

aluminum hydride (0.53 g, 13.94 mmol) in 10 mL of the same solvent. After completion of the addition, the mixture was heated overnight at reflux, cooled, treated with saturated sodium sulfate solution, and filtered. The inorganic solids were repeatedly leached with ether, and the combined filtrates were washed with brine, dried, and evaporated to give the diol as a semisolid (750 mg, 91%). $^1\text{H NMR}$ (CDCl_3) δ 6.49 and 6.16 (m, 2 H), 3.76 and 3.47 (m, 2 H), 2.89 and 2.75 (s, 2 H), 2.05-1.00 (m, 4 H).

Sodium metaperiodate (1.35 g, 6.3 mmol) was dissolved in 15 mL of water, and pH 7 buffer was added (\sim 15 mL) to attain neutrality. Methanol (6 mL) was added followed by a solution of the diol (750 mg, 5.35 mmol) in 4 mL of methanol. The reaction mixture was stirred at room temperature for 5.25 h, filtered, and continuously extracted with pentane for 2 days. The pentane extract was dried and carefully distilled at atmospheric pressure to remove solvent. The norbornenone was obtained by bulb-to-bulb distillation at 110-120 $^\circ\text{C}$ (25 torr), the product being trapped at -78°C . There was obtained 330 mg (75%) of **19**, $[\alpha]_{\text{D}}^{23} +1033^\circ$ (c 1.01, CHCl_3), after purification of a small amount by VPC.

(1S)-2-Norbornanone Tosylhydrazone (20). A solution of **19** (298 mg, 2.76 mmol) in ether (10 mL) containing 15 mg of platinum oxide was hydrogenated at atmospheric pressure. When the uptake of hydrogen ceased, the catalyst was filtered off and the filtrate was concentrated to leave a semisolid mass, VPC analysis of which showed it to be homogeneous.

This material was dissolved in 2 mL of methanol and 617 mg (3.31 mmol) of tosylhydrazine was added. After gentle heating to dissolve the reagents, the solution was allowed to stand overnight, during which time crystals formed. Subsequent to cooling in the freezer, the crystals were filtered to give 300 mg (39% from **19**) of **20** as white crystals: mp 178-180 $^\circ\text{C}$ dec; $^1\text{H NMR}$ (CDCl_3) δ 7.8 and 7.3 (d, $J = 8$ Hz, 2×2 H), 2.85 (br s, 1 H), 2.5 (m, 1 H), 2.4 (s, 3 H), 2.1-1.3 (series of m, 8 H); m/e calculated 278.1089, found 278.1096.

(1S)-[2- ^2H]Norbornene (21). A suspension of **20** (290 mg, 1.04 mmol) in 4 mL of anhydrous tetramethylethylenediamine was cooled to -45°C , and n -butyllithium (4.16 mmol) in hexane was introduced by syringe. The -45°C temperature was maintained for 1 h and subsequently was allowed to rise to room temperature. After 8 h, the reaction mixture was cooled to 0°C , treated with 100% deuterium oxide, and taken up in a mixture of water (10 mL) and pentane (5 mL). The layers were separated, and the organic phase was washed with water (2×10 mL), saturated copper sulfate solution (2×10 mL), and brine (5 mL) prior to drying and careful distillative removal of the pentane. Preparative scale VPC isolation afforded 15 mg of **21**: m/e calculated 95.0845, found 95.0847.

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Deuterium Isotope Effects on the Carbon-13 Chemical Shifts of Carbocations

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Abstract: The study of β -deuterium isotope effects on the carbon-13 chemical shifts of carbocations provides an unambiguous tool for probing the mechanism of charge delocalization in carbocations and a new criterion for differentiating carbocations with different charge-localization mechanisms. β -Deuterium isotope shifts on the cationic carbon centers are positive (downfield shift) for classical static carbonium ions, zero for classical delocalized ions, and negative (upfield shift) for nonclassical σ - or π -bridged nonclassical ions. For classical carbocations, the β effect is related to the demand for hyperconjugative stabilization by the alkyl group. For σ - or π -bridged nonclassical ions in general, the β effect arises from changes in the relative importance of the contributing resonance structures upon deuterium substitution. The observation of a remote γ or δ effect can provide further information as to the nature of the bridging.

Introduction

During the past decade, superacid solutions of carbocations have been prepared in increasing numbers and with increasing diversity. Differentiating between carbocations with classical or nonclassical structures has required considerable effort by numerous investigators using a variety of methods. Carbon-13 and proton NMR spectroscopy have proven to be valuable tools for the investigation of the structure of carbocations. By comparison with values for known compounds and related ions, ^{13}C chemical shifts and ^{13}C -H coupling constants provide information on carbon hybridization and charge density. For a pair of degenerate equilibrating classical carbenium ions, the observed chemical shifts and coupling constants are expected to be the averages of the static shifts and coupling constants of the two sites. For nonclassical ions, however, the cationic carbon centers are unusually shielded, with their chemical shifts differing substantially from the estimated values based on mixtures of equilibrating classical ions. The interpretations of the coupling constants and chemical shifts for these nonclassical ions suffer from the lack of suitable and reliable model compounds from which model values can be obtained.

Recently Saunders and his colleagues¹ have presented a new criterion for differentiating equilibrium processes from resonance phenomena. They have reported deuterium isotope induced splitting in the carbon-13 chemical shifts of some deuterium-substituted carbocations and proposed that the isotopic splitting should be considerably smaller for isotopic perturbation of resonance than for an equilibrium isotope effect. In the equilibrium case, the energy surface has two minima separated by a barrier and one observes a splitting as a result of the isotopic influence on the relative stability of the two minima. In the resonance case, there is only one minimum and one observes a splitting due to the change in a single structure perturbed over vibration upon isotopic substitution. The general applicability of this new criterion remains to be demonstrated. For the examples which have been reported, β -deuterium isotopic splittings for the equilibrium cases were compared with α -deuterium isotopic splittings for the res-

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onance cases. Clearly an α -proton or deuterium unlike the β -proton or deuterium cannot participate in the hyperconjugative interaction with the empty p orbital of the carbocation. Since α - and β -deuterium isotope effects have different origins, a comparison of α - and β -isotopic splittings should not be made.

