CARBONIUM ION INTERMEDIATES FROM ALLYLCARBINYL AND CYCLOPROPYLCARBINYL DERIVATIVES

Thesis by

Warner Bruce Kover

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ABSTRACT

The products of the amine-nitrous acid reaction of (α-methylallyl)-carbinylamine were determined. The deamination of dideutero-(β-methylallyl)-carbinylamine was found to yield apparently unrearranged dideutero-(β-methylallyl)-carbinol and 1-methylcyclobutanol with > 97% of the deuterium in the 3-position. The deamination of dideutero-(α-methylallyl)-carbinylamine was found to yield methylallylcarbinol with 78% of the deuterium in the α-methylene position and (2-methylcyclopropyl)-carbinol with 66% of the deuterium on the cyclopropyl ring. The deamination of dideutero-(2-methylcyclopropyl)-carbinylamine was found to yield methylallylcarbinol with 74% of the deuterium in the vinyl methylene position and (2-methylcyclopropyl)-carbinol with 85% of the deuterium on the carbinyl carbon.

These results are discussed in terms of various intermediates. It is concluded that the experimental evidence appears to require interpretation in terms of the equilibrating nonclassical bicyclobutonium and homoallylic carbonium ions.

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I. INTRODUCTION

The carbonium-ion reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives have been studied extensively over the past 15 years (1). Cyclobutyl and cyclopropylcarbinyl derivatives have been found to have extraordinarily high reactivities and tend to yield very similar product distributions. For example, the nitrous acid deamination in aqueous media of cyclopropylcarbinylamine and cyclobutylamine as well as the solvolysis of cyclopropylcarbinyl chloride and cyclobutyl chloride in lithium carbonate solution yield approximately equal amounts of cyclobutanol and cyclopropylcarbinol together with 5% of allylcarbinol (2).

A study of the reactivities of the respective chlorides in 50% aqueous ethanol at 50° showed that cyclopropylcarbinyl chloride is at least 40 times more reactive than β-methylallyl chloride (3). This latter compound might be considered to provide an upper limit for reactivity of a four-carbon primary chloride, if one takes into consideration only facts affecting the stability of carbonium-ion intermediates. However, the strain intrinsic in the cyclopropyl ring and some partial release of this strain in going to the transition state must also be considered in a discussion of the reactivity of cyclopropylcarbinyl derivatives. The reactivities have been suggested to be better explained on the basis of ground-state stabilities, and the product distributions in terms of rapidly equilibrating classical cat-

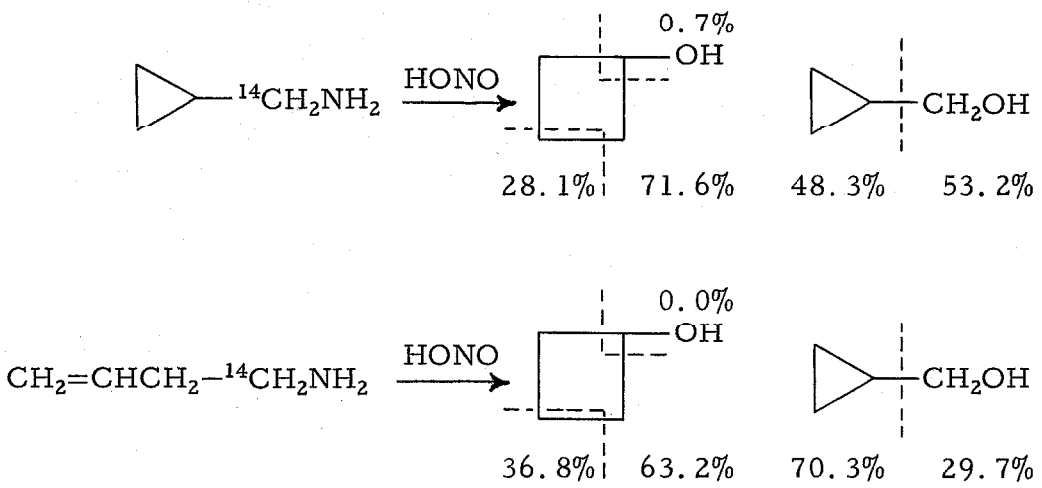
ions (5). An alternative to this explanation is one involving a species with a good deal of charge delocalization as the intermediate in these reactions. Delocalization involving the σ-bonding electrons of the cyclopropyl ring would both stabilize the cationic center and relieve steric strain. A theoretical study of these effects for reasonable configurations of the intermediates has been published by Howden and Roberts (6). Any explanation involving equilibrating classical cations must also be consistent with the relative carbonium-ion stabilities when used to rationalize the observed product distributions.

The postulation of a common intermediate in the carbonium-ion reactions of cyclobutyl and cyclopropylcarbinyl systems prompted a study of methylene group redistribution in the products via ^{14}C labeling experiments. Under conditions of equilibrium control, such as obtain in the reactions of alcohols with the Lucas reagent (zinc chloride-hydrochloric acid), the chloride produced from cyclobutanol, cyclopropylcarbinol and allylcarbinol was allylcarbinyl chloride. The reaction of cyclopropylcarbinol-α-^{14}C with Lucas reagent yielded allylcarbinyl chloride with label statistically distributed among the three methylene positions (2).

In this case, labeled chloride ion is found to be incorporated in cyclobutyl chloride and cyclopropylcarbinyl chloride under the reaction conditions. It is therefore impossible to say whether methylene group shuffling occurs in the initially formed cationic intermediate or partially via the internal- and external-return reactions of the

subsequently formed chloride. Parallel investigations have shown that in acetic acid and 80% aqueous ethanol the systems appear to undergo ion pair formation followed by internal return (7). In reactions which are both free of internal-return isomerization of starting material and give the products of kinetic control, the label distribution in the product gives considerable information about the carbonium-ion intermediates. The label redistribution has been determined for the amine-nitrous acid reactions on cyclopropylcarbinylamine and allylcarbinylamine. This reaction was chosen because the products are those of kinetic control, and the nitrogen molecule, as a neutral leaving group, probably does not give return to an alkyldiazonium ion (8, 9). Unfortunately, escape from pre- and post-carbonium-ion equilibration difficulties does not resolve the question of the relationship between the carbonium ions arising during solvolysis reactions and that from the deamination reaction. The deamination reaction clearly gives rise to special products. Whether these special products arise from "hot" carbonium ions (10) or from concerted reactions of alkyldiazonium ions (11) remains unsettled.

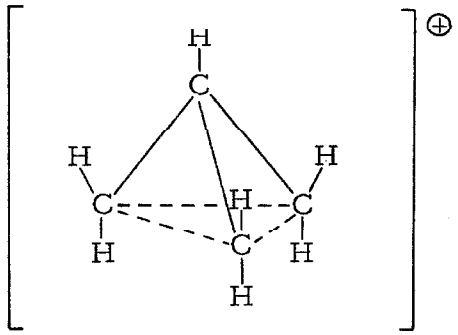
Both cyclopropylcarbinylamine-α-^{14}C (12) and allylcarbinylamine-α-^{14}C (13) have been deaminated in aqueous nitrous acid. The resulting cyclobutanol and cyclopropylcarbinol were degraded to give the following distributions of the ^{14}C label.



These results are fascinating if considered as arising from rapidly equilibrating classical carbonium ions. Obviously, any such equilibration of cyclopropylcarbinyl and cyclobutyl carbonium ions must be relatively rapid but not instantaneous with respect to their rates of reaction with solvent, while at the same time the strain-relieving ring opening to the allylcarbinyl cation must be slower than both these rates of reaction with solvent. Significantly, the ring closure reactions of the allylcarbinyl cation clearly compete successfully with the reaction of the primary cation with solvent. This formulation appears to require the allylcarbinyl cation to be less stable than the cyclopropylcarbinyl cation. In the classical formulations of these two cations, the only vital difference between them is the difference in strain between an allyl system and a cyclopropyl system. On this basis, the allylcarbinyl system is expected to be more stable. The contradiction between the expected and apparent properties of the ions can best be resolved by assuming that the actual intermediates

have reactivities and stabilities different from those expected for classical carbonium ions.

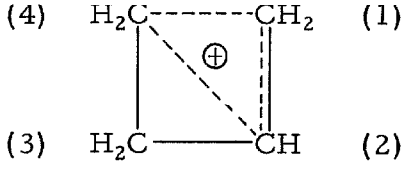
The once appealing delocalized intermediate described as a "tricyclobutonium" (I) has already been rejected as the principal



I

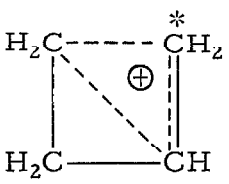
intermediate (12). Its threefold symmetry would predict a symmetrical distribution of ^{14}C in the products, and the observed variation from a statistical distribution of label is experimentally significant.

The data obtained so far on the unsubstituted cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl systems have been successfully rationalized on the basis of a bicyclobutonium ion intermediate (II) (12). When a labeled carbon atom is introduced, this becomes a

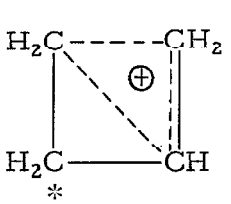


II

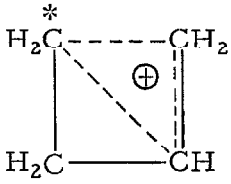
scheme of three equilibrating intermediates (IIa-c) or actually, if all three methylene groups could be distinguished, there would be six different bicyclobutonium ions. For the present, we shall restrict our attention to the ions IIa-c.



IIa



IIb



IIc

Formation of these cations explains the observed reactivities if the assumption is made that the solvolysis transition state closely resembles the intermediates with their delocalized charge. It is likely that there would be a significant release of strain in going from a cyclopropylcarbinyl derivative to a bicyclobutonium cation and probably a significant increase in strain coming from a cyclobutyl compound. The equilibration of cyclobutyl chloride with cyclopropylcarbinyl chloride in the presence of zinc chloride favors cyclobutyl chloride by about 36/1. At the same time cyclobutyl chloride was found to react at 1/30 the rate of cyclopropylcarbinyl chloride in 80% aqueous ethanol at 97° (7). This suggests that the transition states for these two solvolyses have approximately the same energy and may have very similar structures. This is not very surprising, if despite their dissimilar ground state structures, both materials were solvolyzing by the same carbonium-ion intermediate.

The product distribution obtained from the deamination reactions of cyclobutyl, cyclopropylcarbinyl and allylcarbinylamine have been used as a measure of the reactivity of the bicyclobutonium ion at its three different centers of positive charge. It has been assumed, because the reaction of the carbonium ion with solvent is highly exothermic, that the reactivity of the bicyclobutonium ion at its three centers is a fairly accurate measure of the charge distribution over the various centers (14). In this connection, the calculations made by Howden and Roberts (6) predict that the net charges at C-2, C-1, and C-4 would be in the ratio of 1:1.34:2.05, respectively. This predicted charge distribution for the most stable configuration disagrees with the proportion of products corresponding to nucleophilic attack which is usually about 10:10:1 (2, 12). Refinements in calculation techniques might very well produce a significant change in electron distribution without causing large changes in the delocalization energy and hence of the predicted geometry and stability of the intermediate.

Analysis of the possible modes of interconversion of IIa-c and how each would affect the label distribution is important to understanding the reactions under consideration. The activation energy for the interconversion of the labeled bicyclobutonium ions must range between 0 and 5 kcal/mole less than that for the reaction of the ions with solvent. These limits were established by rough calculations (which will be discussed below) of the effect of the variation of the relative barrier heights. It was found that equal rates of re-

arrangement and reaction with solvent of the initially formed bicyclobutonium ion left the majority of the product with its label unscrambled. The assumption that the slowest rate of rearrangement was a thousand times faster than the rate of reaction with solvent led to a label distribution experimentally indistinguishable from that which would arise from the tricyclobutonium ion (I). As has been noted (12), the direct formation of differently labeled initial bicyclobutonium ions should produce predictably different label distributions in the products. A final consideration that should enter into all predictions about the system of equilibrating intermediates is the question of the structures of and relative activation energies for the transition states for interconversion.

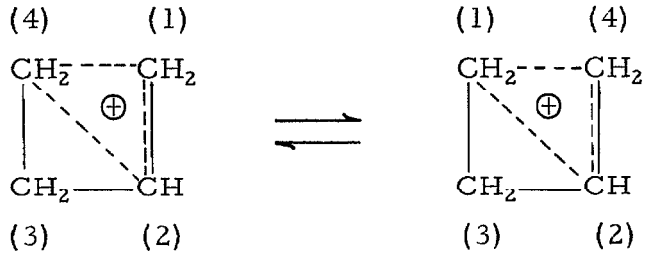
The tricyclobutonium ion has been considered as a possible transition state for the direct interconversion of any one of the bicyclobutonium ions into any other bicyclobutonium ion (12). The calculations of Howden and Roberts show the difference in stability between a bicyclobutonium and tricyclobutonium ion to be of the order of 23 kcal/mole (6). These calculations were made on a completely symmetrical model with two possible orbital configurations being considered. It seems unlikely that refinements in the calculations would change this value sufficiently to make the tricyclobutonium ion a reasonable transition state for the interconversions.

Another proposal is to consider the bicyclobutonium ions as interconvertible in a sequential order. The scheme which will be favored here is one in which IIa can be converted to IIc via interme-

diate IIb only, with the conversion of IIa to IIb (conversion A) being

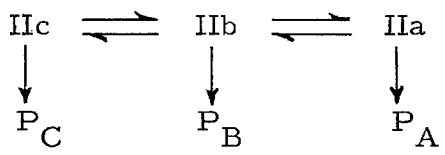
$$\text{IIa} \overset{A}{\rightleftharpoons} \text{IIb} \overset{B}{\rightleftharpoons} \text{IIc}$$

different in kind from that of IIb to IIc (conversion B). An examination of models suggests that conversion A might be very easy, since the changes in atomic positions between the two structures are minor. The electronic changes consist of changing one bond (between C-2 and C-4) from delocalized to localized while changing another (between C-3 and C-2) from localized to delocalized. It has been suggested that conversion B might be accomplished via a transition state resembling the tricyclobutonium ion (12), but this seems unreasonable on energetic grounds unless an unsymmetrical tricyclobutonium-like ion can supply a favorable delocalization energy. Formally, the conversion B involves both a considerable change in the position of two carbon atoms and an electronic change similar to that in conversion A. The new localized bond would be between what had been originally C-2 and C-4. Direct interconversion of IIa and IIc would require at least two of the carbon atoms to change their positions, and at least two localized bonds must be broken simultaneously with the formation of two new bonds.



IIa IIc

It has been shown that the label distribution in cyclobutanol (36.8% at C-3) from the deamination of allylcarbinylamine-α-^{14}C can be used to predict the amount of label in the ring of the accompanying cyclopropylcarbinol (15). As will be seen below, none of the calculated label distributions fit the observed value (13) of 70.4% of the label in the ring very closely. Schemes permitting direct interconversions of all three ions (IIa-c) give 68.4%, which was the best fit to the observed value. The scheme of making barrier B larger than barrier A while not allowing direct interconversion of IIa and IIc gave the same value (68.4%). The assumption of the reverse relative barrier heights leads to 73.6%. These figures bracket the experimental results and suggest that the barriers may be nearly equal. Attempts to integrate directly the equations resulting from a system of three sequential intermediates with equal rates of rearrangement and equal rates of reaction with solvent failed, but suggested that the



rate of approach to equilibrium for IIc and IIb should be three times that of the rate of approach to the second equilibrium. This would in turn suggest that the best fit to the data would be obtained by making barrier B slightly larger than barrier A.

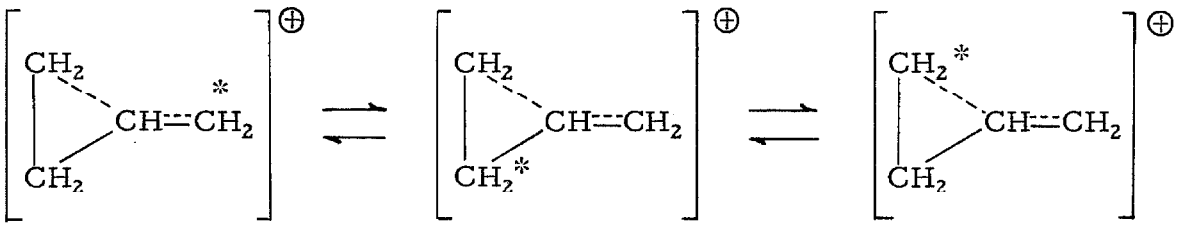
Crude iterative calculations were performed on this system by assuming equal barrier heights, various ratios of the rate of rearrangement to the rate of reaction with solvent, and that the rate of formation of the initial non-classical intermediate is insignificant compared to the rates of rearrangement and reaction with solvent. These assumptions reduce the problem to one of the redistribution of a fixed quantity of material among the three intermediates in the face of a competing reaction with solvent. Initially, each iteration was performed for a unit of reaction in which 1% of the bicyclobutonium ions reacted by its most rapid reaction path. For example, if we choose the rate of rearrangement to be ten times faster than the rate of reaction with solvent, then, after the first iteration, 98.9% of the material would be present as IIc, 1.00% as IIb, and 0.10% as P_C; after the second iteration, 97.82% of the material would be present as IIc, 1.97% as IIb, 0.01% as IIa, 0.199% as P_C, and 0.001% as P_B. The percentage of reaction per iteration was gradually increased when successive iterations led to changes of less than 0.1% in the quantity of each intermediate. It was found that for the conditions given in the example the cyclobutanol from the deamination of allylcarbinylamine-α-^{14}C would have 38.4% of the label in the 3-position while the cyclopropylcarbinol would have 70.6% of the label in

the ring; for a 20:1 ratio the numbers would be 36.0% and 68.8% respectively.

Cyclopropylcarbinylamine-α-^{14}C yielded on deamination cyclopropylcarbinol with its ^{14}C label less extensively scrambled than that of the accompanying cyclobutanol. The ratios of the cyclopropylcarbinol to cyclobutanol obtained from the deaminations of cyclobutylamine and allylcarbinylamine were 1.16 and 1.17 respectively (13). By contrast, the ratio obtained from cyclopropylcarbinylamine deamination was 1.39. This corresponds to a 16% excess of cyclopropylcarbinol which is assumed to arise either from the SN_2 displacement on the diazonium ion or from a "hot" carbonium ion. If correction is made for the non-rearranging path, the cyclopropylcarbinol derived from cyclopropylcarbinylamine-α-^{14}C <u>via</u> the carbonium ion is found to have 42% of its label in the carbinyl methylene. This is in reasonable agreement with the 71.6% of label found in the 2-position of the cyclobutyl system. A calculation in which the barriers for interconversion were assumed equal and the rate of rearrangement was assumed to be 5 times that of the rate of reaction with solvent gave 42.6% and 73.7% for the two quantities. It is interesting to note that in each case the observed deviation from a statistical distribution is in the direction that would be predicted by the direct formation of the appropriate bicyclobutonium ion. The theoretical analysis of the proposed scheme of interconversions suggests that the deamination of allylcarbinylamine-β-^{14}C would be of great interest. The deamination should lead directly to the formation of IIb, which, if the

barriers for interconversion are indeed equal, should yield products with equal amounts of labeling in the carbinyl carbon of the cyclopropylcarbinol and the 3-position of the cyclobutanol. Any deviation from equality would be a measure of the relative barrier heights, while the deviation from a statistical distribution would permit a calculation of the ratio of the rates of rearrangement and reaction with solvent. The need to use two different rate ratios to fit the two cases studied suggests that the barrier heights are not equal but differ by less than 1 kcal/mole. The uncertainty in the amount of direct displacement occurring in the deamination of cyclopropylcarbinyl-α-^{14}C is too large to make a calculation of the two parameters from the available data worthwhile.

Several schemes have been proposed as alternative explanations of the tracer shuffling, product distributions, and reactivities observed in these systems. One proposal is that equilibrating homoallylic cations might provide just as reasonable a set of non-classical cations (16). The formation of cyclobutanol as a major product in the cationic reactions of the unsubstituted cyclopropylcarbinyl system would seem to require an unexpectedly high reactivity at the

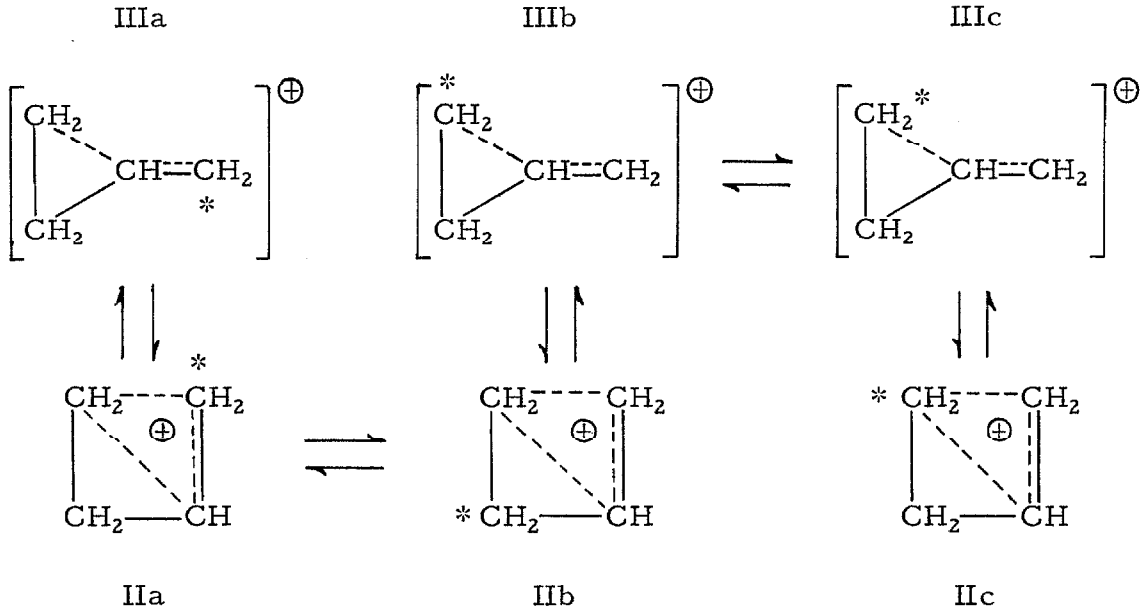


IIIa IIIb IIIc

methinyl carbon atom of the homoallylic cations (IIIa-c). The reactivity of the homoallylic cation at the methinyl carbon atom might well be larger than that of the allylic system but unless a clear-cut example of cyclobutyl formation from a homoallylic intermediate can be found, the argument in favor of IIIa-c as principal intermediates must be considered weak.

