(21) It should be noted, in this connection, that the highest $k_{\text{O-alkylation}} \cdot k_{\Sigma\text{C-alkylation}}$ ratio measured at atmospheric pressure can only be regarded as a *lower limit*, since occurrence of isomerization processes cannot be ruled out, even at 720 Torr.
(22) S. A. Benezra and M. M. Bursey, *J. Am. Chem. Soc.*, **97**, 3600 (1972). More recent evidence for gas-phase O-acetylation, and the possible isomerization of the intermediate oxonium ions to more stable forms, is provided by D. A. Chatfield and M. Bursey, *J. Am Chem. Soc.*, **98**, 6492 (1976).
(23) The relative stability of I and II can be evaluated from (1) the $\Delta H_f°$ values of *tert*-butyl phenyl ether (IV) and respectively of *p*-*tert*-butylphenol (V) and (2) the PA of the oxygen atom of IV vs. that of the alkyl-substituted ring position of V. While experimental $\Delta H_f°$ values of IV and V are not available, the data concerning other isomeric alkyl phenyl ethers/*p*-alkylphenols pairs show that the latter are invariably *more stable* by some 10 kcal/mol; cf. (a) M. Badoche, *Bull. Soc. Chim. Fr.*, **8**, 212 (1941). As to the PA values, the following data are relevant. First, para-protonated phenol is *more stable* in the gas phase with respect to the isomeric oxonium ion; cf. (b) D. J. De Frees, R. T. McIver, and W. J. Hehre, private communication to be published, and (c) B. S. Freise, R. L. Woodin, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6893 (1975), the stability difference obtained with theoretical and ICR methods ranging from 13 to 20 kcal/mol. The preferred ring protonation of phenol is consistent with the small (<5 kcal/mol) difference measured between the gas-phase PA of phenol and anisole; cf. ref 23b and (d) Y. Lau and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 7452 (1976). Furthermore, the ICR isotope exchange experiments of Freiser, Woodin, and Beauchamps show that ring protonation of anisole is energetically preferred with respect to O-protonation. The PA of the oxygen atom is expected to be higher in *tert*-butyl phenyl ether than in anisole, owing to the larger effect of the *tert*-butyl with respect to the methyl group, on the basicity of the n center; cf. (e) J. Long and B. Munson, *J. Am. Chem. Soc.*, **95**, 2427 (1973). On the other hand, the presence of a *tert*-butyl substituent is also expected to increase the PA of the para position of phenol, in accord with the stabilizing effect of an ipso alkyl substituent at the protonated site of a gaseous arenium ion; cf. (f) J. L. Devlin, III, J. F. Wolf, R. W. Raft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976). As these two effects tend to cancel each other, the available evidence strongly suggests, albeit certainly does not prove, that the PA values of the oxygen atom of IV, and of the alkyl-substituted ring position of V are comparable, perhaps with a small preference for the latter, and that their difference, if any, can hardly offset the large stability excess of V over IV. Consequently, our experimental evidence pointing to the higher stability of II with respect to I appears quite reasonable on the grounds of independent thermochemical and mass spectrometric data.
(24) H. J. Shine, "Aromatic Rearrangements", American Elsevier, New York, N.Y., 1967.
(25) M. J. S. Dewar, "Molecular Rearrangements", P. de Mayo, Ed., Wiley, New York, N.Y., 1963, p 306.
(26) D. E. Pearson and C. A. Buchler, *Synthesis*, 460 (1971).
(27) P. Kovacic and J. J. Hiller, *J. Org. Chem.*, **30**, 1581 (1965).
(28) J. H. Ridd and E. F. V. Scriven, *J. Chem. Soc., Chem. Commun.*, 641 (1972).
(29) R. A. Kretchmer and M. B. McCloskey, *J. Org. Chem.*, **37**, 1989 (1972).
(30) E. C. Taylor and A. McKillop, *Acc. Chem. Res.*, **3**, 345 (1970).
(31) P. Heberfield and P. Paul, *J. Am. Chem. Soc.*, **87**, 5502 (1965).
(32) P. A. Spanninger and J. L. von Rosemberg, *J. Am. Chem. Soc.*, **94**, 1070 (1972), and references cited therein.
(33) However, it has been shown (ref 12) that a *gaseous tert*-butyl ion can efficiently attack the ring positions ortho to a methyl group, provided that they are sufficiently activated, and furthermore the steric hindrance of the OH group is smaller than that of the methyl group.