The related kinetic deuterium isotope effects in solvolytic reactions have been investigated in depth and demonstrated to be quite informative.² The effects can be divided into two main categories, α effects and β effects, according to the position of deuterium substitution. For solvolyses involving "rate-determining dissociation of ion pairs", the α -deuterium isotope effects show maxima characteristic of the type of the leaving group but reasonably independent of the type of carbocation involved. The β -deuterium isotope effects have been first demonstrated by Shiner and co-workers³ to be predominantly of hyperconjugative origin. Further studies by Servis, Borcic, and Sunko have established a linear free energy relationship between the CH_3/H rate and the CH_3/CD_3 rate effect.⁴ Based on this linear relationship, Sunko, Szele, and Hehre⁵ have proposed an empirical method for the correlation of the magnitudes of the β effects with the conformations of the solvolytic transition states.

In this paper, we present the deuterium isotope effects on the carbon-13 chemical shifts for a series of representative carbocations. We have attempted to identify the origins of the chemical shift isotope effects on carbocations. Attempts have also been made to correlate the observed chemical shift isotope effects with the trends of charge delocalization, the classical or nonclassical nature, and other properties of the carbocations.

Results

Carbon-13 chemical shifts of the alcohols, which served as the cation precursors, were measured as mixed 1:1 protium to deuterium samples at 25.2 MHz. Peak assignments were based on (i) chemical shift considerations from comparisons of the observed values with the calculated values using additivity parameters,⁶ (ii) multiplicity measurements from off-resonance proton-decoupling experiments, (iii) peak intensity considerations, and (iv) deuterium labeling. Because of reduced NOE enhancements and C-D coupling, the assignments for the carbon resonances at the α and β positions of the deuterated compound are straightforward. The ^{13}C chemical shifts of the alcohols for both the protium and the deuterium compounds are reported and compared in Table I. The ^{13}C chemical shifts (± 0.05 ppm) are reported in ppm downfield from the internal reference, Me_4Si , in CDCl_3 solvent.

For the alcohols, in all cases for which measurable effects were detected, the shieldings at the attached carbon and at the adjacent carbon are increased by deuterium substitution. The isotope effects on the α -carbons are around -0.8 to -1.0 ppm for each methyl- d_3 substitution. The isotope effects on the β -carbons are around -0.0 to -0.3 ppm for each methyl- d_3 substitution.

Carbocations were prepared from their alcohol precursors with superacid SbF_5 or $\text{FSO}_3\text{H}/\text{SbF}_5 = 1:1$ in sulfonyl chloride fluoride, SO_2ClF , at -78 °C (dry ice-acetone slurry temperature). The molar ratio of superacid/alcohol was held at $\geq 4:1$ to ensure complete ionization. The volumetric ratio of superacid/ SO_2ClF was kept at approximately 1:1.

Carbon-13 chemical shifts of the carbocations were also measured as mixed 1:1 protium to deuterium samples at 25.2 MHz. The data were recorded at a temperature varying from -70 to -80 °C.

Data for carbon-13 chemical shifts of deuterated and non-deuterated carbocations are tabulated and compared in Table II. The ^{13}C chemical shifts (± 0.1 ppm) are reported in ppm downfield

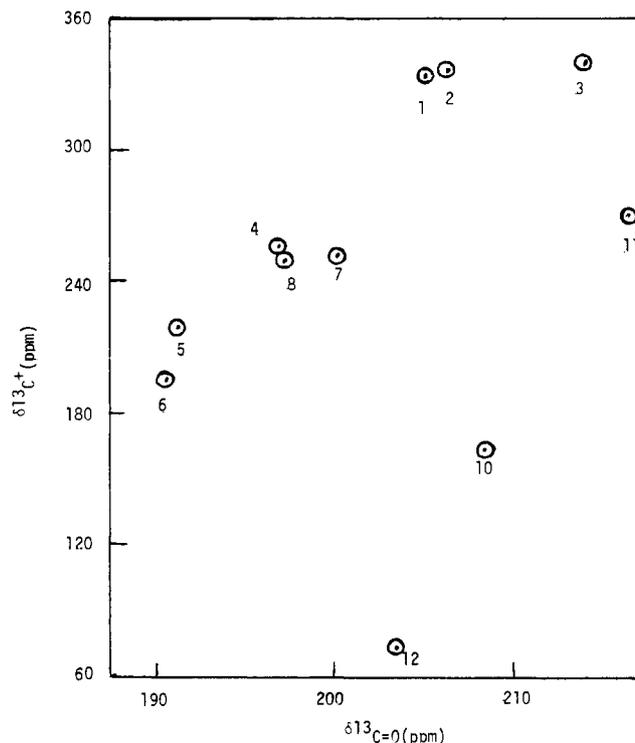
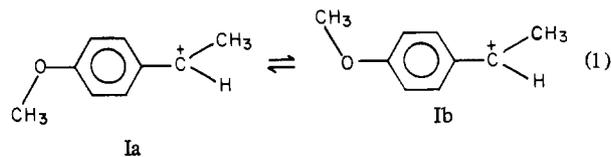


Figure 1. Plot of the cationic carbon chemical shift of the carbocation vs. the carbonyl carbon chemical shift of the corresponding ketone or aldehyde.

from the external reference, Me_4Si , in CD_2Cl_2 or CD_3COCD_3 solvent.