It is possible though that the homoallylic ions (IIIa-c) are present as metastable intermediates along with the bicyclobutonium ions (IIa-c). William of Occam might indeed oppose the introduction of this added complication, but the presence of such intermediates helps make conversion B in the bicyclobutonium ion scheme look more straightforward and energetically favorable. The conversion of a bicyclobutonium ion to a homoallylic ion involves both a loss of delocalization energy due to the exclusion of the 1, 4-interaction and a reduction in strain (6). This transformation should involve a relatively small excess activation energy beyond the difference in stability of the two ions. A crude calculation of this difference gives 8.6 kcal/mole (6). This difference, if correct, is much too large for the homoallylic cations to be important intermediates. The cations (IIIa-c) are included for the sake of completeness and to provide a reasonable route for the transformation of IIb into IIc.

The proposed scheme has the virtue of supplying a transformation process with an activation energy in the neighborhood of 10-15 kcal/mole. The transition states for the "easy" transformation of IIa to IIb, or IIIb to IIIc are difficult to formulate in such a way that



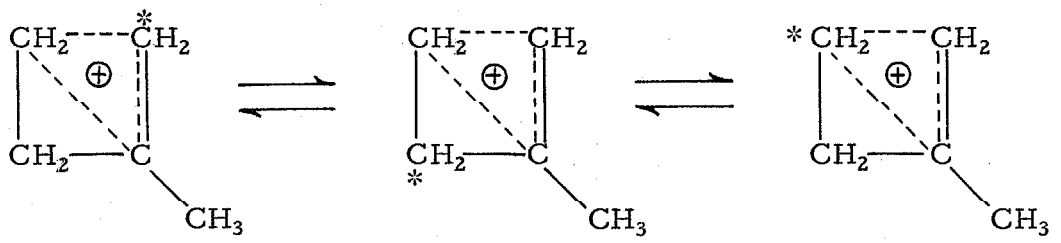
their delocalization energy can be calculated. A simple approximation which might have some validity would be to take the classical cyclopropylcarbinyl and cyclobutyl cations as models for the two transition states.

It is possible that the relations among the intermediates as well as the electronic structure and geometry of the individual intermediates will be severely altered by the substitution of various functional groups. A simple substituent useful in investigating these possibilities is the methyl group. It is obvious that, if the present data is correctly interpreted in terms of bicyclobutonium ions, the fact that most of the charge appears to be evenly distributed between two carbon atoms suggests that the product distribution from the reaction of such cations with solvent might be severely altered by the substitution of a methyl group. Such substitution at the methinyl

hydrogen should affect the charge distribution in both the intermediates and the transition states for their interconversion with the result that a change in the products and in the degree of equilibration of the three bicyclobutonium ions (which must be considered if one of the methylene groups is labeled) would be expected. In a methinyl-substituted bicyclobutonium ion, more charge would be concentrated at the tertiary center, and there would be an increase in the amount of cyclobutyl product observed in all reactions that could lead to this bicyclobutonium ion. For a methinyl-substituted homoallylic cation, theory predicts a substantial increase in the charge at the tertiary center, but as long as 1, 4-interaction is not permitted there would be a significant reactivity at the two methylene positions. A study of the reactivities of the substituted halides and of the products obtained from the methinyl-substituted compounds has been carried out (17). The only product isolated in the deaminations of 1-methylcyclobutylamine and (1-methylcyclopropyl)-carbinylamine was 1-methylcyclobutanol. The only ring-closed product positively identified in the deamination of β-methylallylcarbinylamine was also 1-methylcyclobutanol. These results might be used to argue that the intermediate formed was the classical 1-methylcyclobutyl cation, but they are also consistent with the formation of the 2-methylbicyclobutonium ion. The possible intervention of the methinyl-substituted homoallylic ion as a principal or transient intermediate will be discussed below.

(1-Methylcyclopropyl)-carbinylamine-α-^{14}C on deamination in an aqueous media gives 1-methylcyclobutanol with 2.6% of the ^{14}C at

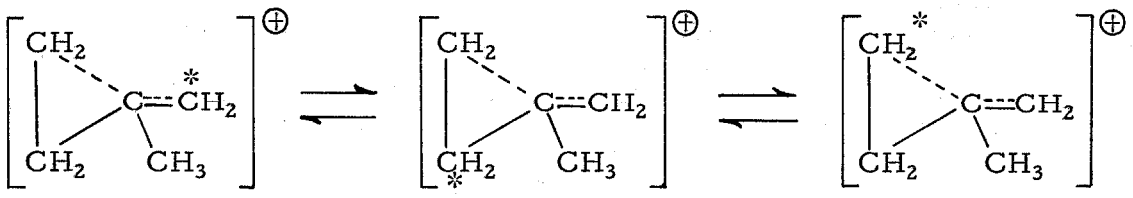
the 3-position of the cyclobutyl ring (17). This distribution of the label is only 7.8% of that expected for complete equilibration. For



IVa IVb IVc

the formulation in terms of the sequential equilibration IVa-c, it corresponds to an increase in either the rate of reaction with solvent or the activation energy for the conversion of IVa to IVc. This latter change could be occurring in one or both of the conversion barriers.

In terms of a formulation involving homoallylic cations (Va-c), there would be the same pair of alternative explanations for the change in degree of label equilibrium relative to the unsubstituted case, with



Va Vb Vc

the only fact being that the conversion of Va to Vc has to be severely inhibited. That these equilibrating cations (Va-c) should yield only 1-methylcyclobutanol seems very unreasonable, but the possibility cannot be eliminated on the basis of present knowledge. An experi-

ment which could eliminate equilibrating homoallylic cations as principal intermediates would be the deamination of carbinyl-labeled (β-methylallyl)-carbinylamine which would give IVc or Vc as the initially formed intermediate in the two schemes. According to the previous study (17) not much conversion of IVc to IVa would be expected, and if conversion B indeed has the higher barrier, then no more than 3% of the label should be found in the 2-position of the resultant 1-methylcyclobutanol. If the barriers are indeed different in the homoallylic case, then the easier conversion would be expected to be that of Vc to Vb. The intermediate Va is not readily converted to Vc, but still we might observe a near equilibration of Vc and Vb which would lead to 1-methylcyclobutanol with a significant amount of label in the 2-position. Such experiments will be described later.

If the homoallylic cations are present only as metastable intermediates, the methyl group would be expected to stabilize the bicyclobutonium ions more than the homoallylic ions, thus increasing the barrier to the interconversion of bicyclobutonium ions IVb and IVc. The barrier between Vb and Vc would be expected to increase by a much smaller amount, if the transition state really resembles the classical (1-methylcyclopropyl)-carbinyl cation. The transition state for the conversion of IVa to IVb, and hence that of Va to Vb, would resemble the 1-methylcyclobutyl cation, with the result that the barrier to this conversion would probably decrease. The data from the deamination of (1-methylcyclopropyl)-carbinylamine is consistent with this formulation, and in general would suggest that if IVc

were the initially formed intermediate, there would still be little label shuffling in the product.

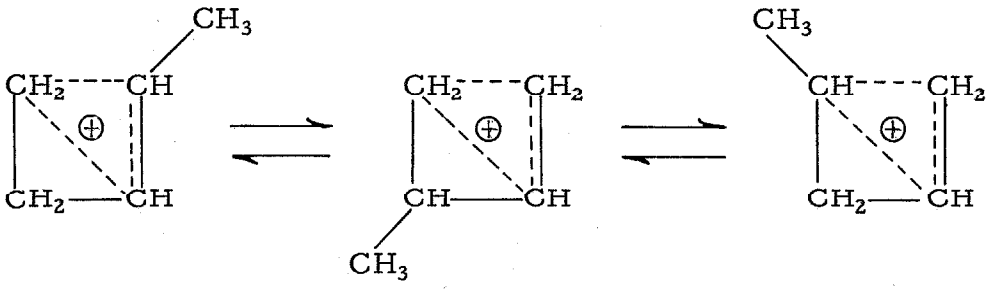
The deamination of (β-methylallyl)-carbinylamine forms 1-methylcyclobutanol, 55%, and (1-methylcyclopropyl)-carbinol, 2 ± 2%, with the rest of the material appearing as open-chain products (17). Since the only observed product in the deamination of (1-methylcyclopropyl)-carbinylamine was 1-methylcyclobutanol, it was assumed that the open-chain products were formed from a precursor of the non-classical carbonium ion such as an alkyldiazonium ion or a "hot" carbonium ion. The non-classical carbonium ion formed might very well be a metastable species which eventually cascades down to the more stable intermediate(s) before reacting with solvent. If the metastable intermediate(s) has a long enough lifetime, one might expect partial equilibration between Vc and Vb to give as the product-forming intermediates, IVc and IVb. The tentative identification by infrared analysis of (1-methylcyclopropyl)-carbinol as one of the products of the deamination of (β-methylallyl)-carbinylamine might be considered evidence of the presence of the homoallylic ion as the first-formed but transient intermediate.

In view of these speculations, the synthesis, deamination, and nuclear magnetic resonance (n. m. r.) examination of the deamination products of dideutero-(β-methylallyl)-carbinylamine were undertaken. Concurrently, the product mixture was to be re-examined for the presence of (1-methylcyclopropyl)-carbinol.

Silver studied the effect of methyl substitution at the methylene

positions of amines which would give rise to the bicyclobutonium ion (14). The investigation showed that the deamination products from the amine-nitrous acid reactions of six such amines could be interpreted in terms of substituted bicyclobutonium ions. Here, as in the previously discussed cases, it was necessary to assume that the alkyldiazonium ion was capable of yielding intermediates of products outside of the bicyclobutonium ion scheme. The results are summarized in Table I.

The most important and obvious modification of the bicyclobutonium ion scheme is that the three bicyclobutonium ions which could only be differentiated by isotopic substitution, now differ by the position of a methyl substituent and consequently differ in energy. Of the three ions (XII-XIV), XII probably has the lowest energy since it has

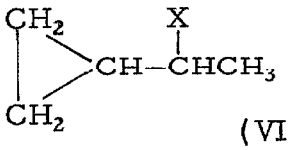
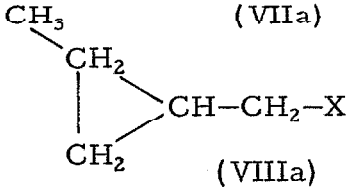
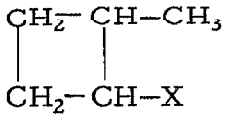
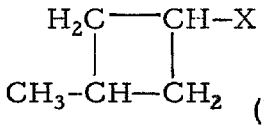


XII XIII XIV

the stabilizing methyl group substituted at the methylene group which appears to bear the most positive charge in the unsubstituted bicyclobutonium ion. Intermediate XIII should be the least stable ion (highest energy) with respect to the interconversions of the three ions because the only stabilizing effect of the methyl group would arise from

TABLE

PERCENTAGES OF ISOMERIC ALCOHOLS FROM AMINE–NITROUS ACID REACTIONS

	VIb	VIIb	VIIIb	IXb	Xb
 (VIa)	100	0	0	0	0
 (VIIa)	17	49	3(?)	0	0[c]
 (VIIIa)	51	35	13	0	0
 (IXa)	100	0	0	0	0
 (Xa)	47	39	9	0	0
 (XIa)	74	0	0	0	0[c, d]

[a]X is $-NH_2$.

[b]X is -OH.

[c]Plus isomeric allylic alcohols via hydride shift.

[d]Plus 10% of crotylcarbinol.

the inductive effect of β-methyl group. XIV should be intermediate in energy because the carbon atom involved appears to bear the least charge of the three charged carbon atoms in the unsubstituted case. Further complications are introduced because the reactivity toward solvent is different for each of the three species (XII-XIV) as well as for each center of partial positive charge. This probably significant variation tends to obscure the relative stabilities of the intermediates when they are studied under conditions of kinetic control. Finally, there is the possibility that both the reactivity and stability of potential intermediates like the homoallylic and classical cations relative to the bicyclobutonium ions may have been altered sufficiently so that one or more of them may actually be a principal intermediate along with the bicyclobutonium ions

The results reported by Silver (14) can be explained on the basis of just the first two types of adjustments of the bicyclobutonium ion scheme. With 2-methylcyclobutylamine (IXa), methylcyclopropylcarbinylamine (VIa) and crotylcarbinylamine (XIa), the only ring-closed product observed is methylcyclopropylcarbinol. This is reasonable in that the intermediate (XII) would be formed directly in each of these cases. Apparently, the methyl group has distorted the charge distribution of the intermediate so that this intermediate behaves as if the charge was localized at C-1, and reaction with solvent occurs before conversion to any other intermediate. This would be reasonable in terms of the proposed sequential order of conversions since then any conversion of XII to XIV must go <u>via</u> the highest-energy

intermediate (XIII). Intermediate XIV might be expected to form only methylallylcarbinol directly from solvent, but conversion to XII and XIII may be relatively easy. Intermediate XIII is expected to give equal amounts of 2-methylcyclobutanol (VIIb) and (2-methylcyclopropyl)-carbinol (VIIIb) by reaction with water since the charge distribution should not vary much from that of the unsubstituted bicyclobutonium ion.

No 2-methylcyclobutanol (IXb) was observed to be found in the deamination of any of the six amines studied by Silver (14). This is not surprising because XIII is either not formed directly or not the only bicyclobutonium ion that can be formed directly from any of these amines. With 2-methylcyclobutylamine (IXb) either XIII or XII could be formed directly, and the only product isolated is that from XII. With (2-methylcyclopropyl)-carbinylamine (VIIIa), where XIII or XIV could have been formed initially, the product distribution does not differ unexpectedly from that obtained from 3-methylcyclobutylamine (Xa) which can give only XIV directly. On the other hand, (2-methylcyclopropyl)-carbinol (VIIIb) was detected among the products obtained from three of the amines. For each of these deaminations, XIV is assumed to be the intermediate formed directly, so it is possible that XIV reacts at more than one carbon, or for some reason, possibly steric in origin, that XIII only reacts at C-1 to give (2-methylcyclopropyl)-carbinol (VIIIb). Of course, this alcohol (VIIIb) may possibly arise from both routes.

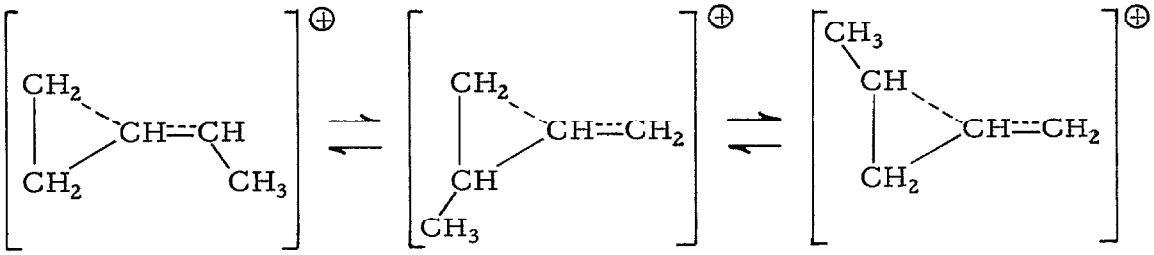
The deamination of 3-methylcyclobutylamine (Xa) affords 5% of

3-methylcyclobutanol (Xb). Since no 3-methylcyclobutanol (Xb) forms in the deamination of either methylallylcarbinylamine (VIIa) or (2-methylcyclopropyl)-carbinylamine (VIIIa), the alcohol (Xb) may arise either from the "hot" carbonium ion or an SN_2 displacement on the diazonium ion. Here the starting material might have been a mixture of cis and trans isomers and the conformation of the cis alcohol might be such as to favor the S_N2-displacement reaction (14). These special reactions also appear with both substituted allylcarbinylamines studied which give a large proportion of direct displacement and hydride-shift products.

The variation in the ratio of (2-methylcyclopropyl)-carbinol (VIIIb) to methylallylcarbinol (VIIb) between the deaminations of 3-methylcyclobutylamine (Xa) and (2-methylcyclopropyl)-carbinylamine can be rationalized by attributing the variation to the formation of about 40% of the (2-methylcyclopropyl)-carbinol (VIIIb) (or 5% of the product mixture) via an S_N2-displacement reaction on the alkyldiazonium ion. Apparently, the primary cyclopropylcarbinyl system does not undergo hydride shift reaction. This phenomenon is surely associated with the high energy of the cyclopropyl cation (18).

No cyclobutyl products other than the 3-methylcyclobutanol (Xb) from 3-methylcyclobutylamine (Xa) were identified among the deamination products from the six amines. The absence of such products might be interpreted as evidence for the intermediacy of homoallylic ions (XV-XVII). These ions when substituted at a methylene group could well give only cyclopropylcarbinyl and allylcarbinyl products

upon reaction with solvent. The energies of the three homoallylic ions (XV-XVII) should depend on the position of the methyl group substitution. The expected order of energies would be XV $\gtrsim$ XVII < XVI. Both XV and XVII might well give a single product each, with XV giving methylcyclopropylcarbinol and XVII giving methylallylcarbinol.

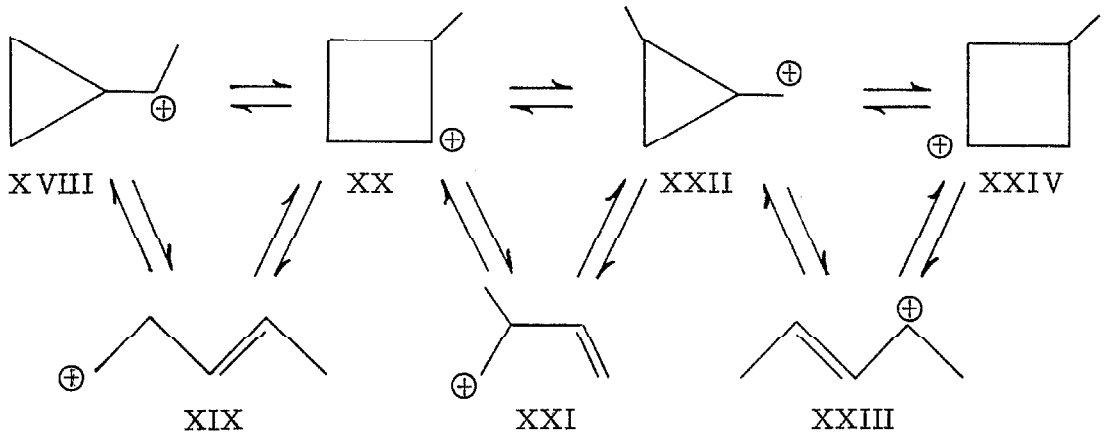


XV XVI XVII

A problem arises in the case of XVI which would be expected to yield similar quantities of both (α-methylallyl)-carbinol and (2-methylcyclopropyl)-carbinol. The failure to detect (α-methylallyl)-carbinol among the products from the three amines that would be expected to give rise to XVI requires a change in the a priori prediction of products. The two alternative reactivity schemes, i.e., to assume that XVII gives both (2-methylcyclopropyl)-carbinol and methyl-allylcarbinol with no products being formed from XVI, or to assume that for some reason XVI gives only (2-methylcyclopropyl)-carbinol, both run contrary to the expected trends in the behavior of these intermediates. The observation that amines which can form XV give only methylcyclopropylcarbinol (VIb) requires that the proposed sequential order of interconversions be followed, or that the reactivity XV toward solvent be much greater than that of the other two ions. In general, the bicyclobuton-

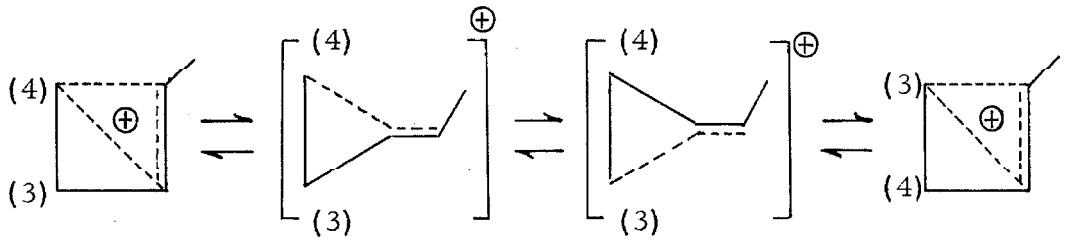
ium formulation appears to fit the pattern of results better than the homoallylic formulation despite the lack of cyclobutyl products.

