I. STRUCTURE AND REACTIONS OF THE 1-CYCLOPROPYLVINYL CATION

II. INTERACTION OF THE FACE OF A CYCLOPROPANE RING WITH POSITIVELY CHARGED CARBON

Thesis by
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In Partial Fulfillment of the Requirements
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And further, by these, my son, be admonished:
of making many books there is no end; and
much study is a weariness of the flesh.

Ecclesiastes 12:12

ACKNOWLEDGEMENTS

Membership in the Bergman research group has been a genuine pleasure. Professor R. G. Bergman has bountifully provided encouragement, talented direction, and contagious enthusiasm during the course of this work. His remarkable abilities as a scientist were complimented by a tolerance for individuality in his students and an obvious concern for their well-being.

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Thesis by Shelby Allen Sherrod

Abstract

I. STRUCTURE AND REACTIONS OF THE 1-CYCLOPROPYLVINYL CATION*

The unusual solvolytic reactivity of cyclopropylcarbinyl derivatives suggested that cyclopropyl substitution should stabilize vinyl cations; accordingly, it has been shown that 1-cyclopropylvinyl iodide ionizes readily under solvolytic conditions, with or without silver catalysis. Comparative kinetic measurements show that the cyclopropyl group enhances the uncatalyzed solvolysis rate by a factor greater than 1.2 x 10^3, apparently by delocalizing the incipient positive charge. The major products result from reactions of the 1-cyclopropylvinyl cation with solvent, but partial rearrangement of this intermediate to the 2-methylenecyclobutyl cation occurs in acetic acid. The enthalpy of activation for this rearrangement exceeds that required for solvent trapping by 2.2 kcal/mol. A small yield of 3,4-pentadien-1-yl acetate may involve rearrangement to the 3,4-pentadien-1-yl cation. Comparative product studies show that 1-cyclopropylvinyl cation is also the major intermediate

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* For published accounts of this work see, S. A. Sherrod and R. G. Bergman, _J. Am. Chem. Soc._, _91_, 2115 (1969); _ibid._, _93_, 1925 (1971).

in the solvolysis of 3,4-pentadien-1-yl derivatives but is not involved in solvolyses of 2-methylenecyclobutyl or 1-cyclobutenylcarbinyl halides. There appears to be a difference between the 2-methylenecyclobutyl cation resulting from rearrangement and that obtained on direct solvolysis.

II. INTERACTION OF THE FACE OF A CYCLOPROPANE RING WITH POSITIVELY CHARGED CARBON**

In order to evaluate the nature of the title interaction, the solvolytic reactivities of 4-tricyclyl, 1-apocamphyl, and 1-methyl-4-tricyclo[2.2.2.$0^{2.6}$]octyl derivatives were compared. Solvolysis of the trifluoromethanesulfonates (triflates) in 60% aqueous ethanol (buffered) provided good first-order kinetic and Arrhenius data. Extrapolated to 25° the relative rates for these substrates (in the order given above) are 1.0, 2.84×10^{4}, and 5.45×10^{7}. In each case, product studies showed that no rearrangement took place, and incorporation of ^{18}O in 4-tricyclenol on solvolysis of 4-tricyclyl triflate in isotopically enriched medium showed that even under the most forcing conditions, carbon-oxygen rather than sulfur-oxygen bond cleavage was occurring. Since the rate data are well rationalized by

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** For a published account of this work see, S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, <u>J. Am. Chem. Soc</u>., <u>92</u>, 3469 (1970).

semiempirical calculations that consider only relative strain energies, interaction of an incipient carbonium ion with the face of a cyclopropane ring apparently affords no significant stabilization.

TABLE OF CONTENTS

PART I

PART II

SECTION TITLE PAGE

II RESULTS

III DISCUSSION

IV EXPERIMENTAL

V REFERENCES

LIST OF TABLES

I. STRUCTURE AND REACTIONS OF THE 1-CYCLOPROPYLVINYL CATION

LIST OF FIGURES

I. STRUCTURE AND REACTIONS OF THE 1-CYCLOPROPYLVINYL CATION

LIST OF TABLES

II. INTERACTION OF THE FACE OF A CYCLOPROPANE RING WITH POSITIVELY CHARGED CARBON

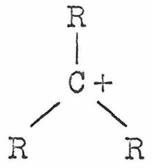
LIST OF FIGURES

II. INTERACTION OF THE FACE OF A CYCLOPROPANE RING WITH POSITIVELY CHARGED CARBON

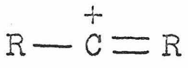
STRUCTURE AND REACTIONS OF THE 1-CYCLOPROPYLVINYL CATION

I. INTRODUCTION

The history of carbonium ions now spans about seventy years (1). It embraces a monumental amount of work, almost certainly more than has been directed toward the elucidation of any of the other intermediates in organic chemistry. Nearly all or this work has dealt with carbonium ions such as I, which have three substituents (here referred to as saturated and trigonal). Relatively little work has dealt with unsaturated or digonal carbonium ions such as II, which have only two substituents. In particular, vinyl cations (III) have received marked attention only during the last decade. It may be instructive to consider why this has been so.

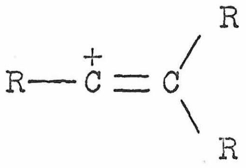


I



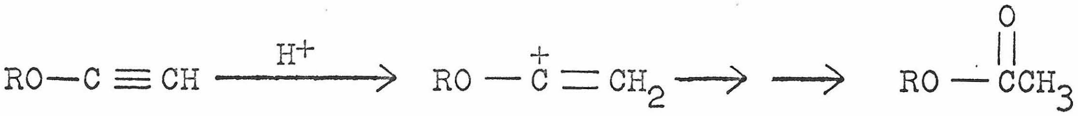
$R{-}\overset{+}{C}{=}R$

II



III

First, one should remember that much of the early work with carbonium ions centered around stable carbonium ion salts (1). Since even today there are no known stable salts of vinyl cations, it is not surprising that they were not a part of the early history of the field. It was not until 1932, less than forty years ago, that the importance of carbonium ions in solution chemistry, and in particular in rearrangements, was first generalized by Whitmore (1). Even then the sentiment against carbonium ions as reactive intermediates was so strong that Whitmore resorted to explicitly describing a carbonium ion without using the term as such. In spite of this ploy, his paper received much criticism from referees (1,2). In this context the vinyl cation does not seem to be such a latecomer, because only twelve years later Jacobs and Searles proposed cation IV as an intermediate in the acid-catalyzed hydration of acetylenic ethers (3). Nevertheless, the general field of



$$RO-C\equiv CH \xrightarrow{H^+} RO-\overset{+}{C}=CH_2 \longrightarrow \longrightarrow RO-\overset{\overset{O}{\|}}{C}CH_3$$

IV

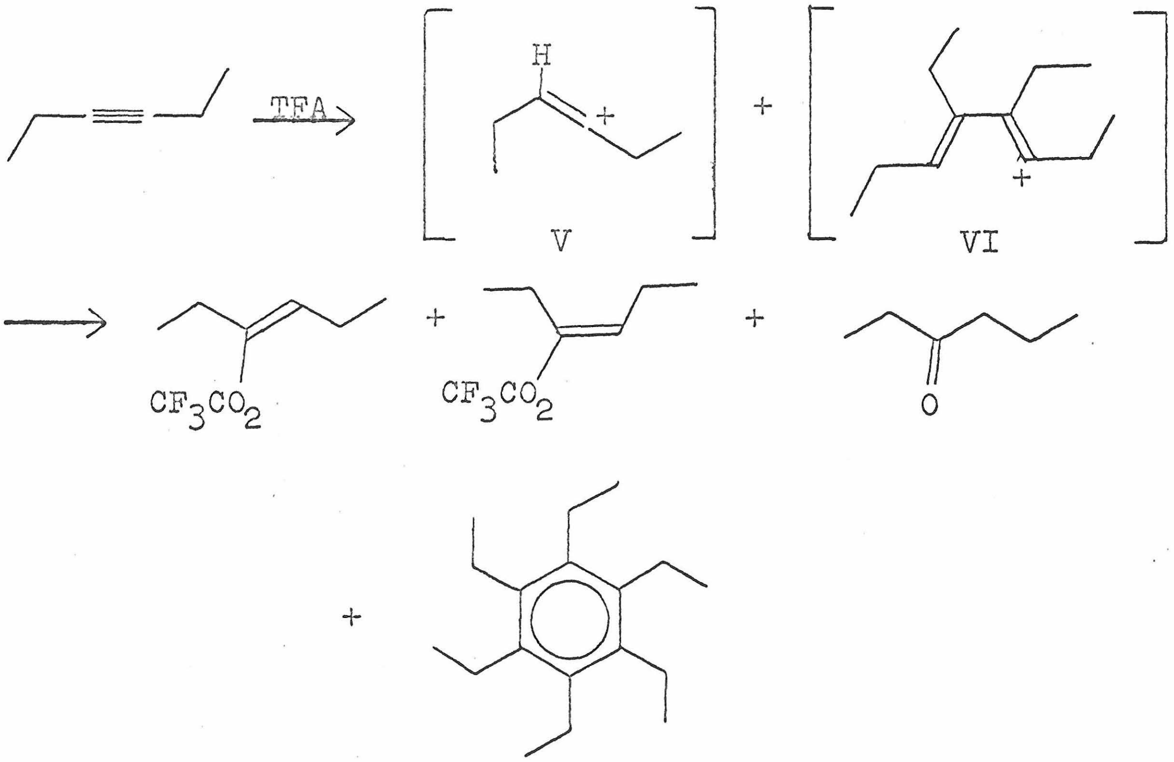
carbonium ions underwent a tremendous expansion during the next twenty years, while vinyl cations remained a rarity.

In retrospect it appears that two factors were to blame for the slow development of the vinyl cation field:

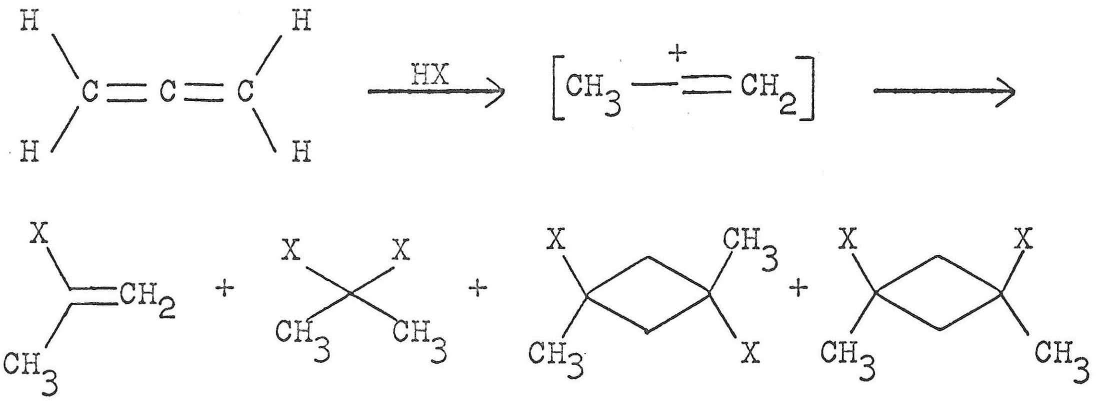
1. Relative to analogous saturated cations, vinyl cations have some inherent instability. 2. Chemists apparently had the misconception that vinyl cations were even less stable than they in fact are. The first of these factors may have inhibited research in the field by making vinyl cations difficult to generate and by making the use of such important techniques as kinetics seem impossible, at least for solvolytic displacement reactions with conventional leaving groups. However, the second factor may have caused the greater inhibition by discouraging chemists from seeking relatively stable vinyl cations or more suitable leaving groups.

In a burst of output occurring mainly after 1960, workers found that they were often able to overcome the problems associated with the instability of vinyl cations by employing one or both of two devices: the use of stabilizing substituents and the use of highly energetic substrates. For example, a number of groups took advantage of the stabilization afforded by substituted phenyl substituents or adjacent heteroatoms and the high energy content of the carbon-carbon triple bond and obtained evidence for the intermediacy of vinyl cations in the acid-catalyzed hydration of ethynyl ethers and ethynyl thioethers (4), phenyl propiolic acids (5), and phenyl acetylenes (6). The techniques that were brought to bear in some of these investigations included kinetics, solvent isotope effects, isotopic labeling, substituent effects, and various linear free energy relationships, and these cases provided the first definitive evidence for vinyl cations.

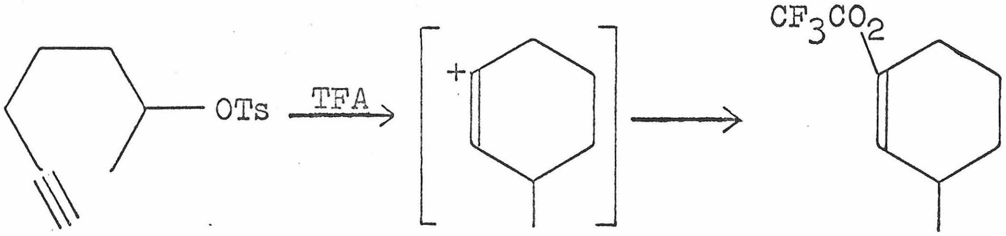
Even in the absence of favorable substituents, the high energy of an acetylene bond is sufficient to facilitate the generation of vinyl cations. Working with normal alkyl acetylenes and trifluoroacetic acid, Peterson and Duddey observed reactions which strongly suggested the intermediacy of vinyl cations V and VI.



Allenes also provide sufficient energy. Griesbaum _et_ _al_. (7) found that the electrophilic addition of hydrogen halides to allene gave products that were most easily explained by initial attack of a proton at a terminal carbon to give a vinyl cation:

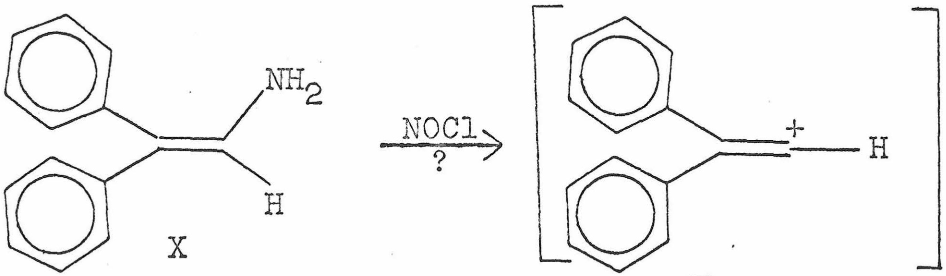


Furthermore, it was shown that acetylene (8) and allene (9) bonds could participate intramolecularly in solvolyses, giving products which suggested that vinyl cations intervene in these reactions. For example, Peterson and Kamat found that the solvolysis of tosylate VII in trifluoroacetic acid led to the cyclic enol trifluoroacetate IX, presumably via the "bent" vinyl cation VIII. Rate studies indicated that the triple bond was participating in the ionization transition state (8c).

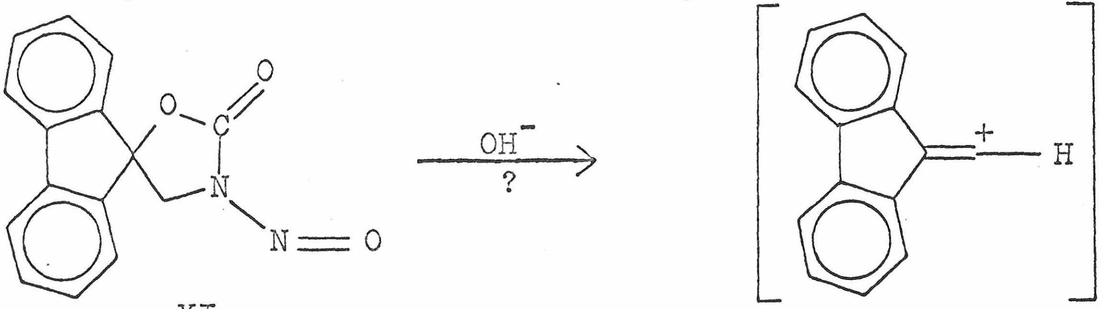


VII VIII IX

Other workers found that the use of nitrogen as a leaving group provided a route to some vinyl cation systems. One problem with this route was the general unavailability of vinyl amines for diazotization. However, some vinyl amines such as X could be obtained. The mechanism in the deamination of X seemed to depend on the reagent used. With nitrosyl chloride a vinyl cation was apparently produced, but isoamyl nitrite seemed to favor a carbene mechanism (10). The base-catalyzed decomposition of the *N*-nitrosooxazolidone XI also gave products that suggested the intermediacy of a vinyl diazonium ion and a vinyl cation, but making a distinction between such a mechanism and one involving a carbene is again subtle (11). The unavailability of vinyl amines was partly circumvented by Jones and Miller, who found that protonation of triazenes such as XII

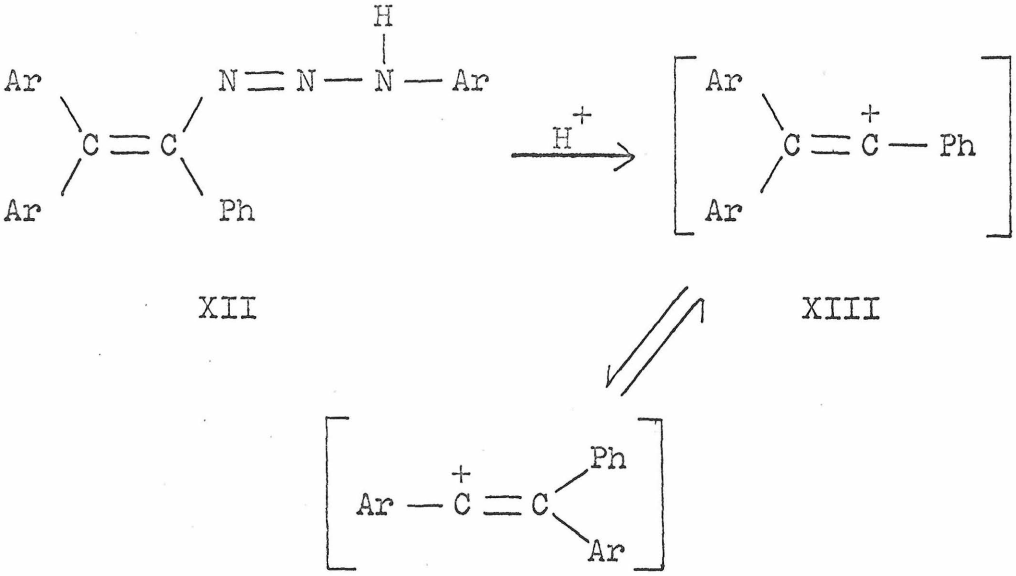


X



XI

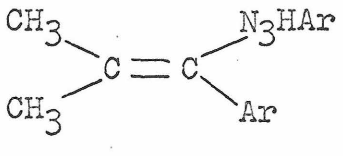
even in weak acids such as acetic results in the immediate liberation of one equivalent of nitrogen. The vinyl cation XIII is produced, presumably from the decomposition of a diazonium intermediate. Aryl migration in XIII to give XIV was observed, this being the first demonstration of a rearrangement with a vinyl cation terminus (12). However, it was not clear that this would provide a general route to vinyl cations, because the procedures used to obtain XII and related compounds were applied with no success in attempts to synthesize XV, XVI, and other compounds (13).



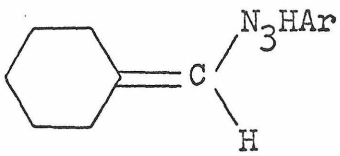
XII

XIII

XIV

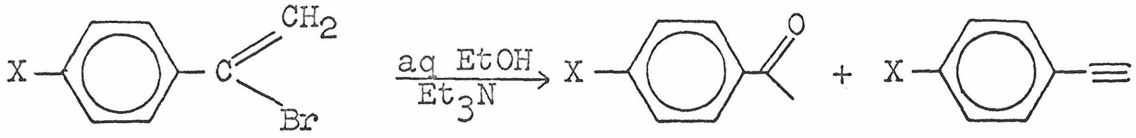


XV



XVI

While they are interesting in their own right, vinyl diazonium ions have a distinct disadvantage in one respect: except in extraordinary cases, such as phenyl diazonium salts, they are too unstable to allow kinetic measurements on the ionization step. However, for some time conventional leaving groups offered no advantage in this respect, since their vinyl derivatives had never been known to ionize in solution. The "well known" inertness of vinyl halides even in the presence of silver nitrate eventually made its way into textbooks (14,15), but a recent literature search revealed no systematic study of the reactivity of vinyl halides in silver nitrate solution (16). This lack of reactivity on the part of vinyl halides probably contributed to the opinion that vinyl cations were particularly unstable, in spite of the fact that other possible factors, such as an unusually strong vinyl halide bond, had been pointed out (17). It was a major breakthrough in the field when in 1964, Grob and Cseh discovered that α-aryl substitution of vinyl halides increased their reactivity, making vinyl cations available throught direct ionization in polar solvents. They found that substituted α-bromostyrenes (XVII) undergo clean unimolecular solvolysis in 80% aqueous ethanol at rates which are independent of the concentration of triethylamine buffer, and give as products the corresponding acetophenones and phenyl acetylenes. The p-amino compound was very reactive, solvolyzing at a convenient rate at room temperature, while the p-nitro compound was inert up to 190°. In addition, marked silver catalysis was noted, and all of these data are consistent with rate-determining ionization to a vinyl cation (18).

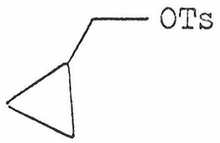


XVII

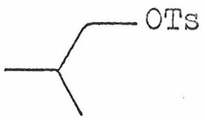
X = H, NH_2, CH_3O, CH_3CONH, NO_2

In the case of the p-amino compound, the vinyl cation mechanism proposed by Grob and Cseh has been attacked recently by Schubert and Barfnecht, who found that in acidic media the solvolysis rate for the amino compound is pH dependent; therefore they propose an addition-elimination mechanism (19). Attempts to extrapolate the data of the two groups to a common solvent at a common pH lead to rate constants which disagree radically. The disagreement has not been resolved in print (19b).

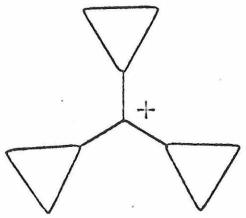
The work of Grob and Cseh suggested that other substituents might render vinyl halides conveniently reactive. A particularly attractive possibility was the use of a cyclopropyl substituent. It was well established in the aliphatic series that substituting a cyclopropyl group for a hydrogen or alkyl group on a potential ionization center results in an enormous increase in reactivity. For example, the acetolysis rate of tosylate XVIII is about a million times greater than that of tosylate XIX (20), and XX is apparently more stable than the triphenylcarbonium ion (21). A further attraction of the cyclopropyl group was that the



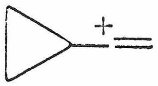
XVIII



XIX



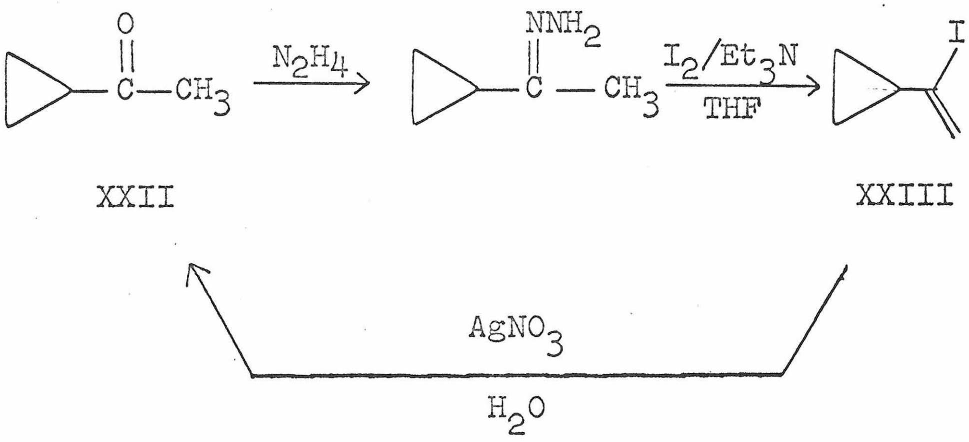
XX



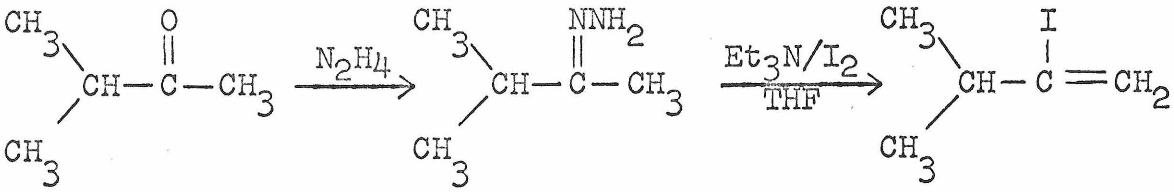
XXI

cation (XXI) that might be obtained bears an obvious resemblance to saturated cyclopropylcarbinyl cations, which often undergo interesting rearrangements and whose structures have been a center of controversy for years (22). One of the most powerful techniques in chemical investigation is that of making an appropriate change in structure and observing the effect of that change on properties such as reactivity or selectivity. In going from the saturated cyclopropylcarbinyl system to the unsaturated cation XXI, one makes a profound change at the reaction center itself, the results of which might be of value in understanding the cyclopropylcarbinyl system in general.

Bergman, using the general method of Barton, O'Brien and Sternhell (23), synthesized 1-cyclopropylvinyl iodide (XXIII) from cyclopropyl methyl ketone (XXII). From preliminary experiments, Bergman found that this vinyl iodide reacts immediately at room temperature with aqueous or aqueous ethanolic silver nitrate; silver iodide precipitates and the major organic product isolated on work-up is ketone XXII (24). Iodide XXIII was also observed to react readily with silver acetate in acetic acid, and in this case gas-liquid chromatography (glc) revealed that a number of products had been formed. At higher temperatures in polar solvents silver catalysis was not necessary; iodide XXIII solvolyzed readily at 150° in 77% aqueous methanol buffered with triethylamine. It was shown that the iodide was thermally stable at this temperature. In order to



confirm the impression that vinyl iodide XXIII was unusually reactive, Bergman synthesized vinyl iodide XXIV from 3-methyl-2-butanone. This model compound reacted very slowly with aqueous silver nitrate, even at 160°. These preliminary results indicated that a careful study of 1-cyclopropylvinyl iodide (XXIII) would be fruitful (24).



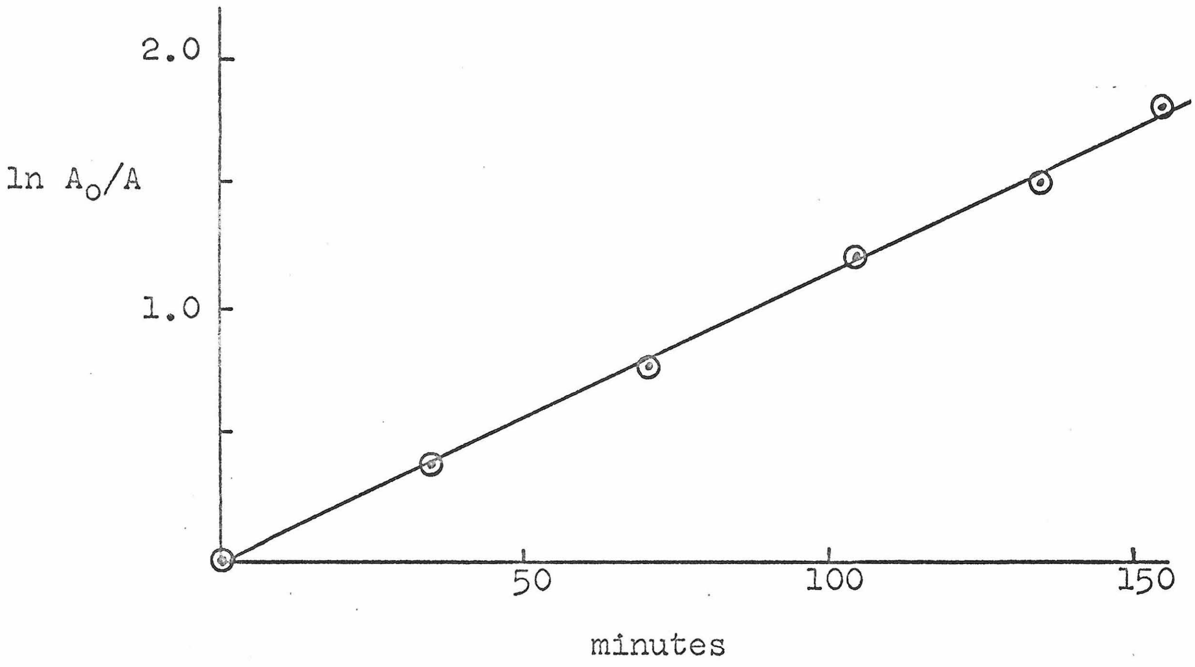
XXIV

II. RESULTS

Reactivity of 1-Cyclopropylvinyl Iodide.

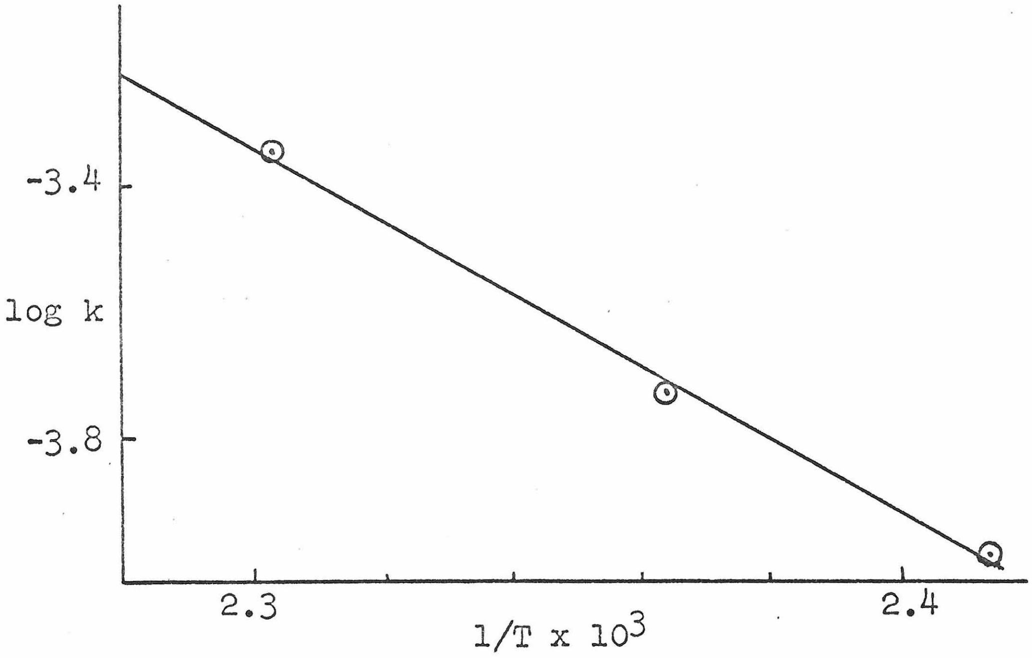
In an effort to quantify the rate acceleration afforded by the cyclopropyl group, a careful kinetic study of the solvolysis of vinyl iodide XXIII and of the model compound XXIV was undertaken. Iodide XXIII was solvolyzed at about 150° in 77.5% aqueous methanol containing 1.1 equivalents of triethylamine. Plots of ln A_0/A versus t were linear for at least two half-lives, which indicates that the reaction is first order in XXIII but independent of the concentration of triethylamine (25). The major product of this

Figure 1. First-order plot for the solvolysis of 1-cyclopropylvinyl iodide (XXIII) in 77.5% aqueous methanol at 150° [a].



[a] Slope of line give $k = 1.94 \pm 0.04 \times 10^{-4}$ sec^{-1}.

Figure 2. Arrhenius plot[a] for solvolysis of 1-cyclopropylvinyl iodide (XXIII) in 77.5% aqueous methanol.[b]



[a] Log k vs. 1/T

[b] Slope of the line gives $E_a = 24.6 \pm 0.7$ kcal/mol, and intercept gives $\Delta S^{\ddagger} = -20.0 \pm 1.7$ eu.

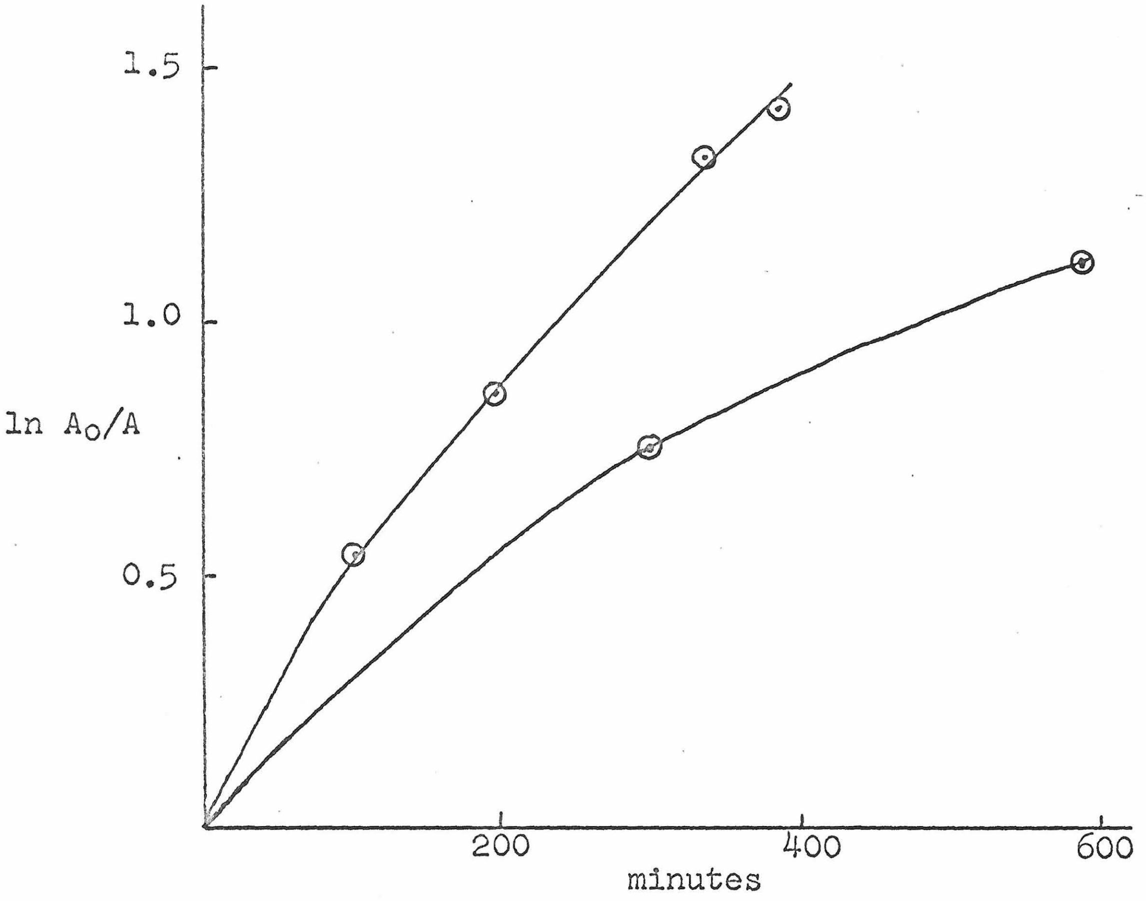
reaction was ketone XXII. The use of three equivalents of triethylamine actually resulted in a slight reduction in the rate relative to that observed with the smaller amount. This is consistent with a medium effect but not with kinetic order in amine. Measurement of the rate at 140.9, 150.0, and 161.1° led to an acceptable Arrhenius plot (log k versus 1/T) which gave values of $\Delta H^{\ddagger} = 23.8 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -20.0 \pm 1.7$ eu (25). A sample rate plot and the Arrhenius plot are given as Figures 1 and 2 respectively.

In the same solvent system, the model compound XXIV required a much higher reaction temperature. At 233.5°, reaction occurred at a convenient rate, but plots of ln A°/A versus t were definitely concave downward, which suggests that the rate is dependent in this case on the concentration of triethylamine. This dependence was more conclusively demonstrated by increasing the triethylamine concentration by a factor of three and observing a comparable change in the initial reaction rate (Figure 3). It could be shown that the corresponding ketone was not a major product in this reaction.

Solvolysis Products of 1-Cyclopropylvinyl Iodide.

A study of the products from silver-catalyzed solvolysis of vinyl iodide XXIII was undertaken. One medium which was considered worth examining was silver tosylate (p-toluenesulfonate) in acetonitrile. In this medium, XXIII

Figure 3. Solvolyses of 1-isopropylvinyl iodide (XXIV) in 77.5% aqueous methanol at 233.5° [a]



[a] Initial concentrations of triethylamine buffer were 0.094 M (upper curve) and 0.036 M.

reacted readily at 0°, and a careful, rapid work-up yielded after two low-temperature recrystallizations from pentane a 17% yield of 1-cyclopropylvinyl tosylate (XXV) (26). This tosylate proved to be unstable, decomposing to a black tar in a few hours at room temperature. The only other product isolated from the reaction mixture was ethynylcyclopropane (XXVI). The instability of the tosylate and the difficulties of the work-up discouraged us from attempting to find and quantify any minor products which may have formed in the reaction.

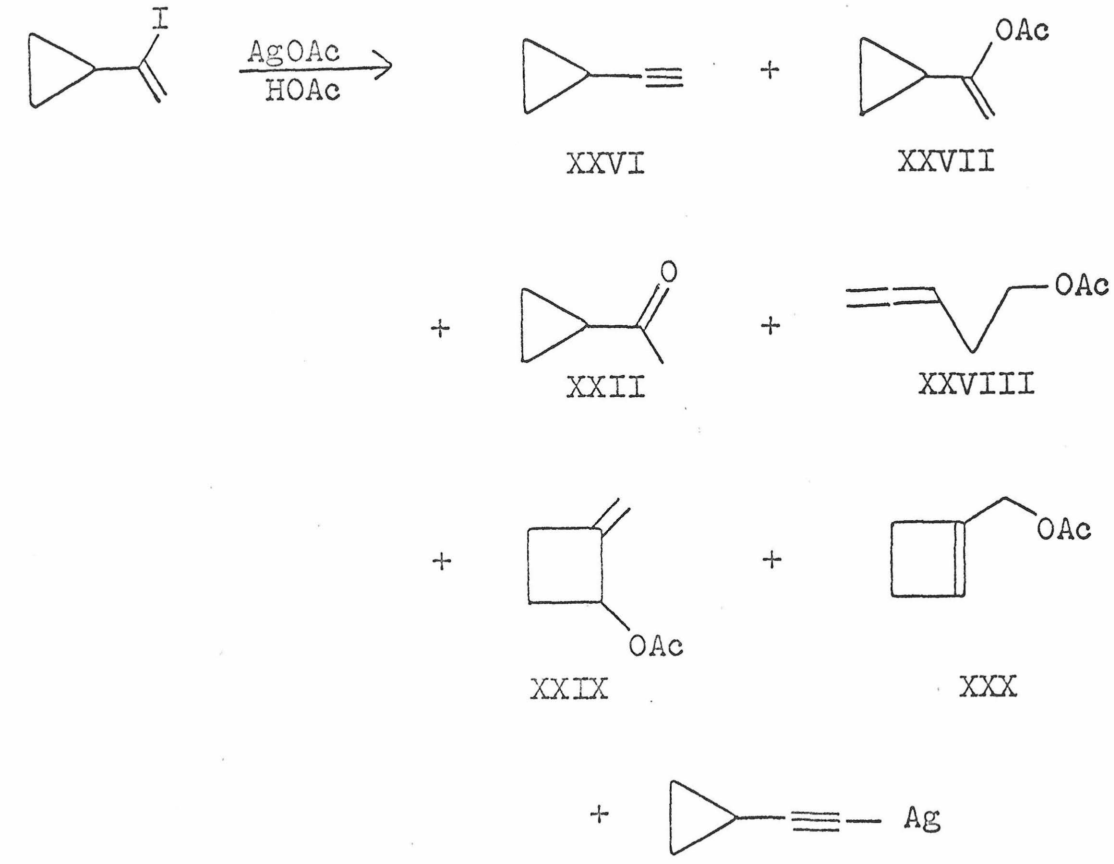
XXIII

XXV
17%

XXVI

There were a number of factors which suggested that silver acetate in acetic acid would be an appropriate medium for a detailed product study. Among them were several features of the medium that favor product stability: 1. Silver catalysis would allow a much lower reaction temperature than would be practical in its absence. 2. Acetic acid is a weak acid. 3. Silver acetate would serve as a buffer in the event that protons are liberated from the substrate, as in an E1 elimination. One might anticipate that even enol acetates would be stable in such a medium. An additional attraction was the low nucleophilicity of acetic acid, which should allow relatively long-lived carbonium ion intermediates and thereby facilitate rearrangements. Indeed, the preliminary experiments with iodide XXIII in this medium had revealed that a number of apparently rather stable products had formed, and it seemed probable that they could be readily isolated by preparative gas-liquid chromatography. Therefore this medium was chosen for detailed product studies.

