I. REARRANGEMENT OF CYCLOPROPYLDIPHENYLMETHYLLITHIUM AND 4,4-DIPHENYL-3-BUTEN-1-YLLITHIUM

II. DEUTERIUM ISOTOPIC PERTURBATION OF THE CYCLOPROPYLMETHYL-CYCLOBUTYL CARBOCATION

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To Helen:

for her steadfast patience,

encouragement,

and continual support

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PART I

ABSTRACT Cyclopropyldiphenylmethyllithium was prepared directly from cyclopropyldiphenylmethane by trimethylsilylmethyllithium metalation or indirectly by transmetalation of cyclopropyldiphenylmethylpotassium. The organolithium is stable in tetrahydrofuran, dimethyl ether, or 2-methyltetrahydrofuran and exists predominatly as loose ion pairs. In diethyl ether or isopropyl methyl ether, cyclopropyldiphenylmethyllithium isomerizes to 4,4-diphenyl-3-buten-1-yllithium; a process that can be reversed by addition of tetrahydrofuran. 4,4-Diphenyl-3-buten-1-yllithium is unstable in most solvents; in cyclopentane, β-elimination of lithium hydride and ortho-cyclisation were major reaction pathways. The solvent dependence of the organolithium rearrangement can be adequately explained by three principle equilibria; the rearrangement occurring in contact ion pairs.

PART II

ABSTRACT Ionization of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol, **9**, in SbF_5–SO_2ClF–SO_2F_2 afforded primarily one stereoisomer (endo-$C_4H_4D_3$+) of the trideuterated cyclopropylmethyl-cyclobutyl carbocation. Ionization of (2,2-d_2-cyclopropyl)-1-d-methanol, **10**, in SbF_5–SO_2ClF–SO_2F_2 produces a 1:1 mixture of endo- and exo-$C_4H_4D_3$+. The low-temperature ^1H, ^2H, and ^{13}C NMR spectra of both $C_4H_4D_3$+ stereoisomers are reported. The methine resonance (^{13}CH) of exo-$C_4H_4D_3$+ is shifted 0.4 ppm downfield from unlabeled cation, C_4H_7+, while the endo-$C_4H_4D_3$+ resonance is coincident with the corresponding carbon in C_4H_7+. This can be taken as evidence for the deuterium isotopic perturbation of the equilibrium between bicyclobutonium, **2**, and bisected cyclopropylmethyl, **4**, structural isomers. The deuterium perturbation of equilibria involving structurally similar, nondegenerate isomers is a larger effect and induces dramatic changes in the methylene carbon resonances. The ^{13}C resonance corresponding to the mondeuterated carbon ($^{13}CH_2$) is shifted in opposite directions relative to C_4H_7+ in endo- and exo-$C_4H_4D_3$+. Endo-$C_4H_4D_3$+ slowly isomerizes to exo-$C_4H_4D_3$+; a lower limit for the rotation barrier in $C_4H_4D_3$+ is 14 ± 1 kcal/mol. The endo-hydrogens in endo-$C_4H_4D_3$+ were assigned to the high-field methylene resonance in the ^1H spectrum of this ion in contrast to previous assignments by other workers. The results of this NMR study of $C_4H_4D_3$+ carbocations are consistent with two rapidly equilibrating structures, **2** and **4**, of $C_4H_4D_3$+ under stable-ion conditions.

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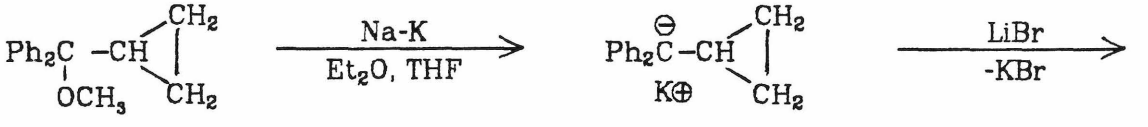
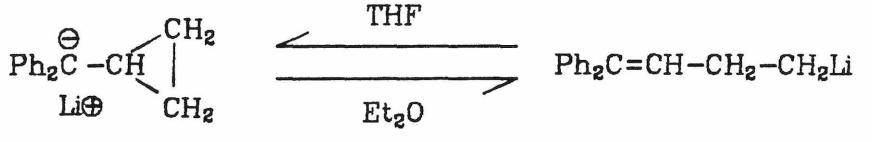
INTRODUCTION

Cyclopropylmethyllithium is unstable at -70°C and quickly rearranges to 3-buten-1-yllithium in a 10:1 mixture of petroleum ether and diethyl ether; tetrahydrofuran is more effective than diethyl ether in promoting isomerization.[1] The reversible character of this rearrangement was demonstrated by Roberts and co-workers with α-labeled 3-buten-1-ylmagnesium bromide; the half-life for equilibration of α and β positions was 30 hours at 27°C.[2] Conjugative delocalization of the cyclic isomer by substituting phenyl or vinyl groups at the 4-positions of 3-butenyl isomer accelerated equilibration of label.[3]



5 **6**



7 **8**

To increase resonance stabilization of the cyclopropylmethyl carbanions, Maercker and Roberts replaced magnesium with alkali metals in the diphenyl substituted system.[4] Cyclopropyldiphenylmethylpotassium (**6**), a deep-red com-

pound, was prepared by Na-K alloy cleavage of cyclopropyldiphenylmethyl methyl ether in tetrahydrofuran or diethyl ether. Cyclopropyldiphenylacetic acid was the only acid product obtained following carbonation. When the organopotassium **6** was transmetalated with lithium bromide in diethyl ether, the color of the solution changed from deep-red to brown. Carbonation gave 5,5-diphenyl-4-pentenoic acid indicating that cyclopropyldiphenylmethyllithium (**7**) had rearranged to 4,4-diphenyl-3-buten-1-yllithium in diethyl ether. Addition of tetrahydrofuran (50% by volume) reversed the color back to deep-red; carbonation gave cyclopropyldiphenylacetic acid. Maercker and Roberts were the first to observe a retro cyclopropylmethyl : 3-buten-1-yl organometallic rearrangement. The ability to control the equilibrium populations with solvent composition was the most interesting aspect of the rearrangement of cyclopropyldiphenylmethyllithium and 4,4-diphenyl-3-buten-1-yllithium system.

Initially, our purpose was to exploit the cyclisation of 4,4-diphenyl-3-buten-1-yllithium for synthesis of related compounds. However, the unique properties of this organolithium rearrangement rekindled our interest in Maercker's work. The results of this reinvestigation are grouped into three chapters. Chapter I describes the development of synthetic methodology for preparation of organolithiums **7** and **8**. The drawback of Maercker's route was the abundance of contaminants in the organolithium solutions. Some preliminary results suggested that the contaminating alkoxide and halide salts present under Maercker's conditions may be influencing the kinetics of rearrangement. Hence, considerable effort was expended to developing new synthetic strategies superior to Maerkcer's original route.

Chapter II presents a nuclear magnetic resonance characterization of cyclopropyldiphenylmethyllithium. 4,4-Diphenyl-3-buten-1-yllithium was not amenable to successful NMR observation because homogeneous solutions could

not be prepared. Chapter II also addresses the existence of delocalization of the carbanionic nonbonding electron pair into low-lying molecular orbitals of the cyclopropyl substituent. In Chapter III, a study of the position of the organolithium equilibrium in six different solvents is evaluated. These results are used to construct a candidate mechanism for rearrangement of cyclopropyldiphenylmethyllithium and 4,4-diphenyl-3-buten-1-yllithium.

Chapter IV describes efforts to characterize the cyclopropyldiphenylmethyl : 4,4-diphenyl-3-buten-1-yl radical rearrangement. The radical rearrangement is interesting in it s own right but also has direct bearing upon the correpsonding organolithium rearrangement. Ortho-cylisation products are observed in products from some organolithium reactions which may be evidence of radical participation.

I. METHODOLOGY FOR ORGANOLITHIUM PREPARATION

In this chapter the synthetic strategies for preparation of 4,4-diphenyl-3-buten-1-yllithium and cyclopropyldiphenylmethyllithium are presented. Emphasis is placed on the success of each method for generating the desired organolithiums in good yields and free of contaminants. A detailed discussion of the product-formation mechanisms is reserved for later chapters.

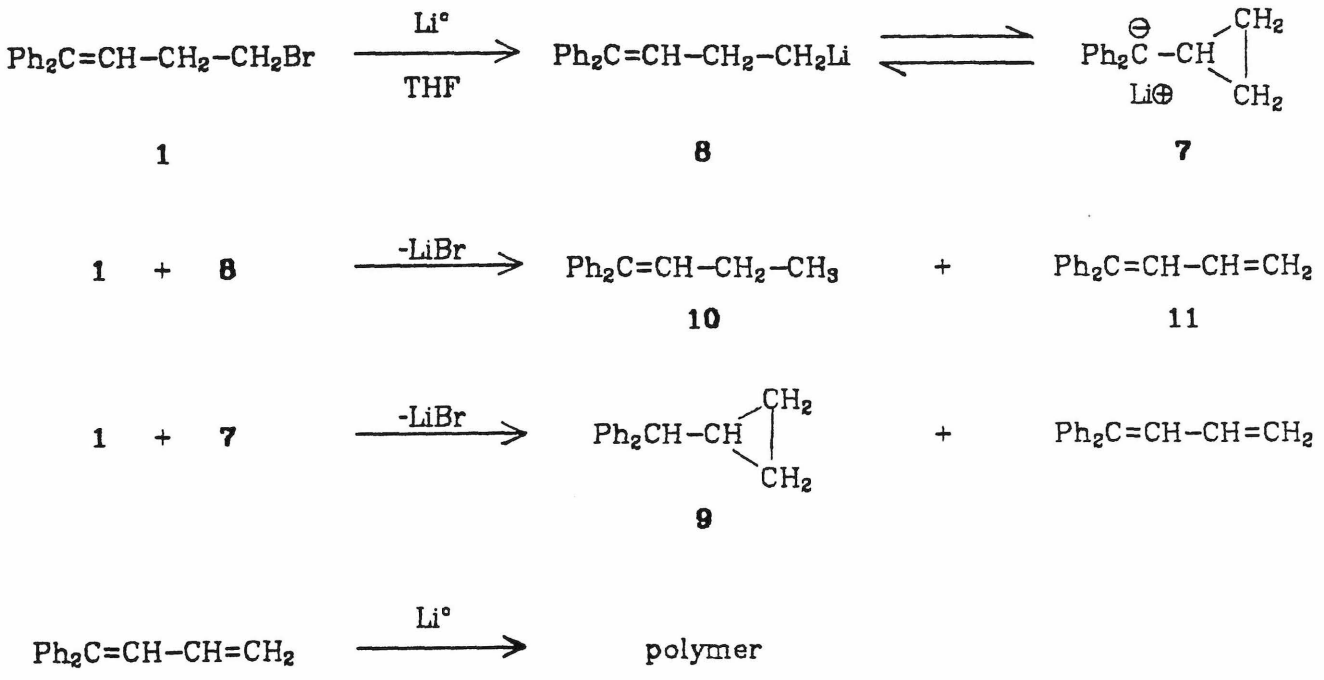
A. Cyclopropyldiphenylmethyl Methyl Ether Cleavage with Lithium

Generally, ether cleavage is an unwanted side reaction; however, both benzyllithium[5] and allyllithium[6] have been prepared from methoxy-precursors. Maercker reported Na-K cleavage of cyclopropyldiphenylmethyl methyl ether, **5**.[4] The cleavage of methyl ether **5** with 140-mesh lithium powder was sluggish. A stirred tetrahydrofuran solution containing 2.6 molecular equivalents lithium, stirred tetrahydrofuran solution containing 2.6 molecular equivalents lithium, after 4 h at 25°C, on carbonation afforded cyclopropyldiphenylacetic acid, **12**, in 22% yield; 45% of the unreacted starting material was recovered. Longer reaction times actually decreased the yields of **12** and produced significant amounts of cyclopropyldiphenylmethane, **9**, and 1,1-diphenyl-1-butene, **10**. These results indicated lithium cleavage of methyl ether **5** was unsuitable for our needs.

B. Reaction of 4-Bromo-1,1-diphenyl-1-butene with Lithium

4-Bromo-1,1-diphenyl-1-butene, **1**, reacts slowly with excess lithium powder (140-mesh) at 25°C in tetrahydrofuran or diethyl ether. No reaction was observed with other forms of lithium metal. A complex mixture of products including 3,4-dihydro-1-phenylnaphthalene, **15**, was obtained from of **1** and lithium(1%)-sodium alloy. A discussion of the formation of phenylnaphthalene compounds in organometallic reactions is presented in a Chapter III. The reaction times necessary for consumption of starting material varied greatly, 3 to 55 h, depending upon the scale and rate of bromide addition to lithium. A trace of acid product was obtained after carbonation; neutral products generally comprised 95% of the mass balance. GC and ^{1}H NMR analysis identified three major products: cyclopropyldiphenylmethane, **9**, 1,1-diphenyl-1-butene, **10**, and 1,1-diphenyl-1,3-butadiene, **11**.

The important difference between lithium powder reaction with **1** in tetrahydrofuran vs. diethyl ether is in the ratio of isomeric hydrocarbons [**9**]/[**10**]. In tetrahydrofuran a 4.0 ratio was produced while in diethyl ether, the ratio of hydrocarbons was 0.3. Refluxing dimethyl ether, bp-18°C, resulted in a hydrocarbon ratio of 0.2 along with traces of unidentified acid product. A mechanism for the reaction of **1** with lithium powder is shown in Scheme 1. Isolated yields of diene **11** varied because polymerization did not occur to same extent under different conditions. Substantial mass inbalance from polymeric resins adhering to glass surfaces in the reaction workup was common. The mechanism shown above is consistent with product analysis and was confirmed by direct ^{1}H NMR analysis of an *in situ* reaction. Figure 1 displays five spectra taken over a 3.4 h period. The spectra in Figure 1 show a decrease in starting material, **1**,



Scheme 1.

with concomitant growth of cyclopropyldiphenylmethane, **9**, and 1,1-diphenyl-1,3-butadiene, **11**. **9** and **11** were formed in roughly equal amounts consistent with the proposed mechanism. After a 1 h reaction time, polymerization of diene **11** was observed; at reaction end, all of **11** was converted to polymer. By a similar procedure, diene **11** in tetrahydrofuran was quickly consumed by 140-mesh lithium powder within 1-2 h, giving the same broad resonances as in Figure 1.

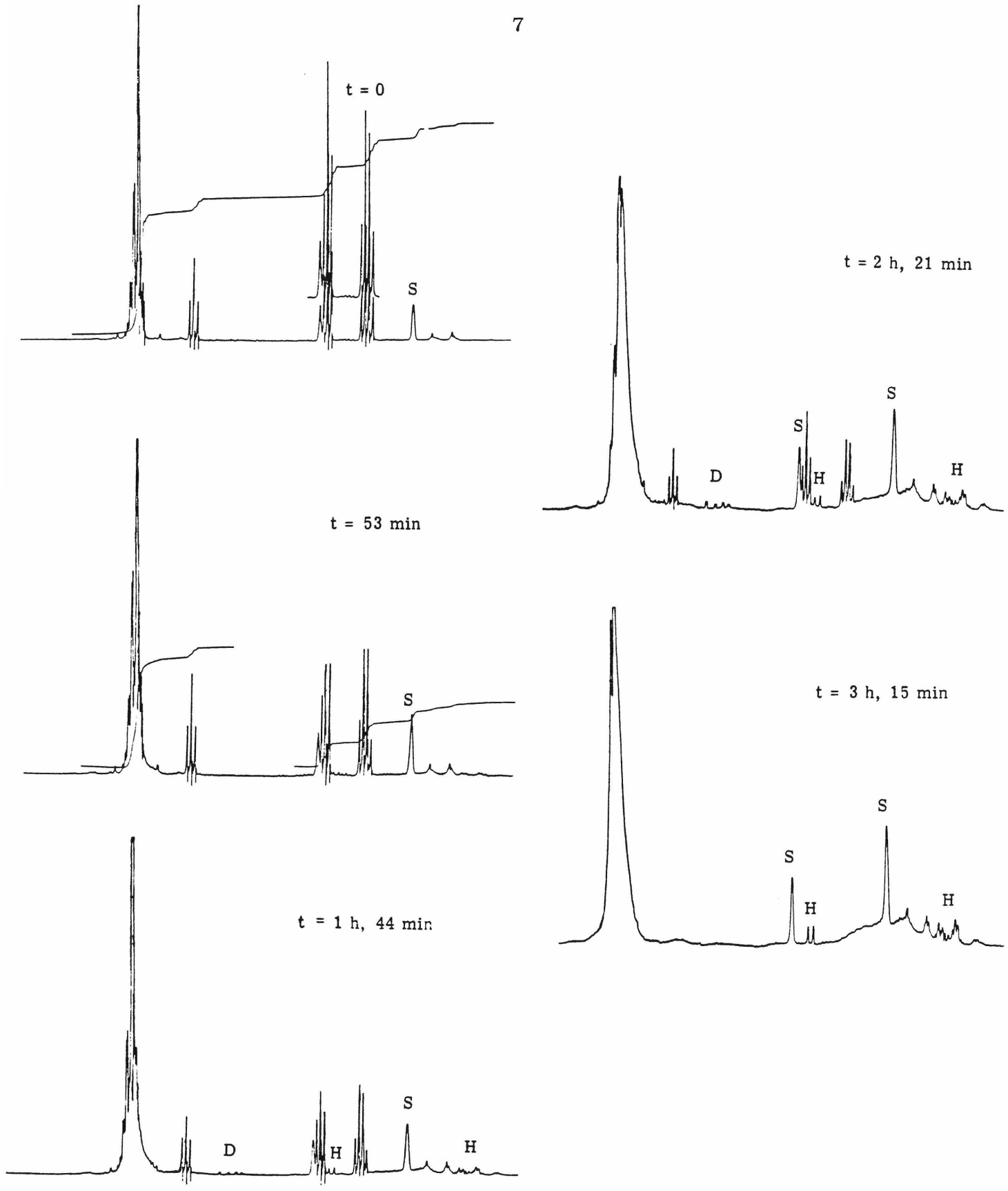
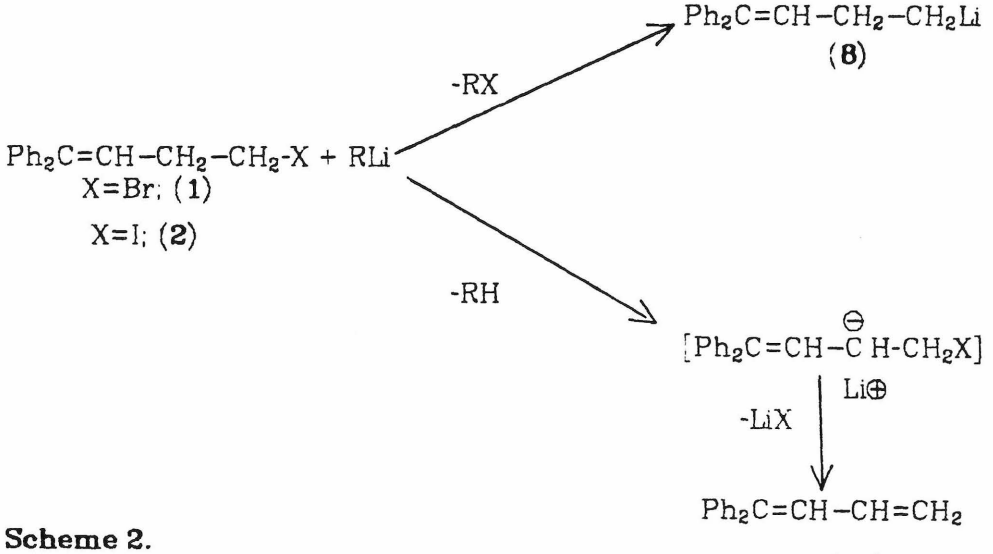


Figure 1. ^{1}H NMR of the *in situ* reaction of 4-bromo-1,1-diphenyl-1-butene with 140-mesh lithium in tetrahydrofuran-d_8 at 25° C as a function of time: residual solvent resonances = S; cyclopropyldiphenylmethane = H; 1,1-diphenyl-1,3-butadiene = D.

Under the conditions used for Figure 1, no **10** was produced. 4,4-Diphenyl-3-buten-1-yllithium is more reactive than cyclopropyldiphenylmethyllithium attacking nondeuterated tetrahydrofuran readily; this accounts for the observation of **10** in reactions run in nondeuterated tetrahydrofuran. NMR analysis of the *in situ* reaction of **1** with lithium powder in diethyl ether was not carried out.

C. Lithium-Halogen Exchange of 4-Halo-1,1-diphenyl-1-butene

Lithium-halogen exchange of 4-iodo-1,1-diphenyl-1-butene, **2**, and 4-bromo-1,1-diphenyl-1-butene, **1**, with an alkyllithium was not competitive with allylic proton abstraction from starting material.



Scheme 2.

The lability of the allylic protons in **1** was demonstrated in the previous section. Attempts to suppress the proton abstraction in favor of the kinetically controlled lithium-halogen exchange met with little success. Results from reactions

run under different conditions are given in Table I.

Table I. Lithium-Halogen Exchange

Conditions[a,b,c]	T,°C	Percent Yield[d]			
		Substrate	**9**	**10**	**11**
X=Br, 1.0 *n*-BuLi, THF	-77	8	0	0	81
X=Br, 1.7 *n*-BuLi, THF	-100	34	0	0	51
X=Br, 1.0 *s*-BuLi, THF	-100	37	7	17	3
X=Br, 1.0 *tert*-BuLi Me_2O/THF(2/1)	-130	33	10	32	2
X=I, 1.0 *tert*-BuLi pet ether/THF(1/2)	-130	13	0	54	22

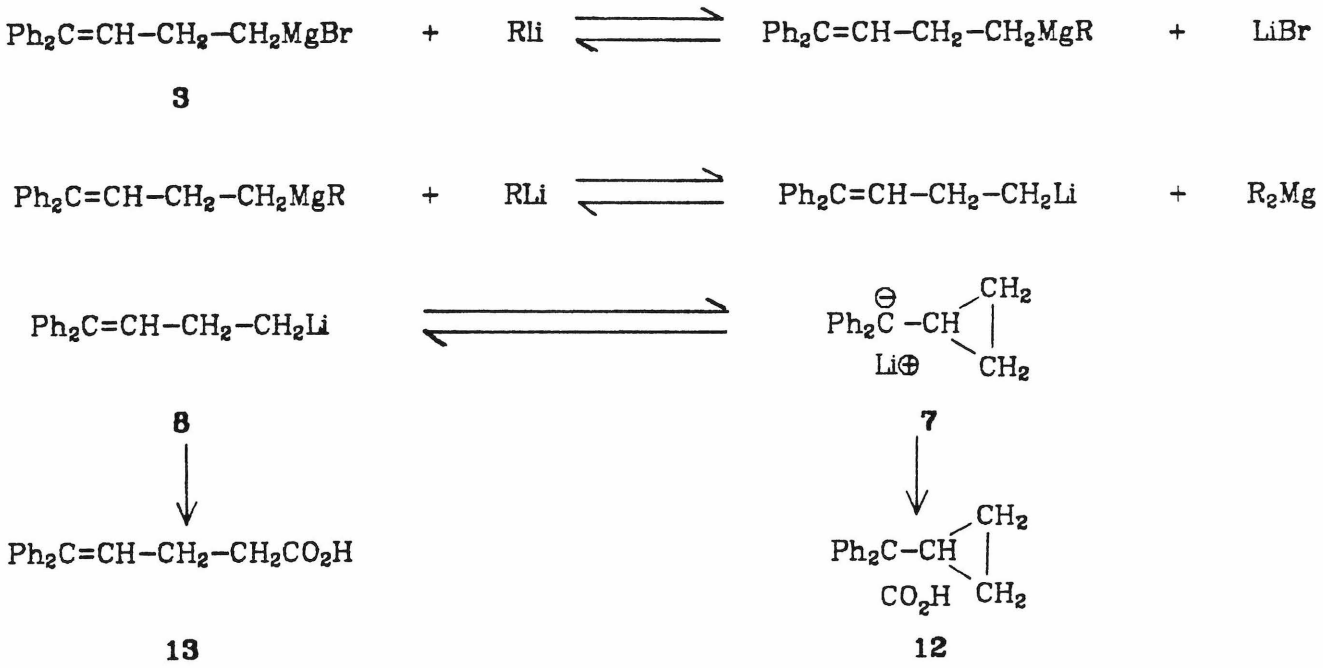
[a]Reaction times were all 5 min. [b]*tert*-Butyllithium exchange was accompanied by four minor, unidentified products each constituting less than 1% of total products. [c]Abbreviations: THF=tetrahydrofuran; Me_2O=dimethyl ether; pet ether=low boiling fraction of petroleum ether; BuLi=butyllithium. [d]Yields based on products from deuterium oxide quench; the "zero" entries mean none was detected by GC or NMR and therefore corresponds to less than 1%.

Under most conditions, the formation of diene **11** was immediate and quantitative upon mixing reactants. Irreversible lithium bromide loss from transient 4-bromo-4,4-diphenylbut-3-en-2-yllithium induced rapid conversion of **1** and **2** to diene **11**.

D. Transmetalation of 4,4-Diphenyl-3-buten-1-ylmagnesium Bromide

Preliminary results suggested transmetalation of 4,4-diphenyl-3-buten-1-yl-

magnesium bromide, **3**, with an organolithium could be a viable preparative method for the desired organolithiums **7**, **8**. The Grignard is easily prepared from **1** in either tetrahydrofuran or diethyl ether. To freshly prepared **3**, two molecular equivalents of organolithium (*tert*-C_4H_9Li, C_6H_5Li, CH_3Li) were added at -78°C (see Scheme 3).



Scheme 3.

In some experiments, lithium bromide was precipitated as a p-dioxane complex from the reaction solution before adding second molecular equivalents organolithium. Following organolithium addition, tetrahydrofuran was added such that the solvent ratio: [tetrahydrofuran]/[diethyl ether]≥ 0.5. The reaction mixture was then warmed to 25°C and stirred for 5-8 h. Table II summarizes the results from transmetalations using three different organolithium reagents. Cyclopropyldiphenylmethane, **9**, is a byproduct of Grignard preparation; yields of **9** in Table II are not relevant in evaluating the transmetalation. 1,1-Diphenyl-1-butene, **10**, also is a Grignard byproduct; but the majority of **10** obtained from

Table II. 4,4-Diphenyl-3-buten-1-ylmagnesium Bromide Transmetalation

Organolithium	Percent Yield[a]			
	12	**13**	**9**	**10**
phenyllithium	32	38	5	25
methyllithium	0	67	5	12
tert-butyllithium	0	70	6	18

[a]Based on products following carbonation; meaning of a zero entry given in previous Table.

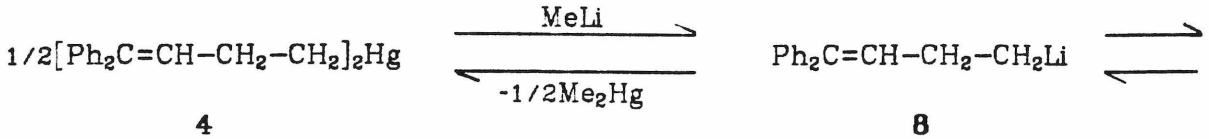
transmetalation is from solvent attack over the extended reaction times. Methyllithium transmetalation was monitored in a separate experiment over a 44 h period by GC analysis of aliquots subjected to hydrolysis. After one hour, [**9**]/[**10**]= 0.2; by the end of 44 h, this ratio had only increased to 0.7. Hoping to catalyze cyclisation of organolithium **8** as it was formed, the effect of added 12-crown-4 was explored. The lithium cation cryptand had no observable effect on transmetalation.

Grignard transmetalation is too slow to be of any practical value. A greater drawback was complex product mixtures; an inevitable consequence of the reversible nature of all Grignard/organolithium transmetalations.[7]

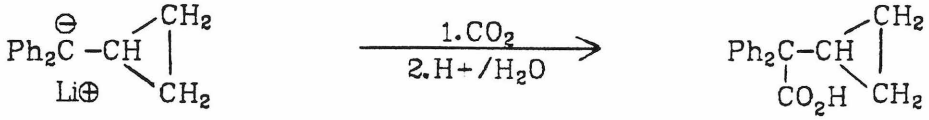
E. Transmetalation of Bis[4,4-diphenyl-3-buten-1-yl]mercury

Bis[4,4-diphenyl-3-buten-1-yl]mercury, **4**, was synthesized from 4-bromo-

1,1-diphenyl-1-butene by a one-pot procedure. Addition of 0.5 molecular equivalents mercuric bromide to Grignard **3** afforded pure **4** in 70% yield.



4 **8**



7 56%**12**

Addition of two molecular equivalents methyllithium to a tetrahydrofuran solution of **4** cooled to -78°C effected immediate deep-red discoloration. Carbonation of the solution gave cyclopropyldiphenylacetic acid, **12**, as the **sole** product. The yield of acid **12** was disappointingly low, 56%. ^{1}H NMR analysis of an *in situ* transmetalation indicated total conversion of bis-mecurial **4** to cyclopropyldiphenylmethyllithium, **7**. Transmetalation is a reversible process and in 100% diethyl ether does not favor the side of organolithiums **7** and **8**. In presence of a more strongly coordinating solvent like tetrahydrofuran, any 4,4-diphenyl-3-buten-1-yllithium formed immediately isomerizes to **7**. Cyclisation **8** in presence of tetrahydrofuran drives the transmetalation in the desired direction. In fact, 15% tetrahydrofuran in diethyl ether (v/v) is sufficient for complete conversion of bis-mercurial **4** to **7**.

Smart[8] prepared 3-butenyllithium by the transmetalation of bis[3-butenyl]mercury with lithium metal. There was no reaction observed for **4** and excess 140-mesh lithium powder. Benzene, cyclopentane, and benzene:diethyl ether (1:1) were tried as reaction medium for lithium transmetalation. The

reaction of **4** with sodium-potassium (Na-K) alloy is rapid at 0°C producing a deep-red solution within minutes. Carbonation of the Na-K reaction gave a mixture of cyclic acid **12** (70%) and cyclopropyldiphenylmethane, **9** (21%).

F. Alkyllithium Metalation of Cyclopropyldiphenylmethane

For a detailed study of cyclopropyldiphenylmethane metalation, moderately large amounts of substrate were needed. Diphenylmethylenecyclopropane was prepared using Utimoto's[9] method. Hydrogenation of this alkene at 50 psi in presence of platinum oxide catalyst afforded cyclopropyldiphenylmethane in good yields.

Alkyllithiums attack tetrahydrofuran and to a lesser degree diethyl ether by α-hydrogen abstraction with subsequent formation of ethylene and a lithium enolate salt. The half-life of *n*-butyllithium in tetrahydrofuran at 25°C is only 10 min.[10] Tetrahydrofuran-d_8 is stable up to ten times longer than nondeuterated tetrahydrofuran.[11] To minimize solvent attack, reactions were carried out at low temperatures. Reaction of **9** with 1.5 molecular equivalents *s*-butyllithium for 90 h at -55°C afforded only traces of cyclopropyldiphenylacetic acid, **12**, upon carbonation. Greater than 95% starting material was recovered. Much better results were obtained using *tert*-butyllithium as the metalating reagent. The yields of cyclopropyldiphenylacetic acid, **12**, from *tert*-butyllithium metalation under different conditions are shown in Table III. In all three experiments, the only product observed was **12**; highest yield obtained was 55%. A major drawback of *tert*-butyllithium metalation is the necessity for excess alkyllithium; the

Table III. *tert*-Butyllithium metalation of cyclopropyldiphenylmethane in tetrahydrofuran.

Substrate Conc, M	Mol Equiv *tert*-BuLi	T°,C	t, h	Percent Yield **12**
0.16	2.2	-18	1	39
0.15	1.0	-28	1	44
0.30	1.0	-66	12	55

desired product, **12**, was inevitably contaminated with di-*tert*-butyl ketone and 2,2-dimethylpropanoic acid, the carbonation products from *tert*-butyllithium. Longer reaction times did not improve yields. A strong ethylene resonance at 5.3 ppm in the ^{1}H NMR spectrum during *in situ* metalation indicated a significant amount of solvent attack over periods greater than 2 h, even at -50°C. Metalation of **9** with *tert*-butyllithium did not occur in 100% diethyl ether.

Bank used *tert*-butyllithium to metalate 1,1-diphenylethane and reported similar drawbacks to the use of such a reactive alkyllithium for hydrocarbon metalations.[12]

G. Trimethylsilylmethyllithium Metalation of Cyclopropyldiphenylmethane

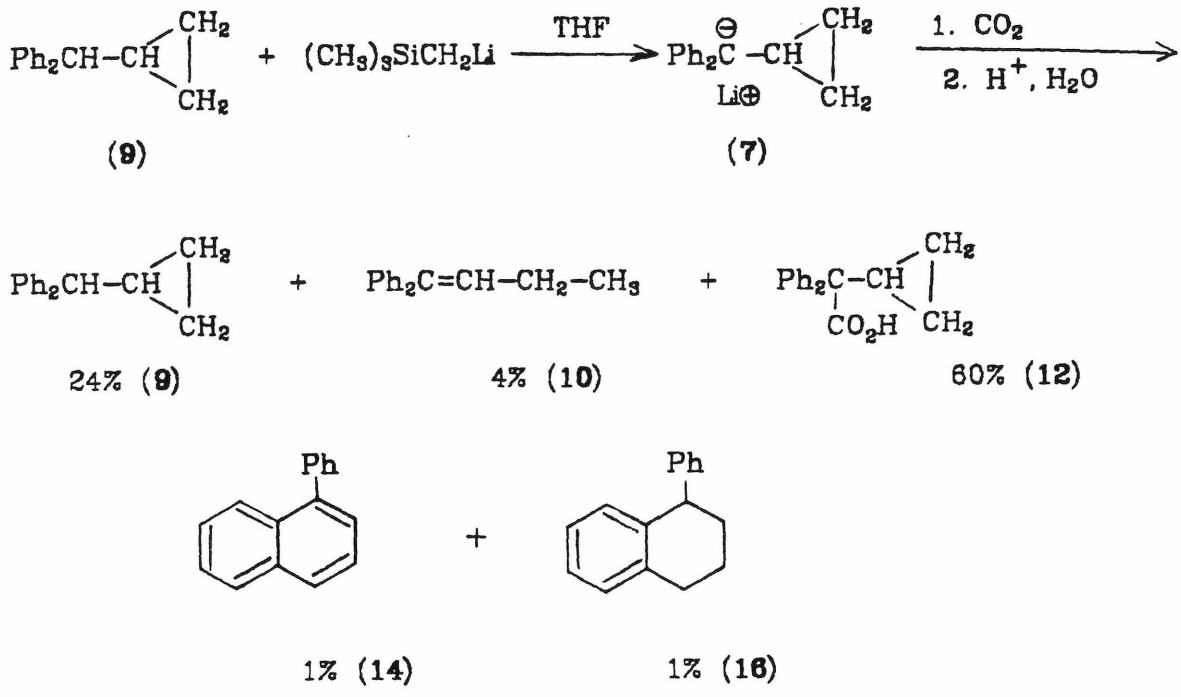
Trimethylsilylmethyllithium is a very unique reagent for metalation of weakly acidic compounds. Trimethylsilylmethyllithium has proven to be the

metalating reagent of **choice** for organolithium preparation directly from cyclopropyldiphenylmethane. From ^{1}H NMR data, the pK_a of tetramethylsilane can be estimated using a relationship reported by Schaeffer[13].

$$pK_a = 3.20\cdot\Delta + 35.12$$
$$\Delta=[\delta(\text{ppm}) \text{ of TMS}]-[\delta(\text{ppm}) \text{ of } Me_3SiCH_2Li]$$

The methylene protons of trimethylsilylmethyllithium are observed at δ = -2.18 ppm; in tetrahydrofuran-d_8; from this a pK_a of 41.2 is estimated for tetramethylsilane. The basicity of trimethylsilylmethyllithium is comparable with primary alkyllithums. Despite the high pK_a value of tetramethylsilane, trimethylsilylmethyllithium displays remarkable stability in tetrahydrofuran solutions. For a 0.33 M solution of trimethylsilylmethyllithium in tetrahydrofuran, 26% had decomposed after 18.5 h at 25°C. Another advantageous property of trimethylsilylmethyllithium is a vapor pressure sufficient to facilitate vacumn sublimations.

The results of a product study of trimethylsilylmethyllithium metalation are shown above in Scheme 4. Direct ^{1}H NMR analysis of an *in situ* trimethylsilylmethyllithium metalation of cyclopropyldiphenylmethane, **9**, indicated 90% conversion to cyclopropyldiphenylmethyllithium, **7**, after 37 h at room temperature. Longer reaction times or additional trimethylsilylmethyllithium did not improve yields of **7**. Metalation did not occur in diethyl ether solutions. For reactions utilized in product studies, there was 24-30% unreacted **9** at reaction end. The reactivity of 4,4-diphenyl-3-buten-1-yllithium, **8**, is demonstrated by the 4% yield of hydrocarbon **10**. The organolithium equilibrium lies heavily toward the side of **7** in tetrahydrofuran; however, attack by **8** is fast enough to afford observable quantities of 1,1-diphenyl-1-butene, **10**.

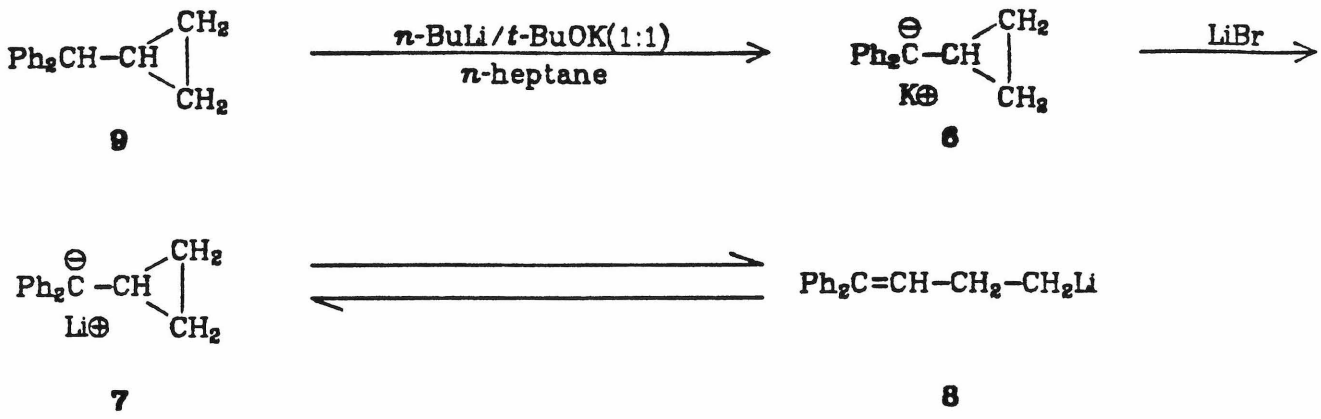


Scheme 4.

H. Transmetalation of Cyclopropyldiphenylmethylpotassium

In the presence of postassium *tert*-butoxide, *n*-butyllithium metalates weakly acidic hydrocarbons.[14] For resonance-stabilized organometallic species, metal-hydrogen exchange leads to an organopotassium which precipitates from nonpolar media. The product can be washed with fresh solvent to remove contaminants. Transmetalation with anhydrous lithium bromide in the solvent of choice cleanly affords the desired organolithium. Schlosser has demonstrated the synthetic utility of this double metal-exchange method to obtain relatively pure organolithiums.[15]

The double-metal exchange route proved to be the only preparative method that did introduce tetrahydrofuran prior to organolithium generation. The



starting material, **9**, was stirred for 2 h at 25°C with 1.05 molecular equivalents *n*-butyllithium/potassium *tert*-butoxide (1:1) in *n*-heptane. Cyclopropyldiphenylmethylpotassium, **6**, precipitated as a brown-red solid which was washed with fresh *n*-heptane seven times. Traces of *n*-heptane were removed under reduced pressure. Dissolving **6** in solvent of choice, 1.05 molecular equivalents lithium bromide was added to the solution at -78°C. Mass balance was consistently low for double metal-exchange. A detailed presentation of results and discussion of operative mechanisms is reserved for Chapter III.

II. NUCLEAR MAGNETIC RESONANCE OF CYCLOPROPYLDIPHENYLMETHYLLITHIUM

A nuclear magnetic resonance study of cyclopropyldiphenylmethyllithium, **7**, is reported in this Chapter. This NMR study will primarily address the degree of cyclopropyl stabilization in **7**, relative to diphenylmethyllithium. There are two conceivable interactions of a cyclopropyl group with a negatively charged center: (1) conjugative delocalization of the electron pair at the carbon with the low-lying MO orbital of cyclopropyl; (2) nonconjugative stabilization from the relatively higher *s*-character in the bond between the anionic center and cyclopropyl. Proton, lithium-7, and carbon-13 nuclear magnetic resonance results are discussed in the first three sections. The chemical shifts of **7** are very similar to diphenylmethyllithium systems indicating that there is little, if any, interaction between the electron pair and cyclopropyl group. Some aspects of the ^{1}H NMR spectrum of cyclopropylphenylmethyllithium are reported in the last section with regard to possible cyclopropyl stabilization. Also in the last section are the results of an equilbrium study involving cyclopropyldiphenylmethyllithium and 1,1-diphenyl-1-ethyllithium. Using ^{1}H NMR analysis, a rough comparision of relative stability in the two diphenylmethyllithium systems is made.