If an attempt is made to explain the data in terms of rapidly equilibrating classical carbonium ions, there are too many problems with respect to the required relative energies of the various ions. The chief problem is the successful competition of (2-methylcyclopropyl)-carbinyl cation (XXII) as a product-forming intermediate with a strain-free, secondary carbonium ion like the methylallylcarbinyl cation (XXIII). This does seem improbable. A priori one might set



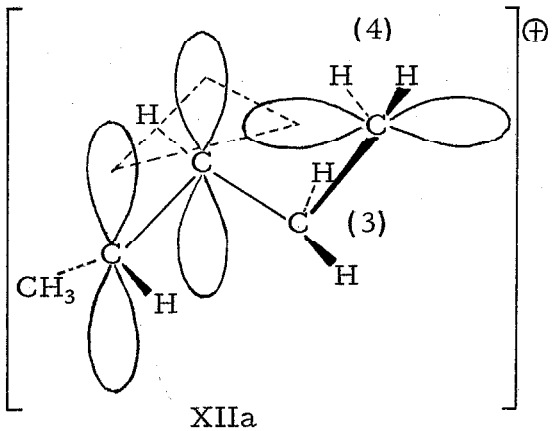
the relative stabilities of the classical carbonium ions at XXIII ≫ XVIII ~ XX ~ XXIV > XIX > XXI > XXII. Nevertheless, in three different reactions, the product from XXII is found as well as that from XXIII. It is also difficult to explain why XXIII is converted to XVIII when the reverse reaction, which certainly would be favored, does not occur. Assuming a significant difference in reactivity toward solvent might smooth out the former difficulties, but certainly not the latter.

Vogel's observation that the deamination of optically active methylcyclopropylcarbinylamine (VIb) gives essentially racemic alcohol can be explained in many ways (19). First, there are the competing S_Ni and S_N2 mechanisms of deamination which could be combined fortuitously in equal parts to give racemic product. Second, an initially formed classical carbonium ion (XVIII) would be racemic. Third, the homoallylic cation (XV) would give racemic product. The observed 4% inversion could be correlated with an S_N2 reaction on the alkyldiazonium ion. The bicyclobutonium ion, XII, is asymmetric and of itself would not be expected to produce racemized product. If this ion were in rapid equilibrium with XIII and XIV, it might be racemized during the rearrangements, but the observation that only methylcyclopropylcarbinol (VIb) is formed (14) suggests that this equilibrium, which would lead to the products of XIV as well as XII, is not established. Actually, failure to observe retention of configuration while isolating VIb is consistent with a formulation in terms of two equilibrating bicyclobutonium ions differing by the interchange of methylene groups labeled 3 and 4 below. Passage through a tran-

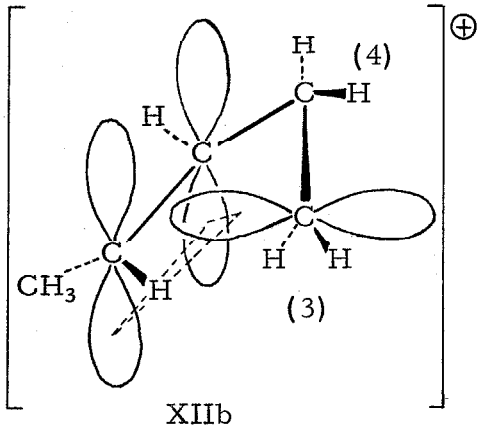


XIIa XVa XVb XIIb

sition state resembling the homoallylic ion would lead to the racemic product observed. Furthermore, direct interconversion of XIIa and XIIb, by processes similar to those that might be invoked to explain conversion B in the unsubstituted case, would also lead to racemization.



XIIa



XIIb

Deamination of (α-methylallyl)-carbinylamine would shed some light on these problems by providing direct entry to the highest energy intermediates in the non-classical formulations.

II. RESULTS AND DISCUSSION

The first synthetic efforts were directed toward preparing (dideutero-α-methylallyl)-carbinylamine by reduction of some precursor with lithium aluminum deuteride to the desired amine. α-Methylallyl cyanide was prepared and converted to α-methylallylcarboxamide with concentrated sulfuric acid. Reduction of both the amide and cyanide yielded only traces of amine and larger amounts of a high-boiling oil. The failure to obtain the desired amine was probably due to proton abstraction followed by condensation reactions.

The successful route was an adaptation of methods previously used for the synthesis of allylcarbinyl derivatives (13, 17). β-Methylallyl magnesium bromide was prepared in a cyclic reactor (20) and carbonated to give 3-methyl-3-butenoic acid in yields ranging from 26 to 56%. The carboxylic acid was esterified with diazomethane and reduced with lithium aluminum deuteride to dideutero-(β-methylallyl)-carbinol. The deuterated alcohol was converted to the benzenesulfonate with benzenesulfonyl chloride in collidine. Dideutero-(β-methylallyl)-carbinyl azide was formed from the benzenesulfonate with sodium azide in dimethyl sulfoxide. The azide was reduced to the amine with lithium aluminum hydride. Dideutero-(β-methylallyl)-carbinylamine was obtained in 34% yield based on the lithium aluminum deuteride.

In order to compare results from vapor phase chromatography (v. p. c.) analysis with those obtained earlier by infrared analysis

(17), the deamination of (β-methylallyl)-carbinylamine was re-examined. The results are given in Table II.

TABLE II

PRODUCTS FROM THE AMINE-NITROUS ACID REACTION OF (β-METHYLALLYL)-CARBINYLAMINE

	Present Work	Cox (17)
1-Methylcyclobutanol	59%	55%
(β-Methylallyl)-carbinol	29%	33%
α, β-Dimethylallyl alcohol	6%	5%
β, γ-Dimethylallyl alcohol	6%	4%
(1-Methylcyclopropyl)-carbinol	0%	2 ± 2%

The agreement between the present work and that of Cox is satisfactory, considering that no attempt was made to correct for differences in the thermal conductivities of the alcohols. The search for (1-methylcyclopropyl)-carbinol was unsuccessful under conditions where a peak due to 0.2% of the alcohol could be detected. The original assignment had been regarded as tenuous (17). The formation of isoprene was observed but not evaluated quantitatively.

Dideutero-(β-methylallyl)-carbinylamine was deaminated with sodium nitrite in aqueous perchloric acid in order to determine the degree of deuterium scrambling in the 1-methylcyclobutanol formed. The mixture of product alcohols was separated by preparative v. p. c. on four 12-foot Carbowax columns at 120° in the Beckman Megachrom.

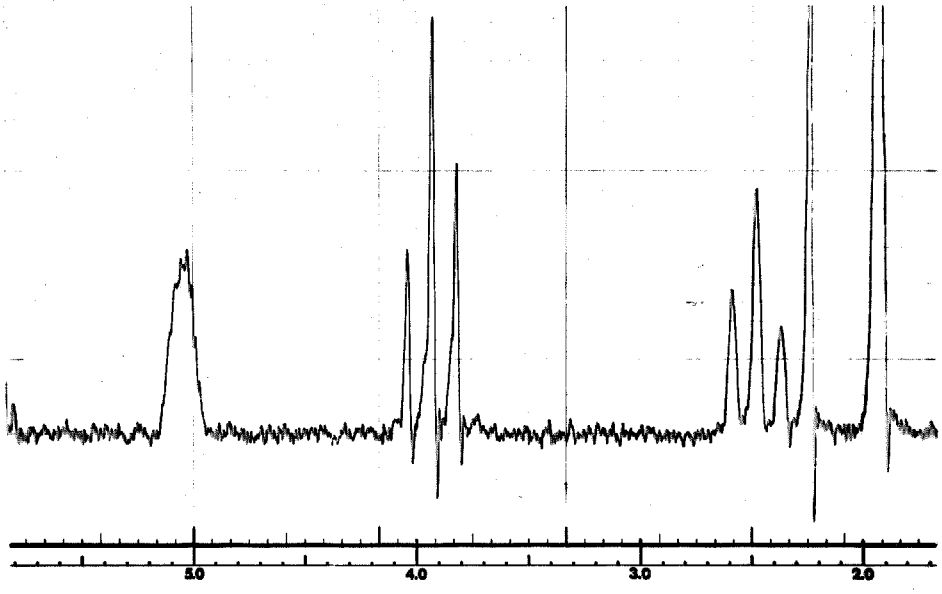


Fig. 1. N. m. r. spectrum of (β-methylallyl)-carbinol in CCl_4.

Fig. 2. N. m. r. spectrum of (β-methylallyl)-carbinol from deamination of dideutero-(β-methylallyl)-carbinylamine.

The (β-methylallyl)-carbinol fraction was homogeneous on the analytical v. p. c. using either a Carbowax (K) or a diisodecyl phthalate (A) column. The n. m. r. spectrum of the fraction was identical with that of the dideutero-(β-methylallyl)-carbinol prepared at the beginning of the synthesis. The alcohol is apparently unrearranged, but less than 2% protium in the carbinyl position would have gone undetected.

α, β-Dimethylallyl alcohol had the same retention time on column K as 1-methylcyclobutanol. Mixtures of the two isomeric alcohols in any proportion gave a v. p. c. peak indistinguishable from that of either pure component. Investigation by v. p. c. on column A showed that the preparative v. p. c. fraction corresponding to 1-methylcyclobutanol actually contained 22% of α, β-dimethylallyl alcohol. The n. m. r. sample was purified by the reaction of the preparative v. p. c. fraction with a 10% solution of bromine in carbon tetrachloride at 0°, followed by flash distillation of the product. The n. m. r. spectrum of the resulting alcohol had a multiplet 12 cps wide and centered 124 cps downfield from tetramethylsilane. The multiplets due to the protons at the 2- and 3-positions were clearly distinguishable in the n. m. r. spectrum of undeuterated 1-methylcyclobutanol. The multiplet in the spectrum of the deuterated 1-methylcyclobutanol was assigned to the protons at the 2-position. The section of spectrum where the protons of the 3-position should appear was devoid of detectable absorptions. Clearly, the expected complicated splitting would make the detection of small quantities of 2, 2-dideutero-1-methylcyclobutanol difficult. A reasonable upper limit would be the 3% found in the

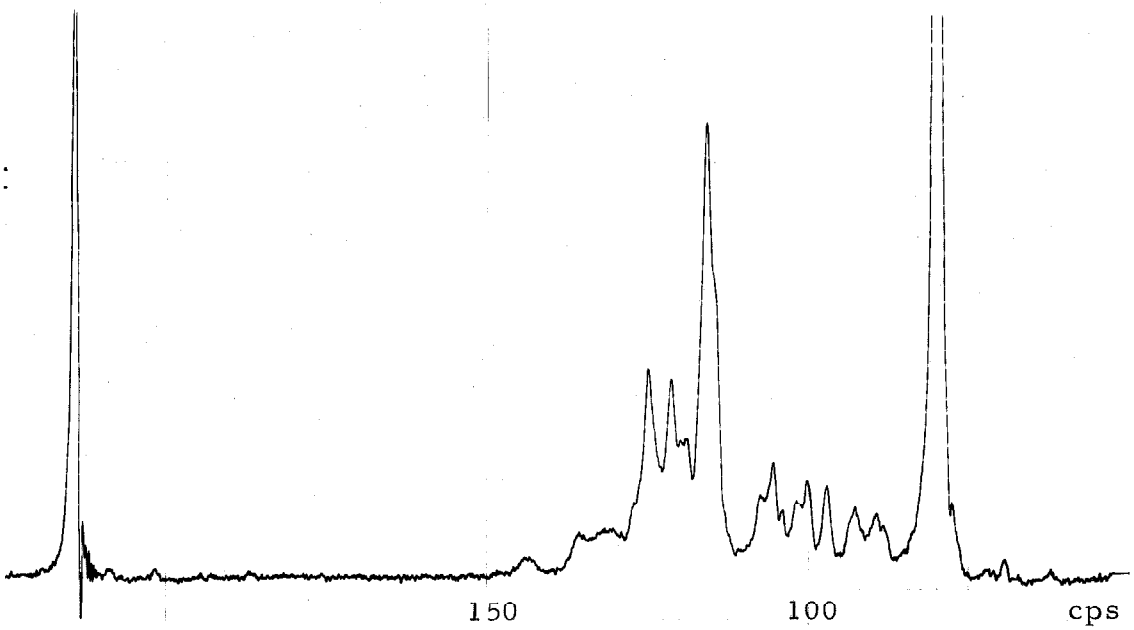


Fig. 3. N. m. r. spectrum of 1-methylcyclobutanol in CCl_4.

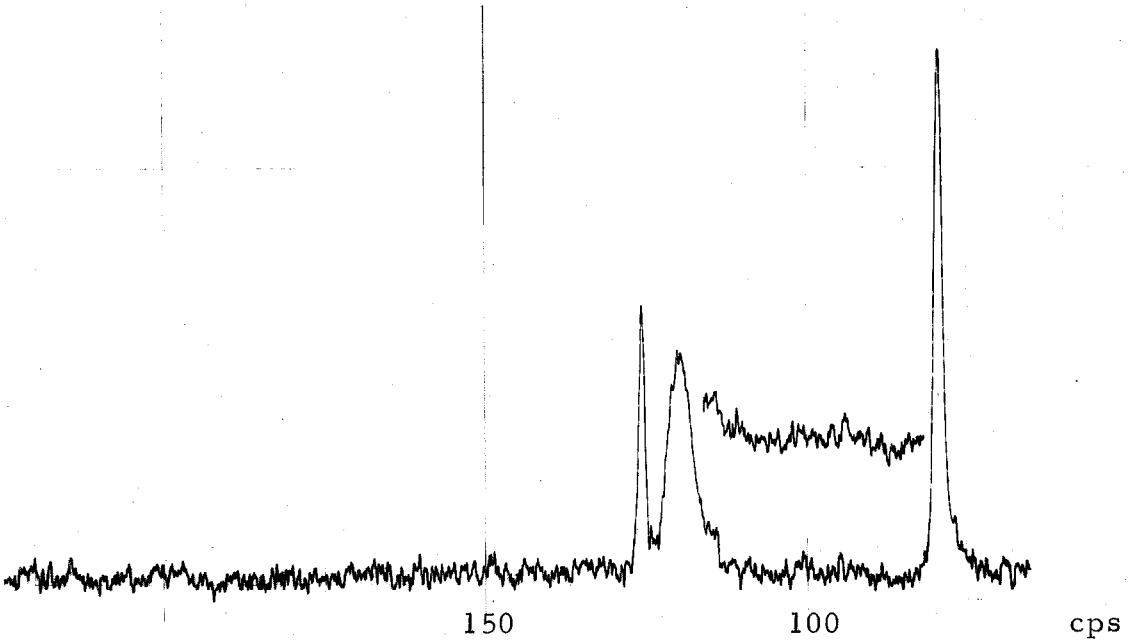


Fig. 4. N. m. r. spectrum of 1-methylcyclobutanol from deamination of dideutero-(β-methylallyl)-carbinylamine.

^{14}C labeling experiments of Cox (17). Analysis by v. p. c. indicated that the sample still contained 4% of an unidentified impurity, possibly the nitrite ester. A more accurate analysis might be possible using mass spectra or ^{14}C tracer techniques.

The observed product distributions are consistent with the initial formation of some species such as a "hot" carbonium ion or an alkyldiazonium ion (8, 10). This species then, by either a concerted reaction that releases nitrogen, or by a reaction faster than the rate of rotation about a carbon-carbon bond (21), undergoes further reactions. The reactive species can undergo a hydride shift to form an allylic cation which reacts with water to give a mixture of α,β-dimethylallyl and β,γ-dimethylallyl alcohols. The experimentally determined ratio, 1.0, of these products is known with only moderate precision but is still rather interesting because it is close to the ratio observed in the silver nitrate-catalyzed hydrolysis of 1- and 3-methylallyl chlorides (22), a reaction which shows a negligible product spread. The similar product distributions suggest that the allylic cation is indeed a solvolytic carbonium ion. The results point up the problem involved in equating the observed product distributions directly to the charge distribution in delocalized intermediates on the assumption that the charge distribution will be highly sensitive to substitution. Certainly, if this had been an equilibrium between two localized species, the secondary alcohol would have been predicted to be the exclusive product. The lack of response to a methyl substituent on a highly delocalized intermediate shows that

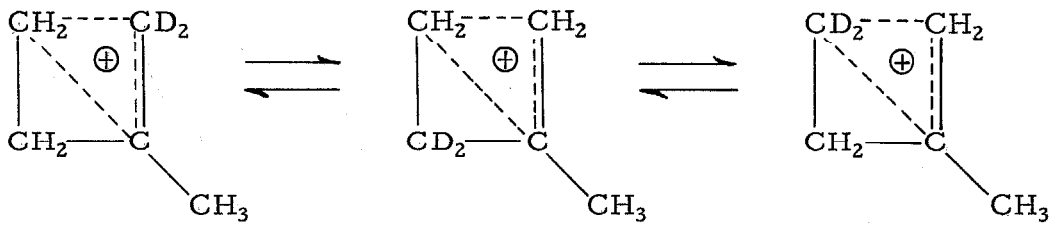
in these systems the delocalization stabilization takes precedence over the stabilization due to a local inductive effect. This conclusion casts some doubt on the reasoning used to predict the reactivities of substituted delocalized species in the Introduction.

The initially formed intermediate can react directly with solvent either by elimination to form isoprene, or by displacement to form (β-methylallyl)-carbinol. The observation that all the recovered (β-methylallyl)-carbinol is unrearranged is tenuous evidence that the product arises from an intermediate prior to the intermediate that forms 1-methylcyclobutanol. The measurement of the absence of protium from the carbinyl methylene of (β-methylallyl)-carbinol is probably more accurate than the measurement of the amount of label in the 2-position of the cyclobutyl ring. The 2.6% of label in the 3-position reported by Cox in the 1-methylcyclobutanol obtained from the (1-methylcyclopropyl)-carbinylamine-α-^{14}C deamination should have been detectable in the spectrum of the alcohol. The conclusion that (β-methylallyl)-carbinol arises from an intermediate prior to the one which forms 1-methylcyclobutanol remains uncertain until a detectable rearrangement of deuterium is found in the deamination of 2, 2, 4, 4-tetradeutero-1-methylcyclobutylamine. The possibility that Cox's measured activity is an artifact of the degradation scheme has not been eliminated (17).

The direct precursor of the 1-methylcyclobutanol in the deamination reactions arises from the initial intermediate and undergoes some label shuffling. It is apparent that the 3% label shuffling ob-

served by Cox represents an upper limit on the amount of label redistribution that occurs in the deamination of dideutero (β methyl allyl)-carbinylamine.

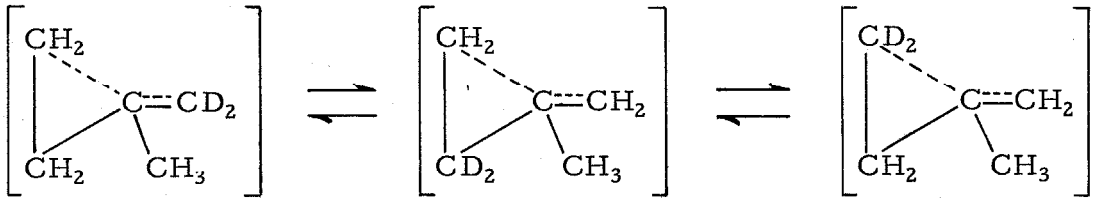
A discussion of the implications of this distribution in terms of the non-classical carbonium ion schemes discussed in the Introduction can be carried out using this 3% of label shuffling as an upper bound. If it is assumed that IVa is converted to IVc only via IVb, then the results amount to a demonstration that the barrier to the conversion of IVa to IVb is not significantly larger than the barrier



IVa IVb IVc

to the interconversion of IVb and IVc, otherwise the generation of IVc as in the present experiment would produce nearly complete label-shuffling. Furthermore, the barrier between IVc and IVb is larger than that between IVb and IVa, otherwise, as will be discussed, the degree of equilibration in the present experiment would have been significantly greater than the 3% previously observed for the conversion of IVa to IVc. A crude iterative calculation, of the type already discussed, in which the rates of rearrangement were chosen to be equal and the rate of reaction with solvent was chosen to be five times faster, gave 86.8% of the product from IVc, 11.6% from IVb

and 1.7% from IVa. Thus, the conversion of 3% of IVa to IVc would require for equal barriers that at least 15% of the deuterium appear in the 2-position of the 1-methylcyclobutanol obtained in the present experiment. It should be noted that this description of the relative difficulty of rearrangement among the three 2-methylbicyclobutonium ions is in agreement with that previously suggested for the unsubstituted case (12).



Va Vb Vc

For the homoallylic formulation, the same data would require the equilibration of Va and Vb to be faster than that of Vb and Vc. A qualitative examination of the changes involved in the two rearrangements predicts the reverse order of equilibration rates, since much less change in bonding and the position of carbon atoms must take place in converting Vb to Vc than in converting Va to Vb.