The ^{13}C chemical shifts of the aromatic carbons of the *p*-methoxystyryl cation (see compound **6a** in Table II) are not listed because the rapid interconversion between the isomers **Ia** and **Ib** (eq 1)⁷ broadens the peaks of the aromatic carbons at the temperature (-70 °C) studied.



The chemical shifts of the methyl carbons of the 1-methylcyclohexenyl and 1,3-dimethylcyclohexenyl ions (see compounds **8a** and **9** in Table II) are 35.2 and 30.7 ppm, respectively. These values do not agree with the published data.⁸ The literature value, 42.7 ppm, for the chemical shift of the CH_3 carbon in 1-methylcyclohexenyl ion is closer to the value which we have assigned to the chemical shift of the C-6 carbon, 41.3 ppm. Since we suspected that the previous assignments were incorrect, off-resonance proton decoupled spectra were obtained. The triplets due to the C-6 methylene carbons and the quartets due to the CH_3 carbons are thus easily differentiated. The results are consistent with the general trend that the methylene carbons adjacent to the positive charge will resonate at lower field than the methyl carbons adjacent to the same positive charge in a 6-membered ring system.

Discussion

The carbocations can be considered as derived from the corresponding aldehyde or ketone by replacement of O^- by $-\text{CH}_3$. Such substituent replacement procedures for estimating carbon chemical shifts work surprisingly well for substituted alkanes and

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cycloalkanes. The ^{13}C chemical shifts of the carbocations and of the related ketone or aldehyde are listed in Table III. The chemical shift change upon substitution of $-\text{CH}_3$ in $\text{RR}'^{13}\text{C}^+-\text{CH}_3$ by O^- to give $\text{RR}'^{13}\text{C}=\text{O}$ varies from -130 to $+130$ ppm. The underlying requirement for structural constancy upon substituent replacement which undoubtedly occurs in the substituted alkanes no longer occurs for the carbocations. If compounds **10**, **11**, and **12** are excluded, a qualitative relationship between $\delta_{^{13}\text{C}^+}$ and $\delta_{^{13}\text{C}=\text{O}}$ does occur (Figure 1). The chemical shifts of the carbocations are much more structurally dependent than are those of the ketones.

Foote⁹ demonstrated some years ago that the acetolysis rates of secondary, saturated (arene)sulfonates could be quantitatively correlated with the infrared stretching frequencies of the corresponding ketones. Since both depend on bond angle and hybridization, a qualitative relationship was said to be expected. Since ^{13}C chemical shifts are also sensitive to bond angle and hybridization, infrared stretching frequencies of ketones corresponding to the carbocations were examined (Table III). The saturated carbocations have ^{13}C chemical shifts at ~ 335 ppm and $\nu_{\text{C}=\text{O}}$ at $1720\text{--}1740\text{ cm}^{-1}$; the conjugated carbocations have $\delta_{^{13}\text{C}^+}$ at $200\text{--}250$ ppm and $\nu_{\text{C}=\text{O}}$ at $1680\text{--}1690\text{ cm}^{-1}$; the third group of carbocations, **10**–**12**, have both $\delta_{^{13}\text{C}^+}$ and $\nu_{\text{C}=\text{O}}$ values outside the above ranges.

In addition to a dependence on bond angle and hybridization, the ^{13}C chemical shifts in the carbocations should also be strongly dependent on the positive charge density at the cation center. The charge density at the cation center will be directly influenced by charge delocalization in the ion. Substituent groups which provide charge delocalization by conjugation, hyperconjugation, or σ -bridging should effect the charge density and thereby the ^{13}C chemical shift at the cation center. If this were the only mechanism by which the ^{13}C chemical shift were effected, then a linear correlation of ^{13}C chemical shifts and charge density might be expected. Such relationships do exist but only within systems with similar geometries and hybridizations.¹⁰ For a diverse series of carbocations, no simple correlations between charge density and ^{13}C chemical shift can be expected.

The substitution of hydrogen by deuterium is the most minimal structural modification which can be made to the carbocations. Such isotopic substitution of a lighter isotope by a heavier isotope has been found to produce small upfield changes on adjacent nuclei.¹¹ Theoretical studies of the chemical shift isotope effect have focused on the way in which vibrational changes due to isotopic substitution affect nuclear shieldings.¹² Gutowsky suggested that different vibrational amplitudes of C–H and C–D systems are the cause of the effect.¹³ Since the C–D bond has a smaller vibrational amplitude, the bonding electrons are on the average closer to the resonating nucleus and hence exert a larger shielding effect. Batiz-Hernandez and Bernheim,¹⁴ on the other hand, explained the effect in terms of slight changes in bond lengths and bond angles associated with the lower zero-point vibrational energy in an anharmonic potential well when the heavier isotope is present. This explanation focuses on wave function changes caused by this small alteration in structure rather than an intramolecular field effect. How to differentiate and evaluate the different factors responsible for the observed overall effect is not definitely known.

Of all the reported data,¹⁵ the effect of deuterium substitution,

if detectable, is to increase the shielding at the attached carbon and at the adjacent carbon. The expected small upfield shift on deuterium substitution is found for the α and β positions in the ^{13}C NMR spectra of the alcohols (Table I).

For the carbocations reported in Table II, the expected upfield ^{13}C chemical shift isotope effect is found for the α position. For the β position, the magnitude and direction of the ^{13}C chemical shift isotope effect depends on the type of ion. Deuterium substitution at the β position in ions **1**–**3** produces a chemical shift isotope effect which is downfield. Positive (downfield) chemical shift isotope effects are unprecedented. The isotopic shift values, ΔC^+ , vary from $+1.4$ ppm for *tert*-butyl- d_9 cation to $+0.4$ ppm for 1-methyl- d_3 -cyclopentyl cation. For the ions **4**–**8**, β -deuterium substitution produces no measurable chemical shift isotope effect. For the ions **10**–**12**, β -deuterium substitution produces a large upfield chemical shift isotope effect. Isotope shift values are -1.1 ppm for 1-methyl- d_3 -cyclobutyl cation, -2.2 ppm for 2-methyl- d_3 -2-norbornyl cation, and -0.8 ppm for 7-methyl- d_3 -7-norbornenyl cation.