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^{13}C Nuclear Magnetic Resonance Spectroscopic Study of Alkyl Cations. The Constancy of ^{13}C Nuclear Magnetic Resonance Methyl Substituent Effects and Their Application in the Study of Equilibrating Carbocations and the Mechanism of Some Rearrangements[1a]

George A. Olah*[1b] and Daniel J. Donovan

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received December 20, 1976*

Abstract: All C_3 to C_8 alkyl cations were prepared in SbF_5/SO_2ClF solution at low temperature (−78 to −130 °C) and their proton decoupled and coupled ^{13}C NMR spectra were studied. The effect of methyl substituents was determined by comparing the ^{13}C NMR shifts of related carbocations and was found to be constant. These substituent effects were applied in estimating the ^{13}C shifts of the degenerate and nondegenerate equilibrating cations. This method gave good agreement for estimating the ^{13}C NMR shifts in tertiary–tertiary equilibrating ions, as compared with the experimental values. Some thermodynamic properties were also measured for the nondegenerate equilibrating cations. Application of the additive substituent effect method to secondary–secondary equilibrating carbocations showed significant deviations from the experimental ^{13}C NMR shifts. Methyl substituent effects in static and equilibrating carbocations are discussed. Additionally, some carbocationic rearrangements were observed during the course of this work and their mechanisms are discussed.

Since our first report in 1962 of the successful preparation of alkyl cations,[2] the structural elucidation of a continuously increasing number of diverse types of stable carbocations has been accomplished by ^1H NMR and ^{13}C NMR spectroscopic studies in low nucleophilic media.[3-5a-c] The NMR methods give particular information about the structure, the trend of charge distribution,[6] bonding,[7] dynamic exchange processes,[4,8] and other properties of carbocations. The NMR chemical shifts and coupling constants have been correlated with the above properties by the molecular comparison of related ions and/or frequently by quantum mechanical molecular orbital calculations.[9-12] The success of these methods has brought about their widespread use in studying carbocations. ^{13}C NMR studies of a significant number of alkyl cations were carried out and reported, as were rearrangements of carbocations. However, no comprehensive, systematic study was made to establish general trends, if any, of substituent effects.

In the course of our continued studies we undertook a systematic investigation of structurally related alkyl cations by ^{13}C NMR spectroscopy, since small changes in structure produce a relatively large change in the chemical shift for the position substituted. A pertinent point in question is that of the ^{13}C shifts of alkanes, where two systematic studies have resulted in excellent empirical methods for predicting the ^{13}C shifts of any carbon atom of the alkanes.[13,14] The methods are based on comparison of the ^{13}C shift of methane and the observed differences as methyl groups are successively substituted. These differences were defined as the methyl substituent effects.

In the present study all the static C_3 to C_8 alkyl cations were prepared at low temperatures and their ^{13}C NMR chemical shifts and J_{C-H} coupling constants were determined. The methyl substituent effects were calculated from comparison of the chemical shifts and were subsequently utilized in estimating the ^{13}C shifts of symmetrical and unsymmetrical equilibrating carbocations. In the latter case, they can be used to measure the equilibrium constants of the different carbenium ions at different temperatures. These applications were also extended to static secondary and equilibrating secondary–secondary carbocations.

The latter part of our study is concerned with the mechanism of carbocationic rearrangements as studied under stable ion conditions on the basis of subsequently found carbocations. ^{13}C NMR is again particularly suitable because of its wide chemical shift range, allowing identification of complex ion mixtures. This is further enhanced by proton decoupling which eliminates peak overlaps by eliminating J_{C-H} coupling and allowing observation of single absorptions. Complicated mixtures of isomeric carbenium ions can be easily identified by their proton decoupled ^{13}C NMR spectra, in contrast to ^1H NMR where overlapping peaks cannot be identified.[15]