In the formulation using the homoallylic ions as metastable intermediates for the interconversions of the bicyclobutonium ions, the transition state for the interconversion of IVb and IVc is the same as the transition state for the interconversion of Vb and Vc, and would resemble a (1-methylcyclopropyl)-carbinyl carbonium ion. The transition state for the other pair of interconversions would be re-

quired to resemble a 1-methylcyclobutyl carbonium ion. Certainly, the latter transition state would be far more stable than the former and, in agreement with the experimental results, would furnish the smaller barrier to rearrangement.

The question of whether the product-forming intermediate might be better formulated as a classical 1-methylcyclobutyl cation cannot be dealt with on the basis of the present results. A transition state resembling the (1-methylcyclopropyl)-carbinyl carbonium ion would certainly be required to account for any methylene shuffling observed in experiments on this system.

It would be reasonable to suggest that the deamination of dideutero-(β-methylallyl)-carbinylamine should have led to a species resembling this (1-methylcyclopropyl)-carbinyl cationic transition state and therefore more label shuffling. Servis has found the solvolysis rate of (β-methylallyl)-carbinyl tosylate in 90% formic acid and 10% pyridine at 50° to be enhanced by a factor of three over the rate of solvolysis of allylcarbinyl tosylate (23). On the basis of the study of allylcarbinyl tosylate (24) it appears reasonable to consider this an S_N1 solvolysis, in which case the acceleration requires the participation of the double bond in the solvolysis in such a way that most of the displaced charge appears at C-4, the unsubstituted vinyl carbon atom. The observation that trans-(γ-methylallyl)-carbinyl tosylate undergoes formolysis 210 times faster than allylcarbinyl tosylate (23) strongly supports this hypothesis. Such a transition state for formolysis would closely resemble a homoallylic carbonium

ion and so it does seem reasonable to postulate that such a homoallylic transition state is involved in the transformation of the alkyldiazonium ion into a nitrogen molecule plus a non-classical intermediate.

The labeling data in itself is too inaccurate and sketchy to permit any firm conclusion as to whether a homoallylic carbonium ion is formed as a transient intermediate in the deamination reaction. If there is any opportunity for such an intermediate to be formed initially, then more shuffling of isotopic label should be observed in the present experiment than in the deamination of (1-methylcyclopropyl)-carbinylamine-α-^{14}C. The accuracy of the experiment does not permit a clean distinction, but it is clear that the results exclude easy equilibration of ions Vb and Vc. Furthermore, if these intermediates are metastable intermediates involved in a cascade from the high energy initial reactive species, either their lifetime is too short or the energy barrier to interconversion is too high to permit significant equilibration.

To supply practice in the experimental techniques and a model for the behavior of saturated amines, two saturated five-carbon amines were deaminated. 2-Pentylamine gave approximately a 2 to 1 mixture of alcohols and alkenes, with the more stable alkene and 2-pentanol being formed as the major products. In the deamination of isoamylamine, the recovery of products was poor and no alkenes were isolated. The product mixture contained rearranged alcohols and isoamyl alcohol in a 1 to 1 ratio. The rearranged alcohols were 2-methyl-3-butanol and t-amyl alcohol in a 1 to 3.5 ratio. These

results are in accord with a special reaction available to the diazonium ion or "hot" carbonium ion, while subsequent rearrangement leads to solvolytic carbonium ions with normal lifetimes. This latter deduction is based on the similarity between the measured ratio of the percentages of t-amyl alcohol and 2-methyl-3-butanol and that of the chlorides in the presence of aluminum chloride (25), or obtained in the Arbuzov reaction (26).

(α-Methylallyl)-carbinylamine was synthesized by the same method as was employed in the synthesis of (β-methylallyl)-carbinylamine. The amine-nitrous acid reaction in aqueous media gave a product mixture which, when analyzed on a gas chromatograph fitted with a flame-ionization detector, appeared to contain at least sixteen substances. Six alcohols and isoprene were identified by their v. p. c. retention times on both column A and column K. The assignments were corroborated by studying the change in product caused by reacting part of the product mixture with bromine in carbon tetrachloride, and also by comparing the n. m. r. spectrum of the mixture with the n. m. r. spectrum of an artificial mixture. The identifications were later confirmed by isolation of the individual materials from the deuterated product mixture. The nine unidentified components totaled 7% of the product mixture. Of these products, one was tentatively identified as the expected γ,γ-dimethylallyl alcohol on the basis of its v. p. c. retention time and its reactivity towards bromine.

The deamination of (α-methylallyl)-carbinylamine was run four times, twice with deuterated amine. The agreement among the runs

as to relative yields of the major products was satisfactory. In one of these runs, a peak representing less than 0.2% of the total area of the product peaks was observed with a retention time equal to that of one of the cis-trans isomers of 2-methylcyclobutanol. The remaining products may be 2-penten-1-ol, nitrite esters of the product alcohols, or products from the addition of nitrogen sesquioxide to alkenols. The relative percentages of the major products detected in three runs are given in Table III. Alcohols that were definitely absent were cis- and trans-crotylcarbinol, cis- and trans-3-methylcyclobutanol, and one of the cis-trans-isomers of 2-methylcyclobutanol.

There was no evidence that more than one isomer of (2-methylcyclopropyl)-carbinol has been formed in the reaction, but whether the isomers are resolvable on the column used is unknown.

The most important single experimental fact in this product study is the apparent absence of 2-methylcyclobutanol. This implies that even when XIII is the only bicyclobutonium ion formed directly, a product which might be presumed characteristic of XIII is not formed. This means that either XIII does not react as might be expected or that it rearranges rapidly.

An alternative explanation of the appearance of (2-methylcyclopropyl)-carbinol as a product, is that it arises from XIV along with methylallylcarbinol. In that case, the intermediates XII and XIV are present in approximately equal amounts, which is consistent with initial formation of a high-energy intermediate which rearranges in

TABLE III

PRODUCTS FROM THE AMINE-NITROUS ACID REACTION OF (α-METHYLALLYL)-CARBINYLAMINE

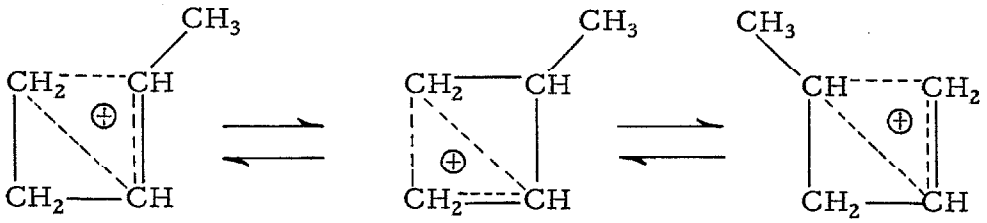
	RUN 1, %	RUN 2, %	RUN 4[a], %
α, α-Dimethylallyl alcohol	20	21	22
Methylallylcarbinol	21	21	21
Ethylvinylcarbinol	4	4	4
(α-Methylallyl)-carbinol	8	8	5
Methylcyclopropylcarbinol	37	35	38
(2-Methylcyclopropyl)-carbinol	10	11	10
γ, γ-Dimethylallyl alcohol	0.3	0.5	0.4 ± 0.2
2-Methylcyclobutanol	-	-	0.2 ± 0.2

[a]This run involved the use of dideutero-(α-methylallyl)-carbinylamine.

a cascade to the two product-forming intermediates. The products could also be explained in terms of homoallylic carbonium ions, or classical cations. In general, the dimethylallyl alcohols would arise by a hydride shift in the initial reactive species to give the allylic cation which reacts with solvent. The preference for the tertiary product is consistent with the products observed in the hydrolysis of the chlorides (27). The (α-methylallyl)-carbinol would be generated by an S_N2 displacement on the diazonium ion. The ethylvinyl carbinol could be formed via a methide shift in the initial intermediate

or alternatively via a hydride shift in a subsequently formed classical methylallylcarbinyl carbonium ion. The isomeric allylic alcohol, 2-penten-1-ol may have been present in the product mixture, but no attempt was made to identify it.

The question of whether 2-methylcyclobutanol could be formed from the most likely amine precursor of XIII has been answered, but the results raise a question as to why such a large amount of (2-methylcyclopropyl) carbinol relative to the amount of methylallylcarbinol should be formed in the reaction. If it is assumed that the ratio of methylallylcarbinol to (2-methylcyclopropyl)-carbinol measured in the product mixture from the deamination of 3-methylcyclobutylamine (Xa) is characteristic of the reactivity of XIV, then the ratio of reactivity of XIV at C-4 to that at C-1 is 4.3. This ratio would be very



XII XIII XIV

sensitive to any experimental error. The study done by Silver (14) does not include a correction for thermal conductivity differences, and there is a good chance that an unidentified material which was found to have a retention time near that of methylallylcarbinol on column K and on 1, 2, 3-tris-(2-cyanoethoxy)-propane (TCEP) in the

current work, may have gone undetected in the earlier work since this peak is not resolved on column A. Still, 4.3 is significantly larger than 2.1 and the possibility that approximately half of the (2-methylcyclopropyl)-carbinol is coming from an intermediate other than XIV should be considered.

The re-examination of the products of the deamination of (2-methylcyclopropyl)-carbinylamine (VIIIa) forms a bridge between the present techniques and those of Silver. The results are given in Table IV. The agreement between the two runs made with deuterated

TABLE IV

PRODUCT PERCENTAGES FROM THE AMINE-NITROUS ACID REACTION OF (2-METHYLCYCLOPROPYL)-CARBINYLAMINE

	Silver (14)	RUN 1	RUN 2[a]
Methylcyclopropylcarbinol	52	50.2	50.1
(2-Methylcyclopropyl)-carbinol	13	16.5	16.9
Methylallylcarbinol	35	33.3	33.0

[a]In this run, dideutero-(2-methylcyclopropyl)-carbinylamine was deaminated.

and undeuterated amines is excellent. After correction was made for thermal conductivity differences, the ratio of methylallylcarbinol to (2-methylcyclopropyl)-carbinol averaged over the individual v.p.c. analyses is 1.9 ± 0.1 as compared to the 2.9 found in Silver's work. The change in the ratio can be ascribed to the factors mentioned

above. The same sort of corrections may also apply to the product mixture obtained in the deamination of 3-methylcyclobutylamine (Xa). Equal amounts of the product from the two different intermediates XII and XIV are reported. Correction for the approximately 5% of product usually obtained by S_N2 displacement or from the "hot" carbonium ion gives the same sort of ratio (1.1) as is observed in the deamination of (α-methylallyl)-carbinylamine.

One way of checking whether the (2-methylcyclopropyl)-carbinol and methylallylcarbinol arise from the same intermediate would be to deaminate dideutero-(α-methylallyl)-carbinylamine and compare the deuterium distribution between the two methylene groups in each of the two products of interest. If both alcohols come from the same intermediate, we would expect identical deuterium distributions in them. If (2-methylcyclopropyl)-carbinol is formed directly from XIII, then there should be an excess of deuterium located in the ring methylene groups of the (2-methylcyclopropyl)-carbinol as compared to the deuterium located in the α-position of the methylallylcarbinol.

The dideutero-(α-methylallyl)-carbinol was prepared and converted to the amine by the method previously employed for the preparation of dideutero-(β-methylallyl)-carbinol (see above). The alcohol mixture from the deamination was distilled and the individual alcohols isolated by preparative v. p. c. The amine was deaminated twice and in neither run was either alcohol of interest obtained entirely pure. Despite this difficulty, reasonably reproducible values for the deuterium distribution were obtained. The presence of dif-

ferent quantities of impurities in the samples and in the case of the methylallylcarbinol, the use of two different integration ratios to calculate the deuterium distribution provides an internal check on the validity of the determinations.

The (2-methylcyclopropyl)-carbinol isolated from the two independent deaminations of dideutero-(2-methylcyclopropyl)-carbinylamine contained 65.3 ± 2.2% and 66.4 ± 3.0% of the deuterium in the ring methylene group. Different impurities were present in the two samples and totaled less than 7% in each case. A systematic error could have been introduced if one of the impurities had an absorption which coincided with the methyl doublet of (2-methylcyclopropyl)-carbinol. At the worst, this would lead to a 5% relative increase in the percentage of ring-methylene deuterated (2-methylcyclopropyl)-carbinol to approximately 69%. An error of this magnitude is unlikely because in the first sample, the impurities were of known structure, and none had absorptions which would conflict with the doublet methyl absorption of (2-methylcyclopropyl)-carbinol. Thus, the product, (2-methylcyclopropyl)-carbinol, is best described as having 66 ± 3% of the deuterium label in the ring-methylene group of the labeled molecules.

The experiments, in which the label distribution in the accompanying methylallylcarbinol was determined, were complicated by the presence of ethylvinylcarbinol in n.m.r. samples. This impurity proved virtually inseparable from the methylallylcarbinol. The quantity of impurity was measured both by v.p.c. and n.m.r. techniques.

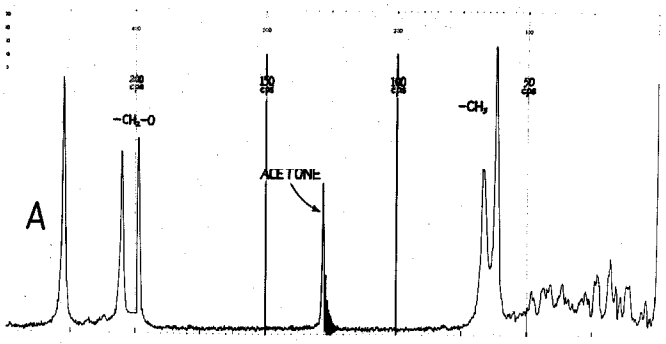


Fig. 5A. N. m. r. spectrum of (2-methylcyclopropyl)-carbinol in CCl_4.

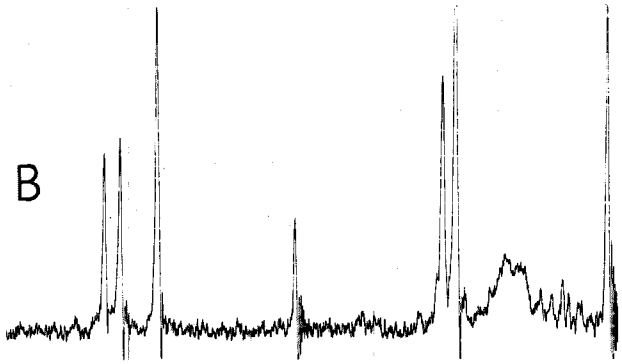


Fig. 5B. N. m. r. spectrum of (2-methylcyclopropyl)-carbinol from dideutero-(2-methylallyl)-carbinylamine.

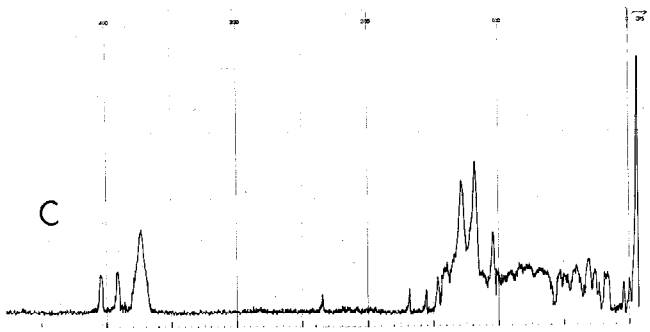


Fig. 5C. N. m. r. spectrum of (2-methylcyclopropyl)-carbinol from dideutero-(2-methylcyclopropyl)-carbinylamine.

The agreement was good between the two methods of measurement. In the two separate deaminations of (α-methylallyl)-carbinylamine the percentage of ethylvinylcarbinol accompanying the methylallylcarbinol varied, and this variation supplied an internal check on the determination of the deuterium distribution.

One method of determining the deuterium distribution was to find the ratio of the α-methylene proton absorption to that of the vinyl methyl proton absorption in the n. m. r. spectrum of the sample. From this ratio, the deuterium distribution could be calculated if it was assumed that a total of 2. 046 protons/molecule were distributed between the two methylene positions in the methylallylcarbinol, and if the vinyl methylene absorption was corrected for that due to the ethylvinylcarbinol present. By this method, the percentage of deuterium in the α-methylene position of the labeled methylallylcarbinol was found to be 77. 1 ± 1. 1% or 78. 3 ± 0. 9% for the two determinations. If the correction for the impurity was ignored or doubled, the percentage of deuterium in the α-methylene position shifted by only 3%. With the second sample, the ratio of the α-methylene proton absorption to that of methyl proton absorption was measured. This ratio should be independent of the impurity concentration. Calculations involving the same assumption of 2. 046 protons distributed between the two methylene positions gave 78. 3 ± 0. 9% as the percentage of deuterium in the α-methylene position of the labeled methylallylcarbinol.

The agreement between the two methods of determining the

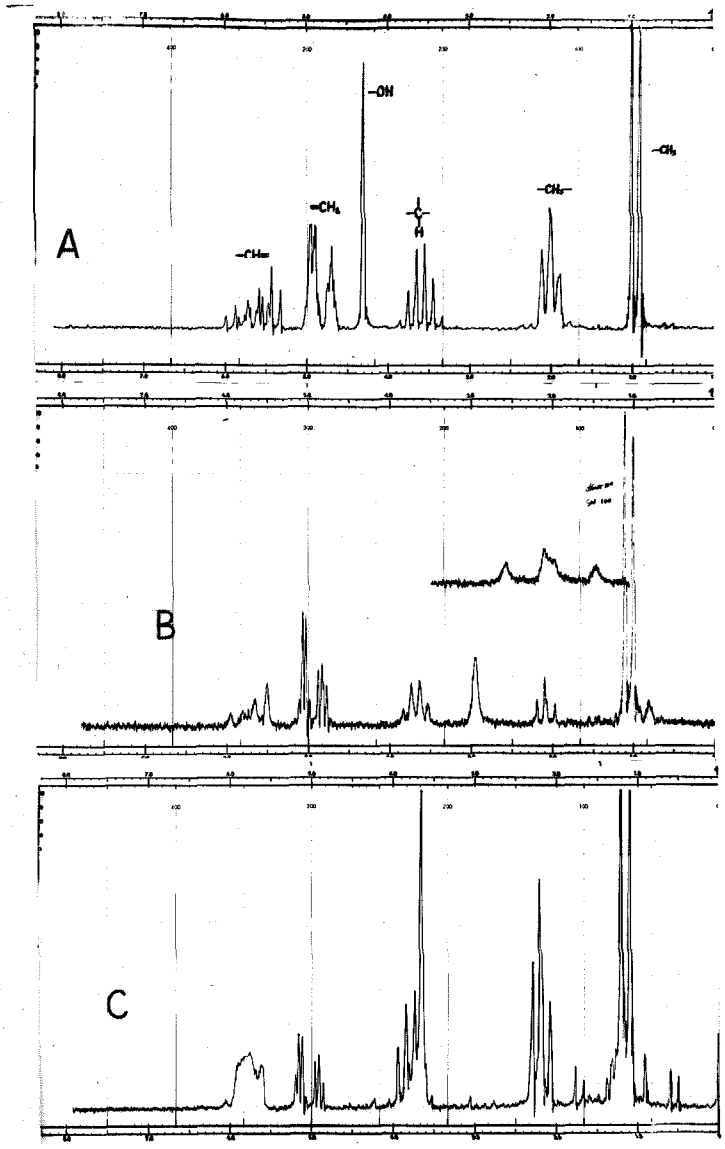
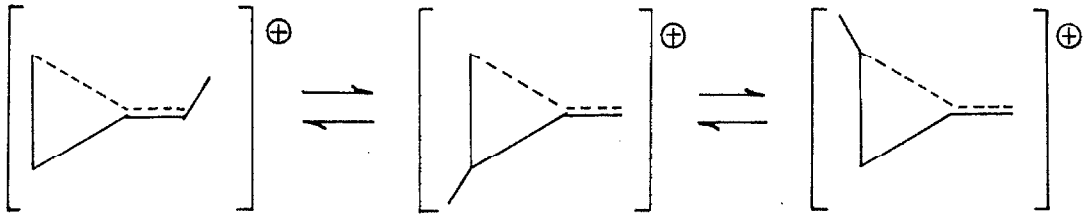


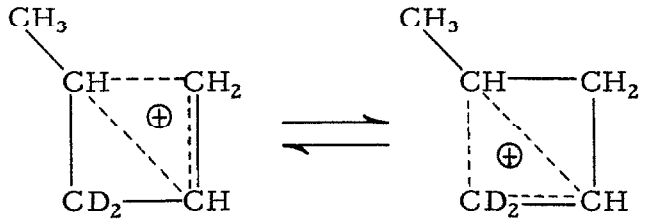
Fig. 6. N. m. r. spectra of methylallylcarbinol in CCl_4: A, undeuterated; B, from dideutero-(α-methylallyl)-carbinylamine; C, from dideutero-(2-methylcyclopropyl)-carbinylamine.



XV XVI XVII

deuterium distribution appears to establish 78 ± 1% as the best figure for the degree of equilibration of the methylene groups in the methylallylcarbinol obtained from the deamination of dideutero-(α-methylallyl)-carbinylamine. This number and the 66 ± 3% found for the (2-methylcyclopropyl)-carbinol are probably different.