The delocalized organolithium, **7**, is stable for days at room temperature in tetrahydrofuran. Regrettably, 4,4-diphenyl-3-buten-1-yllithium, **8**, was not amenable to NMR characterization because it displays high reactivity, decomposing within minutes at 25°C in tetrahydrofuran. More disadvantagous was the heterogeneity of ethereal solutions of **8** preventing preparation of suitable NMR

samples.

Before presenting our NMR results, a brief discussion of the nature of organolithium species in solutions is warranted. Cyclopropyldiphenylmethyllithium is more accurately called a lithium salt of the cyclopropyldiphenylmethyl carbanion. The work of O'Brien indicated the lithium salt of the diphenylmethyl carbanion existed as both solvent-separated and contact ion pairs.[16] For delocalized carbanions having a potassium, sodium, or cesium counterion, the predominant species is the contact ion pair. Both ^{1}H and ^{13}C NMR chemical shifts in carbanions are sensitive to solvent and temperature; this effect is especially pronounced when lithium is the counterion. O'Brien and co-workers utilized variable temperature ^{13}C NMR as a diagnostic probe of solvation in diphenylmethyl carbanions.[16] Low temperatures favored solvent-separated ion pairs. A downfield shift for the charge-bearing carbon and an upfield shift for the aromatic para carbons were taken as evidence for increased participation of solvent-separated ion pairs. The influence of solvent was profound for diphenylmethyllithium. Shielding of the charge-bearing carbon increased in the order: 2-methyltetrahydrofuran (δ=69.9 ppm)> tetrahydrofuran (δ=76.5 ppm)> 1,2-dimethoxyethane (δ=76.7 ppm). From analysis of his data taken at several temperatures, O'Brien determined the equilibrium constant ($\mathbf{K_{eq}}$) for:

$$R^{\ominus}||Li^{\oplus} \underset{}{\overset{K_{eq}}{\rightleftharpoons}} R^{\ominus}Li^{\oplus}$$

solvent-separated ion pair contact ion pair

The value of $\mathbf{K_{eq}}$ for diphenylmethyllithium in a tetrahydrofuran was 2.99 (26° C). The solvated structure of **7** would be similar to that of diphenylmethyllithium; we assume **7** exists predominantly as solvent-separated ion pairs in tetrahydrofuran.

A. Lithium-7 Nuclear Magnetic Resonance

Lithium-7 nuclear magnetic resonance (^{7}Li NMR) has been useful in characterizing structures and exchange processes of organolithium compounds.[17,18] Oliver and co-workers reported a thorough analysis of the contributing factors to the chemical shift of a ^{7}Li nucleus.[19] They also compiled the first comprehensive listing of ^{7}Li chemical shifts for a variety of organolithiums. Simple alkyllithiums (covalent carbon-lithium bonding) have chemical shifts downfield of inorganic lithium (70%lithium bromide in H_2O).

Table IV. ^{7}Li NMR chemical shifts of diphenylmethyllithium derivatives in tetrahydrofuran at 25° C.

Organolithium	δ^a, ppm	Ref
diphenylmethyllithium[b]	-1.36	20
1,1-diphenyl-1-ethyllithium	-1.47	this work
1,1-diphenyl-1-hexyllithium	-1.47	21
cyclopropyldiphenylmethyllithium	-1.35	this work

[a]Chemical shifts (δ) are relative to lithium bromide, 70%aqueous solution; negative shifts are upfield from reference. [b]Original data converted using: δ_{LiBr}, ppm = δ_{LiNO_3}, ppm + 0.2ppm.

Delocalized organolithiums (benzyl-, diphenylmethyl-, and triphenylmethylorganolithiums) display broad resonances upfield from lithium bromide. A tetrahydrofuran solution of cyclopropyldiphenylmethyllithium, **7**, was prepared via *tert*-butyllithium metalation of hydrocarbon **9**. Table IV contains the ^{7}Li NMR

data recorded at 34.8 MHz for **7** and 1,1-diphenyl-1-ethyllithium; literature data for similar ionic organolithium compounds are included for comparision. The chemcial shift of **7**, δ=-1.36 ppm, is typical for diphenylmethyllithium systems. Little is known about the influence of alkyl substituents upon the ^{7}Li shifts of arylmethyllithiums. However, the ^{7}Li NMR data suggest that the lithium-7 nucleus in 1,1-diphenyl-1-ethyllithium and 1,1-diphenyl-1-hexyllithium is more positive relative to **7** or the difference in shifts may reflect a ring current effect which differs for the substituted diphenylmethyllithiums. The ^{7}Li resonance of **7** changed little over the temperature range -90 to 25° C. The ^{7}Li spectra of **7** also contained a broad resonance at δ=+0.75 which is assigned to excess *tert*-butyllithium.

B. Carbon-13 Nuclear Magnetic Resonance

Carbon-13 nuclear magnetic resonance (^{13}C NMR) has been valuable in characterizing the structures and charge distribution of organolithium compounds. Fraenkel exploited the coupling between ^{13}C and ^{6}Li to define the aggregation of propyllithium.[22] Several studies of delocalized organolithiums using ^{13}C NMR have been reported.[8,20,21,23] The ^{13}C NMR characterization of cyclopropyldiphenylmethyllithium, **7**, is presented here. Solutions of **7** in tetrahydrofuran-d_8 were prepared via trimethylsilylmethyllithium metalation of cyclopropyldiphenylmethane, **9**. Figure 2 displays the 125.7 MHz FT ^{13}C NMR spectrum of **7** (proton coupled). The chemical shift data for **7** plus three similar organolithium systems for comparison purposes is presented in Table V.

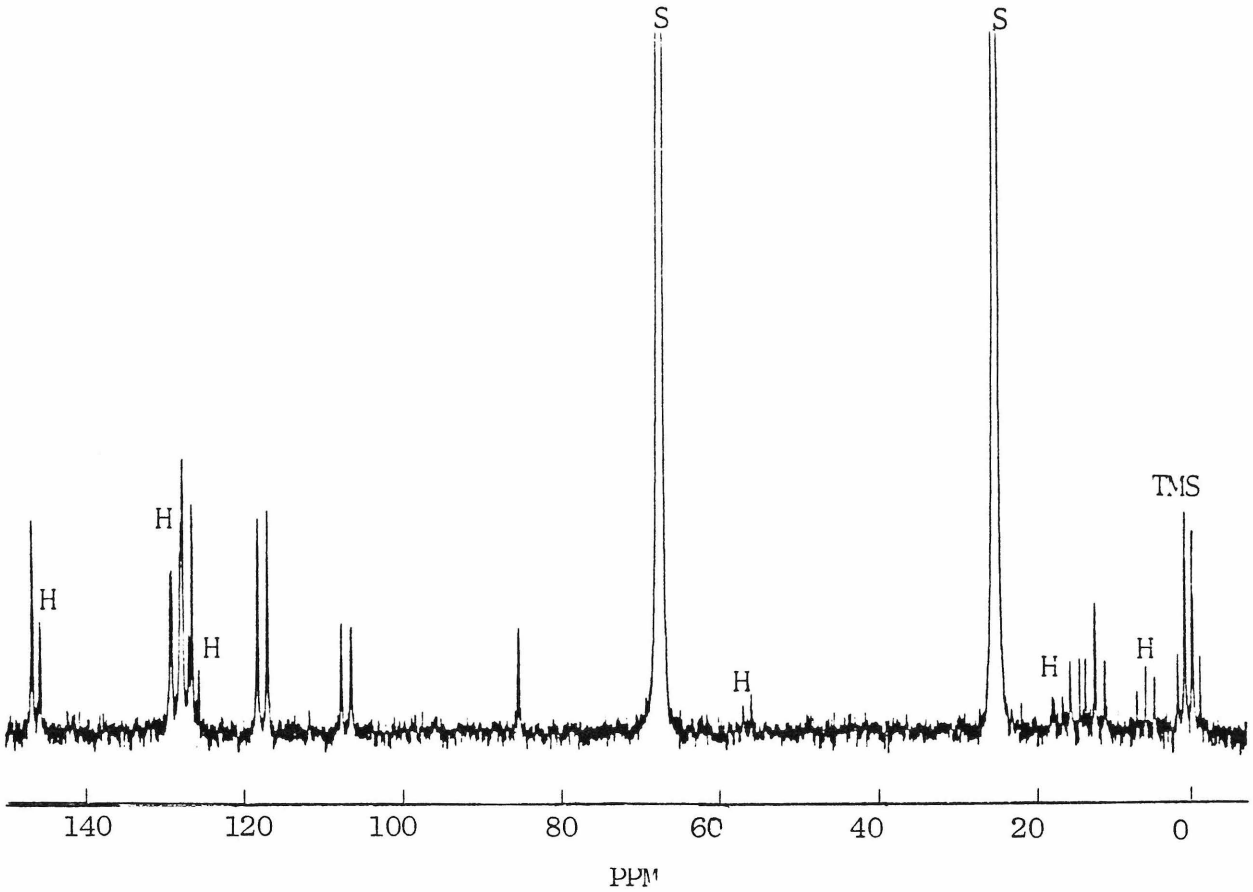
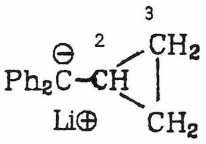


Figure 2. 125.7 MHz ^{13}C FT NMR spectrum of cyclopropyldiphenylmethyllithium in tetrahydrofuran-d_8 (0.7 M) at 25° C: cyclopropyldiphenylmethane=H; solvent=S; tetramethylsilane=TMS.

Inspection of Table V indicates the nature of delocalization in **7** is very similar to that in diphenylmethyllithium and 1,1-diphenyl-1-ethyllithium. In benzyl-, diphenylmethyl-, and triphenylmethyllithium, ^{13}C NMR[24] and ^{1}H NMR[25] data can be used to estimate π-electron density within the delocalized array. The NMR data observed in alkyl-substituted benzyl carbanions did fit a linear chemical shift-π-density relationship very well.[26] Consequently the chemical shifts cannot be used to evaluate distribution of the negative charge in cyclopropyldiphenylmethyllithium.

The ^{13}C NMR chemical shift of the charge-bearing carbon, C(1), in **7** is shifted downfield 28.96 ppm relative to cyclopropyldiphenylmethane, **9**. This

Table V. Carbon-13 chemical shifts[a,b] of 4,4-diphenyl-3-buten-1-yllithium derivatives in tetrahydrofuran at 25°C. Figures in square brackets are for $\Delta\delta$; the shift of the organolithium relative to its hydrocarbon precursor.

Organolithium	δ, ppm						
	C(1)	C(i)	C(o)	C(m)	C(p)	C(2)	C(3)
$Ph_2\overset{\ominus}{C}H$ $Li\oplus$	76.8 [+34.4]	147.3 [+5.4]	117.5 [-11.9]	128.0 [-.8]	107.3 [-19.1]		
$Ph_2\overset{\ominus}{C}-\overset{2}{C}H_3$ $Li\oplus$	81.4 [+35.54]	147.0 [+.6]	116.9 [-11.25]	127.8 [-.03]	106.8 [-19.94]	19.3 [-2.62]	
$Ph_2\overset{\ominus}{C}-(CH_2)_4-CH_3$ $Li\oplus$	82.8						
	85.39 [+28.96]	146.98 [+.98]	117.72 [-11.04]	127.25 [-1.72]	107.14 [-19.28]	14.98 [-2.32]	12.38 [+6.69]

[a]Chemical shifts relative to internal tetramethylsilane; abrreviations for carbons: C(i)=ipso, C(o)=ortho, C(m)=meta, C(p)=para; numbers refer to structures. [b]Diphenylmethyllithium: ref 23; 1,1-diphenyl-1-hexyllithium: ref 21; 1,1-diphenyl-1-ethyllithium: ref 12.

shift is the result of the negative charge residing on C(1) in organolithium **7** which would shield the carbon nucleus and shift the ^{13}C resonance upfield. Opposing this effect is a downfield shift experienced by C(1) due to the hybridization change: $sp^3 \rightarrow sp^2$. If 100 ppm is assumed for a typical hybridization change in diphenylmethyllithium systems,[27] then the localized negative charge on C(1) shifts the resonance 71 ppm upfield. If a similar calculation is performed on 1,1-diphenyl-1-ethyllithium, the localization of charge on C(1) shifts the ^{13}C NMR resonance 63 ppm upfield. The chemical shift of the α-carbon

increases going downward in Table V indicating the partial negative charge residing at the α-carbon is also increasing, the amount of negative charge being greatest in **7**. We emphasize this conclusion assumes the identical hybridization at each organolithium α-carbon.

Steric interactions between ortho hydrogens on different aromatic rings and between these hydrogens and the cyclopropyl substituent prevent formation of a planar delocalized array. The most stabilization would be afforded in a conformation of **7** that maximizes orbital overlap between the charge bearing-carbon, C(1), and the two aromatic ipso carbons, C_i. The average plane formed by these three centers will define the molecular orientation of the delocalized array with respect to other parts of molecule. Examination of a Corey-Pauling-Koltun model of **7** reveals that the methylene cyclopropyl carbons, C(3), lie in the perimeter of this delocalized array. These carbons are subject to the paramagnetic portion of the ring current in the delocalized organolithium. The C(3) carbons are shifted 6.69 ppm downfield in **7** relative to the hydrocarbon, **9**, which is consistent with a paramagnetic ring current effect. The shift experienced by the methine cyclopropyl carbon, C(2), is the result of two opposing influences. An increase in shielding from the localized negative charge on the adjacent carbon, C(1), is felt at C(2) upon organolithium formation. The Corey-Pauling-Koltun model indicates that C(2) also is positioned in the perimeter of the delocalized system. The net result of these two effects is the observed upfield shift, $\Delta\delta_{C(2)}$= -2.32 ppm. This shift is similar to the change in chemical shift observed for the methyl carbon in 1,1-diphenyl-1-ethyllithium $\Delta\delta_{C(2)}$=-2.62 ppm.

C. Proton Nuclear Magnetic Resonance

Proton nuclear magnetic resonance (^{1}H NMR) was extensively utilized in evaluating the various synthetic approaches to organolithiums **7** and **8**. In this section, we wil analyze the characteristics of the ^{1}H NMR spectrum of **7**. Spectra recorded at 90 MHz of cyclopropyldiphenylmethyllithium prepared by four different routes (*tert*-butyllithium and trimethylsilylmethyllithium metalation of **9**, bis-mercurial transmetalation, cyclopropyldiphenylmethylpotassium transmetalation) were not significantly different; chemical shifts were within 0.03 ppm of each other in the aromatic region. Solvent peaks obscured high field resonances in most cases. The best results were obtained from **7** generated by trimethylsilylmethyllithium metalation of **9**. A unique feature of using trimethylsilylmethyllithium is that a tetramethylsilane internal reference is a product. Figure 3 diplays the 500.13 MHz FT ^{1}H NMR spectrum of **7** in tetrahydrofuran-d_8. Unconsumed starting material is also observed in the spectrum.

The aromatic region is first order with two triplets for the meta and para hydrogens and a doublet for the ortho hydrogens. The cyclopropyl methine hydrogen, H(2), is shifted upfield by 0.42 ppm relative to the neutral compound. The methylene cyclopropyl hydrogens cis to the substituent, H'(3), are shifted 0.28 ppm upfield relative to the hydrocarbon. The hydrogens trans to the substituent, H(3), are shifted downfield 0.10 ppm. Complete ^{1}H NMR data for **7** is presented in Table VI along with chemical shifts recorded at 500.13 MHz for 1,1-diphenyl-1-ethyllithium. Some literature data on other diphenylmethyl carbanions is also included for comparision.

The chemical shifts of meta and para hydrogens for all of the diphenyl-

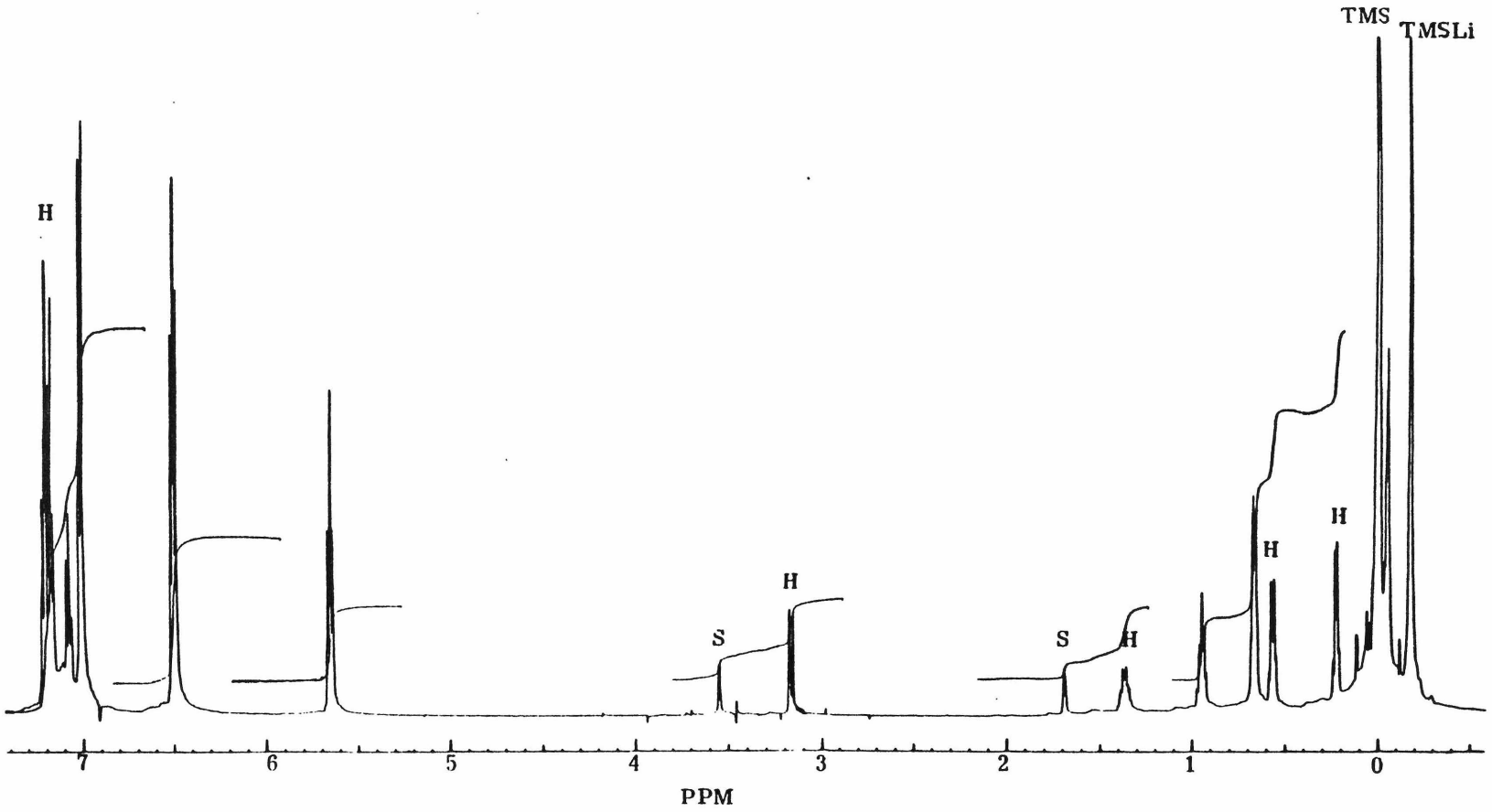


Figure 3. 500.13 MHz FT proton NMR spectrum of cyclopropyldiphenylmethyllithium in tetrahydrofuran-(0.7 M in organolithium) at 25 C: cyclopropyldiphenylmethane=H; residual solvent=S; tetramethylsilane=TMS; trimethylsilylmethyllithium=TMSLi.

Table VI. Proton NMR chemical shifts and coupling constants for diphenylmethyl carbanions in tetrahydrofuran at 25°C.

Anion	Cation	δ,ppm[a]				$^3J_{HH}$,Hz[b]	
		Ortho	Meta	Para	Others	J_{om}	J_{mp}
$Ph_2\overset{\ominus}{C}$-CH(CH_2)-CH_2	K[c]	7.06	6.66	5.78	0.01[CH_2]	8.8	7.0
	Li	7.04	6.52	5.68	0.95[CH] 0.67,-.05[CH_2]	8.0	7.0
$Ph_2\overset{\ominus}{C}$-$(CH_2)_4$-CH_3	Li[d]	6.77	6.37	5.47			
$Ph_2\overset{\ominus}{C}$-CH_3	Li	6.84	6.50	6.52	1.80[CH_3]	8.0	6.9
$Ph_2\overset{\ominus}{C}H$	Li[e]	6.51	6.54	5.65	4.22[CH]	8.2	6.9

[a]Chemical shifts (δ) relative to internal tetramethylsilane. [b]J_{om} = coupling of ortho/meta hydrogens, J_{mp} = coupling of meta/para hydrogens. [c]Ref 4. [d]T = -31°C, Ref 21. [e]Literature data: aromatic shifts from Ref 12; α-hydrogen shift from Ref 20.

methyllithiums in Table VI fall within narrow sets. McKeever's data[21] for 1,1-diphenyl-1-hexyllithium was taken relative to solvent resonance and appears to be discrepant. If a correction of +0.18 ppm is applied, data which have close correspondence with the other compounds are obtained (in ppm): 6.95 (ortho), 6.55 (meta), and 5.65 (para)

The ^1H NMR chemical shifts of the ortho hydrogens vary with organolithium structure. This effect is not a reflection of different charge densities but rather is a steric phenomenon. Steric compression of the ortho hydrogens with each other and with the hydrogens of the alkyl substituent causes the ^1H NMR resonance of the ortho hydrogens to shift downfield. Cheney has described the repulsive interaction between sterically compressed hydrogens.[28] In the ^1H NMR

spectrum, these hydrogens shift to lower field. The data in Table VI support this interpretation and if the corrected δ_{ortho} values for 1,1-diphenyl-1-hexyllithium are used, an ordering of the alkyl substituents with regard to downfield ortho shift (relative to 1,1-diphenyl-1-ethyllithium) can be made; in order of increasing steric demand ($\Delta\delta$, ppm): methyl (0.34) > *n*-hexyl (0.44) > cyclopropyl (0.53). Corey-Pauling-Koltun models are consistent with such a steric ordering.

The upfield shift (relative to **9**) of the methine cyclopropyl hydrogen, H(2), in **7**, is the combined result from two opposing effects: (1) increased shielding from the adjacent negative charge causes and upfield shift; (2) a diamagnetic ring-current effect of the delocalized system. In 1,1-diphenyl-1-ethyllithium, the ring-current effect is more important; the methyl ^{1}H NMR resonance is shifted 2.8 ppm downfield relative to the hydrocarbon.

The methylene cyclopropyl hydrogens are also subject to ring-current effects. Corey-Pauling-Koltun molecular models indicate that the cis hydrogens are above the π system and the trans are in the perimeter, consistent with the observed shifts.

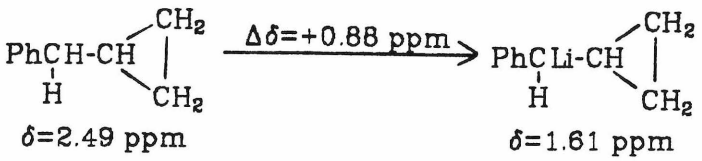
D. Cyclopropyl Stabilization of Organolithiums

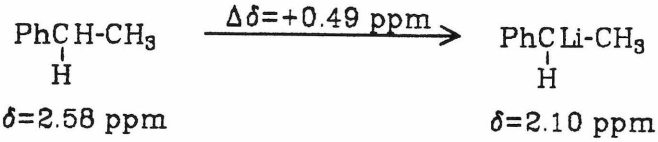
This section reports on two ^{1}H NMR studies which address the possible stabilization of carbanionic centers by cyclopropyl substituents. Perkins and Ward reported a rate enhancement in the base-catalyzed hydrogen exchange of benzylcyclopropane relative to *n*-butylbenzene which they attributed to the

stabilizing influence of cyclopropyl.[29] We present our results for cyclopropylphenylmethane first and secondly, a study on the equilibrium acidity of cyclopropyldiphenylmethane.

The metalation of benzylcyclopropane by trimethylsilylmethyllithium in tetrahydrofuran-d_8 proceeded slowly at room temperature. Analysis by 500.13 MHz ^{1}H NMR indicated a complex solution composition and substantial unreacted starting material. Based on benzyllithium ^{1}H NMR data, cyclopropylphenylmethyllithium was identified. Both the high- and low-field regions of the spectrum were complex; not all of the hydrogens in cyclopropylphenylmethyllithium could be definitely assigned. For this discussion, we will only consider the chemical shift of the α-hydrogen. To serve as a model, ethylbenzene was metalated in a similar manner and the 500.13 MHz spectrum was recorded. Because cyclopropyl might be expected to exert an intrinsic 'alkyl-substituent' influence common to typical alkyl substituents, 1-phenyl-1-ethyllithium is a more accurate comparision relative to benzyllithium. Given below is the pertinent information for both systems. Surprisingly, the α-hydrogen shifts 0.88 ppm upfield in benzylcyclopropane and ethylbenzene shifts only 0.49 ppm upfield; the α-hydrogen of toluene shifts 0.70 ppm upfield. Presumably if the cyclopropyl substituent stabilized charge in a carbanion, the electron density would decrease at the charged center so that a smaller α-hydrogen upfield shift is expected.

On this theory alone, the conclusion is that a methyl substituent accepts more charge density than cyclopropyl in benzyllithiums. However, the shift of the α-hydrogen is determined by more than inductive effects; namely, the ring-current effects of delocalized π-electron arrays in phenylmethyllithiums. It has been suggested that benzyllithium (yellow in ethereal solutions) adopts a pyramidal structure at the charged center while diphenyl- and triphenyl-



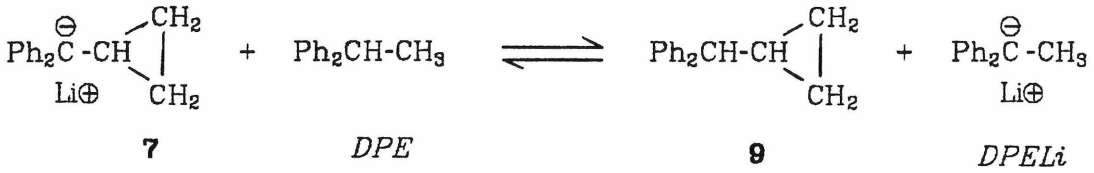


methyllithiums (deep-red in ether) are more nearly planar π-systems.[30] This idea is supported by the downfield shift of the α-hydrogen in diphenylmethyllithium in contrast to the upfield shift for benzyllithium. For a planar organolithium, the α-hydrogen would lie in the perimeter of the delocalized system and would experience a substantial paramagnetic ring current effect (downfield shift). The effect of an alkyl substituent on the charged center of a phenylmethyllithium may be primarily steric distortion of π-system planarity plus any inductive/conjugative influence of the substituent.

For argument's sake, assume cyclopropyl, methyl, and hydrogen have equal inductive influences on the charged center in phenylmethyllithium; then, the results indicate the cyclopropyl distorts planarity the most and methyl the least. This makes no sense in terms of the size of these groups. It would not be justified to draw conclusions regarding cyclopropyl stabilization of negatively charged centers based on NMR data for cyclopropylphenylmethyllithium.

Bank estimated pK_a values for a series of substituted phenyl- and diphenylmethanes by ^1H NMR.[12] Typically, the hydrocarbon of interest was added to *p*-xylylithium; integration of proton spectra then gave a rough estimate of

hydrocarbon acidity. We proposed a similar experiment with cyclopropyldiphenylmethyllithium, **7**. The reference hydrocarbon chosen for the equilibrium study was 1,1-diphenylethane whose pK_a has been reported to be 37.[12] To a solution of **7** in tetrahydrofuran-d_8, 1,1-diphenylethane was added. ^1H NMR analysis at 500.13 MHz was performed on the mixture until the relative integration of cyclopropyldiphenylmethyllithium and 1,1-diphenyl-1-ethyllithium did not change. The results are summarized below in Scheme 5.



7 *DPE* **9** *DPELi*

$$K_{eq} = \frac{[9]\cdot[DPELi]}{[7]\cdot[DPE]} = 0.34$$

given: $pK_a(DPE) \cong 37 \rightarrow pK_a(\mathbf{9}) \cong 36.5$

Scheme 5.

The K_{eq} value of 0.34 was estimated after one week at 25°C and did not change thereafter. While the difference is slight, the equilibrium lies in favor of cyclopropyldiphenylmethyllithium. Cyclopropyldiphenylmethane is more stable relative to 1,1-diphenylethane by approximately 0.6 Kcal (ΔpK_{eq}=0.5). Analysis at 500.13 MHz gave clearly resolved resonances which could be accurately integrated.

^7Li NMR, ^1H NMR, and ^{13}C NMR spectroscopy of cyclopropyldiphenylmethyllithium did not provide support for a cyclopropyl stabilization of the organolithium; spectra were adequately rationalized in terms of an alkyldiphenylmethyllithium. The ^1H NMR data presented on cyclopropylphenylmethyllithium

were not amenable to a reasonable interpretation; incomplete spectral data due to the complex nature of the organolithium solution diminish the relevance of these results. The only supporting evidence for cyclopropyl stabilization is based on the position of equilibrium for a solution of cyclopropyldiphenylmethyllithium, 1,1-diphenyl-1-ethyllithium, and their respective hydrocarbon acids. The enhanced stability of cyclopropyldiphenylmethyllithium is small relative to 1,1-diphenyl-1-ethyllithium.

III. SOLVENT DEPENDENCE OF ORGANOLITHIUM REARRANGEMENT

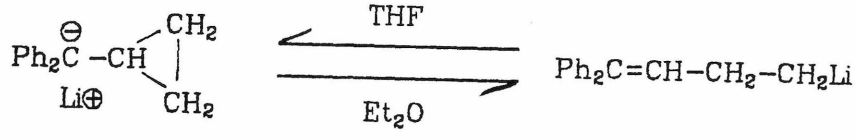
Trimethylsilylmethyllithium metalation and double-metal exchange were used to synthesize the organolithium system of **7**, **8**. Double-metal exchange is superior because tetrahydrofuran is not involved in preparation of the organolithiums. The major drawback of double-metal exchange is the 60-70% mass loss from starting material, **9**, to isolated products. Also, there is always a possibility of trace amounts of alkali *tert*-butoxide salts remaining from the initial preparation of cyclopropyldiphenylmethylpotassium.

Trimethylsilylmethyllithium metalation was followed by ^{1}H NMR to monitor the trimethylsilylmethyllithium consumption and determine the amount of unreacted starting material, **9**, at end of the reaction period. Typically, 25% cyclopropyldiphenylmethane was present after complete consumption of trimethylsilylmethyllithium; the product distributions for trimethylsilylmethyllithium metalation were corrected in each experiment for unreacted **9**. Additional trimethylsilylmethyllithium did not improve yields. The tetrahydrofuran and tetramethylsilane were removed under reduced pressure to give a dark-red gummy residue. If desired, a different solvent could then be added to the residue with vigorous vortex mixing. Complete removal of tetrahydrofuran is impossible because it forms stable complexes with organolithium compounds (one to three molecules of tetrahydrofuran per organolithium molecule). Even at 10^{-4} torr, there will be traces of tetrahydrofuran in the residue. However, trimethylsilylmethyllithium metalation does benefit from high yields, absence of alkoxides during preparation, and experimental simplicity.

All of the experiments were carried out using organolithium concentrations of 0.3-0.35 M. Rigorous product identifications were made by ^{1}H NMR, ^{2}H NMR, and interfaced GC-MS analysis. Percent deuteration in phenylnaphthalene derivatives was not determined. The product distribution was based on the average of three analytical GC analyses.

This chapter is organized by solvent with subsections on side reactions and influence of contaminants. The final section summarizes solvent dependence and proposes a candidate mechanism for the rearrangments of 4,4-diphenyl-3-buten-1-yllithium and cyclopropyldiphenylmethyllithium.

A. Tetrahydrofuran and Diethyl Ether

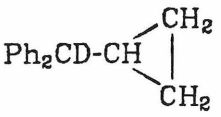
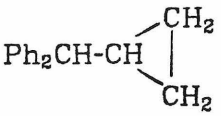
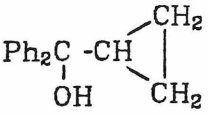


7 **8**

The organolithium equilibrium of **7** and **8** lies heavily to the left side in tetrahydrofuran. The appearance of tetrahydrofuran solutions is deep-red; upon carbonation, the only acidic product obtained is cyclopropyldiphenylacetic acid, **12** (see Chapter I).

The equilibrium lies in favor of the covalent 4,4-diphenyl-3-buten-1-yl-lithium, **8**, in diethyl ether solutions. Diethyl ether solutions have a murky

Table VII. Percent product compositions from organolithium equilibrium in diethyl ether followed by ethanol-O-*d* quench.[a]

Product	TMSLi Metalation[b,c] 10 min, 0°C	Double-Metal Exchange 20 min, 0°C
	5	14
	1	7
$Ph_2C{=}CH{-}CH_2{-}CH_2D$	38	55
$Ph_2C{=}CH{-}CH_2{-}CH_3$	45	15
	8	9

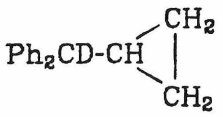
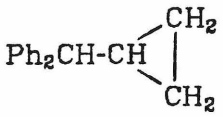
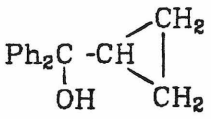
[a]Data corrected for 4% ^1H in ethanol-O-*d*. [b](1) Trimethylsilylmethyllithium metalation for 36 h in tetrahydrofuran, (2) tetrahydrofuran removed under reduced pressure, (3) diethyl ether added to residue. [c]Yields for trimethylsilylmethyllithium metalation corrected for 25% unreacted cyclopropyldiphenylmethane, as determined via ^1H NMR.

brown appearance and upon carbonation afford 5,5-diphenyl-4-pentenoic acid, **13**, as the major product.[4] Table VII presents our results for the organolithium equilibrium in diethyl ether solutions. The data in Table VII corroborate

Maercker's observations in diethyl ether. Our results for tetrahydrofuran were also in agreement. The yield of solvent-cleavage product, 1,1-diphenyl-1-butene, is higher using the trimethylsilylmethyllithium metalation method. Organolithium **8** cleaves the traces of tetrahydrofuran remaining from the trimethylsilylmethyllithium preparation resulting in higher yields of **10**.

With addition of 15% vol equiv or greater of tetrahydrofuran to a diethyl ether solution of 4,4-diphenyl-3-buten-1-yllithium, **8**, the brown solution changes color to deep-red. Table VIII presents data for mixed solvent systems of tetrahydrofuran and diethyl ether. Both 1:1 and 1:2 (v/v) mixtures of tetrahydrofuran : diethyl ether favor the ionic organolithium, cyclopropyldiphenylmethyllithium as demonstrated by the product distribution following an ethanol-O-*d* quench. The equilibrium lies 70% and 80% toward the side of organolithium **7** in 1:2 and 1:1 tetrahydrofuran : diethyl ether solvent mixtures, respectively. One major difference between 50% and 33% tetrahydrofuran in diethyl ether is the higher yield of 1,1-diphenyl-1-butene in the former. 1,1-Diphenyl-1-butene, **10**, is primarily the result of α-proton abstraction from tetrahydrofuran. Higher tetrahydrofuran concentrations (cleaved 10 times faster than diethyl ether) afford higher yields of **10**. The reactivity of 4,4-diphenyl-3-buten-1-yllithium is equal to or slightly more than that exhibited by *n*-butyllithium in tetrahydrofuran (10 min half-life at room temperature).

Table VIII. Percent product compositions from organolithium equilibrium[a] in diethyl ether(Et_2O)/tetrahydrofuran(THF) followed by ethanol-O-*d* quench[b]; preparation via double-metal exchange.

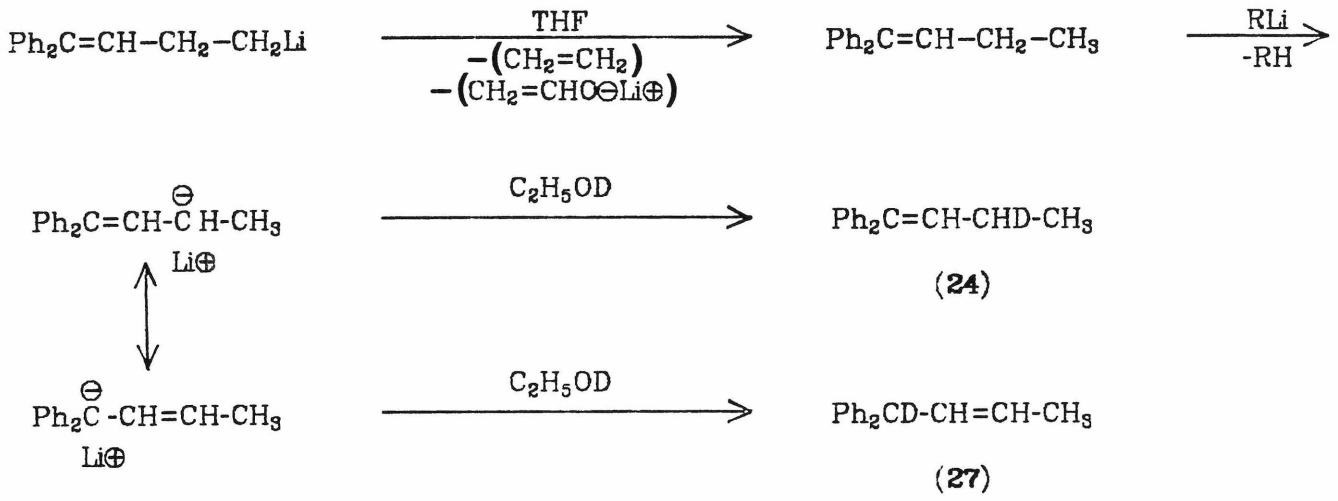
Product	THF/Et_2O(1:1)	THF/Et_2O(1:2)	THF/Et_2O(1:2) LiBr, Na-K
	41	40	36
	10	12	15
$Ph_2C{=}CH{-}CH_2{-}CH_2D$	10	18	8
$Ph_2C{=}CH{-}CH_2{-}CH_3$	26	12	14
$Ph_2C{=}CH{-}CHD{-}CH_3$	0	6	10
$Ph_2CD{-}CH{=}CH{-}CH_3$	0	0	7
	13	14	10

[a]10 min reaction time at 0°C. [b]Data corrected for 4%-^1H in ethanol-O-*d*.

1. Allylic Proton Abstraction from 1,1-Diphenyl-1-butene

Isolation of 1,1-diphenyl-4-d-1-butene, **24**, and 1,1-diphenyl-1-*d*-2-butene, **27**, is evidence that the solvent-cleavage product, **10**, undergoes further reaction under the experimental conditions employed. The abstraction of an α-proton

from tetrahydrofuran gives 1,1-diphenyl-1-butene, **10**, and an unstable α-metalated tetrahydrofuran intermediate which decomposes to ethylene and the lithium enolate of acetaldehyde via a $[_{\pi}4_s + _{\pi}2_s]$ cyclorevision.



Scheme 6. Allylic proton abstraction from 1,1-diphenyl-1-butene.

The allylic hydrogens of **10** are easily removed to give a stable, delocalized allyl organolithium. 4,4-Diphenyl-3-buten-1-yllithium and cyclopropyldiphenylmethyllithium are both viable candidates for allylic hydrogen abstraction. It may be recalled from Chapter I that, in the reaction of lithium powder with 4-bromo-1,1-diphenyl-1-butene, 4,4-diphenyl-3-buten-1-yllithium readily abstracted an allylic proton from starting material. The high yields of **10** and **9** are consistent with the mechanism in Scheme 6. There are two possible products from deuteration of 4,4-diphenyl-3-buten-2-yllithium: 1,1-diphenyl-3-*d*-1-butene, **24**, and 1,1-diphenyl-1-*d*-2-butene, **27**.

2. Cyclopropyldiphenylmethanol Formation

Cyclopropyldiphenylmethanol, **21**, is a frequently observed product in reactions of organolithiums **7** and **8**. Maercker also isolated this alcohol but concluded it was an impurity in his starting material, cyclopropyldiphenylmethyl methyl ether. This cannot be the case here. Both double-metal exchange and trimethylsilylmethyllithium metalation involve removal of solvent under reduced pressure. Leakage of oxygen into the septum-sealed reaction vessels during evacuation results in autoxidation of organometallic compounds. Autoxidation of organoalkali compounds affords the corresponding alcohol in moderate yields.[31] The long evacuation periods (2-3 h) employed in the removal of *n*-heptane from cyclopropyldiphenylmethylpotassium offers an explanation for isolation of alcohol **21** in all the double-metal exchange preparations. On one occasion, inadvertent admission of air into a vessel containing cyclopropyldiphenylmethylpotassium resulted in immediate blackening. Analysis revealed **21** as a major component. Cyclopropyldiphenylmethanol is not obtained in every trimethylsilylmethyllithium metalation preparation. Oxygen leakage during removal of tetrahydrofuran could autoxidize cyclopropyldiphenylmethyllithium; the shorter evacuation times (1 h) lowered the amount of autoxidation relative to double-metal exchange.

3. Effect of Alkoxides, Na-K Alloy in Organolithium Equilibrium

Preliminary results suggested that the behavior Maercker observed for organolithiums **7** and **8** was in part due to catalysis/activation by contaminants.

Maercker prepared the organolithium by Na-K cleavage of cyclopropyldiphenylmethyl methyl ether and subsequent lithium bromide transmetalation; the organolithium solutions were contaminated with varying amounts of lithium methoxide, potassium methoxide, Na-K alloy, elemental lithium, lithium bromide, and potassium bromide. Maercker had to use 3 mol equiv lithium bromide to effect complete transmetalation.