It is convenient to interpret the isotope effects in terms of the conventional substituent electronic effects—inductive, hyperconjugative, steric, etc.¹⁶ Although the energy surface for the deuterated and nondeuterated materials should exactly coincide, small changes in bond lengths and bond angles which result from averaging over a vibrational motion in an anharmonic potential well can be expected to occur. For a bond to sp^3 hybridized carbon, the lower zero-point vibrational energy of deuterium will lead to a reduced bond length and an effectively greater electron density at the carbon. This effect will be experienced predominantly at the α -carbon and can for convenience be termed an “inductive” isotope effect. For a C–D bond adjacent to an empty p orbital, the lower zero-point vibrational energy will lead to reduced electron delocalization to the empty orbital and a reduced electron density at the adjacent carbon. This effect will be experienced predominantly by a cation center β to a site of substitution and can be termed a “hyperconjugative” isotope effect.

In the uncharged neutral alcohols, the inductive isotope effect can be expected to dominate. Thus deuterium substitution increases the electron density at the α - and to a lesser extent the β -carbons and leads to increased shieldings. The upfield shift of the α -carbon by ~ -0.9 ppm and of the β -carbon by ~ -0.1 ppm as a result of $-\text{CH}_3$ by $-\text{CD}_3$ substitution seems adequately explained.

In the positively charged carbocations, hyperconjugative isotope effects can be expected to play a more important role. In studies of secondary β -deuterium isotope effects in solvolytic reactions where the transition states are carbocation like, the solvolytic isotope effects have been demonstrated to arise predominantly through a hyperconjugative mechanism. For the ions **1**–**3**, the reduced hyperconjugative electron release to the cationic carbon by $-\text{CD}_3$ compared to $-\text{CH}_3$ decreases the electron density at the cationic center. The downfield shift at the cationic center, although unprecedented, can be seen to arise from an isotope induced charge concentration. These ^{13}C chemical shift isotope effects are in fact consistent with the hyperconjugative origin of β -deuterium isotope effects.

The ions **4**–**9** all possess cationic centers which are stabilized by conjugation with the well-known stabilizing groups: phenyl, vinyl, and cyclopropyl. Because of the resonance stabilization provided by these groups, there is less demand for further stabilization by the methyl groups. The hyperconjugative demand upon the methyl group by the cationic center is reduced and the isotope effect on the hyperconjugative electron release is reduced.

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Table I. Carbon-13 Chemical Shifts^a of the Cation Precursors

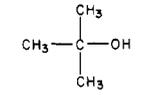
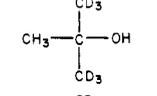
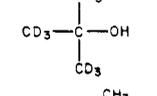
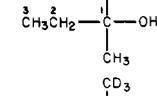
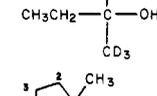
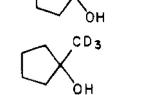
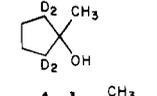
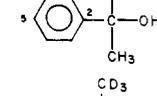
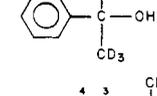
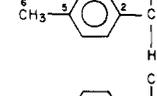
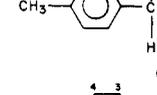
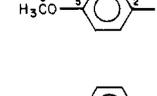
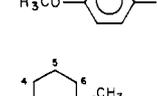
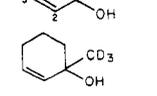
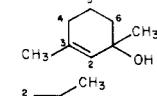
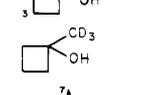
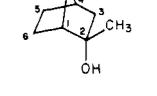
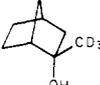
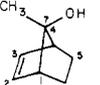
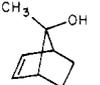
compd	C-1	CH ₃	CD ₃	C-2	C-3	C-4	C-5	C-6	C-7	ΔC_{α}^b	ΔC_{β}^c
	68.7	31.6									
	68.4	31.5	30.7							-0.9	-0.3
	68.3		30.1							-1.5	-0.4
	70.5	28.2		36.0	8.4						
	70.3		27.3	36.0	8.4					-0.9	-0.2
	79.7	28.2		41.2	24.3						
	79.6		27.3	41.2	24.3					-0.9	-0.1
	79.5	28.2		41.0	24.1						-0.1
	72.3	31.6		149.0	127.9	124.2	126.3			-0.9	-0.3
	72.0		30.7	149.0	127.9	124.2	126.3				
	70.4	25.5		143.1	125.6	129.4	137.3	21.5			
	70.4		24.6	143.1	125.6	129.4	137.2	21.5		-0.9	-0.0
	70.2	25.5		138.4	127.0	114.1	159.0	55.7			
	70.0		24.7	138.4	127.0	114.1	159.0	55.7		-0.8	-0.2
	67.7	29.3		133.6	128.5	25.0	19.5	37.8			
	67.6		28.5	133.6	128.5	25.0	19.5	37.8		-0.8	-0.1
	67.8	23.4		128.2	126.3	29.8	19.5	37.2			
	72.2	26.5		37.1	11.4						
	72.1		25.6	37.1	11.4					-0.9	-0.1
	48.4	30.4		77.3	47.1	37.3	22.0	28.4	38.8		

Table I (Continued)

	48.3	29.4	77.0	46.9	37.3	22.0	28.3	38.7	-1.0	-0.3
	50.2	20.2	135.3	135.3	50.2	23.3	23.3	89.7		
	50.2	19.3	135.3	135.3	50.2	23.3	23.3	89.7	-0.9	-0.1

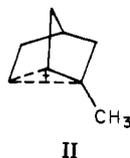
^a Chemical shifts in ppm relative to internal Me₄Si in CDCl₃. ^b Chemical shift difference between α -carbons of the deuterium and protium compounds, $\delta_{\text{CD}_3} - \delta_{\text{CH}_3}$. ^c Chemical shift difference between β -carbons of the deuterium and protium compounds, $\delta^{13}\text{COHCD}_3 - \delta^{13}\text{COHCH}_3$.