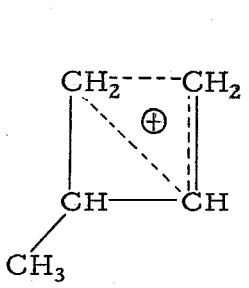
If the two products came from the same intermediate (either XIV or XVII would do), then the label distribution should have been the same in the two molecules. Admittedly, in an equilibrium such as



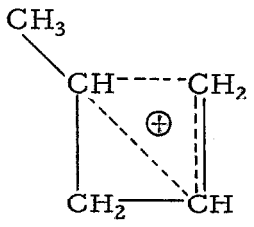
XIVa XIVb

that between XIVa and XIVb, there could be an isotope effect, but this isotope effect should be an order of magnitude smaller than the observed difference. On the other hand, if as previously suggested, some of the (2-methylcyclopropyl)-carbinol is coming from a different intermediate (such as XIII or XVI), then the label distribution

would be expected to be different in the two molecules with the exact magnitude depending on the amount of product coming from this second intermediate. However, this scheme would predict that the isotopic label in the methylene groups of the methylallylcarbinol should be more nearly equilibrated than that of the (2-methylcyclopropyl)-carbinol. There is apparently no way to explain the observed difference in the degree of equilibration of methylene groups in terms of either an equilibration of bicyclobutonium ions or of homoallylic ions alone. The experiments do appear to eliminate from consideration any transition state for the conversion of XIII to XIV in which the methylene groups become equivalent (such as an unsymmetrical



XIII



XIV

tricyclobutonium ion), since the resulting intermediate XIV would then have equivalent methylene groups, and the isotopic label in the methylene groups of the methylallylcarbinol would have been equilibrated.

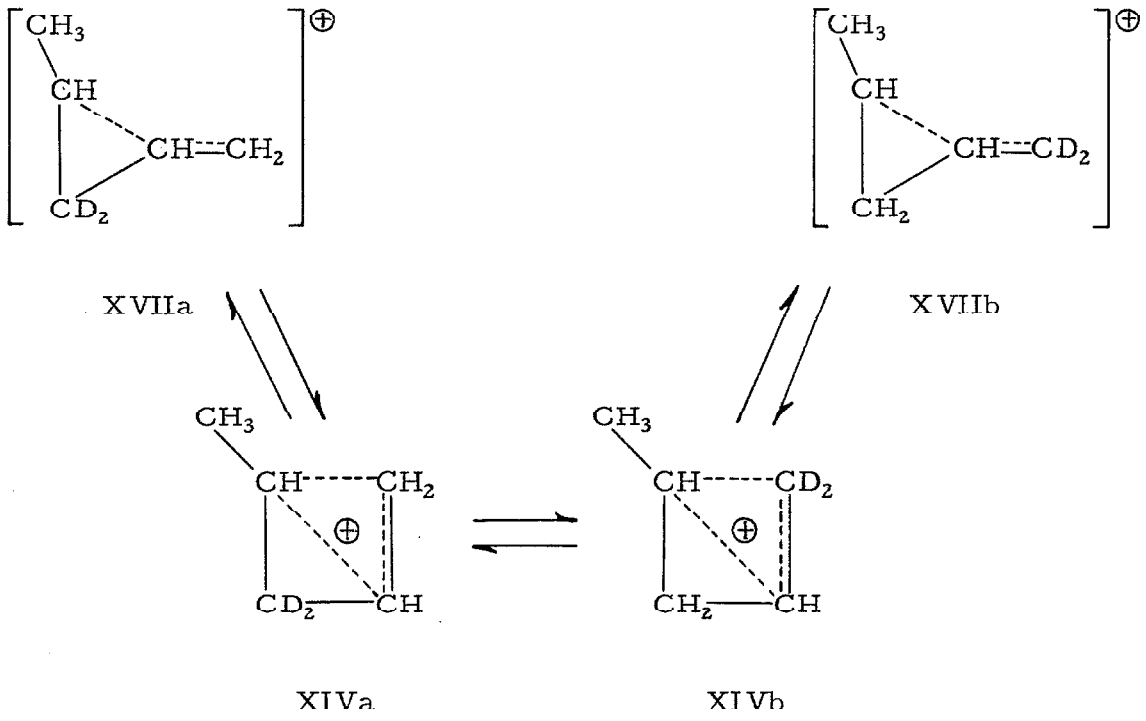
As a further check on this label distribution, dideutero-(2-methylcyclopropyl)-carbinylamine was synthesized and deaminated. The labeled methylallylcarbinol obtained was found to have 74 ± 2%

of the deuterium in the vinyl methylene group and the labeled (2-methylcyclopropyl)-carbinol was found to have 85 ± 1% of the deuterium in the carbinyl methylene group. Interpretation of the data is complicated by the fact that an undetermined amount of the (2-methylcyclopropyl)-carbinol is formed via a direct displacement reaction on the diazonium ion which would give no isotope-position rearrangement. The degree of equilibration of the deuterium in the methylallylcarbinol is similar to that obtained in the methylallylcarbinol from the deamination of dideutero-(α-methylallyl)-carbinylamine. This similar degree of equilibration is consistent with the proposal that methylallylcarbinol arises from the same equilibrating intermediates in both cases.

$$\text{XV} \rightleftharpoons \text{XII} \rightleftharpoons \text{XIII} \rightleftharpoons \text{XVI} \rightleftharpoons \text{XIV} \rightleftharpoons \text{XVII}$$

The proposed formulation of the intermediates in these reactions as involving both homoallylic and bicyclobutonium ions can be used to explain the label redistribution results. The key point in the argument is the proposal that both XIV and XVII are product-forming intermediates in these reactions, with XIV giving a different ratio of methylallylcarbinol to (2-methylcyclopropyl)-carbinol than XVII. This formulation would require that relative energies of the six nonclassical ions should be XII < XV ~ XIV ~ XVII < XIII < XVI. It is assumed that no products are obtained from XIII and XVI. This assumption is partially confirmed by the failure to observe 2-methylcyclobutanol as a product of any of the amine-nitrous acid reactions.

In the deamination of dideutero-(α-methylallyl)-carbinylamine, the initially formed non-classical intermediate would be XVIa which would then rearrange rapidly to either XVIIa or XIIIa. The latter



XIVa XIVb

intermediate would then give XII and eventually methylcyclopropyl-carbinol. Intermediate XVIIa both reacts with solvent and equilibrates with XIVa, XIVb and XVIIb. Obviously, we have a surfeit of parameters and can fit just about any data currently available. For the purposes of simplicity, XVII is taken to give only methylallylcarbinol, while XIV gives a 2:1 ratio of methylallylcarbinol to (2-methylcyclopropyl)-carbinol. An example of a set of parameters that would rationalize the observed equilibration would be a ratio of 1:2:1:0 for products formed from the four intermediates XVIIa, XIVa, XIVb, and

XVIIb, respectively. For 31.0% of the product coming from these intermediates, this would predict that the product would contain 23.3% of methylallylcarbinol with 78% of the deuterium in the α-methylene position (actual numbers 21.6% and 78%) and 7.8% of (2-methylcyclopropyl)-carbinol with 67% of the deuterium in the carbinyl methylene (actual results, 9.2% and 66%).

To fit the results obtained from the deamination of dideutero-(2-methylcyclopropyl)-carbinylamine, it is required that an extra parameter be approximated. For this amine, it was guessed that 8.0% of the product formed would be (2-methylcyclopropyl)-carbinol formed by the direct displacement of the diazonium ions. This number corresponds to the 8% of (α-methylallyl)-carbinol obtained from (α-methylallyl)-carbinylamine and 8.8% of cyclopropylcarbinol estimated from the variation in product ratios (13) as being formed from cyclopropylcarbinylamine. A good set of parameters in this case would result if it is assumed that XVIIb, XIVb, XIVa, and XVIIa form products in the ratio of 3:5:2:1. This set of parameters would predict the formation of 32.9% of methylallylcarbinol with 73% of the deuterium in the vinyl methylene group (actual results, 33.0% and 74%) and 16.9% of (2-methylcyclopropyl)-carbinol with 85% of the deuterium in the carbinyl methylene group (actual results, 16.8% and 85%).

The variation in product ratios from the intermediates would be expected because while the rate of formation of XVIIb from (2-methylcyclopropyl)-carbinyldiazonium ion should be negligible compared to the rates of rearrangement and reaction with solvent of the

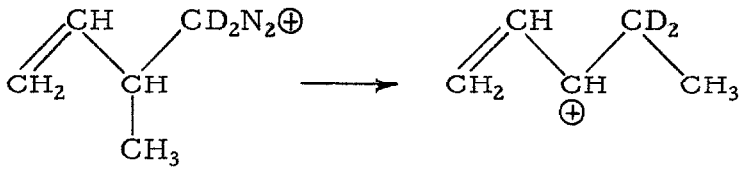
various intermediates, the rate of formation of XVIIa from XVIa should be significant with the result that a change in the proporti of products from the different intermediates would be expected.

In the deamination of 3-methylcyclobutylamine, the initially formed intermediate would be XIV which in the process of forming XII must pass through XVII and give the observed ratio of methylallylcarbinol to (2-methylcyclopropyl)-carbinol, which is definitely greater than 2:1 (14). The formation of XII makes it obvious that the rearrangement of XIV to XII is easier than the rearrangement of XIVa to XIVb. This agrees with the proposal that the transition states for the interconversions resemble the classical ions.

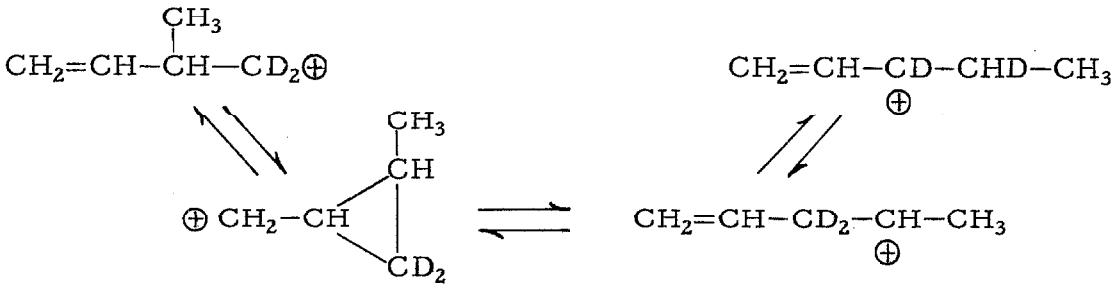
Three of the minor products obtained in the deamination of dideutero-(α-methylallyl)-carbinylamine were isolated from the reaction mixture in varying degrees of purity. The α,α-dimethylallyl alcohol isolated was apparently pure according to the v. p. c. analysis. The n. m. r. spectrum of this alcohol was essentially that which would be expected for α-dideuteromethyl-α-methylallyl alcohol. The vinyl absorptions in the n. m. r. spectrum are essentially unchanged from that of the unsubstituted alcohols, which means that the hydride shift occurs in some step prior to that in which the methylene groups undergo partial equilibration. The label distribution is therefore consistent with the formation of this alcohol via a concerted hydride shift and nitrogen elimination in the (α-methylallyl)-carbinyldiazonium ion.

The triplet absorption due to the methyl group in ethylvinylcarbinol was found to have coalesced to a narrow multiplet in the n. m. r.

spectrum of a 1:1 mixture of deuterated methylallylcarbinol and (2-methylcyclopropyl)-carbinol from the deamination of dideutero-(α-methylallyl)-carbinylamine. This coalescence would be expected if the deuterium was located exclusively on the methylene group adjoining the methyl group and is consistent with the identification of this product as (1, 1-dideuteroethyl)-vinylcarbinol. This label distribution implies that the product arises <u>via</u> a methide shift in an ion having the initial (α-methylallyl)-carbinyl structure. If so, we may



exclude from consideration the possibility that the product arises from an intermediate subsequent to that which equilibrates the methylene groups and also the possibility that this alcohol arises by a



hydride shift in a classical methylallylcarbinyl cation present in a mixture of rapidly equilibrating classical cations.

(α-Methylallyl)-carbinol could only be examined as a 20% impurity in the methylcyclopropylcarbinol isolated from the deamination of dideutero-(α-methylallyl)-carbinylamine. In the n. m. r. spectrum there was no significant increase of the absorption due to the carbinyl methylene protons, so it appears that this product also arises via a direct displacement on the diazonium ion before the equilibration of methylene groups.

The deuterium distribution in these minor products appears to be consistent with the proposed mechanism for the formation of the various partially equilibrated products, in that none of these minor products arises after equilibration.

III. EXPERIMENTAL

Melting points and boiling points are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan, and Elek Microanalytical Laboratories, Los Angeles, California. Infrared absorption spectra were obtained with a Perkin-Elmer Infracord, Model 137, or Beckman Infrared Spectrophotometer, Model IR 7. Vapor chromatographs were obtained with a Perkin-Elmer Vapor Fractometer, Model 154-C, or a Perkin-Elmer Gas Chromatograph, Model 800. All n.m.r. spectra were obtained on a Varian Associates, Model A-60, Analytical NMR Spectrometer.

β-Methylallyl Cyanide. - The method of Reitz for the synthesis of allyl cyanide (28) as adapted by Cox (17) was used. In a three-necked flask fitted with a mechanical stirrer and a reflux condenser were placed 8.0 g. (0.89 equivalents) of freshly prepared cuprous cyanide, 76 g. (0.80 moles) of dried and distilled β-methylallyl chloride and 0.25 g. of potassium iodide. The stirred reaction mixture was refluxed for 8 hours. All volatile liquid products were collected by flash distillation at aspirator pressure.

The crude product mixture was distilled through a Wheeler center-rod distilling column to give 33.7 g. (52%) of liquid, b.p. 134.2-134.5° (745 mm), $n^{23}D$ 1.4196; lit., b.p. 134.5-136.5°, $n^{20}D$ 1.4180 (29). The infrared spectrum agreed with that of Cox. Analysis of this sample by v.p.c. on column A (diisodecyl phthalate) showed it to

contain 2% of an unidentified impurity.

(β-Methylallyl)-carboxamide.- In a 100-ml. three-necked flask fitted with a mechanical stirrer and a dropping funnel was placed 13.2 g. of concentrated sulfuric acid. The acid was cooled to 0° and 10.3 g. (0.127 moles) of β-methylallyl cyanide added dropwise over a period of 1.3 hours. The viscous glass which formed was allowed to stand at 0° for 3 hours. The addition complex was decomposed by adding ice. After the glass dissolved completely, the aqueous solution was neutralized with potassium carbonate. The aqueous layer was continuously extracted with ethyl ether for 72 hours.

The ether extract was dried over anhydrous magnesium sulfate and evaporated on a Rinco rotatory evaporator. Upon standing, the residual oil gave a white precipitate which was extracted with chloroform. The chloroform extract gave 0.85 g. (7%) of white crystals, m.p. 152-156°.

Anal. Calcd. for C_5H_9NO: C, 60.60; H, 9.09; N, 14.14. Found: C, 60.18; H, 9.02; N, 14.03.

β-Methylallyl bromide was prepared many times by the reaction of 54.0 g. (0.59 moles) of β-methylallyl chloride with 94.0 g. (0.82 moles) of sodium bromide at reflux in 220 ml. of absolute methanol for 4 hours. This is essentially the method of Nordlander (33). The reaction mixture was decomposed by adding it to 1 l. of water. The organic layer was separated and dried over anhydrous magnesium sulfate. This layer was distilled through a 1.4 x 25-cm.

vacuum-jacketed Vigreux column with a total reflux head to give 20 - 29 g. (25-37%) of product of b.p. 91-94°.

3-Methyl-3-butenoic Acid. - (a). In a 100-ml. round-bottomed flask fitted with a reflux condenser was placed a mixture of 35 ml. of concentrated hydrochloric acid and 15 g. (0.18 moles) of β-methyl-allyl cyanide. The reaction mixture was refluxed for 0.6 hours and then quenched by adding 15 ml. of water. The organic layer was separated and the aqueous layer was extracted with three 15-ml. portions of ethyl ether. The combined extracts and organic layer were dried over anhydrous magnesium sulfate.

The ether was removed by distillation through a 2.4 x 35-cm. Vigreux column with a total reflux head. The residual liquid was distilled at reduced pressure through a 1.4 x 25-cm. column packed with a wire-spiral to give 6.8 g. of liquid, b.p. 51-55° (8 mm.). By v.p.c., this product contained 5% of the starting material, and by infrared analysis the product appeared to be a complex cyanide with no signs of a carbonyl absorption. There was also obtained 1.2 g. of 3-methyl-2-butenoic acid; b.p. 84-88° (8 mm.).

(b). The acid was prepared many times in the cyclic reactor described elsewhere (21). In the reaction chamber was placed 10 g. (0.41 g. atoms) of magnesium turnings. A solution of 1 g. of mercuric bromide in 40 ml. of ether was added to the reaction chamber after the system had been heated with a flame and flushed with nitrogen. The mercuric bromide solution was permitted to remain in the

reaction chamber for 1 hour and then the cyclic reactor was flushed by cyclic refluxing ether through it for 0.5 hours. One milliliter of ethylene dibromide was added to the magnesium. When a violent reaction set in, the system was flushed again and a new receiving flask was substituted for the old one.

A solution of 18.0 g. (0.133 moles) of β-methylallyl bromide in 75 ml. of absolute ether was added through a pressure-equalizing dropping funnel at such a rate that gas bubbles (ether) rose constantly from the magnesium column. After 1 hour the solution in the collection flask gave a positive Gilman test. Completion of the addition required 7 hours.

The Grignard reagent was carbonated by adding it to a hand-stirred slurry of 300 g. of Dry Ice in 100 ml. of ether. The resultant solid was permitted to come to room temperature and then hydrolyzed with 200 ml. of 1 N hydrochloric acid. The ethereal layer was separated, and the aqueous layer was extracted with three 100-ml. portions of ether. The combined ethereal layers were dried over anhydrous magnesium sulfate.

The drying agent was removed by filtration and the ether removed by distillation. The residual liquid was distilled through a 1.4 x 25-cm. vacuum-jacketed Vigreux column fitted with a total reflux head and gave 2.0 g. of coupling product and 6.0 g. (45%) of acid, b.p. 70-78° (8 mm.), $n^{25}D$ 1.4330; lit. b.p. 49° (3 mm.), $n^{20}D$ 1.4240 (30). This acid gave a reasonable infrared spectrum with absorptions at 1742 and 1654 cm^{-1}. The n.m.r. spectrum gave

a narrow multiplet centered at 271 cps and a sharp singlet at 648 cps. There was about 5% of an unidentified impurity present by n. m. r. analysis.

The p-bromophenacyl derivative had m. p. 44. 5-45. 5°; lit. 42. 0-42. 3° (30) upon recrystallization from ethanol.

(c). It was found that the Grignard reagent could be prepared by adding a solution of 40 g. (0. 44 moles) of β-methylallyl chloride in 300 ml. of absolute ether over a period of 3. 2 hours to a stirred mixture of 200 ml. of absolute ether and 17. 0 g. (0. 70 g. atoms) of magnesium turnings under nitrogen. The resultant Grignard reagent was carbonated and the acid isolated as described above to give 17. 2 g. (39%) of 3-methyl-3-butenoic acid, b. p. 63-67° (6 mm.).

2-Methyl-3-butenoic Acid. - In a preheated 1-l. three-necked flask fitted with a 250-ml. pressure-equalizing dropping funnel, a mechanical stirrer and a bubble condenser terminating in a drying tube were placed 200 ml. of absolute ether and 12. 0 g. (0. 50 g. atom) of magnesium turnings. A solution of 22. 3 g. (0. 166 moles) of crotyl bromide in 200 ml. of absolute ether was added over a period of 3. 5 hours at such a rate that reflux was maintained. The resulting solution, which gave a positive Gilman test, was carbonated by adding it to a vigorously stirred Dry Ice slurry.

The salt, thus formed, was hydrolyzed with 100 ml. of 2 N hydrochloric acid. The layers were separated after extended shaking, and the aqueous layer was extracted with four 50-ml. portions of

ether. The combined ethereal layers were dried over magnesium sulfate. The ether was removed by distillation and the residual liquid distilled to give 10.2 g. (61%) of acid, b.p. 83-85° (10 mm.); lit., 94-95° (30 mm.) (31). The n.m.r. spectrum was consistent with the assigned structure (doublet 69 cps, quintet 180 cps, broad multiplets at 190, 203, and 240 cps, and sharp singlet at 712 cps). This reaction was run several times with yields varying from 26 to 62%.

Methyl 3-Methyl-3-butenoate. - The method of Arndt was used to prepare the diazomethane (32). An ethereal solution of diazomethane, prepared from 0.24 moles of N-methyl-N-nitrosourea, was added in portions over a period of 0.6 hours to a 1-l. Erlenmeyer flask containing a cooled solution of 15 . (0.15 moles) of 3-methyl-3-butenoic acid in 100 ml. of ether. The solution was stirred for two hours, dried over anhydrous magnesium sulfate, and distilled through 1.4 x 25-cm. vacuum-jacketed Vigreux column to give 11.5 g. (67%) of methyl 3-methyl-3-butenoate, b.p. 51-53° (50 mm.). The n.m.r. spectrum showed that the double-bond of the ester had not reacted with diazomethane. In addition, 2.7 g. (18%) of the starting acid was recovered.

Methyl 2-Methyl-3-butenoate was prepared by the reaction of diazomethane, prepared from 50 g. of N-methyl-N-nitrosourea, with 19.5 g. of 2-methyl-3-butenoic acid in ether. The yield was 16.2 g. (73%) of ester, b.p. 60.6-61.5° (103 mm.). The n.m.r. spectrum

showed the product to be the unsaturated ester rather than the pyrazoline.