Lithium alkoxides[32] and lithium bromide[33] form stable complexes with organolithiums. Potassium alkoxides activate organolithiums in metalations; an effect exploited in the double-metal exchange method employed for this work. The active metalating species in potassium alkoxide-organolithium mixtures is either the organopotassium or a mixed organolithium-organopotassium complex.[34] Potassium *tert*-butoxide also catalyzes rearrangement of organolithiums; for example, 2,3,3-triphenyl-1-propyllithium rearranged to 1,1,3-triphenyl-1-propyllithium and 1,2,3-triphenyl-1-propyllithium in tetrahydrofuran with potassium *tert*-butoxide present.[35] Potassium metal also activates organolithium reagents in metalation reactions. The best evidence for alkoxide activation is a report by Maercker and Weber on the kinetics of 3-methyl-1,1-d_2-3-buten-1-yllithium rearrangement.[36]. They found that lithium alkoxide retarded the rate of rearrangement.

The results of an experiment designed to test influence of a mixture of Na-K alloy and lithium bromide upon the rearrangement of the diphenyl-substituted system are given in Table VIII. The combination of lithium bromide and Na-K more accurately simulate Maercker's original conditions. Lithium bromide will react with some of Na-K alloy to give lithium metal and potassium bromide This side-reaction is supported by the formation of a reactive, black metal powder under Maercker's conditions. There is no significant change in product distribution for organolithium solutions when Na-K/lithium bromide is present.

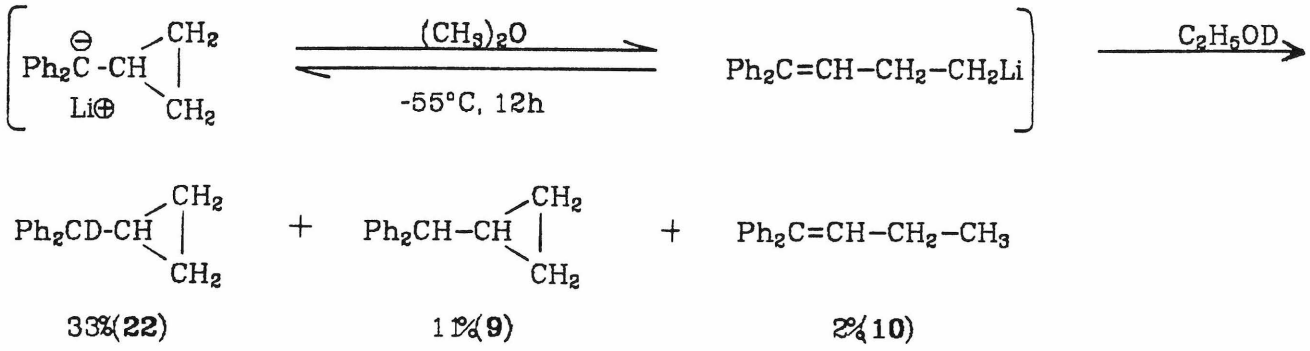
In a different experiment, cyclopropyldiphenylmethylpotassium was prepared by Maercker's method and was washed five times with anhydrous *n*-heptane to remove the by-product of ether cleavage, potassium methoxide. Normally, three mol equiv lithium bromide are required to effect complete transmetalation; only two mol equiv lithium bromide were required in this experiment confirming successful removal of potassium methoxide. The products from ethanol-O-*d* quenching of the diethyl ether reaction mixture were very similar to Maercker's. We obtained 13% cyclopropyldiphenylmethane, (**9**,**22**) 74% 1,1-diphenyl-1-butene (**10**, **23**), and 13% cyclopropyldiphenylmethanol, (**21**); the percent deuterium incorporation was not determined. Maercker quenched a diethyl ether solution with deuterium oxide and reported 25% **9**, 70% **23**, and 5% **21**.[4] The results show that the influence of methoxide salts upon the organolithium rearrangement is not important.

Product distributions are not reproducible to within 3-5% under identical reaction conditions. However, the two experiments just described do not indicate a dominating effect by contaminants present under Maercker's original conditions upon rearrangement of cyclopropyldiphenylmethyllithium and 4,4-diphenyl-3-buten-1-yllithium.

B. Dimethyl Ether

Transmetalation of cyclopropyldiphenylmethylpotassium in dimethyl ether at -55°C produces a deep-red solution. Quenching with ethanol-O-*d* afforded the product distribution shown in Scheme 7. The stability of dimethyl ether in the

presence of organolithium compounds and the low reaction temperature account for the lack of side-products. The relatively low yield of **10** demonstrates that solvent cleavage is minimal.



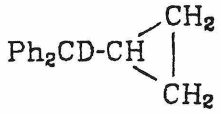
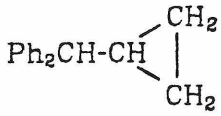
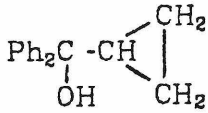
Scheme 7. Product distribution from organolithium equilibrium in dimethyl ether.

Cyclopropyldiphenylmethyllithium, **7**, predominates in dimethyl ether; the only deuterium-containing product is (cyclopropyldiphenyl)-1-d-methane, **22**. Addition of one vol equiv diethyl ether had no observable effect on reaction appearance.

C. 2-Methyltetrahydrofuran

The results for the organolithium rearrangements in 2-methyltetrahydrofuran are given in Table IX. The 2-methyltetrahydrofuran organolithium solutions were deep-red, consistent with the product analyses. Like tetrahydrofuran, the ionic organolithium **7** predominates in 2-methyltetrahydrofuran. Up to 88% of the equilibrating organolithium system had the ionic structure.

Table IX. Product yields from organolithium equilibrium in 2-methyltetrahydrofuran following ethanol-O-*d* quench.

Product	TMSLi Metalation[a,b] 10 min, 0°C	Double-Metal Exchange 10 min, 0°C
	61	22
	1	5
$Ph_2C{=}CH{-}CH_2{-}CH_2D$	10	2
$Ph_2C{=}CH{-}CH_2{-}CH_3$	12	3
$Ph_2C{=}CH{-}CHD{-}CH_3$	0	1
	0	8
$Ph_2C{=}CH{-}CH{=}CH_2$	1	0
1-phenylnaphthalene	4	0
3,4-dihydro-1-phenylnaphthalene	8	0
1,2,3,4-tetrahydro-1-phenylnaphthalene	1	0

[a]See footnote *b* in Table VII. [b]Data corrected for 17% unreacted **9**.

The difference in product distributions between the two preparative methods is primarily in the secondary reactions of 4,4-diphenyl-3-buten-1-yllithium. 1,1-Diphenyl-3-*d*-1-butene, is observed only in double-metal exchange and ortho-cyclisation products are observed only in trimethylsilylmethyllithium metalation, a result which is not understood.

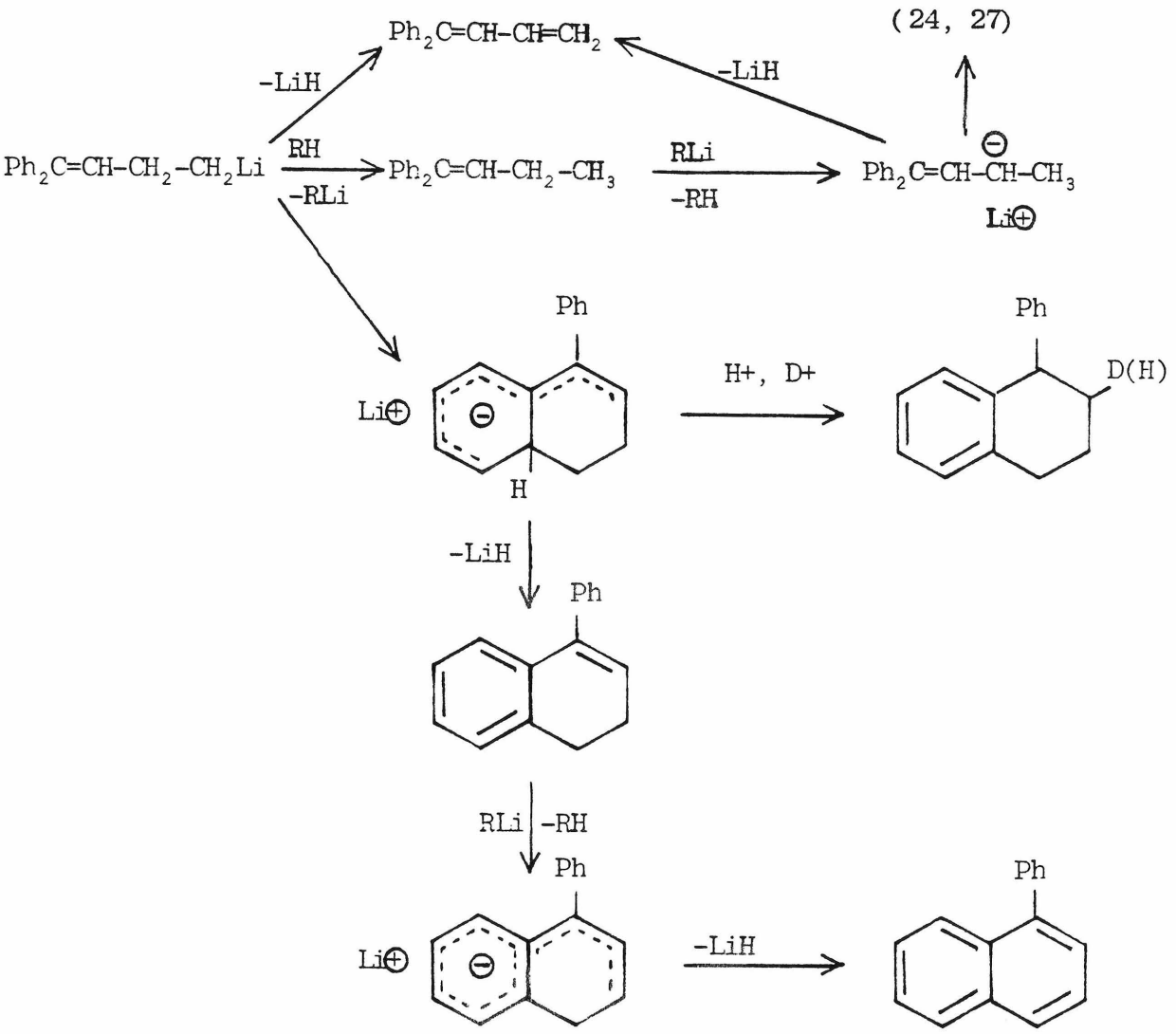
1. Ortho-cylisation and β-Elimination of Lithium Hydride

The formation of 1-phenylnaphthalene, **14**, 3,4-dihydro-1-phenylnaphthalene, **15**, and 1,2,3,4-tetrahydro-1-phenylnaphthalene, **16**, could theoretically occur by ortho-cyclisation of either 4,4-diphenyl-3-buten-1-yllithium or 4,4-diphenyl-3-buten-1-yl radical. Halgren reported **15** in yields up to 35% for *tert*-butyl 5,5-diphenyl-4-perpentenoate thermolysis in diethyl ether and hydrocarbon solvents.[37] He did not observe 1-phenylnaphthalene and could not unambiguously identify one product that he assigned to 1,2,3,4-tetrahydro-1-phenylnaphthalene.[38]

The isolation of **14** is not itself sufficient basis for organolithium ortho-cyclisation because it's formation is not dependent upon the mechanism of ortho-cyclisation. The product distributions reported here, where similar yields of all three phenylnaphthalene derivatives are observed, support the ortho-cyclisation of 4,4-diphenyl-3-buten-1-yllithium, **8** rather than the radical.

Scheme 8 outlines three alternate reaction pathways proposed for 4,4-diphenyl-3-buten-1-yllithium other than cyclisation: (1) β-elimination of lithium hydride; (2) proton abstraction to give 1,1-diphenyl-1-butene; and (3) ortho-cyclisation to intermediate organolithium **28**.

The most common process in alkyllithium pyrolysis is the elimination of lithium hydride to give an alkene. Simple alkyllithiums have been observed to decompose slowly in benzene at room temperature by irreversible β-elimination.[39] Elimination takes place readily when aromatisation provides the driving force.[40] Elimination of lithium hydride directly from 4,4-diphenyl-3-buten-1-yllithium or from the allylic carbanion formed from 1,1-diphenyl-1-butene proton abstraction would afford 1,1-diphenyl-1,3-butadiene, **11**. The



Scheme 8. 4,4-Diphenyl-3-buten-1-yllithium (**8**) decomposition pathways.

considerable conjugation in the diene helps drive its formation; nonpolar media where organolithium **8** is poorly solvated would facilitate lithium hydride elimination to afford **11**.

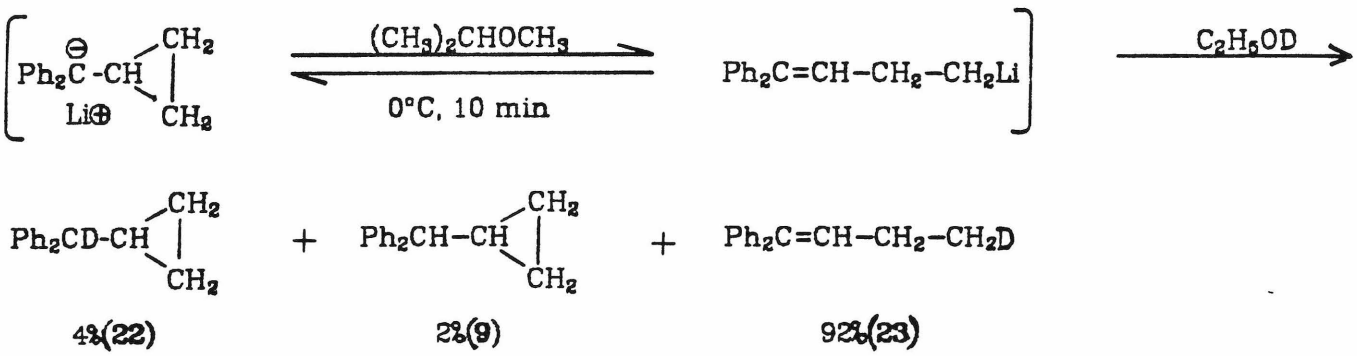
Ortho-cyclisation of organoalkali compounds has ample literature precedence. Burley and Young isolated 1-methyl-2-butyl-3-phenylindane in 5% yield from the reaction of *n*-butyllithium and 1,3-diphenyl-1-butene in *n*-hexane.[41]

The indane was formed by ortho-cyclisation of the organolithium addition product followed by lithium hydride elimination; there was no ortho-cyclisation observed in diethyl ether or tetrahydrofuran. A similar reaction was reported by Margerison and Nyss for a toluene solution of ethyllithium and α-methylstyrene.[42] They isolated 1,3-dimethyl-3-phenyl-1-propylindane as the major product. Grovenstein obtained a 3% yield of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene, the ortho-cylisation product of 4,4,4-triphenyl-1-butyllithium in tetrahydrofuran.[43] When Na-K alloy was substituted for lithium in the carbanion preparation, the yield of the ortho-cylisation product increased to 26%.

Ortho-cyclisation of 4,4-diphenyl-3-buten-1-yllithium, **8**, is proposed as the mechanism of formation for **14**, **15**, and **16**. As depicted in Scheme 8, ortho-cyclisation of **8** affords anion **28** as the initial product which can undergo β-elimination of lithium hydride to afford **15**. Deuteration/protonation of the anion would give **16**. The amount of deuteration in phenylnaphthalene products was determined in the product analyses discussed here. Like **10**, 3,4-dihydro-1-phenylnaphthalene contains an acidic allylic proton which can be removed by either organolithium **7** or **8**. Subsequent lithium hydride elimination from the carbanion formed would give 1-phenylnaphthalene, **14**; aromatisation would be expected to provide sufficient energetic impetus for such an elimination.

D. Isopropyl Methyl Ether

Addition of isopropyl methyl ether to the residue from trimethylsilylmethyllithium metalation gave a brown, heterogeneous solution. The results in Scheme 9 indicate that the organolithium equilibrium lies more than 95% toward the side of the covalent isomer, **8**.

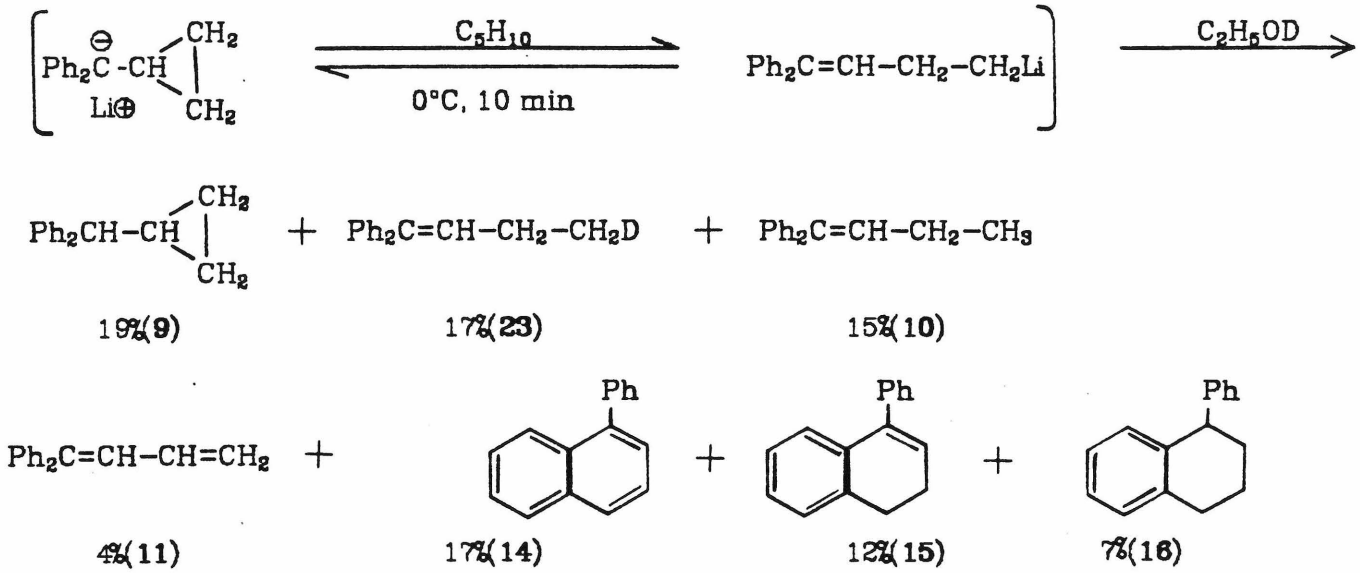


Scheme 9. Product distribution from organolithium equilibrium in isopropyl methyl ether following ethanol-O-*d*; results corrected for 25% unreacted **9**.

Similar to dimethyl ether, the organolithium equilibrium in isopropyl methyl ether was not accompanied by formation of any side-products. Isopropyl methyl ether was the best medium examined for stable solutions of 4,4-diphenyl-3-buten-1-yllithium, **8**. The covalent organolithium is stable in isopropyl methyl ether because the α-hydrogens are less acidic relative either diethyl ether or tetrahydrofuran. There was apparently no solvent-cleavage of traces of residual tetrahydrofuran by **8**.

E. Cyclopentane

Addition of cyclopentane to the residue from a trimethylsilylmethyllithium metalation gave a pale yellow, heterogeneous mixture. Scheme 10 shows the product distribution following ethanol-O-*d* quench.



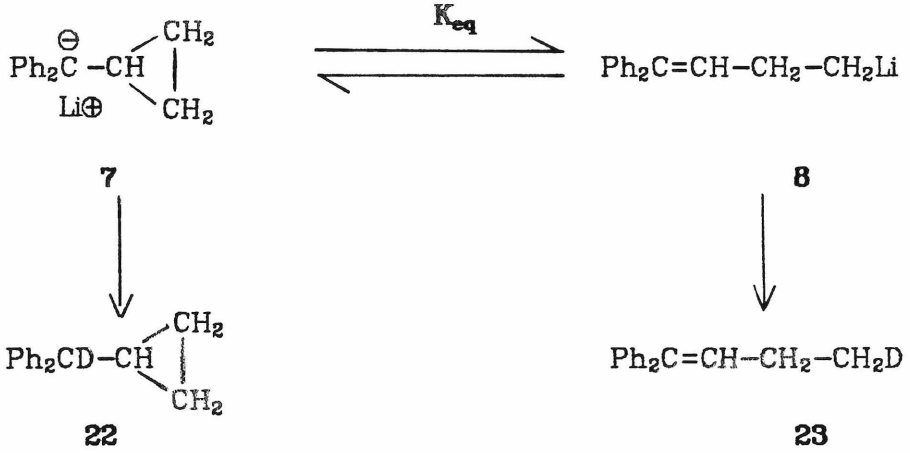
Scheme 10. Product distribution from organolithium equilibrium in cyclopentane.

The only deuterium containing product isolated was 1,1-diphenyl-4-*d*-1-butene, **23**. The equilibrium lies entirely toward the side of the covalent isomer, 4,4-diphenyl-3-buten-1-yllithium as expected for a nonpolar medium. The 17% yield of **23** is low by comparison with yields of organolithium-derived products observed in other solvents. The yields of ortho-cyclisation products are highest in cyclopentane; consistent with the work of Burley and Margerison. The yield of the β-elimination product, **11**, is also highest here. A precipitate was observed during the 20 min reaction time which may well have been lithium hydride. The

yield of 1-phenylnaphthalene, **14**, partially accounts for the unexpectedly high amounts of hydrocarbons **9** and **10** observed. Organolithiums **7** and **8** cannot abstract a proton from cyclopentane. The contention that these hydrocarbon yields offer evidence of radical participation in ortho-cyclisation is invalidated if unreacted starting material can account for some of the yield of **9**.

F. Summary of Solvent Dependence

The influence of solvent in the rearrangment of 4,4-diphenyl-3-buten-1-yl-lithium and cyclopropyldiphenylmethyllithium is dramatic. The quench ratio of 1,1-diphenyl-4-*d*-1-butene to (cyclopropyldiphenyl)-1-*d*-methane, [**23**]/[**22**], is used as a rough estimate of the equilibrium constant ($\mathbf{K_{eq}}$) for the organolithium rearrangement.



The best available empirical parameter for describing the nucleophilic properties of a solvent is donicity as defined by the donor number (DN). Gutmann

defines donor number as the negative ΔH-value in kcal mol^{-1} for the interaction of an electron-pair donor with antimony pentachloride in a highly dilute 1,2-dichloroethane solution.[44]

$$DN = - \Delta H_{EPD \cdot SbCl_5}$$

The extent of lithium-carbon bond polarization should increase with increasing donor number of a solvent. Table X contains a summary of known donor numbers, dielectric constants, and [**23**]/[**22**] ratios observed for the solvents studied.

Table X. Ratios of organolithium-derived products in different solvents and empirical solvent parameters.

Solvent[a]	[**23**][b] / [**22**]	Donor Number, kcal mol^{-1}	Dielectric Constant, ε
THF	≤ 0.008[c]	20	8.23(0°C)[d]
2-MeTHF	0.1-0.16	18	6.92(0°C)[e]
THF/Et_2O(1:2)	0.45		6.0(0°C)[f]
Me_2O	≤ 0.015		5.02(25°C)
Et_2O	7.1	19	4.88(0°C)[e]
i-PrOMe	25		4.45(25°C)[g]
C_5H_{10}	≥ 25	0	1.97(25°C)

[a]Abbreviations used: THF=tetrahydrofuran, 2-MeTHF=2-methyltetrahydrofuran, Et_2O=diethyl ether, Me_2O=dimethyl ether, *i*-PrOMe=isopropyl methyl ether, C_5H_{10}=cyclopentane. [b]Where a single isomeric product was isolated, an inequality sign is used based on the minimum level of detection in product analysis: 0.5%. [c]Ratio of [5,5-diphenyl-4-pentenoic acid]/[cyclopropyldiphenylacetic acid] [d]Ref 45. [e]Ref 46. [f]Estimated assuming additivity for dielectric constants (ε); 0.33[8.23 + 2(4.88)]=6.0. [g]Estimated from the average of ε values for dimethyl ether and di-isopropyl ether (ε = 3.88).

Theoretically, there are four organolithium states which can be described: (1) polar

covalent (R-Li), (2) contact ion-pair (R⊖Li⊕), (3) loose ion-pair (R⊖ || Li⊕), and (4) dissociated free ions. In contact ion-pairs, the interionic distance is slightly

$$R{-}Li \rightleftharpoons R^{\ominus}Li^{\oplus} \rightleftharpoons R^{\ominus} \,||\, Li^{\oplus} \rightleftharpoons R^{\ominus} + Li^{\oplus}$$

greater than the polar covalent carbon-lithium bond length and the lithium cation is peripherally solvated. Contact ion-pairs can be either a σ- or π-complexes. Loose ion-pairs can be differentiated into those having one intervening solvent molecule between ions (shared-solvent ion-pairs) and those having more than one intervening molecule (solvent-separated ion-pairs). Loose ion-pairs are recognized when a carbanion salt displays behavior independent of counterion and ligand. The free ions predominate in strongly polar solvents like hexamethylphosphortriamide, but only minor amounts are in present aliphatic and alicyclic ethers.

The dielectric properties of a solvent (ε) primarily influence loose ion-pair formation; solvents with higher episilon values stabilize charge separation. Donicity of a solvent influences the polarization of the carbon-lithium bond, manifested initially by peripheral solvation to afford contact ion-pairs and later by coordinative saturation of cation to give shared-solvent ion-pairs. Dielectric constants and donicity of a solvent cannot completely describe solvent behavior. Steric accessibility of the oxygen in ethereal solvents is important. From ^{1}H NMR chemical shift data for ethylmagnesium bromide, Blomberg and Bickelhaupt[47] determined the basicity of ethereal solvents, in order of increasing coordinative ability to be:

$$i\text{-}Pr_2O < n\text{-}Bu_2O < Et_2O < THF$$

From the stability of (*n*-butyllithium)-solvent coordinative complexes, Sergutin and co-workers[48] studied severeal ethereal solvents with different steric requirements; they reported the following series (in order of increasing coordinative

ability) :

$$n\text{-}Bu_2O < Et_2O < MeOEt < Me_2O < THF$$

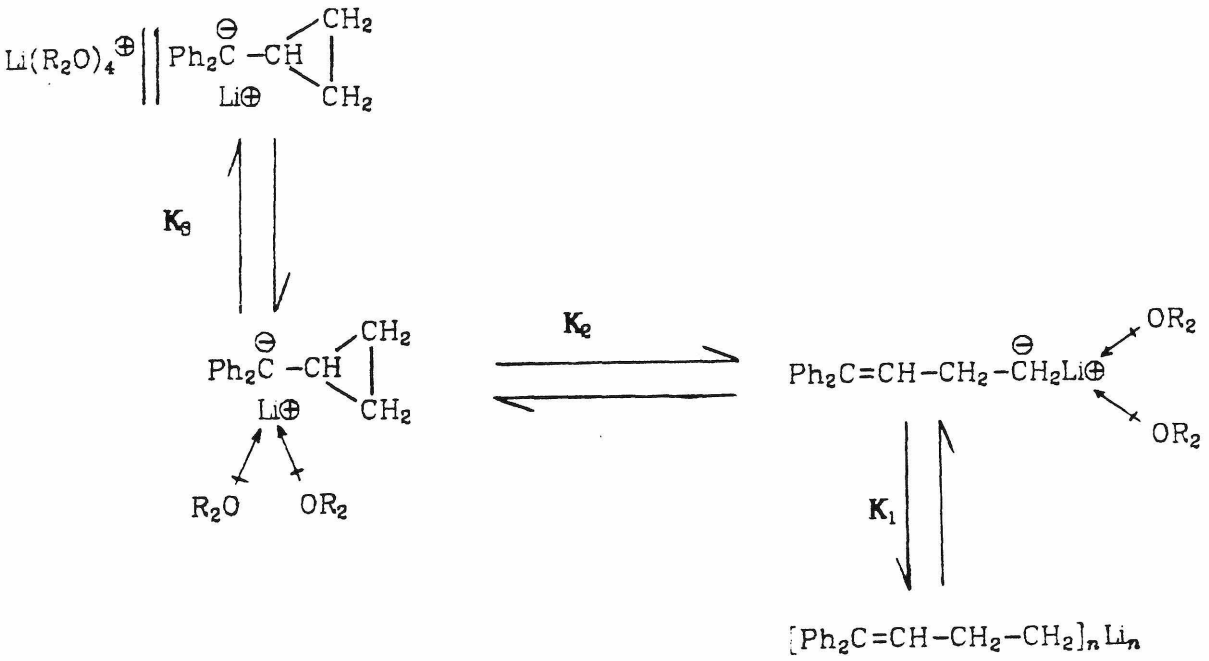
A dramatic example of steric effects was reported by Fraenkel and Hallden-Abberton for the adduct of *tert*-butyllithium and 1,1,2,3,5,6-hexamethyl-4-methylene-2,5-cyclohexadiene.[49] Triethylamine (DN = 61 kcal/mol) was less effective at lithium-ion coordination relative to tetrahydrofuran (DN = 20 kcal/mol). The difference in donicity is offset by the three organic groups on triethylamine versus the two groups of the oxygen ligand.

The product ratio: [**23**]/[**22**], which represents the equilibrium populations of cyclopropyldiphenylmethyllithium and 4,4-diphenyl-3-buten-1-yllithium, seem to correlate with expected solvent coordinative strengths. The steric demands imposed upon solvation are especially important in this organolithium system because **7** has a sterically encumbered α-carbon. Inspection of Table X shows the importance of steric accessibility in ethereal solvents where the greater donicity of diethyl ether is outweighed by its steric bulk, relative to 2-methyltetrahydrofuran. Dimethyl ether is the second best solvent for stabilization of **7**. The lower reaction temperature used normally used for dimethyl ether should be considered; the population of **7** would increase as temperature is lowered because loose ion-pairs become more favorable. While the donor numbers of diethyl ether and isopropyl methyl ether should be similar, the larger steric bulk of an isopropyl group makes isopropyl methyl ether a poorer coordinating ligand.

Cyclopentane is not an electron-pair donor; organolithium compounds generally show low solubility in hydrocarbon solvents. Simple alkyllithiums aggregate in hydrocarbons to hexameric units containing bridged lithium-carbon bonds. 3-Buten-1-yllithium is a hexamer in cylcopentane;[8] however, steric repul-

sions in the diphenyl-substituted system may destabilize hexameric aggregates relative to tetramers.

G. Candidate Mechanism for Organolithium Rearrangment



Scheme 11. Proposed mechanism for the rearrangement of 4,4-diphenyl-3-buten-1-yllithium and cyclopropyldiphenylmethyllithium; double vertical lines indicate a loose ion-pair, ROR represents an aliphatic or alicyclic ether molecule.

As shown in Scheme 11, we propose three principal equilibria in the rearrangement of cyclopropyldiphenylmethyllithium, **7**, and 4,4-diphenyl-3-buten-1-yllithium, **8**: (1) an equilibrium between aggregated and contact ion pair forms of **8** (K_1); (2) equilibrium between contact ion-pairs of **7** and **8** (K_2); and (3) equilibrium between loose and contact ion-pairs of **7** (K_3). It is the perturbation of these three principal equilibria that determine the solvent-dependent

behavior of organolithiums **7** and **8**.

In both trimethylsilylmethyllithium metalation and double-metal exchange, cyclopropyldiphenylmethyllithium, **7**, is the starting point on the rearrangment potential-energy surface. A solvent which has a sterically accessible oxygen and good electron-pair donor and dielectric properties will favor the ionic organolithium isomer, **7**. From the [**23**]/[**22**] ratios in Table X, it can be seen that tetrahydrofuran, 2-methyltetrahydrofuran, and dimethyl ether satisfy these requirements. In these three solvents, **7** is a loose ion-pair with the lithium cation coordinatively saturated as the tetraetherate. The freezing out of ligand motions when the loose ion-pair is formed from a contact ion-pairs decreases the entropy of the system. The steric repulsion between ligand and the cyclopropyl group attached to the α-carbon of **7** destabilizes contact ion-pairs of **7**. Fraenkel reported that contact ion pairing of 4,4-dimethyl-2-lithio-2-phenylpentane was energetically unfavorable in ethereal solvents because of the steric repulsions.[50] By contrast, benzyllithium is a contact ion-pair in most solvents. The important factor in determining organolithium behavior in solvents such as tetrahydrofuran, 2-methyltetrahydrofuran, and dimethyl ether is the preference of **7** to form loose ion-pairs: $\mathbf{K_3} > \mathbf{K_2}$.

The deep-red color of **7** changes to brown in diethyl ether or isopropyl methyl ether indicative of ring-opening; product analysis of quenched reactions substantiates **8** as the major isomer. Relative to tetrahydrofuran, 2-methyltetrahydrofuran, and dimethyl ether, diethyl ether and isopropyl methyl ether differ primarily in steric accessibility of oxygen. Additionally, diethyl ether and isopropyl methyl ether have weaker donor and dielectric properties. The equilibrium population of **7** in diethyl ether or isopropyl methyl ether is low; thus, the major species present would be contact ion-pairs. We expect for **7** that $\mathbf{K_3}$(diethyl ether) << $\mathbf{K_3}$(tetrahydrofuran), and. in general, conjugated

organolithiums give mainly contact ion-pairs in diethyl ether.[51]

In Scheme 11, the contact ion-pairs are depicted as dietherates. There is published evidence for dietherate complexes of contact ion-pairs for delocalized organolithiums. For example, Okamoto and Yuki[52] made a study of 1,1-diphenyl-1-butyllithium in mixtures of benzene and tetrahydrofuran by monitoring changes in the visible absorption and ^{1}H NMR spectra when tetrahydrofuran was added to a benzene organolithium solution. Two stable complexes of the organolithium were observed, a dietherate [R⊖·$(THF)_2$Li⊕] and tetraetherate [R⊖·$(THF)_4$Li⊕]. The spectral characteristics of the tetraetherate were identical to an organolithium solution in tetrahydrofuran alone. Waack and co-workers[53] reported the same stoichiometry for 1,1-diphenyl-1-hexyllithium complexes with tetrahydrofuran.

We propose the contact ion-pair of **7** as a discrete intermediate in the ring-opening to 4,4-diphenyl-3-buten-1-yllithium, **8**. Complete transmetalation of bis-(4,4-diphenyl-3-buten-1-yl)mercury and methyllithium to **7** can be induced by addition of 15% (v/v) of tetrahydrofuran to a diethyl ether solution. This roughly corresponds to a 4:1 molar ratio of tetrahydrofuran to organolithium for a 0.35 M concentration of the organolithium. The cyclisation of **8** is driven by the formation of tetraetherate loose ion-pairs of **7**.

Ring-opening of **7** will give the isomeric contact ion-pair of **8**. It is uncertain whether the contact ion-pair of **8** has two distinct energy minima for a contact ion-pair; one for the externally solvated and the other for the unsolvated contact ion-pair. The existence of unsolvated contact ion-pairs is still an unresolved question in organolithium chemistry. As yet, there is no available experimental method to determine the differences between unsolvated and externally solvated contact ion-pairs.

Rearrangement in the contact ion-pairs is induced by the accumulation of charge at the α-carbon. Charge accumulation decreases the conjugative stabilization of **7** to the degree that the contact ion-pair is less stable relative to the loose ion-pair. The ring-opening of the cyclopropyl is favorable by 4-7 kcal/mol based on estimates from similar systems.[4] Electrophilic attack at the α-carbon is synergistic with charge accumulation in promoting rearrangement. In absence of conjugative stabilization, normal alkyllithiums having primary metal-bound carbons are more stable relative to a tertiary organolithium. It may be recalled from the Introduction, that Lansbury observed rapid ring-opening at -70°C in the parent system, cyclopropylmethyllithium.[1] Tetrahydrofuran accelerated the ring-opening relative to diethyl ether. This solvent effect supports the contention that charge accumulation at the α-carbon induces ring-opening; polarization of the carbon-lithium bond is greater in tetrahydrofuran increasing the partial negative charge at the α-carbon.

The major species of **8**, in diethyl ether and isopropyl methyl ether is a dimeric or tetrameric aggregate with bridged lithium, carbon bonding. Because **8** does not derive stabilization from localized charge at the α-carbon, contact ion-pairs will not be favorable. *n*-Butyllithium and methyllithium are tetrameric in diethyl ether and tetrahydrofuran. As previously mentioned, hexamers predominate in nonpolar solvents. Diethyl ether and isopropyl methyl ether solutions of **8** were not homogeneous. We have no experimental evidence which can be used to assign a cause to the heterogeniety. However, it may be simply be the result low 4,4-diphenyl-3-buten-1-yllithium solubility with the insoluble being **8** itself or more likely as some solvent complex. The ordering of equilibria in diethyl ether and isopropyl methyl ether is: $K_1 \gtrsim K_2 > K_3$

The rearrangement of 4,4-diphenyl-3-buten-1-yllithium and cyclopropyldiphenylmethyllithium was described by Maercker as a reversible process. The

nature of reversibility in the organolithium rearrangement deserves some clarification. To be more accurate, the ring-opening of cyclopropyldiphenylmethyllithium is reversible. We are using reversible to describe ability to effect a retro rearrangement simply by changing solvent composition. In this sense, the cyclisation of 4,4-diphenyl-3-buten-1-yllithium is not reversible. However, removal of solvent from cyclopropyldiphenylmethyllithium and subsequent addition of diethyl ether or isopropyl methyl ether effectively reverses cyclisation. This was the way in which trimethylsilylmethyllithium metalation could be utilized for solvent-dependence studies. Once formed, loose ion-pairs of **7** have no thermodynamic impetus to exchange the lithium ion ligands with more weakly coordinating ligands; e.g. replacement of tetrahydrofuran with diethyl ether.

In summary, the three principal equilibria shown in Scheme 11 provide an adequate basis to account for the equilibrium populations of cyclopropyldiphenylmethyllithium and 4,4-diphenyl-3-buten-1-yllithium in different solvents. Simply stated, if solvent stabilizes the loose ion-pairs of **7**, then the cyclic organolithium predominates. A solvent which does not favor loose ion-pairs will effectively promote ring-opening via contact ion pairs.

IV. REARRANGEMENT OF CYCLOPROPYLDIPHENYLMETHYL RADICAL

There is strong evidence for radical participation in reactions of cyclopropyldiphenylmethyl and 4,4-diphenyl-3-buten-1-yl organometallic derivatives. Most notably, cyclopropyldiphenylmethane, **9**, is always a side-product (3-15% yield) in the preparation of 4,4-diphenyl-3-buten-1-ylmagnesium bromide, **3**.[3] Formation of **9** is best explained by occasional migration of transient radicals from magnesium surface during Grignard formation and subsequent hydrogen abstraction from solvent. Preparation of Grignard **3** is also accompanied by the isomeric hydrocarbon, 1,1-diphenyl-1-butene, **10**, but in lower yields. Maercker reported only ring-opened products upon quenching the transmetalation reaction of cyclopropyldiphenylmethylpotassium and magnesium bromide.[4] This finding demonstrated that **9** does not arise from the cyclic Grignard reagent.

The cyclopropyldiphenylmethyllithium : 4,4-diphenyl-3-buten-1-yllithium rearrangement afforded significant amounts of 1,2,3,4-tetrahydro-1-phenylnaphthalene, **16**; 3,4-dihydro-1-phenylnaphthalene, **15**; and 1-phenylnaphthalene, **14** under some of the reaction conditions. The result of ortho-cyclisation, these substances are formed to the greatest extent in cyclopentane; but they were also observed in diethyl ether and 2-methyltetrahydrofuran. Formation of these naphthalene derivatives implies radical participation. Halgren obtained moderate yields of **15** in thermolyses of *tert*-butyl cyclopropyldiphenylperacetate, **17**, and *tert*-butyl 5,5-diphenylperpent-4-enoate, **18**.[37,38] He obtained his highest yields of **15** in diethyl ether (26-28%) and cyclohexane (23-26%). Chapter III of this work presented a detailed discussion of organolithium ortho-cyclisation.

A. ESR Characterization

The parent cyclopropylmethyl : 3-buten-1-yl radical rearrangment was initially studied by Kochi[54] and more recently by Ingold.[55] Using a kinetic ESR technique, Ingold and co-workers photolytically generated the cyclopropylmethyl radical from the *tert*-butyl perester and determined the rate of isomerization to the 3-buten-1-yl radical; $k=1.3\times10^{8}$ s^{-1} (25°C). In a more recent study, Griller and Ingold reported ESR data for the 1,1-d_2-3-buten-1-yl radical.[56] From the scrambling of deuterium a value for the equilibrium constant was determined to be; $K=1.3\times10^{4}$ (25°C).

$$CH_2{=}CH{-}CD_2{-}CH_2\bullet \underset{k_r}{\overset{k_c}{\rightleftharpoons}} \bullet CH_2{-}CH(CD_2)(CH_2) \underset{k_c}{\overset{k_r}{\rightleftharpoons}} CH_2{=}CH{-}CH_2{-}CD_2\bullet$$

$$K=\frac{k_c}{k_r}$$

Our initial proposal was to apply similar experimental methodology to the diphenyl-substituted system. Because peresters are efficient precursors for photolytic low-temperature radical generation, peresters **18** and **17** were synthesized for the initial work. The **major** experimental problem encountered was the very low perester solubility in otherwise suitable low-temperature solvents; CS_2, CCl_2F_2, $CBrClF_2$, and cyclopropane. In the range of -40 to -160°C, maximum solubility of *tert*-butyl 5,5-diphenylperpent-4-enoate was less than 0.005 M. Outgassed samples of perester **18** produced broad ESR signals upon photolysis (257nm). The ESR spectrum shown in Figure 4 is representative and was assigned to the 4,4-diphenyl-3-buten-1-yl radical, **20**.