Since the cationic carbons in these compounds show no change in shielding as a result of isotopic substitutions, it appears that the reduced electron density brought about by the hyperconjugative isotope effect is compensated for by the increased electron density brought about by the inductive isotope effect.

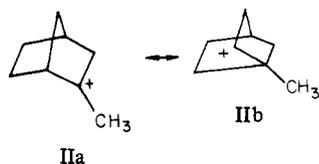
The direction of the shift at the cationic center for **10–12** as a result of β -deuterium substitution is the same as that for neutral compounds. The isotope induced shifts -1.1 ppm for 1-methyl-*d*₃-cyclobutyl cation, -2.2 ppm for 2-methyl-*d*₃-2-norbornyl cations, and -0.8 ppm for 7-methyl-*d*₃-7-norbornenyl cation are 1 order of magnitude larger than the isotope-induced shifts for similar positions in neutral compounds (-0.1 to -0.3 ppm). The isotope-induced shifts appear to be too large to interpret as arising from inductive effects. These abnormally large isotope effects observed for these ions must arise for other reasons.

The 2-methyl-*d*₃-2-norbornyl cation exhibits isotope induced shifts not only at C-2 (-2.2 ppm) but also at C-3 (-0.3 ppm) and C-1 (+0.4 ppm). Isotope-induced shifts at the γ position in a saturated compound appear not to have been previously reported. An explanation of the γ -isotope shifts based on inductive effects does not appear to be reasonable. For an understanding of these unusual isotope shifts, a thorough examination of the detailed electronic structure of the 2-methyl-2-norbornyl cation is required.

The preponderance of evidence accumulated over the past 2 decades indicates that the 2-norbornyl cation exists as a static σ -bridged nonclassical carbonium ion. It has been argued that by methyl substitution at the 2-position, the σ -bridged 2-norbornyl cation is converted to a simple nonbridged tertiary 2-methyl-2-norbornyl cation. One would expect that there would be a continuum of charge delocalization with the extent depending on the particular system. If the 2-methyl-2-norbornyl ion existed as a single static tertiary ion then the isotope induced shifts should be similar to those for the ions **1–3**. The fact that the isotope shifts are of opposite sign argues strongly against this possibility. Another possibility is that the 2-methyl-2-norbornyl cation is nonclassical with σ -bridging by the C₂-C₆ bond as in **II**. A



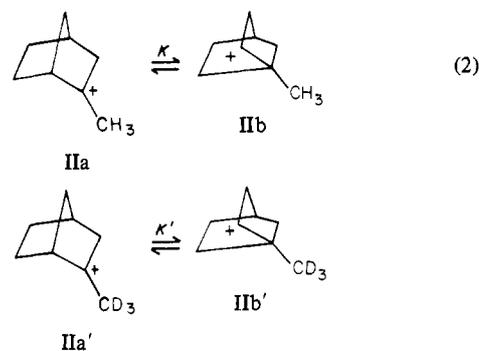
consideration of the two contributing resonance structures, **IIa** and **IIb**, implies that methyl-*d*₃ substitution will selectively increase



the relative contribution of the canonical form, **IIb**. As a result of this, the C-2 carbon will become less positive, the C-1 carbon will become more positive, and the C-3 carbon will become less

positive upon deuterium substitution. Indeed we have observed a β -isotopic splitting (-2.2 ppm) at C-2, a γ -isotopic splitting (+0.4 ppm) at C-1, and another γ -isotopic splitting (-0.3 ppm) at C-3. The observation of these large γ -deuterium chemical shift isotope effects further supports the above arguments.

A final possibility to be considered is that structures **IIa** and **IIb** are in equilibrium with each other (eq 2). A free energy



difference between **IIa** and **IIb** of $\Delta G = 6.5$ kcal/mol can be estimated.¹⁷ The chemical shifts observed for the cationic carbons of the protium and deuterium compounds, δ and δ' , are weighted averages of isomer fractions, giving

$$\delta = \delta_1 A + \delta_2 (1 - A)$$

$$\delta = \delta_1 A' + \delta_2 (1 - A')$$

where δ_1 and δ_2 are chemical shifts of the cationic carbons in **IIa** (or **IIa'**) and **IIb** (or **IIb'**) and A and A' are mole fractions of **IIa** and **IIa'**, respectively. The chemical shift isotope effect observed on the cationic carbon, $\Delta C^+ = \delta' - \delta = (\delta_1 - \delta_2)(A' - A)$, is equal to -2.2 ppm. An approximate value for $\delta_1 - \delta_2$ is 160 ppm obtained from the slope of the linear relationship,^{10d} hence $A' - A = 0.014$.