(β-Methylallyl)-carbinol. - (a). In a 100-ml. three-necked flask fitted with a mechanical stirrer, a condenser with a drying tube, and a pressure-equalizing dropping funnel was placed a mixture of 50 ml. of absolute ether and 3.0 g. (0.315 equivalents) of lithium aluminum hydride. To the stirred cooled reaction mixture was added a solution of 6.00 g. (0.060 moles) of 3-methyl-3-butenoic acid in 23 ml. of ether over a period of 2 hours. The reaction mixture was stirred at room temperature for 10 hours and permitted to stand for 9 hours. The vessel was then cooled again in ice, and the excess lithium aluminum hydride was decomposed by adding 5 ml. of water dropwise. A saturated solution of ammonium chloride was then added until the inorganic salts precipitated as a powder. The ether layer was decanted and the powder was extracted with three 25-ml. portions of ether. The addition of 15 ml. of water freed another portion of adsorbed ether from the powder. This was separated, and the combined ethereal extracts were dried over anhydrous magnesium sulfate.

The drying agent was removed by filtration and the ether by distillation. Distillation of the residual liquid through a Holzman column gave 4.0 g. (76%) of (β-methylallyl)-carbinol, b.p. 128-132°. The product was identified by comparing the infrared and n.m.r. spectra with those of an authentic sample of the alcohol.

(b). The alcohol was also prepared via the reaction of the Grignard reagent obtained from β-methylallyl bromide with gaseous formaldehyde (17) to give a 9% yield of (β-methylallyl)-carbinol.

(c). The reduction of methyl 3-methyl-3-butenoic acid with lithium aluminum hydride also yielded the desired alcohol. The method was the same as in (a) and gave 71% of (β-methylallyl)-carbinol, b.p. 129-132°.

Dideutero-(β-methylallyl)-carbinol. - In a 200-ml. three-necked flask fitted with a mechanical stirrer, a 50 ml. pressure-equalizing dropping funnel, and a calcium chloride drying tube was placed 2.45 g. (0.233 equivalents) of lithium aluminum deuteride (100.0% active deuterium from Metal Hydrides, Inc.). The flask was cooled in ice and 50 ml. of absolute ether was added. A solution of 10.72 g. (0.094 moles) of methyl 3-methyl-3-butenoate was added over a period of 1.8 hours. The resultant suspension was stirred at room temperature for 5 hours. The solution was again cooled in ice and decomposed by adding 5 ml. of water, followed by a solution of 6.5 ml. of concentrated sulfuric acid in 27 ml. of water over a period of 1 hour. The mixture was stirred for another hour, the layers separated, and the aqueous layer subjected to continuous extraction with ether for 8 hours. The ether layers were combined and dried over anhydrous magnesium sulfate. The ether was removed by distillation and 2 ml. of collidine was added. The liquid was distilled through a 1.4 x 60-cm. column packed with a wire spiral and fitted with a total reflux

head. The yield of alcohol was 6.13 g. (74%), b.p. 128-131°. The n.m.r. spectrum (in chloroform) showed that the triplet absorption for the carbinyl protons (217 cps) had completely disappeared, and the triplet at 141 cps had become a narrow multiplet.

(α-Methylallyl)-carbinol. - (a). This alcohol was prepared by the method of Roberts (32). Crotylmagnesium bromide was prepared as previously described for synthesis of 2-methyl-3-butenoic acid (vide supra), and gaseous formaldehyde, obtained by heating paraformaldehyde at 200°, was added. The reaction mixture was hydrolyzed by pouring it over a mixture of ammonium chloride and cracked ice. The layers were separated after the ice melted, and the aqueous layer was extracted with two 100-ml. portions of ether. The combined ethereal layers were dried over anhydrous magnesium sulfate, and the ether was removed by distillation. The residual liquid was distilled through a 1.4 x 60-cm. column with a tantalum wire-spiral packing to give 44% of (α-methylallyl-carbinol, b.p. 121-122°, $n^{25}D$ 1.4246; lit., 120-121°, $n^{20}D$ 1.4261 (32). The v.p.c. on Carbowax showed the product to 99% pure, and the n.m.r. was consistent with the assigned structure.

(b). The carbinol was prepared in 47% yield by the reduction of 2-methyl-3-butenoic acid with lithium aluminum hydride. The (α-methylallyl)-carbinol isolated had b.p. 121-122° (748 mm.).

(c). The carbinol was also prepared by reduction of the methyl ester of 2-methyl-3-butenoic acid to give a 70% yield of unrearranged

alcohol.

Dideutero-(α-methylallyl)-carbinol. - In a 300-ml. three-necked flask fitted with a mechanical stirrer, a solution of 4.00 g. (0.0956 moles) of lithium aluminum deuteride (97.7% deuterium from Metal Hydrides, Inc.) in 125 ml. of absolute ether was prepared at 0°. A solution of 21.6 g. (0.190 moles) of methyl 2-methyl-3-butenoate in 55 ml. of absolute ether was added through a 50-ml. pressure-equalizing dropping funnel over a period of 3 hours.

The reaction mixture was hydrolyzed by adding 5 ml. of water to the ice-cooled reaction mixture followed by saturated ammonium chloride solution until the inorganic material precipitated as a white powder. The ether layer was decanted and the solid was extracted with three 50-ml. portions of ether. The addition of 20 ml. of water freed another portion of ether from the resultant paste. The combined extracts were dried over magnesium sulfate, and the ether was removed by distillation. A 2-ml. portion of collidine was added, and the residual liquid was distilled through a 1.4 x 65-cm. column packed with a wire spiral to give 11.55 g. (64% yield on the deuterium) of dideutero-(α-methylallyl)-carbinol, b.p. 120.5-123.5°. The n.m.r. spectrum showed changes consistent with the spectrum of the undeuterated alcohol.

(β-Methylallyl)-carbinyl Benzenesulfonate. - In a 200-ml. three-necked flask fitted with a 50-ml. pressure-equalizing dropping funnel, a mechanical stirrer and a calcium chloride drying tube was

placed a solution of 5.45 g. (0.063 moles of (β-methylallyl)-carbinol in 22 ml. of collidine. The reaction mixture was cooled in an ice-bath and 15.0 g. (0.085 moles) of benzenesulfonyl chloride added to the stirred solution over a period of 0.5 hours. The resulting viscous pink liquid was stirred for 3.5 hours and then decomposed by adding 22 ml. of 10 N sulfuric acid and stirring for 0.4 hours. The resultant mixture was extracted with four 40-ml. portions of 2 N sulfuric acid and dried over anhydrous magnesium sulfate.

The chloroform was removed on a Rinco rotatory evaporator and the red residual oil extracted with nine 30-ml. portions of ligroin (30-60°). The ligroin was evaporated on a Rinco rotatory evaporator, and 14.06 g. (99%) of a pale yellow liquid was obtained. This liquid gave the proper n.m.r. spectrum for (β-methylallyl)-carbinyl benzenesulfonate; singlet 87 cps, triplets at 129 and 239 cps, a narrow multiplet at 270 cps and two broad multiplets at 440 and 460 cps. The liquid decomposed to a black tar in all attempts to purify it by distillation.

Dideutero-(β-methylallyl)-carbinyl Benzenesulfonate. - The procedure used for preparing the undeuterated-(β-methylallyl)-carbinyl benzenesulfonate was employed without modification. The reaction gave 15.65 g. (99%) of a straw-yellow liquid. The n.m.r. spectrum was the same as that of the undeuterated benzenesulfonate except that the triplet at 239 cps in the spectrum of the sulfonate had disappeared, and the triplet at 129 cps coalesced to a narrow multiplet.

(α-Methylallyl)-carbinyl benzenesulfonate was prepared by the same technique as (β-methylallyl)-carbinyl benzenesulfonate from 6.0 g of (α-methylallyl)-carbinol. The reaction gave 14.70 g. (93%) of a clear colorless liquid. The n. m. r. spectrum showed the expected absorption for an (α-methylallyl)-carbinyloxy compound plus the phenyl absorptions.

Dideutero-(α-methylallyl)-carbinyl benzenesulfonate was prepared from dideutero-(α-methylallyl)-carbinol by the same method as was used to prepare the undeuterated benzenesulfonate. The reaction gave a 100% yield of the deuterated benzenesulfonate. The n. m. r. spectrum was consistent with the changes expected by deuterium substitution in comparison with that of the undeuterated compound.

(β-Methylallyl)-carbinyl Azide. A solution of 8.0 g. (0.12 moles) of sodium azide in 40 ml. of dimethyl sulfoxide (redistilled) was placed in a 200-ml. round-bottomed flask fitted with a magnetic stirrer and a reflux condenser terminating in a calcium chloride drying tube. To this flask was added a solution of 14.06 g. of (β-methylallyl)-carbinyl benzenesulfonate in 35 ml. of dimethyl sulfoxide. The stirred reaction mixture was heated at 79° for 32.5 hours with an oil bath. The contents of the flask was added to 300 ml. of water, and the mixture was extracted with six 75-ml. portions of ethyl ether. The combined ethereal extracts were washed with three 100-ml. portions of water and dried over anhydrous magnesium sulfate. The ethereal solution was concentrated to 50 ml. by careful distilla-

tion. The n. m. r. spectrum of this ethereal azide solution was consistent with a (β-methylallyl)-carbinyl skeleton (the downfield triplet was apparently hidden under the methylene absorptions of the ether). The infrared spectrum showed the expected strong azide absorption at 2125 cm^{-1} and the alkene absorption at 1656 cm^{-1} (33).

(α-Methylallyl)-carbinyl Azide was prepared from the appropriate benzenesulfonate in the manner described above for preparing (β-methylallyl)-carbinyl azide. There was obtained 35 ml. of an ethereal azide solution which showed in its infrared spectrum the absorption at 2120 cm^{-1} characteristic of N-N triple bonds and usually observed in azides (33).

(β-Methylallyl)-carbinylamine. - (a). The following procedure is an adaptation of the one described by Renk and Roberts (13). In a 200-ml. three-necked flask fitted with a pressure-equalizing dropping funnel, a mechanical stirrer and a calcium chloride drying tube were placed 4. 4 g. (0. 46 equivalents) of lithium aluminum hydride and 40 ml. of absolute ether. The solution of (β-methylallyl)-carbinyl azide in 50 ml. of ether prepared from the benzenesulfonate was added slowly to the ice-cooled solution over a period of 0. 8 hours. The reaction mixture was stirred at 0° for 12 hours and then decomposed by adding 10 ml. of water over 0. 5 hours. To this solution was added 40 ml. of 25% aqueous sodium hydroxide and 35 ml. of ether. The ether layer was separated, and the aqueous sludge was extracted with two 20-ml. portions of ether. Another 60 ml. of

water and 70 ml. of ether were added. The ethereal layer was separated and the aqueous layer was extracted with 50 ml. of ether. The final separation was achieved with the aid of a centrifuge. The combined ethereal extracts were dried over magnesium sulfate, and the ether was removed by distillation. The residual liquid was distilled through a 1.4 x 24-cm. column packed with a tantalum wire spiral to give 2.25 g. of liquid, b.p. 45-48° (105 mm.). The distillate contained ethanol as an impurity; by n.m.r. integration the sample was found to contain 0.018 moles of the desired amine which represents a 28% yield on the initial alcohol. The infrared spectrum (chloroform) in agreement with that of Cox showed major absorptions at 3385, 3210, and 1652 cm^{-1}. The n.m.r. spectrum (10% carbon tetrachloride) showed a narrow multiplet at 78 cps, a broad singlet at 88 cps, triplets at 103 and 139 cps, and a broad multiplet at 259 cps.

(b). An attempt was made to prepare the amine from β-methylallyl cyanide. A solution of 10.0 g. (0.125 moles) of β-methylallyl cyanide in 100 ml. of diethyl ether was added to a stirred mixture of 3.7 g. (0.39 equivalents) of lithium aluminum hydride and 200 ml. of ethyl ether at 0° over a period of 1 hour. The solution turned yellow-green as soon as the addition started. The reaction mixture was stirred for 2 hours and then decomposed by adding 30 ml. of water slowly to the ice-cooled reaction mixture. The hydrolysis was completed by adding 35 ml. of 20% sodium hydroxide. The ether layer was separated, and the aqueous layer was extracted with 50 ml. of ether. The combined extracts were washed with 200 ml. of 20%

aqueous sodium hydroxide and dried with anhydrous magnesium sulfate. The ether was removed by distillation and the residual liquid was distilled to give 0.1 g. of a material that smelled like an amine and 6.3 g. of a high boiling liquid.

(c). Three attempts were made to reduce β-methylallylcarboxamide with lithium aluminum hydride. A suspension of 300 mg. (3.03 mmoles) of β-methylallylcarboxamide in 20 ml. of ether was prepared in a 50 ml. round-bottomed flask fitted with a magnetic stirrer, and a small condenser terminating in a calcium chloride drying tube. To the ice-cooled solution was added 240 mg. (6.3 mmoles) of lithium aluminum hydride. The reaction mixture was stirred at room temperature and decomposed by adding 20 ml. of 10% aqueous sodium hydroxide. The layers were separated, and the aqueous layer was extracted with 15 ml. of ether. The combined ethereal layers were washed with 10 ml. of water and dried over anhydrous potassium carbonate. Distillation of the ether left less than 0.1 ml. of an oil which smelled like an amine. This oil dissolved in chloroform but the infrared spectrum disagreed with that reported by Cox (34).

Dideutero-(β-methylallyl)-carbinylamine. - The dideutero-(β-methylallyl)-carbinyl azide was prepared from the benzenesulfonate by the same method as was previously employed to prepare the undeuterated azide (vide supra). The 35 ml. of ethereal azide obtained from 15.65 g. of dideutero-(β-methylallyl)-carbinyl benzenesulfonate

was then added slowly to an ice-cooled stirred mixture of 4.4 g. (0.46 equivalents) of lithium aluminum hydride and 40 ml. of absolute ether over a period of 1.6 hours. The reaction mixture was stirred for 10 hours at room temperature and then decomposed by adding 20 ml. of water to the ice-cooled mixture over 0.7 hours. The addition of 10 ml. of 50% aqueous potassium hydroxide precipitated the inorganic material as a solid. The ether layer was decanted and the solid triturated with two 20-ml. portions of ether. The solid was dissolved in 60 ml. of water and extracted with four 50-ml. portions of ether. The combined extracts were dried over anhydrous magnesium sulfate.

The ether was removed by distillation and the residual liquid was distilled through a modified Claisen distillation flask with a 1.3 x 10-cm. sidearm to give 4.19 g. of liquid, b.p. 43-44° (90 mm.). The n.m.r. spectrum showed this to be the deuterated amine with ethanol as an impurity. Integration of the n.m.r. spectrum showed the mole fraction of ethanol to be 0.3, and this corresponds to 0.039 moles of dideutero-(β-methylallyl)-carbinylamine which is a 34% yield based on the lithium aluminum deuteride.

(α-Methylallyl)-carbinylamine was prepared from the azide in the manner previously described for preparing (β-methylallyl)-carbinylamine from its corresponding azide (vide supra). The reaction gave 2.26 g. of amine, b.p. 89-92° (748 mm.) which is a 36% yield based on the initial alcohol. The infrared spectrum (chloroform) showed a band in 3300-3400 cm^{-1} region and a strong band at 1650

cm^{-1} consistent with the material being an unsaturated amine. The n. m. r. spectrum showed a doublet centered at 63 cps, a mobile broad singlet, a quintet at 133 cps, an unsymmetrical doublet at 153 cps, and two sets of multiplets in the 290-365 cps region, consistent with the assigned structure.

Dideutero-(α-methylallyl)-carbinylamine. - A solution of 14.0 g. (0.215 moles) of sodium azide in 80 ml. dimethyl sulfoxide was placed in a 500-ml. round-bottomed flask fitted with a condenser terminating in a calcium chloride drying tube, and a magnetic stirrer. A solution of 32.5 g. (0.141) moles) of dideutero-(α-methylallyl)-carbinyl benzenesulfonate in 70 ml. of dimethyl sulfoxide was added and the mixture heated at 75° for 21.5 hours.

The reaction mixture was cooled and quenched with 600 ml. of water. This mixture was extracted with seven 100-ml. portions of ether. The combined ether extracts were washed with two 200-ml. portions of water, dried over anhydrous magnesium sulfate and concentrated to 60 ml. by careful distillation of ether.

To a 300-ml. three-necked flask fitted with a mechanical stirrer, a calcium chloride drying tube, and a 50-ml. pressure-equalizing dropping funnel was added a mixture of 6.0 g. (0.16 moles) of lithium aluminum hydride and 125 ml. of absolute ether. This mixture was cooled in ice, and the ethereal solution of azide described above was added over a period of 3.5 hours. The reaction mixture

was stirred at room temperature for another 7 hours. A Dry Ice condenser was substituted for the calcium chloride tube, and the excess lithium aluminum hydride was decomposed by adding 13 ml. of water over a 1-hour period. A 20% aqueous sodium hydroxide solution was added until the inorganic salts came down as a powder. The ethereal layer was decanted, and the powder was washed with four 50-ml. portions of ether. The addition of 30 ml. of water to the powder caused the release of another 50 ml. of ether. The combined ether layers were dried over magnesium sulfate.

The ether was removed by distillation, and the residual liquid was distilled through a modified Claisen head with a 1.3 x 10-cm. Vigreux sidearm to give 5.89 g. of amine, b.p. 42-44° (108 mm.). This represents a 59% yield on the deuterated alcohol and a 35% yield on the lithium aluminum deuteride. The n.m.r. spectrum was that observed for the undeuterated amine except for the change in pattern for the methinyl proton and the reduction in the intensity of the absorption due to carbinyl methylene protons. A good integration of the spectrum was not possible because of the overlap of these two sets of proton absorptions. The analytical value of 2.3% protium given by Metal Hydrides, Inc. was used as the protium content of the carbinyl methylene group

1-Chloro-3-bromo-2-methylpropane was synthesized in a 500-ml. three-necked flask fitted with a magnetic stirrer, a gas dispersion tube and a gas outlet tube. The gas dispersion tube was attached to a cylinder of hydrogen bromide gas through the intermedi-

acy of three scrubbing traps containing sulfuric acid and a tower containing iron filings. The outlet tube was attached in series to an empty trap and a trap containing dilute sodium hydroxide solution. In the reaction flask was placed 130 g. of β-methylallyl chloride and 1.5 g. of benzoyl peroxide. The reaction mixture was tared and irradiated with an ordinary 150 watt bulb. Hydrogen bromide gas was bubbled through the stirred reaction mixture for 10 hours. At the end of this period, the flask and contents had gained 99 g. in weight. The reaction mixture was washed with 100 ml. of water, 100 ml. of 5% sodium bicarbonate, another 100 ml. of water and dried over anhydrous calcium chloride. The reaction mixture was distilled through a 1.4 x 25-cm. vacuum-jacketed column with a total reflux head. A fraction containing 56.9% of starting material, b.p. 54-62° (66 mm.) and one containing 110.0 g. (79%) of the desired product, b.p. 78-82°; lit. 49° (15mm.) (35), 55-63° (26-28 mm.) (17) was obtained. The n.m.r. spectrum was consistent with the assigned structure.

1-Chloro-3-cyano-2-methylpropane was prepared in a 500-ml. round-bottomed flask fitted with a reflux condenser and a magnetic stirrer. A solution of 22.0 g. (0.45 moles) of sodium cyanide in 80 ml. of 50% aqueous ethanol was placed in the flask and a solution of 60.0 g. of 1-bromo-3-chloro-2-methylpropane (0.348 moles) in 100 ml. of 95% ethanol added over a 1-hour period through a dropping funnel. The solution was refluxed for 14 hours. The reaction mixture was diluted with water to 750 ml. and extracted with three

150-ml. portions of chloroform. The chloroform extracts were combined and dried over anhydrous magnesium sulfate.

The drying agent was removed by filtration and the chloroform removed by distillation. The residual red liquid was distilled through a 1.4 x 25-cm. vacuum-jacketed Vigreux column with a total reflux head, and gave 25.2 g. (62%) of colorless liquid, b.p. 66-76° (7-9 mm.); lit. 82-83° (16 mm.) (36), and 74-79° (11.7 mm.) (17). The n.m.r. spectrum was consistent with the assigned structure but not definitive.

1-Cyano-2-methylcyclopropane was prepared by the method of Silver and Roberts (17). The reaction gave 58% of 1-cyano-2-methylcyclopropane, b.p. 54-55.5° (26 mm.); lit. 142-146° (760 mm.) (17). The product gave the expected broad multiplet in the 25-100 cps region of the n.m.r. spectrum and a doublet centered at 68 cps.

(2-Methylcyclopropyl)-carbinylamine was prepared in 27% yield by the reduction of 4.75 g. (0.059 moles) of 1-cyano-2-methylcyclopropane with 1.5 g. (0.040 moles) of lithium aluminum hydride in ether. This low yield seems to confirm the claim (37) that the reduction of a nitrile requires a 1:1 molar ratio of reactants. The liquid obtained had b.p. 97-102°; lit. 102-102.5° (17). The n.m.r. spectrum was consistent with the assigned structure.