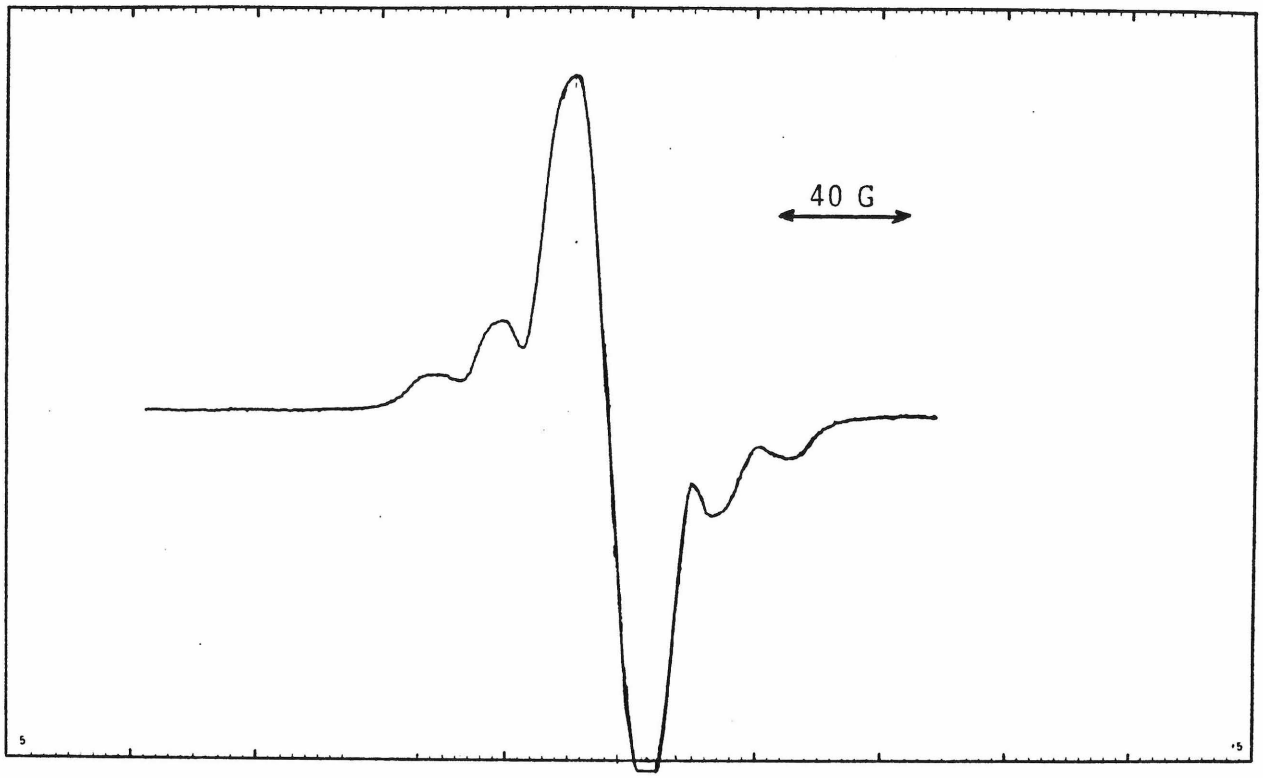
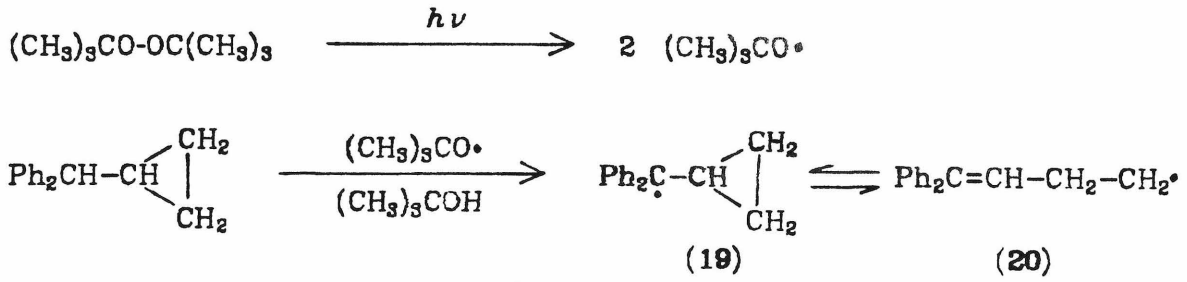


Figure 4. ESR spectrum after irradiating CF_2Cl_2 solution of *tert*-butyl 5,5-diphenylperpent-4-enoate, **18**, for 5 min. The conditions of this ESR spectrum were: microwave frequency, 9.0986 GHz; microwave power, 10 mW; modulation amplitude, 8 G; modulation frequency, 100 KHz; time constant, 0.05 s; sample temperature, -140°C.

The spectrum in Figure 4 had a well-defined center and corresponds to g=2.0025. The pentet is a result of hyperfine splitting by α-hydrogens; a_α=22 G. Raising sample temperature did not improve the spectrum.

In a search for a more soluble precursor, Kochi's method[57] of radical generation from the corresponding hydrocarbon by hydrogen abstraction with the *tert*-butoxy radical was explored; Scheme 12 shows the generation of **19** by this method. The low extinction coefficient for di-*tert*-butyl peroxide is a drawback of Kochi's method. In our work, this was compounded by unavailability of 1 kW



Scheme 12. Cyclopropyldiphenylmethyl radical generation by hydrogen abstraction from the hydrocarbon using *tert*-butoxy radical.

arc lamps. Sample irradiation was performed using a non-collinear arrangement of two 200-watt Xe-Hg arc lamps; both lamps focused on the microwave cavity. An outgassed cyclopropane solution containing 50 mM each of di-*tert*-butyl peroxide and cyclopropyldiphenylmethane was irradiated for 20-30 min. periods at several temperatures in the range of -70 to -120°C. Despite numerous experiments, no ESR signal could be detected.

Recently, Professor David Griller was sent a sample of hydrocarbon **9** for a study of the cyclopropyldiphenylmethyl radical, **19**. He had substantial difficulty in obtaining an ESR spectrum of **19**.[58] At 10°C, irradiation of **9** in di-*tert*-butyl peroxide solution gave the spectrum shown in Figure 5. Rapid sample deterioration made it imposssible to record entire spectrum; hence, Figure 5 is a composite of two samples. From the spectral center, Griller found g=2.00244 for radical **19**. Griller deduced that splitting from β-hydrogens of the cyclopropyl ring was probably less than 5 G. This indicates these hydrogens lie in the nodal plane of the orbital containing the unpaired electron. The geometry implied from this splitting is consistent with radical **19**.

Our dismal results from attempted ESR characterization of this radical system prompted us to abandon the work. While Griller was able to observe the

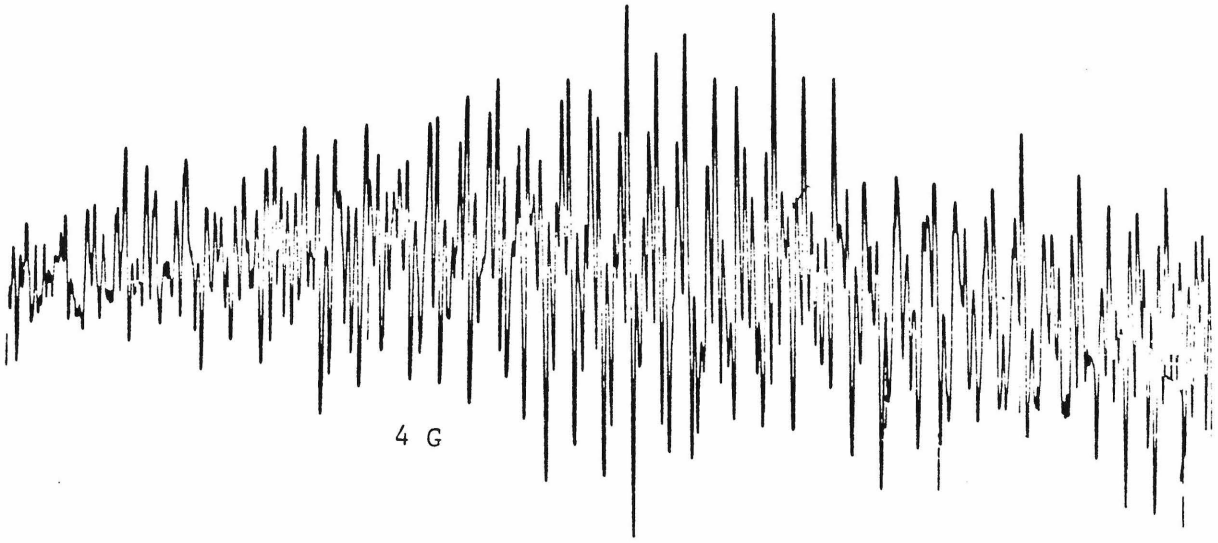


Figure 5. ESR spectrum obtained by Griller of cyclopropyldiphenylmethyl radical using: microwave power, 0.2 mW; modulation amplitude, 0.02 G; sample temperature, 10°C.

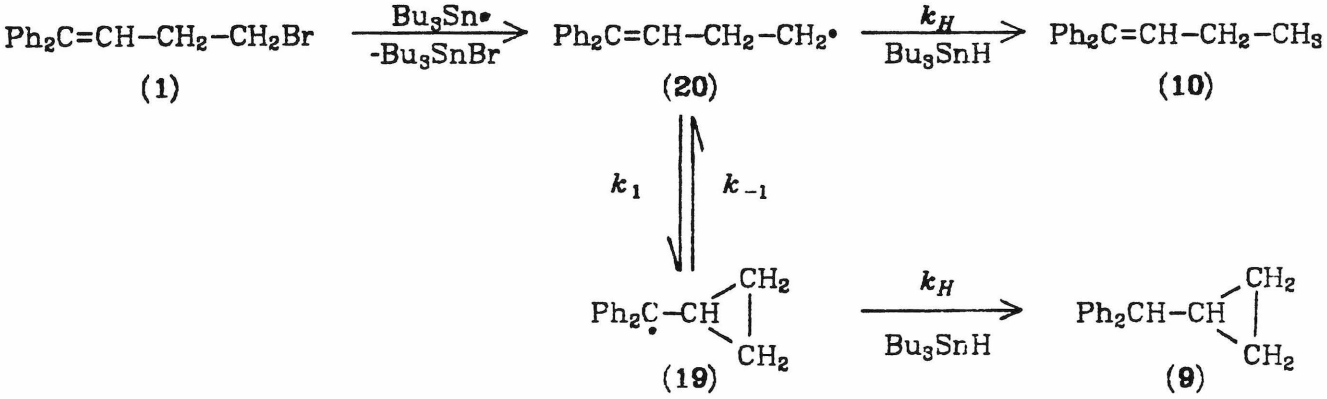
ESR spectrum of the cyclopropyldiphenylmethyl radical, the conditions necessary for his spectrum are not suitable for ESR characterization of the radical isomerization. This reinforces the futility of ESR for gleaning kinetic information on the cyclopropyldiphenylmethyl : 4,4-diphenyl-3-buten-1-yl radical rearrangement.

B. Tri(*n*-butyl)tin Hydride Reduction 4-Bromo-1,1-diphenyl-1-butene

A benzene solution of 4-bromo-1,1-diphenyl-1-butene, **1**, and 1.1 mol equiv tri(*n*-butyl)tin hydride (Bu_3SnH) was irradiated (257 nm) for 9 h at 25°C. GC analysis of reaction products indicated 36% starting material, 54% 1,1-diphenyl-

1-butene, **10**, and 10% cyclopropyldiphenylmethane, **9**. Bromide **1** remained unchanged in absence of irradiation even at elevated temperatures for prolonged periods.

Unsaturated alkyl halides are known to slowly react with trialkyltin hydrides.[59] Reversible hydrostannation of the double bond reduces the steady state concentration of trialkyltin radicals. Scheme 13 outlines the relevant radical processes involved in the Bu_3SnH reduction of **1**.



Scheme 13. Tri(*n*-butyl)tin hydride reduction of 4-bromo-1,1-diphenyl-1-butene.

Ortho-cyclisation of the 4,4-diphenyl-3-buten-1-yl radical, **20**, was not important in the presence of $(n\text{-Bu})_3SnH$, as evidenced from lack of 1-phenylnaphthalene derivatives. Also, disproportionation and bimolecular termination between alkyl radicals were not observed.

At this point, it is worthwhile to mention some results from Halgren's work on the thermolytic decomposition of peresters **18** and **17**. The ratio of the two isomeric hydrocarbons obtained from decomposition of *tert*-butyl cyclopropyldiphenylperacetate in presence of triethyltin hydride displayed a linear dependence on initial tin hydride concentration. The rate of hydrogen abstraction (k_H) from triethyltin hydride should be approximately equal for radicals **20** and

19; from Carlsson and Ingold's work, a value of 10^6 M^{-1} s^{-1} for k_H is not unreasonable.[59] From Halgren's data a rough estimate of the ring-opening rate (k_1) for radical **19** was derived; $k_1 \simeq 10^7$ s^{-1}.

The 10% of cyclopropyldiphenylmethane, **9**, obtained in the reaction of Bu_3SnH and bromide **1** is clear evidence for the enhanced stability of the diphenyl-substituted cyclopropylmethyl radical. To obtain valid kinetic data from the Bu_3SnH reduction of **1**, it would be necessary to demonstrate a linear dependence of the ratio [**10**]/[**9**] upon initial Bu_3SnH concentration. However, some very rough conclusions can be drawn from the 0.19 ratio observed. Assuming complete radical equilibration prior to hydrogen abstraction, the ratio approximates the equilibrium constant for radical rearrangement. From this and the estimated ring-opening rate of radical **19** (k_1), we obtain a ballpark estimate for the cyclisation rate (k_{-1}) of the 4,4-diphenyl-3-buten-1-yl radical; $k_{-1} \simeq 2 \times 10^6$ s^{-1}.

Regretfully time did not permit a detailed product study of perester decompositions using more efficient hydrogen donors than those available to Halgren and/or a thorough product study on the trialkyltin hydride reduction of 4-bromo-1,1-diphenyl-1-butene. Reliable product analysis using interfaced GC-MS could have provided kinetic information on the cyclopropyldiphenylmethyl : 4,4-diphenyl-3-buten-1-yl radical rearrangement. Despite Halgren's commendable efforts, he could not fully describe the rearrangement. This diphenyl-substituted system is a promising candidate to plug the current gap in the organic chemist's repertoire of reliable radical rearrangements for mechanistic studies of fast radical processes.[60] Known rearrangements can be

invaluable for competition experiments which afford rate data on the radical process of interest. Because there is not now a rearranging system known with about a 10^7 s^{-1} rate, the estimated ring-opening rate for the cyclopropyldiphenylmethyl radical makes the title radical rearrangement a viable candidate to fill this gap.

EXPERIMENTAL SECTION

GENERAL. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 90 MHz (JEOL FX-90Q or Varian Associates EM-390) or 500.13 MHz (Bruker WM-500 spectrometer at the Southern California Regional NMR Facility under National Science Foundation Grant Number CHE-7916324). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 22.5 MHz (JEOL FX-90Q) or 125.7 MHz (Bruker WM-500). Deuterium nuclear magnetic resonance (^{2}H NMR) spectra were recorded at 13.7 MHz (JEOL FX-90Q) or 76.7 MHz (Bruker WM-500). Lithium nuclear magnetic resonance (^{7}Li NMR) spectra were recorded at 34.8 MHz (JEOL FX-90Q). Chemical shifts (δ) are reported in parts per million relative to internal tetramethylsilane unless otherwise noted; a "universal referencing method" was utilized for ^{7}Li NMR and ^{2}H NMR spectra.[61] Multiplicities are reported as s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, m=multiplet, br=broad with coupling constants (J) in Hz. Electron spin resonance (ESR) spectra were recorded on a Varian Associates E-Line Century Series spectrometer equipped with a Varian temperature controller. Samples were irradiated with a Hanovia 901-B1 high-pressure Xe-Hg arc lamp (253.7 nm).

Mass spectra were recorded on a Dupont 21-492B spectrometer by the California Institute of Technology Microanalytical Laboratory. Interfaced gas chromatography-mass spectrometry (GC-MS) was performed by the California Institute of Technology Microanalytical Laboratory using an AEI (Kratos) Model MS25 system equipped with a Data General Corporation Nova 3 computer for data processing. A 1.8 m x 6.3 mm (o.d.) glass column packed with 5% Ucon

Ucon Polar 50HB 5100 on Chromasorb W (80/100 mesh) was used in GC-MS analyses. Analytical gas chromatography (GC) was carried out on a Hewlett-Packard Model 5710A gas chromatograph equipped with a flame ionization detector (f.i.d.). Analytical GC was also performed on a Varian Associates Series 1400 gas chromatograph equipped with a f.i.d.; data were collected and analyzed with a Spectra Physics System I computing integrator. Analyses were routinely performed on a 1.8 m x 3.2 mm (o.d.) stainless steel column packed with 10% Ucon Polar 50HB 5100 on Chromasorb W (80/100 mesh). Preparative gas chromatography was performed on a Varian Associates 90-P gas chromatograph equipped with a thermal conductivity detector. Typically, a 3.7 m x 6.4 mm (o.d.) stainless steel column packed with 10% Carbowax 20M on Chromasorb P (60/80 mesh) was used for separations.

Sodium-potassium (Na-K) alloy was prepared by heating a 5:1 (w/w) mixture of potassium:sodium under argon and was stored under diethyl ether. *n*-Butyllithium, *s*-butyllithium, *tert*-butyllithium, methyllithium, and phenyllithium (all from Aldrich Chem. Co.) were standardized by titration with diphenylacetic acid. Potassium *tert*-butoxide was doubly sublimed under reduced pressure and then stored and handled under nitrogen in a drybox. Anhydrous lithium bromide was prepared from the reaction of 1,2-dibromoethane with lithium in diethyl ether and was handled as a solid in a drybox. 12-Crown-4 (Aldrich Chem. Co.) was used without further purification. Di-*tert*-butyl peroxide (Pfaltz and Bauer, Inc.) was passed through a column of aluminum oxide to remove traces of *tert*-butyl hydroperoxide. Tri-*n*-butyltin hydride (Ventron-Alfa Corp.) was used without further purification.

SOLVENTS. Tetrahydrofuran, diethyl ether, dimethyl ether, 2-methyltetrahydrofuran, isopropyl methyl ether, and 1,2-dimethoxyethane were freshly distilled from sodium benzophenone ketyl under argon. Tetrahydrofuran-d_8 (Stohler Isotope Co., 99% D) and diethyl ether-d_{10} (Stohler Isotope Co., 99% D) were handled under nitrogen in a drybox without further purification. Hydrocarbon solvents were treated with concentrated sulfuric acid, water, dried over anhydrous magnesium sulfate, and finally distilled from sodium benzophenone ketyl under argon. The isotopic purity of each ethanol-O-*d* lot (Stohler Isotope Co., 96-99%D) was determined via ^{1}H NMR. 1,4-Dioxane and ethyl acetate were dried over 4A molecular sieves prior to use.

Isopropyl methyl ether was prepared via a Williamson synthesis by addition of dimethyl sulfate to sodium isopropoxide (freshly prepared from sodium and isopropanol) in a di-*n*-butyl ether solution. Following two successive fractional distillations, the product was stored over sodium benzophenone ketyl: bp (760 torr) 30°C; ^{1}H NMR (benzene-d_6, 90 MHz) δ 3.29 (septet, $^3J_{HH}$=6.5 Hz, 1H), 3.15 (s, 3H), 1.06 (d, 6H).

COMPOUNDS. **Trimethylsilylmethyllithium** was prepared from the reaction of 140-mesh lithium with chloromethyltrimethylsilane; an adaptation of Daniels and Port's procedure.[62] The solvent was removed and the crude product purified by two successive vacuum sublimations (10^{-4} torr, 100°C). The purified trimethylsilylmethyllithium was a white solid and was handled in a drybox: ^{1}H NMR (tetrahydrofuran-d_8, 90 MHz) δ -0.16 (s, 2H), -2.2 (s, 9H).

Cyclopropyldiphenylmethanol, 21, (Aldrich Chem. Co.) was recrystallized from carbon tetrachloride; mass spectrum (EI, 70 eV), m/z(rel intensity)

224(1.3), 197(14), 196(93), 183(24), 118(19), 105(100). Cyclopropyldiphenylmethyl methyl ether[4], **5**, and 4-bromo-1,1-diphenyl-1-butene[63], **1**, were prepared using published procedures. **4-Iodo-1,1-diphenyl-1-butene, 2**, was synthesized by treating **21** with anhydrous magnesium iodide,[64] based on the recent work of McCormick.[65] By this method, **2** was obtained free of contaminants in good yield; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.20 (m, 10H), 5.95 (t, 1H), 3.07 (t, 2H), 2.52 (q, 2H). **1,1-Diphenyl-1,3-butadiene** was prepared using Eisch's method;[66] ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.12-7.57 (m, 10H), 6.18-6.82 (6 lines, 2H), 5.00-5.57 (4 lines, 2H). **4,4-Diphenyl-3-buten-1-ylmagnesium bromide, 3**, was prepared using a literature procedure[3]; ^{1}H NMR (diethyl ether, 90 MHz) δ 7.18 (m, 10H), 6.26 (t, $^3J_{HH}$=8 Hz, 1H), 2.30 (q, 2H), -0.44 (t, $^3J_{HH}$=8 Hz, 2H).

Bis[4,4-diphenyl-3-buten-1-yl]mercury, 4, was prepared by adding a tetrahydrofuran solution of mercuric bromide (0.5 mol equiv) to a diethyl ether solution of 4,4-diphenyl-3-buten-1-ylmagnesium bromide and stirring for 14 h at room temperature. The reaction mixture was washed with aqueous ammonium chloride, extracted with ether and the combined ethereal extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue chromatographed on 100 g of silica gel eluting the bis-mercurial with 1-5% acetone/hexane. Recrystallization from *n*-hexane gave the bis-mercurial, **4**, in 70% yield from **1**; mp 57-63°C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.26 (m, 20H), 6.06 (t, 2H), 2.49 (q, 4H, $^2J_{HgH}$= 109 Hz), 1.05 (t, 4H, $^3J_{HgH}$= 93 Hz); mass spectrum (EI, 15 eV), m/z (rel intensity) 207(18), 206(39), 196(100), 183(25), 105(24), 91(58).

Cyclopropyldiphenylmethane, 9, was synthesized from diphenylmethylenecyclopropane. The alkene was prepared according to a published procedure[9]; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.40 (m, 10H), 1.40 (s, 4H); mass spectrum (EI, 15 eV), m/z (rel intensity) 207(16), 206(100), 205(38), 191(49), 178(12), 128(17), 91(36).

A solution of 0.04 moles of diphenylmethylenecyclopropane in 150 ml of ethyl acetate was treated with hydrogen at 3.4 atm pressure using 0.05 mol equiv of platinum oxide (Englehard, 86%) as a catalyst for 9 h. Vacuum distillation afforded pure **9** in 85% yield; ^{1}H NMR (tetrahydrofuran-d_8, 500.13 MHz) δ 7.19 (d, 4H), 7.187 (t, 4H), 7.07 (t, 2H), 3.163 (d, $^3J_{HH}$=9.5 Hz, 1H), 1.362 (m, 1H), 0.563 (m, 2H), 0.224 (m, 2H); ^{13}C NMR (tetrahydrofuran-d_8, 125.79 MHz) δ 145.97 (s), 128.79 (d, $^1J_{CH}$=156 Hz), 128.65 (d, $^1J_{CH}$=159 Hz), 126.42 (d, $^1J_{CH}$=159 Hz), 56.43 (d, $^1J_{CH}$=131 Hz), 17.30 (d, $^1J_{CH}$=170 Hz), 5.69 (t, $^1J_{CH}$=160 Hz); mass spectrum (EI, 15 eV), m/z (rel intensity) 208(4), 180(100), 179(36), 165(22), 115(5), 104(79), 91(7).

1,1-Diphenyl-1-butene, 10, was independently synthesized by quenching Grignard **3** in water: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.15 (m, 10H), 6.00 (t, $^3J_{HH}$=7.5 Hz, 1H), 2.06 (p, 2H), 1.00 (t, $^3J_{HH}$=7.5 Hz, 3H); mass spectrum (EI, 75 eV) m/z (rel intensity) 208(100), 193(65), 178(28), 130(37). **1,1-Diphenyl-4-*d*-1-butene, 23**, was prepared similarly by quenching with ethanol-O-*d*: ^{2}H NMR (acetone, 13.7 MHz) δ 0.93 (s, 1D); ^{1}H NMR (CCl_4, 90 MHz) δ 7.21 (m, 10H), 6.10 (t, $^3J_{HH}$=7.3 Hz, 1H), 2.09 (q, 2H), 1.02 (t, $^3J_{HH}$=5.7 Hz, $^2J_{HD}$=1.7 Hz, 2H); mass spectrum (EI, 15 eV) m/z (rel intensity) 210(18), 209(100), 208(36), 207(9), 193(71), 179(26), 178(26), 131(32), 115(68).

(Cyclopropyldiphenyl)-1-*d*-methane, 22, was prepared by quenching cyclopropyldiphenylmethyllithium in tetrahydrofuran with deuterium oxide. The crude product was purified by preparative GC: ^{2}H NMR (CCl_4, 13.7 MHz) δ 3.19 (s, 1D); ^{1}H NMR (benzene-d_6, 90 MHz) 7.20 (m, 10H), 1.15 (br p, 1H), 0.15,0.43 (m, 4H); mass spectrum (EI, 15 eV) m/z (rel intensity) 209(7), 182(13), 181(100), 180(34), 179(16), 168(8), 166(20), 165(11), 105(46), 104(45).

A mixture of 1-phenylnaphthalene (**14**), 3,4-dihydro-1-phenylnaphthalene

(**15**), and 1,2,3,4-tetrahydro-1-phenylnaphthalene (**16**) was a sample supplied by Dr. A. Maercker; GC-MS analysis facilitated unambiguous identification of ortho-cyclisation products in this work; mass spectra (EI, 70 eV) m/z (rel intensity) [**14**] 204(100), 203(81), 202(52), 101(77), 89(32), 87(46), 59(61), 45(67), 31(79); [**15**] 206(100), 191(40), 128(27), 91(41); [**16**] 208(100), 180(97), 179(73), 130(89), 115(31), 104(35), 91(58).

***tert*-Butyl cyclopropyldiphenylperacetate, 17,** and ***tert*-butyl 5,5-diphenyl-4-perpentenoate, 18,** were prepared using Halgren's synthetic methods.[38]

Cyclopropylphenylmethane (Chemicals Procurement Laboratories, Inc.) was used directly. **1,1-Diphenylethane, 25,** was prepared by treating 1,1-diphenylethylene (Aldrich Chem. Co.) with hydrogen at 50 psi using a Pd/carbon catalyst; ^{1}H NMR (tetrahydrofuran-d_8, 500.13 MHz) δ 7.15 (m, 8H), 7.05 (m, 2H), 4.07 (q, $^3J_{HH}$=7.2 Hz, 1H), 1.55 (d, 3H); ^{13}C NMR (benzene-d_6, 22.5 MHz) δ 141.41 (s), 127.99 (m), 126.75 (d), 44.86(d), 21.92 (q).

PROCEDURES. Organometallic work was performed with Schlenk glassware connected to vacuum manifold or under purified nitrogen in a Vacuum Atmospheres Recirculating drybox using standard air-sensitive techniques.[67] **Reaction of lithium powder with 4-bromo-1,1-diphenyl-1-butene, 1**, was achieved by slowly adding a tetrahydrofuran solution of **1** over one hour to the 140-mesh metal suspended in tetrahydrofuran. A dark-red color was first observed after three hours and persisted for the duration of reaction. After fifty hours, carbonation and standard acid-base workup gave traces of unidentified acids, cyclopropyldiphenylmethane (43% yield), and 1,1-diphenyl-1-butene (4% yield). *In*

situ ^{1}H NMR analysis of the lithium powder reaction was performed directly in a 5-mm NMR tube. With a tetrahydrofuran-d_8 solution of **1** in the bottom of the tube, a plug of glass wool was inserted followed by addition of excess 140-mesh lithium. The tube was sealed and then inverted to initiate reaction. For NMR analysis, the reaction mixture was filtered through the glass wool plug. At the end of the reaction period, the solution had become dark-red and viscous.

Transmetalation of bis-[4,4-diphenyl-3-buten-1-yl]mercury, **4**, was performed by addition of methyllithium (in diethyl ether) via syringe to a precooled solution of **4** in tetrahydrofuran. On addition of methyllithium, the mixture immediately turned deep-red. The reaction mixture was stirred for several minutes and then quenched with excess carbon dioxide.

Metalations of cyclopropyldiphenylmethane, **9**, were performed in a flask sealed with a rubber septum. For metalation with *tert*-butyllithium, *n*-butyllithium or *sec*-butyllithium, the alkyllithium was added via syringe to a precooled tetrahydrofuran solution of **1**. All reactions were magnetically stirred and were cooled with slush baths. For trimethylsilylmethyllithium metalations, the starting material and solid trimethylsilylmethyllithium were added to the reaction flask under nitrogen in a drybox. Tetrahydrofuran was then added to the septum-sealed flask on the bench at room temperature. NMR samples were generally prepared directly in an NMR tube sealed with a septum or transferred from a reaction mixture using a stainless steel cannula. For solvent dependence studies, the reaction was analyzed by transfer to an NMR tube whose contents were returned to reaction mixture after analysis. At end of the reaction period, the amount of unreacted starting material was assayed and confirmation of complete trimethylsilylmethyllithium consumption made. Using a stainless steel hypodermic needle attached to a vacuum line, the tetrahydrofuran was removed over one hour. The solvent of choice was then added to the dark-red

gummy residue with vigorous vortex stirring while maintaining temperature at 0°C with an ice bath. These reactions were quenched by adding excess ethanol-O-*d* to the reaction mixture. The workup procedure consisted of washing organic portions with water, drying ethereal extracts over anhydrous magnesium sulfate and removing solvent under reduced pressure.

Double-metal exchange of **9** was based the procedure described by Schlosser[15] with the following modifications: (1) *n*-heptane was substituted for *n*-hexane as reaction solvent, (2) the intermediate organopotassium was washed seven times with fresh *n*-heptane, (3) the potassium bromide from transmetalation was not filtered from reaction solution. Cyclopropyldiphenylmethylpotassium was washed by centrifuging the insoluble product to bottom of reaction vessel and removing *n*-heptane with a syringe. Fresh solvent was added and the mixture vigorously agitated with a vortex mixer for several minutes. The solvent of choice was added prior to transmetalation with solid, anhydrous lithium bromide. The reaction mixtures were quenched with either carbon dioxide or ethanol-O-*d* and then worked up in the usual manner.

The position and percentage deuterium incorporation in products was determined by integration of 13.7 MHz ^{2}H NMR and line intensities of mass spectral data. ^{2}H NMR peaks were assigned on the basis of measurements of independently synthesized compounds (**22**, **23**) and known ^{1}H NMR chemical-shift data. To determine the percentage of deuterium incorporation from mass spectral line intensities, a series of standards containing varying amounts of labeled/unlabeled compounds were analyzed. The line intensities were correlated with known deuterium content using least-squares analysis (correlation coeficient = 0.85-0.90).

Electron spin resonance samples were prepared by condensing an appropri-

ate solvent into a quartz sample tube containing perester or a mixture of cyclopropyldiphenylmethane and di-*tert*-butyl peroxide. The crystalline perester was finely ground prior to dissolution. The sample tube had a ground-glass joint at the top to which a vacuum stopcock was attached. The sample was outgassed using three freeze-pump-thaw cycles on a vacuum line which could attain a reduced pressure of 10^{-6} torr (higher pressures did not completely outgas samples of dissolved oxygen). The irradiation and spectroscopic studies were carried out using the sample tube with stopcock attached.

Tri-(*n*-butyl)tin hydride reduction of 4-bromo-1,1-diphenyl-1-butene, **1**, was performed in a 5-mm quartz tube. A benzene solution of 2.5 mM of **1** and 2.7 mM of tri-(*n*-butyl)tin hydride was prepared under nitrogen in a drybox. The tube was sealed with a septum and irradiated at room temperature with a 200-watt Hanovia 901-B1 Xe-Hg arc lamp using to a quartz lens to focus the beam on the sample. Periodically, the sample was analyzed by direct NMR analysis. After nine hours, integration indicated that 70% of **1** had reacted. In the workup tri-(*n*-butyl)tin bromide was removed to the insoluble fluoride with a 10% aqueous potassium fluoride wash.[68] The organic extracts were combined, dried over anhydrous magnesium sulfate, and the ether removed under reduced pressure.

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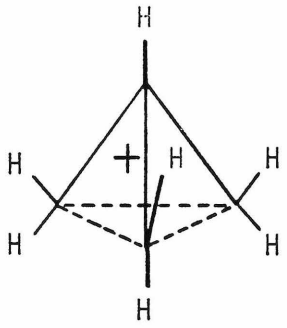
PART II.

DEUTERIUM ISOTOPIC PERTURBATION OF THE CYCLOPROPYLMETHYL-CYCLOBUTYL CARBOCATION

INTRODUCTION

The cyclopropylmethyl carbocation (C_4H_7+) holds a unique position in carbocation history. Bartlett's statement of 1965 is still poignant today: "Among nonclassical ions, the ratio of conceptual difficulty to molecular weight reaches a maximum with the cyclopropylcarbinyl-cyclobutyl system."[1] The pioneering work of Roberts and co-workers showed that cyclopropylmethyl and cyclobutyl derivatives solvolyze with markedly enhanced rates[2] to give rearranged and position-scrambled products of the 3-butenyl, cyclopropylmethyl and cyclobutyl types. The relative ratios of cyclopropylmethyl, cyclobutyl, and 3-butenyl products were similar from deaminations of cyclopropylmethylamine and cyclobutylamine; solvolysis of cyclobutyl and cyclopropylmethyl derivatives; the reactions of cyclopropylmethanol and cyclobutanol with thionyl chloride; the reaction of cyclopropylmethanol with hydrogen bromide or phosphorous tribromide;[2, 3a,b] and the solvolysis of 3-butenyl tosylate in formic acid.[3c]



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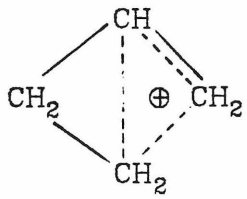
Roberts and Mazur were the first to use the term "nonclassical" in the literature to describe a tricyclobutonium (**1**) intermediate proposed to account for the degree of equivalence achieved by the methylene carbons in the nitrous-acid

deamination of cyclopropylmethylamine-α-^{14}C.[4] Subsequent isotopic labeling experiments indicated extensive, but not statistically random, scrambling of the methylene carbons in the deamination of cyclopropylmethylamine[3a] and 3-butenylamine;[3b] the reaction of thionyl chloride with cyclopropylmethanol and cyclobutanol;[2b] and the reaction of cyclopropylmethanol with Lucas reagent.[3a] The formulation of C_4H_7+ as **1** was later revised in favor of an unsymmetrically bridged, nonclassical bicyclobutonium carbocation, **2**.[3a]



The aim of the present study was to apply Saunders' deuterium isotopic perturbation technique[50] to C_4H_7+. The NMR study of labeled carbocation under stable-ion conditions was investigated with the hope that the major equilibrium geometry of the C_4H_7+ carbocation could be "unambiguously" determined. This thesis provides an opportunity to expound upon the current understanding of the nonclassical concept and also to highlight the drawbacks of Brown's "classical" explanation of the C_4H_7+ problem. It is, however, beyond the scope of this work to provide comprehensive treatments of the cyclopropylmethyl-cyclobutyl or the nonclassical-classical problems; the interested reader is referred to reviews on both subjects.[1,5,6]

I. THE CYCLOPROPYLMETHYL-CYCLOBUTYL CARBOCATION PROBLEM

The purpose of this chapter is to provide a brief overview of the relevant aspects of the cyclopropylmethyl-cyclobutyl (C_4H_7+) problem from both theoretical and experimental perspectives. The various structures proposed for the C_4H_7+ carbocation are evaluated; the geometry and nature of bonding are briefly presented for the two best candidates: the nonclassical bisected cyclopropylmethyl and nonclassical bicyclobutonium carbocations.

A. Definition of Nonclassical-Classical Carbocations

Roberts' usage of the term "nonclassical" was the beginning of one of the most intense controversies in the annals of modern physical-organic chemistry. The longevity of the the nonclassical debate is due, in large part, to the vocal and vigorous crusade of H. C. Brown.[6] Brown doggedly denied the existence of nonclassical carbocations for twenty-six years and at times strained his credibility as an objective, open-minded scientist in his contentious opposition. In 1977, independent solvolytic studies by Brown and Ravindranathan[7] and by Coates and Fretz[8] provided what even Brown regarded as unequivocal evidence for σ-participation in 9-pentacyclo[4.3.2.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoate derivatives. Brown's "own" discovery of σ-participation can best be described as: one small step for carbocation chemistry, one giant leap for H. C. Brown.

The term, **nonclassical**, has been adequate for most purposes but has unfortunately tended to obstruct the proper definition of the underlying con-

cepts. Even today, there is not a unanimous agreement on a definition of nonclassical carbocations. At the heart of this controversy (as with many in the history of organic chemistry) is a fundamental question; namely, just what do chemists mean when they draw structures on paper? To a large extent, the scientific problem pertinent to nonclassical and classical carbocations has been confused by semantic arguments concerning the relationship of lines on paper to molecular structures. Despite the intrinsically fallacious quality of the term, **nonclassical**, it s use in the literature has not waned significantly over the past thirty-one years. Despite the pitfalls, its legacy is continued here for want of more satisfactory nomenclature.

The major elements of the following definition of nonclassical ions were formulated by Schleyer and to a lesser extent, Brown.[9] A **carbocation** generally is defined as a positively charged species in which a significant portion of the positive charge resides on one or more carbon atoms termed the carbocation carbon or carbons. A **classical** carbocation can be adequately represented by a single Lewis structure in which each chemical bond has two electrons. Two subcategories of classical carbocations are:

> [1.] Weak π-complexes[10] which can be adequately represented by a single Lewis structure because the geometries of the acceptor and the donor moieties are not altered significantly by the weak association; an arbitrary enthalpy association criterion of 10 kcal/mole is set as the borderline for such weak complexes.
>
> [2.] Conjugated carbocations like allyl, cyclopropenyl, and benzyl which possess three-center two-electron bonds and are now considered to be classical although clearly they were "nonclassical" fifty years ago. One possible characteristic of a classical structure is to have bond length changes of less than 0.1Å relative to what would be expected of the respective Lewis structure.

The characteristics ascribed to **nonclassical** carbocations include: [1] a hybrid structure which cannot be adequately represented by a single Lewis

structure; [2] bond lengths considerably longer (Schleyer arbitrarily takes the minimum bond length change to be 0.1 Å) than the corresponding classical structure; and [3] existence of at least one "nonclassical bond" between carbons and/or hydrogens. A "nonclassical bond" is defined as: (a) a bond in which a pentacoordinated carbon or dicoordinate hydrogen is involved, or (b) a partial bond between carbons and/or hydrogens which in the reference structure are not nearest neighbors. It is not an absolute requirement that a candidate structure fulfill all three nonclassical criteria to be considered as such. This point will be discussed later in regard to the nonclassical bisected cyclopropylmethyl carbocation, one example of a structure which does not meet all of the listed requirements.

The above definition for nonclassical carbocations is based on structure and is more general than one based on energetics. A definition based on energy was discussed by Ingold.[11] Consider two equal-energy carbocations equilibrating via a Wagner-Meerwein shift over a low barrier; in some systems resonance can occur between zero-order canonical structures which would transform what was the transition state into a local minimum on the potential energy surface. This new local minimum corresponds to a symmetrically bridged nonclassical species. If the local minimum is substantially more stable than the two classical structures consideration of them may become unnecessary. The quantum-mechanical perturbation treatment of Fong[12] is more elegant but leads to the same net result. The situation is less clear for unsymmetrical Wagner-Meerwein carbocationic pairs by either Ingold's or Fong's approach.

Schleyer and Olah[13] have suggested that carbocation behavior is a continuum with classical and nonclassical structures as the extremes. Charge delocalization can range from hyperconjugation (little structural change) to a partially bridged structure. In the bridged structures, significant but unequal bonding to

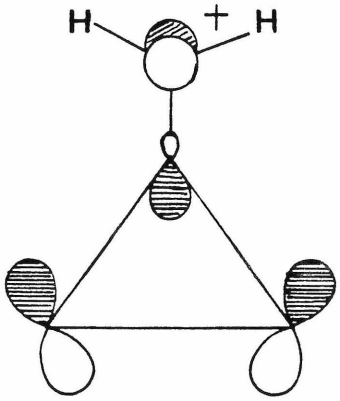
a second atom may take place and this can change into the limiting case where strong and equal bonding of the bridging carbon occurs in an essentially symmetrical fashion. Brown has recommended that the term "nonclassical" be confined to species possessing one or more pentacoordinated carbon or dicoordinate hydrogen bridges with the symmetry properties corresponding to the presence of that bridge.[6,14] However, an increase in symmetry cannot be used as an absolute requirement of nonclassical structures because sometimes inherent symmetry or geometrical constraints prevent symmetrical bridging, for example the nonclassical bicyclobutonium structure of C_4H_7+ and the 1,3,5,7-tetramethyl-2-adamantyl carbocation.[13]

B. Molecular Orbital Theory of C_4H_7+

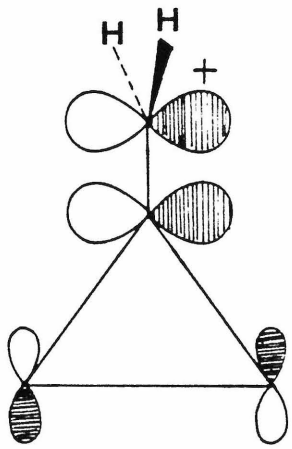
The interactions between the degenerate pair of Walsh orbitals on cyclopropane[15] and the empty p orbital at the carbocation center have been discussed most recently by Hehre.[16] It should be emphasized that the picture of the primary cyclopropylmethyl carbocation which arises out of molecular orbital calculations is classical only in a topological sense (that is, the substitution on H_2C+ of a cyclopropyl group); in fact, the system is one in which a high degree of electron delocalization has occurred. There are two conformations about the ring-carbocation center bond in a hypothetical cyclopropylmethyl carbocation which permit advantageous orbital overlap.