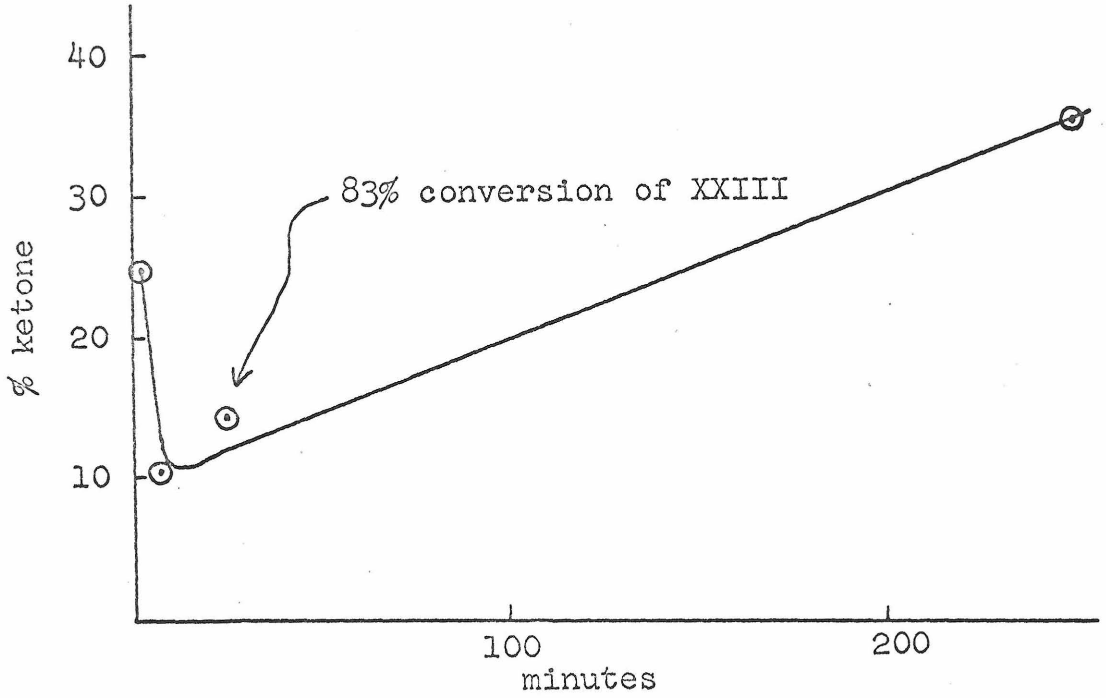
The product mixtures from the reaction of vinyl iodide XXIII with silver acetate in acetic acid were worked up by partitioning between water and ether. Preparative gas-liquid chromatography (glc) allowed the isolation of several products which were identified by comparing their spectral characteristics with those of known or independently synthesized compounds. These included ethynylcyclopropane (XXVI), 1-cyclopropylvinyl acetate (XXVII), cyclopropyl methyl ketone (XXII), and 3,4-pentadien-1-yl acetate (XXVIII). The previously unknown 2-methylenecyclobutyl acetate (XXIX) was also isolated and could be converted to a known compound, 2-methylenecyclobutyl alcohol, by lithium aluminum hydride reduction. A very minor product, 1-cyclobutenylcarbinyl acetate (XXX), was not isolated but could be detected by glc. Its identification was based on the correspondence of its glc retention time with that of known material on two different columns.



XXVI XXVII XXII XXVIII XXIX XXX XXXI

Quantitative glc analysis of the product mixture with the use of an internal standard indicated that the mass balance was poor--about 60%. Relative extraction and glc response factors were determined for all of the products except the acetylene XXVI. As might be expected, the relatively high solubility of ketone XXII in water resulted in very significant losses of this component during the work-up. However, application of the extraction and response factors gave a corrected mass balance of only about 80%. It had been noted that the observed percentage of acetylene XXVI was not reproducible from run to run. Also, it had been noted that in the course of the work-up, the addition of water and ether to the acetic acid solution resulted in formation of a copious white precipitate. Qualitative work with this precipitate suggested that it was silver cyclopropylacetylide (XXXI), which apparently is formed from acetylene XXVI under the reaction conditions. It was assumed that the remaining discrepancy in the observed mass balance was due to the formation of XXXI, and calculation of the corrected yield of acetylene XXVI was based on this assumption. A second problem in the product determination concerned cyclopropyl methyl ketone (XXII) It soon became evident that the percentage of this component was greater with long reaction times. Therefore, enol acetate XXVII was submitted to the reaction conditions with care being taken to exclude all water, and a slow conversion to XXII was observed. In an effort to determine whether or not all of the observed ketone comes from the enol acetate, aliquots were taken during the solvolysis of iodide XXIII. Analysis showed that the observed percentage of ketone XXII went through a minimum at about 80% conversion of XXIII and then slowly increased (Figure 4). This result was obtained in spite of careful efforts to dry the acetic acid and the silver acetate used. A control experiment in which a few

Figure 4. Cyclopropyl methyl ketone (XXII) as percentage of the products[a] of silver-catalyzed acetolysis[b] of 1-cyclopropylvinyl iodide (XXIII) as a function of time.

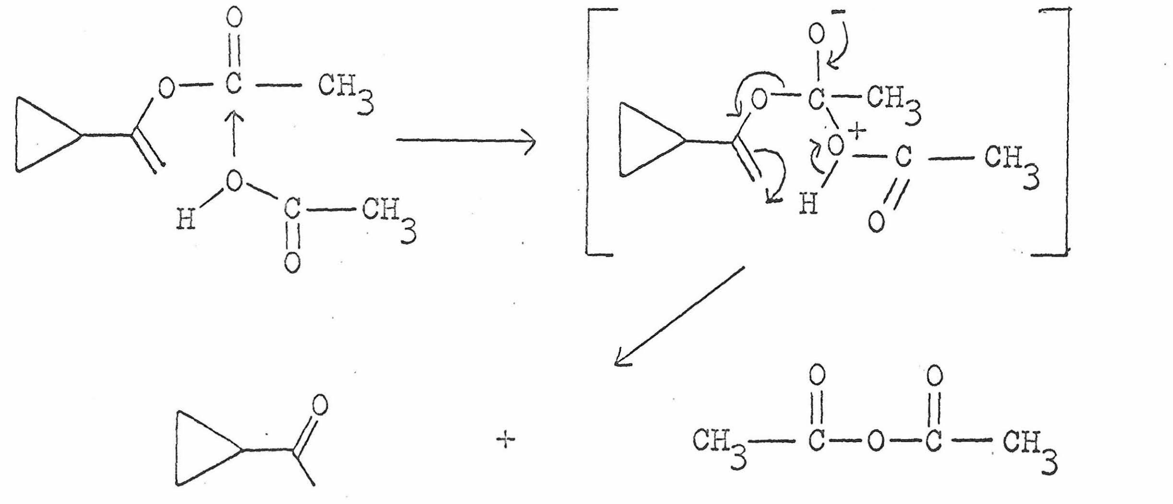


[a] Other than acetylene XXVI.

[b] Reaction temperature 45°.

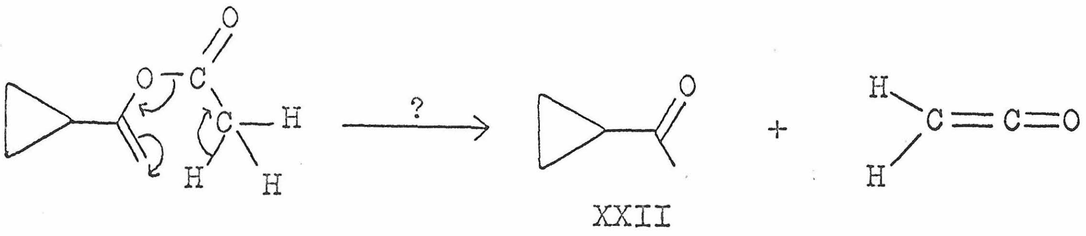
percent of water was intentionally added to the solvent resulted in only a moderate increase in percentage of ketone, which suggests that water is not a significant source of ketone in the original experiments. Perhaps the reaction of iodide XXIII with some minor impurity in the reaction mixture occurs at a greater rate than the reaction which gives the other products, and results in the observed initial "burst" in ketone formation, which is followed by a slow increase in ketone due to the secondary reaction of enol acetate. We thought silver oxide might be this impurity, but a control experiment in which silver oxide was intentionally added resulted in no increase in the percentage of ketone.

The mechanism of the XXVII to XXII conversion may involve an attack on the carbonyl carbon of the enol acetate by acetic acid, followed by what may be an intramolecular proton transfer. This would result in the illustrated



XXII

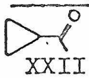
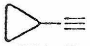
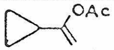
cleavage to ketone XXII and acetic anhydride. That these steps need occur in the given order is not obvious; an initial protonation of the double bond to give a cyclopropylcarbinyl cation, followed by acetate attack on the carbonyl carbon also seems reasonable. A concerted electrocyclic reaction to give ketone XXII and ketene is a less attractive mechanism in view of the observation that enol acetate XXVII is stable indefinitely in ether; a protic solvent seems to be a requirement for the conversion to ketone.



The product distribution obtained from the silver-catalyzed acetolysis of iodide XXIII is given in Table I. A noteworthy fact is the preponderance of cyclopropyl products, which account for 97.8% of the mixture.

As a mechanistic probe, iodide XXIII was solvolyzed under the same conditions as in the above except for the use of O-deuterioacetic acid as the solvent. After isolation from the reaction mixture, the enol acetate XXVII contained no deuterium within the limits of detection (<1%)

Table I. Product Distributions from Substrates Leading to the 1-Cyclopropylvinyl Cation System Under Solvolytic Conditions.

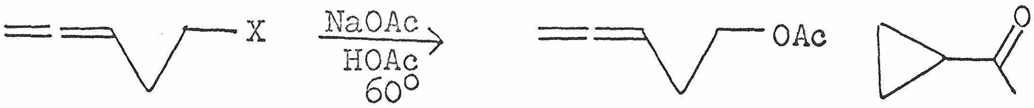
Substrate	Conditions	Products, (%)							
		 XXII	 XXVI	 XXVII	 XXVIII	 XXIX	 XXX	Unident.	Ref.
3,4-pentadien-1-yl β-naphthalenesulfonate (XXXII)	H_2O, DMK, $CaCO_3$, 60°	37						11	9b
	HOAc/NaOAc, 60°	20			61			7,12	9b
	HCOOH/NaOOCH, 60°	80			5[a]			15	9b
	CH_3OH, $CaCO_3$, 60°				92[b]			8	9b
3,4-pentadien-1-yl tosylate (XXXIII)	HOAc/NaOAc, 100°	11		3	76	6			28 1
	HOAc/NaOAc, 100°	55.9	0.92	0	37.8	4.67	0.38	0.17	This work
3,4-pentadien-1-yl bromide	H_2O, Ag_2O, rm. temp.	32			44[c]				9b
3,4-pentadien-1-yl iodide (XXXVI)	AgOAc, HOAc 25°	4.8	23	61.5	9.4	1.21	0.14	0	This work
1-cyclopropylvinyl iodide (XXIII)	AgOAc, HOAc 25°	12.6	27	58.2	0.97	1.15	0.13	0	This work

[a] formate; [b] methyl ether; [c] alcohol

by infrared, nuclear magnetic resonance, and mass spectrometric analysis.

The Solvolysis Products of 3,4-Pentadien-1-yl Derivatives.

Hanack and Häffner were the first to show that 3,4-pentadien-1-yl (homoallenyl) derivatives solvolyze with kinetically detectable participation and give significant amounts of cyclopropyl products. For example, on solvolysis in buffered acetic acid at 60°, 3,4-pentadien-1-yl β-naphthalenesulfonate (XXXII) was reported to give the unrearranged acetate XXVIII, ketone XXII, and two other unidentified products (9). Since this reaction at least formally suggests the intermediacy of the cyclopropylvinyl cation XXI, which might be formed directly in the solvolysis of vinyl iodide XXIII, a careful comparison of the product distributions from these reactions seemed desirable. Generation of formally the same ion from a number of different



XXXII

XXVIII
61%

XXII
20%

X = β-naphthalenesulfonate

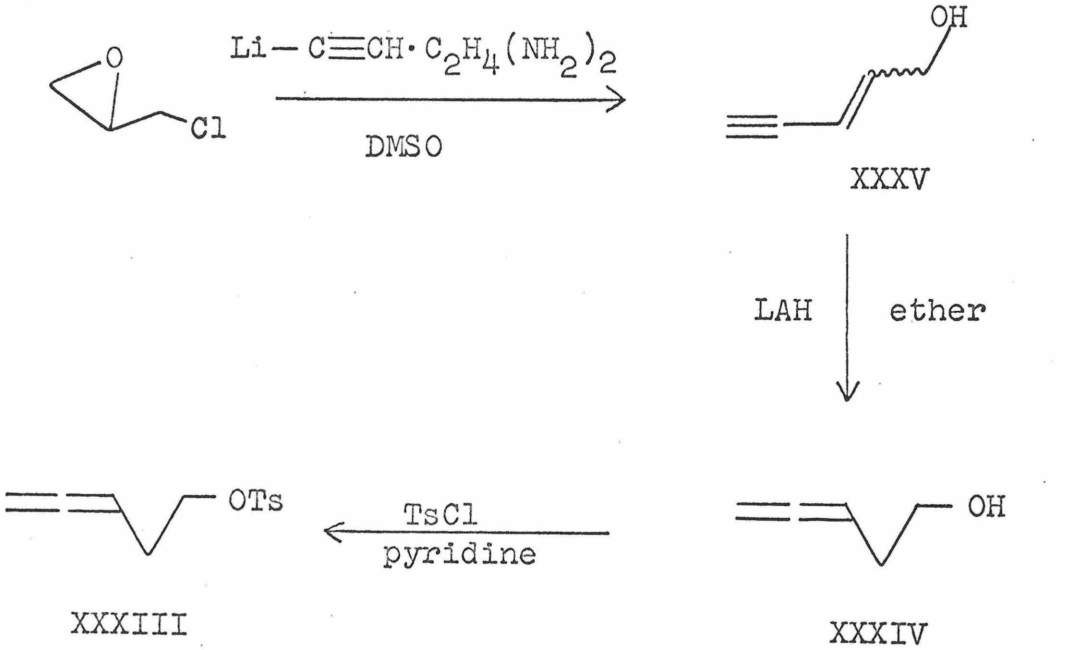
+ 19% unidentified

sources is a technique often used in studying carbonium ion mechanisms (27). A general correlation between the product distributions would suggest basically a common intermediate in the reactions, while subtle differences in distribution might be interpretable in terms of ion-pair phenomena, parallel reaction pathways, or intermediates of closely related structure. Radically different intermediates might be expected to give distinct product distributions

Hanack and Häffner had carried out the solvolysis of XXXII in a number of media and the reported products are presented in Table I. The conditions which most resembled those we used in the acetolysis of vinyl iodide XXIII were the above-mentioned buffered acetic acid and 60°, but the respective product distributions are not at all similar. Whereas Hanack and Häffner found acetate XXVIII to be the major product, we found less than one percent of this component. However, in the reaction of XXXII there is an obvious possibility that a direct displacement to give acetate XXVIII competes with participation by the allenyl moiety to give cyclic products. Thus one might wish to compare only the ratios among cyclic products. This cannot be done with the data given for the solvolysis of XXXII, since ketone XXII is the only cyclic product reported and two products remain unidentified. Hanack and Häffner felt that the enol acetate XXVII was formed but that it was hydrolyzed in the work-up. We have found that XXVII is stable to our work-up, but as described above, is converted to ketone XXII in dry acetic acid. In the long reaction time employed by Hanack and Häffner (12 days) all enol acetate would have been converted to ketone.

Since the work of Hanack and Häffner, a number of publications have appeared reporting solvolyses of homoallenyl derivatives (28), but only those by Jacobs and Macomber (28k,l) included a product study with an unsubstituted derivative, 3,4-pentadien-1-yl tosylate (XXXIII). The product distribution reported for the solvolysis of XXXIII in buffered acetic acid at 100° is given in Table I (page 24). They too report the unrearranged acetate (XXVIII) as the major product. In addition they found acetate XXIX but report a much higher percentage of this component than we observe in the solvolysis of iodide XXIII. Identification of one of the components as enol acetate XXVII seemed strange to us since our experience indicated that XXVII would not have survived the reaction conditions. They did not observe acetylene XXVI or acetate XXX. We decided to repeat the acetolysis of tosylate XXXIII.

For the synthesis of 3,4-pentadien-1-ol (XXXIV) a slight modification of the method of Hanack and Häffner (9b) proved valuable. Treatment of epichlorohydrin with lithium acetylide-ethylenediamine complex in dimethyl sulfoxide (DMSO) gave a better yield (49%) of pent-2-en-4-yn-1-ol (XXXV) than that reported for the use of sodium acetylide in liquid ammonia (29). The reduction of XXXV to XXXIV was carried out in 84% yield using lithium aluminum hydride (LAH) in diethyl ether as reported (9b). Pyridine and p-toluenesulfonyl chloride converted alcohol XXXIV to the tosylate (XXXIII).



XXXV

XXXIII

XXXIV

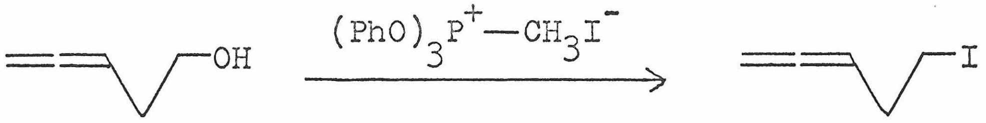
Tosylate XXXIII was solvolyzed in acetic acid at 100° using the same concentrations of sodium acetate buffer and substrate reported by Jacobs and Macomber, but a work-up identical to that used in the acetolysis of iodide XXIII was employed so that the correction factors for extraction and response determined earlier would still be valid.

Analysis by glc and application of the correction factors gave the product distribution shown in Table I (page 24). Noteworthy is the large amount of ketone XXII relative to that reported by the earlier workers. This apparently results from the large correction factor we found necessary to apply for the incomplete extraction of this component. No such correction was made in the earlier work. Our analysis detected some of acetate XXX but none of acetate XXVII. From tosylate XXXIII one obtains 0.92% acetylene XXVI and 37.8% acetate XXVII: from iodide XXIII one obtains 27% XXVI and 0.97% XXVIII. The virtual inverse relationship suggested the unlikely possibility that acetylene XXVI is rather efficiently converted to XXVIII in acetic acid at 100°. Indeed XXVI was found to be unstable under these conditions, but it is converted to a mixture of the other products in which ketone XXII predominates. This latter fact alone would make a careful comparison of the product distributions from tosylate XXXIII at 100° and iodide XXIII at 25° difficult if not meaningless. Additional complicating factors are the different leaving groups, the presence in one case and absence in the other of silver catalysis, and the possibility that even the kinetic product ratios might be different at the widely differing temperatures.

Except for its unusual thermal instability, vinyl tosylate XXV might have been solvolyzed in acetic acid at

100° to provide data possibly more suitable for comparison. Before the thermal instability of XXV was discovered (page 17), its synthesis had been attempted with no success by treating either the sodium enolate (31) of ketone XXII or its lithium enolate (32) with tosyl chloride in dimethoxyethane.

Even more attractive was the possibility of comparing the product distributions under the milder conditions allowed by silver catalsis. Therefore, 3,4-pentadien-1-yl iodide (XXXVI) was synthesized by treating alcohol XXIV with triphenylphosphite methiodide (33), and the silver-catalyzed



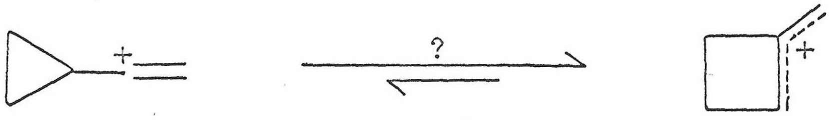
XXXIV

XXXVI

acetolysis of XXXVI was carried out under conditions essentially identical to those used in the acetolysis of XXIII. Again ethynylcyclopropane (XXVI) was a major product but was mostly lost as the silver acetylide (XXXI). As before, the yield of XXVI was estimated from the mass balance. The product distribution is given in Table I (page 24). In general, a close correspondence to the products from XXIII may be noted.

An Examination of the Rearrangements.

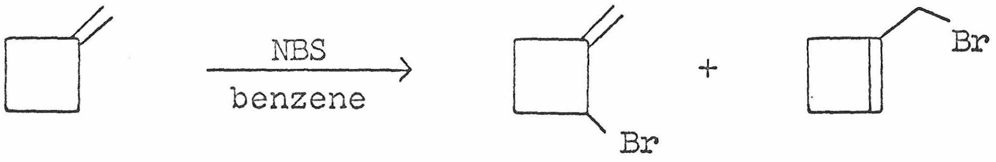
That cyclobutyl products comprise such a small fraction of the total products obtained in the solvolyses of iodides XXIII and XXXVI was surprising. If 1-cyclopropylvinyl cation (XXI) is the principal intermediate in these reactions, its rearrangement to the allylically stabilized 2-methylenecyclobutyl cation (XXXVII) apparently should be strongly favored by thermodynamic factors. Thus it seemed probable that the observed product distribution was a result of kinetic control, and ways were sought to confirm this hypothesis. One approach was to change the solvent; if acetic acid traps most of intermediate XXI before it can



XXI XXXVII

rearrange to XXXVII, then changing to a less nucleophilic solvent should allow the rearrangement process to compete more efficiently and result in an increase in the yield of cyclobutyl products. Trifluoroacetic acid is such a solvent, but in a preliminary test the addition of iodide XXIII to this solvent at room temperature quickly resulted in severe discoloration and the separation of dark solid material. Another solvent of low nucleophilicity (35), 2,2,2-trifluoroethanol, offered the added advantage of being much less acidic, but solvolysis of iodide XXIII in this solvent at 160° with triethylamine as a buffer resulted in an 85% yield of acetylene XXVI. The large increase in the yield of this component relative to that observed under other conditions may be due to the favorability of proton loss from a cationic intermediate in the absence of a good nucleophile, or to an E2 elimination involving triethylamine. The remaining 17% of the product mixture consisted of several components which were not examined further because of their low yields. This reaction, however, did provide a welcome synthesis of acetylene XXVI. Attempts to prepare this acetylene by treating iodide XXIII with potassium _t_-butoxide in DMSO had resulted in the formation of apparently polymeric material and only very low yields of XXVI. Attempts to use sodium methoxide as base and methanol as solvent had resulted in the disappearance of XXIII and the appearance of a product having a much longer glc retention time, but only traces of XXVI were detected.

A more fruitful probe into the energetics of the rearrangement was achieved by entering the presumed ionic manifold from the "other side" through solvolyses of 2-methylenecyclobutyl bromide (XXXVIII) and 1-cyclobutenylcarbinyl bromide (XXXIX). Bromides XXXVIII and XXXIX were synthesized by the reaction of N-bromosuccinimide (NBS) with methylenecyclobutane as reported by Buchman and Howton (34). When bromide XXXVIII was obtained, its proton nuclear magnetic resonance (nmr) spectrum was an ambiguous indication of structure because the signals corresponding to the vinyl protons and to the bromomethylene protons were superimposed. Definitive evidence for the structure was found in the proton-decoupled ^{13}C nmr spectrum (26). The silver-catalyzed acetolysis of bromides XXXVIII and XXXIX gave only the cyclobutyl products XXIX and XXX, but in different ratios as shown in Table II. The limits of detectability of cyclopropyl products was shown to be less than 0.3% for ketone XXII and less than 0.1% for enol acetate XXVII.



XXXVIII
14%

XXXIX
1%

The data in Table II also show that the XXIX/XXX ratios obtained from bromides XXXVIII and XXIX, although different from one another, are even more different from the corresponding ratios obtained in the solvolyses of iodides XXIII and XXXVI. In the interest of determining whether or not this might be an element effect, 2-methylenecyclobutyl iodide (XL) and 1-cyclobutenylcarbinyl iodide (XLI) were prepared by treating bromide XXXVIII with lithium iodide in anhydrous acetone. The iodides were obtained as an 83:17 mixture. An attempt was made to separate this mixture by preparative glc, but the components rapidly interconverted (perhaps in the glc detector) to regenerate what is apparently the equilibrium composition. Silver-catalyzed acetolysis of this mixture gave a value of XXIX/XXX intermediate between those obtained from bromides XXXVIII and XXXIX. This value, shown in Table II for comparison, is close to that predicted based on the assumption that the components react at the same rate and individually give the same values for the ratio XXIX/XXX as do the analogous bromides. The rapid equilibration of these iodides raised the suspicion that the bromides XXXVIII and XXXIX might also be interconverting during their solvolyses. This possibility was ruled out in the case of bromide XXXVIII.by demonstrating that no detectable conversion of this bromide

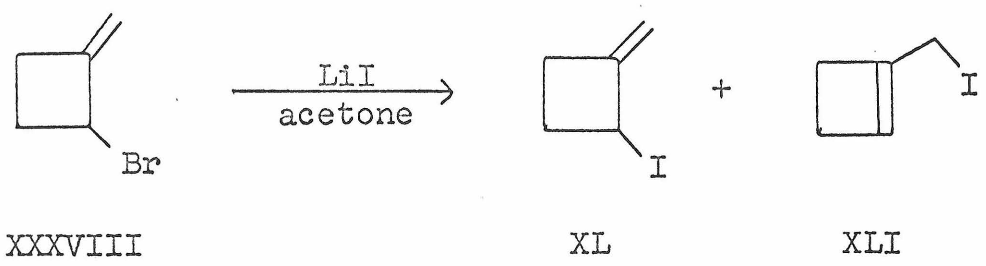
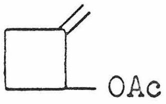
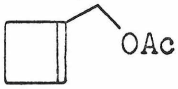
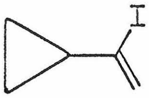
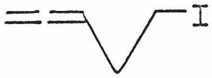
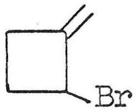
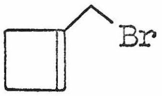
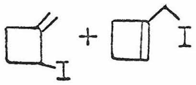


Table II. Cyclobutyl Products Formed in Silver-Catalyzed Acetolyses of Some Halides at 25°.

Substrate	Products[a] (%)		Ratio, XXIX/XXX
	 (XXIX)	 (XXX)	
 XXIII	1.15	0.13	8.85 ± 0.8
 XXXVI	1.21	0.14	8.65 ± 0.8
 XXXVIII	71.9	27.5	2.61 ± 0.09
 XXXIX	46.3	48.2	0.96 ± 0.09
 [b] XL XLI	67.8	31.9	2.12 ± 0.08

[a] Stability of the products under the reaction conditions was demonstrated.

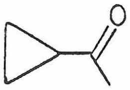
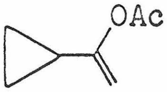
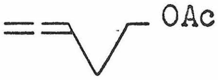
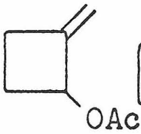
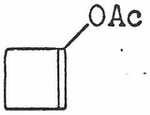
[b] An 83:17 mixture (see text).

to its allylic isomer occurred in acetic acid in the presence or absence of silver iodide. Thus the product ratio given for XXXVIII corresponds to the solvolysis of the pure bromide.

Turning again to the product ratios obtained in the solvolysis of tosylate XXXIII at 100° and iodide XXIII at 25° (Table I, page24), one finds that the percentage of cyclobutyl products obtained in the former case is greater than in the latter. In spite of all the factors that have been cited (page 27) as potentially responsible for any observed differences in those distributions, it was tempting to think that one of them, a temperature effect, might be particularly important in this case. There is obviously some energy barrier involved in the rearrangement that results in cyclobutyl products, and it seemed reasonable that this barrier might be enthalpic in nature, i.e. that the rearrangement process requires more activation energy than solvent trapping. This would account for the increased amounts of rearranged products at the higher temperature. We decided to study the product distribution from the silver-catalyzed acetolysis of vinyl iodide XXIII as a function of temperature. A product ratio that was potentially suitable as a focal point in this study was that of cyclopropyl products to cyclobutyl products. However, the problems associated with determining the amount of ethynylcyclopropane (XXVI) have been described. Therefore analysis for this component was not included in the temperature study, and in practice the ratio that was observed as a function of temperature was (XXVII + XXII)/(XXIX + XXX).

A number of precautions had to be taken in order to obtain reliable data. The uncorrected product percentages were determined by disc integration of gas-liquid chromatograms. A dissection of the barrier to rearrangement into enthalpic and entropic contributions was desired, and in order to determine $\Delta\Delta S^{\ddagger}$ one must determine molar product ratios. Therefore the crude chromatographic integrals has to be corrected for extraction and response. The fact that the minor products were only a few percent of the major products made desirable the use of different attenuation of the chromatographic response in the course of each analysis. Thus the response factors had to account for the difference in attenuation and the errors associated with very dissimilar absolute sample sizes, such as result from column hold-up. Particularly large and important was the extraction factor for ketone XXII, which was relatively water soluble and only partially recovered in the work-up. This in turn demanded that the rather involved work-up be duplicated as accurately as possible from run to run. Since the rate of conversion of enol acetate XXVII to ketone XXII increased as the temperature was raised, progressively shorter reaction times were allowed at the higher temperatures in order to keep the relative amounts of XXVII and XXII approximately constant. This avoided the need to calibrate the response factors for XXVII and XXII over wide ranges of concentration. It was also necessary to correct the observed amount of ketone XXII for that portion which did not come from XXVII. The corrected data were obtained at five temperatures, ranging from 25.0 to 64.8°, and are presented in Table III. The log of (XXVII + XXII)/(XXIX + XXX) was plotted versus the reciprocal of temperature (Figure 5), and the function was found to be reasonably linear. From the slope of this plot one can calculate that the enthalpy of activation for rearrangement exceeds that for solvent trapping by 2.2 kcal/mol (36).

Table III. Products[a] Formed in Silver-Catalyzed Acetolyses of 1-Cyclopropylvinyl Iodide (XXIII) at Various Temperatures

	Products, mol %[a]				
Temp. (°C)					
	XXII	XXVII	XXVIII	XXIX	XXX
25.0[b]	17.3	79.7	1.33	1.58	0.18
25.0[c]	34.5	62.8	1.11	1.38	0.20
34.9[d]	13.0	83.8	1.37	1.76	0.19
44.6[d]	15.9	80.7	1.40	1.87	0.21
55.0[d]	17.1	78.7	1.66	2.28	0.25
64.8[d]	28.1	67.7	1.80	2.34	0.26

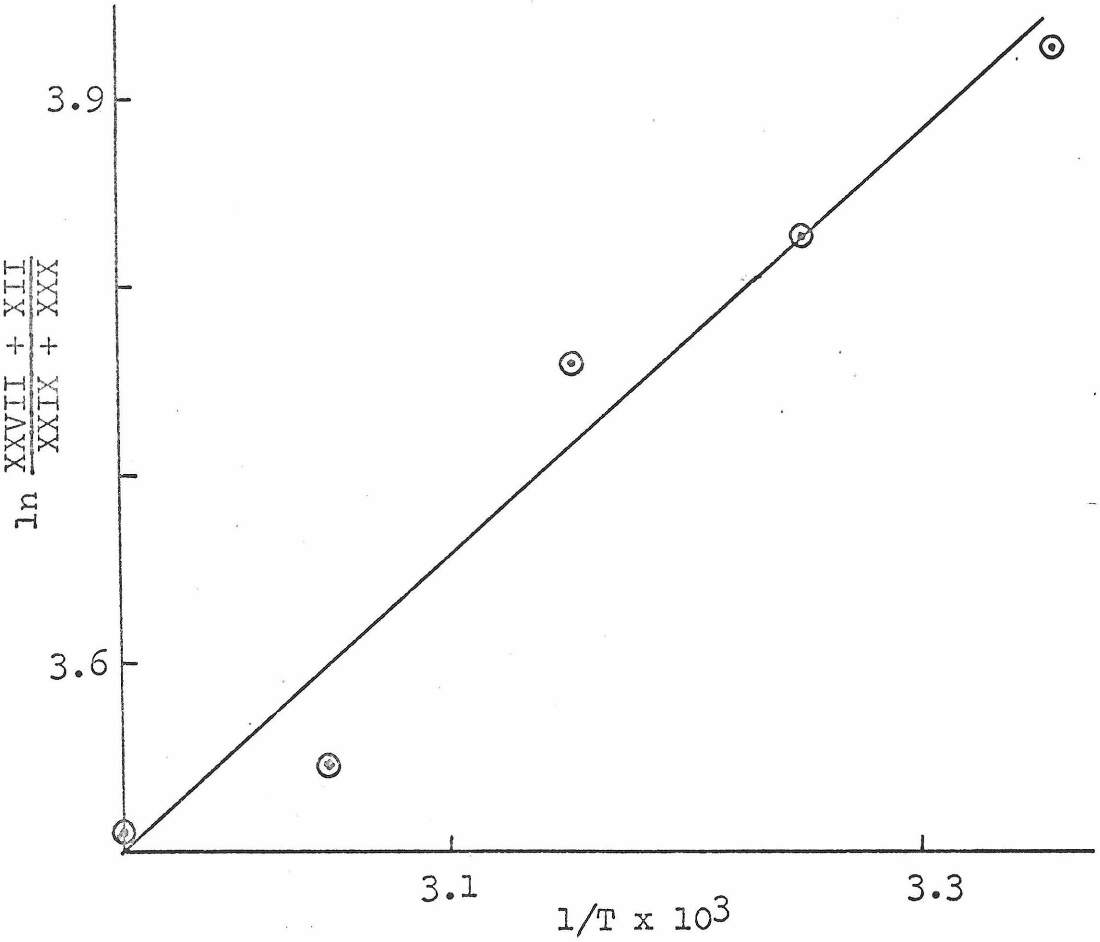
[a] Other than acetylene XXVI

[b] Reaction time 250 min

[c] Reaction time 1320 min

[d] Reaction time adjusted to give about 20% XXII

Figure 5. Log of cyclopropyl to cyclobutyl product ratio versus the reciprocal of temperature for silver-catalyzed acetolysis of 1-cyclopropylvinyl iodide (XXIII).

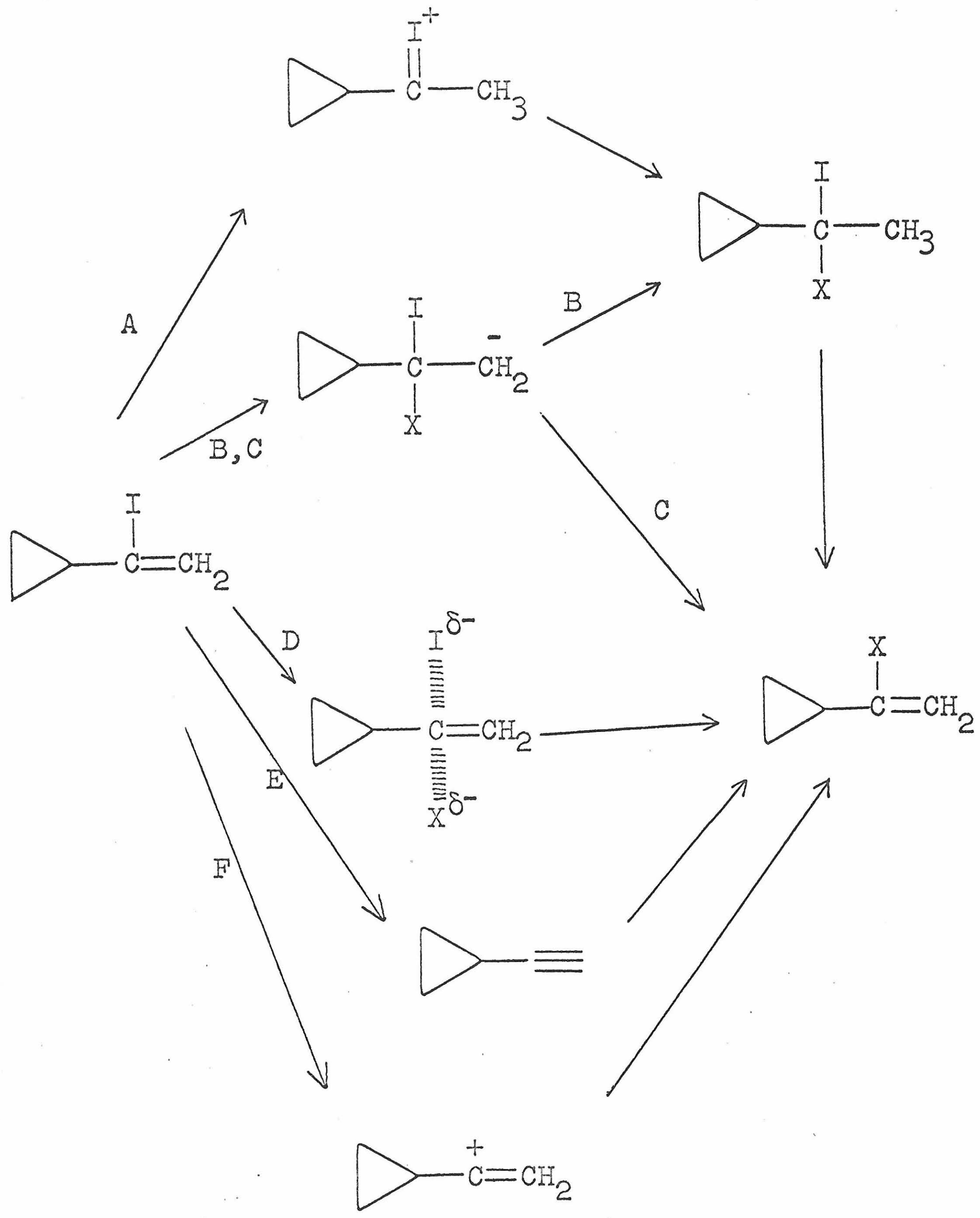


III. DISCUSSION

Mechanism of 1-Cyclopropylvinyl Iodide Solvolyses.

Substitution at a vinyl center can occur by a number of different mechanisms. These have been discussed in several papers (18a, 19b, 37, 38, 39) but will be presented here also in order to provide background for the mechanistic arguments that follow. Figure 5 illustrates these mechanisms for the case of vinyl iodide XXIII. Paths A, B, and C are addition-elimination mechanisms. In path A protonation of the double bond to give a carbonium ion is followed by nucleophilic trapping and then eliminations of hydrogen iodide. This mechanism has been shown to be active in some systems (19a, 40) and can be readily distinguished from a vinyl cation mechanism on the basis of a number of criteria (19b). In paths B and C addition of a nucleophile to the double bond to give a carbanion is followed either directly by elimination (path C) or by protonation and then elimination (path B). Until recently all nucleophilic displacements at vinyl centers were thought to occur by path C (38). Path D is a direct displacement of the leaving group by nucleophile. Hypothetically, a number of transition state geometries might be possible in this mechanism. In addition to a conventional backside displacement, a special case of path C has been proposed, in which the geometry of nucleophilic

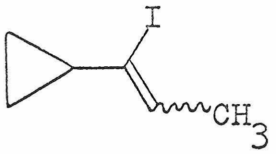
Figure 6. Possible mechanisms for nucleophilic substitution reactions at a vinyl center.



approach is the same but no discrete intermediate is formed (41). In path E elimination of hydrogen iodide, giving an acetylene, is followed by addition of some acid, "HX". And finally, in path F heterolysis of the carbon-iodine bond gives a vinyl cation, which is trapped by some nucleophile.

We may now consider the data obtained from the solvolyses of vinyl iodide XXIII in an effort to decide which of these mechanisms is involved. In the solvolyses in aqueous methanol, the concentration of triethylamine buffer was varied by a factor of three and this in turn must have resulted in significant variation in the concentrations of both hydroxide and hydronium ions. The observed constancy of the reaction rate in spite of variation in the concentrations of these three species shows that none of the three can be involved in the rate limiting step of the reaction. If one is willing to assume that the solvent (water or methanol) is the only important nucleophile, base, or proton source in the rate determining step, then the observed kinetic behavior does not allow a distinction among any of the mechanisms. However, this assumption seems very unreasonable, and in its absence a combination of the observed kinetics and chemical intuition argues strongly against paths A, B, C, D, and E. In path A, the protonation step, whether it be rate limiting or rapid and reversible, should have caused the rate of disappearance of starting material to be dependent on the concentration of hydronium ion. This was not observed. In paths B and C the addition of the nucleophile must be either rate limiting or reversible, because it is most unlikely that the anionic intermediate accumulates during the course of the reaction. The reversibility of this step is untenable since it requires that the anion repeatedly eject hydroxide or methoxide rather than iodide. Therefore the addition of nucleophile must be rate limiting in paths B and C, and if either of these paths were important a dependence of rate on the concentration of the most likely nucleophiles, triethylamine or hydroxide, should have been noted. In path D the nucleophile is present in the only transition state and therefore should have been detected kinetically. If path E is to go through the acetylene without involving a vinyl cation some base is required, but rate dependence on bases was not observed. Thus the kinetic data and reasonable assumptions eliminate all mechanisms for the solvolysis of vinyl iodide XXIII in aqueous methanol except path F, the vinyl cation mechanism.

In the silver-catalyzed acetolysis of XXIII, path A was explicitly ruled out by demonstrating that no deuterium was incorporated from O-deuterioacetic acid. For path B the observation of silver catalysis seemingly demands that loss of iodide from the saturated intermediate be rate determining. This in turn would demand that one of the following be true: 1. The addition of acetic acid to XXIII is relatively fast and irreversible. 2. The addition of acetic acid is fast and reversible. 3. The anionic intermediate must accumulate. The first of the possibilities was ruled out by observing no disappearance of XXIII in acetic acid in the absence of silver acetate. The latter two possibilities are unreasonable on the grounds discussed above. Rationalizing the silver catalysis in terms of path C requires the very improbable accumulation of the anionic intermediate. Path D is unlikely, since Kelsey and Bergman have found that the <u>cis</u> and <u>trans</u> isomers of the closely analogous 1-iodo-1-cyclopropylpropene (XLII) give essentially identical product distributions on silver-catalyzed acetolysis (42). Which stereochemistry one should expect in the direct displacement mechanism is unclear, but it would be most unusual if the reaction resulted in no stereospecificity at all. That path E is unimportant is indicated by the fact that the acetylene XXVI is stable under the reaction conditions except for its reaction with silver acetate to form the silver salt. Thus the vinyl cation mechanism is the only reasonable one in the light of the above data and is also consistent with the observed



XLII

rearrangements, which are difficult to rationalize in terms of any other mechanism. It must be noted, however, that the rearranged products constitute only a small percentage of the total product mixture and taken alone would not be strong evidence for a vinyl cation as the principal intermediate.