Dideutero-(2-methylcyclopropyl)-carbinylamine. - In a 200-ml. three-necked flask fitted with a 50-ml. pressure-equalizing dropping funnel, a calcium chloride drying tube and a mechanical stirrer was

placed 3.5 g. (0.83 moles) of lithium aluminum deuteride (97.7% active deuterium, Metal Hydrides, Inc.). The flask was cooled in ice, and 75 ml. of absolute ether was added. A solution of 6.72 g. (0.083 moles) of 1-cyano-2-methylcyclopropane in 40 ml. of ether was added over 2 hours. The solution was stirred at room temperature for 12.5 hours and then permitted to stand for 12.5 hours. A Dry Ice condenser was substituted for the calcium chloride tube, and the ice-cooled reaction mixture was hydrolyzed by adding 4 ml. of water, 6 ml. of 20% aqueous sodium hydroxide and then more water until the inorganic salts precipitated as a powder. The ether was decanted, and the powder was extracted with three 40-ml. portions of ether. Another 20 ml. of water was added to release adsorbed ether. The combined ether extracts were dried over anhydrous magnesium sulfate.

The ether was removed by distillation and the residual liquid distilled through a modified Claisen flask with a 1.3 x 10-cm. Vigreux sidearm to give 3.59 g. of amine, b.p. 42-44° (107 mm.). The n.m.r. spectrum was consistent with the expected changes in the spectrum of the undeuterated amine. The amount of amine obtained represented a 25% yield on deuterium and a 51% yield on nitrile.

<u>α,β-Dimethylallyl alcohol</u> was prepared in 21% yield by the addition of methylmagnesium iodide to α-methacrolein; the alcohol had b.p. 113-114°; lit., 112-113° (38). The product was found to be only 90% pure by v.p.c. on column K, but the n.m.r. spectrum was

consistent with the structural assignment, doublet at 53 cps, narrow multiplet at 88 cps, quartet at 238 cps and multiplets centered at 265 and 277 cps.

2-Methyl-3-buten-2-ol. - In a 500-ml. round-bottomed flask fitted with a condenser and a magnetic stirrer were placed a mixture of 200 ml. of 1% aqueous sodium carbonate and 15.3 g. (0.146 moles) of a mixture of α,α-dimethylallyl chloride and γ,γ-dimethylallyl chloride (b.p. 80-102°). The stirred solution was heated at 47° for 42.5 hours, then cooled, saturated with sodium carbonate, and extracted with three 50-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, and the ether was removed by distillation. The residual oil was distilled through a 1.3 x 65-cm column packed with a tantalum wire spiral. The middle fraction, 5.4 g. of liquid, b.p. 93-97°, lit., b.p. 94-96° (39), was 98% pure by v.p.c. on column K. The n.m.r. spectrum of this fraction gave the sharp singlet and normal monosubstituted vinyl absorptions expected for 2-methyl-3-buten-2-ol. The tail fraction was 0.7 g. of essentially pure 3-methyl-3-buten-1-ol by v.p.c. and n.m.r. This compound was used as a v.p.c. standard.

Methylcyclopropylcarbinol was prepared by reduction of methylcyclopropyl ketone (10 g., 0.12 moles) with lithium aluminum hydride. The isolation of the alcohol condition gave 5.5 g (54%) of carbinol, b.p. 119-120°. The compound gave an n.m.r. spectrum in agreement with that of an authentic sample.

The deamination reactions were run in an appropriate three-necked flask fitted with a magnetic stirrer and a Friedrich condenser set for downward distillation with an outlet from the collecting flask attached to a Dry Ice trap, protected by a calcium chloride drying tube. In the reaction flask was placed the amine and 4 parts by volume of water. To the ice-cooled reaction vessel were added 1.2 equivalents of 1 N perchloric acid and 2.4 equivalents of 5 N aqueous sodium nitrite. The solution was stirred at 0° for 0.5 hours and then a heating mantle was substituted for the ice bath, and the reaction mixture was distilled as rapidly as possible. After 25% of the original volume was distilled, it was replaced with an equivalent volume of water and the distillation was continued until the distillate equalled half of the volume of the original reaction mixture. The distillation usually required 0.5 hours. The distillate was saturated with anhydrous potassium carbonate and extracted with four equivalent portions of ether totaling twice the volume of the distillate. The ethereal solution was dried over anhydrous sodium sulfate and analyzed on the v.p.c. to give a measure of the product distribution. In the experiments where individual deuterated products were isolated, the ether was distilled and the residual liquid was distilled through a modified Claisen flask with a 1.3 x 10-cm. Vigreux sidearm at reduced pressure without fractionation. The products were then separated by preparative v.p.c. and analyzed by n.m.r.

Deamination of (β-Methylallyl)-carbinylamine. - The deamination was performed on 0.0142 moles of amine and gave a 70% yield

of high boiling products plus an undetermined amount of isoprene. The ethereal product mixture contained peaks that overlapped on column K and column A. It was necessary to use a combination of the results on K at 105 and 117°, and on A at 50 and 97°. By using the ratios of the α,β-dimethylallyl alcohol peak to the 1-methylcyclobutanol peak on column A, it was possible to obtain values for the four identified components with standard deviations on 18 analyses of 1%. There were three unidentified peaks, possibly nitrites, totaling 11% of the product mixture.

The relative yields of the identified products were: (β-methylallyl)-carbinol, 29%; 1-methylcyclobutanol, 59%; α,α-dimethylallyl alcohol, 6%; and α,β-dimethylallyl alcohol, 6%. No peak with a retention time corresponding to that of (1-methylcyclopropyl)-carbinol was observed in any analysis. Three analyses were made using exceptionally large samples to confirm this observation.

Deamination of Dideutero-(β-methylallyl)-carbinylamine was carried out on a sample of amine which contained ethanol as an impurity. The amine content was 0.0205 moles of amine. The deamination gave 1.81 g. of high-boiling liquids (70% recovery, assigned on the basis of exclusive formation on alcohols). The alcohols were separated by preparative v.p.c. on four 12-foot Carbowax columns in a Beckman Megachrom. By this means, 0.060 g. of (β-methylallyl)-carbinol and 0.382 g. of 4:1 mixture of 1-methylcyclobutanol and α,β-dimethylallyl alcohol were isolated.

The v. p. c. of the (β-methylallyl)-carbinol fraction showed that it was essentially pure, and the n. m. r. spectrum confirmed this. If there had been any (1-methylcyclopropyl)-carbinol present, it would have been collected in this fraction and detected in the v. p. c. Identification of the alcohol via the characteristic high field absorption in the n. m. r. would have been possible. The n. m. r. spectrum of the dideutero-(β-methylallyl)-carbinol was virtually identical with that of the synthetic precursor of the amine. It was concluded that no observable rearrangement of the carbon skeleton had occurred in the deamination process leading to (β-methylallyl)-carbinol.

The n. m. r. spectrum of the 1-methylcyclobutanol fraction in carbon tetrachloride was obtained after treating 100 ml. of the fraction with a slight excess of a 10% solution of bromine in spectro quality carbon tetrachloride at 0° and flash distilling the reaction mixture at an oil bath temperature of 45° and a pressure of 100 mm. The only n. m. r. absorption observed in the 115 to 85 cps region was insignificant absorption in the position where the dibromide of α, β-dimethyl-allyl alcohol was known to absorb. To the accuracy possible by n. m. r. integration, the product was entirely 3, 3-dideutero-1-methylcyclobutanol.

Deamination of 2-pentylamine was run on 9.0 g. (0.106 moles) of the amine and gave 2.45 g. of alkenes in the Dry Ice trap and 5.50 g. of alcohol. These quantities correspond to a 92% recovery of products. The observed product distribution on column K was: 2-pentanol, 53%; 3-pentanol, 11%; 2-pentene, 32%; 1-pentene, 4%.

Deamination of isoamylamine was performed on 0.78 g. (0.009 moles) of amine and gave a 34% recovery of alcohols. The alcohol mixture contained: t-amyl alcohol, 37%; 2 methyl-3 butanol, 11%; isoamyl alcohol, 52%.

Deamination of (α-methylallyl)-carbinylamine was run twice. In each run 0.018 moles of amine was deaminated. The alcohols were isolated in only 15 and 23% yields. Isoprene was formed in undetermined quantities in the reaction. The analysis of the ethereal solution was carried out on column K at 89°. Seven major products were tentatively identified on the basis of v.p.c. retention times. An artificial mixture of alcohols gave an n.m.r. spectrum in reasonable agreement with the spectrum of the product mixture (in carbon tetrachloride). The observed alcohols and the relative percentage yield of each for both runs are given in Table III. All these identifications except those of 2-methylcyclobutanol and γ,γ-dimethylallyl alcohol were later confirmed by partial isolation and n.m.r. spectra.

Deamination of (2-methylcyclopropyl)-carbinylamine was carried out on 1.36 g (0.016 moles) of the amine. The product ratios were determined by v.p.c. on an ethereal solution, and the product was isolated. There were at least seven substances present, of which only three alcohols totaling 88% of the product mixture were identified. The other products were possibly nitrites, cis-(2-methylcyclopropyl)-carbinol or the nitrogen sesquioxide adduct of (α-methylallyl)-carbinol. The relative percentages of products formed are

given in Table IV.

Deamination of dideutero-(α-methylallyl)-carbinylamine was run twice. In the first run (Run 3), 2.41 g. (0.028 moles) of amine was deaminated to give 2.15 g. (88%) of high-boiling products. In the second run (Run 4), 5.65 g. (0.064 moles) of amine was treated with nitrous acid to give a 78% yield of high-boiling products and 12% of isoprene. In Run 3 the alcohols were isolated by preparative v.p.c. on a 12-foot Carbowax column in the Autoprep (Aerograph Model, A-700). In Run 4 the separation was carried out on four 12-foot TCEP columns in the Megachrom. at 120°.

The sample of α, α-dimethylallyl alcohol obtained from Run 4 was indicated to be pure by v.p.c. on TCEP. It showed the expected n.m.r. spectrum (carbon tetrachloride) for α-dideuteromethyl-α-methylallyl alcohol and consisted of a normal vinyl region for a monosubstituted vinyl group, a sharp singlet for the methyl group, and a multiplet at approximately the same chemical shift. Also, from Run 4 a sample containing a 1:1 mixture of deuterated ethylvinylcarbinol and deuterated methylallylcarbinol was obtained. The n.m.r. spectrum of this sample showed that the methyl triplet of the ethylvinylcarbinol is present in the deuterated alcohol as a relatively narrow multiplet. The spectrum is consistent with the identification of this product as (1, 1-dideuteroethyl)-vinylcarbinol.

The (2-methylcyclopropyl)-carbinol obtained in the two runs was impure. The sample from Run 3 contained 3% of α, α-dimethylallyl alcohol, 1% of methylallylcarbinol and 2.5% of methylcyclo-

propylcarbinol. The sample from Run 4 contained 5% of an unidentified impurity, possibly the nitrite ester or the other isomer of the alcohol. The presence of these impurities made the evaluation of the proper integral for the cyclopropyl ring protons risky. The method of choice for evaluating the deuterium distribution while minimizing the systematic error due to impurities was to compare the integral of the methyl doublet absorption with the integral of the doublet absorption due to the carbinyl methylene. For the purposes of calculation, it was assumed that 2.046 protons were distributed between the two methylene positions. In the case of the sample from Run 3, the integration was performed 15 times using the automatic integrator. This gave a ratio of methylene absorption to methyl absorption of 0.441 ± .015, which corresponds to 65.3 ± 2.2% of the labeled molecules with deuterium in the ring methylene group. For the sample from Run 4 the ratio for 26 separate integrations made using a digital voltmeter was 0.448 ± .020 which corresponds to having 66.4 ± 3.0% of the deuterium label in the ring methylene group of the labeled carbinol.

The methylallylcarbinol fraction obtained in the first experiment was only 80% pure by v.p.c. The sample contained 15% of ethylvinylcarbinol. Only three integrations using the automatic integrator were performed on the sample before it was lost while attempting to purify it by a further pass through the Autoprep. With the integration data available there were two reasonable approaches to calculating the deuterium content. The first is to compare the methyl group integral to the integral of α-methylene group absorptions and the second is to compare the α-methylene group absorptions to the vinyl methyl-

ene group absorptions with a correction being made for the amount of absorption from the 15% of ethylvinylcarbinol present. The ratio of methylene protons to methyl protons was not available from the three runs, but the ratio of α-methylene absorption to vinyl methylene absorption was 0.266 ± .017. This corresponds to having 77.1 ± 1.1% of the protium in the vinyl methylene group of the deuterated α-methylallylcarbinol. If the correction had not been made, the value would have been 80%, and if the estimated quantity of ethylvinylcarbinol from the v.p.c. had been double, the value would have been 74%. The sample from Run 4 was found to be 90% pure by v.p.c. and this purity checked with an 8% value of ethylvinylcarbinol found by comparing the n.m.r. integrals of their two methyl absorptions. The sample was subjected to 29 independent integrations with the aid of a digital voltmeter. The ratio of the α-methylene protons to the methyl protons was 0.157 ± .006. The ratio corresponds to 78.3 ± 0.9% of the deuterium being in the α-methylene position. The ratio of the absorptions due to the two methylene groups was found to be 0.271 ± .016, which also corresponds to 78.3 ± 0.9% of the deuterium being in the α-methylene position. For this sample, ignoring the ethylvinylcarbinol impurity in the calculation gives 80% and doubling it gives 76%. A measure of the success involved in the integration is found in the observation that the ratio of the vinyl methinyl absorption to the carbinyl methinyl absorption was 1.002 ± .036.

Deamination of dideutero-(2-methylcyclopropyl)-carbinylamine was carried out on a 3.41 g. (0.039 moles) sample of amine. The

ethereal solution of the product was studied by v. p. c. on TCEP at 60°. The results are reported in Table III. From the ethereal solution, 2. 74 g. of high boiling liquid was isolated which corresponds to an 81% recovery.

The (2-methylcyclopropyl)-carbinol isolated by preparative v. p. c. on four 12-foot TCEP columns in the Megachrom was shown by analytical v. p. c. to contain a total of 19% of impurities, including 11% of methylallylcarbinol, and 4% of methylcyclopropylcarbinol. The n. m. r. spectrum was integrated with the aid of a digital voltmeter. The ratio of the carbinyl methylene absorption to the methyl absorption was used to calculate that 14. 5 ± 0. 9% of the deuterium was located at the ring methylene group.

The methylallylcarbinol obtained contained 12% of an unidentified impurity. Since the impurity did not produce any noticeable changes in the n. m. r. spectrum from that of deuterated methylallylcarbinol by itself, it was assumed that the impurity was the nitrite ester of methylallylcarbinol. A total of 67 independent integrations were made using a digital voltmeter. It was found that the ratio of α-methylene proton absorptions to the methyl proton absorptions was 0. 496 + . 009, and this ratio corresponds to 73. 8 ± 2. 0% of the deuterium being located in the vinyl methylene group. The ratio of the vinyl methylene proton absorptions to the α-methylene proton absorptions was 0. 347 ± . 022 which corresponds to 74. 8 ± 2. 2% of the deuterium being located at the vinyl methylene group. The ratio of the vinyl methinyl proton absorption to the carbinyl methinyl proton

absorption was found to be 1.034 ± .046.

Calibration of V.P.C. Results. - It was found that the Perkin-Elmer models 154C and 800 gave widely differing values for the integration of the same samples. A brief study of the model 800 showed the integral to be sensitive to slight variations of the hydrogen flow rate to the detector and to small variations in the structure of isomeric alcohols. Calibration with samples containing equal parts by weight of the various isomeric alcohols was carried out on the model 154C which uses a thermal conductivity detector. The percentages of the various isomers on TCEP or column K varied by 1% and so it was assumed that all variation in areas were due to variations in thermal conductivities. The thermal conductivities relative to α,α-dimethylallyl alcohol were:

α,α-dimethylallyl alcohol	1.00
(α-methylallyl)-carbinol	0.99
ethylvinylcarbinol	0.88
methylallylcarbinol	1.02
methylcyclopropylcarbinol	0.92
(2-methylcyclopropyl)-carbinol	0.85

All data reported in this thesis have already been corrected according to these calibrations.

Stability of Product Alcohols. - Silver (17) previously replaced the amine with some of the isomeric alcohols under the deamination

conditions. It was found that 2-methylcyclobutanol, 3-methylcyclobutanol, (2-methylcyclopropyl)-carbinol, methylcyclopropylcarbinol, and methylallylcarbinol were stable under these conditions which are certainly more acidic than those that the alcohols are subjected to during the deamination reaction. In the present work, an artificial mixture of the alcohols obtained in the deamination of (α-methylallyl)-carbinylamine was subjected to this stability test. The average of the three v. p. c. analyses for both starting mixture and product mixture is given below.

	Initial %	Final %
α,α-dimethylallyl alcohol	20	19
methylallylcarbinol	20	14
methylcyclopropylcarbinol	46	55
(α-methylallyl)-carbinol	11	8
(2-methylcyclopropyl)-carbinol	4	4

It was noted that several low-boiling materials, including isoprene, were present in the ethereal product. The variations probably are smaller for the actual deamination conditions.

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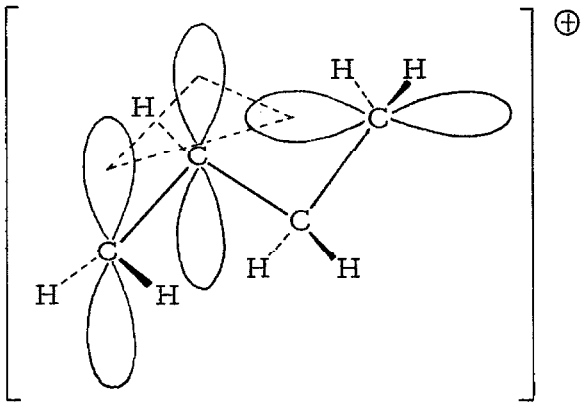
V. PROPOSITIONS

PROPOSITION I

An experiment is proposed to distinguish on the basis of their stereochemical properties between two schemes of intermediates used to explain the reactivity of and products obtained from cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives.

A scheme of equilibrating bicyclobutonium ion intermediates has been used to rationalize the available data on the reactions of allylcarbinyl, cyclobutyl and cyclopropylcarbinyl derivatives (1).

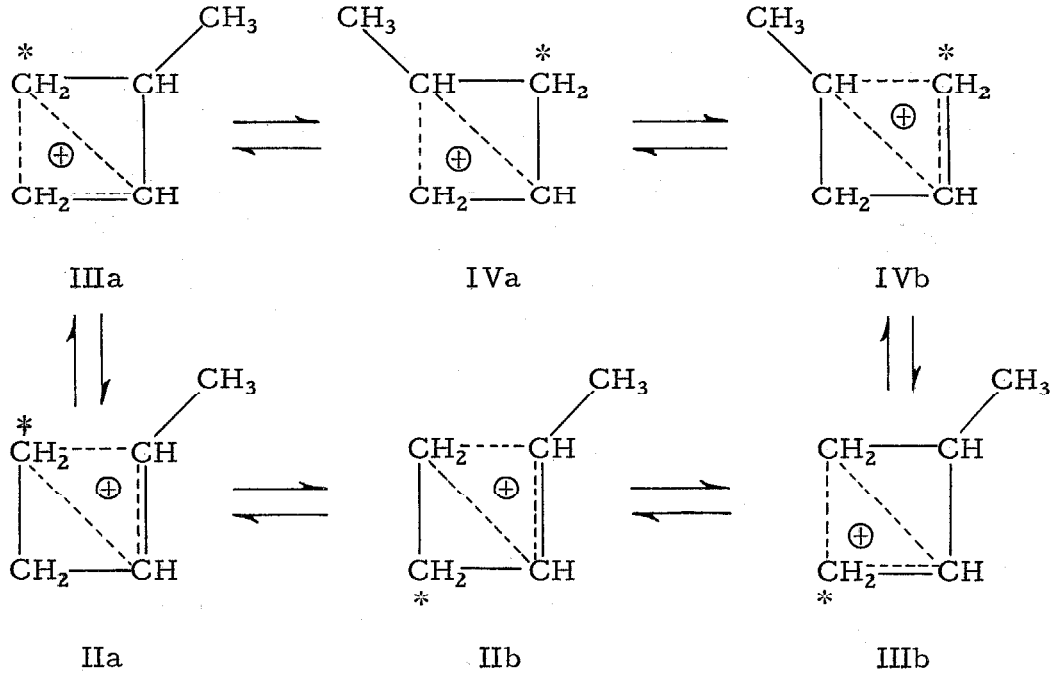


I

A similar scheme has been successfully used to explain the products and reactivities of the methyl-substituted cyclopropylcarbinyl, allylcarbinyl and cyclobutyl derivatives (2, 3). The present results appear to suggest that it may be necessary to invoke the intermediacy of a homoallylic ion to explain the labeling data obtained in the deamination of dideutero-(α-methylallyl)-carbinylamine (4).