In the eclipsed conformation, **3a**, the symmetric component of the set of degenerate Walsh orbitals on cyclopropane interacts with p orbital at C+. Twisting the carbocation center by 90° gives a bisected conformation, **3b**, which

makes the antisymmetric component of the degenerate Walsh orbitals available for interaction. Simple perturbational models regarding the difference in stabilizing abilities of the two Walsh cyclopropane orbitals indicate that the bisected conformation is more favorable for optimal overlap and hence affords the most



3a
Eclipsed



3b
Bisected

energetic stabilization of the system. In other words, the points of higher electron density in the symmetric Walsh orbital are farthest from the carbocation center so that the orbital overlap in the eclipsed conformation is less than the bisected conformation.

In a simple sense, the energy difference between the eclipsed and bisected conformations is experimentally equivalent to the barrier to rotation about the ring-carbocation center bond. Investigation of the temperature dependence of the ^1H spectrum of the tertiary dimethylcyclopropylmethyl carbocation gave an experimental value of 13.7 kcal/mol for the rotation barrier[17] which is quite close to the 12.3 kcal/mol obtained by molecular orbital calculations at the minimal basis set STO-31G level.[16a] The same theoretical method yields a higher value of 25.7 kcal/mol for the rotation barrier in the parent C_4H_7+ system with

full optimization of geometry.[16a] Other semiempirical and *ab initio* molecular orbital procedures which have been applied to the same problem have yielded similar results.[18-20]

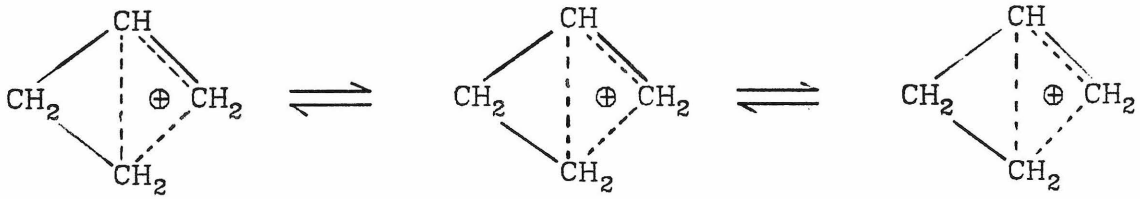
Theoretical investigations to date indicate that the bisected cyclopropylmethyl carbocation is a local minimum on the potential surface and the puckered cyclobutyl carbocation and the 3-butenyl carbocation require no activation energy to collapse to the bisected form[16a,21] No evidence was obtained for other stable forms of C_4H_7+ at the STO-31G level of theory. From these calculations, Hehre and Hiberty[21] proposed that C_4H_7+ exists as a set of rapidly equilibrating classical structures with a puckered cyclobutyl transition state. In a more recent *ab initio* molecular orbital study, Levi, Blurock and Hehre[22] reported two local minima on the potential surface of C_4H_7+ in the vicinity of the bisected cyclopropylmethyl carbocation. All previous theory had found only one minimum for C_4H_7+, the bisected form, but Hehre and co-workers found a new minimum 0.5 kcal/mol higher in energy at the 6-31G*//4-31G level. Hehre described the new minimum as a hybrid structure of a 3-butenyl and eclipsed cyclopropylmethyl resonance forms[22] (see Figure 1 on page 87). This structure bears remarkable resemblance to the previously postulated nonclassical bicyclobutonium carbocation. The symmetrical puckered cyclobutyl carbocation was found to be 3.7 kcal/mol higher in energy relative to the bisected carbocation and represented a maximum on the potential energy surface.

It is fair to say that theory has not been a highly effective tool for the study of the structures of C_4H_7+. Theoretical calculations would surely benefit from inclusion of electron correlation when considering C_4H_7+. Indeed, Pople, Schleyer and co-workers[23] found that inclusion of electron correlation into calculations of the ethyl carbocation had dramatic effects, one of which was a

change in the energy ordering of the classical and bridged, nonclassical structures; inclusion of electron correlation lowered the energy of the nonclassical structure. Hehre's reports on C_4H_7+[16,21,22] have seemed to improve and agree, perhaps only coincidently, with each new significant piece of experimental evidence accumulated, but this is not the same as a decisive and convincing argument for a particular favored C_4H_7+ geometry.

C. Nonclassical Bicyclobutonium and Bisected C_4H_7+ Structures

Roberts, et. al. proposed a set of rapidly equilibrating nonclassical bicyclobutonium structures, **2a-c**, rather than the more symmetrical tricyclobutonium carbocation (**1**) to explain the statistically nonrandom distribution of label in the solvolyses of cyclopropylmethyl, cyclobutyl, and 3-butenyl derivatives. It is necessary to assume that the equilibration of structures **2a-c** is rapid but not instantaneous compared to the rate of reaction with solvent. Each bicyclobutonium isomer is expected to give the same proportions of cyclopropylmethyl, cyclobutyl, and 3-butenyl products. To illustrate more clearly the geometrical arrangement of atoms in **2**, Figure 1 displays a stereoscopic ORTEP (Oak Ridge



2a **2b** **2c**

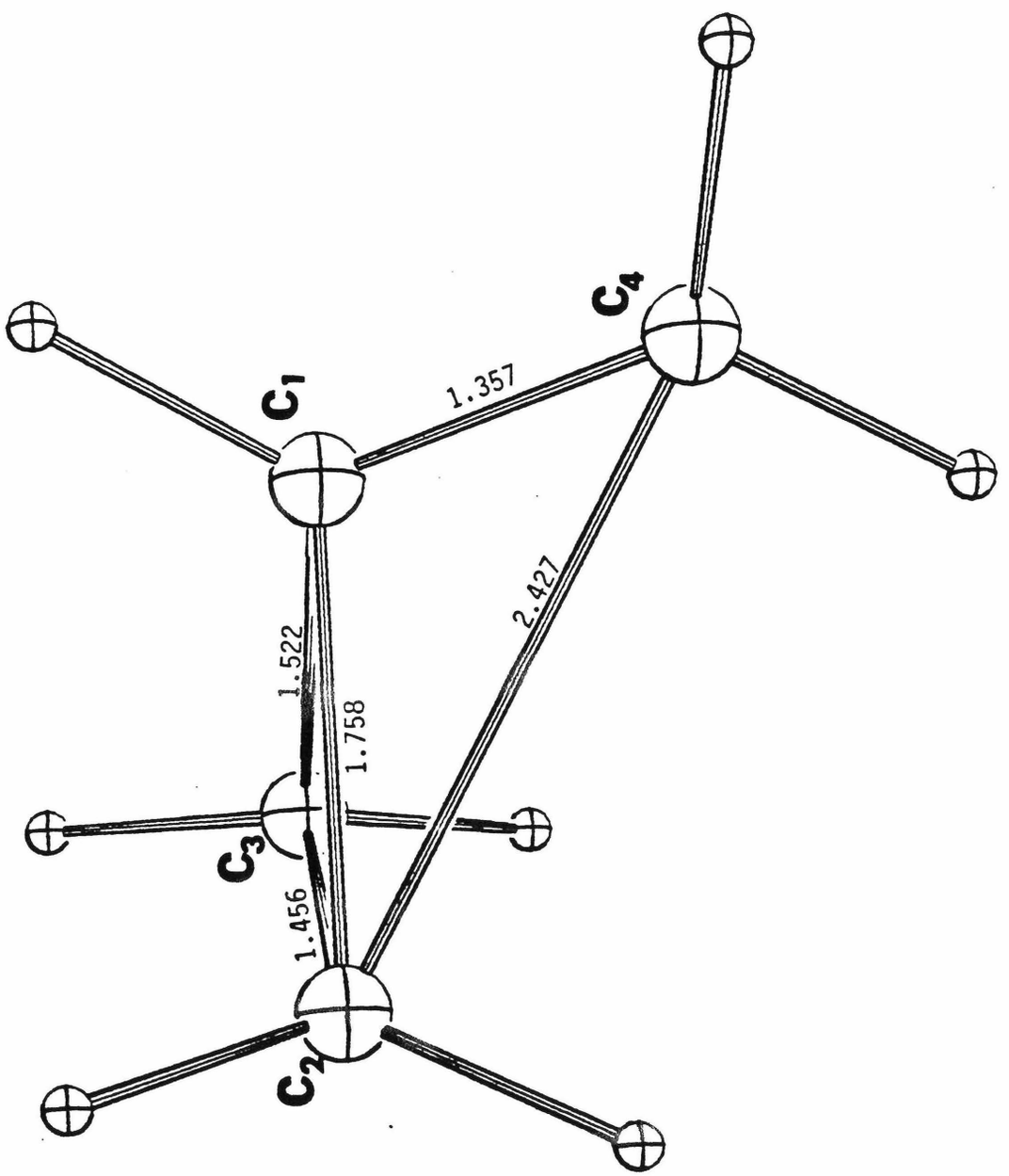


Figure 1. ORTEP drawing of the $C_4H_7^+$ bicyclobutonium structure, based on Cartesian coordinates calculated at 4-31G level of theory (point group C_1); see ref 24.

Thermal Ellipsoid Plot Program) drawing. The structural parameters were calculated by Hehre at the 4-31G level of molecular orbital theory[24] and the bond lengths are indicated; dotted-line formalism is omitted from Figure 1 (normal convention would show the C1-C2 and C2-C4 bonds as dotted-lines and the C1-C4 bond as one solid and one dotted-line). Structure **2** possesses a pentacoordinate carbon (C2) unsymmetrically bridging two electron-deficient carbons (C1, C4). The bicyclobutonium structure differs slightly from the bisected cyclopropylmethyl structure, **4** in that the C2-C1-C4 angle has decreased, the C1-C2 bond is longer, and the C1-C4 bond is shorter. Formally, one can convert the bisected structure **4** to **2** with a slight twist in the exo methylene carbon so that the empty p orbital can effectively overlap the C1-C2 or C1-C3 σ-bond. Figure 2 shows Streitwieser's description of the transition state leading to the nonclassical bicyclobutonium carbocation.[25]

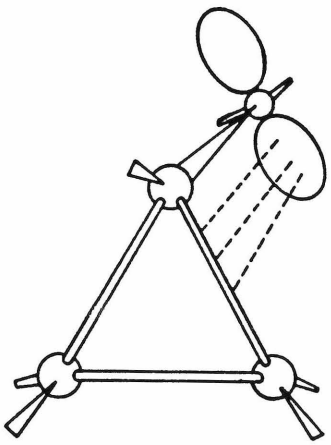
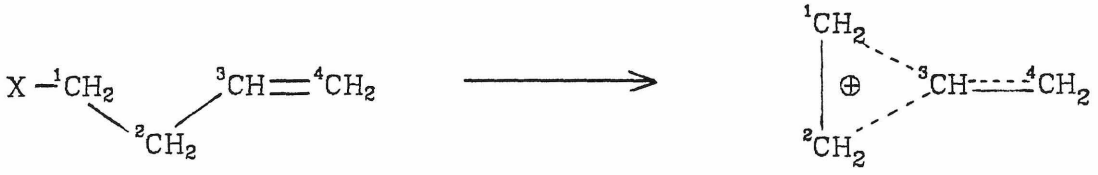


Figure 2. σ-Bridging leading to proposed bicyclobutonium carbocation.

Based on MO calculations, Roberts and Howden[26] found that the net atomic charges on C1, C2, and C4 were in the ratio 1:2.05:1.34, respectively.

The nonclassical structure which has been the subject of the most disagree-

ment is the bisected cyclopropylmethyl carbocation, **4**. It only meets the first two criteria previously given for a nonclassical structure. If **4** is formed from a 3-butenyl precursor, the coordination number of the methine carbon (C3) increases because in the bisected carbocation, it still maintains primarily sp^2 hybridization. This increase in coordination at C3 is akin to pentacoordinate car-

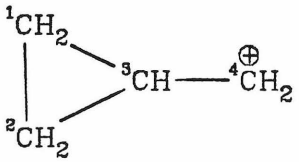


4

bon formation from a sp^3 hybridized carbon. In this sense, **4** also satisfies the last criterion of a nonclassical carbocation. More importantly, there is the fact that such a large barrier to rotation about the cyclopropane-carbocation carbon bond in **4** indicates that this bond has a high double-bond character and hence the carbocation is not classical. Without belaboring the issue, there seems to be ample justification for designating the bisected cyclopropylmethyl carbocation as nonclassical. Schmitz and Sorenson[27] calculated charge delocalizations for the bisected cyclopropylmethyl structure at the STO-3G level of theory. They report formal charges 0.014 and 0.487 for atoms C3 and C4, respectively and a combined charge of 0.499 for atoms C1 and C2. The charge distributions in the bicyclobutonium and bisected cyclopropylmethyl are very different; in the former two methylene carbons bear partial positive charge while all three methylene carbons bear charge in the latter.

D. Mechanisms Involving Classical C_4H_7+ Intermediates

Brown has frequently expressed reservations about the invocation of non-classical carbocations to explain the enhanced rates and the product distributions in the solvolysis of cyclopropylmethyl, cyclobutyl and 3-butenyl derivatives. In 1962, he suggested that the rapid rate of solvolysis observed for cyclopropylmethyl derivatives could be ascribed to relief of steric strain in the transition states leading to formation of C_4H_7+ intermediates which had an unspecified but "classical" structure.[28] There can be **no** relief of steric strain in a "classical" sense unless solvolysis of cyclopropylmethyl derivatives occurs with rearrangment to cyclobutyl or 3-butenyl intermediates. If this were the case, it becomes very difficult to explain the enhanced rates of solvolysis for the corresponding cyclobutyl or 3-butenyl derivatives. Brown's most recent position on the rate accelerations was based on a solvolytic study of 1-aryl-1-cyclopropyl-1-ethyl *p*-nitrobenzoates.[29] Using his "tool of increasing electron demand," Brown concluded that the formation of the cyclopropylmethyl carbocation is stabilized by σ-conjugation. Brown distinguishes between σ-conjugation which is equivalent to hyperconjugation and σ-participation which is equivalent to nonclassical electron delocalization. With regard to the solvolysis of cyclopropylmethyl derivatives, he restricts σ-participation to electron supply only from the C2-C3 bond and σ-conjugation to electron supply from either the C1-C2 or C1-C3 bonds.



Brown claims that the confusion over the nature of electron delocalization in

the cyclopropylmethyl system has resulted from the failure to properly distinguish between σ-conjugation and σ-participation. This form of logic is characteristic of Brown's strategy in defending classical intermediates for C_4H_7+ where he redefines descriptive nomenclature for electronic interactions in an apparent attempt to confuse or obscure the issue. In this regard, it is relevant to compare his latest position of σ-conjugation with his 1965 statement:[30] "the cyclopropylcarbinyl carbocation is highly stabilized by some sort of electron release, but this stabilization has nothing to do with any bonding between the carbonium carbon and either the two carbons of the ring or with one of the three carbon-carbon bonds of the ring."

Brown's explanation of product distributions and the extent of label scrambling observed in the solvolysis of cyclopropylmethyl derivatives is no more satisfactory. He proposes a rapidly equilibrating set of cyclopropylmethyl and puckered cyclobutyl carbocations with a small, essentially irreversible, diversion to 3-butenyl derivatives.[31] Several facts cast doubt upon this mechanistic hypothesis. If "classical" intermediates are involved, then the observed 10:10:1 product ratio for cyclopropylmethyl:cyclobutyl:3-butenyl products[2a,b] reflects an approximate relative ordering of stability for the corresponding classical carbocations: cyclopropylmethyl $\approx$ puckered cyclobutyl >> 3-butenyl. It is difficult to explain how a primary cyclopropylmethyl carbocation has comparable stability to the secondary puckered cyclobutyl carbocation. Currently available evidence indicates that primary carbocations are incapable of existence, that is, they are not local minima on the potential-energy surface.[32] Furthermore, the involvement of 3-butenyl carbocations should result in formation of α- and γ-methylallyl derivatives via a facile 1,2-hydride shift. The Brown mechanism also does not explain the internal return effects and the effect of methyl and phenyl substituents upon the solvolysis rates of

cyclopropylmethyl derivatives.

The strongest evidence supporting involvement of nonclassical intermediates in the solvolysis of cyclopropylmethyl derivatives is the high degree of formation of cyclobutyl products. It is difficult to rationalize this fact in terms of either a classical or a bisected C_4H_7+. Formation of cyclobutyl products was the primary impetus for the original postulation of the nonclassical bicyclobutonium intermediate by Roberts and co-workers. It is unfortunate that Brown has not seriously addressed this issue.

E. NMR Evidence for Nonclassical Structures under Stable-Ion Conditions

Cyclobutyl or cyclopropylmethyl chloride or the corresponding alcohols react with antimony pentafluoride to give stable-ion solutions with identical ^{1}H and ^{13}C NMR spectra.[33] These spectra are consistent with either a three-fold symmetric ion, the tricyclobutonium carbocation, **1**, or a set of rapidly equilibrating, less symmetric carbocations with the same effective averaged symmetry. The tricyclobutonium structure was abandoned by Roberts, et. al. as the result of the nonrandom ^{14}C distribution in solvolysis products and simple MO calculations.[26] The conclusion has been fortified by the finding that the exactly symmetric tricyclobutonium carbocation must be a maximum in energy as a consequence of the Jahn-Teller theorem.[34]

Another problem with Brown's proposed participation of a classical cyclobutyl carbocation is the ^{1}H spectrum of C_4H_7+ under stable-ion conditions. There are two sets of nonequivalent methylene hydrogens which do not undergo exchange at low-temperatures in $SbF_5-SO_2ClF-SO_2F_2$ or under solvolytic conditions.[35] Cyclobutanone with one sp^2 hybridized carbon is planar;[36] a cyclobutyl carbocation would have nonequivalent hydrogens only if it were to possess a puckered conformation. Furthermore, such a puckered cyclobutyl carbocation would have to have a large inversion barrier to maintain nonequivalence of methylene hydrogens. There are problems with this because the inversion barrier in cyclobutane is only 1.4 kcal/mol.[37]

The ^{13}C NMR spectrum of C_4H_7+ shows a single resonance for the methine carbon and an averaged resonance for the three methylene carbons. Staral, Roberts, Olah and co-workers[38] studied the temperature dependence of the ^{13}C spectrum of C_4H_7+ under stable-ion conditions. The temperature dependence

was larger than expected for a "normal" chemical shift dependence and was taken as evidence for a temperature-dependent equilbrium between two or more energetically similar structural isomers of C_4H_7+ interconverting rapidly on the NMR time scale. Assuming only two species were involved, optimization of a least-squares fit of the observed chemical shifts versus population of the lower-energy isomer was used to derive values for the chemical shifts of the lower energy isomer for the averaged methylene carbons as 47± 3 ppm and for the methine carbon as 115± 3 ppm. Comparison of these values with those anticipated for cyclobutyl, nonclassical bisected cyclopropylmethyl, and nonclassical bicyclobutonium carbocations[33b] showed that they were consistent with a nonclassical bicyclobutonium carbocation as the major structural form of C_4H_7+ under stable-ion conditions. The data also suggested that the minor form of C_4H_7+ was the nonclassical bisected cyclopropylmethyl carbocation, roughly 1 kcal/mol higher in energy.

Brown has claimed that the coupling constant ($J_{^{13}C_{CH}}$) observed for the methine carbon in C_4H_7+ under stable-ion conditions is a useful criterion for accessing nonclassical character.[39] but makes several logical errors in arriving at the conclusion that this coupling constant supports classical C_4H_7+ structures. The argument is based on expected change in $J_{^{13}C_{CH}}$ if the bicyclobutonium structure were formed; Brown contends that an increase in strain would be attendant on formation of **2** which should increase $J_{^{13}C_{CH}}$ and points to the fact that $J_{^{13}C_{CH}}$=180 Hz for C_4H_7+ is smaller than either the dimethyl ($J_{^{13}C_{CH}}$=190 Hz) or monomethyl ($J_{^{13}C_{CH}}$=187 Hz) substituted cyclopropylmethyl carbocations. The problem with the argument is that there is no justification in assuming more strain in structure **2** than in the bisected cyclopropylmethyl ion. Furthermore, the change in structure in going from the methyl-substituted systems to

the parent C_4H_7+ carbocation will have as serious ramifications for $J_{^{13}C_{CH}}$ as strain alone. The related methine carbon in the bridged 2-norbornyl carbocation has a $J_{^{13}C_{CH}}$=184.5 Hz comparable to the methine carbon value in C_4H_7+.[40] In a later study, Kelly[41] presented a different view than the one earlier reported in collaboration with Brown.[39] Using an equation for the angular dependence of $J_{^{13}C_{CH}}$ in C_4H_7+, Kelly[41] concluded that the C_4H_7+ carbocation must be distorted by $\approx 20°$ from the bisected arrangement. This new criterion proposed by Brown to fuel his classical polemics has thus only served to strengthen the validity of nonclassical C_4H_7+ structures.

II. EFFECT OF DEUTERIUM SUBSTITUENTS ON CARBOCATIONS

A. Intrinsic and Hyperconjugative Deuterium Isotope Effects in NMR

Three probable effects of deuterium substitution on ^{13}C resonances[42] are: (1) *intrinsic* isotope effects resulting from α- or β-^{2}H substitution; (2) *hyperconjugative* effects of β-^{2}H substitution; and (3) deuterium isotopic perturbations of equilibria or symmetries. For polyatomic molecules, the intrinsic effect of ^{2}H-substitution arises from the anharmonic vibrational term of the chemical shielding.[43] For compounds which do not form intermolecular hydrogen bonds, α- and β-^{2}H intrinsic isotope effects are always negative (upfield). Typically, a ^{13}C resonance undergoes a 0.3 ppm shift for each α-^{2}H and a 0.05-0.1 ppm shift for each β-^{2}H.[44] Intrinsic effects of γ-^{2}H substitution are usually negative but there have been numerous recent reports of positive (downfield) shifts.[44,45] For example, the C1 carbon of cyclobutene-3-*d* experiences a 0.075 ppm shift to lower field.[44] Intrinsic isotope shifts have been thought of as through-bond effects, but a recent report by Ernst, Eltamany, and Hopf[46] seems to demonstrate a through-space effect in deuterated cyclophanes.

Intrinsic deuterium isotope effects on ^{13}C chemical shifts in some neutral cyclopropyl and cyclobutyl deuterium-substituted derivatives which were measured in the course of this study are given in Table I. Most of these compounds were intermediate products in the preparation of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol (the synthesis is described later in this thesis). The intrinsic effects induced by deuterium substitution were measured at 125.76 MHz and the

Table I. The effect of deuterium substitution upon ^{13}C NMR chemical shifts[a] at 125.76 MHz.

Compound[b]	$\Delta\delta$, ppm[c]				$^1J_{CD}$, Hz			
	C1	C2	C3	C4	C1	C2	C3	C4
3*Z*-*d*-2,2-dichloro-1-phenylcyclopropane	0.00		-0.31					
3*E*-*d*-2,2-dichloro-1-phenylcyclopropane	0.00		-0.31					
2*E*,2*Z*,3*Z*-d_3-1-phenylcyclopropane	-0.30	-0.72	-0.53			24	25	
2*E*,2*Z*,3*E*-d_3-1-phenylcyclopropane	-0.30	-0.72	-0.49			25	25	
2*E*,2*Z*,3*E*-d_3-cyclopropanecarboxylic acid	-0.27	-0.67	-0.43					
2*E*,2*Z*,3*E*-d_3-cyclopropylmethanol	-0.29	-0.66	-0.48	-0.08			24	
cyclopropyl-1,1-d_2-methanol	-0.18			-0.77				21
1,2*E*-d_2-cyclobutanol	-0.57	-0.45	-0.15	-0.15	22	21		*d*
2,2,4,4-d_4-cyclobutanol	-0.36	-0.72	-0.13	-0.72		20		20

[a]Values of $\Delta\delta$ are ± 0.01 ppm. [b]C1, C2, and C3 refer to cyclopropyl group and C4 is the exocyclic carbon. [c]Negative values correspond to an upfield isotopic shift. [d]$^2J_{CD}$=1.7 Hz.

shifts are relative to the respective unlabeled compounds as internal standards. The intrinsic isotope shifts shown in Table I are not particularly unusual except for the two stereospecific phenylcyclopropanes where there is a 0.04 ppm greater shift for the ^{13}CHD when the deuterium is cis to the phenyl than when it is trans.

Hyperconjugative deuterium isotope effects are important in carbocations.[47,48] For the change from a β-C-H bond to a β-C-D bond in a carbocation, the lower zero-point vibrational energy is expected to lead to a reduction in electron donation to the empty p orbital and consequently a reduced electron density (deshielding) at the cationic center. Servis and Shue[49] have observed such deshielding hyperconjugative effects in classical, static carbocations. They report a downfield shift of $\approx$ 0.4 ppm at the cationic center for replacement of an α-methyl by trideuteriomethyl. In nonclassical π- or σ-bridged systems, the direction and magnitude of the chemical-shift isotope effect depends on the relative importance of the contributing resonance structures, the extent of hyperconjugative interaction and also the chemical shifts expected for each of the canonical forms. Servis and Shue concluded that the β-deuterium effect in nonclassical, bridged carbocations arises **mostly** from changes in the relative importance of the contributing resonance structures.

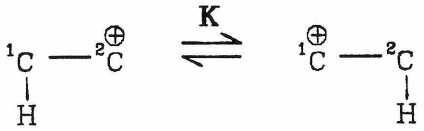
B. Deuterium Isotopic Perturbation of Carbocation Degeneracy

Nuclear magnetic resonance spectroscopy has been a powerful tool in the study of internal molecular processes. Changes in lineshape as a function of reaction rate made possible determination of a variety of torsion, inversion and

molecular rearrangement rates. Measureable uncertainty broadening may occur when the rates are greater than a few times a second. However, when a process which interchanges the nuclei responsible for different NMR shifts becomes faster than a limit which is roughly equal numerically to the square of the frequency separation in Hz, sharp peaks appear at positions which are the weighted averages of the separate NMR frequencies. Depending upon the observation frequency, the accessible temperature range, and the frequency separation of the signals of interest, rearrangement barriers as low as 3 kcal/mol have been measured. The issue of whether rearrangement is occurring over a barrier on a double- or multiple-minimum surface or whether there is a single energy minimum with a hybrid structure is a fundamental question in physical organic chemistry. The NMR lineshape cannot usually differentiate between these situations. If the NMR resonances of a carbocation are far removed from the positions predicted by the average of shifts chosen from suitable model systems, the conclusion may be drawn that the carbocation is not a set of rapidly equilibrating classical ions, but rather a bridged nonclassical carbocation. Olah has used the "discrepancy of chemical shift" as evidence for nonclassical character in several carbocations.[13,33,38] However, the discrepancy between predicted and observed chemical shifts is not always convincing evidence for a nonclassical structure.

Saunders and co-workers at Yale University[50] have developed an important and sensitive experimental probe of carbocation charge delocalization in which the validity of nonclassical structures is much more directly addressed. Deuterium substitution is a very small structural change to make in a carbocation and this is an important advantage of the Saunders method. The central theme is the idea that introduction of deuterium into carbocations undergoing rapid **degenerate** rearrangement will cause the equilibrium constant for the

rearrangement to other than unity, because the energies of the equilibrating structures will be perturbed to different extents by isotopic substitution. As a consequence, nuclei which gave a single, averaged peak in the unlabeled compound should now be observed with separate resonance lines. Saunders has observed perturbational effects for both $^{1}H^{51}$ and ^{13}C NMR spectra. This discussion will be limited to the effect of deuterium substitution on ^{13}C spectra; however, the general concepts are also applicable to ^{1}H spectra. The observed splitting (δ) between the carbon peaks of the deuterium-substituted carbocation is related to the chemical-shift difference of the nuclei in the slow-exchange limit (Δ) and the equilibrium constant (**K**) of the perturbed system. For the most simple case, a carbocation undergoing a rapid degenerate 1,2-shift, an equation expressing this relationship can be derived. If the rearrangement is fast, Δ cannot be determined directly and must be estimated from suitable model systems. This can be a significant problem in nonclassical systems because of the paucity of appropriate chemical-shift information. At low temperatures, ln **K** should



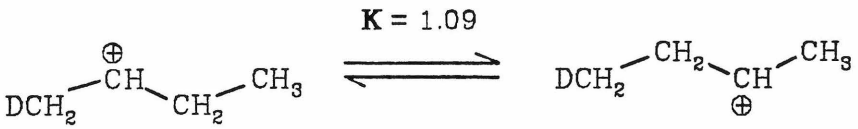
I II

$$\delta = \frac{[(\delta_1 I + \delta_2 II) - (\delta_2 I + \delta_1 II)]}{(I + II)}$$

$$\mathbf{K} = \frac{II}{I} \qquad \Delta = \delta_2 - \delta_1$$

$$\delta = \frac{\Delta(\mathbf{K}-1)}{\mathbf{K}+1} \qquad \frac{\delta}{\Delta} = \frac{\mathbf{K}-1}{\mathbf{K}+1} \qquad \mathbf{K} = \frac{\Delta+\delta}{\Delta-\delta}$$

vary linearly with 1/T which is a useful criterion for establishing that a deuterium isotopic perturbation of an equilibrium is in fact being observed. The largest deuterium isotopic perturbation effects are seen in the ^{13}C NMR spectra of carbocations where the resonances of carbon atoms, alternating between positively charged and neutral centers in a classical structure, are expected to be characterized by particularly large frequency differences (Δ). Deuterium-induced splittings (δ) in 1,2-dimethylcyclopentyl carbocation are 25 ppm for each β-deuterium on a methyl and 50 ppm for each β-deuterium on a methylene carbon. For rearrangements occurring over barriers of less than 3-4 kcal/mol, NMR lineshapes cannot, in general, determine the rates; however, large deuterium-induced splittings are observed. For example, deuterium substitution in the labeled *sec*-butyl carbocation produces an 11 ppm splitting of the C2-C3 carbon resonances at -111°C; assuming Δ = 206 ppm, the equilibrium constant of the monodeuterated system can be calculated.[52]



Deuterium isotopic perturbation of **symmetry** as contrasted to perturbation of an equilibrium produces splittings (δ) two orders of magnitude smaller on carbon-13 NMR shifts. Thus, cyclohexenyl-d_1 carbocation, which has a single-minimum potential-energy surface, shows only small splitting in the ^{13}C spectrum, δ = 0.33 ppm.[50b] β-Deuterium isotopic splittings in the cyclohexenyl-4,4-d_2 carbocation are of similar magnitude, δ = 1.68 ppm. Deuterium substitution increases the effective importance of one canonical form over the other; and in the cyclohexenyl carbocation, the effect on the shifts indicates that the charge

prefers to reside on the carbon bearing the proton. The Born-Oppenheimer approximation implies energy surfaces are unaffected by isotopic substitution and isotopes have equal electronegativity. However, isotopes do affect zero-point bond vibrations and because NMR chemical shifts are averages over bond vibrations, they are perturbed by isotopic substitution. In the 9-pentacyclo[4.3.2.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl carbocation reported by Coates,[53] the ^{1}H and ^{13}C spectra established that the carbocation has a nonclassical structure. The ^{13}C spectrum of (9-d)-9-pentacyclo[4.3.2.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl carbocation displays a splitting (δ) less than 0.1 ppm (the line-width of the averaged NMR peak).[52] This is consistent with a symmetrical nonclassical carbocation having a single-minimum potential-energy surface.

Deuterium isotopic perturbation produces relatively large splittings in carbocations undergoing a rapid, degenerate rearrangement. If the carbocation possesses true symmetry rather than time-averaged molecular symmetry, then deuterium-induced splittings are at least one order of magnitude smaller. Saunders has shown this to be the case for several controversial carbocations including the 1-d-bicyclo[2.2.1]heptyl carbocation where $\delta \leq 2$ ppm.[54] The 1-d-bicyclo[2.1.1]hexyl carbocation displays a splitting of 1.2 ppm at -115°C[50c] which is far smaller than a typical δ for perturbation of equilibrium and thus supports a nonclassical structure for this carbocation.

As the barrier to rearrangement in a carbocation becomes lower, **K** approaches unity and Δ decreases, both changes reducing δ. Saunders has proposed that the ratio δ/Δ be used as an indicator of the extent of delocalization in a carbocation.[50b] Values of δ/Δ range from 0.18 for the 3,3-d_2-1,2-dimethylcyclopentyl carbocation to 0.0058 for the 1-d-bicyclo[2.1.1]hexyl carbocation and 0.0035 for the 1-d-cyclohexenyl carbocation.[50c]

III. EQUILIBRIUM ISOTOPIC PERTURBATION OF C_4H_7+

A. C_4H_7+ ^{13}C Chemical Shifts in the Slow-Exchange Limit

The interpretation of deuterium isotopic perturbation results for labeled C_4H_7+ carbocations ultimately rests upon estimated chemical shifts for the carbons of candidate structures in the slow-exchange limit. While the criticisms made of such estimates warrant consideration, it seems reasonable to assume that any error in "static" shift values will not affect qualitative deductions concerning the geometry of C_4H_7+. Chemical-shift estimates used here are based on NMR data for the best available carbocation models. However, given the current state of understanding of the chemical shifts of nonclassical bridged structures, there could easily be an 10-20 ppm error in some estimates.

The chemical shift ($\delta_{^{13}C}$) of a carbon atom in a carbocation depends upon the hybridization (sp^2-carbons generally resonate $\approx$ 120 ppm to lower field relative to sp^3-carbons), the coordination number, and the degree of partial positive charge on the carbon. The degree of partial positive charge is determined by the number and type of atoms involved in charge delocalization. Carbon atoms in nonclassical structures which are directly associated with three-center two-electron bonding exhibit significant smaller deshielding than charge-bearing

carbons in classical structures. Ditchfield and Miller[56] used an *ab initio* method to calculate the carbon-13 chemical shifts of the classical and hydrogen-bridged ethyl carbocations. The sum of the chemical shifts of the two carbons of the classical C_2H_5+ was predicted to be 100 ppm less than that of the nonclassical bridged structure. Unfortunately, the same method of calculation has not as yet been applied to systems with a bridging carbon atom.

1. Nonclassical Bicyclobutonium Carbocation

For the three methylene carbons of the nonclassical C_4H_7+ bicyclobutonium carbocation, **2**, two model systems were chosen. Shown below are the reported ^{13}C chemical shifts for the nonclassical bicyclo[2.2.1]heptyl (**5**)[57] and nonclassical 1-methylcyclobutyl (**6**)[58,59] carbocations.

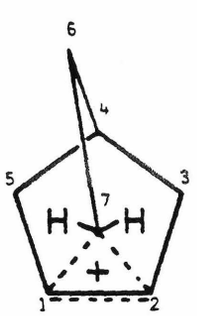
$\delta_{1,2}$= 125.2 ppm

$\delta_{3,5}$= 47.9 ppm

δ_4= 33.3 ppm

δ_6= 27.9 ppm

δ_7= 22.3 ppm

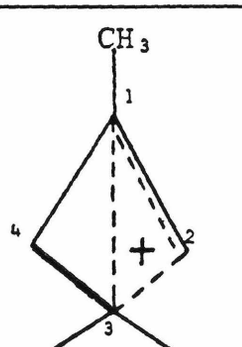


5
(-150°C)

δ_1= 162.08 ppm

$\delta_{2,4}$= 72.72 ppm

δ_3= -2.83 ppm

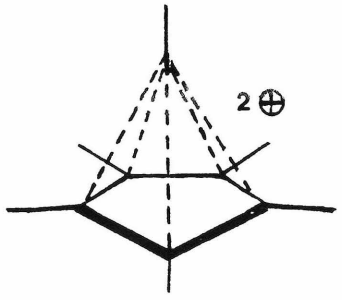


6
(-156.4°C)

The unsaturated carbons (C1, C2) of the 2-norbornyl structure, **5**, should provide a reasonable estimate for the C4 atom of bicyclobutonium structure **2**.

Substitution of methylene by hydrogen typically reduces a ^{13}C chemical shift by ≈ 10 ppm so that the predicted value for C4 in **2** is 115 ppm. The chemical shift (δ_3) of the methylene carbon (C3) in **2** seems reasonably estimated from the average chemical shift for the two types of methylene carbons (C3, C6) in the 2-norbornyl carbocation; $\delta_3 \approx (47.9 + 27.9)/2 \approx 38$ ppm.

Olah's[58] assignment of the ^{13}C spectrum of the 1-methylcyclobutyl carbocation (**6**) is used to estimate δ_2 in **2**. Above -156°C, carbocation **6** displays an averaged resonance ($\delta \approx 48$ ppm) for the three methylene carbons. Kirchen and Sorenson[59] were the first to observe separation of the averaged methylene resonance into two peaks having chemical shifts of 72.72 and -2.83 ppm. Sorenson, et.al. assigned the high-field methylene resonance to a sp^3-hybridized carbocationic center in a classical 1-methylcyclobutyl structure. Based on the ^{13}C spectra of a series of 1-alkylcyclobutyl carbocations which are considered classical, Olah and co-workers[58] surmised that the high-field methylene resonance was more likely the pentacoordinated, bridging carbon in a pair of rapidly equilibrating nonclassical bicyclobutonium structures. Hogeveen has observed highly shielded carbons in the spectra of pyramidal carbodications.[60] For example, the carbon which is positioned above the ring in the pyramidal dication shown below has a ^{13}C chemical shift at δ -2.0 ppm.[60b] Olah's interpretation of the 1-methylcyclobutyl carbocation seems more reasonable and hence, the value for δ_2 in the "static" bicyclobutonium structure is taken to be ≈ -3 ppm.



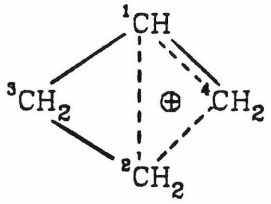
The ^{13}C chemical shifts estimated for the bicyclobutonium carbocation, **2**, are summarized below; the value for the methine carbon has been reported by Staral, Roberts, Olah, and co-workers.[38] The average of the "static" methylene chemical shifts given here is 50 ppm, in reasonable agreement with the 56 ppm average of Staral, et.al.[38] who estimated the chemical shifts entirely from the 2-norbornyl carbocation.

$\delta_1 \approx$ 114 ppm

$\delta_2 \approx$ -3 ppm

$\delta_3 \approx$ 38 ppm $\quad \delta_{av} \approx$ 50 ppm

$\delta_4 \approx$ 115 ppm



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2. Nonclassical Bisected Cyclopropylmethyl Carbocation

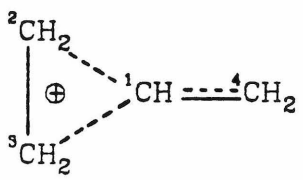
An estimate for the carbon-13 chemical shift of C1 in the "static" (slow-exchange limit) nonclassical bisected cyclopropylmethyl carbocation, **4**, has been reported by Staral, Roberts, Olah, and co-workers.[37] The shift of C4 in **4** was estimated from the unsubstituted terminal carbon (C3) in the 1,1-dimethylallyl carbocation (δ_{13_C}=160 ppm).[61] The "static" chemical shift for C4 in the bicyclobutonium structure (115 ppm) is used for δ_2 and δ_3 in the bisected cyclopropylmethyl carbocation. The estimated ^{13}C shifts for the nonclassical C_4H_7+ bisected cyclopropylmethyl carbocation are summarized below. The aver-

age ^{13}C methylene shift for **4** is 130 ppm.

Compare the two average ^{13}C methylene shifts for **2** and **4** with the experimentally observed value for C_4H_7+, δ=54.68 ppm at -94°C. The correspondence of the experimental δ with structure **2** formed the basis for the contention of Staral, et.al.[37] that the nonclassical bicyclobutonium structure was the major form of C_4H_7+ under stable-ion conditions.