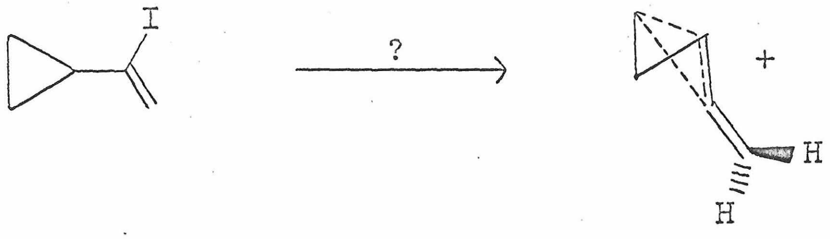
The mechanism in the silver nitrate-catalyzed solvolysis of XXIII is less clear. A vinyl cation probably is involved, but the reaction produces an equivalent of unbuffered nitric acid. Therefore path A may become predominant, the reaction becoming autocatalytic. This suggests a general note of caution regarding the use of the silver nitrate test in assessing the reactivity of vinyl halides. The silver nitrate test is generally useful with alkyl halides but there the system is not complicated by the possibility of the path A mechanism. The use of the silver salt of a weak acid such as acetic may be advisable when testing the reactivity of vinyl halides. The same criticism may be offered regarding the reaction of XXIII with silver tosylate in acetonitrile, but here the weakly basic solvent probably prevents path A from becoming important. The weak nucleophilicity of the tosylate anion argues against the importance of paths B, C, and D in this system. The vinyl tosylate obtained probably results from trapping of a vinyl cation by tosylate. A precedent is found in the work of Jones and Miller, who generated the 1,2,2-triphenylvinyl cation by decomposing a corresponding triazene with p-toluenesulfonic acid and obtained the vinyl tosylate in 20% yield (12).

One should also consider the possible involvement of silver complexes in these reactions. In a recent investigation no evidence was found for a stabilizing interaction between cyclopropanes and silver ion (43); such an interaction probably is not important in the above solvolyses. Silver ions are known to complex with olefins, but the formation of such a complex with vinyl iodide XXIII seemingly should retard ionization rather than accelerate it. Reversible formation of such complexes may well occur in this system, but it is unlikely that they are on the reaction coordinate leading to ionization and products.

Nature of the 1-Cyclopropylvinyl Cation.

Evidence for Cyclopropyl Stabilization. The apparent relative reactivities of 1-cyclopropylvinyl iodide (XXIII) and the model compound XXIV with silver catalysis show that the cyclopropyl group can dramatically accelerate the ionization of a vinyl iodide. One might reason that silver catalysis would attenuate the difference in reactivity between the two compounds, i.e., that their reactivities should differ even more in uncatalyzed solvolyses. Our efforts to measure the rate ratios for first-order reactivity of these compounds in aqueous methanol provided only a lower limit for the magnitude of acceleration. The data show that the tendency of XXIV to undergo a first-order solvolysis is so low that ultimately a second-order reaction intervenes involving triethylamine, perhaps as the base in an E2 elimination. Other workers have provided evidence that an E2 mechanism intervenes when trans elimination is possible and the vinyl cation that would form otherwise is not stabilized. This is true even with the remarkably facile triflate (trifluoromethanesulfonate) leaving group (44). Extrapolation of the Arrhenius plot for solvolysis of vinyl iodide XXIII to 233° allows one to calculate that even at this temperature the first-order rate ratio of XXIII to XXIV is at least 1.2×10^3. The actual value may be much higher.

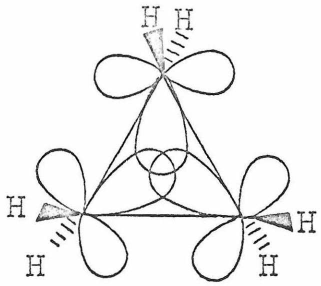
Source of Cyclopropyl Stabilization. Thus a cyclopropyl group accelerates ionization of a vinyl iodide just as it does that of saturated derivatives, and it is of interest to consider the factors that result in this acceleration. Perhaps some understanding of the factors that shape the phenomenon in the unsaturated case can be gleaned by considering examples from the mass of data and explanations that have resulted from studies of saturated cases. A fundamental question is whether the acceleration is principally a ground state effect or a transition state effect; i.e., relative to an acyclic model, does cyclopropyl substitution lower the energy barrier for ionization by increasing the energy content of the ground state molecule, or by decreasing the energy of the transition state. In that the cyclopropyl ring adds over 20 kcal of strain energy to the ground state, the possibility for a ground state effect is obvious. However, in order to be effective a portion of this strain energy must be lost in going to the transition state. The formation of mainly cyclopropyl products in the solvolyses of some saturated cyclopropyl derivatives has been used as evidence for the unimportance of the ground state effect (22b). The reasonable deduction involved here is that the ionization gives cyclic intermediates, and in turn, that the transition state for ionization is essentially cyclic and affords little strain relief. This reasoning can be applied equally well to the vinyl system involving XXIII, where cyclopropyl products account for greater than 95% of the product mixture under all of the conditions examined. Some strain relief might be expected if the ionization of vinyl iodide XXIII initially produced the bicyclobutonium-like ion XLIII (45, 28 1), but this apparently could not account for the minimum of 7.1 kcal/mole for the difference in free energies of activation required by the first-order rate ratio above.



XXIII XLIII

Furthermore, Wiberg and co-workers have reported cyclopropyl systems that are constrained so as to make the bicyclobutonium ion inaccessible. Nevertheless considerable acceleration is noted and the intermediate traps to give unrearranged cyclopropyl product (46). The ground-state strain effect fails to account for the influence of the cyclopropyl group on ionization rates.

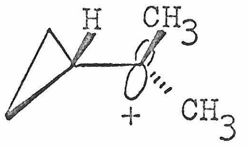
Among the factors which might be involved in a transition state effect is the electron-withdrawing inductive effect of the cyclopropyl group. Insight into the origin of this effect is provided by the Walsh model for cyclopropane (XLIV), in which the hybridization at carbon is represented as sp^2 (47). The sp^2 hybrid orbital used in bonding the cyclopropyl group to another atom is more electronegative than the sp^3 orbital used in bonding an acyclic alkyl substituent. With certain fixed geometries a cyclopropyl group can retard ionization rates in alkyl derivatives



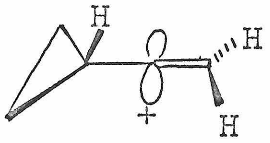
XLIV

remarkably (48). This suggests that a rate-retarding inductive effect is present in the ionization of XXIII and that in its absence an even greater acceleration would be observed. The Walsh model portrays the carbon-carbon bond as consisting of central overlap of three sp^2 hybrid orbitals and peripheral overlap of three p orbitals. This implies a high p character (effectively sp^5) in the carbon-carbon bonds and indicates that these bonds should be relatively electropositive. This is apparently the major source of acceleration and stabilization in cyclopropylcarbinyl systems.

Structure of the 1-Cyclopropylvinyl Cation. As might be expected, effective overlap is required for interaction with the electron-rich orbitals of the cyclopropyl group; this restricts the geometries of the transition states for ionization and of the intermediates as well. In the saturated series some cyclopropylcarbinyl cations are stable enough to allow direct nmr investigation in highly ionizing, non-nucleophilic solvents. In this way it was found that the cyclopropyldimethylcarbinyl cation prefers the "bisected" geometry shown in XLV (49a). This geometry optimizes the overlap between the empty p orbital and the bent cyclopropyl bonds. More recently the parent cyclopropylcarbinyl cation has been studied in the same way, and one interpretation of the nmr evidence is in terms of rapidly equilibrating ions analogous in structure to XLV (49b). By analogy, cation XXI may prefer the geometry shown in XLVI, and if this geometry is approached in the ionization the loss of rotational freedom in the transition state at least partially accounts for the low entropy of activation ($\Delta S^{\ddagger} = -20$ eu). Of course



XLV



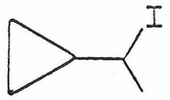
XLVI

the nmr evidence does not eliminate the possibility that XLV is merely the time average of two rapidly equilibrating bicyclobutonium ions, and such may also be the case with XLVI. However, nuclear motion is not necessary for stabilization by a cyclopropyl group; Traylor and co-workers have shown that stabilizing interactions with a cyclopropyl group can occur on the time scale of electronic excitation, which precludes significant nuclear motion (50). Nmr data on vinyl cation XXI would be desirable, but under the highly ionizing, non-nucleophilic conditions required for nmr studies of cations, the ions usually cascade into a most stable form unless the barriers to rearrangement are significant. The rearrangement of vinyl cation XXI to the 2-methylenecyclobutyl cation under solvolytic conditions is apparent from the products, and the small barrier involved in this rearrangement (vide infra) probably would not allow nmr observation of XXI; furthermore, although many unsaturated cations have been successfully generated for instrumental observation (49c), current techniques are not successful in all cases. For example, styrene polymerizes in antimony pentafluoride-fluorosulfonic acid, even at -60° (49d).

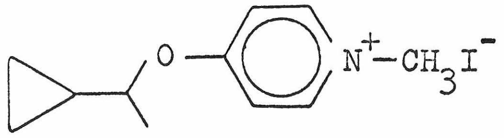
Some idea of the relative stabilities of ions XXI and XLIII, at least in the gas phase, could be obtained from quantum mechanical calculations. Some calculations of the extended Hückel type have been done on ion XXI. These predicted a preference for the geometry in XLVI over that of its 90° rotamer (51, 42b) and indicated that the species is more stable when the cationic center is linear (sp hybridized) than when it is bent (42b). No attempt was made to determine the relative energies of XXI and XLIII. Ideally this would require a detailed investigation of the energy surface in the vicinity of both ions, taking into account all degrees of freedom. Such a calculation, even with the extended Hückel approximation, would be expensive. Furthermore, semiempirical calculations that are considerably more refined than the extended Hückel method still tend to seriously overestimate the stability of bridged ions relative to the results of more accurate ab initio calculations (52), and detailed ab initio calculations on cations XXI and XLIII would be extremely expensive and difficult. Thus a reliable quantum mechanical estimate of the relative energies of XXI and XLIII seems to be beyond reach at the present. Our data do not indicate which of these species is obtained on ionization of XXIII, but the work of Kelsey and Bergman with the closely related vinyl iodides XLII suggests that if XLIII is the initial ion formed, it must rapidly relax to XXI or equilibrate with its enantiomer (42b). Also recent studies have supported the symmetrical, "bisected" structure as the first intermediate in solvolyses of saturated cyclopropylcarbinyl derivatives (53). In the absence of compelling evidence for XLIII it is assumed that the ion initially formed in the solvolyses of vinyl iodide XXIII is XXI, where that formulation is taken to represent a structurally classical, symmetric ion with electronic delocalization.

Stability of Vinyl versus Saturated Cations. The relative stability of analogous vinyl and alkyl cations is a point of interest, and thus a comparison of the solvolysis rate of vinyl iodide XXIII to that of cyclopropylmethylcarbinyl iodide (XLVII) would be desirable. However, cyclopropylmethylcarbinyl halides and esters, being difficult to purify and undergoing rearrangement readily, are poor substrates for kinetic study (54). The only directly related compound for which a rate constant has been obtained is N-methyl-4-(cyclopropylmethylcarbinyloxy)pyridinium iodide

(XLVIII), which hydrolyzes at 30° with a first-order rate constant of 0.16 hr^{-1} (54). An effort to obtain a meaningful rate ratio from XXIII and XLVIII would require presumptuous corrections for differences in leaving group, solvent, and temperature and therefore is not justified. In other systems it has been possible to obtain rate ratios for analogous vinyl and alkyl cations and these seem to be relatively insensitive to substituents. For example, the relative rates of cis-2-buten-2-yl tosylate and 2-butyl tosylate in aqueous methano (55) and of 1,2,2-triphenylvinyl tosylate and 1,2,2-triphenylethyl tosylate in acetic acid (56) have been determined. In each case the rate of the alkyl derivative is about 10^6 times that of its vinyl analog. It follows that in the absence of complications, such as ion-pair return, iodide XLVII would be expected to solvolyze at a much higher rate than vinyl iodide XXIII. Nevertheless it must be noted that these rate ratios may be only a partial reflection of the relative stabilities of the respective ions. In rate measurements, differences in ground state



XLVII



XLVIII

energies, ease of solvation, and degree to which the transition state resembles the intermediate may be superimposed on the difference in inherent cationic stability. As an example of ground state effects, the possibility that the carbon-halogen bond in vinyl halides is unusually strong due to resonance effects or to the sp^2 hybridization at carbon has been discussed (17,57,58).

A better indication of the inherent relative stability of simple vinyl and alkyl cations is found in hydride affinities, given in Table IV. These suggest that the unsubstituted vinyl cation is less stable than the ethyl cation but more stable than the methyl cation. Accordingly, vinyl cation XXI may be closer in stability to the cyclopropylmethylcarbinyl cation than to the cyclopropylcarbinyl cation. The use of hydride affinities as a measure of cation stability avoids the problem of unknown relative solvation energies, but the method is still open to criticism on the grounds that it includes unknown ground state differences. Hydride affinities reflect not only the relative stabilities of the cations but also the relative strengths of the respective carbon-hydrogen bonds (vinyl carbon-hydrogen bonds are apparently stronger than aliphatic carbon-hydrogen bonds (60)). This suggests that the electron affinities of the cations, or conversely the ionization potentials of the corresponding radicals, would be a better measure of the relative intrinsic stabilities of the cations. This measure

Table IV. Hydride Affinities[a] for Some Simple Cations[b,e]

Cation	$-\Delta H$ (kcal/mol)
CH_3^+ [d]	312
$C_2H_3^+$ [c]	290
$C_2H_5^+$ [d]	272
$C_6H_5^+$ [c]	298
$PhCH_2^+$ [c]	237

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[a] ΔH for the reaction $R^+ + H^- \longrightarrow RH$ in the gas phase; calculated from $\Delta H = \Delta H_f(R^+) + \Delta H_f(H^-) - \Delta H_f(RH)$.

[b] Heats of formation of hydride anion (33 kcal/mol) and the hydrocarbons were taken from ref 59a.

[c] Heat of formation of the cation was taken from ref 59a.

[d] Heat of formation of the cation was taken from ref 59b.

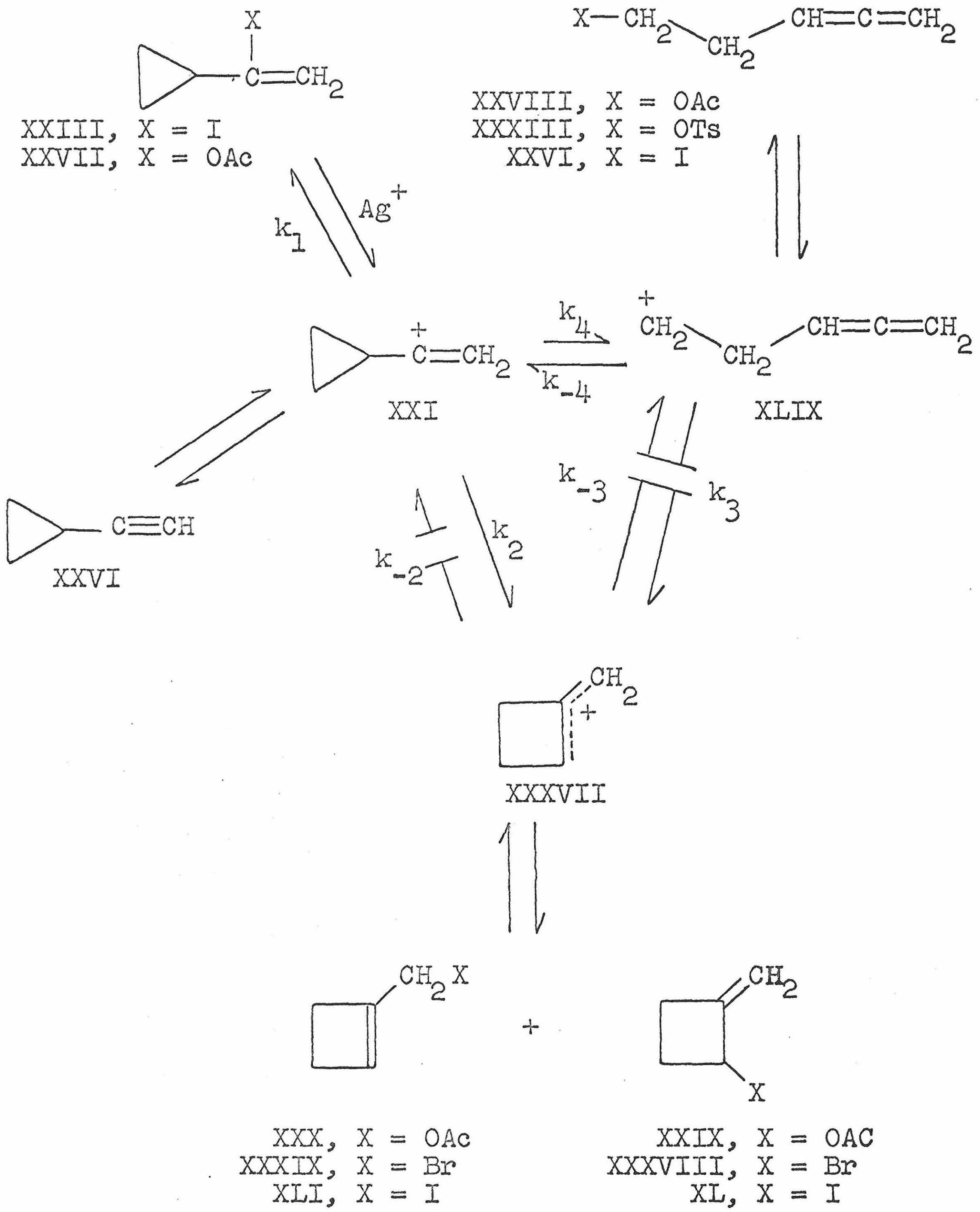
[e] We are grateful to Dr. J. L. Beauchamp for helpful discussions on hydride affinities.

was chosen by Miller and Kaufman, who pointed out that the ionization potential of the vinyl radical is 0.7 ev (16 kcal/mol) greater than that of the ethyl radical (61). Based on this value, alkyl derivatives should solvolyze $10^{8.6}$ times as fast as their vinyl counterparts at 130°, which reasonably corresponds to the observed value of about 10^{6} (55). The somewhat greater difference between the hydride affinities (18 kcal/mol) would predict a difference in solvolysis rates of $10^{9.7}$ at 130°. However, it is the difference in hydride affinities that should correlate better with solvolysis rates, since a solvolysis rate is more closely related to the energy difference between a cation and a corresponding ground state molecule than to the energy difference between a cation and its corresponding radical. This suggests that vinyl cations may be more highly solvated than their alkyl counterparts, which provides another rationale for the low entropy of activation seen in the solvolysis of vinyl iodide XXIII and some other vinyl derivatives (56, 61).

Nature of the Rearrangements.

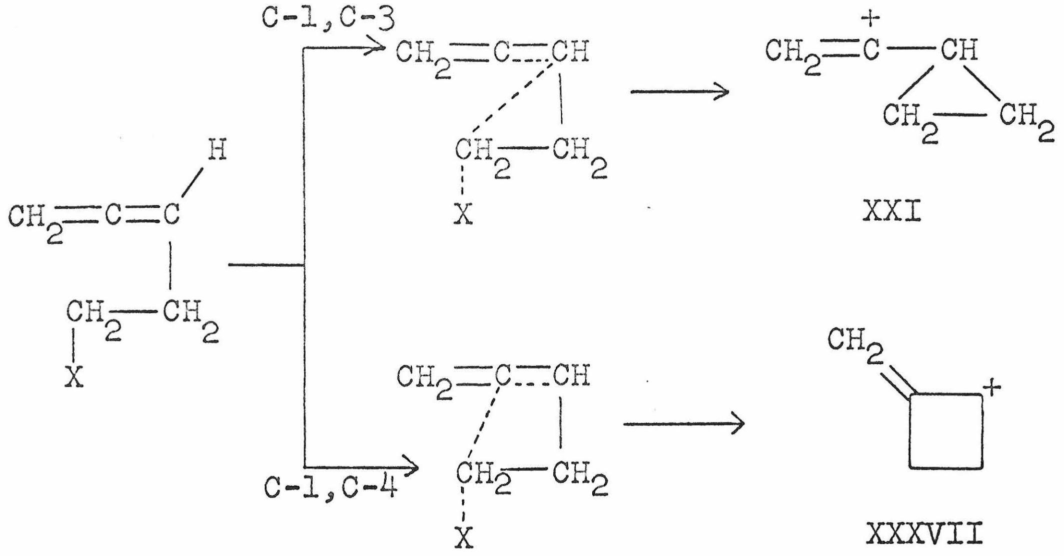
The mechanistic pathways that apparently are important in the 1-cyclopropylvinyl cation system in acetic acid are summarized in Figure 7. The catalyzed ionization of vinyl iodide XXIII produces initially the 1-cyclopropylvinyl cation (XXI), most of which either is trapped to give the

Figure 7. Mechanistic pathways in the 1-cyclopropylvinyl cation system in acetic acid.



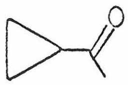
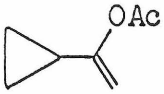
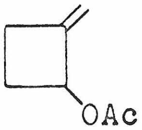
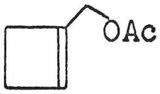
unstable enol acetate XXVII or loses a proton to give the acetylene XXVI. A smaller fraction of cation XXI competitively rearranges to the 2-methylenecyclobutyl cation XXXVII, which is trapped to give acetates XXIX and XXX. Also a small fraction of XXI ultimately results in the formation of acetate XXVIII. Whether this involves the indicated rearrangement to the primary cation XLIX or nucleophilic attack on the ring methylene carbons of XXI to give XXVIII directly is open to speculation. Since there is ample kinetic evidence for participation of the allenyl moiety in the solvolysis of 3,4-pentadien-1-yl derivatives (9b,28 l), direct attack on XXI to give acetate XXVIII seems quite reasonable; the latter process is essentially the microscopic reverse of the former. The solvolyses of the cyclobutyl substrates, bromides XXXVIII and XXXIX and iodides XL and XLI, give only the cyclobutyl products XXIX and XXX, which indicates that the rate constants for rearrangement of the 2-methylenecyclobutyl cation (XXXVII) are experimentally insignificant.

A priori, homoallenyl participation in the solvolysis of 3,4-pentadien-1-yl derivatives, or cyclization of the possible intermediate XLIX, could be thought to proceed by one or both of two paths. The decisive interaction could occur between the primary carbon and the third carbon of the chain (path C-1,C-3) to give ion XXI or between the primary carbon and the central carbon of the allene (path C-1,C-4) to give ion XXXVII. Since rearrangement of vinyl cation XXI



to methylenecyclobutyl cation XXXVII occurs to only a small extent and rearrangement of XXXVII to XXI is virtually nonexistent, the product distribution obtained on solvolysis of 3,4-pentadien-1-yl derivatives should reflect the extent to which each pathway is taken in the cyclization. The major difference between the product distributions from iodides XXIII and XXXVI (Table I, page 24) is the larger amount of homoallenyl acetate (XXVIII) obtained from XXVI, which presumably is the result of direct displacement. The more important comparison is of the relative amounts of cyclopropyl and cyclobutyl products that are obtained from each substrate. The pertinent percentages, taken from Table I, and the calculated ratios are presented in Table V. Because the accuracy with which we could determine the denominators (which represent only about 1% of the product mixtures) is limiting, the values obtained probably are equal within

Table V. Profile of Cyclized Acetate Products Formed in Cyclopropylvinyl and Homoallenyl Systems.[a]

Substrate	Conditions	Products (%)		$\frac{XXII + XXVII}{XXIX + XXX}$
		 XXII +  XXVII	 XXIX +  XXX	
3,4-pentadien-1-yl tosylate (XXXIII)	HOAc NaOAc 100°	55.9	5.05	11
3,4-pentadien-1-yl iodide (XXXVI)	HOAc AgOAc 25°	64.0[b]	1.35	47.4
1-cyclopropylvinyl iodide (XXIII)	HOAc AgOAc 25°	65.8[c]	1.28	51.4

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[a] Ethynylcyclopropane (XXVI) is not included in these ratios because its percentage was measured only indirectly.

[b] From the reaction time allowed and the observed rate of XXVII to XXII conversion at 25°, it may be estimated that at least 2.5 of the 4.8% XXII observed came from XXVII. Only this amount is included.

[c] Corrected for the amount of XXII which apparently is not derived from XXVII.

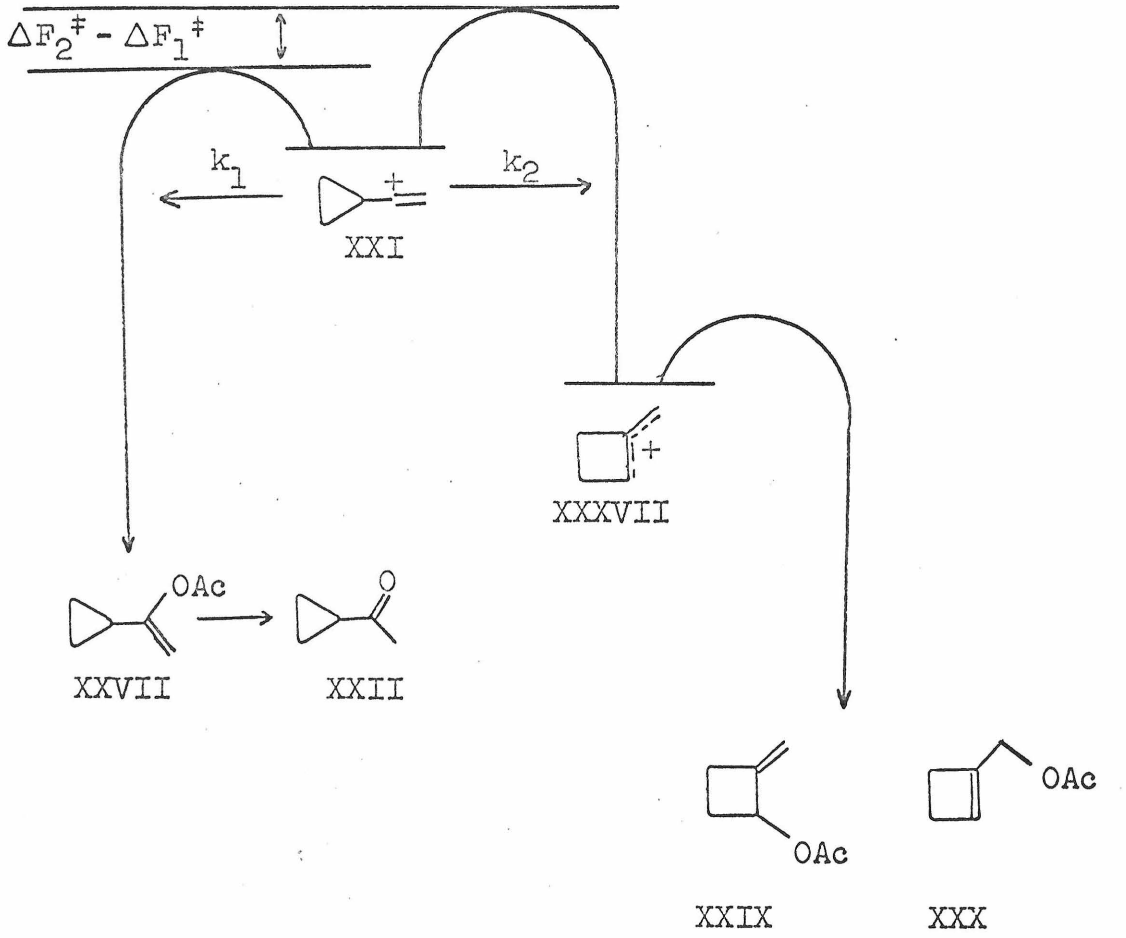
experimental error. However, because cation XXXVII gives only cyclobutyl products, the cyclized product ratios provide such a sensitive test for the C-1,C-4 pathway that a strong conclusion still may be drawn from the data. For example, if in the solvolysis of iodide XXXVI only 0.5% of the cyclized products resulted from the C-1,C-4 pathway and the remainder from the C-1,C-3 pathway, the expected value for the product ratio would be only 36.4, which is far smaller than the observed value of 47.4. We therefore can say with some confidence that less than 0.5% of the C-1,C-4 pathway is required to explain the silver-catalyzed solvolytic behavior of homoallenyl iodide XXXVI.

If one can assume that the rates for solvent trapping of XXI and XXXVII are comparable, then the product distributions show that XXXVII is the more stable ion in that its rearrangement to XXI is undetectable whereas some rearrangement of XXI to XXXVII is observed. This energetic relationship is presented in Figure 8. For entry into the system from XXI, the ratio of cyclopropyl to cyclobutyl products should be given by the following equation:

$$\frac{[\mathrm{XXVII} + \mathrm{XXII}]}{[\mathrm{XXIX} + \mathrm{XXX}]} = \frac{k_1[\mathrm{HOAc}]}{k_2} = [\mathrm{HOAc}]\, e^{(\Delta F_2^{\ddagger} - \Delta F_1^{\ddagger})/RT}$$

$$= [\mathrm{HOAc}]\, e^{(\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger})/R}\, e^{(\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger})/RT} \qquad \text{eq 1}$$

Figure 8. Thermodynamic relationships governing the fate of the 1-cyclopropylvinyl and 2-methylenecyclobutyl cations.



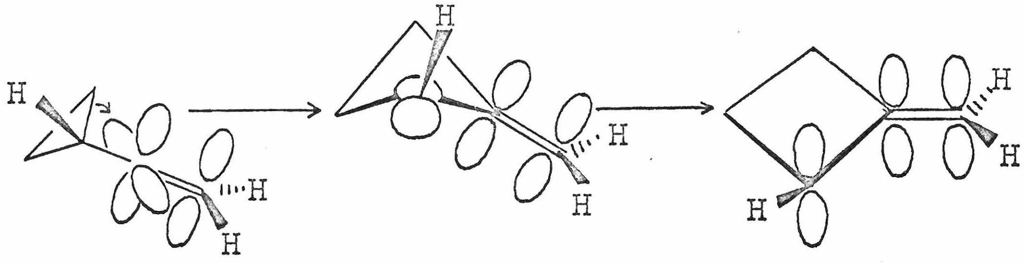
Thus it is seen that the natural logarithm of the product ratio should be a linear function of the reciprocal of temperature:

$$\ln\frac{[\mathrm{XXVII} + \mathrm{XXII}]}{[\mathrm{XXIX} + \mathrm{XXX}]} = \ln[\mathrm{HOAc}] + (\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger})/R + (\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger})/RT \qquad \text{eq 2}$$

A plot (Figure 5, page 40) based on the temperature dependence data in Table III is reasonably linear and from its slope the value of $\Delta H_2 - \Delta H_1$ is calculated to be 2.2 kcal/mol; i.e., the activation energy required for rearrangement of XXI to XXXVII exceeds that required for solvent trapping by 2.2 kcal/mol.

Knowledge concerning the rates of solvent trapping of carbonium ions is scanty. Although the trapping rates of extraordinarily stable cations, such as the triphenylcarbonium ion, have been measured directly (62), no similar feat has been accomplished with cations of normal stability. For the 2-norbornyl cation, Winstein has estimated a pseudo-first-order trapping rate of 10^9 $\sec^{-1}$ (63) and Berson et al. have calculated a minimum value of 4.65 kcal/mol for the energy of activation for trapping (64). If a comparable energy is required in trapping XXI, then the rearrangement barrier associated with k_2 would be over 6 kcal/mol. Examination of the geometries involved in the rearrangement suggests a rationale for this barrier. One might envision

L, in which ring expansion has occurred but not relaxation to the planar form XXXVII, to be approximately the transition state in the rearrangement of XXI to XXXVII. The strain energy of L is probably comparable to that in XXI, but delocalization of the positive charge may be less effective since the symmetry in XXI has been lost while the allylic delocalization has not yet been gained; the empty p orbital is nearly orthogonal to the π cloud of the double bond.

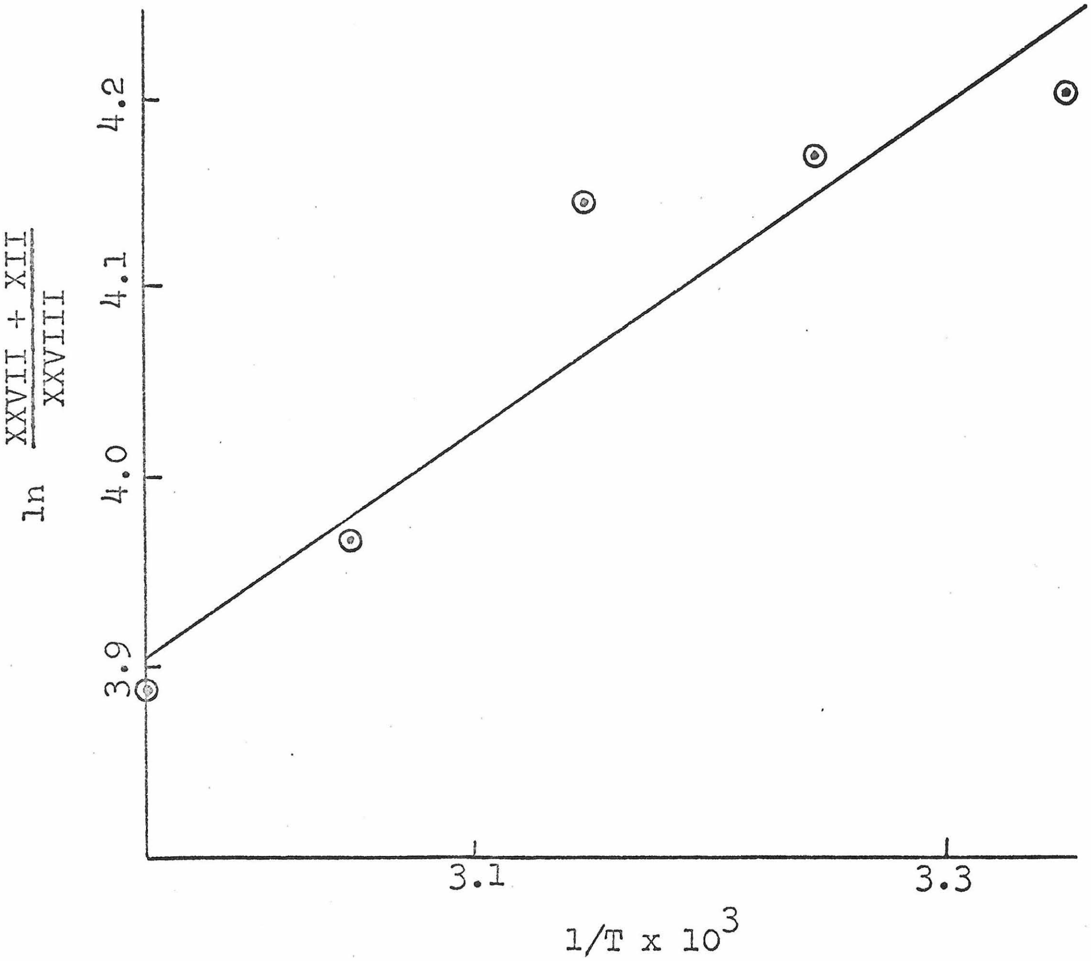


XXI L XXXVII

Calculation of the entropic parameter from the intercept of the plot in Figure 7 and the relationship expressed in equation 2 is complicated by the need to express the concentration of acetic acid. With reference to the usual standard state (65), concentration may be expressed in mol/cc and $\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger}$ is found to be 8.5 eu. Seemingly, the transition state for rearrangement could not be significantly more ordered than the highly ordered intermediate XXI (assuming restricted rotation in XXI); neither would one expect large changes in the entropy of the solvent shell during the rearrangement. Therefore, since it is difficult to see why the entropic activation parameter for rearrangement should be significantly negative, the corresponding parameter for solvent trapping is apparently positive. The latter circumstance might stem from significant loss of electrostriction in the solvation shell during solvent trapping.

The product data in Table III (page 39) show a similar increase in the proportion of the homoallenyl acetate XXVIII at higher reaction temperatures, and a similar numerical treatment may be applied. A somewhat less linear plot is obtained (Figure 9), and its significance in this case is much less clear. If acetate XXVIII is formed via intermediate XLIX, as is indicated in Figure 7 (page 59), the recyclization of XLIX probably is competitive with solvent trapping, in which case equations 1 and 2 would no longer apply. On the other hand, if acetate XXVIII is formed by a direct solvent attack on vinyl cation XXI, then its formation would be irreversible and directly competitive with solvent trapping of XXI to give cyclopropyl products. In this case equations 1 and 2 would apply with the exception that the concentration of solvent would no longer appear, because both reactions are pseudo-first-order. In terms of this assumption, the enthalpy of activation for trapping at a ring methylene carbon exceeds that for trapping at the vinyl

Figure 9. Log of cyclopropyl to homoallenyl product ratio versus the reciprocal of temperature for silver-catalyzed acetolysis of 1-cyclopropylvinyl iodide (XXIII).

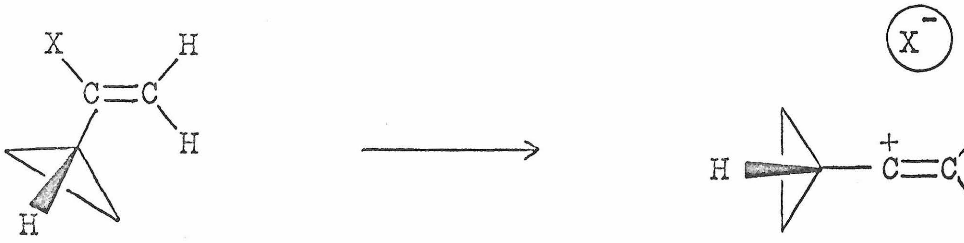


cationic center by 1.6 kcal/mol, and trapping at the vinyl cationic center is favored entropically by 2.9 eu.

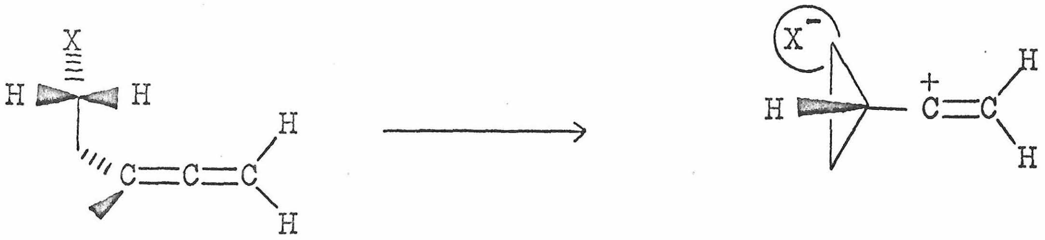
The ratio of cyclopropyl to cyclobutyl products expected at 100° can be calculated from equation 2 and the measured values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ to be 24.2, whereas the ratio obtained in the acetolysis of tosylate XXXIII at 100° was 11 (Table V, page 62). Apparently the major reason for the lower ratio obtained from the tosylate at 100° as compared with those obtained from iodides XXIII and XXXVI at 25° is the temperature effect; other factors which may account for the rest of the observed difference were mentioned on page 29.

The data in Table II (page 35) show that the ratio of 2-methylenecyclobutyl acetate (XXIX) to 1-cyclobutenylcarbinyl acetate (XXX) obtained in the products depends on the substrate solvolyzed. In solvolyses of vinyl iodide XXIII and homoallenyl iodide XXXVI these products are obtained in the same ratio within experimental error, this ratio being about 8.7, whereas solvolyses of bromides XXXVIII and XXXIX result in ratios of 2.6 and 0.96 respectively. The major difference seems to be associated with whether the presumed intermediate, 2-methylenecyclobutyl cation (XXXVII) is produced on rearrangement of vinyl cation XXI or is produced directly, as in the solvolyses of the cyclobutyl derivatives. Berson and co-workers have observed such "memory effects" in other systems and have discussed in detail a number of factors which may be responsible, including ion pairs, assymetric solvation, conformational barriers in intermediates , and non-classical ions (66). In the present case the product ratio obtained from solvolysis of the equilibrium mixture of iodides XL and XLI is intermediate between those obtained with the isomeric bromides, which shows that the principal difference is not merely due to an element effect.

In attempting to explain the observed differences in product ratios one is tempted to designate one set of ratios as "normal" and the other as "unusual". The ratios obtained from the allylic bromides are normal in the sense of showing the order typical of allylic solvolysis products. Such allylic "product spreads" are well documented and invariably involve a greater proportion of product with the nucleophile bound to the primary center when the solvolyzed substrate is a derivative of the primary alcohol. The same trend has been noted even in silver-catalyzed solvolyses, although to a lesser extent (67). One might prefer to take as "normal" the natural trapping ratio for the dissociated, planar ion XXXVII.In this sense the ratios obtained from bromides XXXVIII and XXXIX obviously cannot both be "normal" since they are far from identical. Among the factors which might keep the 2-methylenecyclobutyl ion obtained by rearrangement from giving the natural ratio are ion-pair effects. However, as illustrated below the anions in the hypothetical ion pairs which might be formed in solvolyses of XXIII and XXXVI would be in very different orientations relative to the cation XXI. If the anion is present and influences the product distributions at all, one might expect its influence to be different according to its orientation. Thus the nearly identical product ratios obtained from XXIII and XXXVI may be taken as evidence that ion pairs are not important in these systems. Then one possibility is that the rearrangement of XXI provides the planar, dissociated 2-methylenecyclobutyl cation, in which case the observed product ratio of 8.6 would be the natural trapping ratio for this species, and the "unusual" product ratios obtained with bromides XXXVIII and XXXIX could be explained in terms of ion pairs or mixed mechanisms.