The equilibrium constant, K , for **IIa** \rightleftharpoons **IIb** can be calculated to give $K = 6.3 \times 10^{-6}$ from the value of $\Delta G = 6.5$ kcal/mol. The equilibrium constant, K' , and the free energy difference, $\Delta G'$, for **IIa'** \rightleftharpoons **IIb'** can then be calculated to give eq 3 and 4. The free

$$K' = \frac{1 - A'}{A'} = \frac{1 - A + 0.014}{A - 0.014} = \frac{0.014}{0.986} = 0.014 \quad (3)$$

$$\Delta G' = -RT \ln K' = 1.47 \text{ kcal/mol} \quad (4)$$

energy change upon deuterium substitution, $\Delta \Delta G = \Delta G - \Delta G' = 6.5 - 1.47 = 5.0$ kcal/mol, is apparently unacceptable when compared to that value for 1-methyl-*d*₃-2-methylcyclopentyl cation, 174 cal/mol.^{1a} Therefore the isotope effect, -2.2 ppm, observed for the 2-methyl-2-norbornyl cation, must arise from an "isotopic perturbation of resonance" instead of an equilibrium isotope effect. This isotopic perturbation of resonance results from averaging over

Table II. Carbon-13 Chemical Shifts^a of Carbocations

no.	compd	C-1	CH ₃	CD ₃	C-2	C-3	C-4	C-5	C-6	C-7	ΔC ^{+b}
1a		335.7	48.3								
1b		336.5	48.7	47.5							0.8
1c		337.1		47.6							1.4
2a		336.0	45.4		58.4	10.3					
2b		336.6		44.7	58.4	10.3					0.6
3a		337.3	37.5		64.1	27.2					
3b		337.7		36.6	64.1	27.2					0.4
3c		337.8	37.5			27.2					0.5
4a		254.1	32.4		139.3	141.1	131.8	154.8			
4b		254.1		31.4	139.3	140.9	131.8	155.0			0.0
5a		217.0	24.5		139.5	153.1 141.9	134.0 ^d 134.8	181.7	25.5 ^c		
5b		217.0		23.4	139.5	153.0 141.9	134.0 ^d 134.8	181.9	25.5		0.0
6a		194.2	20.5						59.6		
6b		194.2		19.4					59.6		0.0
7a		250.5	32.6		67.4	59.6					
7b		250.5			67.4	59.6					0.0
8a		249.1	35.2		140.7	207.6	33.5	19.5	41.3		
8b		249.1			140.7	207.6	33.5	19.5	41.3		0.0
9		230.3	30.7		137.7	230.0	36.3	18.7	36.3		
10a		162.4	24.3		47.6	47.6					
10b		161.3		23.5	47.6	47.6					-1.1
11a		79.9	26.6		268.3	54.2	41.8	22.4	34.6	39.1	
11b		80.3	25.8		266.1	53.9	41.8	22.4	34.6	39.1	-2.2
12a		57.6	12.5		134.4		57.6	25.6	25.6	72.4	
12b		57.6		11.7	134.4		57.6	25.6	25.6	71.4	-0.8

^a Chemical shifts in ppm relative to external Me₄Si in acetone-*d*₆ or CD₂Cl₂ at a temperature of -70 to -80 °C. ^b Chemical shift difference between the cationic carbon centers of the deuterium and protium compounds. ^c Chemical shift of the CH₃ carbon in the tolyl group. ^d Alternate assignment possible, for the two nonequivalent meta positions. The ortho position syn to the -CH₃ group occurs at higher field.

Table III. ^{13}C Chemical Shifts of the Carbocations and Precursor Alcohols and ^{13}C Chemical Shifts and Infrared Carbonyl Stretching Frequencies of the Corresponding Ketones or Aldehydes

no. ^a	carbocation series type	RR'C ⁺ (CH ₃)		RR'C(OH)CH ₃		RR'C=O	
		$\delta^{13}\text{C}^+$	$\delta\text{C}^+-^{13}\text{CH}_3$	$\delta^{13}\text{C-OH}$	$\delta\text{C(OH)}^{13}\text{CH}_3$	$\delta\text{C=O}$	$\lambda_{\text{C=O}}, \text{cm}^{-1}$
1	<i>tert</i> -butyl	335.7	48.3	68.7	31.6	205.1	1718
2	<i>tert</i> -amyl	336.0	45.4	70.5	28.2	206.3	1721
3	1-methylcyclopentyl	337.3	37.5	79.7	28.2	213.9	1740
4	2-phenylpropyl	254.1	32.4	72.3	31.6	196.9	1687
5	α -(<i>p</i> -tolyl)ethyl	217.0	24.5	70.4	25.5	190.9	1689
6	α -(<i>p</i> -anisyl)ethyl	194.2	20.5	70.2	25.5	190.2	1683
7	α -methylcyclopropylcarbonyl	250.2	32.6			199.9	
8	1-methyl-2-cyclohexenyl	249.1	35.2	67.7	29.3	197.1	1686
10	1-methylcyclobutyl	162.4	24.3	72.2	26.5	208.2	1791
11	2-methyl-2-norbornyl	268.3	26.6	77.3	30.4	215.3	1751
12	7-methyl-7-norbornenyl	72.4	12.5	89.7	20.2	203.3	1779

^a The numbering is the same as that in Table II.

a vibrational motion in an anharmonic potential well which effectively perturbs the averaged electron distribution.

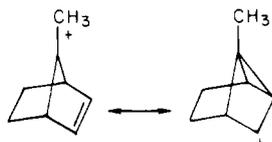
The nonclassical nature of the 2-methyl-2-norbornyl cation can be further supported by a consideration of the chemical shifts of the C-1 and CH₃ carbons. The C-1 carbon (with a chemical shift = 79.9 ppm) is more deshielded than the corresponding carbons of classical static carbenium ions. The CH₃ carbon (with a chemical shift of 26.6 ppm) is, on the other hand, less deshielded than those of the classical static carbenium ions. The chemical shift data are therefore also consistent with σ bridging by the C₂-C₆ bond in the 2-methyl-2-norbornyl cation.