$\delta_1 \approx$ 76 ppm
$\delta_2 \approx$ 115 ppm
$\delta_3 \approx$ 115 ppm
$\delta_4 \approx$ 160 ppm

$\delta_{av} \approx$ 130 ppm



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B. Monodeuterated and Dideuterated C_4H_7+

Saunders and Siehl[63] recently reported their investigation of the cyclopropylmethyl-cyclobutyl carbocation using deuterium isotopic perturbation. They examined the ^1H and ^{13}C NMR spectra of the carbocations formed by ionization of cyclopropyl-1-*d*-methanol and cyclopropyl-1,1-d_2-methanol at low temperatures. The isotopic perturbation was temperature-dependent which they regarded as definitive evidence for rapidly equilibrating C_4H_7+ structures. The most interesting aspect of their report was with reference to the methylene portion of the proton-decoupled ^{13}C NMR spectrum of the monodeuterated carbocation (C_4H_6D+) which is reproduced in Figure 3. There are two triplets and

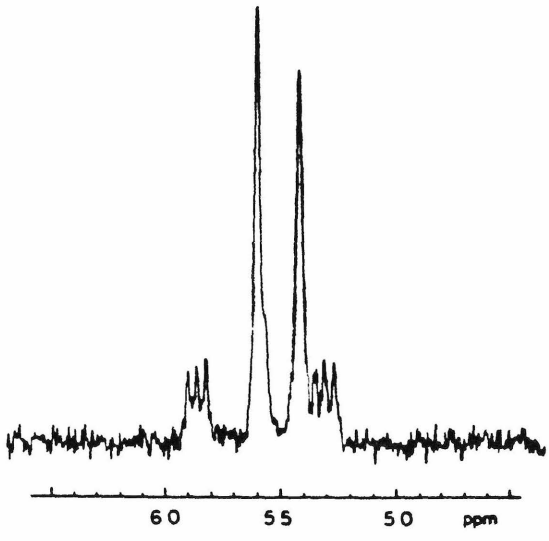


Figure 3. ^{13}C NMR spectrum of $C_4H_6D^+$ at -96°C reported by Saunders and Siehl[63].

two singlets, twice the number of resonances one might expect. There were also two methine carbons separated by 0.4 ppm in the ^{13}C spectrum of $C_4H_6D^+$. Saunders and Siehl took this as evidence for the existence of stereoisomeric forms of $C_4H_6D^+$, differing in the orientation of the C-D bond, although they could not assign specific resonances to the two $C_4H_6D^+$ stereoisomers. Deuterium isotopic perturbation of the equilibrium involving one $C_4H_6D^+$ stereoisomer is clearly different from perturbation of the equilibrium involving the other stereoisomer in both magnitude and sign.

In the ^1H NMR spectrum of $C_4H_6D^+$, deuterium isotopic perturbation of the upfield methylene resonance was evident but the downfield methylene peak was unaffected. At -135°C, the upfield methylene resonance of $C_4H_6D^+$ consisted of three peaks: one of area two (nondeuterated methylene hydrogens) shifted upfield and one of intensity one shifted downfield (the difference in chemical shift between these was 0.357 ppm). The remaining peak of area two was shifted slightly downfield (0.04 ppm relative to unlabeled carbocation, $C_4H_7^+$). These

results suggest that the value of Δ (chemical-shift difference between hydrogens in the slow-exchange limit) is very different in magnitude for the two types (exo and endo) of rapidly equilibrating hydrogens.

Saunders and Siehl[63] also reported ^1H and ^{13}C NMR data for the carbocation generated upon ionization of cyclopropyl-1,1-d_2-methanol in $SbF_5-SO_2ClF-SO_2F_2$. As in the ^1H spectrum of $C_4H_6D^+$, deuterium isotopic perturbation was observed only for the upfield set of hydrogens of $C_4H_5D_2^+$. Relative to the unlabeled carbocation, $C_4H_7^+$, the upfield methylene hydrogens were shifted to higher field by between 0.087 (-130°C) and 0.057 ppm (-80°C). Under the conditions used by Saunders, et.al., the deuterated methylene carbon resonance was not observed, so that the direction and magnitude of the deuterium ^{13}C chemical-shift effect were measured by observing the change in the position of the unlabeled methylene carbon relative to internal $C_4H_7^+$. The CH_2 resonance of $C_4H_5D_2^+$ shifted by between 1.77 (-135°C) to 1.24 ppm (-107°C).

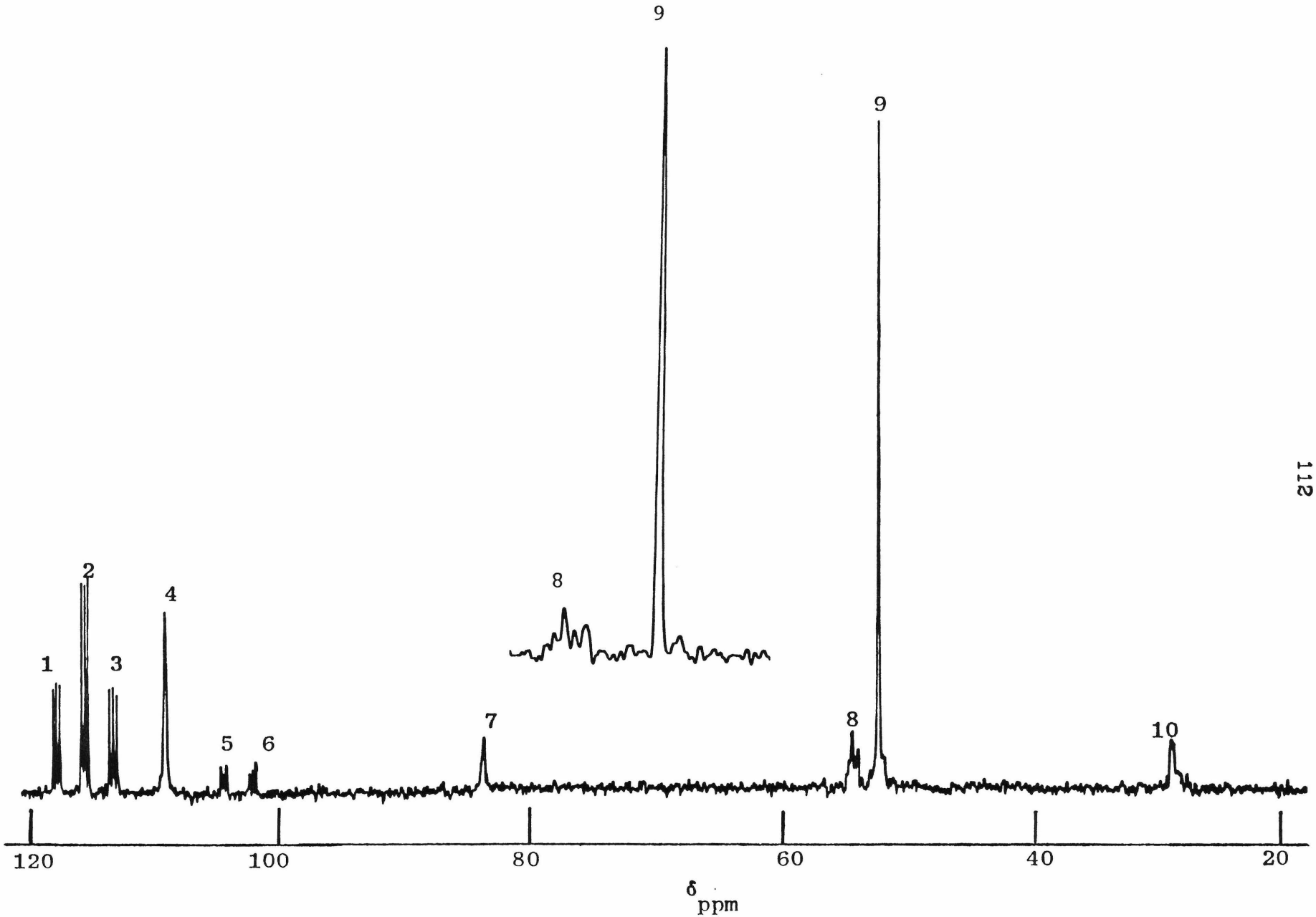
Saunders and Siehl[63] concluded that the deuterium isotopic perturbation of equilibria involving $C_4H_5D_2^+$ and $C_4H_6D^+$ was best interpreted in terms of a bicyclobutonium structure, **2**, as the major geometry for the cyclopropylmethylcyclobutyl carbocation. The opposite sign of deuterium chemical-shift effects in the ^{13}C spectrum of $C_4H_6D^+$ and the different magnitudes of deuterium chemical-shift effects in the ^{13}C and ^1H spectra of the two $C_4H_6D^+$ stereoisomers suggested a structure which contained a carbon with C-H bonds having different force constants. Because the carbon and proton chemical shifts of pentacoordinated carbons are very unusual, it is probable that the vibration frequencies of the CH bonds attached to a pentacoordinated carbon are different. The only viable candidate structure of $C_4H_7^+$ which contains a pentacoordinated carbon is **2**.

C. 125.76 MHz ^{13}C FT NMR of $C_4H_5D_2^+$

The ^{13}C FT NMR spectrum of the geminally dideuterated carbocation, $C_4H_5D_2+$, has been examined in this research but at much higher field (125.76 MHz). The ^1H-decoupled carbon spectrum of the solution formed by ionization of cyclopropyl-1,1-d_2-methanol in SbF_5–SO_2ClF–SO_2F_2 is shown in Figure 4. There are resonances assigned to O-protonated [d_2]cyclobutanol[64] with $\delta_{^{13}C}$ 84.05, 29.30 and 10.08 ppm as well as the resonances of the methine and methylene carbons of $C_4H_5D_2+$ at $\delta_{^{13}C}$ 109.54, 54.69 (pentet, $^1J_{CD}$=28 Hz) and 52.60 ppm, respectively. A mixture of dichlorofluoromethane-d and difluorochloromethane-d contained in a centered capillary was used to provide both field-frequency lock and reference signal ($\delta_{^{13}C}$= 116.52 ppm). The mechanism of formation for O-protonated cyclobutanol is not known although the scrambling of label observed in the ionization of cyclopropylmethanol-1-^{13}C suggested a transalkylation by way of the conjugate acid of cyclobutyl cyclopropylmethyl ether.[64]

The difference in chemical shift for the methylene carbons of $C_4H_5D_2+$ ($\Delta\delta_{CD_2}$) in Figure 4 is 2.09 ppm. The results of Saunders and Siehl[63] are equivalent to $\Delta\delta_{CD_2}$ values of 1.86 (-107°C) and 2.65 ppm (-135°C). The magnitude of $\Delta\delta_{CD_2}$ reported here for $C_4H_5D_2+$ at -90°C is larger than Saunders' value at -107°C. The difference in temperature control of samples and procedures for measurement of the NMR shifts are probable reasons for the lack of agreement. A reasonable correction for the intrinsic effect of α-deuterium substitution at the $^{13}CD_2$ carbon of $C_4H_5D_2+$ is +0.6 ppm judging from the data given in Table I (Chapter II) for intrinsic effects in neutral small-ring compounds. The corrected value of $\delta_{^{13}C}$ for the $^{13}CD_2$ carbon of $C_4H_5D_2+$ is 55.3 ppm; corrected value of $\Delta\delta_{CD_2}$ is 2.7 ppm.

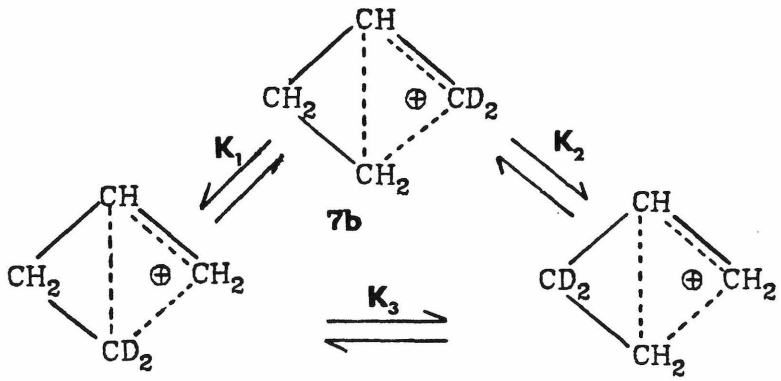
Figure 4. 125.76 MHz ^{13}C FT NMR (^{1}H-decoupled) spectrum (at -90°C of a $SbF_5-SO_2ClF-SO_2F_2$ solution): of $C_4H_5D_2+$ and O-protonated [d_2]cyclobutanol prepared from cyclopropyl-1,1-d_2-methanol. Resonance lines are assigned as follows: 1,2,3=CDF_2Cl used as field-frequency lock signal and reference ($\delta_{^{13}C}$ 116.52 ppm); 4=methine carbon of $C_4H_5D_2+$ ($\delta_{^{13}C}$ 110.12 ppm); 5,6=$CDFCl_2$, a by-product of CDF_2Cl preparation; 7,10=O-protonated [d_2]cyclobutanol 8=$^{13}CD_2$ of $C_4H_5D_2+$ ($^{1}J_{CD}$=28 Hz, $\delta_{^{13}C}$ 55.26 ppm); 9=$^{13}CH_2$ of $C_4H_5D_2+$ ($\delta_{^{13}C}$ 53.17 ppm). A resonance ($\delta_{^{13}C}$ 125.23 ppm)from an unknown impurity in $SbF_5-SO_2ClF-SO_2F_2$ and the high-field resonance ($\delta_{^{13}C}$ 10.67 ppm) of O-protonated [d_2]cyclobutanol are not shown.


9
9
8
2
4
1
3
5
6
7
8
10
120
100
80
60
40
20
δ ppm

D. Interpretation of $C_4H_5D_2$+ Results

The interpretation of deuterium isotopic perturbation of the equilibria involving $C_4H_5D_2$+ will be considered individually for two C_4H_7+ candidate geometries: the nonclassical bicyclobutonium (**2**) and the nonclassical bisected cyclopropylmethyl (**4**) structures. There are two equilibria which can be effectively perturbed by introduction of deuterium into C_4H_7+: (1) the equilibrium between different structures (**2** $\rightleftharpoons$ **4**) and (2) the equilibrium among structurally similar, nondegenerate isomers. Saunders and Siehl[63] did not find evidence for perturbation of the equilibrium between structures **2** and **4**. The relative importance of the deuterium substitution on these two types of C_4H_7+ equilibrium processes is evaluated in more detail later (Chapter IV, Section E). For the present discussion, it is assumed that the deuterium chemical-shift effects in $C_4H_5D_2$+ can be adequately described in terms of one major structural form of $C_4H_5D_2$+.

For a nonclassical bicyclobutonium $C_4H_5D_2$+ ion, there would be three rapidly equilibrating nondegenerate isomers (**7a-c**). The populations of **7a-c** can



7a **7c**

be defined by any two of the three equilibrium constants. The chemical shift of the deuterated methylene carbon in $C_4H_5D_2+$ ($^{13}CD_2$) is given by equation [1]. Equation [2] is obtained from equation [1] by substitution of $\mathbf{K_1}$[**7b**] for [**7a**] and $\mathbf{K_2}$[**7b**] for [**7c**].

$$\delta_{CD_2} = \frac{([\mathbf{7a}]\delta_3 + [\mathbf{7b}]\delta_4 + [\mathbf{7c}]\delta_2)}{[\mathbf{7a}] + [\mathbf{7b}] + [\mathbf{7c}]} \qquad [1]$$

$$\delta_{CD_2} = \frac{\mathbf{K_1}\delta_3 + \delta_4 + \mathbf{K_2}\delta_2}{1 + \mathbf{K_1} + \mathbf{K_2}} \qquad [2]$$

The chemical shift for the two $^{13}CH_2$ carbons in $C_4H_5D_2+$ is derived in a similar manner.

$$\delta_{CH_2} = \frac{\delta_3 + \delta_2 + \mathbf{K_2}(\delta_2 + \delta_4) + \mathbf{K_1}(\delta_3 + \delta_4)}{2(1 + \mathbf{K_1} + \mathbf{K_2})} \qquad [3]$$

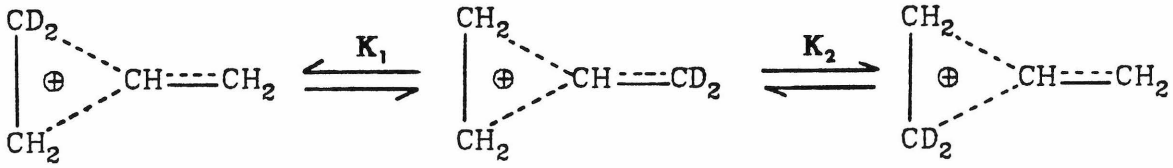
Subtracting equation [3] from equation [2] gives an expression for the deuterterium chemical-shift splitting ($\Delta\delta_{CD_2}$) in terms of the "static" chemical shifts and equilibrium constants.

$$\Delta\delta_{CD_2} = \frac{\delta_2(\mathbf{K_1} - 1) + \delta_3(\mathbf{K_2} - 1) + \delta_4(2 - \mathbf{K_2} - \mathbf{K_1})}{2(1 + \mathbf{K_1} + \mathbf{K_2})} \qquad [4]$$

Equation [4] cannot be used to estimate an accurate population distribution among isomers **7a-c** without knowledge of the relative values of $\mathbf{K_1}$ and $\mathbf{K_2}$. However, for the sake of argument, it will be assumed that $\mathbf{K_1} \approx \mathbf{K_2}$. Substitution of the experimental value for $\Delta\delta_{CD_2}$ and the values for δ_2, δ_3 and δ_4 for a bicyclobutonium structure (first section of this chapter) into equation [4] gives: $\mathbf{K_1} \approx \mathbf{K_2} \approx 0.9$. While the assumption that $\mathbf{K_1} \approx \mathbf{K_2}$ has little justification; the reason for calculating these equilibrium constants is for comparision purposes with the same calculation for a bisected structure. Hopefully, the error introduced

by assuming $K_1 \approx K_2$ is not greater than the difference between the equilibrium constants calculated for bicyclobutonium and bisected cyclopropylmethyl structures.

For a $C_4H_5D_2+$ bisected cyclopropylmethyl carbocation, there would be three isomers, **8a-c**, in rapid equilibrium.



8a **8b** **8c**

Isomers **8a** and **8c** are structurally indistinguishable so that the equilibrium constant for **8a** **8c** isomers is unity; furthermore, $K_1=K_2$ and $\delta_2=\delta_3$. For the bisected structure of $C_4H_5D_2+$, equation [4] can be reduced to equation [5], where $\Delta = \delta_4 - \delta_2$.

$$[\Delta\delta_{CD_2}] = \frac{\Delta(1 - K_1)}{1 + 2K_1} \qquad [5]$$

$$K_1 = \frac{\Delta - (\Delta\delta_{CD_2})}{\Delta + 2(\Delta\delta_{CD_2})} \qquad [6]$$

From the first section of this chapter, $\Delta = 45$ ppm for the C_4H_7+ bisected structure; from equation [6], $K_1=K_2 \approx 0.8$.

This analysis of $C_4H_5D_2+$ for two hypothetical cases, rapidly equilibrating bicyclobutonium ions or rapidly equilibrating bisected cyclopropylmethyl ions, is intended to show how the value of Δ (chemical-shift difference in the slow-

exchange limit) implies different magnitudes of perturbation. For example, because the bicyclobutonium structure has static chemical shifts ranging over a 118 ppm range, the population differences among possible isomers that would have to be assumed to account for the experimentally observed value of $\Delta\delta_{CD_2}$ is less than the population difference required for interpretation in terms of the bisected cyclopropylmethyl structure. This principle is a very rough qualitative distinction between the bicyclobutonium and bisected structures which will be more useful later in interpretation of the trideuterated carbocation.

The values of equilibrium constants reported in other isotopic perturbation studies of carbocations have all been for interconversion of classical structures. For example, the equilibrium constant for the Wagner-Meerwein rearrangement in 1-(methyl-d_3)-2-methyl-2-norbornyl carbocation is 0.85 at -89°C (where the charge prefers to be adjacent to the unlabeled methyl group)[50c] and the equilibrium constant for a 1,2-hydride shift in 2-butyl-1-d carbocation at -111°C is 0.92.[50c] There is no information regarding the magnitudes of perturbation induced by deuterium substitution into rapidly equilibrating nonclassical structures. Consequently, the question of how reasonable are the values calculated above for an equilibrium involving isomers **7a-c** in one case and isomers **8a-c** in the other cannot be addressed properly at this time.

The direction of the deuterium chemical-shift effect for the $^{13}CD_2$ carbon of $C_4H_5D_2$+ reflects the change in the weighted average of possible environments for $^{13}CD_2$. Because the $^{13}CD_2$ resonance is downfield relative to the methylene resonance of C_4H_7+, this carbon is spending a greater proportion of its time at a site which, in the slow-exchange extreme, has a $\delta_{^{13}C}$ higher than the averaged methylene resonance in rapidly equilibrating C_4H_7+. In other words, if the major equilibrium $C_4H_5D_2$+ structure is assumed to be bicyclobutonium, then the most populated isomer would be **7b**. The position of $^{13}CD_2$ in **7b** is at the C4 site which

had the highest predicted chemical shift in the slow-exchange extreme (Section A, this chapter). If these estimated shifts for **2** are correct, then only a greater weighting of isomer **7b** into the $^{13}CD_2$ chemical-shift averaged over all isomers could cause the $^{13}CD_2$ resonance to move to lower field. Placing the $^{13}CD_2$ preferentially at C3 or C4 would cause an upfield shift with respect to the average.

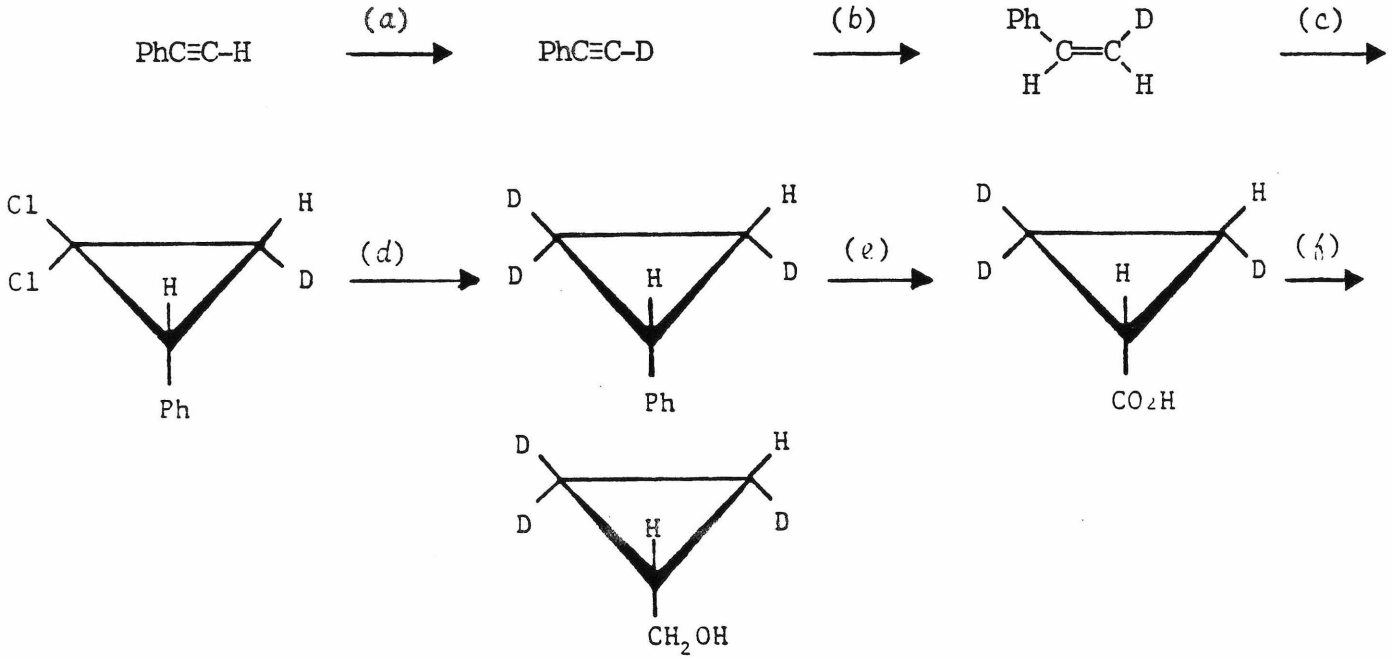
For an equilibirum situation involving C-H bonds with different force constants, substitution of a deuterium and the concomitant lower zero-point energy is expected to lead to a perturbation such that the deuterium would preferentially occupy the position where the bond has the greatest amount of s-character. The percent s-character of C-H bonds becomes higher as the amount of partial positive charge at a carbon increases. Theoretical[22,26] work has suggested that C4 in the bicyclobutonium structure bears the most partial positive charge of the three methylene carbons, consistent with the most populated isomer being **7b**. Product distributions in the solvolytic studies of the cyclopropylmethyl-cyclobutyl derivatives strongly suggest that the methine carbon of C_4H_7+ may actually bear the greatest partial positive charge of all four carbons in C_4H_7+.

IV. TRIDEUTERATED CYCLOPROPYLMETHYL-CYCLOBUTYL CARBOCATION

A. Synthesis of $C_4H_4D_3^+$ Precursors

(2*E*,2*Z*,3*Z*-d_3-Cyclopropyl)methanol, **9**, was synthesized in six steps as outlined below in Scheme 1. The overall yield of **9** was 13% from phenylacetylene. The stereochemistry of the product was confirmed with the aid of 500.13-MHz ^{1}H NMR and 76.7-MHz ^{2}HNMR in conjunction with a lanthanide-induced chemical-shift study using optically active tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium.

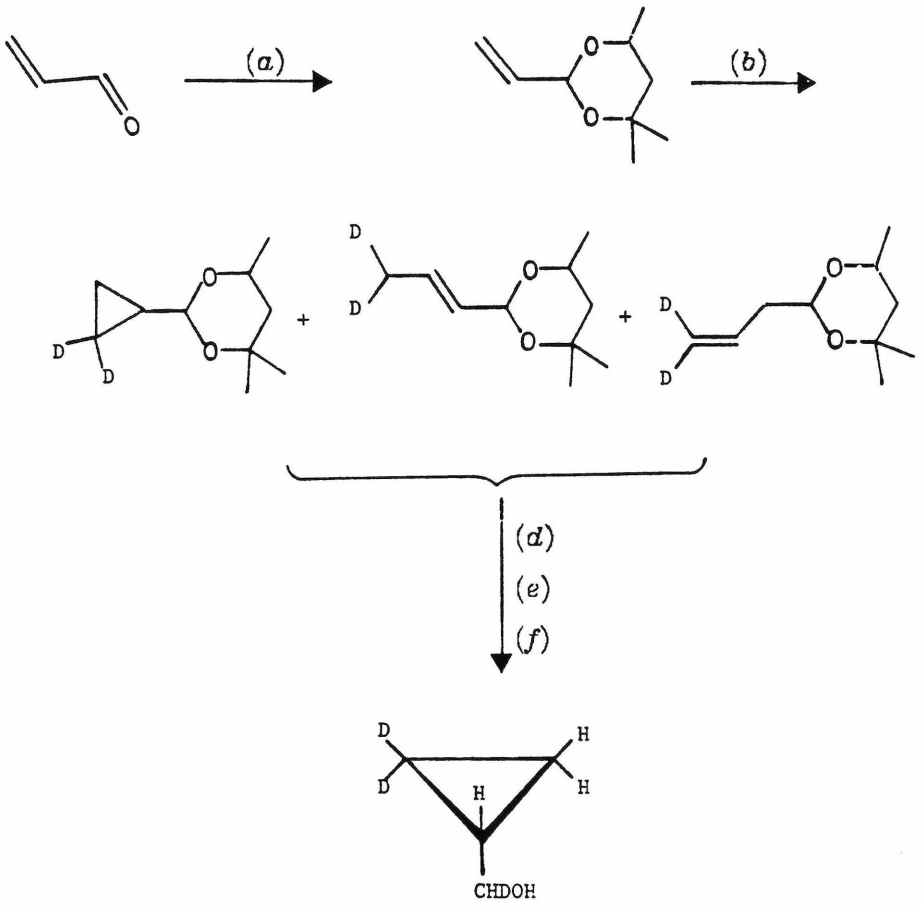
Scheme 1.



(*a*) NaOD, D_2O; (*b*) H_2, Pd(Pb); (*c*) $CHCl_3$, NaOH, $Et_4N^{\oplus}Cl^{\ominus}$; (*d*) Na°, CH_3OD, D_2O; (*e*) O_3, CH_3CO_2H; (*f*) $LiAlH_4$.

(2,2-d_2-Cyclopropyl)-1-d-methanol, **10**, was synthesized by Dr. Michael Squillacote[64] in six steps as outlined in Scheme 2. The pyrolysis of the pyrazolines obtained from addition of dideuteriodiazomethane to the protected acrolein was accompanied by 34% isomerization to open-chain derivatives. The GC separation of the cyclopropyl isomer was most efficient for the final alcoholic products.

Scheme 2.



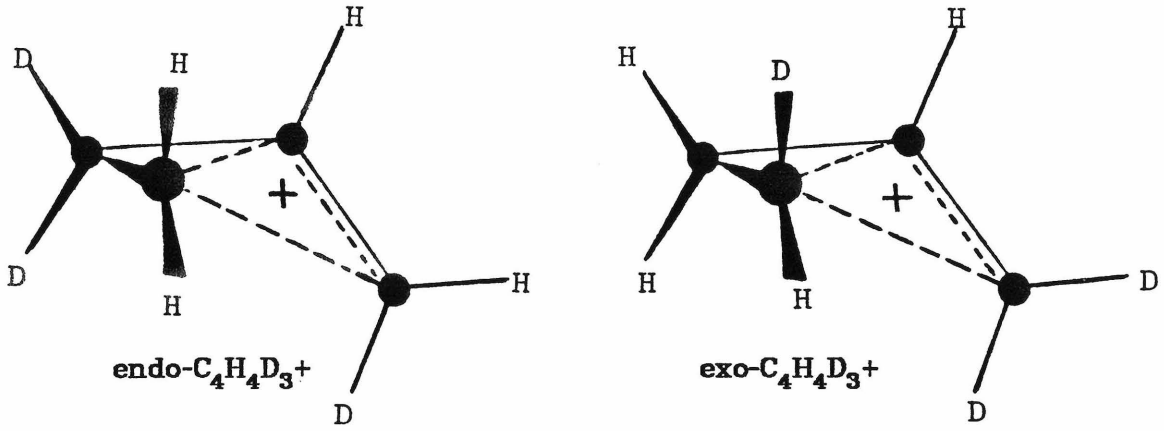
10

(*a*) 2-methyl-2,4-pentanediol; (*b*) CD_2N_2; (*c*) 450°C, 0.3 torr; (*d*) 1*N* CCl_3CO_2H; (*e*) $LiAlD_4$; (*f*) GC separation on 30% SE-30.

B. 125.76 MHz ^{13}C FT NMR of $C_4H_4D_3+$

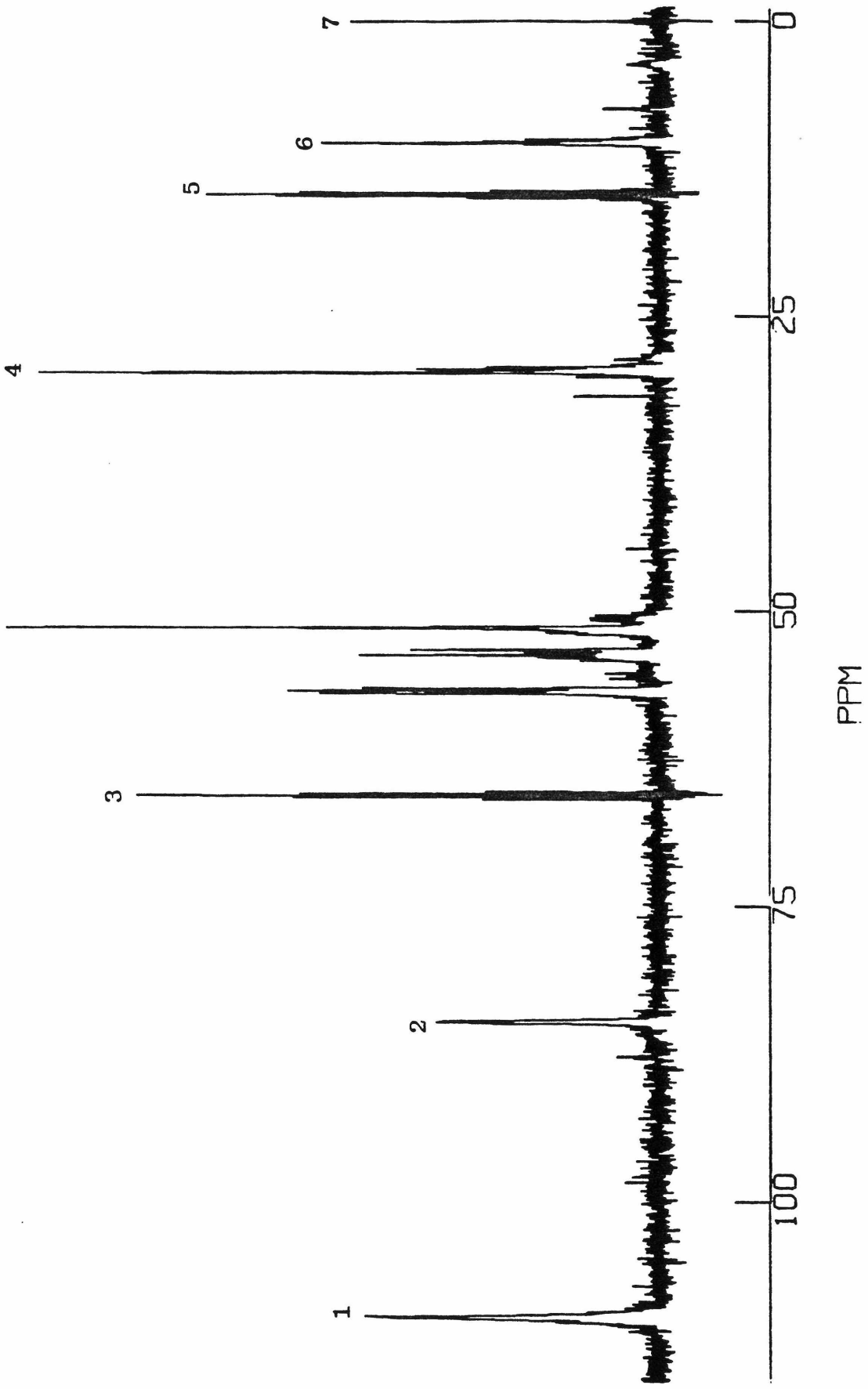
1. $C_4H_4D_3+$ Preparation from (2*E*,2*Z*,3*Z*-d_3-Cyclopropyl)methanol

The ^1H-decoupled ^{13}C NMR spectrum observed for the carbocation solution formed by ionization of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol, **9**, in SbF_5–SO_2ClF–SO_2F_2 is shown in Figure 5. Three resonances in the methylene region and one in the methine region are assigned to a sterospecific carbocation structure which will be termed "endo-$C_4H_4D_3+$". Bicyclobutonium structures are used to illustrate the geometry of both endo- and exo-$C_4H_4D_3+$ carbocations.



The chemical shift of the methine carbon (^{13}CH) of endo-$C_4H_4D_3+$ is 109.81 ppm in the Figure 5 spectrum, while the methylene carbons display resonances at 56.69 ppm (^{13}CHD, triplet, $^1J_{CD}$=27 Hz), 53.68 ppm ($^{13}CD_2$, pentet, $^1J_{CD}$=27 Hz), and 51.35 ppm ($^{13}CH_2$, singlet). The methylene region (49-58 ppm) of the ^{13}C spectrum in Figure 5 is shown in an expanded form in Figure 6. There are smaller resonances in the ^{13}C spectra which are assigned to the exo-$C_4H_4D_3+$

Figure 5. 125.76-MHz ^{13}C FT NMR (^{1}H-decoupled) spectrum of $C_4H_4D_3^+$ prepared from (*2E*,*2Z*,*3Z*-d_3-cyclopropyl)methanol (SbF_5–SO_2ClF–SO_2F_2 solution at -95°C). Resonances are assigned as follows: 1=^{13}CH of $C_4H_4D_3^+$; 2,4,6=O-protonated [d_3]cyclobutanol; 3,5=diethyl ether-d_{10} used as field frequency lock; 7=tetramethylsilane. The assignment of the methylene region is made in the Figure 6 legend. A resonance at $\delta_{^{13}C}$ 125.14 ppm (an unidentified impurity in SbF_5–SO_2ClF–SO_2F_2) is not shown.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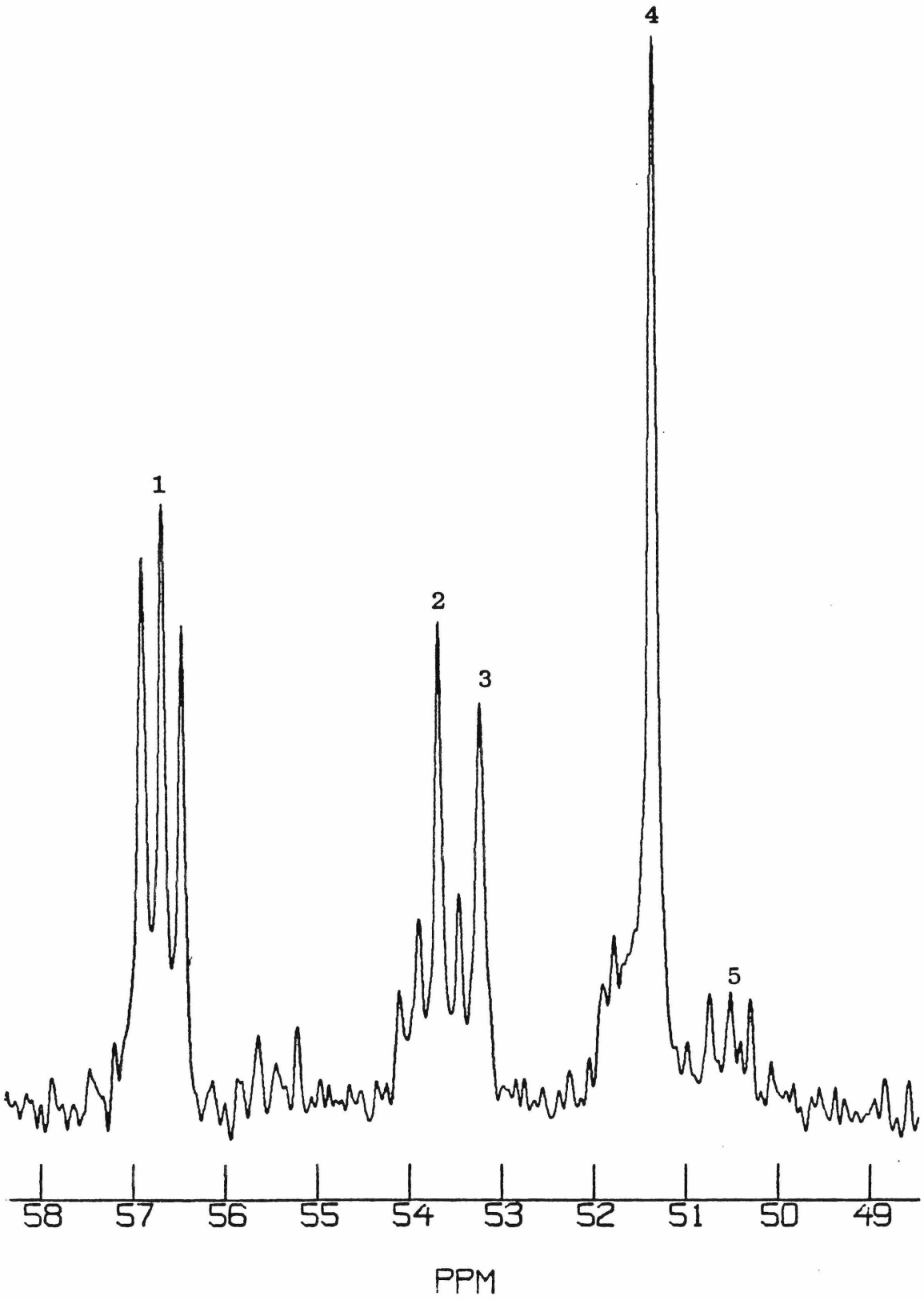


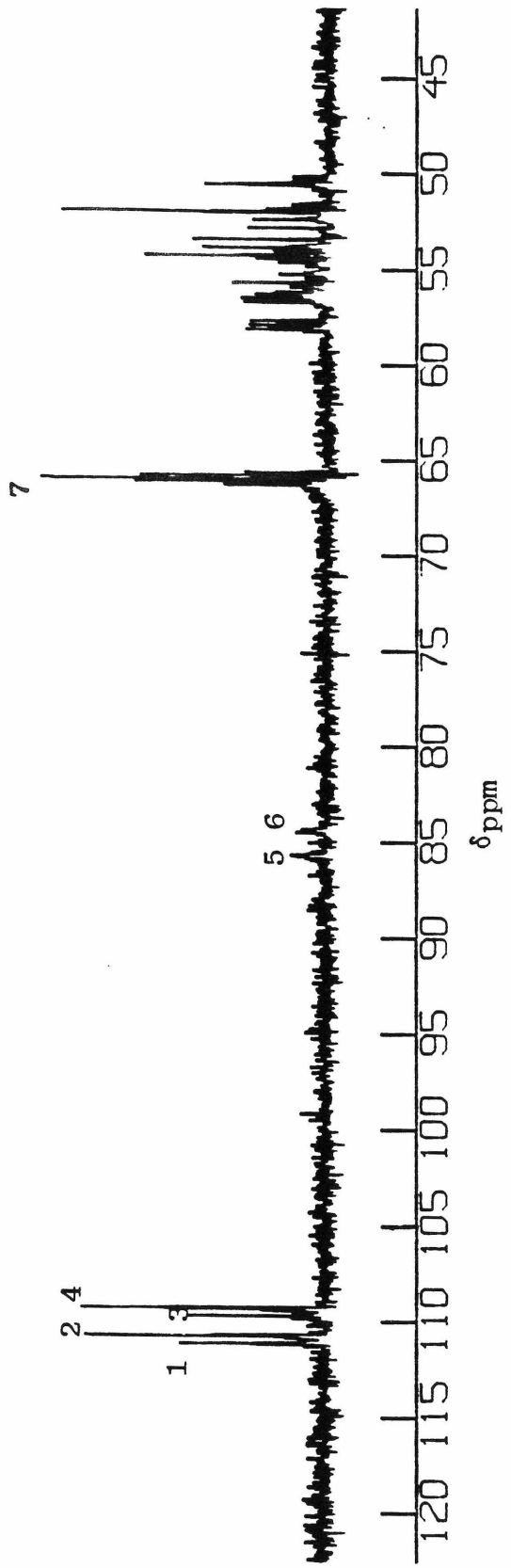
Figure 6. Methylene region of the 125.76-MHz ^{13}C FT NMR spectrum of $C_4H_4D_3+$ shown in Figure 5. Resonance lines are assigned as follows: 1= ^{13}CHD of endo-$C_4H_4D_3+$ ($^1J_{CD}$= 27 Hz, $\delta_{^{13}C}$= 56.69 ppm); 2= $^{13}CD_2$ of endo-$C_4H_4D_3+$ ($^1J_{CD}$= 27 Hz) coincident with $^{13}CH_2$ of exo-$C_4H_4D_3+$ ($\delta_{^{13}C}$= 53.68 ppm); 3= unknown ($\delta_{^{13}C}$= 53.23 ppm); 4= $^{13}CH_2$ of endo-$C_4H_4D_3+$ ($\delta_{^{13}C}$= 51.35 ppm); 5= ^{13}CHD of exo-$C_4H_4D_3+$ ($\delta_{^{13}C}$= 50.51 ppm).

carbocation: a triplet slightly upfield of the singlet of endo-$C_4H_4D_3$+ and a singlet coincident with the $^{13}CD_2$ carbon of endo-$C_4H_4D_3$+. The methine carbon of exo-$C_4H_4D_3$+ is observed 0.43 ppm downfield from endo-$C_4H_4D_3$+. The amount of the exo stereoisomer varied with different sample preparations; the $^{13}CD_2$ carbon of this stereoisomer can be observed in solutions having moderate amounts of exo-$C_4H_4D_3$+.