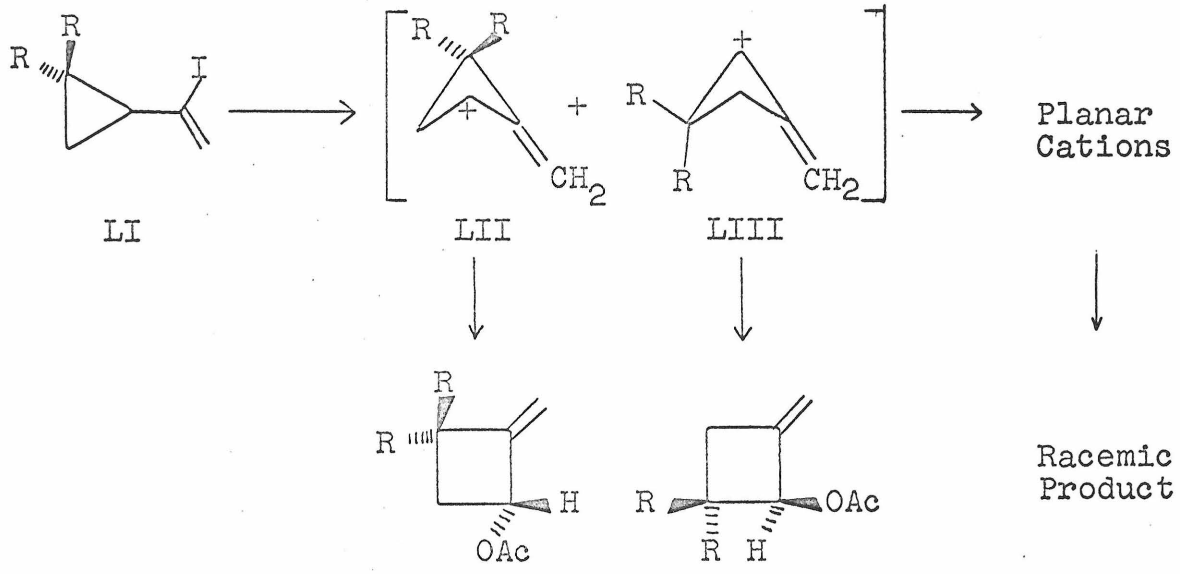
XXIII XXI



XXXVI XXI

On the other hand, it is possible that the product ratio from bromide XXXVIII is the natural ratio for the free cation, and the greater proportion of primary acetate obtained from bromide XXXIX might be the result of a competitive direct displacement. This explanation has been offered for product spreads in other allylic systems (67). If this explanation is true, we must seek a reasonable explanation, which does not involve ion pairs, for the unusual product ratio obtained from the rearrangement entry to ion XXXVII. The rearrangement of XXI to XXXVII must involve at some point a structure similar to L (page 66). If there were some energy barrier associated with the relaxation of L to the planar ion XXXVII, then L might have the status of an intermediate. As such it might be trapped by solvent in competition with its relaxation. One possible source of such a barrier might be residual delocalization of the migrated σ bond, in which case L might be better formulated as the methylenebicyclobutonium ion XLIII. The intermediate L should trap exclusively at the secondary center, since delocalization of positive charge to the primary position is precluded by the orthogonal orientation. Under the above assumptions, including the assumption that the natural product ratio from XXXVII is 2.6, it can be calculated from the observed product ratio of 8.6 that 63% of L is trapped before it can relax to XXXVII.

The inherently lower symmetry of L as compared to XXXVII suggests an experimental test for this mechanism. If an optically active substituted 1-cyclopropylvinyl iodide (LI) were solvolyzed, the dissymmetric intermediates LII and LIII might intervene. Solvent trapping of these intermediates should occur preferentially on the less hindered "<u>exo</u>-" side (an analogous trapping stereospecificity in the cyclobutyl cation was demonstrated recently (53b)). To the extent that trapping rates of these intermediates were competitive with relaxation to the planar cations, the illustrated enantiomers of the structurally isomeric secondary acetates should predominate.



In conclusion we wish to acknowledge that Michael Hanack and Tilmann Bässler have conducted a similar investigation of 1-cyclopropylvinyl chloride and we thank them for an exchange of information prior to publication (68). In addition it should be noted that many papers dealing with vinyl cations have appeared since the inception of our work, and not all of these have been cited above. References to most of these may be found in a recent review (69).

IV. EXPERIMENTAL

General

Acetic acid (DuPont reagent) was purified by refluxing 500 ml with 10 ml of acetic anhydride and 25 g of chromic oxide for 2 hr and then fractionally distilling under nitrogen. Silver acetate (J. T. Baker, purified) was purified by stirring 5 g in 75 ml of 20% acetic anhydride in acetic acid for 12 hr at 110°. The liquid was decanted and after drying for 4 hr at 85° and 0.05 mm the solid was transferred to an oven dried bottle in a nitrogen dry-bag. All boiling points are uncorrected. Infrared (ir) spectra were determined on a Perkin-Elmer IR 257 instrument, as approximately 10% solutions in carbon tetrachloride unless otherwise indicated. Proton nuclear magnetic resonance (nmr) spectra were obtained on a Varian A60-A spectrometer; carbon tetrachloride was the solvent and chemical shifts are reported in ppm downfield from tetramethylsilane. Carbon-13 nmr spectra were recorded on a Varian DSF-60 spectrometer; dioxane was the solvent and chemical shifts are reported in ppm upfield from carbon disulfide. Mass spectra were obtained on a CEC-21-103C instrument at 10 μa ionizing current and 70 v ionizing potential; the inlet temperature was 250°. Elemental analyses were performed by Spang Microanalytical Lab., Ann Arbor, Michigan, unless otherwise noted. Qualitative and preparative vapor phase chromatography (glc) was carried out on Varian Aerograph 90-P3 instruments. Quantitative analytical vpc was carried out on a Hewlett-Packard 5750 (flame ionization detector) equipped with a Disc integrator. The following columns were used: column A, 8 ft x 3/8 in. 5% SE-30 on 60/80 Chromosorb P; column B, 21 ft x 1/4 in. 15% Carbowax 20M on 60/80 Chromosorb P; column C, 12 ft x 1/4 in. 20% Carbowax 20M on 60/80 Chromosorb P; column D, 12 ft x 1/4 in. 8% SE-30 on 60/80 Chromosorb P; column E, 5 ft x 1/4 in. 3% SE-30 on 100/120 Varaport 30; column F, 12 ft x 1/8 in. 15% Carbowax 20M on 100/120 Chromosorb WAWDMCS; column G, 12 ft x 1/8 in. 15% TCEP on 100/120 Chromosorb WAWDMCS; column H, 6 ft x 1/8 in. 10% UCC-W98 on Chromosorb WAWDMCS; column I, 20 ft x 3/8 in. 30% Carbowax 20M on 60/80 Chromosorb P; column J, 10 ft x 1/4 in. 20% SE-30 on 60/80 Chromosorb P.

Syntheses

1-Cyclopropylvinyl Iodide (XXIII). Cyclopropyl methyl ketone (XXII) (Aldrich) was treated with hydrazine hydrate to obtain the hydrazone (70), which was converted to the desired iodide by the general procedure of Barton *et al.* (23) as follows: In a 1-l. round-bottomed flask, 14 g of the hydrazone and 140 ml of triethylamine were dissolved in 350 ml of tetrahydrofuran (THF). While stirring this solution magnetically and cooling it in an ice bath, a solution of 70 g of iodine in 280 ml of THF was added dropwise from an unstoppered pressure-equalizing addition funnel until a red color persisted. Sodium thiosulfate (0.5 g in 100 ml of water) was added and then the reaction mixture was poured into 2000 ml of ice water, followed by extraction with 1 x 150 ml and 2 x 75 ml of pentane. The combined pentane solution was washed with 1000 ml of ice water, 2 x 175 ml of 1 N HCl, 500 ml of ice water, 250 ml of saturated aqueous sodium bicarbonate, and 500 ml of water. After drying over sodium sulfate, most of the pentane was removed by distillation through a Vigreux column under nitrogen at atmospheric pressure. The crude product was distilled under pump vacuum into a dry ice-cooled receiver and was obtained in pure form by preparative gas-liquid chromatography (glc) on column A at 90° in a yield of 5.7 g (about 20% when roughly corrected for impurities in the hydrazone). The colorless iodide slowly became red even when stored at -10°; so samples were freshly purified by glc on column C at 140° for critical applications such as kinetics and quantitative product determinations.

The nmr spectrum of the pure iodide showed a vinyl proton triplet (1H) at 6.3 ppm, a vinyl proton broad singlet (1H) at 5.9 ppm, a cyclopropyl methine multiplet (1H) from 1.5-2.0 ppm, and a cyclopropyl methylene multiplet (4H) from 0.75 to 1.1 ppm. The infrared spectrum showed absorptions at 3090, 3015, 1620, and 1605 cm^{-1}, and the mass spectrum exhibited a parent peak at m/e 194 and a base peak at m/e 67. *Anal*. Calcd for C_5H_7I: C, 30.95; H, 3.64; I, 65.41. Found: C, 30.96; H, 3.66; I, 65.28.

1-Isopropyl-1-iodoethylene (XXIV). The conversion of isopropyl methyl ketone (Matheson Coleman and Bell) to the hydrazone has been reported (71). A 250 ml round-bottomed flask was charged with 100 ml of triethylamine and 3.64 g of the crude hydrazone (contaminated with 36% ethanol according to nmr). The solution was stirred magnetically and cooled in ice while 12.5 g of iodine in 50 ml of THF (distilled from LAH) was added over a period of about 5 min from an unstoppered, pressure-equalizing addition funnel. After stirring 1 hr at room temperature, the mixture was poured into 400 ml of ice and water and extracted with 100 ml of pentane. The pentane solution was washed with 4 x 100 ml of cold 1 N HCl; during the fourth wash the color of the solution turned from yellow to orange. The pentane was then washed with 100 ml of saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. The concentrate was distilled for 1 hr under pump vacuum at room temperature into a dry ice-cooled receiver. The pot residue was a red viscous liquid the nmr of which indicated only a trace of olefin.

The distillate was analyzed on column I at 190°. Four major components were observed: first component, 4.5%; second component, 10.1% (retention time of starting ketone);

third component, 62%; fourth component, 23.5%. The third and fourth components were isolated by preparative glc on the same column. The third component was identified as XXIV. Its infrared spectrum exhibited bands at 2965, 2930, 2880, 1615, and 898 cm^{-1}. The mass spectrum gave a parent peak at m/e 196. The nmr spectrum indicated a vinyl proton as an apparent triplet at 6.05 ppm, a vinyl proton doublet at 5.62 ppm (1H, J = 1.5 Hz), a methine proton septet (1H, J = 6.5 Hz) from 1.77 to 2.55 ppm, and a methyl doublet centered at about 1.04 ppm (6H, J = 6.5 Hz). Also observed in the spectrum was a small singlet (0.34H) at 3.58 ppm which could be attributed to column bleed (the nmr spectrum of Carbowas 20M is a singlet at 3.58 ppm). Analytical samples could be obtained by preparative glc on column D at 140°. *Anal.* Calcd for C_5H_9I: C, 30.64; H, 4.63; I, 64.74. Found: C, 30.59; H, 4.63; I, 64,66. The fourth component was apparently 3-methyl-2-iodo-2-butene. Its infrared spectrum exhibited bands at 2190, 2850, 1645, 1440, 1375, 1210, 1057, and 880 cm^{-1}. The nmr spectrum displayed a very poorly resolved methyl quartet at 2.47 ppm (3H) and a total of six protons as a multiplet at about 1.90 ppm partly overlapping a broad singlet at 1.80 ppm. The total yield of the vinyl iodides after glc isolation was 15.3%.

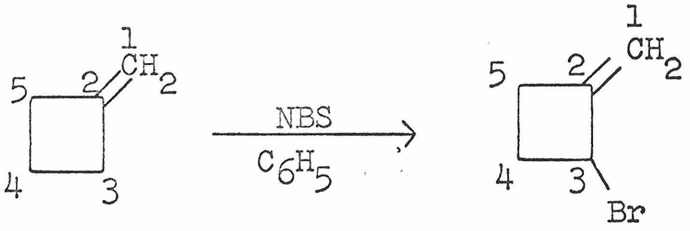
2-Penten-4-yn-1-ol (XXXV). The procedure of Hanack and Häffner (9b) was modified by the use of lithium acetylide-ethylenediamine in place of sodium acetylide. A 500 ml three-necked flask was equipped with a pressure-equalizing addition funnel, an adapter with a thermometer and gas inlet tube, a drying tube, and a magnetic spin bar. After purging the flask with nitrogen it was charged with 200 ml of dimethyl sulfoxide (distilled from calcium hydride) and 70.3 g (0.74 mol) of lithium acetylide-ethylenediamine (Foote Mineral Co.). While stirring and cooling externally as needed to keep the reaction temperature from 30-35°, 34.2 g (0.37 mol) of freshly distilled epichlorohydrin was added dropwise over a period of 2 hr. The reaction mixture was then heated for 1/2 hr at 40° and poured into 1 l. of ice and water. After extraction with 3 x 400 ml of ether, the combined ether solution was washed with 2 x 200 ml of saturated sodium chloride solution, dried over sodium sulfate, and concentrated on a rotary evaporator. Distillation through a short Vigreux column (58° at 5 mm; lit., 65-66° at 12 mm) gave 14.8 g of a clear liquid the infrared and nmr spectra of which were appropriate for a mixture of the cis and trans isomers of XXXV but suggested the presence of an impurity. Glc analysis on column F showed that the desired cis and trans isomers comprised 89% of the sample and that there was an 11% impurity. The yield corrected for the impurity was 49%.

3,4-Pentadien-1-ol (XXXIV). A 500 ml three-necked flask equipped with a pressure-equalizing addition funnel, a cold water condenser with a drying tube, and a magnetic spin bar, was charged with 5.8 g of lithium aluminum hydride (LAH) and 100 ml of dry ether (distilled from LAH). A solution of 12.6 g of alcohol XXXV (89% pure, vide supra) in 125 ml of dry ether was added dropwise to the stirred reaction mixture over a period of 1 hr. The mixture was then heated under reflux for 18 hr. The excess LAH was decomposed by dropwise addition of saturated aqueous sodium sulfate and the ether layer was separated, dried over sodium sulfate, and concentrated on a rotary evaporator. Distillation of the concentrate through a short Vigreux column (57° at 10mm; lit. 52-53° at 10.5 mm (28 1) gave 10.9 g of a colorless liquid which was 90% pure by glc analysis on column F. The infrared and nmr spectra of this sample agreed with those reported except for apparent impurity (a weak infrared band at 3310 cm^{-1} suggested some acetylene). Pure samples of XXXIV and of the major impurity were isolated by preparative glc on column C. The impurity showed absorption at 3640 and 3310 cm^{-1} in its infrared spectrum; it is probably 4-pentyn-1-ol. A second impurity of considerably longer retention time was not further examined. The yield corrected for impurities was about 85%.

3,4-Pentadien-1-yl Tosylate (XXXIII). The tosylate XXXIII was obtained by conventional means through the reaction of the alcohol XXXIV with tosyl chloride in pyridine (dried over molecular sieves) at -10°. When the tosylate was prepared from 90% pure XXXIV (vide supra) the infrared and nmr spectra were in general accord with those reported (28 l) but impurity was apparent even after two recrystallizations from pentane. This impure tosylate was used only for preparative solvolyses. For quantitative product studies pure tosylate was prepared from glc purified XXXIV.

3,4-Pentadien-1-yl Iodide (XXXVI). Triphenylphosphite (J.T. Baker) was purified by dissolving it in ether, washing with 2 M sodium hydroxide and saturated aqueous sodium chloride, and drying for 2 hr over magnesium sulfate with stirring. The ether was then removed on a rotary evaporator at about 50° for 2 hr. A 250 ml three-necked flask equipped with a magnetic stir bar, a gas inlet tube, a pressure-equalizing addition funnel, and a reflux condenser with a drying tube was charged with 16 g of purified triphenylphosphite and 16 g of methyl iodide and was heated while stirring under a nitrogen atmosphere in an oil bath. The bath temperature was kept at 70° for 10 hr, brought to 120° over a period of 5 hr, and kept at 120° for 3 hr. The mixture was cooled in ice and 50 ml of DMSO (dried over molecular sieves and distilled from calcium oxide) was added; a bright red color resulted. A solution of 3 g of XXXIV (90% pure) in 20 ml of DMSO was added dropwise to the reaction mixture while stirring and cooling in ice. After stirring at room temperature for 12 hr, the reaction mixture was partitioned between 500 ml of water and 100 ml of pentane, and the separated pentane solution was washed with 3 x 150 ml of 2 M sodium hydroxide, 3 x 150 ml of water, and 1 x 150 ml of saturated sodium chloride and was dried over magnesium sulfate. The pentane was removed on a rotary evaporator and the product was flash distilled at 0.1 mm with a heat gun into a dry ice-cooled receiver; 1.35 g of a colorless liquid was obtained which was 96% pure by glc analysis on column H at 100°. Attempted analysis on column F at 160° resulted in almost total decomposition of the sample. The yield corrected for impurities was about 25%; a better yield might have been obtained if dimethylformamide had been used instead of DMSO (42b). Pure samples of iodide XXXVI were obtained as needed by preparative glc on column E at 75°. The nmr spectrum of the pure iodide showed vinyl multiplets at 4.82 to 5.35 ppm (1H) and 4.50 to 4.82 ppm (2H), a perturbed triplet (J = 7 Hz) at about 3.15 ppm (2H) due to the iodomethylene protons, and a methylene multiplet at 2.15 to 2.92 ppm (2H). The infrared spectrum showed absorptions at 3060, 3000-2800, 1954, 1425, 1245, 1235, 1170, and 850 cm^{-1}. The mass spectrum gave a parent peak at m/e 194. Anal. Calcd for C_5H_7I: C, 30.95; H, 3.64. Found: C, 30.79; H, 3.49.

2-Methylenecyclobutyl Bromide (XXXVIII) and 1-Cyclobutenylcarbinyl Bromide (XXXIX). In accord with the method of Buchman and Howton (34), bromides XXXVIII and XXXIX were prepared by the benzoyl peroxide-catalyzed reaction of methylene-cyclobutane with N-bromosuccinimide in benzene. Distillation of the product through a 12 cm vacuum-jacketed Vigreux column gave a colorless liquid which was 83% XXXVIII by analysis on column H; the major impurity was benzene. The 60 MHz nmr spectrum of this sample showed a complex multiplet from 2.0 to 2.9 ppm (4H), a multiplet from 4.6 to 5.1 ppm (3H) roughly consisting of a two proton multiplet centered at about 4.83 ppm and a one proton multiplet centered at about 5.0 ppm, and a singlet at 7.18 ppm due to benzene. A pure sample of XXXVIII was obtained by preparative glc on column D; its 220 MHz nmr spectrum exhibited a multiplet (1H) centered at about 2.31 ppm, a multiplet (3H) from 2.5 to 2.84 ppm consisting of a perturbed doublet (about 2H, J = 2 Hz) at 2.7 ppm overlapping a complex multiplet (about 1H), and a doublet (1H, J = 2 Hz) with further poorly resolved coupling at about 5.06 ppm. The infrared spectrum of pure XXXVIII displayed bands at 3090, 1678, 1180, and 900 cm^{-1}, and its mass spectrum gave a parent peak at m/e 146 with the p + 2 peak at m/e 148 being 97.7% as large. The base peak was m/e 67. The above evidence is in accord with the structure of XXXVIII but does not definitively exclude the isomeric 3-methylenecyclobutyl bromide as a possibility. An argument based on chemical shifts could be invoked but more conclusive is the ^{13}C nmr spectrum (in dioxane, proton decoupled) which shows distinct chemical shifts for each of the five carbon atoms and eliminates the symmetrical structure from consideration. The assignments for this spectrum and its appropriate analogy to that of methylenecyclobutane are presented below (72). For subsequent studies pure samples of XXXVIII were obtained as needed by preparative glc on column D.



Carbon		XXXVIII
1	87.9	83.7
2	42.7	41.7
3	160.7	147.3
4	176.0	163.9
5	160.7	162.2

Chemical Shift (in ppm upfield from CS_2)

Preparative glc of the above-mentioned distillate on column J at 90°C revealed two poorly resolved minor components with somewhat longer retention times than that of XXXVIII. These were collected together and could be separated by rechromatographing on column C at 90°. The component of longer retention time was found to be XXXIX. Its infrared spectrum displayed bands at 3050, 2960, 2930, 2840, 1430, 1260, 1198, 916, 862, and 676 cm^{-1}. Its nmr showed a vinyl proton triplet ($J = 1$ Hz, 1H) at 5.95 ppm, a broad doublet ($J = 1$ Hz, 2H) at 3.80 ppm due to the bromomethylene protons, and a multiplet from 2.0 to 2.95 ppm (4H) due to the methylene protons on the ring.

Ethynylcyclopropane (XXVI). A mixture of 149 mg of iodide XXIII and 94 mg of triethylamine in 2 ml of 2,2,2-trifluoroethanol was sealed in 1/4-in. heavy-walled Pyrex tubing and heated at 150° for 21.5 hr. Analysis on column C revealed two volatile products (2.25% and 82.5%), one other major product (15.25%) and some minor products. This solution was partitioned between 8 ml of water and 0.75 ml of decane. After separation, the aqueous solution was extracted with 0.25 ml of decane and the combined decane solution washed with 2 ml of 10% aqueous sodium bisulfate, dried over magnesium sulfate, and subjected to preparative glc on column E with temperature programming from 100-160°. The two volatile products were collected together. The infrared spectrum of this fraction displayed bands at 3320, 3100, 3025, 2140, 1430, 1355, 1195, 1060, 1040, and 945 cm^{-1}, in reasonable agreement with the Raman spectrum reported for ethynylcyclopropane (73). The nmr spectrum showed the acetylenic proton as a doublet (J = 2 Hz) centered at 1.53 ppm, the cyclopropyl methine proton as a complex multiplet from 0.95 to 1.45 ppm, and the cyclopropyl methylene protons as two multiplets from 0.55 to 0.88 ppm (4H).

2-Methylenecyclobutyl Iodide (XL) and 1-Cyclobutenylcarbinyl Iodide (XLI). An impure sample of XXXVIII (containing about 70 mg of XXXVIII and about 3 ml of a 25% solution of lithium iodide in dry acetone were sealed in stainless steel tubes and heated at 70° for 15 hr. The combined solution was diluted with 10 ml of water and extracted with 6 x 1 ml pentane. The combined pentane solution was dried over magnesium sulfate and concentrated to a volume of about 1 ml on a rotary evaporator. Analysis on column J at 120° revealed a small amount of remaining XXXVIII followed by a major and a minor component which could almost be resolved. However, after collection of each new product, reinjection showed that each of the two fractions had the same composition as the starting mixture. The nmr spectrum of the "isolated" major component showed that it was a mixture of 83% XL and 17% XLI. The following assignments could be readily made by comparison with the spectra of XXXVIII and XXXIX: a broad singlet at 6.0 ppm (0.176 H) due to the olefinic proton in XLI, a multiplet from 4.7 to 5.4 ppm

(2.54 H) due to the terminal methylene protons and the protons α to iodine in XL, a broad singlet at 3.75 ppm (0.353 H) due to the protons α to iodine in XLI, and a multiplet from 2.0 to 3.04 ppm (4.33 H) due to the ring-methylene protons in XL and XLI. The infrared spectrum of this sample displayed bands at 3080, 2985, 2950, 2925, 2830, 1672, 1425, 1140, 890, and 650 cm^{-1}. The infrared spectrum of the "isolated" minor component was essentially identical.

Kinetics.

1-Cyclopropylvinyl Iodide (XXIII) in Aqueous Methanol. For each kinetic run about 0.5 ml of a 0.2 M solution of XXIII in 77.5% aqueous methanol was prepared, and the appropriate amounts of triethylamine as a buffer and o-dichlorobenzene as an internal standard were added. The solution was divided into six equal portions, which were then sealed in sections of 1/4-inch, heavy-walled Pyrex tubing under aspirator pressure while frozen in liquid nitrogen. The tubes were placed simultaneously in a kinetic bath (Gebrüder Haake Ultra-thermostat, model NBB) equilibrated to $\pm$ 0.1°. Beginning after about ten minutes, tubes were pulled at appropriate intervals and quenched in ice water. Each tube was opened, 60 μl of pentane was introduced and agitated, and the pentane layer was analyzed on column H at 100°. The concentration of XXIII found in the first tube was taken as the initial value. One run was conducted with 1.1 equivalents of triethylamine at 150.0°

($k = 2.17 \pm 0.08 \times 10^{-4}$ sec^{-1}) and three runs were conducted with 3.0-3.2 equivalents of triethylamine at 140.9, 150.0 and 161.1° ($k = 1.10 \pm 0.01$, 1.94 ± 0.04, and $4.40 \pm 0.06 \times 10^{-4}$ sec^{-1} respectively) (74). The thermal stability of XXIII in the absence of an ionizing solvent was demonstrated by heating a mixture of XXIII and o-dichlorobenzene in a tube sealed at aspirator pressure for 12 hr at 150°. Glc analysis before and after heating revealed no change in composition.

1-Isopropylvinyl Iodide (XXIV) in Aqueous Methanol. For each kinetic run, about 18.5 mg of XXIV, the appropriate amount of triethylamine, and 4 mg of n-nonane as an internal standard were dissolved in 77.5% (by wt) aqueous methanol to make 3 ml. The amounts of triethylamine used were 28.4 mg (3.0 equivalents) and 11.0 mg (1.13 equivalents), giving initial concentrations of 0.0937 M and 0.0363 M, respectively. Portions (0.5 ml) of this solution were sealed in stainless steel tubes (these tubes have a volume of 1.5 ml, a wall thickness of 4 mm, and are sealed by threaded caps which employ teflon gaskets), and the samples were heated at 233.5 ± 0.1° in the kinetic bath described above. Beginning after 15 min tubes were removed at intervals and quenched in ice water. The contents of each tube were agitated with 2 ml of 10% sodium bisulfate and 0.1 ml of pentane, and the pentane layer was analyzed on column H at 90°.

Product Studies.

Reaction of 1-Cyclopropylvinyl Iodide (XXIII) with Aqueous Silver Nitrate. About 0.1 g of XXIII and 3 ml of 0.3 M aqueous silver nitrate were stirred magnetically while heating in a stoppered flask at 55° for 2 hr. The yellow precipitate, which has begun to form immediately upon mixing of the reactants, was filtered off and the solution was extracted with ether. The ether solution was dried over sodium sulfate and concentrated. Analysis of the concentrate on column C showed that no starting material remained and that two products were evident. These were isolated by preparative glc on the same column and the major product was identified as cyclopropyl methyl ketone (XXII) by means of its infrared spectrum. The infrared spectrum of the minor product indicated that it was an alcohol. No further work was done on this reaction.

Reaction of 1-Cyclopropylvinyl Iodide (XXIII) with Silver Tosylate. A 100 ml three-necked flask, equipped with a gas inlet and a drying tube and charged with 0.725 g (2.6 mmol) of silver tosylate and 5 ml of acetonitrile, was purged with nitrogen and cooled in an ice bath. After adding 0.5 g (2.58 mmol) of XXIII, the flask was swirled and allowed to stand in ice for 6 hr. With the flask still cooled in ice, the acetonitrile was distilled under pump vacuum into a dry ice-cooled receiver. The solid residue was washed vigorously with 2 x 75 ml of cold ligroin (30-60° fraction) which was then filtered into a flask blanketed with nitrogen. Upon cooling this solution slowly in dry ice-acetone with scratching, white crystals separated and the ligroin was decanted. After a recrystallization from 40 ml of ligroin, the crystals were dried at 0° under pump vacuum. All evidence suggests that the 104 mg (17% yield) of nearly pure white solid was 1-cyclopropylvinyl tosylate (XXV). The compound could be stored for days at -78°, but a sample kept at room temperature was observed to become a black tar in a few hours. The nmr spectrum (in $CDCl_3$) exhibited an aromatic AA'BB' pattern (4H) from 7.28 to 8.0 ppm, vinyl protons (2H) from 4.6 to 4.82 ppm as an approximate AB quartet (J = about 2.2 Hz) with finer unresolved coupling, a methyl singlet (3H) at 2.49 ppm, a cyclopropyl methine multiplet (1H) from 1.17 to 1.72 ppm, and a cyclopropyl methylene multiplet (4H) from 0.50 to 0.63 ppm. The infrared spectrum had bands at 1700, 1600, 1370, 1190, and 1180 cm^{-1}. By delivering a freshly recrystallized sample stored in dry ice to the nearby Elek Microanalytical Lab., Torrance, California it was possible to obtain reasonable analytical data. Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60,50; H, 5.92. Found: C, 59.74; H, 5.95. Preparative glc of the acetonitrile distillate on column B at 200° allowed collection of a volatile component which was shown to be mainly ethynylcyclopropane by ir.

Reaction of 1-Cyclopropylvinyl Iodide (XXIII) with Silver Acetate in Acetic Acid.

I. Analytical Solvolyses and Temperature Dependence of Product Ratios. A 5 ml flask containing a magnetic spin bar, 0.75 ml of dry acetic acid, and about 45 mg of silver acetate was sealed with a rubber septum cap, placed in a constant temperature bath (consisting of an insulated vessel through which water from a Lauda Ultra-thermostat, type K-2, was circulated; temperature control was observed to be better than ± 0.1°) and stirred magnetically. After 15 minutes, about 20 mg of XXIII was introduced with a hypodermic syringe. After several half-lives the flask was removed and 0.5 ml of the contents was squirted into a centrifuge tube containing 2 ml of water and 1 ml of ether (during this and the following extractions the tubes were kept in an ice bath at all times except when transferring or centrifuging). After vigorously agitating with a pipette, the tube was centrifuged and the ether layer transferred to a second tube. The aqueous solution was extracted with 0.5 ml of ether and the combined ether solution was washed with 2 x 0.5 ml of saturated sodium bicarbonate solution and 1 ml of saturated sodium chloride solution and was dried over anhydrous potassium carbonate. Analysis on column F resolved all the products except acetates XXVII and XXX,which exhibited identical retention times. These components could be separated on column G, however, so that through analysis of the samples on both columns the relative amounts of all components could be ascertained. The retention times in minutes of the products on column F at 120° and a flow rate of 12 ml/min were: XXVI, 2.45; XXII, 6.2; XXIII, 10.7; XXIX, 12.2; XXVII, 14.7; XXVIII, 19.0. The retention times in minutes of the products on column G at 100° and a flow rate of 12 ml/min were: XXVI, 2.2; XXIII, 9.0; XXII, 9.8; XXIX, 15.2; XXX, 18.0; XXVII, 23.0; XXVIII, 24.6. Correction factors for relative extraction and response were determined for all components except XXVI, and where necessary, on both analytical columns. Also, correction factors for deviations from linearity of response versus absolute sample size were determined where necessary. Because of a secondary reaction of cyclopropyl acetylene (XXVI) with silver acetate to form the silver salt (*vide infra*), the relative amount of XXVI observed in the glc analysis varied from run to run and it was not possible to determine precisely the mol percentage of this component. In one run at 25° which employed pentyl acetate as an internal standard, only 6.4% of XXVI was observed but the products other than XXVI accounted for only 73% of the starting material; thus XXVI is a maximum of 27 mol percent of the total products (in one run at about 100° in which the reaction was worked up after only 2 minutes, 24.2% of XXVI was observed). The product distribution for 25° given in

Table I of the text incorporates the estimate of 27% XXVI.

The solvolysis, as described above, was carried out at five different temperatures from 25.0 ± 0.1 to 64.8 ± 0.1°. No effort to estimate the percentage of XXVI formed at temperatures other than 25° was made. The molar ratios of XXIX/XXX at 25° and 64.8° determined on column G were 9.97 and 8.58 respectively. Considering the difficulties involved in measuring the amount of acetate XXX, which was less than 0.3% of the total products, it is felt that these values are within experimental error of one another. Therefore, for the product distributions at the intermediate temperatures the average value of 9.22 was used in calculating the amount of acetate XXX (hidden under the XXVII peak) from the amount of acetate XXIX observed on column H. The product mixture obtained at 64.8° was analyzed three times in order to obtain an estimate of the reproducibility in the determination of the minor components. The values and standard deviations were: 28.1 ± 0.7% ketone XXII, 2.34 ± 0.14% acetate XXIX, and 1.80 ± 0.06% acetate XXVIII. The mol percentages of products other than acetylene XXVI are summarized in Table III of the text.

It was found that about 8 mol percent of the reaction products at completion was ketone XXII from a source other than the decomposition of vinyl acetate XXVII, and that this percentage was rather independent of temperature (vide infra). Therefore the amount of XXII coming from XXVII was estimated as the mol percent of XXII produced minus 8 mol percent.

II. Preparative Solvolysis. In a 5 ml flask containing a magnetic stir bar were placed 1.1 ml of dry acetic acid, 239 mg of iodide XXIII, and 206 mg of silver acetate (1 equivalent); the flask was stoppered and stirred for 23 hr after which the contents were rinsed into a centrifuge tube with 1 ml of acetic acid. After centrifuging, the clear acetic acid solution was transferred to a clean tube and 5 ml of water was added. A rather copious white precipitate resulted. The solution was extracted with 2 ml and 3 x 1 ml of ether and the combined ether solution was washed with 4 x 1 ml of saturated sodium bicarbonate and 2 ml of saturated sodium chloride and was dried over sodium sulfate as sample A. To the aqueous solution containing the white precipitate were added 1 ml of 20% sodium iodide solution and 1 ml of ether. A dense yellow precipitate formed. After agitating for a few minutes the ether layer was removed and worked up as above to provide sample B. Analysis of sample A on column F revealed a product distribution analogous to that observed in the analytical run at 25° except for 26.5% of remaining starting material. Analysis of sample B on the same column revealed a considerable amount of a component with the same retention time as the volatile product in sample A and as acetylene XXVI obtained from base-catalyzed dehydrohalogenation of XXIII as described above. A sample of this product was isolated by preparative glc on column B and its infrared spectrum was found to be identical to that of XXVI.

No effort was made to collect the small amount of XXVI in sample A. The other five products and the remaining starting material in sample A were collected in four fractions by preparative glc on column C at 140°; they are discussed in order of increasing retention time. The first fraction was identified as cyclopropyl methyl ketone by comparison of its infrared spectrum and glc retention time with those of an authentic sample (Aldrich). The second fraction consisted of a mixture of iodide XXIII and 2-methylenecyclobutyl acetate XXIX, which were not resolved on this column. The identity of the components in the mixture was established by comparing its infrared spectrum with that of pure XXIII and that of XXIX isolated and fully characterized from the acetolysis of bromide XXXVIII. On column F the components were resolved and the acetate product was observed to have the same retention time as known XXIX.

The third fraction, which was the major product, was identified as 1-cyclopropylvinyl acetate (XXVII). Its infrared spectrum exhibited bands at 3090, 3010, 1755, 1655, and 1200 cm^{-1} and was identical to that of a sample independently synthesized by treating the lithium enolate of cyclopropyl methyl ketone (prepared through the reaction of the ketone with triphenylmethyl lithium in dimethoxyethane) with acetic anhydride. Its nmr spectrum consisted of a broad vinyl singlet (2H) at 4.62 ppm, a methyl singlet (3H) at 2.08 ppm, a cyclopropyl methine multiplet (1H) from 1.2 to 1.7 ppm, and a cyclopropyl methylene multiplet (4H) from 0.5 to 0.8 ppm. The mass spectrum gave a parent ion at m/e 126. Careful efforts to obtain good analytical data were frustrated. Anal. Calcd for $C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 67.11; H, 8.29; C, 65.70; H, 7.89. The third fraction also presumably contains about 0.2% of 1-cyclobutenylcarbinyl acetate (XXX), since XXVII and XXX have identical retention times on column C. No attempt to isolate this minor component was made; its presence was concluded from the observation of a glc peak on column G with a retention time identical to that of acetate XXX which was isolated and fully characterized from the acetolysis of bromide XXXVIII.

The fourth fraction was identified as 3,4-pentadien-1-yl acetate (XXVIII) by comparison of its infrared spectrum and retention time with those of an authentic sample prepared from the alcohol and acetic anhydride.

III. Solvolysis in O-Deuterioacetic Acid. To a 5 ml flask containing a magnetic stir bar were added 250.4 mg of iodide XXIII, 618 mg of silver acetate, and 2 ml of *O*-deuterioacetic acid (International Chemical and Nuclear).

The stoppered flask was stirred for $2\frac{1}{2}$ hr at room temperature and then the contents was worked up in the same manner as was the preparative solvolysis. Preparative glc on column C was used to isolate vinyl acetate XXVII from the product mixture. The infrared spectrum of a 20% solution of this sample in carbon tetrachloride showed negligible absorption in the region appropriate for a vinyl carbon-deuterium stretching mode. In the nmr spectrum the integral ratio of the acetate methyl protons to the vinyl protons was compared to that observed in XXVII obtained from undeuterated medium and within the error limits of the nmr integration no incorporation was detected. Comparison of the corresponding mass spectra suggested -0.45% incorporation.

Silver Acetate-Catalyzed Acetolysis of 2-Methylenecyclobutyl Bromide (XXXVIII).

I. Analytical Solvolyses were carried out and analyzed in the same way as those with iodide XXIII, except XXXVIII was notably less reactive and a reaction time of 72 hr at 25° was allowed in order to assure completion, and because of silver bromide formation the reaction was protected from light. The product mixtures were analyzed on column F. The averages of two runs and the observed deviations were: 71.9 ± 0.8 mol percent of acetate XXIX, 27.5 ± 0.6 mol percent of acetate XXX, and about 0.4% of an unidentified product. Analysis of the mixture on column G revealed no other products and demonstrated that neither ketone XXII nor acetate XXVII was present. Analysis of a solution of XXIX and XXII in known concentrations indicated that 0.3 mol percent of XXII (corrected for extraction and response) could have been detected. Studies of the stability of XXVII under the reaction conditions (*vide infra*) showed that over half of any XXVII formed in the above reaction would have been converted to XXII. The more favorable extraction factor of XXVII would put the limit of its detectability at about 0.1 mol percent. Thus less than 0.4 mol percent of cyclopropyl products was formed in this reaction.

II. *Preparative Solvolysis.* A 50 ml flask equipped with a magnetic spin bar was charged with 0.485 g of bromide XXXVIII, 1.0 g of silver acetate, and 25 ml of dry acetic acid, and the mixture was stirred at room temperature with protection from light for 72 hr. The acetic acid solution was decanted, diluted with 100 ml of water, and extracted twice with ether. The combined ether solution was washed twice with saturated sodium bicarbonate, once with saturated sodium chloride, and dried over anhydrous potassium carbonate. Concentration on a rotary evaporator was followed by preparative glc on column C at 145°. Impurities known to be in the XXXVIII used were ignored, while the two major products observed in the analytical solvolysis were isolated in pure form. The first fraction was identified as

2-methylenecyclobutyl acetate (XXIX). Its infrared spectrum exhibited bands at 3055, 1740, 1680, 1370, 1235, 1078, and 895 cm^{-1}. The nmr showed the cyclobutyl proton α to the acetate function as a multiplet (1H) from 5.07 to 5.65 ppm, vinyl multiplets centered at about 4.92 ppm (1H), and 4.76 ppm (1H), and a complex pattern from 1.6 to 2.7 ppm (7H) in which a singlet (about 3H) at 1.94 ppm was evident. The mass spectrum gave a parent ion at m/e 126. Anal. Calcd for $C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 66.72; H, 8.16. A sample of this product was treated with excess lithium aluminum hydride (LAH) in dry ether for 1 hr. Following a typical aqueous work-up, the ether solution was subjected to preparative glc on column C. The infrared spectrum of the isolated product was identical to that of 2-methylenecyclobutanol (75).

The second fraction was identified as 1-cyclobutenylcarbinyl acetate (XXX). Its infrared spectrum exhibited bands at 3040, 1740, 1437, 1372, 1230, and 1030 cm^{-1}. The nmr spectrum showed a broad vinyl singlet (1H) at 5.9 ppm, a broad singlet due to the methylene protons α to the acetate function (2H) at 4.42 ppm, a broad cyclobutyl methylene singlet (4H) at 2.46 ppm, and a sharp methyl singlet (3H) at 2.02 ppm. The mass spectrum gave a parent ion at m/e 126. Anal. Calcd for $C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 66.44; H, 8.24. A sample of this product was reduced with LAH as above, and the isolated alcohol gave an infrared spectrum identical to the published spectrum of 1-cyclobutenylcarbinol (76).

Reaction of 1-Cyclobutenylcarbinyl Bromide (XXXIX) with Silver Acetate in Acetic Acid. A freshly chromatographed sample (about 0.5 mg) of XXXIX, 8.2 mg of silver acetate, and 150 μl of acetic acid were sealed in a 2 in. length of 1/4-inch Pyrex tubing. The sealed tube was placed in a magnetically stirred 100 ml round-bottomed flask full of water in a constant temperature bath at 25° with protection from light. After 72 hr, 100 μl of the solution was subjected to the usual work-up (appropriately scaled down). Analysis of the resulting sample on column F revealed four components: 46.3 mol percent of acetate XXIX, 4.13 percent of an unknown (this component has a retention time which is different from those of all the products studied in this work; it is probably the result of a minor contaminant), 48.2 mol percent of acetate XXX, and 1.4 percent of the unknown observed in the solvolysis of bromide XXXVIII.

Silver Acetate-Catalyzed Acetolysis of 3,4-Pentadien-1-yl Iodide (XXXVI).

I. Analytical Solvolyses were carried out as with iodide XXIII, and the same problems were encountered in efforts to quantitate acetylene XXVI. Again, pentyl acetate was used in one run as an internal standard and the mass balance based on products other than XXVI was determined to be 77%. Thus a maximum of 23% of XXVI was formed in the reaction. The product distribution given in Table I for this reaction at 25° is the result of an accurate determination of the relative molar amounts of all products other than XXVI adjusted in accord with an estimated 23% yield of XXVI.

II. Preparative Solvolysis. A 10 ml flask was charged with 250 mg of XXXVI, 430 mg of silver acetate, 3 ml of dry acetic acid and a magnetic stir bar. After stirring the mixture for 12 hr at room temperature a work-up analogous to that used in the preparative solvolysis of iodide XXIII was employed. Again, a white precipitate was formed on addition of water to the decanted acetic acid solution. Treatment of this precipitate with sodium iodide solution liberated acetylene XXVI, which was isolated as before and identified by means of its infrared spectrum. Preparative glc of the main product mixture allowed the isolation of XXII, XXIX, XXVII, and XXVIII, which were identified by comparison of their infrared spectra and glc retention times with those of known samples. Also isolated in about 2.3% yield was 4-pentyn-1-yl acetate, which presumably comes from a small amount of 4-pentyn-1-yl iodide present in the impure XXXVI used for the preparative solvolysis. This product was not found when pure XXXVI was solvolyzed as in the analytical runs. The minor product XXX was not isolated. Evidence for its presence in the product mixture consists of the observation of a peak with the correct retention time on column G.