The structure of the 7-methyl-7-norbornenyl cation, III, is



III

similar to the parent secondary 7-norbornenyl cation which has been confirmed to have the "bishomocyclopropenyl"¹⁸ type structure from solvolytic¹⁹ and NMR spectroscopic studies.²⁰ A consideration of the possible resonance structures, IIIa and IIIb,



IIIa

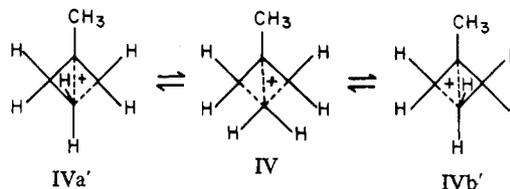
IIIb

suggests that methyl-*d*₃ substitution will increase the relative contribution of the canonical form, IIIb. Consequently, the C-7 carbon of the deuterium compound will have less positive charge and hence will be less deshielded than that of the protium compound.

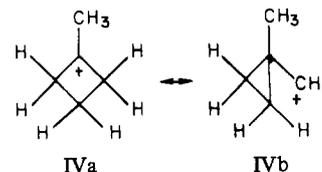
The reason we do not observe a δ -isotopic splitting on C-2 and C-3 carbons is because the static chemical shift of C-2 and C-3 in the "frozen" structure IIIa is perhaps very close to that in the "frozen" structure IIIb, since there is very little change (only +0.9 ppm, see Tables I and II) in the chemical shift of C-2 and C-3 upon ion formation from the alcohol precursor.

1-Methylcyclobutyl cation has been proposed²¹ to be a degenerate set of σ -delocalized bicyclobutonium like ions, IVa' and

IVb', rapidly interconverting through a symmetrical σ -delocalized puckered species, IV, or the symmetric ion itself.



If the structure IV is accepted, the 1-methylcyclobutyl cation may be considered as having the following contributing canonical forms, IVa and IVb. Methyl-*d*₃ substitution will decrease the



IVa

IVb

relative contribution of IVa compared to the protium compound, because a CH₃ group is a better hyperconjugative electron donor than a CD₃ group. As a result of this, the C-1 carbon of the deuterium compound will have less positive charge and hence be less deshielded than that of the protium compound.

The magnitude of the chemical shift isotope effect in the nonclassical ion is a complicated factor which depends on the relative importance of the contributing resonance structures, the extent of hyperconjugative interaction and also the static chemical shifts in each of the canonical forms. Considering only the relative importance of the contributing resonance structures alone, one may expect that the greater the contribution of the structure having the methyl group directly attached to the positive center (such as IIa, IIIa, or IVa), the greater the β -isotope effect will be. The observed relative magnitude of the β -isotope effect increases in the order 2-methyl-2-norbornyl ion > 1-methylcyclobutyl ion \geq 7-methyl-7-norbornenyl ion, suggesting that the relative percent contribution increases in the order IIa > IVa > IIIa.

The differences in percent contribution of IIa, IIIa, and IVa may be due to the ring angle strain in the cyclobutyl compounds and at the 7-position of the norbornenyl systems, which will be accentuated in going to the trigonal carbonium ions. The unusual bond angle and hybridization at the cyclobutyl and the 7-position of the norbornenyl systems can be seen from a comparison of the infrared carbonyl stretching frequencies, $\nu_{\text{C=O}}$, and the ^{13}C carbonyl carbon shieldings, $\delta_{\text{C=O}}$, of the corresponding ketones (Table III).

Our data show that α -deuterium chemical shift isotope effects in carbocations are rather insensitive to the nature of charge delocalization. Some representative values of α -isotopic splittings are -0.7 ppm for dimethyl-*d*₆ ethyl carbenium ion, -0.9 ppm for 1-methyl-*d*₃-cyclopentyl carbenium ion, -1.0 ppm for dimethyl-*d*₆-phenyl carbenium ion, -0.8 ppm for 1-methyl-*d*₃-cyclobutyl carbenium ion, and -0.8 ppm for 7-methyl-*d*₃-7-norbornenyl carbenium ion.

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We also note that α -deuterium chemical shift isotope effects of the carbocations differ very little, if any, from those of the corresponding alcohols. 2-Methyl- d_3 -2-butanol-1,1,1- d_3 , 1-methyl- d_3 -cyclopentanol, 2-phenyl-2-propanol-1,1,1,3,3,3- d_6 , 1-methyl- d_3 -cyclobutanol, and *syn*-7-methyl- d_3 -2-norbornen-7-ol all give an α -isotopic splitting of -0.9 ppm. It appears that within experimental error limits, these α -methyl- d_3 isotope shifts are all around -0.9 ppm in spite of changes in charge densities, hybridizations, and other structural effects.

Experimental Section

General Data. Melting points were determined in a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on the Perkin-Elmer Model 281 spectrometer. Routine ^1H NMR spectra were taken on a Varian T-60 spectrometer. ^1H chemical shifts are reported in ppm down field from internal tetramethylsilane in CDCl_3 solvent.

Materials. (1) Superacid Solutions. Antimony pentafluoride (SbF_5) and magic acid ($\text{SbF}_5/\text{FSO}_3\text{H} = 1:1$) were obtained from Cationics, Inc. Sulfuryl chloride fluoride (SO_2ClF) was obtained from Columbia Organic Chemicals Co., Inc.

(2) Deuterated Reagents. Methyl- d_3 iodide was purchased from Aldrich. Acetone- d_6 was obtained from Stohler Isotope Chemicals. Deuterium oxide (99.7% D) was obtained from Merck Sharp & Dome.

(3) Ketones. Cyclobutanone, cyclopentanone, 2-cyclohexen-1-one, 3-methyl-2-cyclohexen-1-one, and 2-norbornanone are commercial chemicals from Aldrich.