The ^{1}H-coupled ^{13}C NMR spectrum of the carbocation solution from **9** is shown in Figure 7. The superior resolution of ^{1}H-coupled ^{13}C spectra of $C_4H_4D_3$+ made it possible to more accurately access the relative amounts of endo- and exo-$C_4H_4D_3$+ in solution. The line-broadening which results from temperature gradients (created by simultaneous high-power decoupling and external cooling of the sample) is evident from comparision of Figures 5 and 7. Figure 8 displays the methylene region of the ^{1}H-coupled ^{13}C spectrum in Figure 7 in an expanded form. The methylene region of the ^{13}C (^{1}H-coupled) spectrum of a different $C_4H_4D_3$+ sample is shown in Figure 9. Comparision of the line intensities in Figures 8 and 9 demonstrates the basis for endo- and exo-$C_4H_4D_3$+ assignments. The spectral differences can be attributed to changes in the relative intensity of exo-$C_4H_4D_3$+ resonances (the exo-$C_4H_4D_3$+ concentration is lower in the sample used to obtain the Figure 9 spectrum).

The concentration of the exo stereoisomer increased *slowly* with time. Experimental exigencies limited the time for continual observation of a sample to roughly six hours. At a temperature of -90°C, no changes in ^{13}C NMR line intensities were observed over four hours within 5% experimental error. However, the sample whose spectrum is shown in Figures 5 and 6 was stored for several days at liquid-nitrogen temperatures; the subsequent ^{13}C NMR spectrum is the one shown in Figure 7.

Figure 7. 125.76 MHz ^{13}C FT NMR (^{1}H-coupled) spectrum of $C_4H_4D_3+$ prepared from (*2E*,*2Z*,*3Z*-d_3-cyclopropyl)methanol (SbF_5–SO_2ClF–SO_2F_2 solution at -95°C). The resonances are assigned as follows: 1,3=^{13}CH of exo-$C_4H_4D_3+$ ($^{1}J_{CH}$=182 Hz); 2,4=^{13}CH of endo-$C_4H_4D_3+$ ($^{1}J_{CH}$=182 Hz); 5,6=O-protonated [d_3]cyclobutanol; 7=diethyl ether-d_{10}, used as field-frequency lock. For assignment of the methylene carbons, see Figure 8 which displays the methylene region of this spectrum in an expanded form. Resonances for a solvent impurity ($\delta_{^{13}C}$ 124.99 ppm), the other diethyl ether-d_{10} resonance ($\delta_{^{13}C}$ 14.72 ppm), and the tetramethylsilane resonance are not shown in this figure.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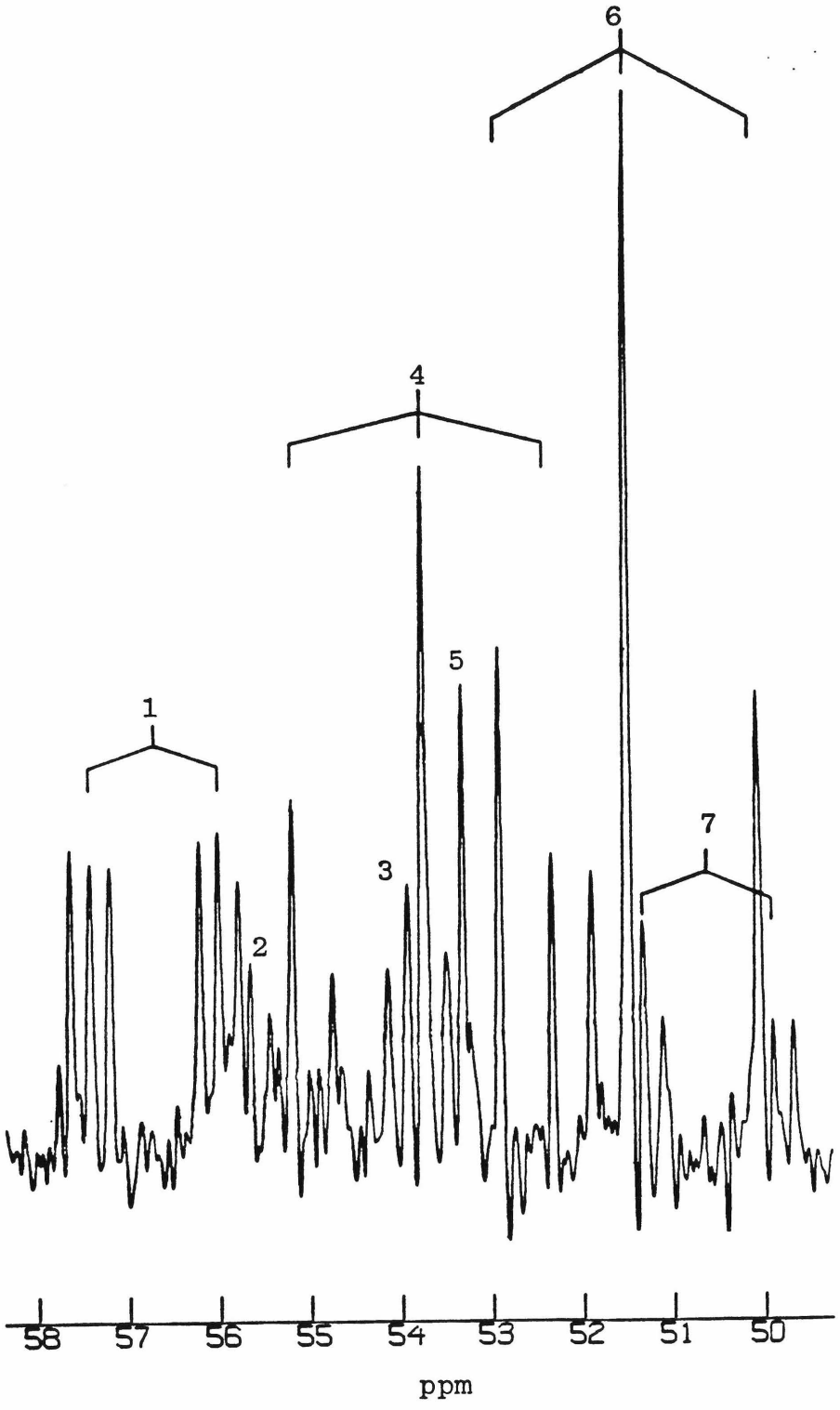


Figure 8. The methylene region of the 125.76 MHz ^{13}C FT NMR (^{1}H-coupled) spectrum shown in Figure 7. Resonances are assigned as follows: 1,3,6=^{13}CHD, $^{13}CD_2$ and $^{13}CH_2$, respectively of endo-$C_4H_4D_3$+; 2,4,7=$^{13}CD_2$, $^{13}CH_2$ and ^{13}CHD, respectively of exo-$C_4H_4D_3$+; 5=unknown. $^{1}J_{CH}$=179 Hz for ^{13}CHD and $^{13}CH_2$ of $C_4H_4D_3$+.

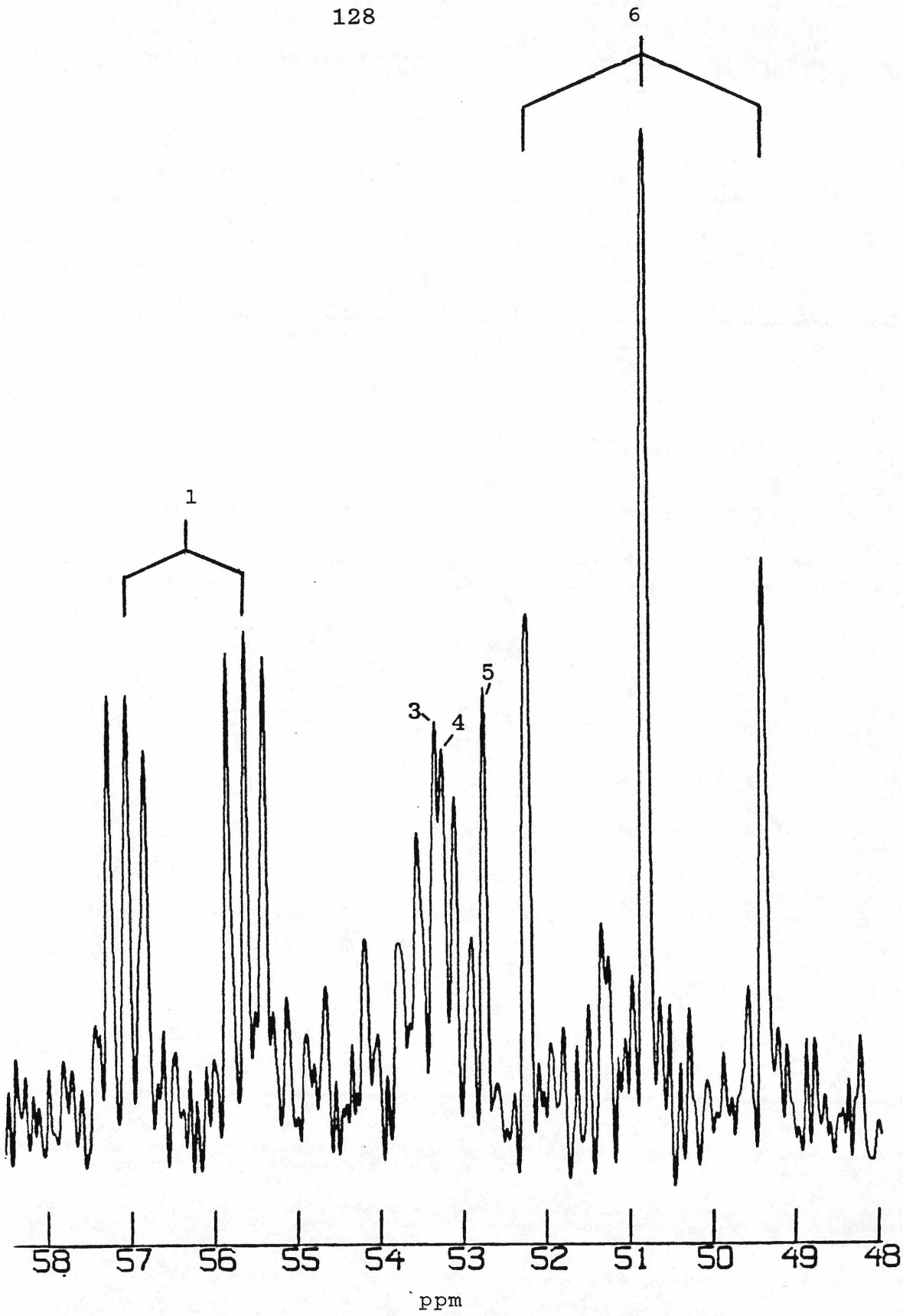


Figure 9. The methylene region of a 125.76 MHz ^{13}C FT NMR (^{1}H-coupled) spectrum of $C_4H_4D_3+$ prepared from (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol (SbF_5–SO_2ClF–SO_2F_2 solution at -95°C). Resonances are assigned as follows: 1=^{13}CHD of endo-$C_4H_4D_3+$; 3=$^{13}CD_2$ of endo-$C_4H_4D_3+$; 4=$^{13}CH_2$ of exo-$C_4H_4D_3+$; 5=unknown; 6=$^{13}CH_2$ of endo-$C_4H_4D_3+$.

The chemical shifts of both stereoisomers show temperature-dependent behavior similar to that observed for the unlabeled carbocation. The methine peaks move toward lower field and the methylene peaks toward higher field as the temperature is lowered. A compilation of the chemical shift data observed for both stereoisomers is given in Table II for carbocation solutions prepared from (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol.

Table II. Carbon-13 NMR shieldings[a] for the carbocation obtained from ionization of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol in SbF_5–SO_2ClF–SO_2F_2 at various temperatures.[b,c]

temp,°C	δ_{ENDO}				δ_{EXO}			
	^{13}CH	$^{13}CH_2$	^{13}CHD	$^{13}CD_2$	^{13}CH	$^{13}CH_2$	^{13}CHD	$^{13}CD_2$
-90	109.34	52.47	57.35	54.56	109.67	54.57	51.44	
-94[d]	109.85	51.70	56.90	53.84	110.25	53.96	51.08	
-95	109.81	51.35	56.69	53.68	110.28	53.68	50.51	55.70
-102	109.89	50.64	56.23	53.20	110.28	53.09		
-104[e]	110.38	50.43	56.17		110.77	52.95	50.07	
-110	110.70	49.75	55.83	52.82		52.40	49.27	55.07
-115	110.98	48.89	55.47	52.38	111.36	51.83	49.02	54.75

[a]Chemical shifts are ± 0.01 ppm relative to external tetramethylsilane. [b]The BVT thermocouple in the NMR probe was calibrated using a methanol sample, while observing the proton spectrum with the decoupler coils; experimental error ± 2.0 °C. [c]Data obtained using a single-band 125.76-MHz probe. [d]Internally unlabeled C_4H_7+ displayed resonances at 109.85 and 54.68 ppm. [e]Internally unlabeled C_4H_7+ displayed two resonances at 110.38 and 53.75 ppm.

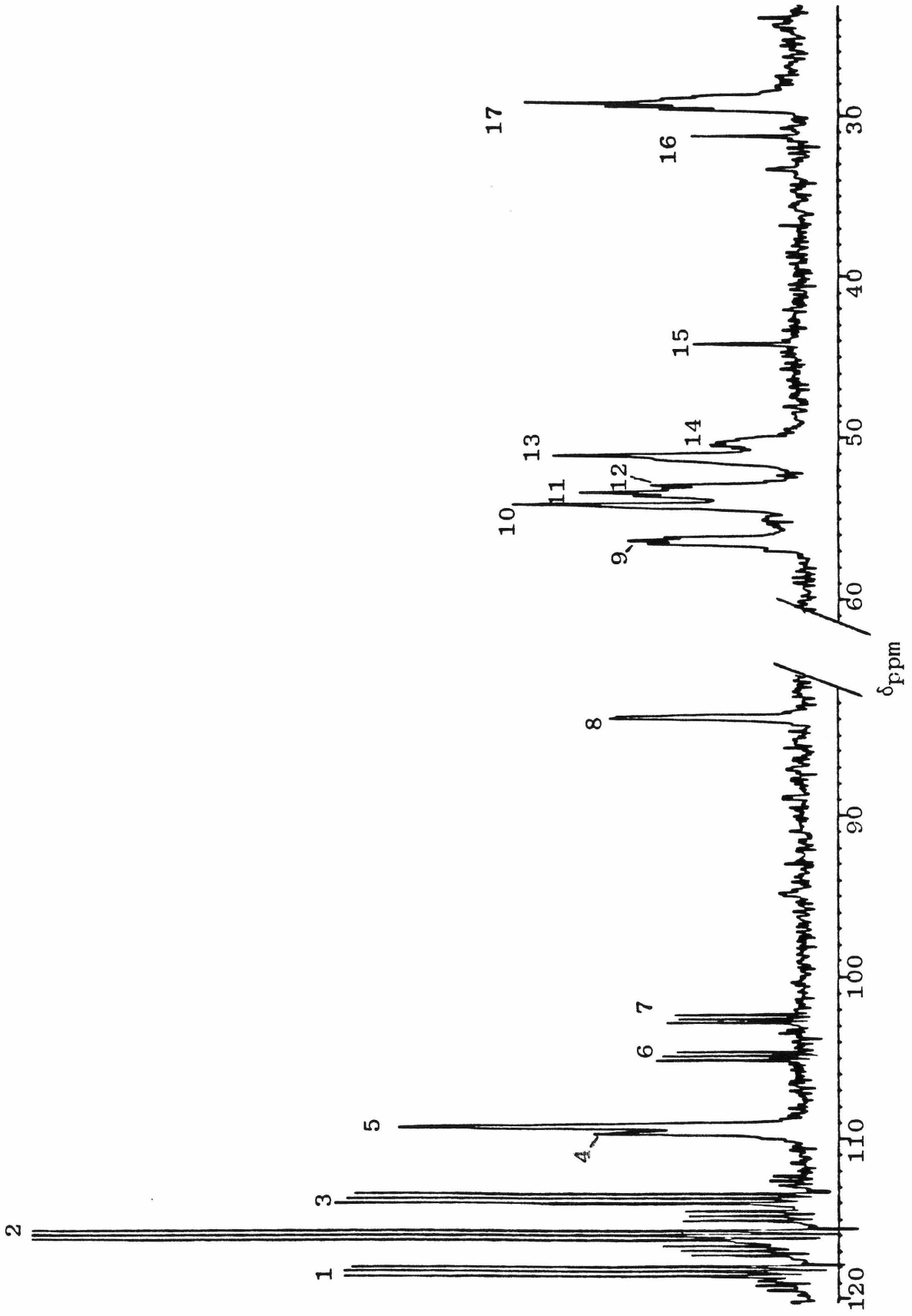
A second sample was prepared under the same conditions from a 1:5 mixture of unlabeled cyclopropylmethanol:(2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol; the

^{1}H-decoupled ^{13}C NMR spectrum is shown in Figure 10. From such samples the direction and magnitude of shifts induced by deuterium substitution could be measured relative to internal unlabeled C_4H_7+ (δ^*=^{13}C chemical shift relative to C_4H_7+). For endo-$C_4H_4D_3$+, the following shifts were observed at -94°C (negative sign indicates an upfield shift): δ^*_{CH}=0.0, $\delta^*_{CD_2}$=+0.84 ppm, δ^*_{CHD}=+2.22 ppm, and $\delta^*_{CH_2}$=-2.98 ppm. Exo-$C_4H_4D_3$+ displayed deuterium-induced shifts of δ^*_{CH}=+0.40 ppm, $\delta^*_{CD_2}$=+0.91 ppm, $\delta^*_{CH_2}$=-0.72 ppm and δ^*_{CHD}=-3.60 ppm.

The ^{13}C NMR spectra also contained resonances attributable to O-protonated [d_3]cyclobutanol.[65] These are seen in Figure 5 at 84.75, 29.67, and 10.38 ppm. O-protonated [d_3]cyclobutanol was slowly converted to $C_4H_4D_3$+ under the NMR conditions used. The stereochemistry of the deuterium substituents in the trideuterated O-protonated cyclobutanol could not be determined. Hence, it was not possible to determine whether the conversion of O-protonated [d_3]cyclobutanol retained stereochemistry. Integration of the ^{1}H NMR spectrum of the carbocation solution indicated that the O-protonated [d_3]cyclobutanol was present as a mixture of O-protonated 2,2,3-d_3-cyclobutanol and O-protonated 2,3,3-d_3-cyclobutanol.

One unidentified resonance was seen in the methylene region which had no $^1J_{CD}$ coupling and triplet multiplicity in a proton-coupled spectrum ($\delta_{^{13}C}$ 53.23 ppm in the Figure 5 spectrum). If this peak is a $C_4H_4D_3$+ carbocation which has undergone scrambling of deuterium to the methine carbon, there are two possible structures: (1) a carbocation containing one $^{13}CD_2$ and two $^{13}CH_2$ methylene carbons, or (2) a carbocation containing two ^{13}CHD and one $^{13}CH_2$ methylene carbons. We did not observe any other resonances in either the methine or methylene regions which could be ascribed to either possibility. Judging from the intensity of the unknown resonance, the first possiblity is the more likely.

Figure 10. 125.76 MHz ^{13}C FT NMR (^{1}H-decoupled) spectrum of $C_4H_4D_3+$ and C_4H_7+ prepared from a 5 : 1 mixture of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol:cyclopropylmethanol (SbF_5–SO_2ClF–SO_2F_2 solution at -94°C). Resonances are assigned as follows: 1,2,3=CDF_2Cl used as field frequency lock and reference ($\delta_{^{13}C}$=116.52 ppm); 4=^{13}CH of exo-$C_4H_4D_3+$; 5=^{13}CH carbons of endo-$C_4H_4D_3+$ and C_4H_7+; 6,7=$CDFCl_2$, a by-product of CDF_2Cl preparation; 8, 17=O-protonated [d_3]cyclobutanol; 9, 11, 13=^{13}CHD, $^{13}CD_2$ and $^{13}CH_2$ carbons, respectively of endo-$C_4H_4D_3+$; 10=$^{13}CH_2$ of C_4H_7+; 11, 14=$^{13}CH_2$ and ^{13}CHD carbons, respectively of exo-$C_4H_4D_3+$; 12, 15, 16=unknown. Resonances at $\delta_{^{13}C}$ 125.20 ppm (SbF_5–SO_2ClF–SO_2F_2 impurity) and 10.56 ppm (O-protonated [d_3]cyclobutanol) are not shown in this figure.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2. $C_4H_4D_3$+ Preparation from (2,2-d_2-Cyclopropyl)-1-d-methanol

The $C_4H_4D_3$+ carbocation was also prepared from (2,2-d_2-cyclopropyl)-1-d-methanol, **10**, by ionization in SbF_5–SO_2ClF–SO_2F_2. The ^{1}H-decoupled ^{13}C NMR spectrum of the carbocation solution prepared from **10** is shown in Figure 11 (-80°C). The carbocation solution prepared from **10** contained approximately equal amounts of exo- and endo-$C_4H_4D_3$+ as judged by the line intensities of the methine carbons. The two methine carbons have a chemical-shift difference of 0.44 ppm in Figure 11. The ^{13}C spectra for carbocation solutions prepared from **10** were generally of poorer quality than those from **9**. This is partly the result of fewer experiments using **10** as a carbocation precursor because of the limited amount of **10** available.

The two most intense singlets and the two triplets seen in the methylene region of the spectrum in Figure 11 are assigned to the $^{13}CH_2$ and ^{13}CHD carbons of exo- and endo-$C_4H_4D_3$+ (see Figure 11 legend for a complete assignment). Generally, it was not possible to assign the $^{13}CD_2$ resonances of $C_4H_4D_3$+ for samples prepared from **10** because of the poor signal/noise ratio in the spectra. There are two unidentified resonances in the ^{13}C spectrum of $C_4H_4D_3$+ prepared from **10** at $\delta_{^{13}C}$ 57.59 and 55.96 ppm, one of these is in the same relative position as the unidentified resonance observed in $C_4H_4D_3$+ solutions prepared from **9** (seen at $\delta_{^{13}C}$ 53.23 ppm in Figure 6). A summary of the ^{13}C NMR results is given in Table III. Different NMR probes were used to obtain the data reported in Table II and the data in Table III; consequently, the discrepancy between the two sets of data is likely a result of differences in temperature measurement and thermal properties of the two NMR probes.

Figure 11. 125.76 MHz ^{13}C FT NMR (^{1}H-decoupled) spectrum of $C_4H_4D_3+$ prepared from (2,2-d_2-cyclopropyl)-1-d-methanol (SbF_5–SO_2ClF–SO_2F_2 solution at -80°C). Resonances are assigned as follows: 1,2,3=CDF_2Cl used as field frequency lock and reference ($\delta_{^{13}C}$=116.52 ppm); 4= ^{13}CH of exo-$C_4H_4D_3+$; 5= ^{13}CH of endo-$C_4H_4D_3+$; 6,7= $CDFCl_2$, a by-product of CDF_2Cl preparation; 8=O-protonated [d_3]cyclobutanol; 9,13=^{13}CHD and $^{13}CH_2$ carbons, respectively, of endo-$C_4H_4D_3+$; 11,14=$^{13}CH_2$ and ^{13}CHD carbons, respectively, of exo-$C_4H_4D_3+$; 10,12=unknown.

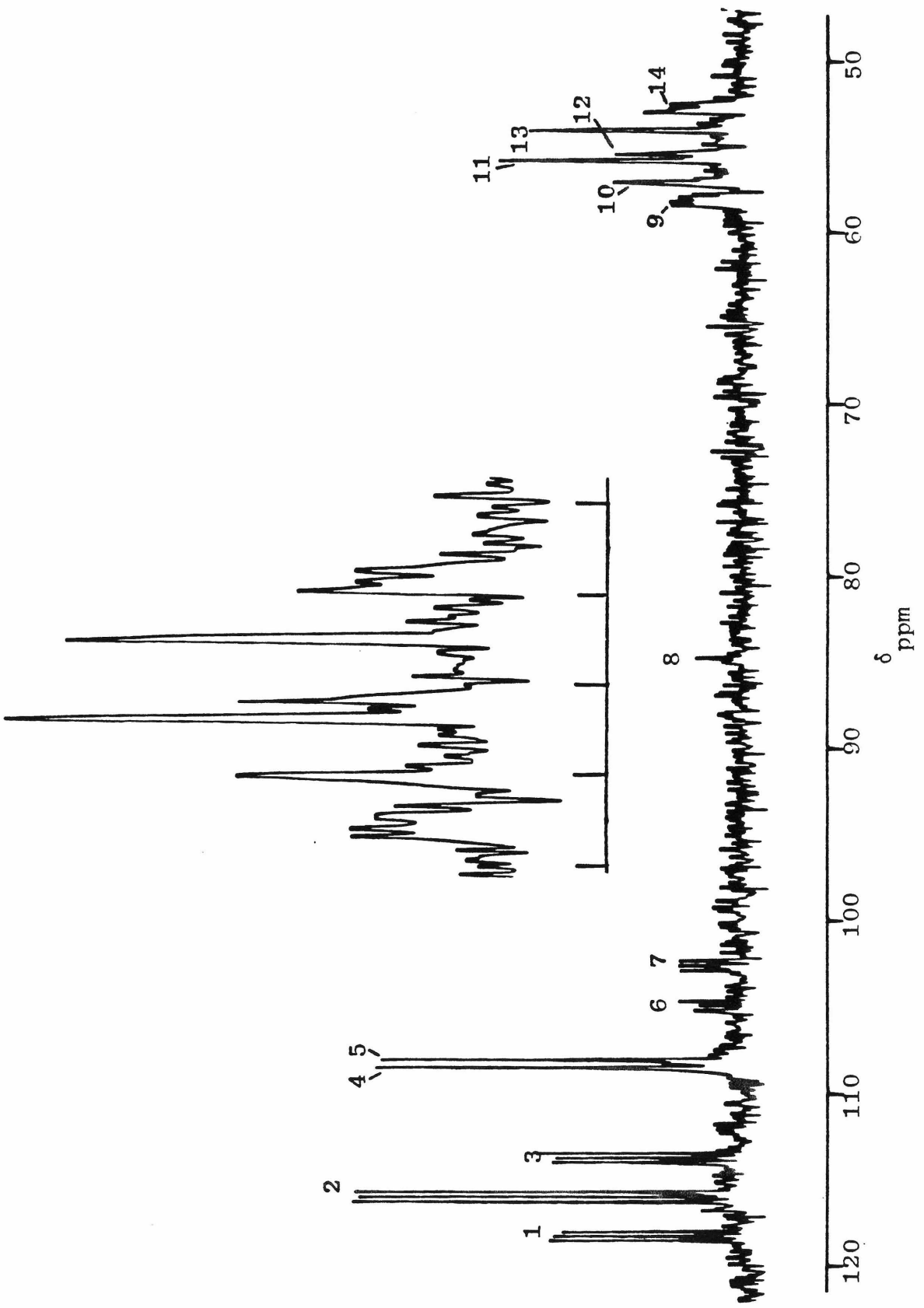
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Table III. Carbon-13 NMR shieldings[a] for the carbocation obtained from ionization of (2,2-d_2-cyclopropyl)-1-d-methanol in SbF_5–SO_2ClF–SO_2F_2 at various temperatures.[b,c]

temp,°C	δ_{ENDO}				δ_{EXO}			
	^{13}CH	$^{13}CH_2$	^{13}CHD	$^{13}CD_2$	^{13}CH	$^{13}CH_2$	^{13}CHD	$^{13}CD_2$
-80	108.55	54.59	58.72		108.99	56.34	53.28	
-90	109.29	52.86	57.65	54.46	109.71	54.93	51.73	56.31
-100	109.41	52.58	57.41	54.23	109.82	54.66	51.56	

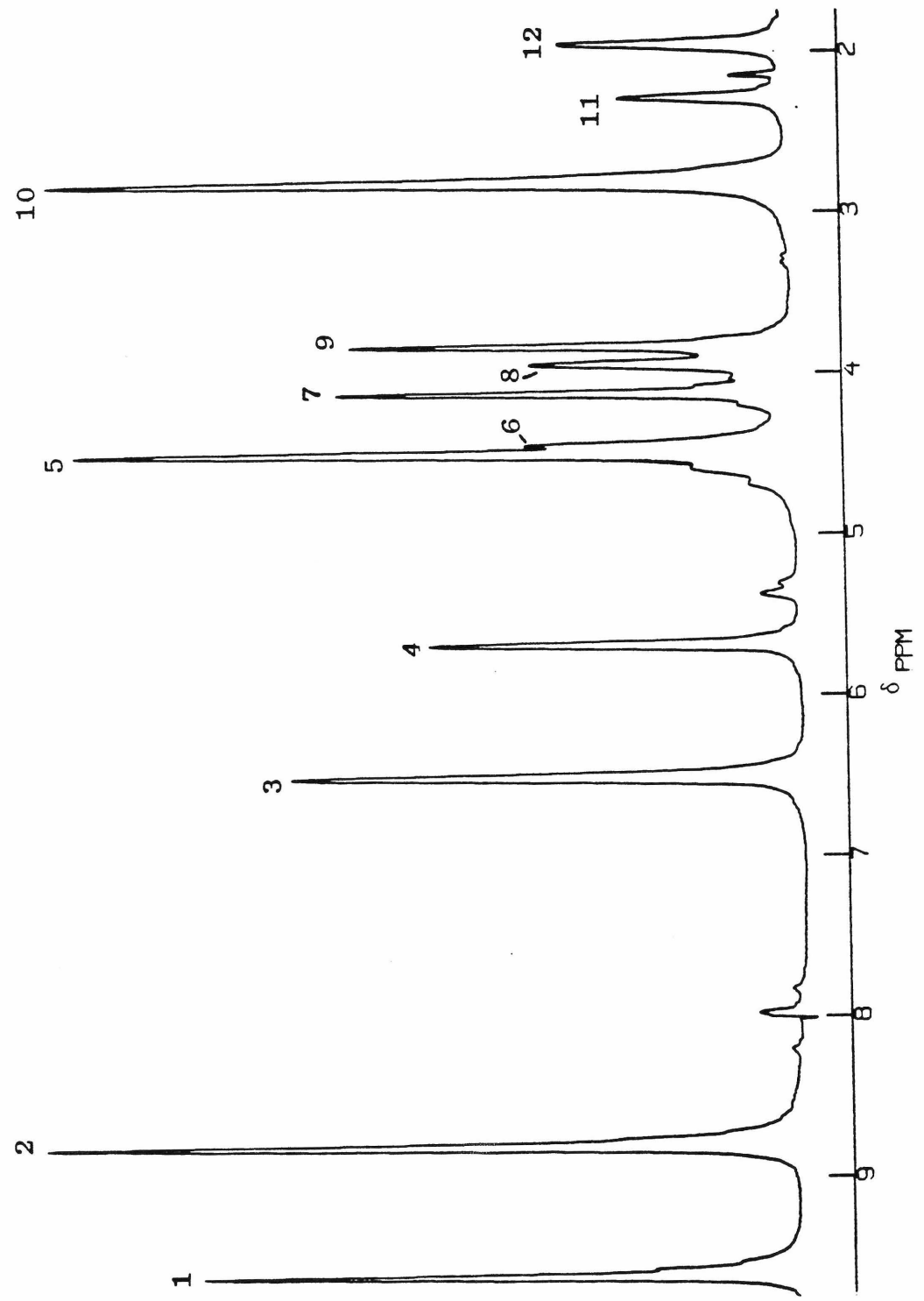
[a]Chemical shifts are ± 0.01 ppm relative to external tetramethylsilane. [b]The BVT thermocouple in the NMR probe was calibrated using a methanol sample, while observing the proton spectrum with the decoupler coils; experimental error ± 2.0 °C. [c]Data obtained using a broad-band probe tuned to 125.76-MHz.

C. 500.13 MHz ^{1}H FT NMR of $C_4H_4D_3$+

The 500.13-MHz ^{1}H FT spectra of the $C_4H_4D_3$+ carbocation prepared from **9** and **10** were recorded. The best resolution was obtained using 5-mm sample tubes. For all samples, transfer of the solutions to NMR tubes was accompanied by some decomposition, a more severe problem for 5-mm tubes than for the 10-mm size routinely used for ^{13}C spectra. It was difficult to obtain carbocation solutions in 5-mm tubes prepared from (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol without a moderate degree of isomerization to exo-$C_4H_4D_3$+.

The 500.13-MHz proton spectrum of the carbocation solution obtained from ionization of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol in SbF_5–SO_2ClF–SO_2F_2 is shown in Figure 12. At -121°C, there are five peaks in the methylene region of the proton spectrum and one methine resonance. Under the conditions used to take the spectrum, hydrogen-hydrogen coupling is not discernible. The chemical shift of the methine hydrogen is the same (δ_{1H} 6.50 ppm) for both $C_4H_4D_3$+ stereoisomers. Two peaks of similar intensity (δ_{1H} 3.83 and 4.12 ppm) and a smaller resonance (δ_{1H} 3.94 ppm) comprise the high-field set of $C_4H_4D_3$+ methylene hydrogens. The two larger resonances are assigned to the hydrogens which occupy the exo carbon-hydrogen bonds in endo-$C_4H_4D_3$+. The larger of the two resonances which comprise the low-field set of methylene hydrogens is actually two coincident resonances, the endo-hydrogen of endo-$C_4H_4D_3$+ and one of the endo-hydrogens of exo-$C_4H_4D_3$+. Exo-$C_4H_4D_3$+ is assigned to the resonances at 4.49, 4.44 and 3.94 ppm.

Figure 12. 500.13 MHz ^1H FT NMR spectrum of $C_4H_4D_3^+$ prepared from (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol (SbF_5–SO_2ClF–SO_2F_2 solution at -121°C). Resonances are assigned as follows: 1=H_3O^+; 2,4,9,10= O-protonated [d_3]cyclobutanol; 3= methine hydrogen of $C_4H_4D_3^+$ (used as reference, $\delta_{^1H}$= 6.50 ppm); 5,7,9= methylene hydrogens of endo-$C_4H_4D_3^+$; 5,6,8= methylene hydrogens of exo-$C_4H_4D_3^+$; 12= unknown. The origin of the smaller resonances in the spectrum is not known.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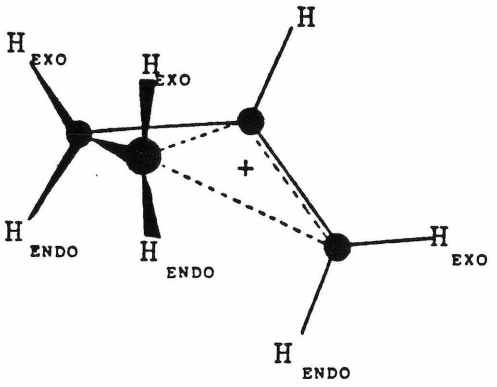


This interpretation of the spectrum in Figure 12 is supported by the 500.13 MHz ^1H spectrum of $C_4H_4D_3+$ prepared from (2,2-d_2-cyclopropyl)-1-d-methanol, **10**. The ^1H spectra of $C_4H_4D_3+$ prepared from **10** were obtained using 10-mm sample tubes and consequently are less well resolved. Despite the broadness of the resonances, the general features of the methylene region are consistent with the expected line intensities for an equal mixture of exo- and endo-$C_4H_4D_3+$ in solution . For example, there are three resonances of comparable intensity in the upfield methylene region.

The 60-MHz proton spectrum of unlabeled C_4H_7+ carbocation has a methine resonance (pentet) at 6.50 ppm and two methylene doublets centered at 4.64 and 4.21 ppm.[33] The 500.13 MHz ^1H NMR results for $C_4H_4D_3+$ can be used to unambiguously assign the two nonequivalent sets of hydrogens in C_4H_7+ for the first time. The methylene endo-hydrogens of $C_4H_4D_3+$ are assigned to resonances at lower field and the exo-hydrogens are assigned to the high-field methylene resonances. This assignment contrasts with that of Olah and coworkers.[33] In two separate reports on C_4H_7+, the endo-hydrogens were assigned to the doublet at 4.21 ppm and the exo-hydrogens to the doublet at 4.64 ppm without basis.

As in the ^{13}C NMR spectrum, resonances were observed for O-protonated [d_3]cyclobutanol (δ_{1H} 8.79, 5.66, 2.55, and 2.27 ppm in Figure 12). It was not possible to determine whether stereochemistry was preserved in the formation

of this ion from the ^{13}C NMR data. The high-field protons of O-protonated [d_3] cyclobutanol were assigned to the resonance at 2.27 ppm on the basis of previously reported ^1H shifts.[65] However, there is an unidentified resonance at δ_{1H} 1.9 ppm which may be attributable to the protonated cyclobutanol. The possibility that the resonances at 1.9 and 2.27 ppm reflect stereoisomeric O-protonated [d_3]cyclobutanol ions differing in the orientation of the hydrogen attached to the ^{13}CHD carbon cannot be discounted. Integration of the ^1H NMR spectrum of the carbocation solution indicated that the O-protonated [d_3]cyclobutanol was present as a mixture of O-protonated 2,2,3-d_3-cyclobutanol and O-protonated 2,3,3-d_3-cyclobutanol.

^1H NMR resonances are subject to intrinsic deuterium isotope shifts and for geminal ^2H-substitution, the remaining hydrogen normally experiences a small upfield shift.[46,66] Thus, the ^1H NMR resonance of the methyl hydrogens in (methyl-d_1)benzene is 0.015 ppm upfield of toluene.[66] There are some rare examples of downfield intrinsic isotope shifts for ^1H NMR signals.[67] The deuterium chemical-shift effects observed for the methylene hydrogens in the ^1H spectrum of $C_4H_4D_3+$ are primarily the result of equilibrium perturbation of the carbocation and, to a much lesser extent, of intrinsic isotope effects. The ^1H NMR chemical shifts for $C_4H_4D_3+$ are not corrected for the intrinsic effect of ^2H-substitution.