Acetolysis of 3,4-Pentadien-1-yl Tosylate (XXXIII).

I. *Analytical Solvolysis.* A mixture of 16.1 mg of XXIII and 0.37 ml of 0.201 *M* sodium acetate in acetic acid (1.1 equiv of acetate) was sealed under aspirator pressure in 1/4-inch, heavy-walled Pyrex tubing, and this sample was heated at 100° for 54.4 hr. Then the contents of the tube were diluted with 0.7 ml of water and extracted with a total of 0.7 ml of ether in three portions. The combined ether solution was washed with 3 x 0.7 ml of saturated sodium bicarbonate and 0.7 ml of saturated sodium chloride and was dried over sodium sulfate. The sample was analyzed by glc on column F. The extraction factor for ketone XXII relative to pentyl acetate under the conditions of the above work-up was determined to be only 0.46. It was assumed that the extraction factors of the other products, being five-carbon acetates (except for acetylene XXVI), were about equal to that of pentyl acetate. The product distribution corrected only for the extraction factor of XXII was: XXVI, 0.92%; XXII, 55.9%; XXIX, 4.67%; unident., 0.17%; XXX, 0.38%; XXVIII, 37.8%.

II. Preparative Solvolysis. In a 50 ml flask, 1.0 g of tosylate XXXIII and 1.1 equivalents of sodium acetate were dissolved in 23 ml of dry acetic acid, and the solution was heated at 100 ± 5° for 49 hr. After cooling in ice water, the contents was diluted with 50 ml of water and extracted with a total of 50 ml of ether in three portions. The combined ether solution was extracted with 3 x 50 ml of saturated sodium bicarbonate and 50 ml of saturated sodium chloride and was dried over sodium sulfate. The presence of acetylene XXVI and ketone XXII in the product mixture was indicated by observation of the correct retention times (compared with known samples) on column F. Four other components of the reaction mixture were isolated by preparative glc on column C. The first was identified as acetate XXIX by comparison of its retention time and its infrared and nmr spectra with those of a known sample. The second and third components were identified as acetates XXX and XXVIII, respectively, by comparison of their infrared spectra and retention times with those of known samples. The infrared spectrum of the fourth component indicated that it was 4-pentyn-1-yl acetate, which presumably came from the corresponding tosylate as an impurity in XXXIII; this product was not observed in the analytical solvolyses which employed pure XXXIII.

Silver Acetate-Catalyzed Acetolysis of a Mixture of 2-Methylenecyclobutyl Iodide (XL) and 1-Cyclobutenylcarbinyl Iodide (XLI). The silver-catalyzed reaction of the 83:17 mixture of XL and XLI with acetic acid was carried out as with the other substrates. The usual light-stable yellow precipitate of silver iodide was noted. Reaction times of 5.5 hr and 72 hr were allowed at 25°. The following product percentages are the averages of the two runs given with the observed deviation: 67.8 ± 0.6 mol percent XXIX, 31.9 ± 0.8 mol percent XXX, and 0.4 ± 0.1 percent of an unknown.

The reaction of XL and XLI with acetic acid in the absence of silver acetate was found to be very slow: When 5 mg of the mixture of XL and XLI was stirred in 0.8 ml of acetic acid 0.4 M in sodium acetate for 2.2 hr at 25°, glc analysis showed only a very small conversion to XXIX and XXX. Silver iodide (12 mg) was added and after stirring an additional 2.7 hr analysis showed little or no increase in conversion.

Stability of Products Under the Reaction Conditions. When the silver acetate-catalyzed acetolysis of iodide XXIII at 25° or 45° was followed by taking aliquots at various intervals, it was obvious after long reaction times that vinyl acetate XXVII was being converted to ketone XXII, and extrapolation showed that most but not all of the XXII observed had this origin. The observation that XXII as a percentage of the observed products exhibited a minimum at about 80% conversion of XXIII (Figure 4) also requires another source for part of the observed XXII. In an effort to discover this source it was demonstrated that under the conditions of the work-up and analysis, XXIII was stable whereas XXVII gave less than 0.5% XXII. The amount of XXII apparently arising from the unknown source was about the same at the two temperatures, being an average of about 8 mol percent of the products. This amount persisted even when freshly dried silver acetate and acetic acid and freshly chromatographed XXIII were used with all transfers being made under nitrogen. Catalysis of the reaction by a 1:2 mixture of silver oxide and silver acetate again resulted in about 8 mol percent ketone XXII at completion. Intentional inclusion of 3.77% water in the reaction mixture resulted in 21.3% ketone at completion. Thus if the initial 8% yield of ketone XXII were coming from water in the solvent, then the solvent must contain about 1.4% water. This is difficult to accept in view of the care that was taken to dry the reagents; furthermore this would not explain the higher percentage of ketone observed at partial reaction. The rate of conversion of XXVII to XXII at 45° was about 5 times as fast as that at 25°. When a sample of XXVII with pentyl acetate as an internal standard was heated in acetic acid 0.201 M in sodium acetate at 100° for 17 hr, quantitative conversion to XXII was observed. Therefore, XXII is stable to the reaction conditions.

Evidence for the stability of acetates XXVIII, XXIX, and XXX under the silver-catalyzed acetolysis conditions may be seen in Table III, where the product distributions from the solvolysis of XXIII for 250 min. and 1320 min. at 25.0° show almost identical amounts of these components. The similar percentages obtained in the acetolysis of tosylate XXXIII at 100° suggest that these components are at least reasonably stable even under those more stringent conditions.

A sample of acetylene XXVI with pentyl acetate as an internal standard was stirred with silver acetate and silver iodide in acetic acid at 25° for 280 min. In the course of the work-up, a copious white precipitate (apparently the silver salt of ethynylcyclopropane) was observed; glc analysis of the ether solution obtained in the work-up showed negligible conversion of XXVI to any of the other products. However, when XXVI and pentyl acetate were heated in acetic acid 0.201 M in sodium acetate at 100° for 49 hr (the solvolysis conditions for tosylate XXXIII), analysis revealed conversion to a mixture of the other products in the following yields: XXII, 57.8%; XXVIII, 1.1%; XXIX, 1.1%; XXX, 0.07%.

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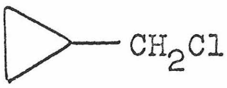
INTERACTION OF THE FACE OF A CYCLOPROPANE RING WITH POSITIVELY CHARGE CARBON

I. INTRODUCTION

Interaction of a cyclopropyl ring with a carbonium ion is often stabilizing. Particularly illustrative of this fact are the accelerations noted in many solvolytic rate studies of cyclopropylcarbinyl derivatives (1). The first study of this kind was by Roberts and Mazur (2), who found that the solvolysis rate of cyclopropylcarbinyl chloride (I) in 50% aqueous ethanol was 40 times that of α-methyallyl chloride (II). A striking example from more recent work is the difference of 10^6 between the acetolysis rates of tosylates III and IV (3). Recently a vinyl analog (V) of the cyclopropylcarbinyl system has been examined, and here too the cyclopropyl group provides an impressive stabilization (4).



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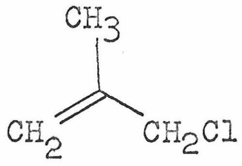

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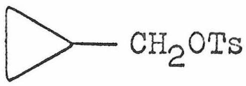

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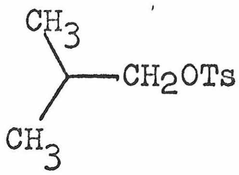

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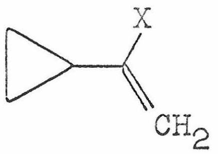
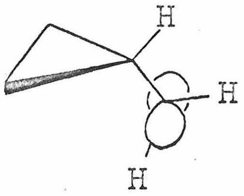


V

Not all interactions between a cyclopropyl ring and a carbonium ion are so stabilizing, however, and it has become apparent that the orientation of the interacting moieties is a key factor in determining the energetic nature of the interaction. In cyclopropylcarbinyl cations there are two extremes of orientation available. They are the "bisected" conformer (VI) and the "perpendicularly twisted" conformer (VII). There has been considerable controversy



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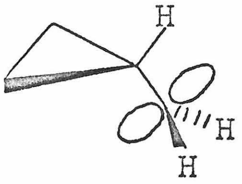
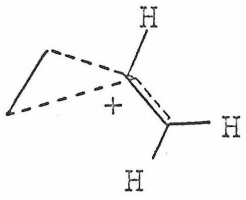
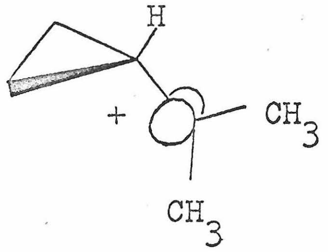


VII

concerning whether either of these is the principal intermediate in solvolyses of cyclopropylcarbinyl derivatives (1). However, in the light of both theoretical (5) and experimental evidence it is clear that of the two the bisected conformer would be preferred, apparently because it optimizes overlap between the empty p orbital and the "bent" cyclopropyl carbon-carbon bonds to give a non-classical ion (VIII). Olah and co-workers have obtained evidence for this conformational preference in the dimethyl derivative IX through low temperature nuclear magnetic resonance (nmr) study of the cation in non-nucleophilic solvents (6). More recently they have observed the parent cyclopropylcarbinyl cation by nmr (7) and the data obtained are consistent, though not uniquely so (8), with rapidly equilibrating non-classical ions of structure VI. Schleyer and Van Dine (10) have found that the effects of progressive substitution of methyl groups for ring-methylene hydrogens on the solvolysis rates of cyclopropylcarbinyl derivatives are multiplicative, and they have taken this as evidence for a symmetric ionization transition state analogous to VI, as opposed to less symmetric structures analogous to a bicyclobutonium ion (9). Strong evidence against favorability of the orientation in VII was found in studies of adamantyl derivatives where the

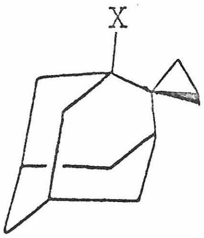


VIII

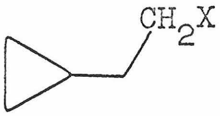


IX

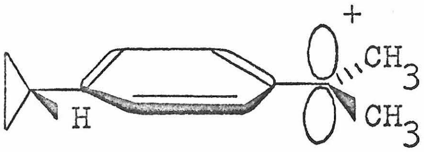
cyclopropylcarbinyl unit is constrained to the perpendicular orientation (X) resulting in a rate *retardation* of about 10^3 relative to the unsubstituted 1-adamantyl derivative (11). Interposing an aromatic nucleus between the three-membered ring and the ionization center in the *para* sense, as in *p*-cyclopropylcumyl chloride, preserves essentially the same possibilities for orientation, and a study by Brown and Cleveland (12) indicated a preference in the ion for conformer XI, analogous to the bisected structure VI.



X

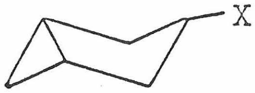


XII



XI

On the other hand, interposing a methylene group between the three-membered ring and the ionization center, as in β-cyclopropylethyl derivatives (XII), allows many new orientations of these moieties. So varied are the possibilities in fact that it would be difficult to study the role of orientation in this system if it were not possible to focus attention on a variety of fixed geometries. Fortunately this is easily done by incorporating the β-cyclopropylethyl unit into fairly rigid, multicyclic systems. Among such systems that have been investigated are XIII through XXI (13). Solvolyses of these substrates result in most cases in at least some rearrangement, and the influence of the cyclopropyl group on the solvolysis rates varies from negligible or slight retardation in XIV (13a) and XXI (13f) to an acceleration of $10^{2.4}$ in XIX (13e), and to an impressive acceleration of 10^{14} in XX (13g,h). A generalization which may be drawn from these studies is that



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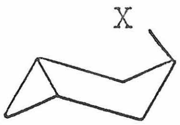

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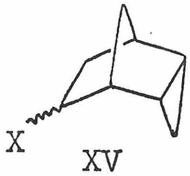
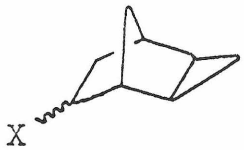
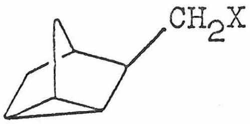


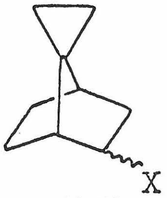
XV



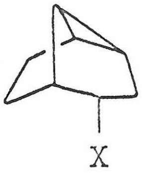
XVI



XVII



XVIII



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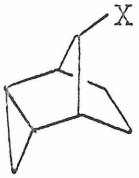

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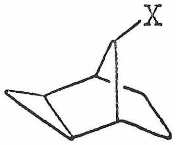
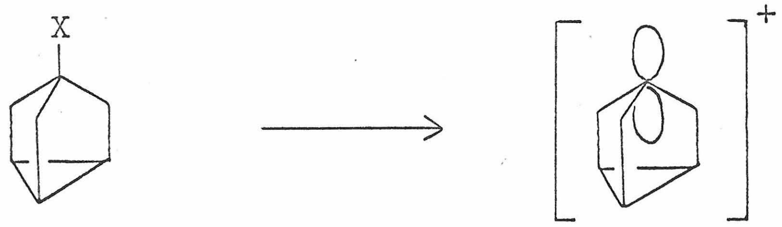


XXI

orientations which favor interaction of the positive center with the edge of the cyclopropyl ring result in stabilization.

A fundamental orientation which was not explicitly explored in these studies is that which allows a symmetrical interaction of the positive charge with the face of the cyclopropane ring. Solvolysis of a substrate having the nortricyclene skeleton with a leaving group in the 4-position (XXII) would rigidly assure this orientation (XXIII).



XXII XXIII

Examination of this interaction would be attractive from a theoretical standpoint; the Walsh model of cyclopropane suggests considerable electron density in the center of the ring (14), and on a naïve level a stabilizing interaction between a positive charge and this region would be expected. Such a study also would bear an interesting relationship to the question of face-protonated cyclopropanes (15) and might shed light on that area; obviously direct kinetic evidence related to the energetics of the interaction in question should be more readily available in the carbonium ion system.

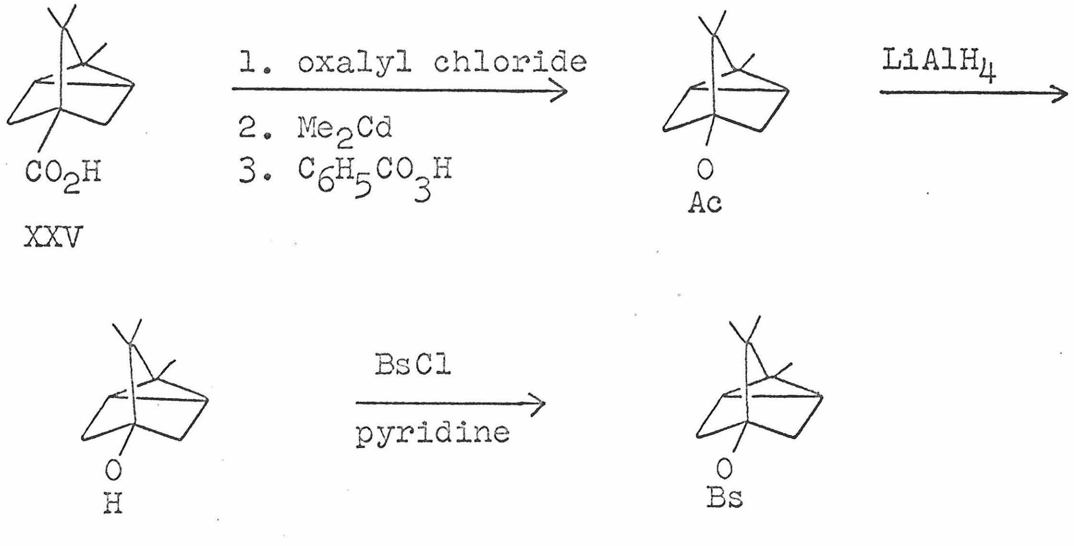
One might argue that the solvolytic studies involving XIV and XXI had already served to probe the nature of the above interaction. However, XIV has conformational freedom which is undesirable for our purposes, and furthermore models show that neither in the appropriate conformer of XIV nor in XXI is the bond to the leaving group symmetrically oriented toward the face of the cyclopropane ring as it is in XXII. The profound effects which can accrue from rigidly prescribing orientation seemingly could not be overemphasized; both XII and XIII can assume the orientation fixed in XX, but whereas the rate acceleration observed in XX is 10^{14}, the acceleration in XIII is only a factor of about 10, and XII solvolyzes predominantly without participation, even in formic acid (16).

Of course the tricyclic system XXII places the incipient carbonium ion at a bridgehead of a highly strained system, and it is well documented that attendant strain effects can severely retard solvolysis rates in such systems (17). This would complicate interpretation of an observed rate in terms of cyclopropyl influence, but Gleicher and Schleyer have provided a generally useful method of correlating bridgehead solvolysis rates with calculated strain energies (18). Use of this method should allow one to separate the electronic influence of the cyclopropyl ring from the strain effects inherent in the system. With these considerations in mind we undertook a study of solvolytic reactions of substances related to XXII.

II. RESULTS

Kinetic Study of 4-Tricyclyl and 1-Apocamphyl Brosylates.

4-Tricyclenol (XXIV) was synthesized for us by Dr. David G. Morris (19) via 4-tricyclenecarboxylic acid (XXV) by the route outlined below. Alcohol XXIV was converted to the p-bromobenzenesulfonate (brosylate) with the usual



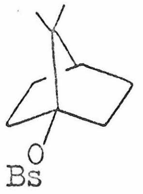
XXV

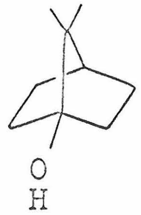
XXIV

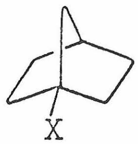
XXVI

reagents, but an abnormally high reaction temperature was required, apparently due to steric hindrance. The closely related 1-apocamphyl brosylate (XXVII) was chosen as a model compound for kinetic studies. Preparation of 1-apocamphanol (XXVIII) was from 1-apocamphanecarboxylic acid (20) by a modification of the method of Hawthorne, Emmons, and McCallum (21), and alcohol XXVIII was converted to brosylate

XXVII as above.


XXVII


XXVIII


XXIX

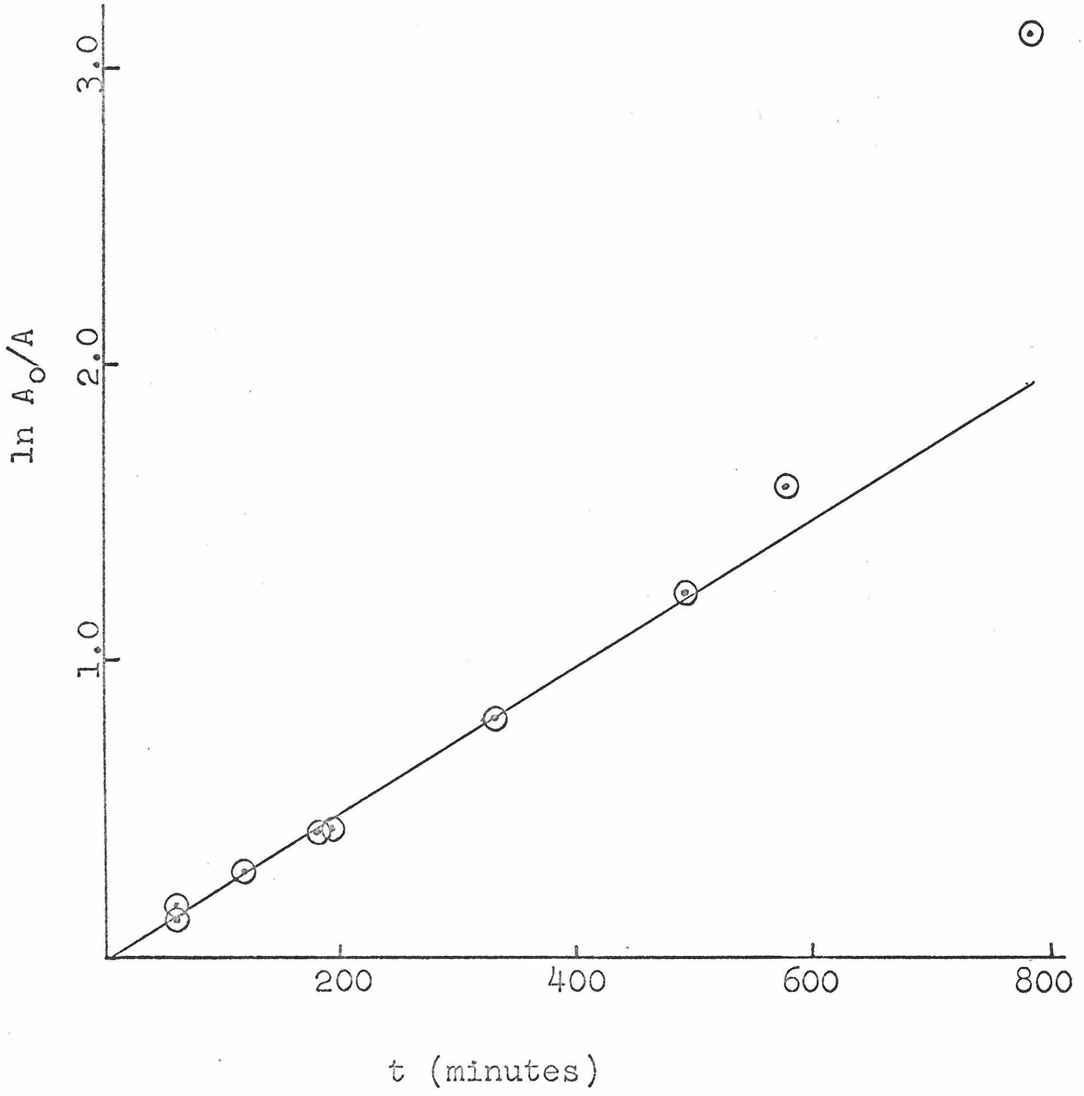
Conditions were sought which would allow a comparative kinetic study of brosylates XXVI and XXVII. Until recently the 1-norbornyl system (XXIX) was the least reactive tertiary alkyl system known (22). Solvolysis of 1-norbornyl bromide in 40% aqueous ethanol required a reaction temperature of 216° (23), and solvolysis of the corresponding chloride has been carried out in *m*-cresol at 322° (24). Extremely unreactive substrates often present experimental difficulties, and the present systems were no exception.

We initially intended to follow the solvolyses titrimetrically. In the case of brosylate XXVII an unbuffered solvolysis allowing direct titration of forming *p*-bromobenzenesulfonic acid probably would have been experimentally facile. However, in the interest of comparability it was desirable to solvolyze brosylates XXVI and XXVII under as nearly identical conditions as possible, and we had been warned that at high temperatures even buffered acetic acid attacks the cyclopropane ring in XXVI (25). Thus it was necessary to seek a buffered medium that would be compatible with both XXVI and XXVII. Initially use of sodium hydroxide as a "buffer" was explored (26). Aliquots of a solution of brosylate XXVII in 70% aqueous dioxane containing sodium hydroxide were heated in sealed Pyrex tubes for a few hours at about 200°. Titration showed that the samples had a pH less than 8, in spite of the fact that a considerable excess of sodium hydroxide had been used. Controls showed that sodium hydroxide apparently reacts rapidly with Pyrex under these conditions; recently a detailed account of similar observations in another laboratory has appeared (27). Attempts to use triethylamine as a buffer also failed; we could not find conditions which would allow titration of aqueous triethylamine at low concentrations to sharp end points.

The titrimetric approach was abandoned and a modification of the ultraviolet (uv) spectrophotometric method of Swain and Morgan (28) was adapted to the solvolysis of brosylate XXVII in 70% aqueous dioxane buffered with triethylamine. The long wavelength maxima of brosylate XXVII and brosylate anion differ appreciably in intensity but not in position. An algebraic treatment of absorbance data on the mixtures of brosylate and brosylate anion formed in the course of solvolysis would have allowed interpretation in terms of first-order kinetics (28), but an extraction procedure which would allow measurements on solutions of brosylate anion alone was deemed more attractive. The kinetic measurements were complicated by a side reaction of the solvent system which resulted in impurities having appreciable absorbance at 265 nm, the wavelength that was monitored, but an approximate correction for this could be made. The first-order rate plot obtained for solvolysis of brosylate XXVII at 200.1° is given as Figure 1. The linearity is reasonable for two half-lives but beyond that curvature is marked. The design of the analytical method caused data points determined late in the reaction to represent relatively small differences between large numbers; rather small errors in the initial concentration of brosylate XXVII, in the extinction coefficient measured for brosylate anion, or in the corrections applied for the side reaction of the solvent system could account for the curvature observed after two half-lives. Therefore this curvature is not thought to be mechanistically significant, and the slope determined in the first two half-lives is thought to be a reasonably accurate measure of the first-order rate constant for solvolysis of brosylate XXVII. The only product observed under these conditions was the unrearranged alcohol XXVIII.

Attempts to solvolyze brosylate XXVI under the same conditions gave no reaction. Even at 200° a disturbing fraction of the Pyrex sample tubes were exploding the kinetic bath, and it was apparent that a considerably higher

Figure 1. First-order rate plot[a] for the solvolysis of 1-apocamphyl brosylate (XXVII) in 70% (by wt) aqueous dioxane[b] at 200.1°.



[a] Slope of the least-squares line based on all but the last point gives $k = 4.44 \pm 0.25 \times 10^{-5}$ sec^{-1}.

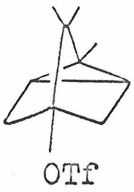
[b] Buffered with 0.015 M triethylamine and 0.01 M in substrate.

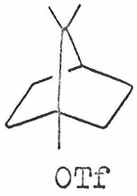
[c] Log of the ratio of the initial concentration of substrate to the concentration at time t .

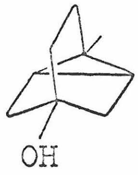
reaction temperature would be needed for brosylate XXVI; therefore we resorted to stainless steel sample tubes with threaded caps that employ teflon gaskets. These allowed us to explore much higher reaction temperatures. After brosylate XXVI was heated in the same solvent at 250° for 12 hr more than 95% of the starting material could be recovered. Even at 292° the reaction was very slow, allowing about 50% recovery after 14 hr. At the higher temperature the reaction mixture became dark and three products were observed, none of which was alcohol XXIV, but the instability of XXIV under the reaction conditions was demonstrated. The mode of reactivity exhibited by brosylate XXVI at 292° is not known but obviously its first-order reactivity with respect to heterolytic cleavage of the bridgehead carbon-oxygen bond must be vastly lower than that of brosylate XXVII.

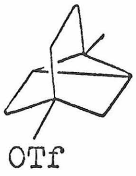
Kinetic and Product Studies with the More Reactive Triflate Leaving Group.

In order to measure the difference in reactivity more accurately we turned to the trifluoromethanesulfonate (triflate) leaving group. Triflates have been found to be more reactive than tosylates by a factor of 10^4 to 10^5 (22,29), and with this much more reactive leaving group we hoped to be able to measure a first-order solvolysis rate for the 4-tricyclyl system. Triflates XXX and XXXI were prepared by treating the corresponding alcohols in pyridine with trifluoromethanesulfonic anhydride (30). A sample of 1-methyl-4-tricyclo[2.2.2.$0^{2,6}$]octanol (XXXII) (32) became


XXX


XXXI


XXXII

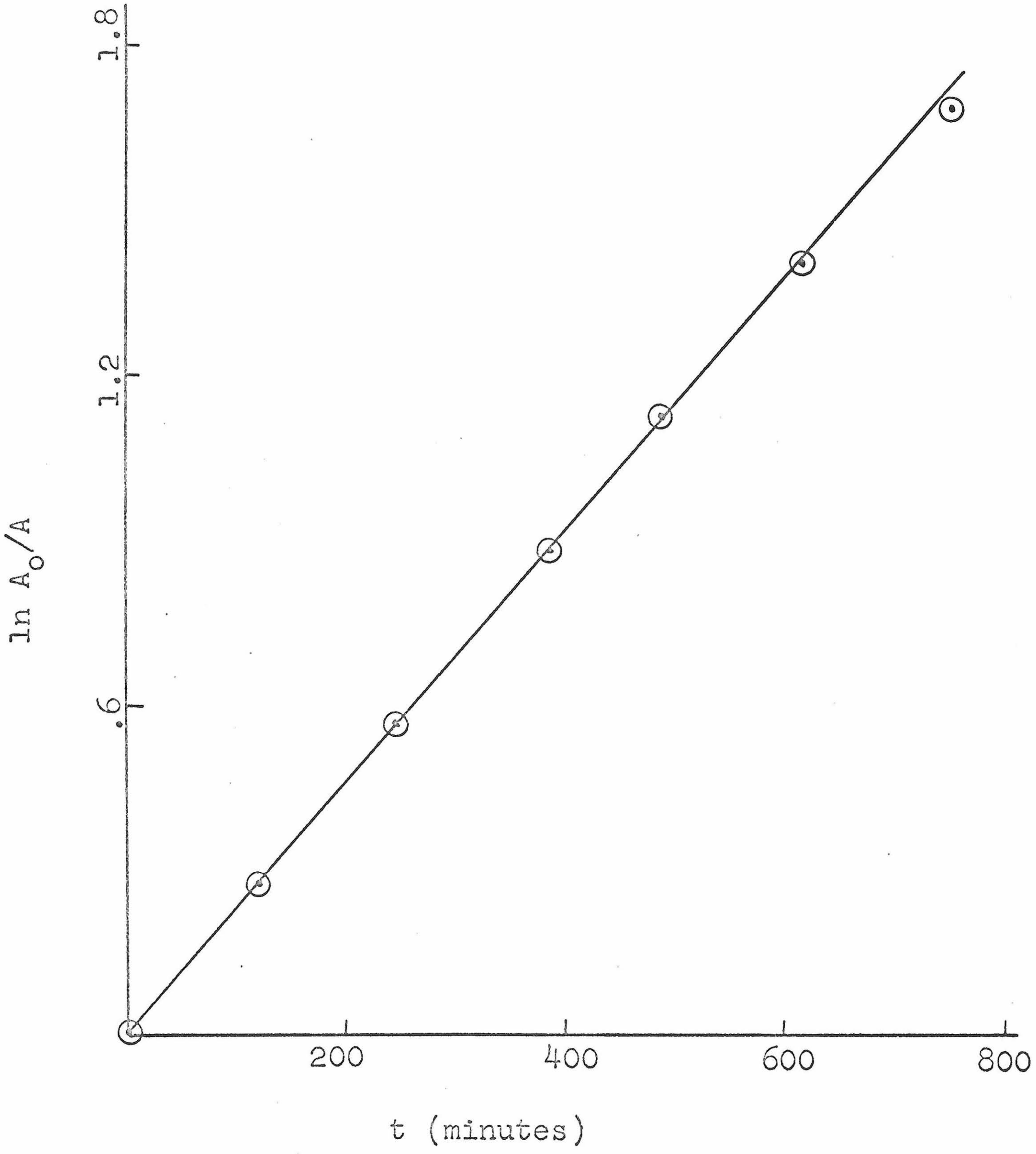

XXXIII

(-OTf = OSO_2CF_3)

available (33) so its triflate (XXXIII) was prepared in like manner and included in the study. With some difficulty the triflates could be purified by gas-liquid chromatography (glc).

The triflates were solvolyzed in 60% aqueous ethanol buffered with triethylamine, and by taking certain precautions (see Experimental) it was possible to follow the reactions quantitatively by glc. Triflate XXXI reacted at a convenient rate at 100°, and triflate XXXIII was even more reactive, requiring only about 40°. However, in order to obtain a comparable reaction rate with triflate XXX temperatures near 250° were required. In all cases the reactions were cleanly first-order; examples of the rate plots are given as Figures 2, 3, and 4. The reaction rates for each triflate were measured at three temperatures covering in each case a range of about 20°, and good Arrhenius plots

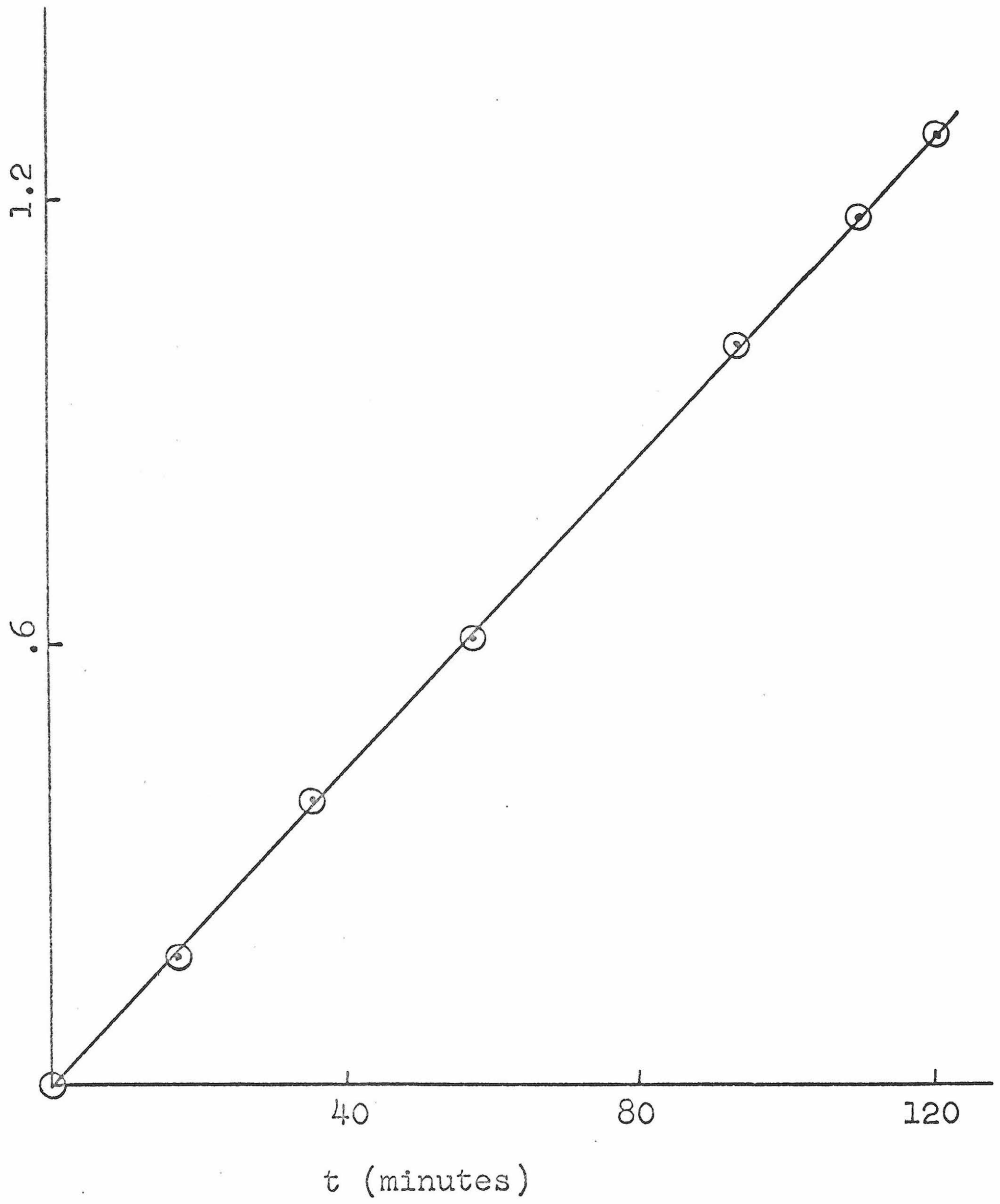
Figure 2. First-order rate plot[a] for the solvolysis of 4-tricyclyl triflate (XXX) in 60% (by wt) aqueous ethanol[b] at 221.1°.



[a] Slope of the line gives $k = 3.74 \pm 0.05 \times 10^{-5}$ sec^{-1}.

[b] Buffered with triethylamine.

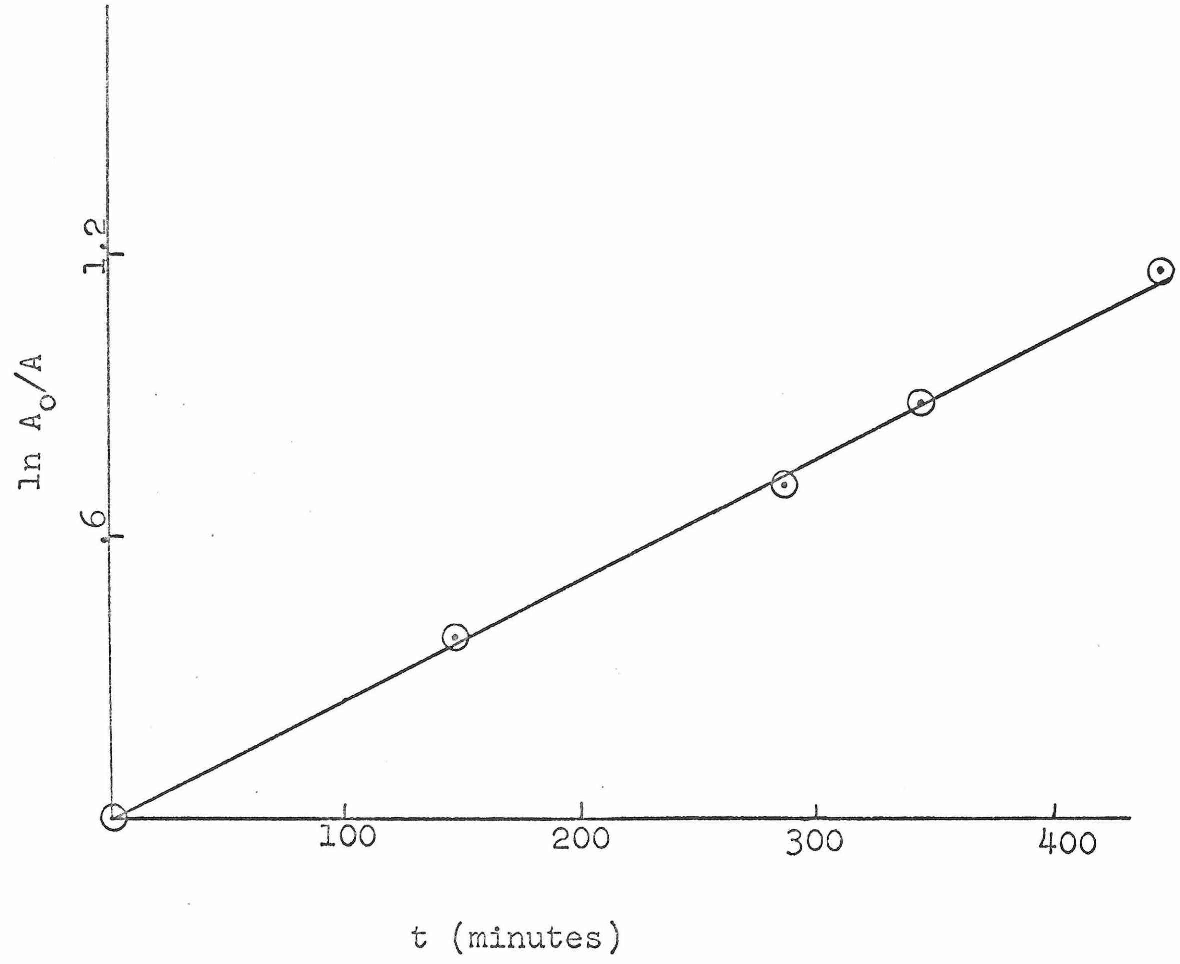
Figure 3. First-order rate plot[a] for the solvolysis of 1-apocamphyl triflate (XXXI) in 60% (by wt) aqueous ethanol[b] at 99.0°.



[a] Slope of the line gives $k = 1.78 \pm 0.01 \times 10^{-4}$ sec^{-1}.

[b] Buffered with triethylamine.

Figure 4. First-order rate plot[a] for the solvolysis of 1-methyl-4-tricyclo[2.2.2.0^{2,6}]octyl triflate (XXXIII) in 60% (by wt) aqueous ethanol[b] at 31.3°.



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[a] Slope of the line give $k = 4.16 \pm 0.08 \times 10^{-5}\ sec^{-1}$.

[b] Buffered with triethylamine.

were obtained (34). Table I presents the measured rate constants and calculated activation parameters, and the Arrhenius plots are shown in Figure 5. The Arrhenius plot for solvolysis of triflate XXX can be used to extrapolate the reaction rate to 25°, and correction for the average triflate-tosylate reactivity difference of $10^{4.8}$ (29) leads to a calculated rate constant of 4.77×10^{-18} $\sec^{-1}$ for 4-tricyclyl tosylate in 60% aqueous ethanol at 25°. This represents the least reactive tertiary alkyl system known (35) and corresponds to a half-life of 4.6×10^{9} years, approximately the radioactive half-life of ^{238}U!

The major products from the solvolyses of the triflates were in each case the unrearranged alcohol and the corresponding ethyl ether. The ratios of alcohol to ether were measured by glc and are reported in Table I. The products were isolated and identified by comparison of their infrared (ir) and in some cases nuclear magnetic resonance (nmr) and mass spectra with those of the starting alcohols and of samples of the ethyl ethers independently synthesized from the starting alcohols.

A sample of 1-apocamphyl ethyl ether (XXXIV) was readily obtained by treating alcohol XXVIII with triethyloxonium tetrafluoborate (36) in methylene chloride, but treatment of alcohol XXIV under the same conditons gave camphor (XXXV) as the only isolated product (its spectra

Figure 5. Arrhenius plots for solvolysis of 4-tricyclyl, 1-apocamphyl, and 1-methyl-4-tricyclo[2.2.2.0^{2,6}]octyl triflates in 60% aqueous ethanol.