Cyclopentanone-2,2,5,5- d_4 ²² was prepared by a procedure similar to that reported by Lambert and Greifenstein.²³ Cyclopentanone (5.6 g, 0.067 mol) was stirred for 24 h at 60 °C in a solution of D_2O (5 g) containing NaCl (1 g) and K_2CO_3 (0.1 g). The organic layer was then taken up in the ether layer and the aqueous layer was extracted with three portions of ether. The combined ether extracts were dried over MgSO_4 . The ether solvent was then removed. The exchange was repeated six times until the α proton (δ 2.1) was no longer observable in the NMR spectrum.

Methyl *p*-tolyl ketone was synthesized by Friedel-Crafts acylation of toluene from acetic anhydride and aluminum chloride.²⁴ The product has a bp of 74–76 °C (2 mmHg).

Methyl- d_3 *p*-tolyl ketone was prepared from the nondeuterated ketone by acid-catalyzed exchange with deuterium oxide.²⁵ Ordinary nondeuterated methyl *p*-tolyl ketone (0.04 mol) was stirred for 24 h in a mixture of D_2O (5 mL) and a stock solution of deuterated acid (5 mL). The acid solution was prepared by adding 1 g of PCl_5 to 50 mL of D_2 . The procedure was repeated five times until the α -proton signal (δ 2.41) disappeared in the NMR spectrum.

Methyl *p*-anisyl ketone was prepared from anisole, acetic anhydride, and a catalytic amount of iodine according to the literature procedure.²⁶ The product has a bp of 106–108 °C (2 mmHg).

Methyl- d_3 *p*-anisyl ketone was prepared by the same acid catalyzed exchange procedure²⁵ described above for methyl- d_3 *p*-tolyl ketone. After

five exchanges, the α -proton signal (δ 2.47) was no longer observable in the NMR spectrum.

Bicyclo[2.2.1]hept-2-en-7-one²⁷ was synthesized following the procedure of Gassman and Pope by using the starting material hexachloropentadiene, except for the dechlorination step, in which the modified method suggested by Jung and Hudspeth²⁸ was used.

(4) Alcohols. The alcohols were prepared by Grignard additions or lithium aluminum hydride reductions from the corresponding ketones.

tert-Butyl- d_6 alcohol, 1-methylcyclobutanol, 1-methylcyclopentanol, 1-methylcyclopentanol-2,2,5,5- d_4 , 2-methyl-*endo*-2-norbornanol, *syn*-7-methyl-2-norbornen-7-ol, and their methyl- d_3 analogues were prepared by Grignard reactions by using samples of methylmagnesium or methylmagnesium- d_3 iodide from the corresponding ketones.

1-Methyl-2-cyclohexen-1-ol or its methyl- d_3 analogue was synthesized from 2-cyclohexen-1-one by using methylolithium or methylolithium- d_3 . 1-Methyl- d_3 -3-methyl-2-cyclohexen-1-ol was prepared from 3-methyl-2-cyclohexen-1-one by using methylolithium- d_3 .

2-Methyl- d_3 -2-butanol-1,1,1- d_3 was synthesized by Grignard addition of ethylmagnesium iodide to acetone- d_6 .

2-Phenyl-2-propanol and 2-phenyl-2-propanol-1,1,1,3,3,3- d_6 were prepared by addition of phenyl magnesium bromide to acetone and acetone- d_6 , respectively.

Methyl-*p*-tolylcarbinol and methyl- d_3 -*p*-tolylcarbinol were prepared by reduction of methyl *p*-tolyl ketone and methyl- d_3 *p*-tolyl ketone with lithium aluminum hydride in anhydrous ether.

Methyl-*p*-anisylcarbinol and methyl- d_3 -*p*-anisylcarbinol were prepared by reduction of methyl *p*-anisyl ketone and methyl- d_3 *p*-anisyl ketone with lithium aluminum hydride in anhydrous ether.

Preparation of Carbocations. The alcohols (with the exception of 1-methyl- d_3 -3-methyl-2-cyclohexen-1-ol) were prepared as mixed 1:1 protium to deuterium samples. A solution of 0.8 mL (2.4 g, 0.011 mol) of SbF_5 or magic acid ($\text{FSO}_3\text{H}/\text{SbF}_5 = 1:1$) and 0.8 mL of SO_2ClF was prepared in a 12-mm NMR tube cooled to -78 °C (dry ice–acetone slurry temperature). About 0.0026 mol of the mixed alcohol was added, with continuous stirring on a Vortex mixer, slowly into a super acid solution.

Carbon-13 Nuclear Magnetic Resonance Measurements. ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL-100 NMR spectrometer. Samples of alcohols were measured as 1:1 protium to deuterium mixtures. In order to get more accurate relative intensity ratios and to obtain enough signal to noise ratio for the low intensity CD_3 heptet, we obtained ^{13}C NMR spectra with a pulse delay (5–10 s) and in the absence of the NOE effect. The instrument was run with a pulse width 20 μs , where a 75 μs pulse is equivalent to a 90° pulse. Acquisition times used were 1.638 s for a spectrum width = 2500 Hz or 0.819 s for a spectrum width = 5000 Hz on the basis of 8K data points. Chemical shifts are reported in ppm referenced to internal Me_4Si in CDCl_3 solvent. The data were obtained at an ambient probe temperature (37 °C) for samples of alcohols. Resolution achieved varies from 0.024 to 0.05 ppm for different runs.

For samples of carbocations, the acquisition times used varied from 0.4–0.8 s depending on spectral widths. Chemical shifts were measured in ppm referenced to external TMS in CD_2Cl_2 or acetone- d_6 contained in a 5-mm NMR tube held concentrically inside the 12-mm NMR tube with a Teflon spacer. In case isotopic splittings were observed, chemical shift assignments were based on consideration of relaxation times; i.e., the peak with lower intensity was assigned to the deuterated compound. The data were obtained at a temperature of -70 to -80 °C. Resolution achieved varies from 0.05 to 0.10 ppm depending on spectral widths.

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