The chemical-shift difference ($\Delta\delta$) between the two exo-hydrogens of endo-$C_4H_4D_3+$ is 0.29 ppm (Figure 12) compared to 0.05 ppm for the endo-hydrogens of exo-$C_4H_4D_3+$. Deuterium isotopic perturbation of the equilibria involving $C_4H_4D_3+$ has a greater effect on the exo-hydrogens (the upfield resonance). Saunders and Siehl[63] did not detect any peak separation in the low-field methylene hydrogens of the lesser substituted carbocations (C_4H_6D+, $C_4H_5D_2+$) in the 270-MHz ^1H NMR spectrum. The magnitudes of deuterium isotopic pertur-

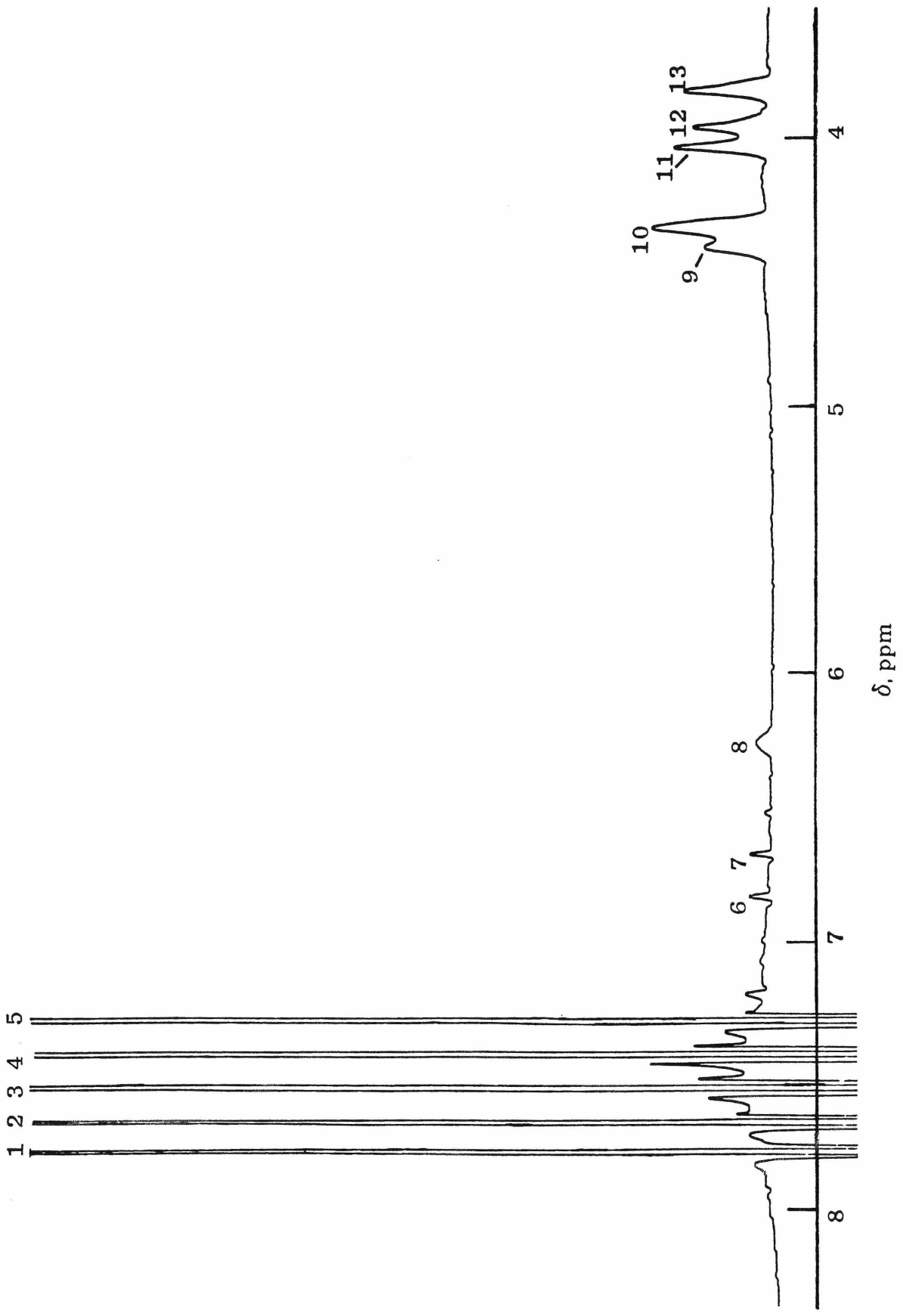
bations are dependent on the equilibrium constants of the processes being perturbed and on the magnitude of Δ (the difference in methylene hydrogen chemical shifts in the slow interconversion extreme). The ^1H NMR results for $C_4H_4D_3+$ indicate that Δ is larger for the exo-hydrogens than the endo-hydrogens. One of the more important puzzles to resolve is why the Δ is so different for the two sets of nonequivalent methylene hydrogens in $C_4H_4D_3+$.

D. 76.7 MHz ^{2}H FT NMR of $C_4H_4D_3$+

The primary purpose of recording the ^{2}H NMR spectra of $C_4H_4D_3$+ was to determine the extent of hydride migrations by monitoring scrambling of deuterium to the methine position. The 76.7 MHz ^{2}HNMR spectrum of $C_4H_4D_3$+ prepared from (2,2-d_2-cyclopropyl)-1-d-methanol, **10**, is shown in Figure 13. Experimental difficulties with low-temperature operation of the broadband spectrometer probehead generally resulted in not well resolved ^{2}H spectra of $C_4H_4D_3$+. However, in most experiments, it was possible to access the extent of deuterium scrambling to the methine position. Scrambling was minor under the NMR conditions used; the spectrum in Figure 13 had the most intense methine resonance (with an integrated area ≈ 5% of total area of all carbocation resonances) observed in any experiment.

The ^{2}H spectra of the carbocation prepared from **10** are consistent with approximately equal concentrations of exo- and endo-$C_4H_4D_3$+ in solution. The resonances at $\delta_{^2H}$ 4.62 (area=1), 4.47 (area=2) and 4.13 ppm (area=1) in Figure 13 are assigned to the endo-$C_4H_4D_3$+ carbocation. Exo-$C_4H_4D_3$+ is assigned to resonances at $\delta_{^2H}$ 4.47 (area=2, coincident with one of the endo-$C_4H_4D_3$+ resonances), 4.27 (area=1) and 3.99 ppm (area=1). An earlier proposal that the unidentified ^{13}C resonance in the methylene region of the ^{13}C spectra of $C_4H_4D_3$+ ($\delta_{^{13}C}$ 53.23 in Figure 6) might be deuterium-scrambled $C_4H_4D_3$+ carbocation is ruled out by the ^{2}H spectra. The amount of rearranged carbocation that would be predicted based on the intensity of the unidentified carbon resonance does not seem consistent with 5% or less deuterium scrambling to the methine position.

Figure 13. 76.7 MHz ^2H FT NMR (^1H-decoupled) spectrum of $C_4H_4D_3+$ prepared from (2,2-d_2-cyclopropyl)-1-d-methanol (SbF_5–SO_2ClF–SO_2F_2 solution at -76°C). Resonances are assigned as follows: 1,2=$CDFCl_2$, a by-product of CDF_2Cl preparation; 3,4,5=CDF_2Cl used for optimizing field homogeneity; 6,7= CDF_3, a by-product of CDF_2Cl preparation; 8= methine-^2H of $C_4H_4D_3+$ (used as reference, $\delta_{^2H}$= 6.50); 9,10,12=methylene deuteriums of exo-$C_4H_4D_3+$; 10,11,13=methylene deuteriums of endo-$C_4H_4D_3+$.


1
2
3
4
5
6
7
8
9
10
11
12
13
8
7
6
δ, ppm

Deuterium resonances should experience intrinsic isotope effects when geminally substituted by a second deuterium. Integration of the ^{2}HNMR spectrum in Figure 13 indicates an equal number of deuteriums in the upfield and downfield methylene regions. The ^{2}H spectrum of exo-$C_4H_4D_3$+ is equivalent to the ^{1}H spectrum of endo-$C_4H_4D_3$+; likewise, the ^{2}H spectrum of endo-$C_4H_4D_3$+ is equivalent the ^{1}H spectrum of exo-$C_4H_4D_3$+. For $C_4H_4D_3$+ prepared from **10**, a 2:1 ratio of integrated areas for the proton resonances at δ_{1H} 4.49 and 4.44 ppm which is opposite of the ratio observed for the ^{2}H resonances at δ_{2H} 4.62 and 4.47 in Figure 13. The correlation between the ^{2}H and ^{1}H spectra of $C_4H_4D_3$+ lends support to the assignment of resonances.

E. Discussion of $C_4H_4D_3$+ Results

The NMR evidence accumulated to date on C_4H_7+ under stable-ion conditions supports the nonclassical bicyclobutonium (**2**) and the nonclassical bisected cyclopropylmethyl (**4**) as the best candidate C_4H_7+ structures.[33,38,58,63] The results reported here for $C_4H_4D_3$+ reinforce this view.

The chemical-shift data are not corrected for the intrinsic isotope effect of β-^{2}H substituents because the effect is a small one ($\leq$ 0.1 ppm). The effect of α-^{2}H on $\delta_{^{13}C}$ can be estimated from the compilation of intrinsic shifts observed for small-ring, neutral compounds (Table I, p 97). A reasonable correction for intrinsic chemical-shift effect is $C_4H_4D_3$+ is +0.3 $\pm$ 0.1 ppm for each α-^{2}H substituent.

1. Perturbation of the Equilibrium Between Different C_4H_7+ Structures

Deuterium isotopic perturbation of $C_4H_4D_3$+ can affect two major interconversion processes: (1) the equilibria between nondegenerate isomers of a single structure (**2** or **4**) and (2) the equilibrium between structures **2** and **4**. The ^{13}C NMR results for $C_4H_4D_3$+ suggest perturbation of both types of equilibria. The methine resonance of exo-$C_4H_4D_3$+ is observed downfield relative to internal C_4H_7+ while the ^{13}CH carbon of endo-$C_4H_4D_3$+ is coincident with the unlabeled carbocation. Comparison of this downfield shift with the values predicted for structures **2** and **4** in the slow-exchange limit indicates that deuterium perturbs the equilibrium in favor of the bicyclobutonium isomers.

A change in chemical-shift for the methine resonance of $C_4H_4D_3$+ is proposed as a measure of perturbation between **2** and **4**. The shielding at the methine carbon should be much less sensitive to the population distribution among isomers of the same structure than the shielding at the $^{13}CH_2$, ^{13}CHD and $^{13}CD_2$ carbons. A single resonance with a line width of 0.1 ppm is observed for the methine carbons of C_4H_7+ and endo-$C_4H_4D_3$+ (-80 to -115°C). The ^{13}CH carbon of exo-$C_4H_4D_3$+ becomes more shielded upon deuterium substitution, appearing 0.4 ppm downfield of the the corresponding carbon in C_4H_7+. Therefore, the shift observed for the methine carbon exo-$C_4H_4D_3$+ is ascribed to a change in the $C_4H_4D_3$+ equilibrium between bicyclobutonium, **2**, and bisected cyclopropylmethyl, **4**, isomers. In the slow-exchange extreme, the $\delta_{^{13}C}$ values estimated for the methine carbons (Section A, Chapter III) of **2** and **4** are 115 ppm and 76 ppm, respectively. The methine carbon of $C_4H_4D_3$+ is shifted toward the estimated static chemical shift of structure **2**.

Saunders and Siehl[63] observed a similar effect in the methine region of the ^{13}C spectrum of C_4H_6D+. Like the direction of isotope shifts observed in the methylene region for $C_4H_4D_3$+, it appears as though the influence of deuterium is very different for the endo and exo stereoisomers of the monodeuterated carbocation. That is, for a carbocation containing a ^{13}CHD carbon, the bicyclobutonium structure is more stable for the exo stereoisomer and the chemical shift of the ^{13}CHD carbon can vary by 10 ppm depending upon the orientation of the deuterium. The data reported here and by Saunders, et.al. [63]for $C_4H_5D_2$+ were measured in the absence of internal C_4H_7+ (the most reliable measure of a deuterium chemical-shift effect) and so it cannot determined to what extent the equilibrium between structures **2** and **4** is perturbed in a carbocation containing a dideuterated carbon.

The methylene carbons subtantiate the perturbation of this equilibrium for the trideuterated carbocation. In the absence of intrinsic deuterium chemical-shift effects, the carbons effectively perturbed by introduction of deuterium would be split symmetrically about the corresponding resonance in the unlabeled compound. At -95°C, the average of the three $C_4H_4D_3$+ methylene shifts provides a value for comparision with C_4H_7+; corrected for intrinsic α-^{2}H effects, the average methylene δ_{13C} of endo- and exo-$C_4H_4D_3$+ are 54.2 and 53.6 ppm, respectively. At -94°C, the methylene resonance of C_4H_7+ has a chemical shift of 54.68 ppm. That the average δ_{13C} methylene resonances for $C_4H_4D_3$+ are not split about the $^{13}CH_2$ of C_4H_7+ could be the result of error in corrections for intrinsic isotope effects. Even if an unreasonable error of 0.4 ppm is assumed for this correction, there is still a 0.7 ppm discrepancy between C_4H_7+ and exo-$C_4H_4D_3$+. A change in the average methylene shift for exo-$C_4H_4D_3$+ is consistent with the methine resonance and is proposed to also be the result of a perturbation of the equilibrium of **2** and **4**. The averages of the methylene shifts estimated for structures **2** and **4** in the slow-exchange limit are ≈ 47 for **2** and ≈ 130 ppm for **4**. The upfield shift of the methylene resonances supports the contention that the equilibrium perturbation increases the relative population of bicyclobutonium isomers. While there appears to be some evidence that a similar perturbation is operative for endo-$C_4H_4D_3$+, the effect is much smaller in magnitude.

2. Deuterium Chemical-Shift Effects on Methylene Carbons

Assignments of the resonances in the 125.76 MHz ^{13}C NMR spectrum of endo- and exo-$C_4H_4D_3$+ can be used to analyze the ^{13}C spectrum of C_4H_6D+

reported by Saunders and Siehl[63] (shown in Figure 3). The $^{13}CH_2$ and ^{13}CHD methylene carbons of $C_4H_4D_3$+ display NMR line patterns very similar to that observed for the methylene carbons of C_4H_6D+. As with the $^{13}CH_2$ and ^{13}CHD resonances of $C_4H_4D_3$+, the downfield triplet (^{13}CHD) and upfield singlet ($^{13}CH_2$) can be assigned to the endo-C_4H_6D+ carbocation. Henceforth, the difference in chemical shift between the $^{13}CH_2$ and ^{13}CHD carbons will be designated as: $\Delta\delta_{CHD} = (\delta^{13}CH_2-\delta^{13}CHD)$, where a negative sign indicates a downfield shift for the ^{13}CHD carbon relative to $^{13}CH_2$ carbon. Values of $\Delta\delta_{CHD}$ can be estimated roughly from the published spectrum of C_4H_6D+;[63] $\Delta\delta_{CHD}$ = -4.7 ppm for endo-C_4H_6D+ and $\Delta\delta_{CHD}$ =+2.7 ppm for exo-$C_4H_4D_3$+ (-96°C). These are comparable with $\Delta\delta_{CHD}$ values of -5.34 ppm for endo-$C_4H_4D_3$+ and +3.17 ppm for exo-$C_4H_4D_3$+ (-95°C).

Table IV. Isotopic chemical-shift splittings for deuterium-substituted C_4H_7+ carbocations, corrected for α-^2H intrinsic effects.[a]

Carbocation	$\Delta\delta_{CHD}$[b,c]	$\Delta\delta_{CD_2}$[c,d]	T,°C
Exo-C_4H_6D+	+2.4[e]		-96
Endo-C_4H_6D+	-5.0[e]		-96
$C_4H_5D_2$+		-2.7	-90
Exo-$C_4H_4D_3$+	+2.9	-2.6	-95
Endo-$C_4H_4D_3$+	-5.6	-2.9	-95

[a] The corrections for intrinsic deuterium effect used are +0.6 ppm for δ_{13C} of $^{13}CD_2$ carbons and +0.3 ppm for δ_{13C} of ^{13}CHD carbons. [b] $\Delta\delta_{CHD}=\delta_{CH_2}-\delta_{CHD}$. [c] A negative splitting corresponds to a downfield shift for the deuterium-substituted methylene carbon relative to the $^{13}CH_2$ carbon. [d] $\Delta\delta_{CD_2}=\delta_{CH_2}-\delta_{CD_2}$. [e] Measured from the published spectrum of C_4H_6D+, see ref 63.

The dideuterated methylene carbons of exo- and endo-$C_4H_4D_3$+ are shifted to lower field in a similar manner to the corresponding carbon in $C_4H_5D_2$+. Corrected for α-^2H intrinsic isotope effects, the chemical-shift splittings

observed for the methylene carbons of deuterium-substituted C_4H_7+ carbocations are given in Table IV.

A straightforward additivity of C_4H_6D+ and $C_4H_5D_2$+ ^{13}C chemical shifts is observed in the $C_4H_4D_3$+ carbocation. Comparison of the direction and magnitude of deuterium chemical-shift splittings for the deuterated methylene carbons in Table IV indicates that $\Delta\delta_{CD_2} \approx \Delta\delta_{CHD}(\text{endo-}^2H) + \Delta\delta_{CHD}(\text{exo-}^2H)$.

The opposite sign and magnitude of the deuterium isotope effect on the chemical shifts of the ^{13}CHD carbons has been the most difficult question to address. Whatever the major structure of C_4H_7+, it must be capable of configurational stability. While several *ad hoc* conclusions regarding the population distributions and discrimination of deuterium for different carbocation sites could be inferred by comparison with static chemical shifts for the candidate structures **2** and **4**, a plausible phenomenon for the profound dependence of equilibrium pertubation on the orientation of the deuterium attached to the ^{13}CHD carbon has not been found. This particular experimental observation is likely the crux to a full comprehension of deuterium isotope effects in the C_4H_7+ carbocation.

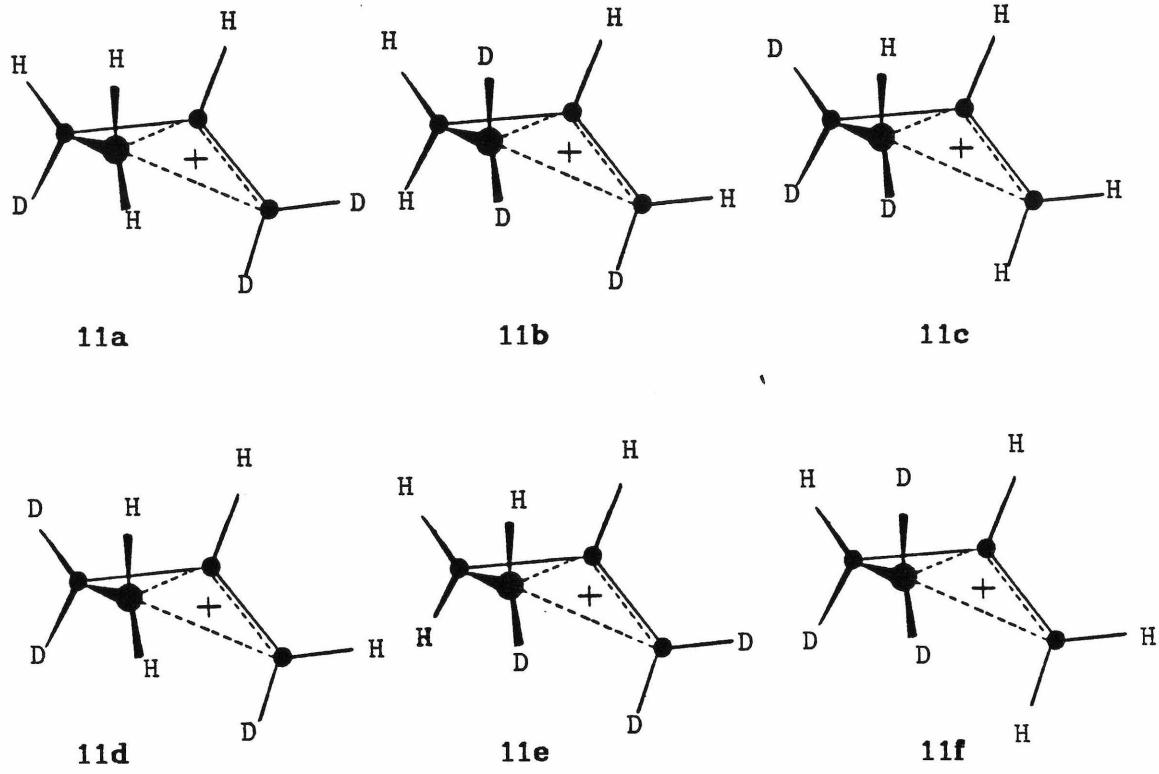
Classical formulations for the structure of C_4H_7+ do not seem reasonable in light of the unusual stereochemical properties of the trideuterated carbocation. The effect that bridging in a nonclassical C_4H_7+ carbocation would have upon the C-H(D) bonds is a matter of speculation given the paucity of information concerning the nature of C-H bonds at a pentacoordinate carbon.

3. Endo-Exo $C_4H_4D_3$+ Isomerism

The likely mechanism for endo-$C_4H_4D_3$+ conversion to the exo stereoisomer involves a higher energy, "classical" cyclopropylmethyl carbocation; conceivably, an intermediate in either the equilibrium between **2** and **4** or between structurally similar isomers. The conversion of endo-$C_4H_4D_3$+ to the exo stereoisomer was too slow to directly observe via NMR; changes in relative intensity for the methine resonances of $C_4H_4D_3$+ were no greater than 12% based on signal/noise ratio of the ^{13}C spectrum. Assuming ≈ 12% conversion of endo-$C_4H_4D_3$+ to exo-$C_4H_4D_3$+ over four hours at -90°C, a 14 kcal/mol lower limit is calculated for the activation energy required for isomerization of endo-$C_4H_4D_3$+. This E_a for the isomerism of endo-$C_4H_4D_3$+ to exo-$C_4H_4D_3$+ is equivalent to the energy necessary for rotation about the bond joining the ring to the carbocation center in a "classical" cyclopropylmethyl structure. The energy barrier, in a simple sense, is the energy difference between the perpendicular and bisected conformations in the classical cyclopropylmethyl carbocation. Compare this 14 kcal/mol lower limit with the 25.7 kcal/mol rotation barrier calculated by Hehre and Hiberty with STO-31G.[16a] Raising the sample temperatures in an effort decrease the half-life of endo-$C_4H_4D_3$+ were accompanied by significant carbocation decomposition.

4. Perturbation of Equilibria Involving Structurally Similar Isomers

It is proposed that the changes observed for the methylene carbons of $C_4H_4D_3$+ relative to one another is largely a result of a deuterium isotopic perturbation of the equilibria involving nondegenerate isomers with the same structure but different positions of label. For each $C_4H_4D_3$+ stereoisomer there are six possible nondegenerate bicyclobutonium isomers, shown below for endo-$C_4H_4D_3$+ (**11a-f**). Six analogous nondegenerate bisected cyclopropylmethyl isomers can be drawn for each $C_4H_4D_3$+ stereoisomer, shown below for endo-



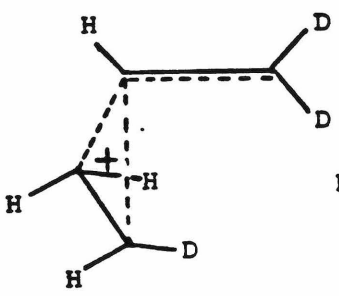
11a **11b** **11c**

11d **11e** **11f**

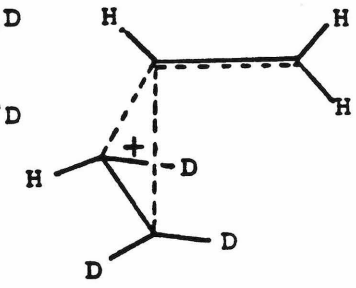
$C_4H_4D_3$+ (**12a-f**). Because **4** (C_s symmetry) has a higher symmetry than **2** (C_1 symmetry), half of the possible bisected cyclopropylmethyl isomers are mirror images of the other three; hence, there are only three nondegenerate structures having unique NMR shieldings involved in the rapid equilibration of each bisected cyclopropylmethyl $C_4H_4D_3$+ stereoisomer.

The direction of deuterium chemical-shift effects in $C_4H_4D_3$+ could be discussed in terms of most populated isomers for a set of rapidly equilibrating bicyclobutonium structures or a set of rapidly equilibrating bisected structures. Such an approach is too simplistic because it is the weighted average of sites which a methylene carbon can occupy that dictates the position of the observed resonance. Upon initial inspection of the methylene region of the ^{13}C spectrum

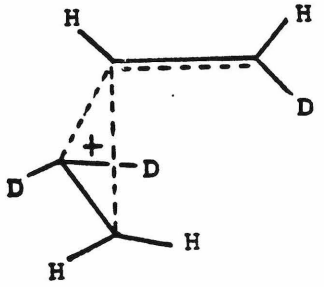
lated bisected cyclopropylmethyl isomers of $C_4H_4D_3+$ to give rise to three different weighted averages for the methylene carbons. Therefore, in no way does the separation of the methylene carbons into three distinct resonances in the $C_4H_4D_3+$ carbon spectrum rule out the possibility of structure **4**.



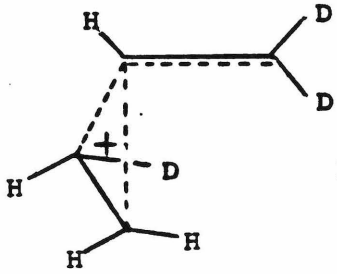
12a



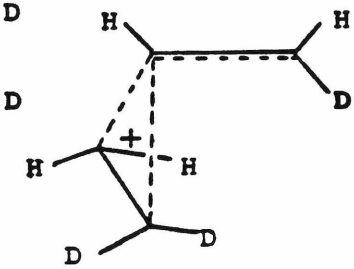
12b



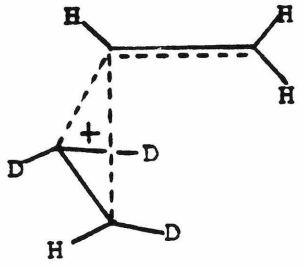
12c



12d



12e



12f

5. Summary

The NMR investigation of the trideuterated cyclopropylmethyl-cyclobutyl carbocation, $C_4H_4D_3+$, has provided additional information regarding this unusual carbocation. The initial goal of this work was to provide definitive evidence for the major equilibrium structure of C_4H_7+ and possibly write the final chapter in the cyclopropylmethyl-cyclobutyl debate. However, the results obtained from the deuterium isotopic perturbation of $C_4H_4D_3+$, albeit enticing and thought provoking, have raised more questions than they have answered.

Based on the 500.13 MHz NMR spectrum of endo-$C_4H_4D_3+$ the upfield set of methylene resonances can be assigned to the exo-hydrogens, contrasting earlier assignments reported by Olah.[33] The effect of equilibrium perturbation on the proton spectrum is largest for the upfield methylene resonance which indicates that Δ is larger for (the difference in proton shifts for a static structure) for the exo-hydrogens. The exo-hydrogens apparently experience a greater variation in shielding between one another than do the endo-hydrogens.

Exo-$C_4H_4D_3+$ appears to be more perturbed by the deuterium at the ^{13}CHD carbon than endo-$C_4H_4D_3+$ on the basis of two observations: (1) $\Delta_{exo\text{-}H} >> \Delta_{endo\text{-}H}$ for the methylene hydrogens, and (2) the perturbation of the equilibrium between structures **2** and **4** is larger for exo-$C_4H_4D_3+$.

The above observations are wholly consistent with the conclusions of Staral, et.al.[38] in which two rapidly equilibrating C_4H_7+ structures (**2**, **4**) were proposed for the C_4H_7+ carbocation under stable-ion conditions. The results obtained in the isotopic perturbation of $C_4H_4D_3+$ do not offer indisputable evidence for a major equilibrium geometry of C_4H_7+. However, a few pieces of evidence may

suggest that the major structure is bicyclobutonium, **2**. The profound ^{13}CHD dependence on ^{2}H orientation suggests that there is at least one methylene carbon which has two very different C-H bonds. The best candidate for such a requirement is the pentacoordinate carbon in structure **2**. A small difference in the force constants for these two C-H bonds of the bridging carbon would give rise to a discrimination of the deuterium for endo or exo orientations. The existence of carbon-hydrogen bonds with different force constants would also be consistent with the ^{1}H NMR effects observed for the two nonequivalent sets of methylene hydrogens.

In Chapter III, the interpretation of the ^{13}C spectrum of $C_4H_5D_2+$ was based, in part, on the population differences that must be assumed two extreme cases: (1) rapidly equilibrating bisected cyclopropylmethyl ions, or (2) rapidly equilibrating bicyclobutonium ions. Because the value of Δ (chemical-shift difference in slow-exchange limit) for **4** is less than half that of **2**, the changes in population required to account for the observed isotopic splittings in the ^{13}C methylene resonances are considerably larger for a $C_4H_4D_3+$ carbocation with structure **4**. It is proposed that the deuterium chemical-shift splittings observed for $C_4H_4D_3+$ and C_4H_6D+ are more in accord with the population changes which must be assumed for a bicyclobutonium structure to account for the magnitude of the splitting.

The elusive C_4H_7+ carbocation still remains somewhat clouded in mystery after several decades of investigation and discussion by many workers. This study makes a significant contribution to the understanding of C_4H_7+ in that it has been shown with NMR spectra that the trideuterated species can exist as a configurationally stable ion and contains at least one carbon which has two very different carbon-hydrogen bonds. Definitive assignment of ^{1}H and ^{13}C NMR resonances to two stereoisomeric forms of $C_4H_4D_3+$ was made. A more complete understanding of the structural characteristics of C_4H_7+ shall be elucidated in future work.

EXPERIMENTAL

Cyclopropyl-1,1-d_2-methanol was prepared by reduction of cyclopropanecarboxylic acid with lithium tetradeuterioaluminate (99%-D, Stohler Isotope Chemicals) in diethyl ether. The product was purified by two successive GC separations on a 3.7 m x 6.4 mm (o.d.) stainless steel column packed with 30% Carbowax SE-30 on Chromasorb P (60/80 mesh).

(2,2-d_2-Cyclopropyl)-1-d-methanol was synthesized from acrolein (Aldrich Chemical Co.). The acrolein carbonyl function was protected with 2-methyl-2,4-pentanediol.[68] 2-Vinyl-4,4,6-trimethyl-1,3-dioxolane was treated with dideuteriodiazomethane prepared by exchange of diazomethane with four washes of $NaOD/D_2O$. The diazomethane was generated by addition of an aqueous potassium hydroxide solution to *N*-*p*-tolylsulfonyl-*N*-methyl-*N*-nitrosoamide (Aldrich Chemical Co.). The reaction of dideuteriodiazomethane and 2-vinyl-4,4,6-trimethyl-1,3-dioxolane afforded a mixture of Δ^1- and Δ^2-pyrazolines based on comparison of infrared, ^{1}H NMR, and ^{13}C NMR analysis with published spectroscopic data.[69] The pyrazoline mixture was passed through a column packed with glass beads at 450°C under reduced pressure (0.3 torr) to extrude the nitrogen in the pyrazolines.[69] Three pyrolysis products were identified using ^{1}H, ^{2}H, and ^{13}C NMR, the percentage composition based on integration of the ^{2}HNMR spectrum (the ^{2}HNMR chemical shifts are given in parentheses): 66% 2-(2,2-d_2-cyclopropyl)-4,4,6-trimethyl-1,3-dioxolane (δ=0.35 ppm), 15% 2-(3,3-d_2-prop-1-enyl)-4,4,6-trimethyl-1,3-dioxolane (δ=1.69 ppm), 19% 2-(3,3-d_2-prop-2-enyl)-4,4,6-trimethyl-1,3-dioxolane (δ=5.06 ppm). A pure sample of 2-(2,2-d_2-cyclopropyl)-4,4,6-trimethyl-1,3-dioxolane was isolated via preparative GC; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.23 (d, $^3J_{HH}$=6 Hz, 1H), 3.80 (q, 1H), 1.23 (m, 12H), 0.47 (m, 2H); ^{13}C NMR

(22.5 MHz, $CDCl_3$) δ 98.13 (d), 71.49 (s), 68.63 (d), 43.54 (t), 31.71 (q), 22.23 (q), 14.95 (d), 1.23 (t); mass spectrum (EI, 15 eV), m/z 171 (P+), 129, 83 (base), 73, 71, 56, 55, 45, 43, 41. Acidic hydrolysis with 1*N* trichloroacetic acid removed the protecting group to afford a mixture of the three corresponding aldehydes. Reduction with lithium tetradeuterioaluminate (99%-D, Stohler Isotope Chemicals) in diethyl ether gave a mixture of alcohols which were separated via preparative GC on a 3.7 m x 6.4 mm (o.d.) stainless steel column packed with 30% Carbowax SE-30 on Chromasorb P (60/80 mesh). Following two sucessive GC separations, pure (2,2-d_2-cyclopropyl)-1-*d*-methanol was obtained: ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.41 (m, 1H), 1.50 (d, $^3J_{HH}$=5.6 Hz, 1H), 1.08 (br q, 1H), 0.51 (m, 1H, trans), 0.19 (m, 1H, cis); ^{2}HNMR (13.7 MHz, $CDCl_3$) δ 3.44 (1D), 0.52 (1D), 0.20 (1D); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 67.1 (t, $^1J_{CD}$=21 Hz), 13.5, 2.60;[70] mass spectrum (EI, 25 eV) m/z 75 (P+), 45 (base), 44, 32, 28. The deuterium incorporation was at least 95% for each position.

(2*E*,2*Z*,3*Z*-d_3-Cyclopropyl)methanol was synthesized from phenylacetylene-*d*. Phenylacetylene-*d* was prepared by vigorously stirring 0.5 mol phenylacetylene with a NaOD solution prepared from 7.5 g sodium and 100 ml deuterium oxide for 7 h; the procedure was repeated once. Distillation was used to purify the phenylacetylene-*d*; ^{2}HNMR indicated 98% deuterium incorporation. phenylacetylene-*d* (0.43 mol), 2.5 g Lindlar's catalyst,[71] and 4.5 ml quinoline were combined in 375 ml *n*-hexane. The mixture was attached to a hydrogenation apparatus capable of monitoring hydrogen uptake. When 95% theoretical amount of hydrogen had been consumed, the mixture was filtered through Celite to remove the catalyst. The *n*-hexane was removed by distillation and the residue distilled under reduced pressure; bp 45-55°C (20 torr). The relative amounts of four purified products were determined by integration of ^{2}HNMR

spectrum: 85% 2*Z*-***d***-styrene, 8% 2*E*-***d***-styrene, 5% phenylacetylene-***d***, and 2% (2-***d***-ethyl)benzene. The following spectroscopic properties were observed for the major component: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.42 (m, 5H), 6.69 (d, $^2J_{HD}$=2.9 Hz, 1H), 5.21 (d, $^3J_{HH}$=11 Hz, $^2J_{HD}\approx$ 0, 1H); ^{2}HNMR (13.7 MHz, $CDCl_3$) δ 5.71 (d, $^2J_{HD}$=2.9 Hz). The ratio of deuterium in the *cis*:*trans* positions was 10.2:1.0. This mixture of four products was used without further separation in the next procedure. The two-step conversion of 2*Z*-***d***-styrene to 1-phenyl-2*E*,2*Z*,3*Z*-d_3-cyclopropane followed the published procedures of Kobayashi and Lambert.[72] 1-Phenyl-2*E*,2*Z*,3*Z*-d_3-cyclopropane was purified by distillation; bp 100-110°C (20 torr); ^{1}H NMR (500.13-MHz, $CFCl_3$) δ 7.132 (t, 2H), 7.025 (t, 1H), 6.961 (d, 2H), 1.789 (d, 1H), 0.843 (d, $^3J_{HH}$=8.6 Hz, 1H); ^{2}HNMR (76.7-MHz, $CFCl_3$) δ 0.592, 0.367. Based on the integration of the ^{2}HNMR peaks, the ratio of deuterium in *cis*:*trans* positions was 1.85:1.0. The ozonolysis of 1-phenyl-2*E*,2*Z*,3*Z*-d_3-cyclopropane was the most difficult step of the overall synthesis; the conditions necessary to oxidize the aromatic ring also oxidized the product. The choice of solvent was crucial; both methanol[73] and acetic acid[72] were tried and the latter found much better. The ozonolysis proceeded slowly enough in acetic acid to prevent accidental destruction of the product if the reaction were allowed to proceed too long. A solution of 15 g of 1-phenyl-2*E*,2*Z*,3*Z*-d_3-cyclopropane in 200 ml of glacial acetic acid and 20 ml water was magnetically stirred in reaction vessel having a jacket for cooling the reaction. The reaction was run at 0°C for periods of 24-36 h. The ozone was generated by electric discharge using a Welsbach ozonator and was admitted into the reaction solution through a gas dispersion tube. Any excess ozone was destroyed by bubbling the exit gases through an aqueous potassium iodide solution. Two reactions were run separately and product residues combined. Bulb-to-bulb distillation afforded (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)acetic acid in 29% yield; ^{1}H NMR (500.13-MHz, diethyl

ether-d_{10}) δ 11.38 (br s, 1H), 1.55 (d, 1H), 0.82 (d, $^3J_{HH}$=8.1 Hz, 1H); ^{13}C NMR (22.5 MHz, neat) δ 182.03, 13.06, 9.26 (p, $^1J_{CD}\approx$ 25 Hz), 8.99 (t, $^1J_{CD}$=25.6 Hz); ^{2}HNMR (76.7-MHz, $CDCl_3$) δ 1.03 (br).

The reduction of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)acetic acid with lithium tetrahydridoaluminate in diethyl ether gave the final product, (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol. The overall yield of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol. from phenylacetylene was 13%. The product was initially purified by distillation: bp 120°C (760 torr) followed by two succesive GC preparations; ^{1}H NMR (90 MHz, neat) δ 5.31 (br s, 1H), 3.36 (m, 2H), 0.995 (q, $^3J_{HH}$=7 Hz, 1H), 0.41 (d, $^3J_{HH}$=7.9 Hz, 1H); ^{13}C NMR (22.5 MHz, neat) δ 66.75, 13.3, 2.44 (t, $^1J_{CD}$=24.4 Hz), 2.28 (p, $^1J_{CD}$=25.6 Hz); ^{2}HNMR (13.7 MHz, $CDCl_3$) δ 0.39, 0.09; mass spectrum (CI, CH_4), m/z (relative intensity) 75 (1), 59 (18), 58 (100), 46 (10), 45 (19), 44 (97), 43 (34), 42 (10), 41 (17), 40 (17), 31 (41). For comparision a sample of unlabeled cyclopropylmethanol (Aldrich Chemical Co.) was analyzed: mass spectrum (EI, 25 eV) m/z (relative intensity) 72 (1), 70 (16), 55 (100), 44 (86), 43 (31), 39 (20), 31 (19); (CI, CH_4) m/z (relative intensity) 72 (1), 70 (15), 67 (9), 55 (100), 44 (77), 43 (35), 42 (9), 41 (13), 39 (33), 31 (30), 27 (23).

The optical activity of (2*E*,2*Z*,3*Z*-d_3-cyclopropyl)methanol. was checked by addition of optically active tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium to a solution of the alcohol in carbon tetrachloride. As shift reagent was added, the ^{1}H NMR resonance for the cyclopropyl methylene hydrogen shifted downfield from 0.5 to 2.76 ppm; no peak was observed for hydrogens *cis* to the substituent. In the ^{2}HNMR spectrum, the *trans* deuterium resonance similarly shifted downfield from 0.48 to 2.66 ppm and the *cis* deuterium resonance shifted from 0.16 to 3.51 ppm. Integration of peaks areas for the *cis* and *trans* resonances in the 76.7-MHz ^{2}HNMR spectrum indicated a ratio of 1.0:1.8 for *trans*:*cis*.

Preparation of Carbocations. Two methods were used for carbocation preparation in superacid media. A technique routinely used by Olah[33a] gave samples having better spectral properties than samples prepared using Saunder's molecular-beam technique.[74] Our best results were obtained by slow dissolution of 90 μl of labeled cyclopropylmethanol in a mixture of 1 g of antimony pentafluoride (Aldrich Chemical Co.), 1 ml of sulfuryl chloride (Aldrich Chemical Co.), and 1 ml of sulfuryl fluoride (Matheson Gas Co.). The sample temperature was maintained at -120°C (*n*-pentane slush bath) and the alcohol was frozen slightly above the superacid solution on the inner walls of sample tube. The sample was withdrawn briefly from the slush bath and vortexed gently. The procedure was repeated until the alcohol had been completely dissolved, typically 3-4 h. The light yellow carbocation solution was transferred to a 10-mm or 5-mm NMR tube using a Teflon cannula.

Nuclear Magnetic Resonance Spectra. All of the nuclear magnetic resonance spectra of carbocation samples were taken with Bruker WM-500 spectrometer at the Southern California Regional NMR Facility under National Science Foundation Grant Number CHE-7916324. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500.13-MHz (Bruker WM-500) or 90 MHz (JEOL FX-90Q). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125.7 MHz (Bruker WM-500) or 22.5 MHz (JEOL FX-90Q). Deuterium nuclear magnetic resonance (^{2}HNMR) spectra were recorded at 76.7-MHz (Bruker WM-500) or 13.7 MHz (JEOL FX-90Q). A high-field spectrometer necessitates high decoupler power to fully decouple all hydrogens from ^{13}C resonances.

Sample heating was minimized by employing a two-level decoupling sequence in which the decoupler power was 5 watts during acquisition and was reduced to 0.5 watts during a long pulse delay. The spectra still displayed

significant line-broadening, the result of temperature gradients set up by cooling the sample from outside and heating it internally.[75] Because the molecules under investigation contain slowly relaxing deuterium-substituted carbons, the primary advantage of the WM-500 was its sensitivity making possible spectra using 30-45° pulse angles and long pulse delays (4-10 s).

Chemical shifts (δ) are reported in parts per million relative to internal, or in the case of carbocations, external tetramethylsilane. Multiplicities are reported as s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, m=multiplet, For carbon-13 spectra, field stabilization was achieved using a coaxial tube (3 mm o.d. stem) containing diethyl ether-d_{10} (Stohler Isotope Chemicals), acetyl chloride-d_3 (Stohler Isotope Chemicals) or chlorodifluoromethane-d. Chlorodifluoromethane-d was prepared by addition of chloroform-d to antimony pentafluoride:hydrogen fluoride (1:1). Typical acquisition parameters for the carbon-13 NMR spectra were: spectrum width=20KHz, total data points=32K, pulse widths equivalent to 30-45° pulse angle, and a repetition rate of 5-11 s. A coaxial tube for 5-mm sample tubes containing propane-d_8 was used to lock the spectrometer for acquisition of proton NMR; ^{1}H NMR were obtained using 16K total data points and spectrum width=5 KHz. ^{2}HNMR spectra were obtained with 8K total data points and spectrum width=800 Hz. A Gaussian multiplication which applies an optimum resolution enhancement function[76] was performed on free induction decays of all carbocation data. For carbon-13 data, a line broadening of -8 Hz and Gaussian broadening of 0.05 Hz were used; proton and deuterium spectra were typically subject to -5 Hz line broadening and 0.1 Hz Gaussian broadening.

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