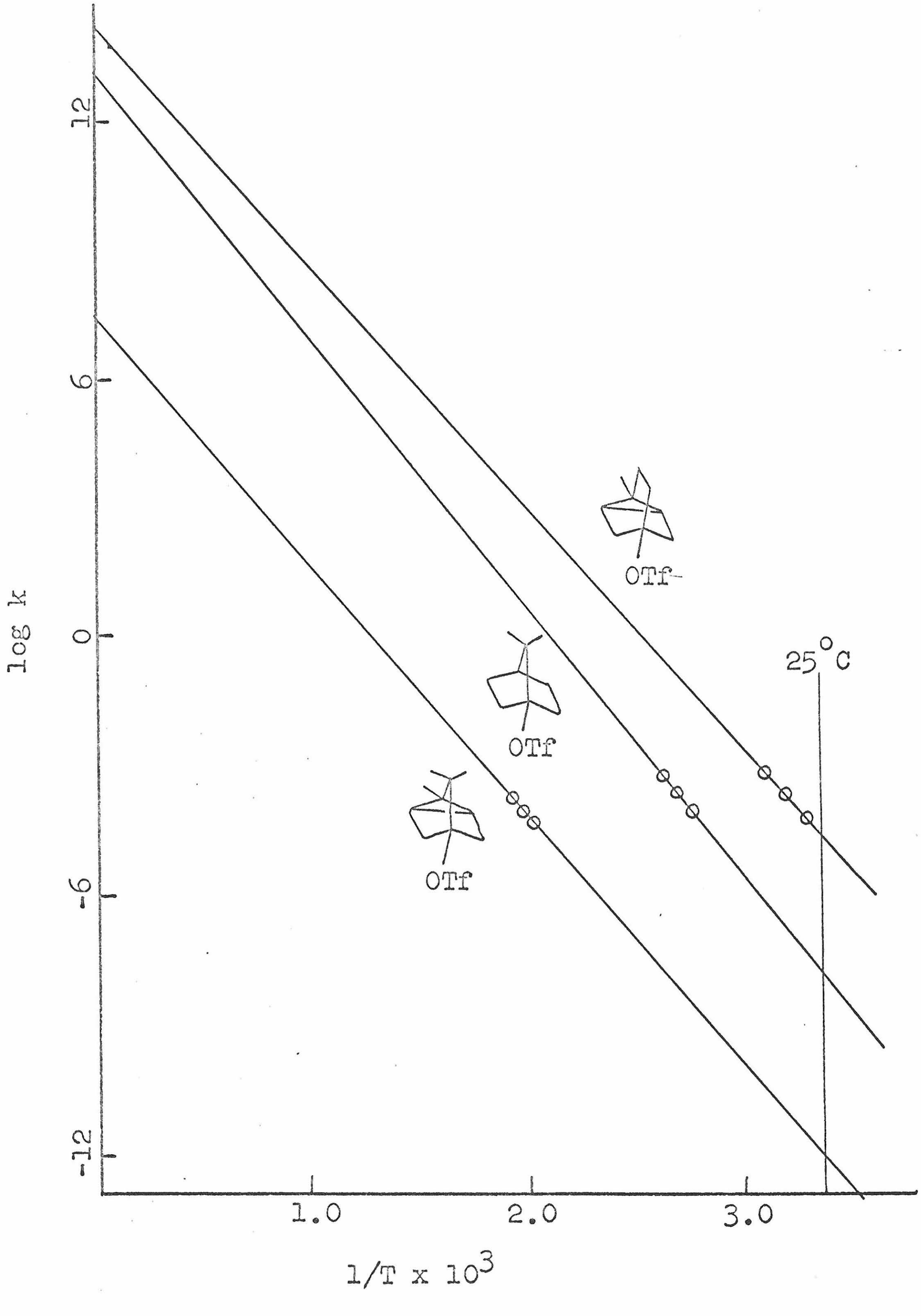
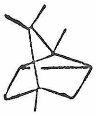
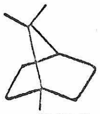
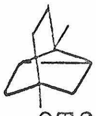


Table I. Kinetic and Product Data from Solvolyses of Some Bridgehead Triflates.[a]

Substrate	T, °C[b]	10^5 k, $\sec^{-1}$	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Pdt ratio[c] (ROH:ROEt)
 OTf XXX	246.0 232.8 221.1	14.6±0.3 7.35±0.1 3.75±0.05	26.9±0.9	-25.2±1.7	72:28
 OTf XXXI	108.5 99.0 89.0	46.5±0.7 17.8±0.1 6.02±0.06	28.0±0.4	-0.8±1.1	63:37
 OTf XXXIII	50.4 41.0 31.3	52.8±0.4 14.8±0.3 4.16±0.08	25.5±0.4	5.0±1.3	69:31

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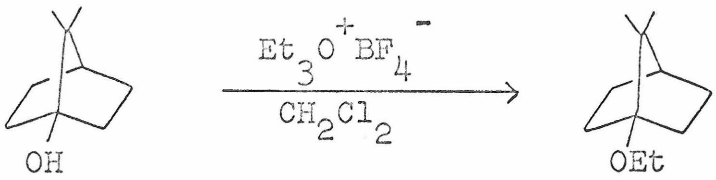
[a] Trifluoromethanesulfonates (0.02 M) solvolyzed in 60% (by wt) aqueous ethanol containing 0.06 M triethylamine.

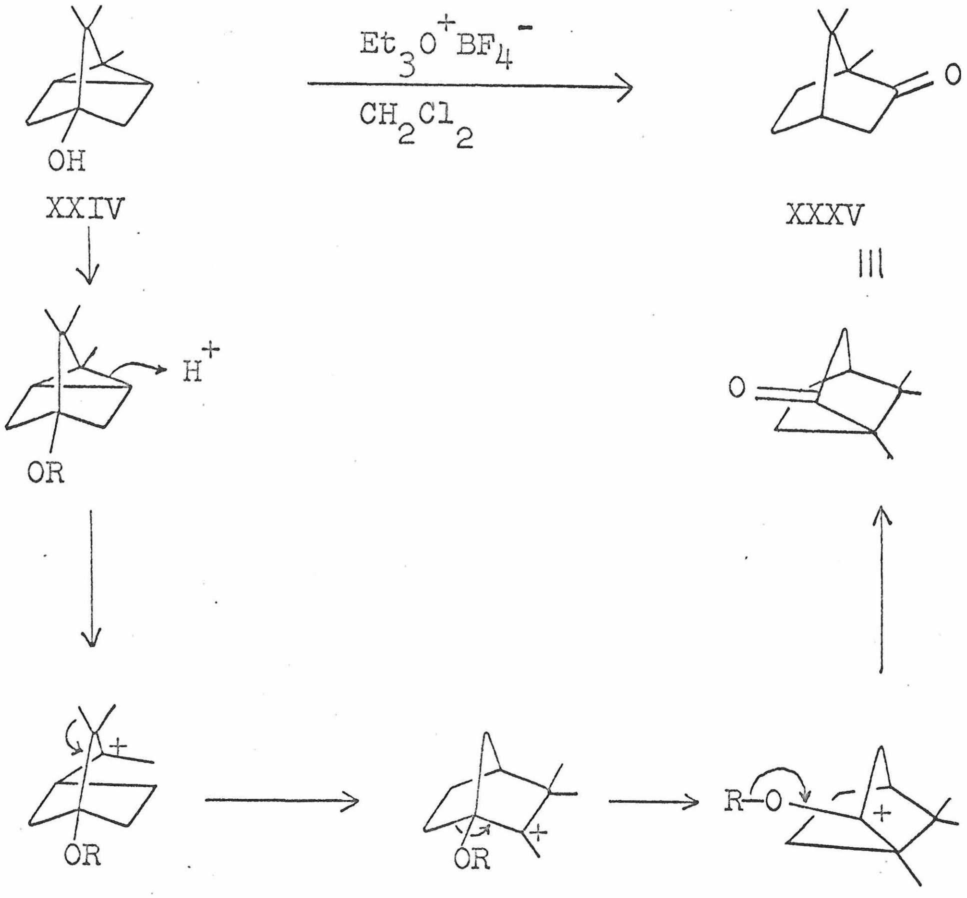
[b] ±0.1°

[c] In all cases the products were the unrearranged alcohol and corresponding ethyl ether.

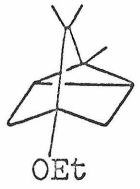


XXVIII XXXIV

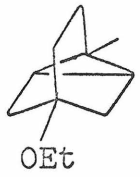
were compared with those of a known sample). The mechanism of the latter reaction is unknown but probably involves catalysis by the equivalent of fluoboric acid produced in the alkylation and might occur as shown below:



It is amusing that the synthesis of 4-tricyclenol begins with camphor and involves 13 steps! Samples of ethers XXXVI and XXXVII were synthesized in low yield (about 20%) by preparing the lithium alkoxides of the corresponding alcohols in dimethyl sulfoxide and then treating with ethyl iodide.



XXXVI



XXXVII

Comparison of Solvolysis Rates with Calculated Strain Energies.

At least a semiquantitative understanding of the role of strain energy in determining the solvolysis rates is of fundamental importance if we are to decide what the role of the cyclopropyl groups has been. At this point we turn to the method of Gleicher and Schleyer for calculating the increase in strain resulting from ionization at a bridgehead (18). This method semiempirically calculates the minimum strain energies of a carbonium ion and of the corresponding hydrocarbon; the difference is taken as the change in strain energy that accompanies ionization at the given center and should roughly correlate with the change in strain energy on going to the ionization transition state.

These calculations take into account strain associated with deformation of bond lengths and bond angles, torsional effects, and nonbonded interactions. The force constant for out-of-plane bending at the carbonium ion has been assigned empirically the value that gives the best linear correlation between calculated strain energies and the logs of the relative solvolysis rates of a number of bridgehead systems (18). Professor Gerald J. Gleicher (37) carried out such calculations for us on the 4-nortricyclyl, 4-tricyclyl, and 1-methyl-4-tricyclo[2.2.2.$0^{2,6}$]octyl systems; the respective strain energies are given in Table II. The calculations for the nortricyclyl and tricyclyl systems indicate that almost the entire strain energy associated with ionization is the result of distortion of carbon-carbon bond angles at and adjacent to the cationic center. The change in strain energy associated with the 1-apocamphyl system can be estimated as about 1 kcal greater than that calculated previously for the 1-norbornyl system (18), based on the observation that a similar difference is calculated between the tricyclyl and nortricyclyl systems and is primarily associated with the geminal methyl groups.

Having obtained Arrhenius data for triflates XXX, XXXI, and XXXIII, one can extrapolate the respective reaction rates to any given temperature and thereby obtain the relative rates at that temperature. This can be done roughly by using the Arrhenius plots in Figure 5 or more accurately by calculating the extrapolated rates based on the measured values of the frequency factors, A , and the energies of activation, E_a , and the Arrhenius equation (37):

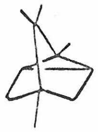
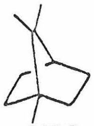
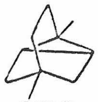
$$k = A\,e^{-E_a/RT}$$

The relative rates for the triflates at 25° are given in Table II.

A plot of the calculated change in strain energy versus the negative of the log of the relative rate constants is reasonably linear (Figure 6), having a slope of 1.45(kcal/mol)/$\log_{10}$, but having only three nearly colinear points is not very convincing. Perhaps the electronic effects of the cyclopropyl groups in triflates XXX and XXXIII are of comparable magnitude but differ in direction due to the difference in cyclopropyl orientation in the molecules. If this were the case then the linearity of the plot would be fortuitous and not indicative of a straightforward correlation between rates and strain energies.

More convincing would be a correlation of the rate and strain data of triflates XXX, XXXI, and XXXIII with those of other bridgehead systems. One difficulty in this regard is the paucity of rate data for bridgehead triflates, but knowledge of a triflate-bromide rate ratio would allow estimation of the solvolysis rates of bromides XXXIX, XL

Table II. Relative Solvolysis Rates and Calculated Strain Energies of Ionization for Some Bridgehead Triflates.

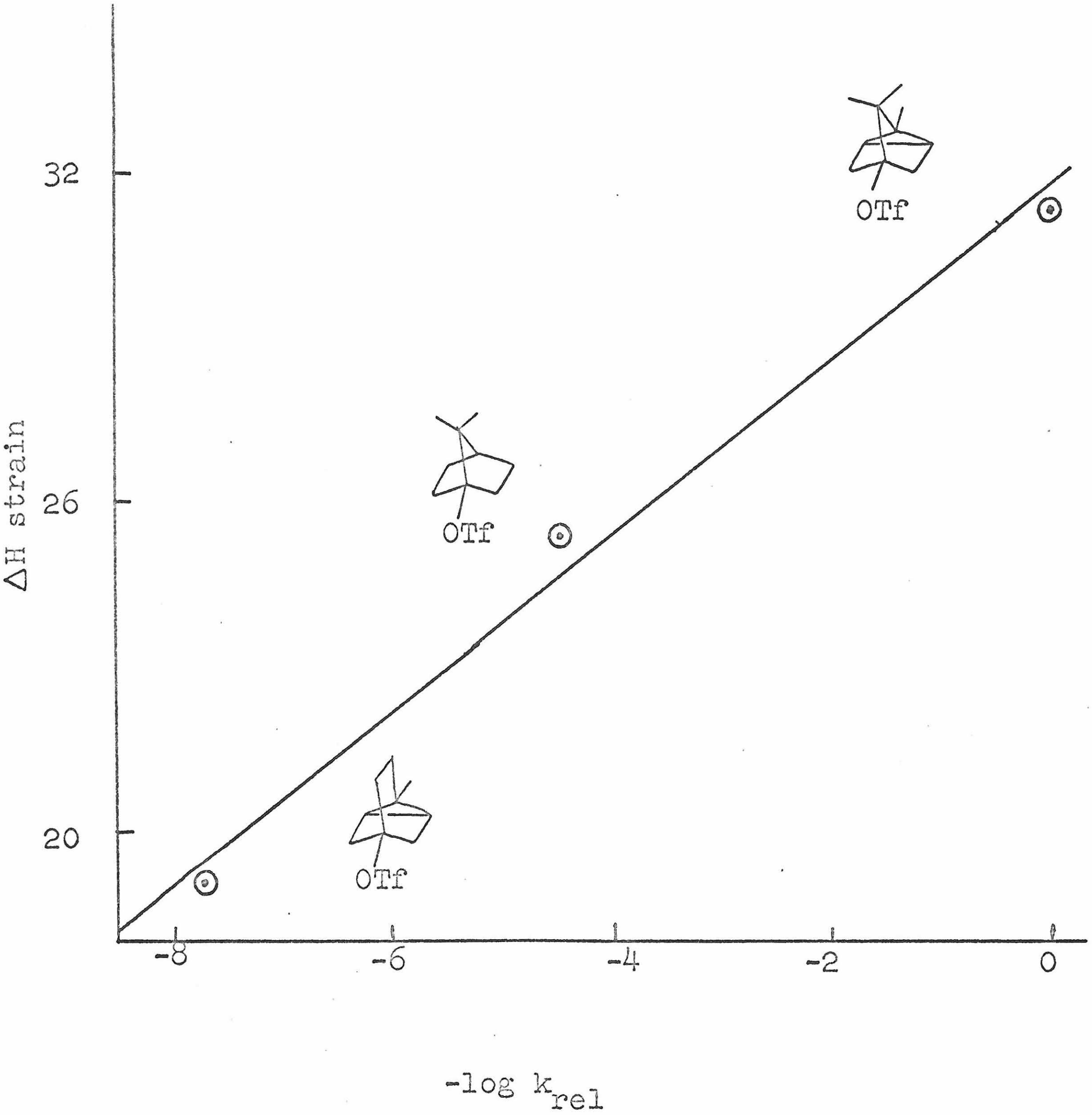
Substrate	k, sec^{-1}, 25°[a]	k_{rel}, 25°	H strain,[b] kcal/mole
 OTf XXX	3.01×10^{-13}	1.0	31.26[c]
 OTf XXXI	8.57×10^{-9}	2.84×10^{4}	25.39
 OTf XXXIII	1.65×10^{-5}	5.45×10^{7}	19.07

[a] Extrapolated from higher temperatures for reaction in 60% (by wt) aqueous ethanol buffered with triethylamine.

[b] Calculated strain energy difference between the carbonium ion and the analogous hydrocarbon.

[c] The corresponding value for the nortricyclyl system is 30.44 kcal/mol.

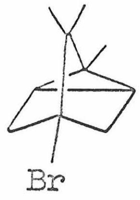
Figure 6. Plot of the calculated strain energies of ionization versus -log of the experimental relative rate con-constants for three bridgehead triflates.



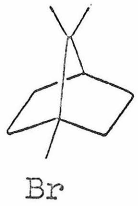
and XLI. An approximate triflate-bromide rate ratio (1.86×10^6) can be obtained from the solvolysis rates of 1-apocamphyl triflate (XXXI) and 1-norbornyl bromide (23, 39), and the strain energies and estimated rate data (39) for the tricyclyl, apocamphyl, and tricyclooctyl systems can then be correlated together with those for several bridgehead systems included by Gleicher and Schleyer in their original treatment (18). The appropriate rates and strain energies appear in Table III and are plotted in Figure 7. The new values fit rather nicely with the earlier ones. The slope base on all points is 1.88 (kcal/mol)/$\log_{10}$, and the intercept appropriately is very close to the change in strain energy calculated for the _t_-butyl system. The relative rate constants predicted by the correlation for the tricyclyl, apocamphyl and tricyclooctyl systems can be obtained from Figure 7 and are shown in Table III; these compare favorably with the experimental relative rates.

Verification of Carbon-Oxygen Bond Cleavage in the Solvolysis of 4-Tricyclyl Triflate (XXX).

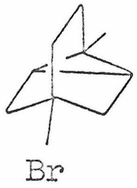
A number of studies have shown that aryl sulfonates, which have extraordinarily low S_N1 reactivity, undergo reactions involving sulfur-oxygen bond cleavage. Some of these studies employed particularly strong nucleophiles and activated aryl groups (41), but the hydrolysis of phenyl tosylate in the presence of dilute sodium hydroxide (42) and



XXXIX



XL



XLI

Table III. Relative Solvolysis Rates and Calculated Strain Energies of Ionization for Some Tertiary Systems.

System	ΔH strain[a] kcal/mol	Experimental k_{rel}, 25°	Calculated[e] k_{rel}, 25°
t-butyl	2.85[b]	1.0[b,c]	
3-homoadamantyl	0.23[b]	0.46[b,c]	
1-adamantyl	10.16[b]	1.2×10^{-3} [b,c]	
1-bicyclo-[2.2.2] octyl	12.93[b]	2.4×10^{-7} [b,c]	
1-methyl-4-tricyclo[2.2.2.0^{2,6}]-octyl	19.07	4.3×10^{-9} [d]	1.1×10^{-9}
1-norbornyl	24.39[b]	2.0×10^{-12} [b,c]	
1-apocamphyl	25.39	2.0×10^{-12} [d]	0.33×10^{-12}
4-tricyclyl	31.26	7.8×10^{-17} [d]	35×10^{-17}

[a] Calculated difference in strain energy between the carbonium ion and the analogous hydrocarbon.

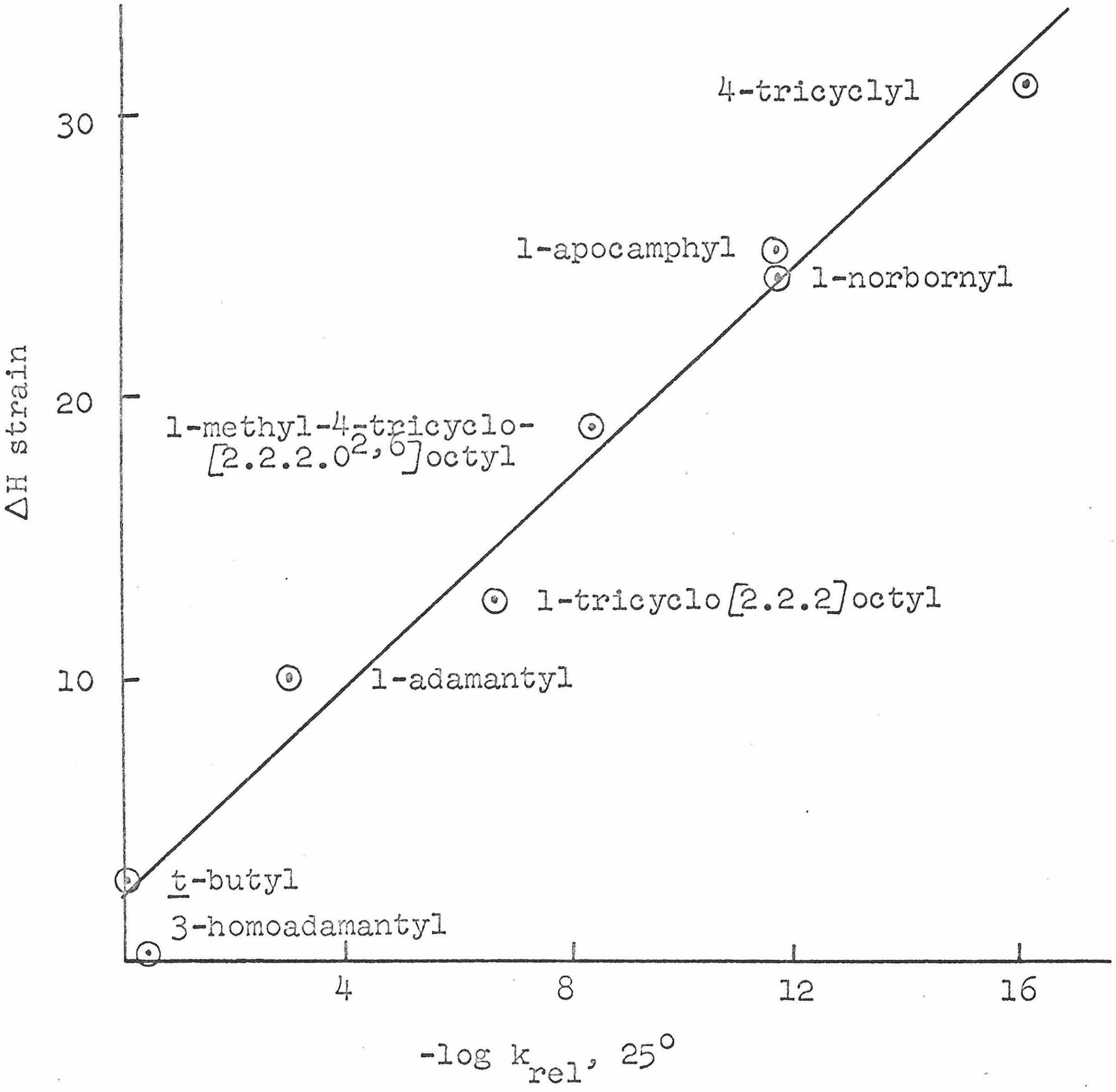
[b] Given in ref 18.

[c] Based on solvolyses of bromides in 80% aqueous ethanol.

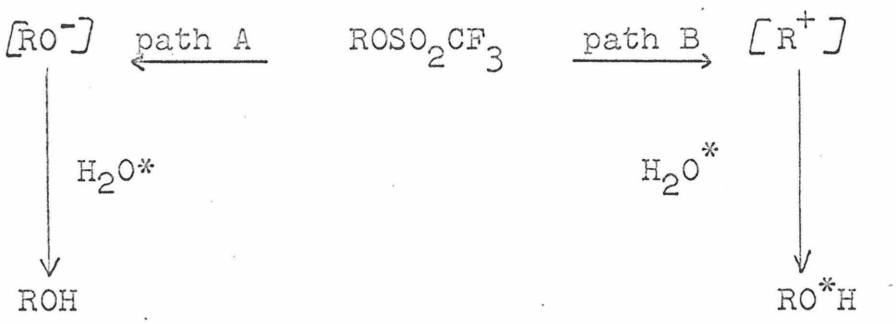
[d] From estimated rates for the bromides based on experimental rates for the triflates (39).

[e] Calculated from the plot in Figure 7.

Figure 7. Plot of the calculated strain energies of ionization versus -log of the experimental relative rate constants for some tertiary systems.



the hydrolysis of phenyl benzenesulfonate in the presence of hydrochloric acid (43) also have been shown to go by this route. This raised the question of whether some or all of the above triflate solvolyses might involve sulfur-oxygen cleavage (path A). Other groups have considered this problem in general and have cited the extreme unreactivity of phenyl triflates in a number of media (22) as evidence against the likelihood of sulfur-oxygen bond cleavage in other triflates (22,29c). This argument is rather convincing, but the remarkable difference between the entropy of activation for solvolysis of triflate XXX and those for the solvolyses of the other triflates (Table I, page 127) suggests that a different, perhaps bimolecular, mechanism might be involved in the solvolysis of XXX. In order to justifiably base an assessment of the nature of the interaction depicted in XXIII on the solvolytic behavior of triflate XXX, it is obviously of paramount importance to know that this solvolysis involves carbon-oxygen bond cleavage. Therefore we



carried out a labeling experiment to check this point; when triflate XXX was solvolyzed in ^{18}O enriched medium the sample of alcohol XXIV produced was found by mass spectrometric analysis to have incorporated the label quantitatively (44). Possible reasons for the anomolous activation entropy of XXX are discussed below.

III. DISCUSSION

Mechanism of the Triflate Solvolyses

Incorporation of ^{18}O into alcohol XXIV on solvolysis of triflate XXX shows that even under the most forcing conditions used in this study carbon-oxygen bond cleavage is occurring and resulting in displacement at the 4-carbon. As a result one can safely assume that carbon-oxygen bond cleavage is involved in the other triflate solvolyses. The first-order kinetics observed for these systems is consistent with a carbonium ion mechanism or with any pseudo-first-order mechanism that involves solvent. Involvement of solvent in a backside nucleophilic displacement is inconceivable owing to the geometric constraints in these substrates. Seemingly the only reasonable mechanism directly involving solvent would be a frontside nucleophilic displacement. This mechanism would be compatible with the observation of ^{18}O incorporation in alcohol XXIV; furthermore, if the frontside nucleophilic displacement occurred only in the case of triflate XXX and the carbonium ion mechanism predominated in the solvolyses of the other triflates, one would have an explanation for the anomolous entropy of activation associated with solvolysis of XXX (Table I, page 127), i.e., the bimolecularity of this displacement together with possible orientational constraints would be expected to result in a much lower entropy of activation than a rate-limiting ionization. However, other studies have led to the generalization that frontside displacements are unimportant in solvolyses of bridgehead substrates (17,23b), and the predominance of a different mechanism in the solvolysis of triflate XXX from that involved in the solvolyses of triflates XXXI and XXXIII could be only fortuitously consistent with closely similar alcohol-ether product ratios such as are observed. The solvolysis rate constant for triflate XXXI in pure water has been measured as 2.95×10^{-3} sec^{-1} at 65.04° (45). From this value and our kinetic data for solvolysis in 60% aqueous ethanol a value of 1.1 can be calculated for Winstein's <u>m</u>, which is consistent with a rate-limiting ionization mechanism (the <u>m</u> value for solvolysis of 1-tricyclo[2.2.2]octyl bromide is 1.13 (17,23b)). We conclude that the solvolyses of all three triflates proceed via carbonium ion mechanisms.

Anomolous Entropy of Activation for Solvolysis of 4-Tricyclyl Triflate (XXX).

Having concluded that a carbonium ion mechanism is common to the solvolyses of triflates XXX, XXXI, and XXXIII, we have yet to explain the anomolous entropy associated with XXX. In that the solvolysis of XXX was carried out with a reaction temperature about 130° higher than that used with XXXI, the possiblity that the $\Delta\Delta S^{\ddagger}$ of 24.4 eu is the result of a temperature effect should be considered. Lending credence to this explanation is the further change in $\Delta S^{\ddagger}$ by 5.8 eu on going from XXXI to XXXIII, which was solvolyzed at a temperature about 60° lower; in all cases the lower $\Delta S^{\ddagger}$ is associated with the higher temperature. The temperature dependence of entropies and enthalpies of activation for solvolysis reactions is well known (46), and by analogy to ground state thermodynamics this dependence may be expressed by the following equations:

$$d\,\Delta S^{\ddagger}/dT = \Delta C_p^{\ddagger}/T$$

$$d\,\Delta H^{\ddagger}/dT = \Delta C_p^{\ddagger}$$

where $\Delta C_p^{\ddagger}$ is the change in heat capacity at constant pressure associated with activations. For example Robertson and co-workers have measured a decrease in $\Delta S^{\ddagger}$ by 10.8 eu and a decrease in $\Delta H^{\ddagger}$ by 3.2 kcal/mol over the temperature range 5 to 40° in the hydrolysis of α-methylallyl chloride (47). These changes are nearly compensatory, resulting in a $\Delta\Delta F^{\ddagger}$ of only 0.2 kcal/mol, and they require a $\Delta C_p^{\ddagger}$ of -92 cal/mol deg (47). In all of the solvolysis reactions for which $\Delta C_p^{\ddagger}$ has been determined, it has been found negative (46).

If $\Delta C_p^{\ddagger}$ for XXX were -79 cal/mol deg, then at 99° $\Delta S^{\ddagger}$ for solvolysis of XXX would be -0.8 eu as it is for XXXI. We may ask whether or not this is a reasonable value for $\Delta C_p^{\ddagger}$ under the circumstances. Robertson and co-workers have generalized that for S_N1 hydrolyses $\Delta C_p^{\ddagger}$ is about -90 cal/mol deg (47), but for a given reaction $\Delta C_p^{\ddagger}$ varies in a complicated way on going from pure water to mixed aqueous solvents. Robertson and Sugamori have shown that for the solvolysis of t-butyl chloride $\Delta C_p^{\ddagger}$ varies from -83 cal/mol deg in pure water to -136 cal/mol deg in 20.8% (v/v) aqueous ethanol, and to -34 cal/mol deg in 50% aqueous ethanol (48). For solvolysis of t-butyl chloride in aqueous isopropanol $\Delta C_p^{\ddagger}$ is -135 cal/mol deg in 18% isopropanol, increases to only -21 cal/mol deg in 32% isopropanol, and decreases again to -52 cal/mol deg in 51.5% isopropanol (48). The studies with aqueous ethanol did not employ greater than 50% ethanol, but by analogy to the results with isopropanol, use of more than 50% ethanol might cause a decrease in $\Delta C_p^{\ddagger}$. Apparently it is not unreasonable to think that a $\Delta C_p^{\ddagger}$ of -79 cal/mol deg might be associated with solvolysis of XXX in our solvent system (65.5% (v/v) aqueous ethanol), but one must also consider a possible temperature effect on $\Delta C_p^{\ddagger}$ in that the measured values given above were all obtained at 10° whereas the average of the solvolysis temperatures used with XXX and XXXI is about 165°. According to the solvent-structural hypothesis offered for the origin of $\Delta C_p^{\ddagger}$ by Robertson and co-workers (48), the absolute value of $\Delta C_p^{\ddagger}$ should decrease with increasing temperature and might be small at our solvolysis temperatures, but the few cases for which sufficiently accurate data have been obtained indicated that $d\,\Delta C_p^{\ddagger}/dT$ was very small and in some cases positive (49,50). Thus a $\Delta C_p^{\ddagger}$ of -79 cal/mol deg might be reasonable even at our high temperature, and we feel that most if not all of the differences between the entropies of activation of XXX and XXXI are just a temperature effect.

With a desire to have this possibility tested we collaborated with Professor Robertson. An attempt to obtain kinetic measurements of the required accuracy with triflate XXX would have been doomed to failure because of experimental difficulties associated with the high reaction temperature required; so we provided Professor Robertson with samples of triflate XXXI. Attempts to measure $\Delta C_p^{\ddagger}$ for hydrolysis of this triflate failed, apparently because the low solubility of XXXI resulted in rate constants of inadequate reproducibility (45).

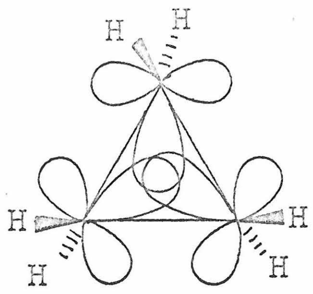
The present case suggests a general note of caution: <u>one should not attach mechanistic significance to a difference in the entropies of activation measured for two compounds at different temperatures unless the temperature effect can be shown to be unimportant</u>.

Interaction of a Carbonium Ion with the Face of a Cyclopropane Ring.

The quality of the correlation between calculated strain energy and reactivity shown in Figure 7 (page 145) is limited to the extent that a measured rate constant would have to differ from the predicted rate by at least $10^{1.76}$ before the difference could be considered statistically significant (beyond the 95% confidence level). The measured relative rates for triflates XXX and XXXIII are well within this limit from the predicted rates, differing by only $10^{0.7}$ and $10^{0.6}$ respectively; in fact these cyclopropane-containing systems fit the correlation better than 1-adamantanyl and 3-homoadamantyl derivatives, compounds the solvolyses of which would not be expected to indicate pronounced electronic effects. Thus one can conclude that within the error limits of the method neither XXX nor XXXIII gives evidence of cyclopropyl stabilization or destabilization in the respective carbonium ions.

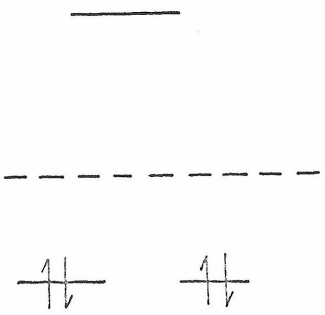
The distance between the ionization center and the face of the cyclopropane ring in triflate XXX apparently is not so great as to preclude a substantial interaction; from the crystal structure of the analogous chloride (51) this distance can be estimated as only 2.1 Å, and in the strain-minimized calculated structure for ion XXIII this distance is only 1.96 Å. Seemingly, either the interaction is prohibited on other grounds or else by its nature little net effect on the stability of the species results.

A crude understanding of the theoretical nature of this interaction can be had with the help of the Walsh model for cyclopropane. Walsh found that much of the available chemical evidence pertaining to cyclopropanes could be rationalized in terms of the model for cyclopropane shown in XLII (14). In this model the hybridization at each methylene group is taken as sp^2, with two sp^2 hybrid orbitals participating in bonds to hydrogen and the third lying in the plane of the ring and directed toward its center. The three p orbitals also lie in the plane of the ring. Walsh showed that the p orbitals would interact to give three molecular

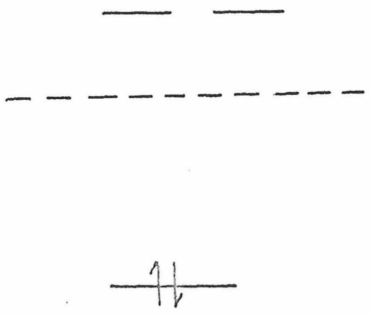


XLII

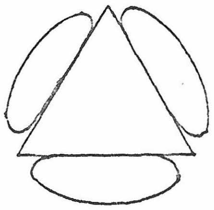
orbitals (MO's), one strongly antibonding and two weakly bonding, having the probability pattern shown in XLIII, whereas the sp^2 hybrids overlap to give one strongly bonding MO and two weakly antibonding MO's having the probability pattern shown in XLIV.



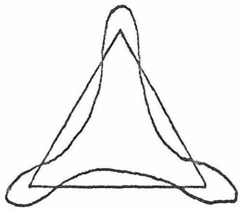
MO's from p orbitals



MO's from sp^2 hybrids



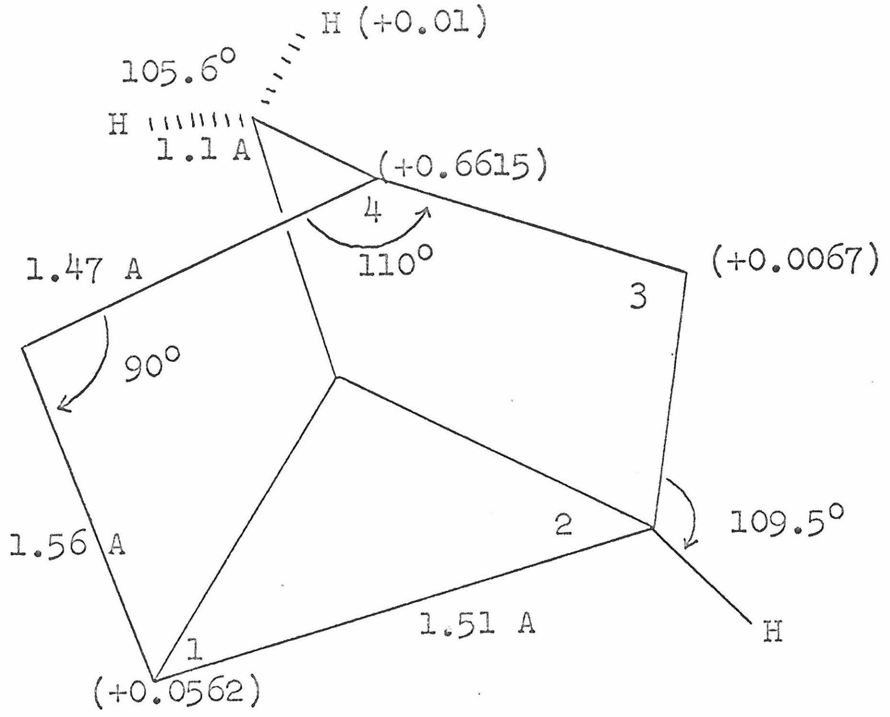
XLIII



XLIV

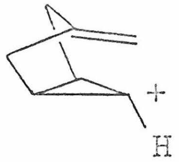
The six electrons of the carbon-carbon bonds were assigned to the three bonding MO's. More recently Hoffmann applied his extended Hückel theory to cyclopropane and obtained results compatible with the predictions of the Walsh model; the highest occupied level was degenerate and composed almost entirely of in-the-plane p orbitals, and the total electron density distribution had maxima in the regions indicated in XLIII (5b). In bringing an empty p orbital perpendicularly onto the face of a cyclopropane ring the interaction in question will be that with the MO illustrated in XLIV. Although the electrons in this MO have a high probability of being in the region of interaction, there are only two electrons distributed over the three nuclear centers of this MO, making it analogous to a cyclopropenium cation. Thus one has in effect an interaction between two cations; furthermore, the higher s character of this MO makes it much more electronegative than a p orbital (52), and accordingly it will be reluctant to delocalize its electrons to the incoming p orbital. These considerations suggest that lack of cyclopropyl stabilization in the solvolysis of triflate XXX should not be surprising.

An extended Hückel calculation (54) on 4-nortricyclyl cation in the conformation (XLV) predicted by the strain-minimizing empirical treatment (described on page 137) also suggests little favorable interaction with the face of the cyclopropane ring. As shown below only a small fraction of the positive charge is delocalized to the cyclopropyl carbons. Still more revealing is the fact that the overlap population (roughly corresponding to a bond order) between carbons 1 and 4 is slightly negative (-0.03)--hardly what one would expect from a favorable interaction with the MO in



XLV

XLIV. This suggests that the small delocalization of charge to the cyclopropyl carbons that does occur may be the result of hyperconjugation, i.e., the charge on carbon 2 may result from interaction of the empty p orbital with the strained σ bond between carbons 2 and 3, as illustrated in the possible resonance contributor XLVI.



XLVI

Another possible contribution to the overall interaction in the solvolysis of triflate XXX is the inductive effect of the cyclopropyl group. Rhodes and Takino have estimated that a "nonconjugated" cyclopropyl ring has a rate retarding inductive effect of 6 to 15 (16a). Since the ionization center in XXX is connected to a cyclopropyl ring through all three methylene groups, one might expect a total rate retardation of 6^3 to 15^3 ($10^{2.3}$ to $10^{3.5}$), but the effect would probably be attenuated in this case because the bonds to the cyclopropane ring are strained and therefore have higher p character. Within our experimental error any inductive effect must be canceled by other electronic effects, perhaps principally by hyperconjugation as in XLVI.

In conclusion, we have found no evidence for a significantly stabilizing interaction between positively charged carbon and the face of a cyclopropane ring (55). An analogous case is that of face-protonated cyclopropane, a theoretical intermediate for which no definitive evidence has been found (15) and which, according to a number of quantum mechanical calculations, appears to be less stable than edge-protonated cyclopropane by more than 100 kcal/mol (56).

IV. EXPERIMENTAL

General. Infrared (ir) spectra were determined on a Perkin-Elmer IR 257 instrument, the samples being 10% solutions in carbon tetrachloride. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian A60-A spectrometer; carbon tetrachloride was the solvent and chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained on a CEC-21-103C instrument at 10 u ionizing current and 70 v ionizing potential; the inlet temperature was 250°. Ultraviolet (uv) spectra were obtained on a Cary 14 spectrophotometer. Elemental analyses were performed by Spang Microanalytical Lab., Ann Arbor, Michigan. Boiling and melting points are uncorrected. Qualitative and preparative gas-liquid chromatography (glc) was carried out on Varian Aerograph 90-P3 instruments. Quantitative analytical glc was carried out on a Hewlett-Packard 5750 (flame ionization detector) equipped with a Disc integrator. The following columns were used: column A, 5 ft x 1/4 in. stainless steel, 3% SE-30 on 100-120 Varaport 30; column B, 12 ft x 1/4 in. aluminum, 8% SE-30 on 60-80 Chromosorb P; column C, 10 ft x 1/4 in. glass, 3% SE-30 on 60-80 Chromosorb WAWDMCS; column D, 2.5 ft x 1/4 in. aluminum, 8% TCEP on 60-80 Chromosorb G; column E, 6 ft x 1/8 in. stainless steel, 10% UCC-W98 on 100-120 Chromosorb WAWDMCS; column F, 6 ft x 1/4 in. glass, 6% SE-30 on 60-80 Chromosorb WAWDMCS.