The bicyclobutonium ion (I) is of itself asymmetric, and if the three methylene groups can be distinguished, there are two inde-

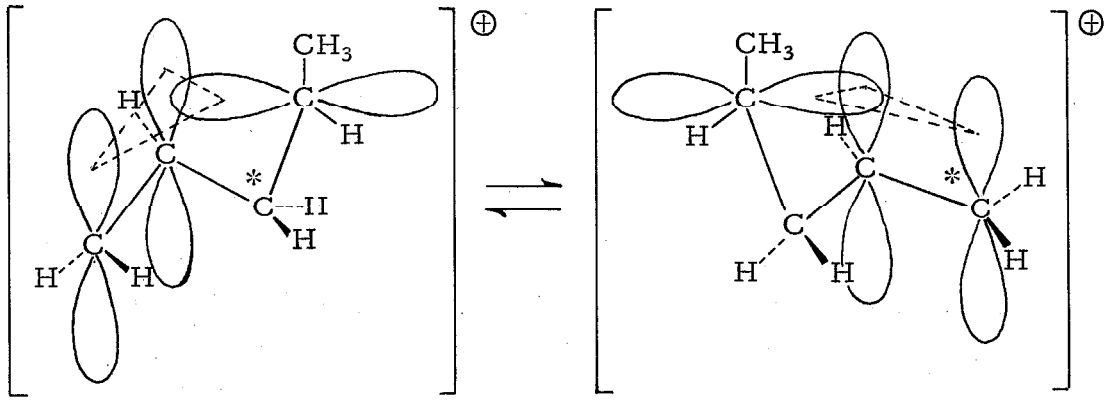
pendent sets of six different bicyclobutonium ions (5), with the second set containing the mirror images of the first set. If all conversions



IIIa IVa IVb

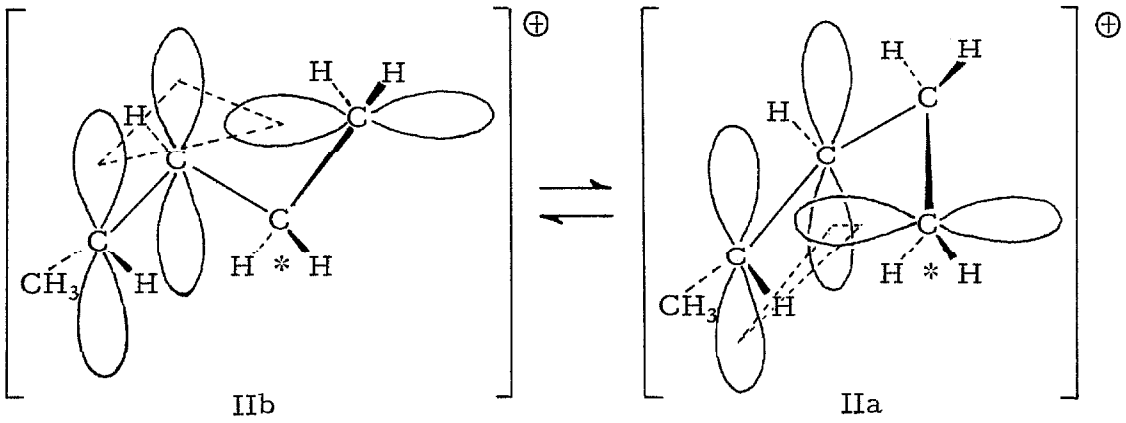
IIa IIb IIIb

between are made by converting one bond from a delocalized to a localized bond while a second bond initially localized is delocalized,



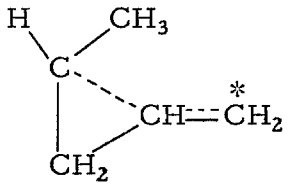
IVa IVb

then the two sets of bicyclobutonium ions will not mix. On the other



IIb IIa

hand, the intervention of a homoallylic ion like V would mix or racemize the bicyclobutonium ions.



V

The deamination of optically active trans-(2-methylcyclopropyl)-carbinylamine-α-^{14}C would yield directly either V or IVa. If IVa is obtained, then in accord with the labeling data obtained for the deamination of dideutero-(2-methylcyclopropyl)-carbinylamine ca. 12% of the material will be converted to IVb (6). The methylallylcarbinol obtained via this route would be about 50% optically pure. Furthermore, if the methylallylcarbinol is resolved, it

should be found that the predominant enantiomer should have all its ^{14}C in the vinyl methylene carbon atom, while the other enantiomer should have all of its label in the α-methylene position. The homoallylic ion, V, would yield racemic methylallylcarbinol, and both enantiomers upon resolution should be found to have identical distribution of ^{14}C between the two methylene carbons. The same racemic methylallylcarbinol would be predicted by classical carbonium ion intermediates.

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PROPOSITION II

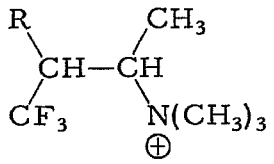
A method is proposed for determining the relative importance of steric and inductive effects as directive influences in the Hofmann elimination reaction.

The relative importance of various effects in determining the direction of elimination in the pyrolyses of quartenary ammonium hydroxides has been debated extensively for the past fifteen years. There are two extreme points of view on the issue. Ingold states that the Hofmann elimination pattern is based almost exclusively on the inductive effect of substituents on the acidity of the β-protons, and that steric effects only become important in very highly branched molecules (1-3). Brown maintains that "the direction of the Hofman elimination is controlled by steric factors even down to the simplest cases. (4, 5). Cope, in his review article, has argued for a blending of the two types of effects in explaining the reactivity details (6). More recently, Cope has used conformational preference as controlled by steric factors in order to explain patterns of elimination (7). At the same time, he suggested that the older data of Smith and Frank (8) should be used as evidence for a steric effect rather than for an inductive effect. The main steric effect considered by Cope arises from repulsions between the β-alkyl groups and the leaving group in the required trans configuration (9).

The issue is difficult to resolve because the inductive and steric effects of alkyl groups act in the same direction. Other

functions whose steric and inductive effects act in opposing directions have a tendency to stabilize the incipient double bond and, thereby, threaten to change the timing of the reaction to that of the E_1 mechanism.

It is proposed that a study be made of the Hofmann elimination reaction of compounds having the general structure I in order to determine the relative yields of 1- and 2-alkenes. The simplest mole-



I

cule of this structure, (γ,γ,γ-trifluoro-s-butyl)-trimethylammonium hydroxide, should enable us to eliminate one of the two mechanistic extremes. Trifluoromethyl has been shown to be strongly electron withdrawing and would increase the acidity of the β-proton. On the other hand, it should have a steric effect larger than that of a methyl group (10). Cope found 94.4% of the 1-alkene in the product from the pyrolysis of s-butyltrimethylammonium hydroxide (8). Brown must predict that the yield of 1-alkene should be at least as large in the case of I. Ingold's theory would predict that the yield of 2-alkene must be considerably in excess of 40% (the statistical expectation) because of the large inductive effect of the trifluoromethyl group. A yield of 2-alkene between 20 and 60% would suggest

that both extreme positions are defective.

If a large yield of 2-alkene is isolated, the inductive effect must be assigned a major role in determining the direction of elimination. The variation of the R group from methyl to t-butyl should have little effect on the acidity of the β-proton and so such a variation would be a useful way of measuring the importance of the steric effect virtually independently of the acidity change. Ingold would predict that the effect would be small until substitution of the t-butyl group.

It might be argued that the effect of adding the trifluoromethyl group would be to change the timing of the reaction toward that of the E_{1cb} mechanism. This possibility could be checked by running the reaction in a deuterated solvent. If this mechanism shift occurs, then it would be reasonable to use (δ, δ, δ-trifluoro-2-pentyl)-trimethylammonium hydroxide to evaluate the relative importance of steric and inductive effects.

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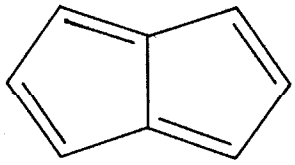
PROPOSITION III.

It is proposed that pentalene be synthesized by a route analogous to that used to prepare heptalene.

The hydrocarbon pentalene (I) is of theoretical interest because the interior bond connects two non-alternant carbon atoms, and because it is an example of an alternant conjugated 4n π-system. The

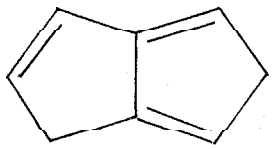


I

wave function for the ground state will be antisymmetric with respect to rotation about an axis perpendicular to the central bond (1). The alternate carbon atoms will have partial positive and negative charges in the ground state (2). For this molecule, valence-bond calculations predict that the bond order for the π-electron system across the central bond will be negative, but the molecular orbital (LCAO) calculations predict a positive bond order across this central bond (1).

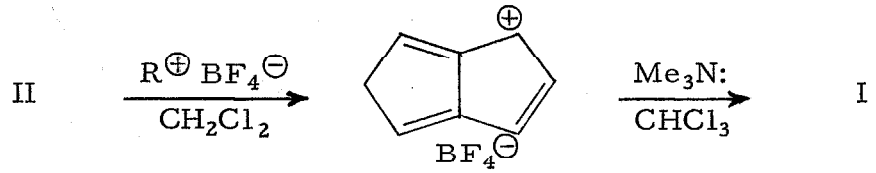
A synthesis of heptalene via a "1-heptalenium" tetrafluoroborate (3) has been reported by Dauben and Bertelli (4). LCAO calculations predict that pentalene will have both a smaller delocalization energy (by 1.16 β) and a larger strain energy than heptalene (1, 4), but since heptalene appears to be a fairly stable compound the possibility of forming and isolating pentalene is not precluded. In fact, the method used by Dauben and Bertelli to synthesize heptalene

should be readily adaptable to preparing pentalene from the dihydropentalene, II, which has been recently synthesized by Katz as a precursor of pentalene dianion (5).



II

The main difficulty in applying Dauben's synthetic scheme to the formation of pentalene is that the hydride abstraction from dihydropentalene might be more difficult than the abstraction from



III

dihydroheptalene. The hydride abstraction, which leads in the dihydroheptalene system to a carbonium ion resembling the tropylium ion, leads in the dihydropentalene system to either a cation resembling an allylic cation or one resembling a cyclopentadienyl cation. The triphenylcarbinyl tetrafluoroborate used by Dauben and Bertelli may not be a strong enough Lewis acid to give 1-pentalenyl tetrafluoroborate in good yield. If this reaction fails, then the desired conversion may be effected by adding silver tetrafluoroborate in small portions to a mixture of t-butyl bromide and dihydropentalene

in sulfur dioxide.

If the t-butyl tetrafluoroborate should decompose faster than it reacts with dihydropentalene, then it would be reasonable to try to form pentalenyl tetrafluoroborate (III) by a less direct route. A method that might be tried would be to react the dihydropentalene (II) with a stoichiometric amount of N-bromosuccinimide in hopes of forming a monobromodihydropentalene which can then be reacted with silver tetrafluoroborate in sulfur dioxide to give a protonated pentalene species. The reaction of any protonated pentalene species with trimethylamine should give pentalene without difficulty.

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PROPOSITION IV

An experiment is proposed to elucidate the timing of the base-catalyzed elimination reaction of 1-chloro-2, 2, 2-triphenylethane.

The reaction of 1-chloro-2, 2, 2-triphenylethane with amyl-sodium yields triphenylethylene (1). There is little question that

$$\phi_3C{-}CH_2Cl \;+\; \text{Amyl-Na} \longrightarrow \phi_2C{=}CH\phi$$

the initial step in this reaction is the abstraction of a proton from

$$\phi_3C{-}CH_2Cl \;+\; \text{Amyl-Na} \longrightarrow \phi_3C{-}\overset{\ominus}{C}HCl \;+\; Na^{\oplus}$$

(I)

the halide to give anion I and pentane. The chief question is one of the timing of the elimination of the chloride ion relative to the rearrangement of the phenyl group. The phenyl group could rearrange

$$\text{I} \longrightarrow \phi_2\overset{\ominus}{C}{-}CHCl\phi \longrightarrow \phi_2C{=}CH\phi \;+\; Cl^{\ominus}$$

(II) (Path 1)

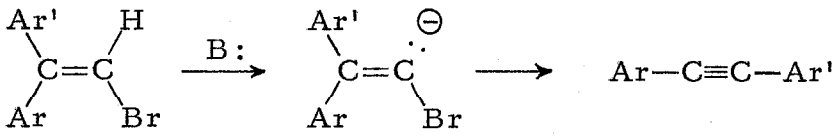
before the elimination of halide (Path 1) or the halide ion could be eliminated from I (Path 2) to give the carbene III, which would then

$$\text{I} \longrightarrow \phi_3C{-}CH{:} \;+\; Cl^{\ominus} \longrightarrow \phi_2C{=}CH\phi$$

(III) (Path 2)

rearrange to the triphenylethylene. There is little doubt that primary alkyl halides can underto an α-elimination reaction to give

carbenes in the presence of strong base (2), but there is also good evidence that β, β, β-triphenylethyl carbanions can undergo phenyl migrations to give the more stable diphenylalkyl anion (1). Furthermore, it has been demonstrated that the base catalyzed rearrangement of 1, 1-diaryl-2-haloethylene, which could be formulated as an α-elimination reaction proceeding via a carbene intermediate, proceeds via a stereospecific path probably involving rearrangement in the initially formed anion (3, 4).



In the 1-halo-2, 2, 2-triarylethane system, testing for a stereospecific rearrangement would involve both a tenuous assumption about the relative rates of carbanion inversion and aryl migration and an extremely difficult synthesis. A more reasonable approach to the problem would be to attempt to run the reaction under conditions where the carbene III is known to be trapped.

2, 2, 2-Triphenyldiazoethane is known to rearrange thermally or in the presence of copper to give triphenylethylene (5). This rearrangement probably goes via the carbene III, and certainly III could be generated from it by irradiation. It is proposed that this diazo compound be decomposed in the presence of triphenylphosphine. The carbene should be trapped as the Wittig reagent which can then be characterized by its reactions with carbonyl compounds. (6, 7).

The carbonyl compound should be tested for behavior in the absence of triphenyl phosphine from the reaction mixture. The carbene III could also be trapped by forming it in the presence of fluoroenyltriphenylphosphine ylide which would react with the carbene to give an easily characterized hydrocarbon (8).

Once it has been established that the carbene can be trapped by these methods, then the base catalyzed reaction of 1-chloro-2, 2, 2-triphenylethane should be run in the presence of the two trapping agents. If the method involving the use of an ylide as a trapping agent is successful with the diazo compound, then a failure to trap carbene, III, by this second mechanism must be regarded as excellent evidence for the absence of this carbene despite the negative nature of the evidence.

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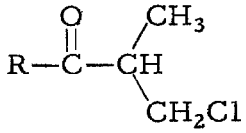
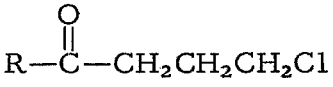
PROPOSITION V

An experiment is proposed to distinguish between two possible mechanisms for the Friedel-Crafts reaction between acetyl chloride and cyclopropane.

In the reaction of cyclopropanes with a solution of the 1 : 1 complex of aliphatic chlorides and aluminum chloride in chloroform at 0°, the major product in each case was a β-chloroketone (I) rather than the expected γ-chloroketone (II) which did appear as a minor product (1). It was shown that alkyl cyclopropyl ketones and γ-chloroketones,

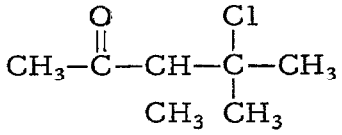


I



II

such as II, are not intermediates in this reaction. The reaction of 1, 1-dimethylcyclopropane with the acetyl chloride and aluminum chloride mixture (2) yielded only 4-chloro-3, 4-dimethyl-2-pentanone (III).

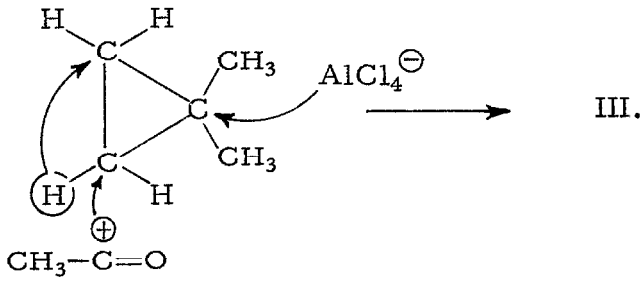


III

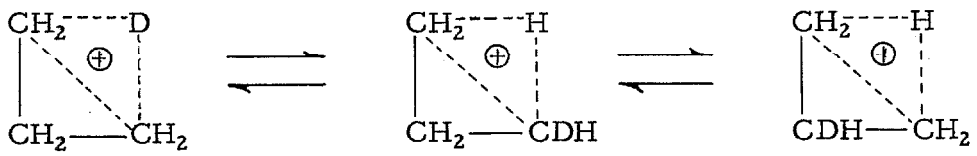
The hydrocarbon, trimethylethylene, would also react with the acetyl chloride and aluminum chloride reaction mixture to give III (2), but even if the isomerisation of 1, 1-dimethylpropane to tri-

methylethylene can be invoked for this reaction, it cannot be used to explain the reaction of cyclopropane because propylene gives the wrong product, 3-chloro-2-pentanone.

Hart proposed, as a general reaction scheme, that the products could be explained by assuming attack of an acyl cation on the most negative ring carbon, transfer of hydrogen to the more negative of the remaining ring carbons and attack of the aluminum tetrachloride ion at the most positive ring carbon, for example:

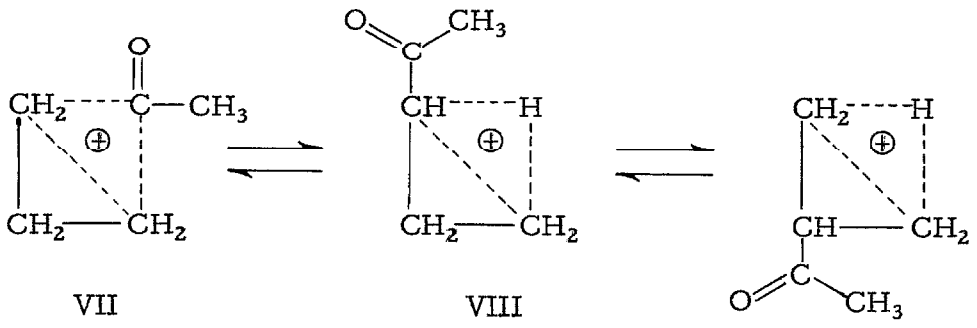


Another mechanism that would yield the desired product would be one invoking a set of bridged cyclopropyl ions (VII-IX), analogous to that utilized by Baird and Aboderin (IV-VI) to explain the deuterium scrambling observed in the formation of 1-propanol from cyclopropane in 8.4 M deuterosulfuric acid (3, 4). The basic dif-



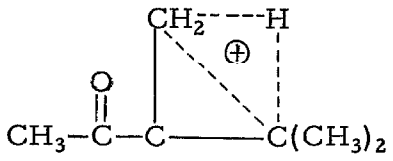
IV V VI

ference in the reactions is that the acyl ion used is a worse bridging species than the deuteron, and, apparently, the ion (IX) in which the acyl carbon has nothing to do with stabilizing the charge is the most stable intermediate. The observed products I and II (R = CH_3)



VII VIII IX

would be formed from IX and VIII, respectively. For the reaction of 1, 1-dimethylcyclopropane, the most stable ion, X, gives product



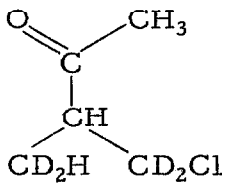
X

exclusively by reacting at the most positive center.

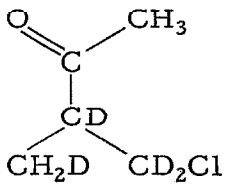
The basic difference between Hart's mechanism and the bridged cyclopropyl cation mechanism is that in the latter mechanism the hydrogens can become completely scrambled while in Hart's mechanism there are limitations on the kinds of scrambling possible.

A study is proposed of protium distribution in products having structure I obtained from the reaction of 1, 1, 2, 2-tetradeuterocyclo-

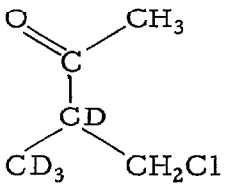
propane with a 1 : 1 acetyl chloride–aluminum chloride complex in chloroform. The mechanism proposed by Hart would lead to three different products, XI, XII, and XIII. The equilibration through all



XI

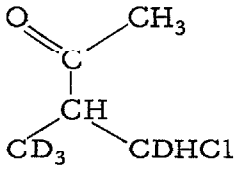


XII

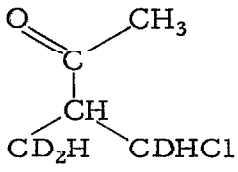


XIII

the various isotopically different bridged ions, which have the carbon skeleton of ion IX, would give the same three β-haloketones (XI–XIII) and two others, XIV and XV.



XIV



XV

The two species XIV and XV are the only ones in the product mixture with mixed methylene groups. Unfortunately, the non-acyl methyl proton of XV absorption would coincide in behavior to that of XII. The methylene absorptions would follow that of XIII.

It would be possible to use double resonance n. m. r. to detect XIV in the presence of XI and XIII. The detection would involve two alterations in the spectra upon double irradiation, both of which alterations have to be observed for a satisfactory identification.

The sample should be irradiated with a broad band deuterium frequency and the non-acyl methyl proton resonance frequency. If both XIV and XIII are present, the methinyl proton which is originally a broad multiplet should become three sharp lines with the sharp doublet of XIV centered on the sharp singlet due to XII and XV. Furthermore, the methylene absorption should sharpen from a broad multiplet to three lines with the outer two lines being again due to XIV and the inner singlet due to XIII. Irradiating with just the broad band deuterium decoupler should give overlapping doublets for the methinyl proton spectrum but the methylene spectrum should still show three lines.

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