Syntheses

1-Apocamphanol (XXVIII) was prepared from 1-apocamphanecarboxylic acid (57) in accord with the method of Hawthorne, Emmons, and McCallum (21) with the exception that *m*-chloroperbenzoic acid instead of pertrifluoroacetic acid was used in the Baeyer-Villiger step as follows: Crude 1-apocamphyl phenyl ketone (3.6 g) and *m*-chloroperbenzoic acid (4.8 g) were dissolved in 50 ml of dichloroethane. The solution was refluxed for 6 hr and allowed to stand overnight. Solvent was removed on a rotary evaporator, and 80 ml of cold 20% sodium hydroxide solution was added to the residue. Vigorous agitation of the mixture was followed by extraction with ether. The ethereal solution was washed with water and brine and dried over anhydrous magnesium sulfate; removal of solvent on a rotary evaporator afforded 3.8 g of crude 1-apocamphyl benzoate as a yellow oil. The benzoate was hydrolyzed as reported (21) and 1.27 g (about 58% yield from 1-apocamphyl phenyl ketone) of alcohol XXVIII was obtained (mp 153-157°). Recrystallization from pentane afforded pure samples (mp 163-164.5°; lit, 160° (21)). A more efficient synthesis was reported recently (58).

1-Apocamphyl Brosylate (XXVII). In a 10 ml flask a mixture of 260 mg of alcohol XXVIII, 2.3 ml of pyridine (dried over molecular sieves), and 700 mg of *p*-bromobenzenesulfonyl chloride (recrystallized from carbon tetrachloride) was heated at 58° for 20 hr and then after addition of 5 ml of water was allowed to stand at room temperature for 24 hr. A 5 ml portion of 6 N hydrochloric acid was added and the mixture was extracted with ether. The ethereal extract was washed with water, saturated sodium bicarbonate solution, water, and brine, and was dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator left 331 mg of an off-white solid (mp 90-110°), which was dissolved in the minimal amount of warm pentane. Cooling the solution to -78° and scratching gave a white precipitate. A second recrystallization from pentane afforded 194 mg (32% yield) of white crystals (mp 118-118.5°). The ir spectrum displayed bands at 2960, 2880, 1263, 1020, and 870 cm^{-1}. The nmr spectrum consisted of an aromatic multiplet (4H) centered at 7.6 ppm, a multiplet from 1.0 to 2.2 ppm (9 H) due to methylene and methine protons, and a singlet (6 H) at 0.97 ppm due to the methyl protons. *Anal.* Calcd for $C_{15}H_{19}O_3SBr$: C, 50.11; H, 5.33; S, 8.92; Br, 22.24. Found: C, 50.17; H, 5.11; S, 8.99; Br, 22.26.

4-Tricycyl Brosylate (XXVI). A mixture of 300 mg of 4-tricyclenol (XXIV) (59), 750 mg of *p*-bromobenzenesulfonyl chloride and 3 ml of dry pyridine was heated at 62° for 30 hr. Treatment of the reaction mixture in the manner described for the preparation of brosylate XXVII gave 261 mg (36% yield) of brosylate XXVI as a white solid (mp 99-100°).

The ir spectrum displayed bands at 3060, 1580, 1395, 1382, 1360, 1285, 1205, 1195, 1067, and 880 cm^{-1}. The nmr spectrum consisted of an aromatic multiplet (4H) centered at 7.68 ppm, a singlet at 1.84 ppm (4 H) due to the methylene protons, a singlet at 1.02 ppm (3H) due to the bridgehead-methyl protons, a singlet at 0.93 ppm (2 H) due to the cyclopropyl methine protons, and a singlet at 0.83 ppm (6 H) due to the protons of the geminal methyl groups. Anal. Calcd for $C_{16}H_{19}O_3SBr$: C, 51.75; H, 5.16; S, 8.64; Br, 21.52. Found: C, 51.86; H, 4.96; S, 8.67; Br, 21.68.

1-Apocamphyl Triflate (XXXI). To a solution of 164 mg of alcohol XXVIII in 3 ml of pyridine contained in a 5 ml flask, was added dropwise under nitrogen 642 mg (1.96 equiv) of trifluoromethanesulfonic anhydride (30). During the addition the solution was stirred magnetically and cooled in an ice bath. A white solid which precipitated soon dissolved and the solution became pink. The flask was stoppered and allowed to stand in a freezer overnight. The dark red reaction mixture was poured into ice water, which was then extracted with ether. The ethereal extract was washed with 6 N hydrochloric acid, water, saturated sodium bicarbonate, and brine, and was dried over anhydrous magnesium sulfate. Concentration on a rotary evaporator left 272 mg of a yellow oil. On standing several hours at room temperature an orange resinous material precipitated; the oil was taken up in pentane and decanted from the resin.

Concentration on a rotary evaporator gave a colorless oil which remained clear on standing. Pure triflate XXXI (159 mg; 50% yield) was isolated from a solution of the above oil in carbon tetrachloride by preparative glc on column A at 100° and a flow rate of 2 ml/sec. The ir spectrum of XXXI displayed bands at 2975, 2900, 1415, 1247, 1215, 1150, 1000, 968, and 908 cm^{-1}. The nmr spectrum consisted of a multiplet from 1.85 to 2.40 ppm (5 H), a multiplet from 1.17 to 1.85 ppm (4 H), and a singlet at 1.1 ppm (6 H) due to the methyl protons. The mass spectrum showed the parent ion (0.74%) at m/e 272, the base peak at m/e 55, and other major peaks at m/e 69 and 41. Anal. Calcd for $C_{10}H_{15}O_3SF_3$: C, 44.11; H, 5.55; S, 11.78. Found: C, 44.26; H, 5.58; S, 12.01. Subsequent attempts to purify other samples of triflate XXXI revealed that it is sensitive to the glc conditions. During preparative glc an oily substance accumulated in the glass injector insert which, unless removed at regular intervals, resulted in severe decomposition of XXXI. Also, a column which worked well on one occasion subsequently resulted in decomposition of XXXI and had to be replaced.

4-Tricycyl Triflate (XXX). Under the above reaction conditions 192 mg of 4-tricyclenol (XXIV) in 4 ml of pyridine was treated with 1.16 g (3.2 equiv) of trifluoromethanesulfonic anhydride. After working up the reaction mixture as described above, pure triflate XXX (188 mg; 52.6% yield) was obtained through preparative glc on column B at 155° and a flow rate of 2 ml/sec. Under these conditions the triflate had a retention time of 18 min and was followed closely by a minor product which was also a triflate according to its ir spectrum but was not identified. The ir spectrum of triflate XXX displayed bands at 3070, 2965, 1440, 1250, 1215, 1155, 1090, 1045, 960, and 910 cm^{-1}. The nmr spectrum consisted of a broad singlet at 2.04 ppm (4H) due to the methylene protons, a broad singlet at 1.07 ppm (5H) due to the bridgehead-methyl and cyclopropyl methine protons, and a singlet at 0.94 ppm (6H) due to the protons of the geminal methyl groups. The mass spectrum showed the parent peak (24.1%) at m/e 284, the base peak at m/e 41, and major peaks at m/e 43, 69, 119, and 269. Anal. Calcd for $C_{11}H_{15}O_3SF_3$: C, 46.47; H, 5.32; S, 11.28. Found: C, 46.78; H, 5.27; S, 11.44.

1-Methyl-4-tricyclo[2.2.2.$0^{2,6}$]octyl Triflate (XXXIII). A solution of 1.57 g (5.8 equiv) of trifluoromethanesulfonic anhydride in 5 ml of dry pyridine in an ice bath was stirred magnetically under nitrogen. A solution of 134 mg of 1-methyl-4-tricyclo[2.2.2.$0^{2,6}$]octanol (32,33) in 2 ml of pyridine was added dropwise. After 40 min the reaction mixture was poured into a separatory funnel containing ice, water, and ether. Shaking was followed by addition of cold

6 N hydrochloric acid, shaking, and separation of the ether layer. The ethereal solution was washed with 6 N hydrochloric acid, saturated sodium bicarbonate, and brine, and was dried over magnesium sulfate and concentrated on a rotary evaporator. Initial attempts at glc purification showed that triflate XXXIII decomposes readily. Glc purification of 149 mg (60.4% yield) of XXXIII was achieved by using a glass injector insert, which had to be replaced after each few injections, and a glass column (column C) at 115° and a flow rate of 1 ml/sec. The ir spectrum displayed bands at 3030, 2950, 2870, 1405, 1245, 1205, 1145, 1020, 925, and 905 cm^{-1}. The nmr spectrum consisted of broad singlets at 2.23 ppm (4H) and 2.06 ppm (4H) due to methylene protons, a broad singlet at 1.24 ppm (2H) due to cyclopropyl methine protons, and a sharp singlet at 0.92 ppm (3H) due to bridgehead-methyl protons. The mass spectrum showed the appropriate parent peak at m/e 270 but also showed peaks from m/e 281 to 285. The latter peaks may be due to a minor impurity or to decomposition of the triflate in the heated inlet system of the mass spectrometer. The base peak was at m/e 105 and other major peaks were at m/e 69, 92, and 120. Anal. Calcd for $C_{10}H_{13}O_3SF_3$: C, 44.44; H, 4.85; S, 11.86. Found: C, 44.35; H, 4.91; S, 11.78.

1-Apocamphyl Ethyl Ether (XXXIV). A 10 ml round-bottomed flask was charged with 80 mg of alcohol XXVIII, 400 mg (3.7 equiv) of triethyloxonium tetrafluoborate (36), and 5 ml of methylene chloride and was fitted with a reflux condenser. The reaction mixture was refluxed for 12 hr and then partitioned between water and ether. The ethereal extract was washed with saturated sodium bicarbonate and brine and dried over anhydrous magnesium sulfate. Most of the solvent was carefully removed on a rotary evaporator. Pure ether XXXIV (78.3 mg; 82% yield) was obtained through preparative glc on column B at 170°. Its ir spectrum displayed bands at 2960, 2880, 1480, 1468, 1453, 1385, 1365, 1210, 1140, and 1075 cm^{-1}. The nmr spectrum consisted of a quartet at 3.33 ppm (2 H, J = 6.5 Hz) due to the methylene protons of the ethyl group, a multiplet from 1.27 to 2.10 ppm (about 3 H, J = 6.5 Hz) due to the methyl protons of the ethyl group, and a singlet at 0.90 ppm (6 H) due to the protons of the geminal methyl groups. The mass spectrum showed the parent peak at m/e 168 (p + 1, 11.7%; p + 2, 0.88%. $C_{11}H_{20}O$ requires: p + 1, 12.25%; P + 2, 0.89%). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.44; H, 12.20.

4-Tricyclyl Ethyl Ether (XXXVI). A 10 ml flask containing 94 mg of alcohol XXIV in 3 ml of dry ether (distilled from LAH) was purged with nitrogen. The solution was stirred magnetically while 0.40 ml of 1.75 M methyllithium (1.14 equiv) was added, producing a white precipitate. The ether was removed under pump vacuum and the white solid was dissolved in 2 ml of dimethyl sulfoxide (distilled from calcium hydride). Addition of 105 mg (1.1 equiv) of ethyl iodide was followed by stirring for 2 hr. The reaction mixture was poured into water and then extracted with pentane. The pentane extract was washed with 1 N hydrochloric acid and saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. Analytical glc revealed mainly starting material but also a minor product. Preparative glc on column D with temperature programming from 50 to 130° and a flow rate of 1 ml/sec allowed isolation of 21.7 mg (19.5%) of ether XXXVI. The ir spectrum of XXXVI displayed bands at 3050, 2950, 2870, 1465, 1295, 1197, 1145, 1125, and 840 cm^{-1}. The nmr spectrum consisted of a quartet at 3.37 ppm (2 H, J = 6.5 Hz) due to the methylene protons of the ethyl group, a triplet centered at 1.11 ppm (J = 6.5 Hz) with a singlet at 1.0 ppm superimposed on one element of the triplet (total of 6 H) due to the methyl protons of the ethyl group and the bridgehead-methyl protons, and a singlet at 0.75 ppm (8 H) due to the cyclopropyl methine protons and the protons of the geminal methyl groups. The mass spectrum showed the parent peak at m/e 180. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.78; H, 11.20.

1-Methyl-4-tricyclo[$2.2.2.0^{2,6}$]octyl Ethyl Ether (XXXVII) was prepared by the method used in preparing ether

XXXVI. Starting with 55 mg of alcohol XXXII, a 20% yield (13.4 mg) of ether XXXVII was obtained after glc purification on column D. The ir spectrum displayed bands at 3020, 2935, 2860, 1445, 1360, 1175, 1120, 1050, and 845 cm^{-1}. The nmr spectrum consisted of a quartet at 3.25 ppm (2 H, J = 6.5 Hz) due to the methylene protons of the ethyl group, a multiplet from 1.1 to 2.1 ppm (about 8 H) due to methylene protons, a triplet at 1.05 ppm (J = 6.5 Hz) due to the methyl protons of the ethyl group overlying a multiplet due to the cyclopropyl methine protons (total of about 5 H), and a singlet at 0.87 ppm due to the bridgehead-methyl protons. The mass spectrum showed the parent peak (16.7%) at m/e 166 and the base peak at m/e 151. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.72; H, 11.16.

Reaction of 4-Tricyclenol (XXIV) with Triethyloxonium Tetrafluoborate. A mixture of 25.5 mg of alcohol XXIV, 0.3 g of triethyloxonium tetrafluoborate, and 2 ml of methylene chloride was refluxed for 2 hr and then partitioned between water and ether. The ethereal extract was washed with saturated sodium bicarbonate and brine and was dried over anhydrous magnesium sulfate. Analysis of the concentrated sample on column E showed one major product, which had the same retention time as ether XXXVI. However, this product was isolated by preparative glc (column B at 170°, 2 ml/sec), and its ir and nmr spectra were identical to those of an authentic sample of camphor (XXXV) (Eastman).

Solvolysis of Brosylates in Aqueous Dioxane.

Solvolysis of 1-Apocamphyl Brosylate (XXVII). The rate of solvolysis of brosylate XXVII in 70% (by wt) aqueous *p*-dioxane was determined using a modification of the uv spectrophotometric method described by Swain and Morgan (28). For each run a solution 0.01 *M* in brosylate and 0.015 *M* in triethylamine in 70% aqueous dioxane (*p*-dioxane was Matheson Coleman and Bell Spectroquality) was prepared. Portions (1.05 ml) of this solution in sections of 1/4-in. heavy-walled Pyrex tubing (previously washed with 5% sodium hydroxide, glacial acetic acid, ammonium hydroxide, and distilled water, and dried in a vacuum over at 100° for at least 24 hr) were cooled in liquid nitrogen and sealed under aspirator vacuum. The sealed samples were placed simultaneously in a kinetic bath (Gebrüder Haake Ultra-thermostat, model NBB) previously equilibrated at 200.1°. After a 15 min equilibration period, samples were removed at intervals and quenched in water. Each sample was treated as follows: By pipette 1.00 ml of the sample was transferred to a 3 ml volumetric flask and to the flask were added 1 ml of reagent diethyl ether and 1 ml of solution A (an aqueous solution 0.05 *N* in sodium hydroxide and 10% by weight sodium chloride). After extraction, the ether layer was removed by pipette and the aqueous layer was extracted with a second 1 ml portion of ether and finally with 1 ml of cyclohexane (Matheson Coleman and Bell Spectroquality). The above extraction sequence was effective in avoiding troublesome emulsions. After removal of the cyclohexane extract the aqueous solution was diluted to the line with solution A, and the uv spectrum (1 cm cell) was measured. The absorbance at 265 nm, the longest wavelength maximum of the brosylate anion, was determined as a function of reaction time. From the extinction coefficient for brosylate anion (measured as 337 at 265 nm; a Beer's law plot was linear over the required concentration range), and the absorbance data, the concentrations of brosylate anion and in turn the extent of reaction of brosylate XXVII could be calculated. When a 1 ml portion of the solution of brosylate XXVII was worked up as above prior to solvolysis a uv sample was obtained which exhibited an absorbance of only 0.005 at 265 nm. This required only a small correction of the raw absorbance data. However, the absorbance measured after 7 half-lives exceeded the expected infinity "titer" by about 30%, and tailing beyond 300 nm was observed, whereas brosylate anion does not absorb appreciably at 300 nm. When samples of 70% aqueous dioxane, 0.015 M in triethylamine were heated under the same conditions and subjected to the above work-up, uv analysis revealed a broad absorption that tailed beyond 300 nm. Since in these samples the ratio of the absorbance at 265 nm to that at

300 nm was essentially constant (about 2.3) and since brosylate anion does not absorb at 300 nm, it was possible to approximately correct the absorbance data at 265 nm obtained in the solvolysis to brosylate anion absorbance by subtracting 2.3 times the absorbance at 300 nm. This correction gave approximately the correct infinity "titer." The first-order rate plot is given as Figure 1. A number of the sample tubes exploded in the kinetic bath during each run; the rate plot includes data points from several runs.

In order to determine the reaction products several samples were heated for seven half-lives and worked up as above. The combined ethereal extracts were dried over magnesium sulfate and analyzed by glc on column E. The one product observed had the retention time of alcohol XXVIII, and comparison with a solution of XXVIII of known concentration suggested a yield of greater than 80%. A sample of the product was isolated by glc and its ir spectrum was identical to that of XXVIII.

<u>Solvolysis of 4-Tricyclyl Brosylate (XXVI)</u>. A solution of brosylate XXVI in 70% aqueous dioxane buffered with triethylamine was prepared as described in the case of brosylate XXVII. A sample of this solution was sealed in a stainless steel tube (these tubes have a volume of 1.5 ml and a wall thickness of 4 mm, and are sealed by threaded caps which employ teflon gaskets) and was heated for more than 12 hr at 250° in a tube oven. The sample was diluted

with solution A (vide supra) and extracted with ether. The extract on evaporation to dryness left a white solid, the ir spectrum of which was essentially identical to that of brosylate XXVI. The recovery was about 97%. A second sample sealed in a steel tube was heated for more than 14 hr at 295°. After a work-up as above, analysis of the ethereal extract on column E at 150° revealed three products the retention times and relative percentages of which follow: 1.9 min, 3%; 2.1 min, 13%; 2.3 min, 84%. Comparison with a solution of alcohol XXIV of known concentration showed that the minor (3%) product had the retention time of XXIV and that this product had formed in less than 1% absolute yield. Concentration of the ethereal extract left a yellow oil, the ir spectrum of which suggested that it was mostly brosylate XXVI. The recovery was apparently about 50%. In a second run under the same conditions but allowing only an 8 hr reaction period, three products were again observed, but none had the retention time of alcohol XXIV. Under the same conditions solvolysis of a mixture of brosylate XXVI and alcohol XXIV gave a mixture of these three products with no remaining XXIV. Alcohol XXIV is apparently unstable under the reaction conditions; therefore, the 3% component observed in the first run is probably not XXIV, although it has the same retention time. The products were not identified.

Solvolyses of Triflates in Aqueous Ethanol.

Kinetics. The solvent used in the solvolysis of triflates XXX, XXXI, and XXXIII was 60% (by wt) aqueous ethanol (ethanol was U. S. I. absolute reagent). For each kinetic run a solution 0.02 M in triflate, 0.06 M in triethylamine, and 0.01 M in biphenyl (internal standard) was prepared, and 0.65 ml aliquots were sealed in stainless steel tubes (described above). The tubes were placed simultaneously in a kinetic bath (Gebrüder Haake Ultra-thermostat, model NBB) previously equilibrated at the desired temperature. After a 15 minute equilibration period tubes were withdrawn at intervals and quenched in ice water. For the kinetic run with triflate XXXIII at 31.3°, the entire sample contained in a 10 ml volumetric flask was placed in a Sargent water bath (S-84810) controlled by a Sargent Thermonitor , model SW (S-82055). Aliquots were taken at intervals by pipette.

In all kinetic runs each sample was transferred to a 2 ml ampoule, to which was added 100 μl of ether and about 1 ml of a solution prepared by mixing 100 g of saturated brine with 100 g of 20% aqueous sodium bisulfate. The ampoule was shaken and the ethereal layer analyzed by glc on column F at 130°. It was necessary to inject the first sample of each series several times before a reproducible ratio of triflate to biphenyl could be obtained. Then each sample was analyzed at least twice and the averages were used in calculating the ratio of the initial concentration of triflate, A_o , to the observed concentration, A , as a function of time, t . The data points were computer fitted to the first-order rate equation (60), $\ln A_o/A = kt$, by the method of least squares (61). The rate constants are presented in Table I; the error limits given are the standard deviations of the slopes (61). Examples of the rate plots are given as Figures 2, 3, and 4.

In the case of triflate XXXI it was shown that stainless steel has no effect on the rate. When samples in a stainless steel tube and in a Pyrex tube were simultaneously solvolyzed at 97°, analysis after one half-life showed the ratios of triflate to internal standard to be essentially identical.

Each of the triflates was solvolyzed at three temperatures covering a range of about 20°. The Arrhenius plots (log of the rate constant versus the reciprocal of temperature) are presented in Figure 5. The activation parameters given in Table I are weighted averages based on the differential error analysis given by Benson (62). The error limits given are standard deviation.

Products of Triflate Solvolyses. The product distributions shown in Table I are based on glc analysis (column F at 120°) of samples taken after one half-life and are not corrected for relative response. There was no apparent change in the product distributions during the course of the reactions. The sum of the glc integrals of the products was approximately equal to the decrease in the integral of the starting triflate; although these integrals were not corrected for relative response, this observation suggests a reasonable material balance. The retention times of the major products from each triflate were shown to be the same as those of the corresponding alcohols and ethyl ethers by co-injection of authentic or independently synthesized samples. In order to isolate the products, in the case of each triflate the samples from the kinetic runs were combined; the ether layer was separated and washed with saturated sodium bicarbonate and brine, dried over sodium sulfate, and concentrated on a rotary evaporator. Preparative glc on column A with temperature programming from 100 to 160° and a flow rate of 2 ml/sec allowed collection of the solvent and products together and separate collection of the unreacted triflate. Then the major products were isolated through preparative glc on column D with temperature programming from 50 to 120° and a flow rate of 1 ml/sec.

The products isolated from the solvolyses of triflates XXX and XXXI were shown to be the corresponding alcohols and ethers by comparison of their ir spectra with those of known samples. However, the products isolated in this way from the solvolysis of triflate XXXIII gave ir and nmr spectra that were different from those of the expected alcohol XXXII and ether XXXVII. One of the products was an alcohol. Its ir spectrum displayed bands at 3600, 3310 (broad), 3000, 2925, 2850, 1448, 1334, 1165, and 1092 cm^{-1}, and its nmr spectrum consisted of a multiplet from 5.10 to 5.25 ppm (1 H), a sharp singlet at 2.95 ppm (1 H), a multiplet from 2.0 to 2.5 ppm (3H), and a multiplet from 1.2 to 2.1 ppm (9 H). The other product was apparently an ethyl ether. Its mass spectrum displayed the parent peak (99.7%) at m/e 166 and the base peak at m/e 151, indicating that it is isomeric with ether XXXVII. Its ir spectrum displayed bands at 2930, 2860, 1450, 1390, 1335, 1186, 1165, 1109, and 1050 cm^{-1}. Due to the small amount of material available, its nmr spectrum could not be integrated accurately but consisted of multiplets at about 5.1, 2.3, and 1.7 ppm, a quartet centered at 3.51 ppm (J = 7Hz), and a triplet at 1.14 ppm (J = 7 Hz). The absence of absorption at 3020 cm^{-1} in the ir spectra of these compounds suggests that neither has a cyclopropyl ring. The absence of a bridgehead-methyl signal in their nmr spectra suggests that deep-seated rearrangements have occurred. When the solvolysis was repeated and worked up immediately, two major products could be isolated by the above procedure; these were identified as alcohol XXXII and ether XXXVII by comparison of their ir and nmr spectra with those of known samples. In the former product study the kinetic samples had been allowed to stand in a refrigerator for two weeks before work-up; perhaps contact with aqueous sodium bisulfate over that period was sufficient to cause the observed rearrangements. The rearranged products were not identified.

Solvolysis of 4-Tricyclyl Triflate (XXX) in ^{18}O Enriched Medium.

A sample of 60% (by wt) aqueous ethanol was prepared from absolute ethanol and ^{18}O enriched water (Bio·Rad; reportedly 50 atom % ^{18}O and 7 atom % ^{2}H). In 0.6 ml of this solvent were dissolved 23 mg of triflate XXX and 26 mg of triethylamine. Samples of the solution were sealed in stainless steel tubes and heated at 246° for 10 hr (about 8 half-lives). The combined samples were partitioned between water and ether, and the ethereal extract was washed with 1 N hydrochloric acid, saturated sodium bicarbonate, and brine, dried over sodium sulfate, and concentrated. Preparative glc on column D allowed isolation of a sample of 4-tricyclenol (XXIV), the identity of which was indicated by its ir spectrum. In high resolution mass spectra (63a) of this sample and of a sample of the ^{18}O enriched water, separate peaks corresponding to each of the isotopic species in the respective parent ions could be observed. This allowed direct comparison of the abundance of corresponding ^{18}O and ^{16}O components. The enriched water contained 68.68 ± 0.44 atom % ^{18}O, and the sample of alcohol XXIV contained 69.94 ± 0.49 atom % ^{18}O (63b). Thus the incorporation of ^{18}O in product XXIV on solvolysis of triflate XXX was 101.8 ± 1.4%.

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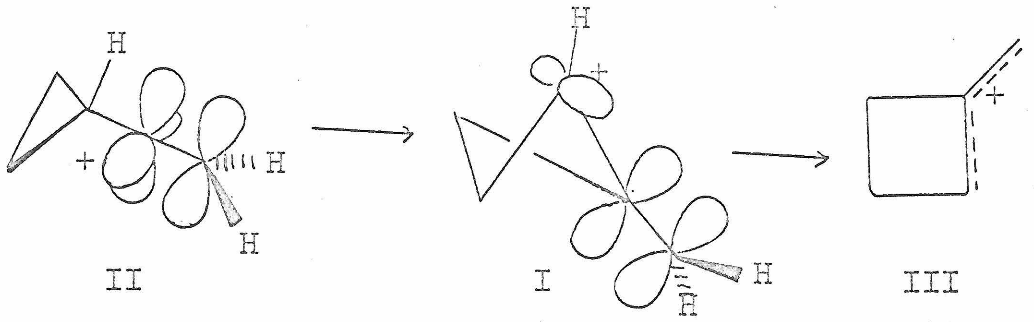
(b) Error limits are standard deviation based on five mass spectra.

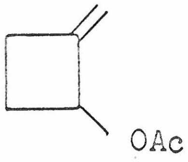
PROPOSITION I

It is proposed that stereoselective trapping of an asymetric 2-methylenecyclobutyl cation (I), which may be formed in the rearrangement of the 1-cyclopropylvinyl cation (II), could be detected by a combination of deuterium labeling and nmr spectroscopy. If this stereoselectivity is substantial, a related study employing both deuterium labeling and optical activity would be capable of detecting rotation about the cyclopropyl-vinyl bond in II.

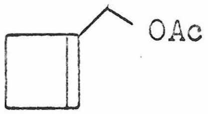
Presented and discussed in Part I of this thesis (1) was the observation that the product ratio 2-methylenecyclobutyl acetate (IV)/1-cyclobutenylcarbinyl acetate (V) was higher (~9) when rearrangement from the 1-cyclopropylvinyl cation (II) was involved than when these products were produced more directly through solvolyses of cyclobutyl derivatives (~1 to 2.7). One rationale given for this result involved a "buckled" 2-methylenecyclobutyl cation (I) as an intermediate in the rearrangement of II to the planar 2-methylenecyclobutyl cation (III);



II I III

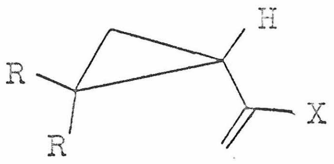


IV

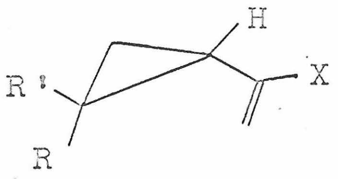


V

The product ratios could be rationalized by assuming that 63% of intermediate I is trapped before it can relax to the planar ion III (2). This trapping should occur almost exclusively at the secondary center, because delocalization of charge to the primary center is geometrically restricted; furthermore, one might expect steric effects and perhaps σ delocalization in I to restrict solvent trapping to the "exo" p lobe (the analogous rearrangement of the parent cyclopropylcarbinyl cation to the cyclobutyl cation has been shown to be highly stereoselective (3)). In this hypothesis I is effectively asymetric and leads to the prediction that solvolysis of an optically active cyclopropyl derivative such as VI should result in optically active methylenecyclobutyl acetates (4). Alternatively, if the substituents, R, on the cyclopropyl ring were not identical (VII) the structures which would have to be distinguished in the analysis would be diasteriomeric; this would avoid the necessity of using optical activity as the analytical criterion. This approach has the disadvantage that



VI



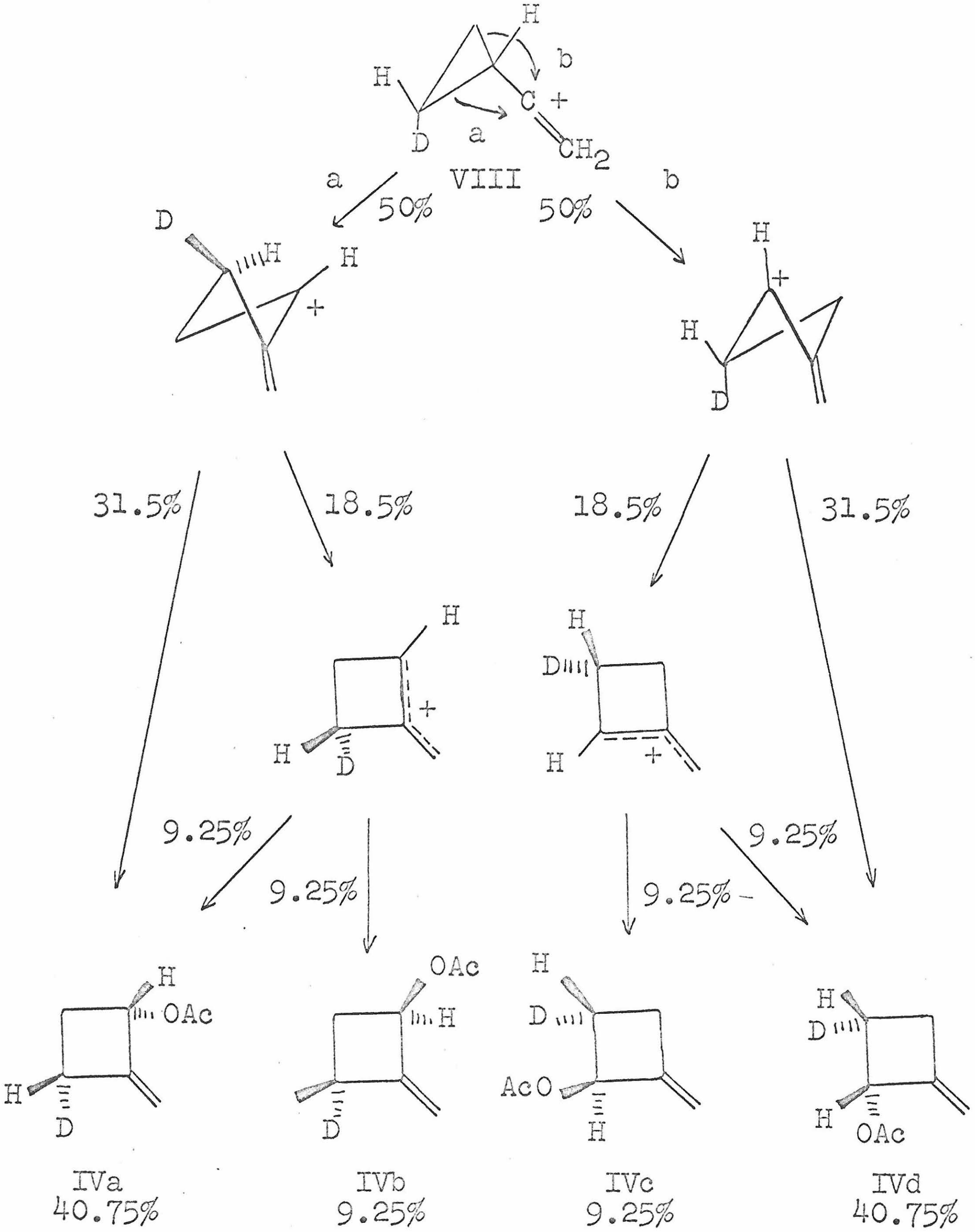
VII

the dissimilar substituents would make the trapping rates on the two faces of the planar cation inherently different, but letting R' and R be hydrogen and deuterium would essentially eliminate this difficulty; such a substrate would lead to ion VIII (Figure 1).

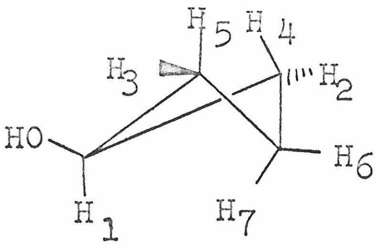
If the methylenecyclobutyl cations from the rearrangement of VIII become effectively planar before being trapped, one would expect the product acetate IV to consist of 25% each of IVa, IVb, IVc, and IVd (assuming negligible secondary deuterium isotope effects). However, the suggestion that 63% of the initially formed cation I is trapped before relaxation to the planar form predicts the percentages shown in Figure I. The required differentiation of the diasteriomeric pairs IVa and IVb, and IVc and IVd should be possible by nmr. The analysis would be facilitated by having the second methylene group of the cyclobutane ring dideuterated.

The nmr spectrum of cyclobutanol (IX) has been completely analyzed (5) and is consistent with a puckered ring

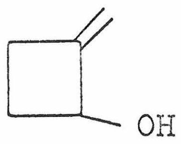
Figure 1. Some rearrangement and trapping pathways for deuterium labeled 1-cyclopropylvinyl cation.



and an exo hydroxyl group. Acetate IV may be readily converted to alcohol X (6); this conversion might not be required for the nmr analysis but will be assumed in the following discussion to strengthen the grounds for the comparisons to be made. Alcohol X would be less inclined to

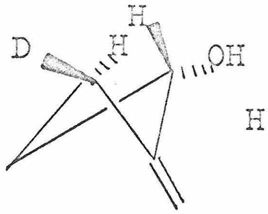


IX

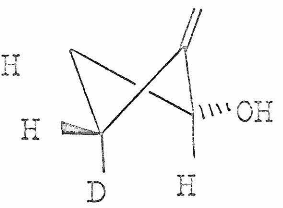


X

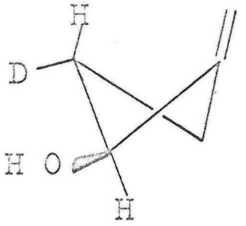
pucker than IX owing to increased angle strain but more inclined to pucker owing to freedom from the non-bonded interaction between hydrogens 4 and 5 in IX; X is probably puckered at least somewhat and may be more puckered than IX. The following discussion describes how the analysis could be carried out if alcohol X is puckered to about the same degree as IX, but the required differentiation could still be made even if X were planar. Assuming X is puckered, the preferred conformers of the labeled species are shown below:



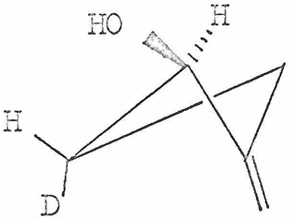
Xa



Xb

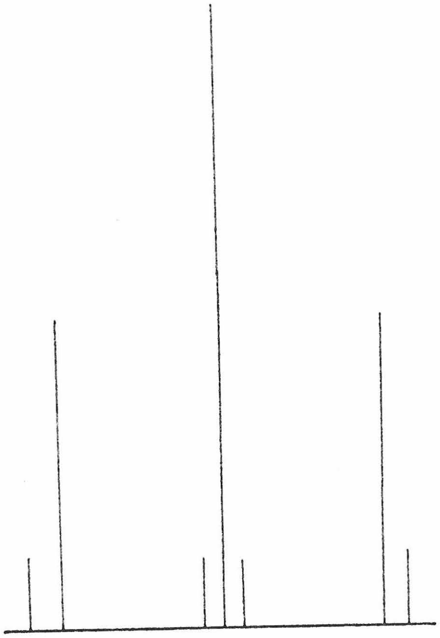


Xc

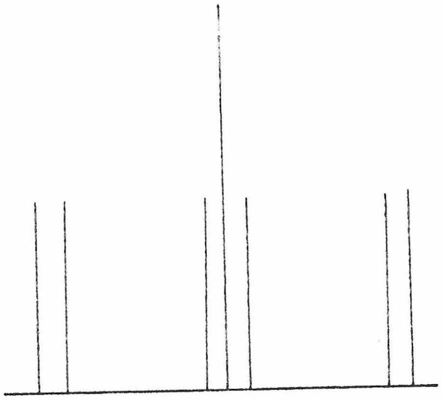


Xd

In Xc the orientation of the proton geminal to deuterium with respect to the hydroxyl group and to the π cloud of the double bond is such that the effects of these substituents should combine in shifting this proton's resonance upfield from that of the analogous proton in Xd (even in IX, where the effect of the double bond is absent, the resonance position of hydrogen 5 is 0.32 ppm upfield from that of hydrogen 3 (5)). In this case the ratio of Xc to Xd could be obtained by spin-decoupling these protons from the proton α to acetate and integrating the resulting singlets. In like manner Xb could be distinguished from Xa (in IX protons 6 and 7 differ in chemical shift by 0.22 ppm). If the degree of pucker in I is equal to or greater than that in IX, a check on the above assignments and calculations would be available. Based on the analogous values for IX, the vicinal coupling constants in Xa, Xb, Xc, and Xd would be ~0 Hz, ≥9 Hz, ≥8.1 Hz, ≤7 Hz. Then depending on whether the formation of acetate IV is entirely via planar cations, or for example involves 63% trapping prior to relaxation of a bent ion, the nmr signal (drawn to scale) for the proton α to the acetate would be one of the following:



63% trapping prior to relaxation

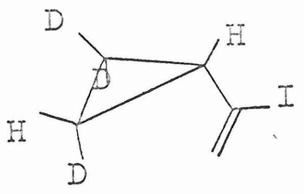


via planar cations

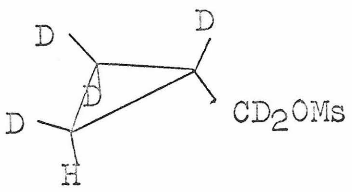
The diasteriomeric purity could be estimated from the integrals of the appropriate doublets.

The starting material (XI) for this study could be obtained through appropriate modification of the method used by Majerski and Schleyer (3) in the synthesis of XII.

If the above test revealed a useful level of stereoselectivity, the study could be extended in an effort to detect rotation in II about the bond between the cyclopropyl

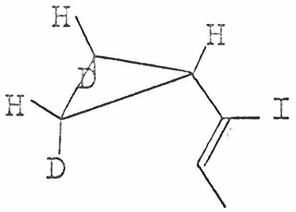


XI

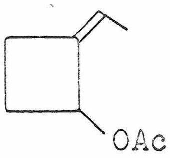


XII

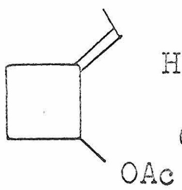
ring and the cationic center. Calculations have predicted that the barrier to such rotation is substantial (7,8). In order to test for such rotation one could repeat the above experiment with homolog XIII--hopefully again finding considerable stereoselectivity manifested in both the *syn* and the *anti* cyclobutyl acetates XIV and XV. Then homoallenyl iodide XVI would be prepared optically active and solvolyzed (9). The stereoselectivity involved in the formation of each of acetates XIV and XV in this case could be deduced from their optical purities and that of the starting allene. Both the nmr label and the optical activity label are potentially capable of measuring the same stereoselectivity--that of the trapping steps giving acetates XIV and XV. However, the optical activity label is destroyed by rotation about the bond between the cyclopropane ring and the vinyl cationic center; thus the difference between the stereoselectivities measured by the above methods would be a measure of rotation about this bond.



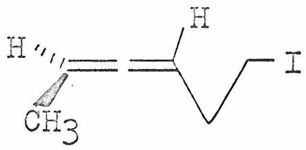
XIII



XIV



XV



XVI

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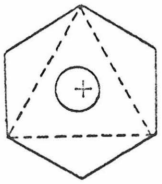
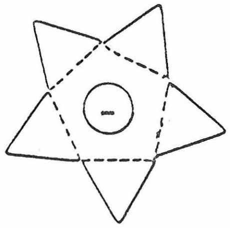
PROPOSITION II

The synthesis of 1,4,7-cyclononatriyne (XI), potentially a trishomobenzenoid aromatic species having a predicted delocalization energy of 46 kcal/mol, is proposed.

A number of years ago, experimental evidence for the existence of a trishomocyclopropenyl cation (I) prompted Winstein to predict that the phenomenon of homoaromaticity (1) would become a general one and to suggest that structure II, III, and IV might someday be counted among those which exhibit this property (2). Since then a number of homoaromatic ions, such as homotropylium ion V (3), bishomotropylium ion VI (4) and bishomocyclopentadienide ion VII (5), have been generated. However, attempts to observe homoaromaticity in neutral species have been less fruitful. Winstein's proposed hexahomobenzene (III) has been



I



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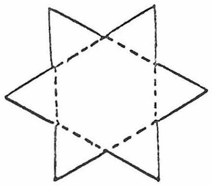
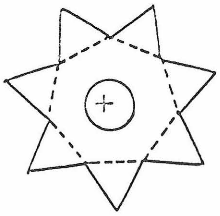
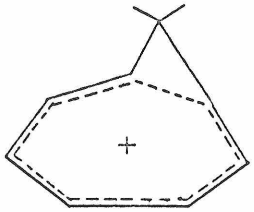


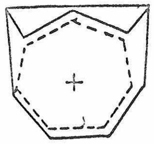
III

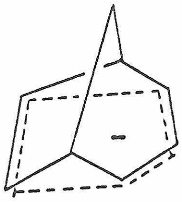


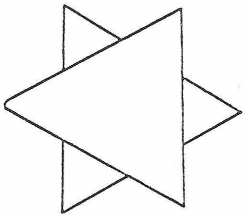
IV

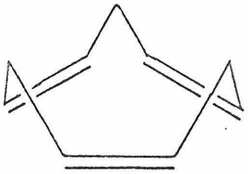
synthesized, but its ir and nmr spectra suggest that it exists as the classical form (VIII) (6). *Cis*-*cis*-*cis*-1,4,7-cyclononatriene (IX), a formal trishomobenzene, has also been made, but no evidence for significant delocalization energy in its ground state has been obtained (7).

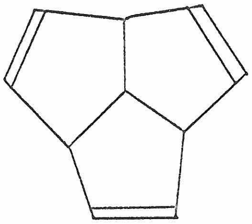

V


VI


VII

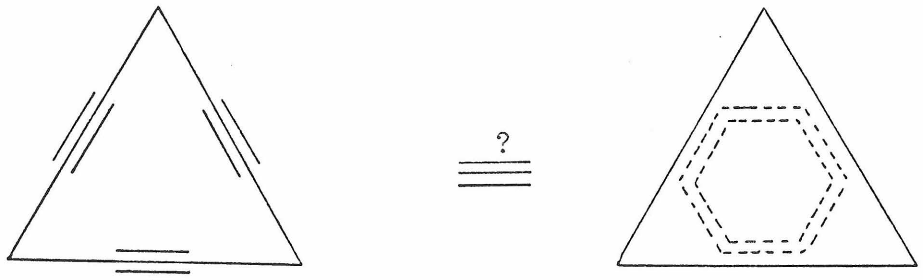

VIII


IX


X

Hückel molecular orbital calculations predict that the delocalization energy (DE) in IX should be about 3 kcal/mol, but it was suggested that this small value might not be detected in heats of hydrogenation owing to the difficulties involved in the selection of a good model compound, including the possibility that steric effects are similar in magnitude to the energy difference in question (8). Similar conclusions have been drawn concerning triquinacene (X), synthesized by Woodward and co-workers (9).

It is proposed that the synthesis of 1,4,7-cyclononatriyne (XI), a trishomobenztriyne, be attempted. In theory this molecule should have a remarkable DE since it contains two orthogonal, cyclic, 6-π-electron systems which are rather well situated for overlap. In attempting to predict whether or not a potentially homoaromatic molecule will exist in its delocalized form, one must weigh the expected DE against the destabilization, in the form of increased strain and steric interaction, associated with the geometry required for delocalization (2). An effort to do this has been made in the present case. To facilitate an

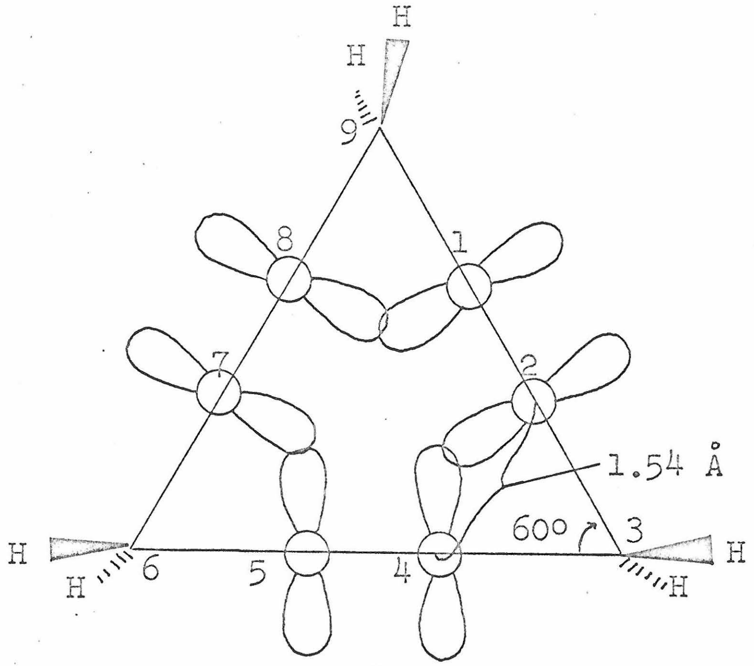


XI

XIa

estimation of the strain energy, the molecule was presumed to be a triangle. In this form the total strain energy should rest in the three 60° C-C-C bond angles at the methylene carbons. Therefore, the total strain energy sould be close to 27.6 kcal/mol, the strain energy of cyclopropane (10).

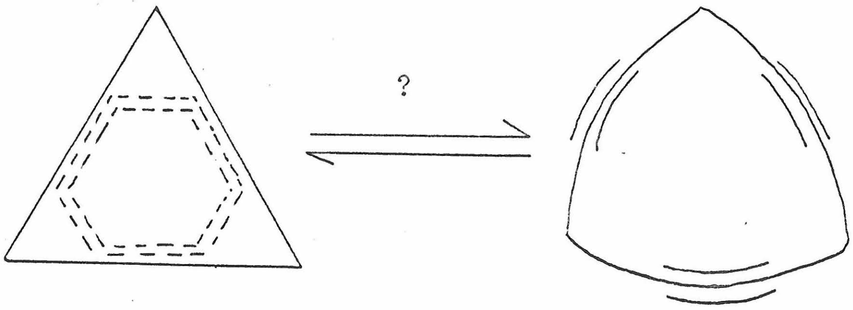
In order to estimate the DE of the species, simple molecular orbital theory was used. In keeping with the triangular geometry, the C_2-C_4 distance was taken as 1.54 Å, i.e., equal to the normal C_2-C_3 σ-bond distance. The benzene-like π system and the co-planar π lobes, being orthogonal, were treated independently. In each case β_{12} was taken as 1.0. For the benzene-like system, β_{24} is approximately 0.5 at the chosen distance (11a). The



XI

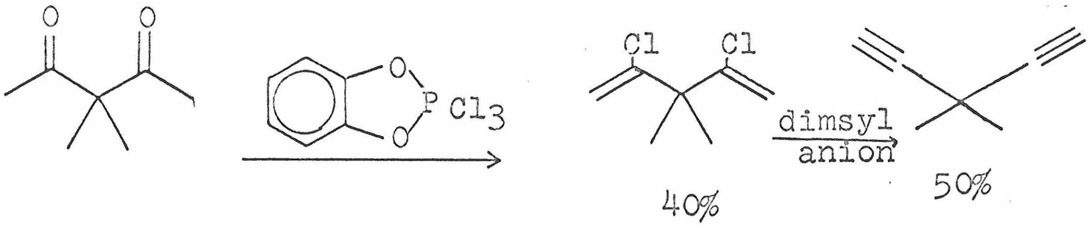
calculated DE for the benzene-like system is 0.46 β. In the co-planar π system, β_{24} was estimated as 1.065 using the method of Roberts (11b). The DE calculated for the co-planar π system is 2.10 , making the total DE for both systems 2.56 β. If β is taken as 18 kcal/mol, the total delocalization energy expected is 46 kcal/mol or 18.4 kcal/mol more than the strain energy involved in obtaining the triangular geometry. This suggests that the molecule should be homoaromatic to an extent easily detectable in heats of hydrogenation.

If contrary to this prediction the DE is only about equal to the stabilization afforded by strain minimization in the nonaromatic, puckered form XIb, there would be the intriguing possibility of observing an equilibrium between XIa and XIb.

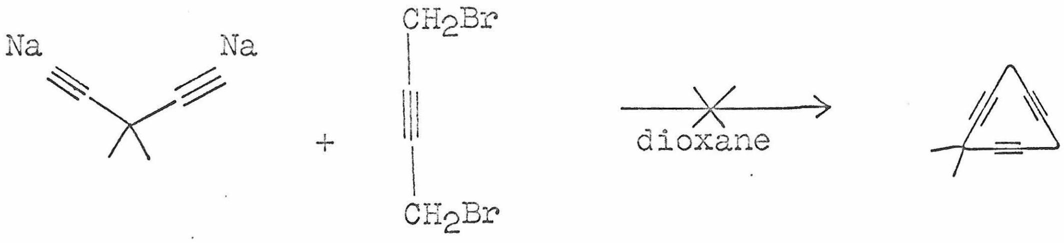


XIa XIb

The above proposition was submitted at my candidacy examination. Since then I have been given an opportunity to attempt the synthesis of XI. In collaboration with my advisor, Dr. R. G. Bergman, the following approach was investigated. Diyne XII was prepared as shown below (the gem-dimethyl compound was chosen to prevent isomerization to conjugated species), and its disodium salt in dioxane was treated with dibromide XIII. Analysis of the product mixture



XII

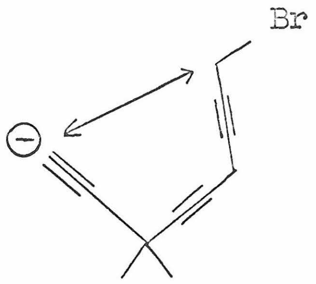


XIII

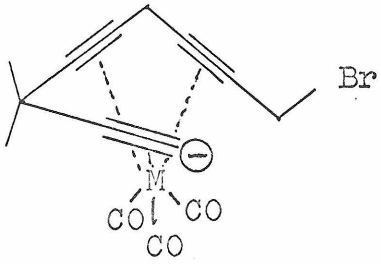
XIV

by glc-mass spec failed to detect the dimethyl derivative XIV; the only component having the correct molecular weight was isolated and its infrared spectrum showed it to be a terminal acetylene.

A number of reasons for the failure of this attempt can be suggested. Even for the eclipsed conformer XV, required for the cyclization step, one can estimate that the reaction centers are initially at least 5 Å apart. This taken together with the losses of rotational freedom must constitute a sizable entropic barrier to closure. The enthalpic barrier probably includes most of the strain energy in XIV (which may be only partially recompensed by delocalization energy in the transition state) and steric hindrance, perhaps involving sodium since it is unlikely that the salt is dissociated in dioxane. The net barrier is apparently sufficient to favor the available side reactions, which may include isomerization, elimination, and polymerization.

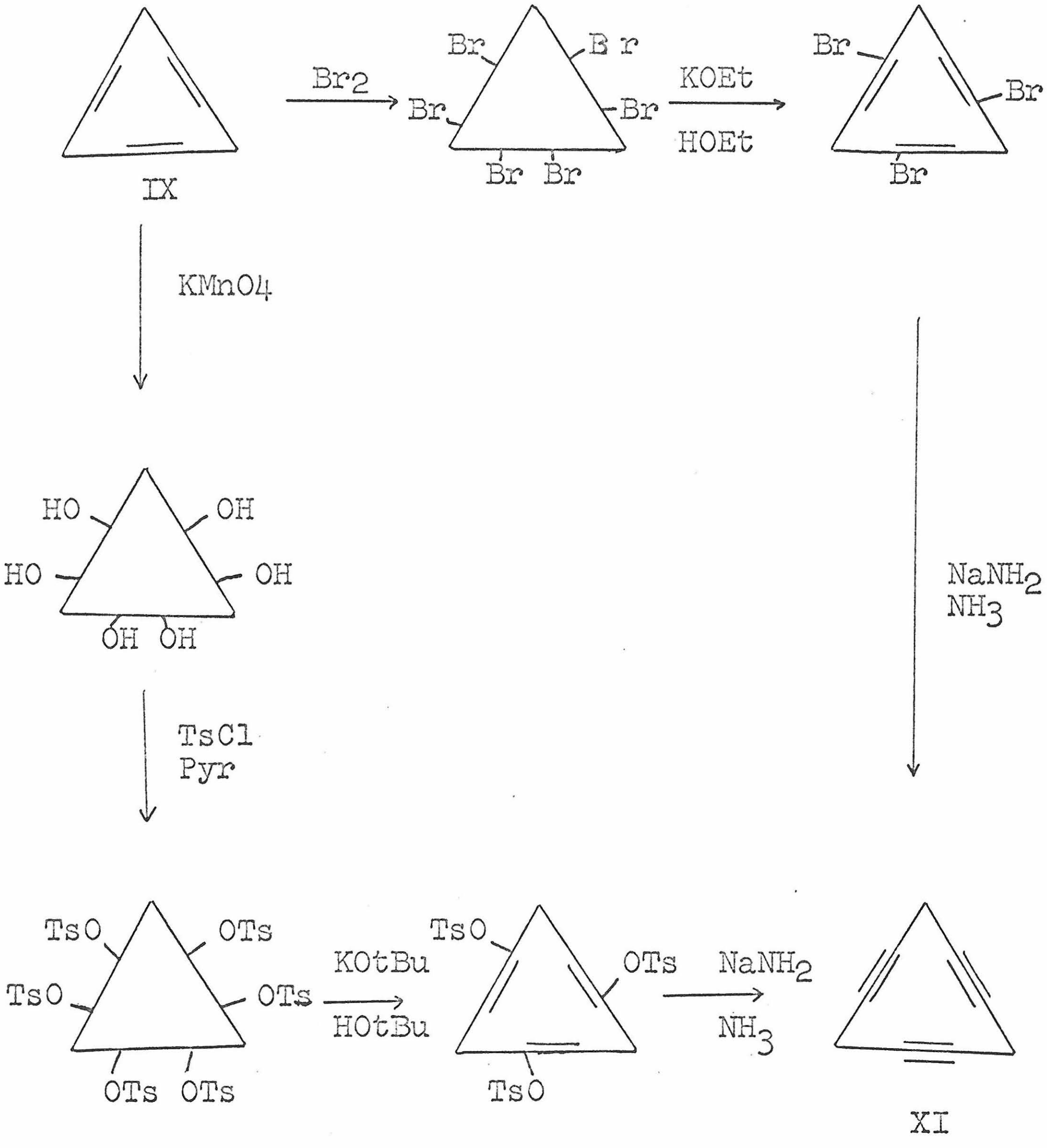


XV



XVI

The use of a crown ether (12) might overcome part of the steric problem suggested above. Perhaps more is to be gained, however, from the use of a metal-atom "template" capable of accepting three π bonds from XIV as ligands; this might achieve the geometry shown in XVI and alleviate a significant portion of the entropic and enthalpic barriers to closure (13). Another synthetic approach which remains o be tested would involve an attempt to increase the unsatuation in IX by an addition-elimination sequence; possible outes are suggested below.



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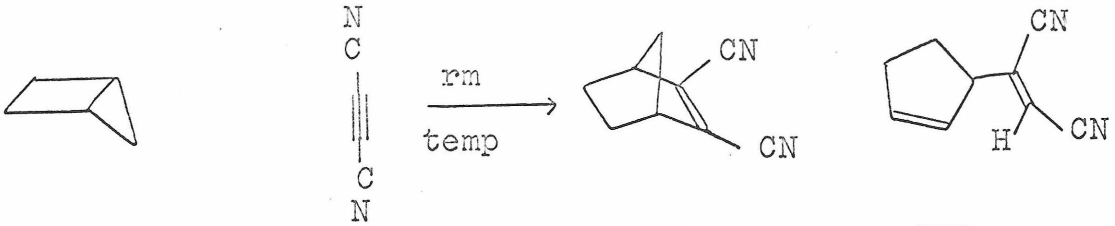
PROPOSITION III

A study of the reactivity of singlet oxygen toward strained, carbon-carbon, σ bonds is proposed. Included would be a stereochemical investigation of the reaction of singlet oxygen with [2.1.0]bicyclopentane.

In the past few years the apparent significance of singlet oxygen ($^1\Delta g$, the lowest excited state of molecular oxygen) in a number of areas intimately related to health has been revealed. For example, Pitts has shown that singlet oxygen is involved in the mechanisms of photochemically enhanced air pollution (1,2), and Murray has found that the reaction of ozone with hydrocarbons produces singlet oxygen (3). Also, it has been found that the biosynthesis of prostaglandin E_1 involves incorporation of molecular oxygen (4) in a manner which resembles the usual reaction of singlet oxygen with olefins (5), and it has been suggested that an enzyme-bound form of singlet oxygen may be involved in such biosynthetic mechanisms (3a,5). In addition it has been pointed out that photosensitizing dyes can sensitize the oxidation of nucleic acids and cause skin cancer (6). In view of these fundamentally health-relevant aspects of singlet oxygen, the relative paucity of our chemical knowledge of the species must be regarded as unfortunate and intolerable. Rarely if ever does our understanding of biological mechanisms exceed the level allowed by our basic knowledge of the chemical species involved. The following proposal is directed at increasing our knowledge of the reactivity and mechanistic inclinations of singlet oxygen.

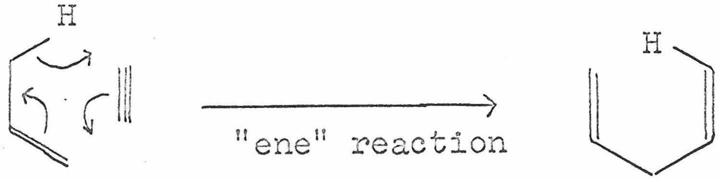
Although the reactivity of singlet oxygen toward olefins has been studied in some detail (6), no systematic study of its reactivity toward strained, carbon-carbon, σ bonds has been undertaken. It is proposed that such a study be conducted, initially involving [2.1.0]bicyclopentane (I). Hydrogenation of the bridge bond in I liberates 48.1 kcal/mol of strain energy, implying the highest strain content of any known carbon-carbon σ bond (7), and therefore it is not surprising that I is quite reactive. For example, I reacts with dicyanoacetylene at room temperature to give



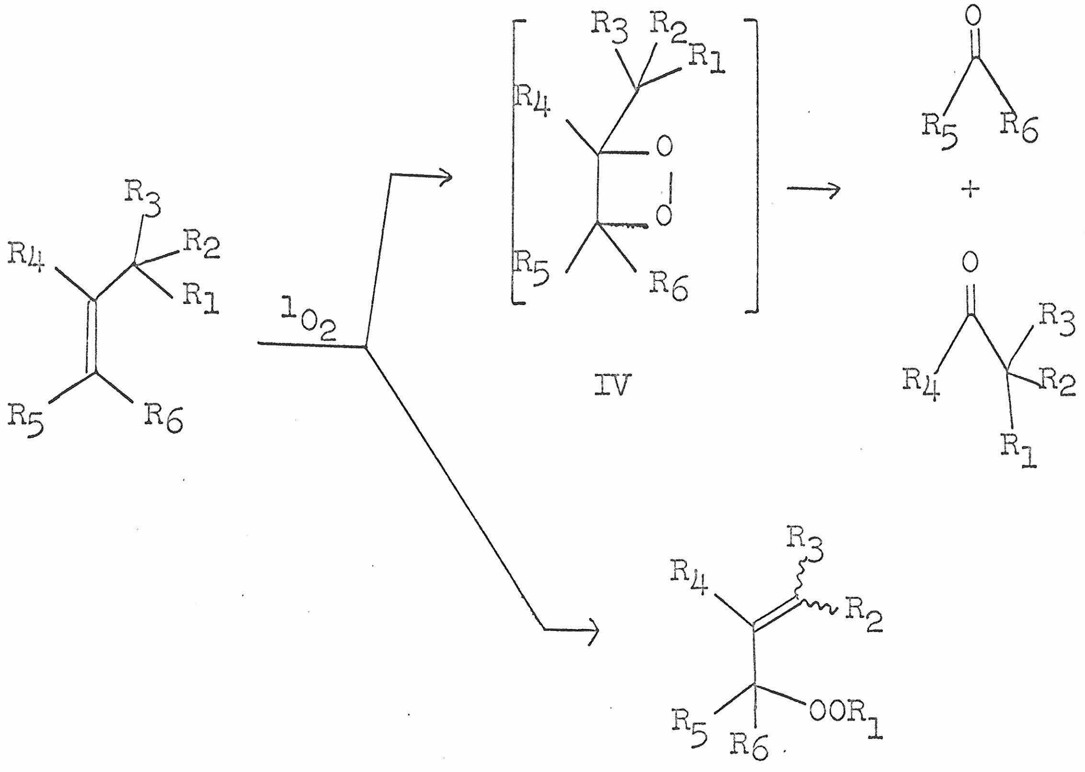
I

II 11%

III 58%

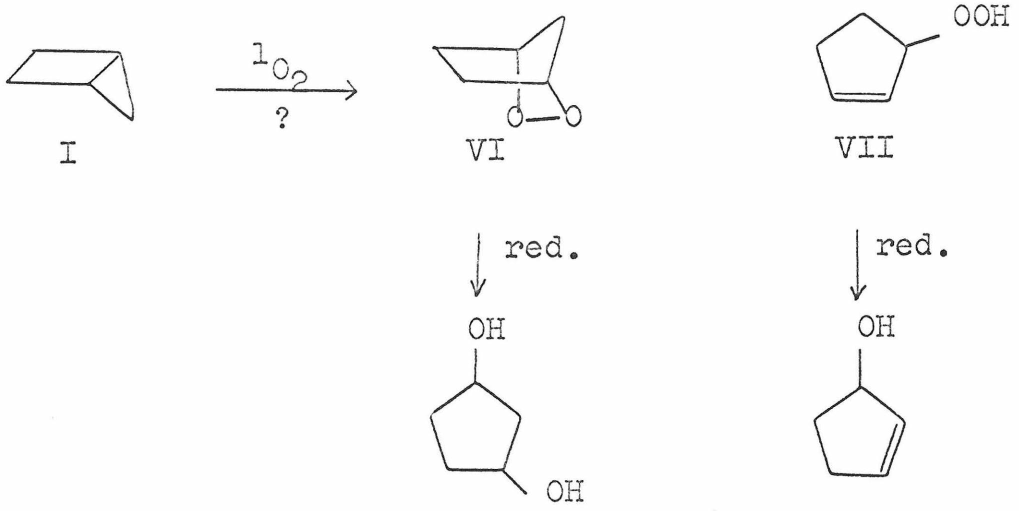


a cycloaddition product, II, and the product, III, of a reaction formally analogous to the "ene" reaction (8). These reactions are similar to those which occur between singlet oxygen and olefins, where cycloaddition products (dioxetanes, IV) and "ene" products (allylic hydroperoxides, V) are formed (5).



V, R_1 = H

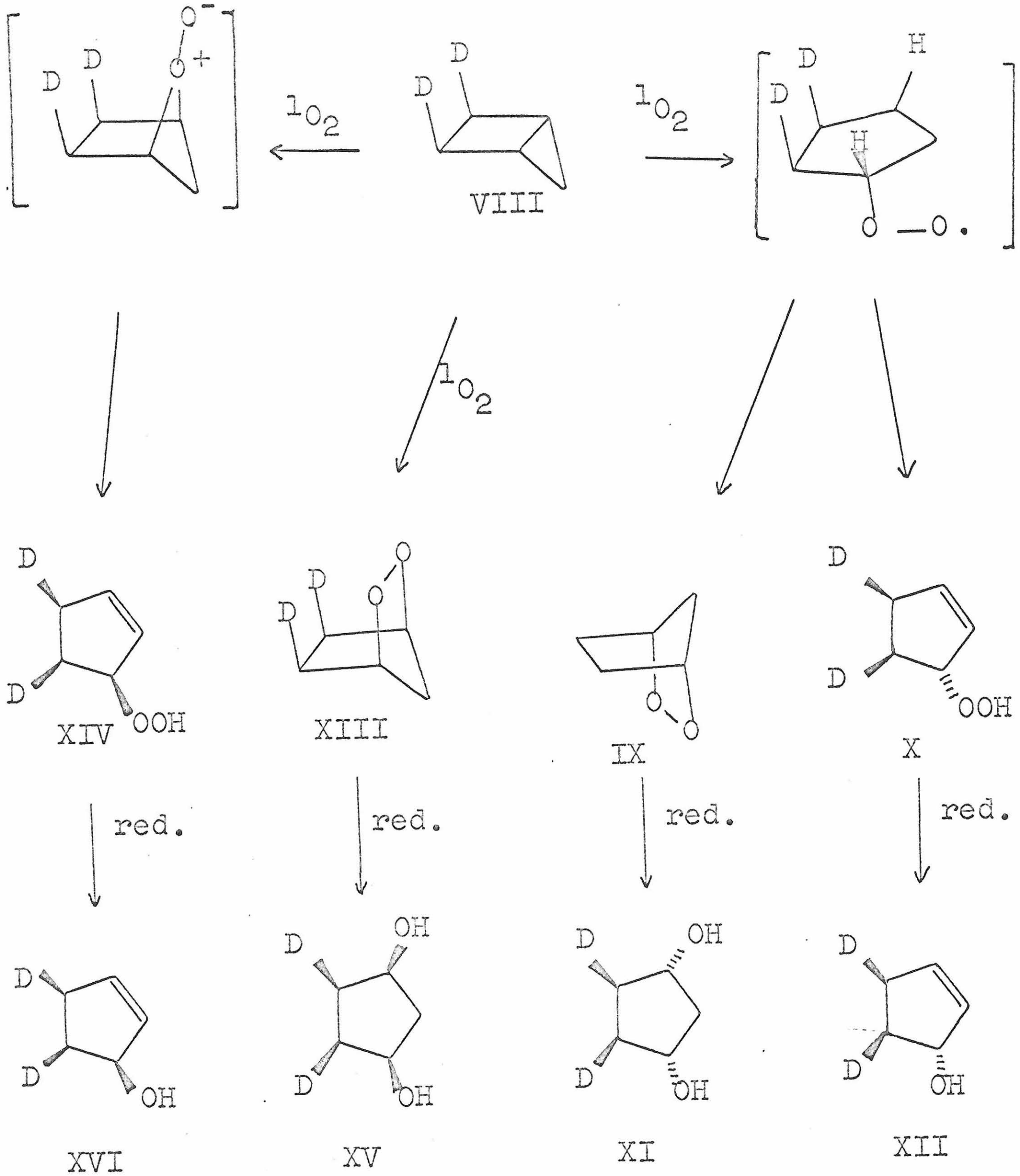
By analogy one might expect the reaction of I with singlet oxygen to give VI and VII. Whether or not the peroxide VI could be isolated is an open question. The analogous dioxetanes IV with care can be isolated in some



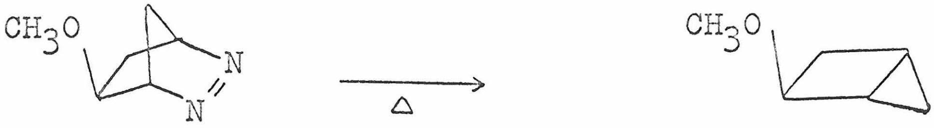
cases (9, 10), but cleavage to carbonyl compounds in what appears to be a concerted process is usually facile (5,9,10, 11,15,19); this process is not open to VI, which thus may be relatively stable. One would expect the hydroperoxide VII to be reasonably stable. Should isolation of VI and VII prove unfeasible, reduction of the product mixture should give the readily characterizable alcohol and diol.

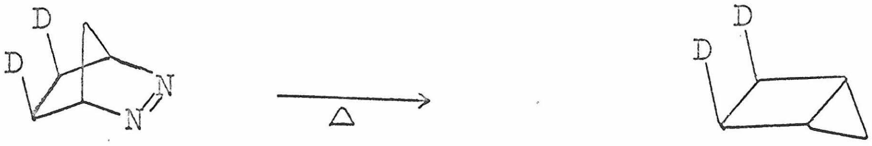
Considerable evidence has been provided to show that the reaction between I and electron deficient acetylenes or olefins involves a diradical mechanism, beginning with a backside attack on the bridging bond, and in the case of the cycloaddition products, such as II, results in double inversion at the bridgeheads (12,13). The reaction with singlet oxygen might take the same course, but the electronic configuration of $^1\Delta g$ oxygen is such that the species should exhibit less radical character than ground state oxygen (5). The concerted $_{\sigma}2_s + _{\pi}2_s$ cycloaddition of an acetylene or olefin to I is orbital-symmetry forbidden (14), resulting in the diradical mechanism observed, but the predictions of orbital symmetry in the case of singlet oxygen are less clear. It had been stated in the literature that the cycloaddition of singlet oxygen to an olefin is "probably nonconcerted" (5), but from a close examination of the correlation diagram for this reaction Kearns has concluded that its barrier might be small, depending on the ionization potential of the olefin (15a). Kearns also examined the concerted addition of singlet oxygen to olefins to give a perepoxide and found that the correlation diagram suggests little or no barrier (15b). An experiment which might differentiate these concerted mechanisms from the radical mechanism in the addition of singlet oxygen to I is available.

The stereoselectively dideuterated bicyclopentane VIII has been reported (13). Reaction of VIII with singlet oxygen by the diradical mechanism, by analogy to the acetylene addition, should result in the diexodideutero peroxide IX and the cyclopentenyl hydroperoxide X with deuteriums <u>trans</u> to the oxy-function. Reduction would produce XI and XII respectively. However, the concerted cycloaddition, for reasons of maximal orbital overlap, might occur with

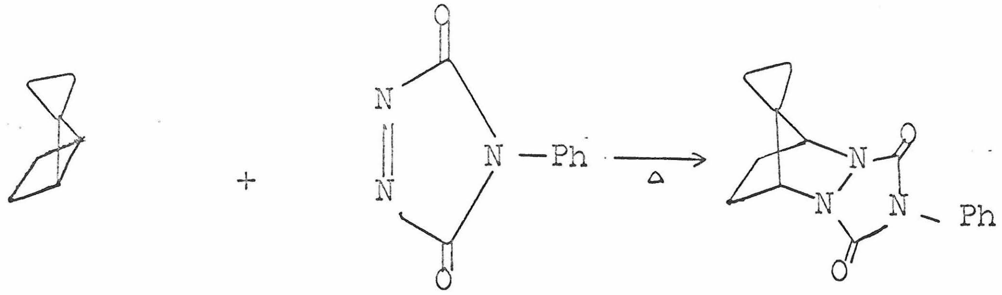


retention, which would result in the diendodideutero peroxide XIII and hydroperoxide XIV, and on reduction in the diol XV and alcohol XVI. It should be possible to distinguish between XI and XV and to assign the configurations of XII and XVI through the use of nmr spectrometry. The outcome of this experiment also would be interesting in the light of the current controversy regarding the rationale for the unusual stereochemistry that has been observed in decompositions of some bicyclic azo compounds (examples below) (16, 17, 18).



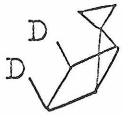


The preferred reaction of singlet oxygen with an olefin where an allylic hydrogen is available is the "ene" analog. If this type of reaction predominates with I to the exclusion of cycloaddition, it should be possible to block the "ene" reaction by placing alkyl groups at the 5-position in I. This is very effective in the case of XVII, which reacts with XVIII to produce XIX almost quantitatively (18). The stereoselectively dideuterated compound



XVII XVIII XIX

XX has also been reported (18). Finally, an extension of this work would be the determination of the relative reactivity of singlet oxygen toward XXI and other less strained alkanes.



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XXI

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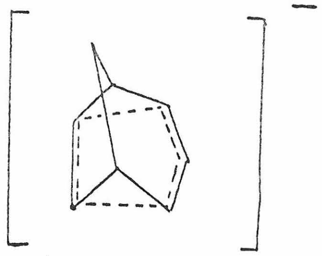
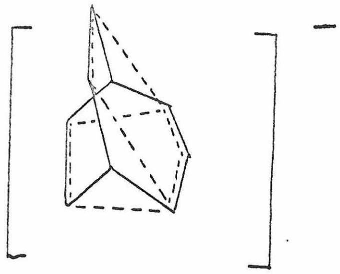
PROPOSITION IV

Synthesis and characterization of 4-azabicyclo[3.2.1]-octa-2,6-diene (III), a bishomopyrrole, and of 4-azabicyclo-[3.2.2]nona-2,6,8-triene (V), a supposed bicycloaromatic species, are proposed.

Studies of the bishomocyclopentadienyl anion (I) (1) and of the bicyclo[3.2.2]nonatrienyl anion (II) (2) have suggested that both of these species are stabilized by delocalization. Anion I was described by Winstein as "homoaromatic" (3), whereas in the terminology of Goldstein, anion II was predicted to be "bicycloaromatic" (4).

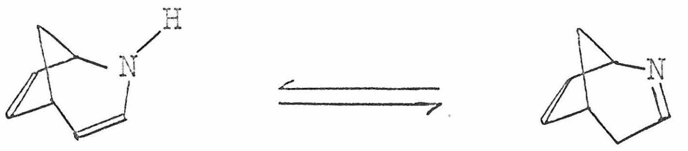


I

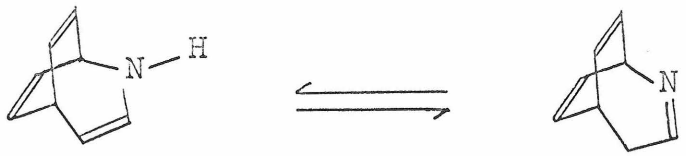


II

Synthesis and characterization of the isoelectronic but neutral, nitrogen analogs of these anions, III and V, are proposed. The evidence available for homoaromaticity in neutral species is scanty compared to that in the case of charged species (5), which suggests that the need for charge



III IV



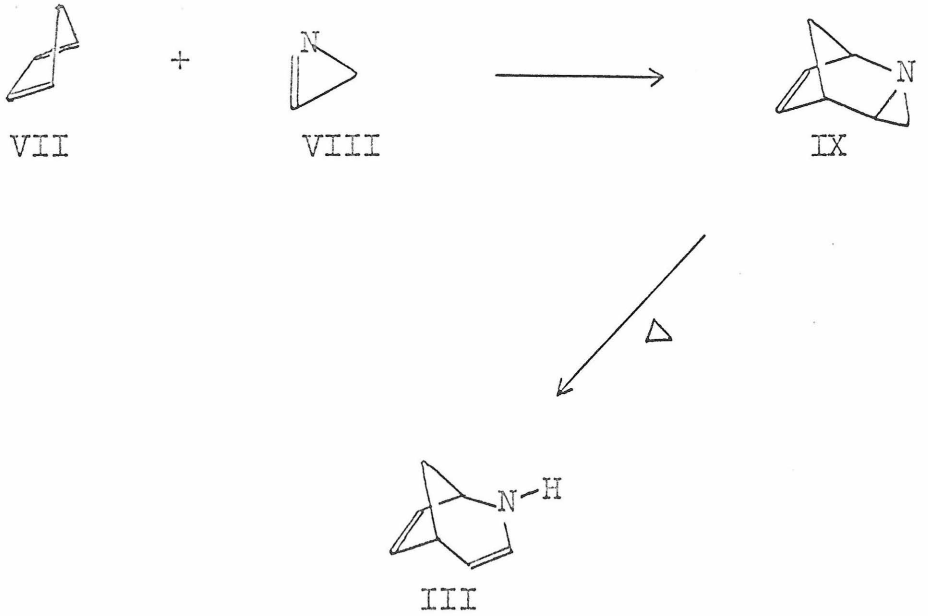
V VI

delocalization may be a prerequisite for marked homoaromatic character. In this respect the character of III and V should be enlightening. The equilibrium composition of III and IV and of V and VI might provide a crude indication of the importance of resonance stabilization in III and V; normally an imine is more stable than the corresponding enamine (6). Hopefully III and V would be reasonably stable and provide an opportunity for measurements not possible with the sensitive anions I and II. These might include determination of X-ray structures, diamagnetic susceptibility exaltations (7), and heats of combustion. Both pK_a and pK_b of these species would be interesting, as would be the positions of protonation and exchange.

Nmr studies of anion II indicated 11.8 kcal/mol as an upper limit for the barrier to "bridge flipping". The lowest temperature used in this study was -35°, the limitation apparently being the solubility of the anion (2). Thus the important question of whether II is most stable as a symmetrical, bicycloaromatic system or as a distorted, partially delocalized system remains unanswered. Solubility should not be a major problem in the case of V, which should allow nmr study at much lower temperatures and in turn either observation of the distorted species or assignment of an even smaller upper limit for the barrier to flipping.

A possible synthetic approach to III and V might be based on the following, recently reported reaction (8):

An alternative approach to III would be reaction of VII with VIII in the hope of obtaining IX (by analogy to a reported reaction of cyclopropene (9)), which might thermally rearrange to III.



+
N
N
VII
VIII
IX
Δ
N–H
III

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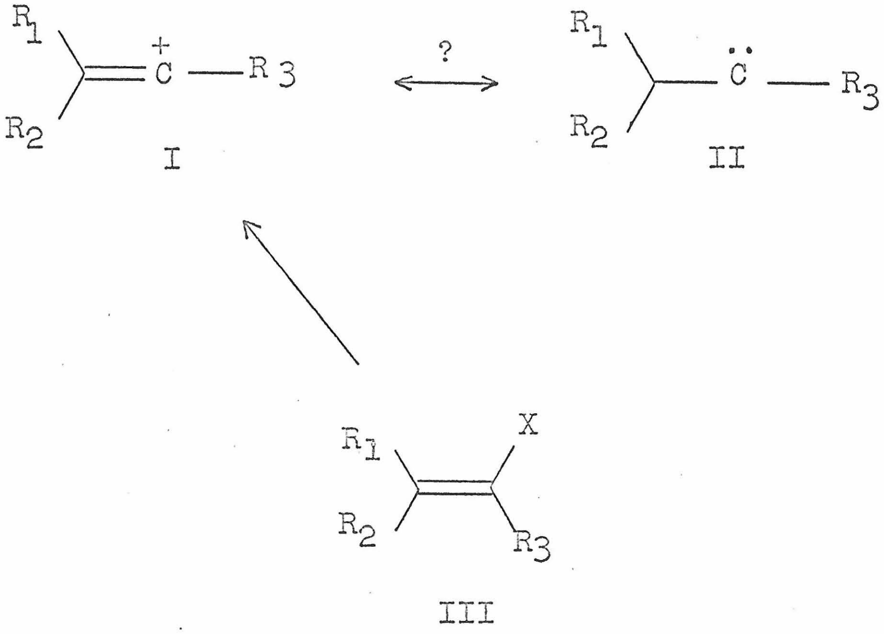
PROPOSITION V

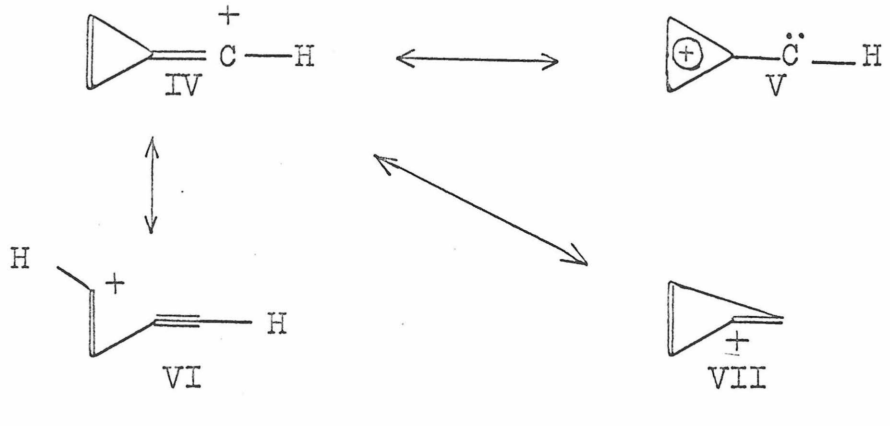
Quantum mechanical and solvolytic studies of the 4-methylenecyclopropenyl cation (IV) are proposed. Of particular interest would be evidence for importance of a cyclopropenium-carbenoid resonance contributor (V).

Evidence against importance of the carbenoid resonance form (II) in vinyl cations (I) has appeared in the literature. For example, Miller and Kaufman noted that the



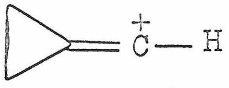
solvolysis rate of 1,2,2-triphenylbromoethylene (III, $R_1 = R_2 = R_3 = Ph$; $X = Br$) is less than that of α-bromostyrene by a factor of four (1). Interpretation of this result is complicated by the unknown importance of solvation and strain effects, but the implications of the fact that 2-anisyl-1,2-diphenyliodoethylene (III, R_1 = Ph or An; R_2 = An or Ph; R_3 = Ph; X = I) solvolyzes only 40% faster than 1,2,2-triphenyliodoethylene (III, $R_1 = R_2 = R_3$ = Ph; X = I) (1) are at least somewhat clearer. Analogous tosylates (2) and fluorosulfonates (3) give similar results, and evidence against the importance of β-aryl inductive effects in vinyl systems has been presented by Rappoport and Gal (4).

Nevertheless, one could argue that because of steric problems of the β substituents and because of the stabilizing α substituent, the above systems provide little driving force for an important contribution from II. On the other hand, one might expect such a driving force to be appreciable in the case of IV. Here the carbenoid resonance form (V) benefits from the unusual stability of

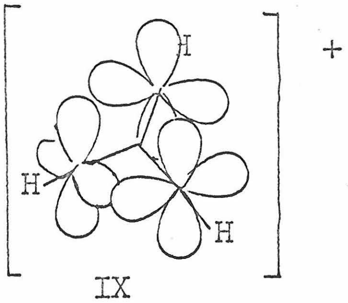


the cyclopropenium cation (5), whereas IV is a primary vinyl cation in which the stabilization normally associated with a cyclopropyl substituent may be lacking owing to the relatively unfavorable resonance forms VI (a bent primary vinyl cation) and VII (a cyclobutadienoid, bent vinyl cation).

The probable instability of precursors to IV may present formidable barriers to conventional wet-chemical studies of this ion. One "solution" to this problem is the possibility of carrying out approximate molecular orbital calculations, beginning with the extended Hückel approach (6) and progressing to more refined methods (7). IV is nicely suited to such calculations because of its small size and limited degrees of freedom. In these calculations IV might be compared to the related ion VIII (CNDO calculations on this species have been done (8)) and to the threefold-symmetric ion IX. Intuitively, it seems likely that IX would be less stable than IV, but perhaps not prohibitively so with respect to the possible degenerate rearrangement.

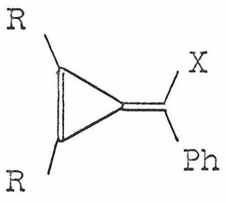


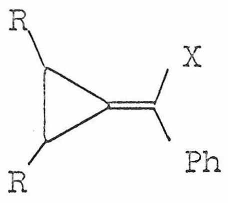
VIII

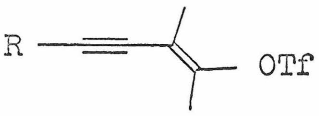


IX

A wet-chemical study perhaps should begin more conservatively, with attempts to synthesize and solvolyze substituted precursors of IV. For example, a comparative study of X and XI should be possible (9), and by analogy to work by Hanack and co-workers (10), solvolysis of substrates such as XII might provide a cyclization route to derivatives of IV.







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