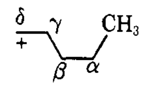
Results

The static C_3 to C_8 alkyl cations (**1–13**) were prepared from either their alcohol or chloride precursor with SbF_5 in SO_2ClF or SO_2ClF/SO_2F_2 solutions at temperatures ranging from −80 to −130 °C. The ratio of precursor to antimony pentafluoride was held at 1:4 (all ratios are molar), while the precursor to solvent ratio varied from 1:19 to 1:30.5 in SO_2ClF and 1:~12.5:6.6 in SO_2ClF/SO_2F_2. The ratio of precursor to antimony pentafluoride was based on previous experience that the secondary and tertiary alcohols or chlorides are completely ionized by excess SbF_5 in a 1:4 ratio to the corresponding alkylcarbenium ions. As this ratio is lowered to 1:2, the ionization of precursor can become incomplete and either the precursor can be alkylated by an already formed carbenium ion to give dialkylhalonium or oxonium ions or deprotonation can be increasingly dominant in the system to form alkenes. Alkyl fluorides do not form dialkyl fluoronium ions, but these precursors are less accessible, particularly considering the large variety of precursors needed in this systematic study. Even though the precursors could be ionized at a lower ratio with SbF_5, such as 1:3, the higher ratio was used throughout to ensure against undesirable side reactions. The solvent and its concentration was not critical for the tertiary carbocations. Only the secondary isopropyl cation showed any interactive association with solvent SO_2ClF. This was minimized by using a low concentration of SO_2ClF or by using SO_2F_2 alone where there is no solvent interaction.

The present systematic study of substituent effects and their additivity in alkyl cations is based on Fourier transform (FT) ^{13}C NMR measurements. The proton decoupled (Table I) and off-resonance (partially coupled) or fully coupled with some nuclear Overhauser enhancement (NOE) (Table II) ^{13}C NMR spectra of the static C_3 to C_8 cations completely ionized between −80 and −130 °C to the corresponding cation from the starting alcohol or chloride.

The ^{13}C spectra were measured at −80 °C for the C_3 to C_5 cations. In the case of C_6, C_7, and C_8 carbenium ions the initially formed carbocations tended to rearrange to their more stable structural isomers. This was overcome by preparing the ions at −130 °C (in a liquid N_2/ethanol slush bath).[16] Above −110 °C these static ions would equilibrate with their isomers.

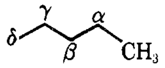
Individual peak assignments were based on the NMR data (coupled and decoupled spectra), their comparison with related cations of known structure, and when needed on peak intensities in the decoupled spectra. It was generally observed that substituent effects on the carbenium center (C^+) decreased substantially after a γ-type effect:



This observation helped in assignments for ions **6**, **10**, **12**, and **13** by comparing the cations with the parent alkanes or by calculating the methyl substituent effect from carbocations whose ^{13}C spectra can be assigned unequivocally.

Methyl Substituent Effects from the ^{13}C NMR Chemical Shifts of Alkyl Cations. ^{13}C methyl substituent effects have been used to empirically calculate ^{13}C shifts for a variety of compounds.[17] Part of our study involved that of the methyl substituent effects from the secondary C_3 isopropyl cation through the static C_4 to C_8 tertiary cations, whose results are summarized in Table III. A comparison of the ^{13}C shifts for the individual cations measured between −110 and −120 °C showed less than a 0.5-ppm difference for the mixtures of isomers measured at −80 °C. It was not expected that there is any appreciable temperature dependence of the ^{13}C shifts between −80 and −110 °C. Thus substituent effects do not vary over this range.

Since the effect of a methyl substituent falls off substantially after the γ position



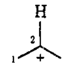
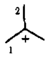
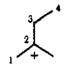
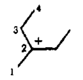
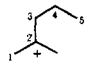
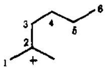
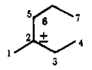
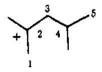
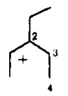
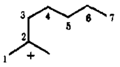
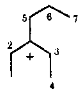
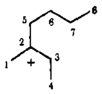
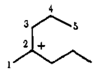
as in the alkane series, the emphasis of substituent effects in carbocations will be centered on the methyl effect on the α, β, and γ positions. From Table I, the effects of methyl groups on the ^{13}C NMR chemical shifts were calculated in replacing H with CH_3 such as going from the isopropyl cation to the *tert*-butyl cation, etc. It was found that the methyl substituent effects (α, β, γ, etc.) could be divided into different sets, where each set consists of methyl groups that are substituted in the same position from the carbenium ion center (Table III). Unfortunately, there is only one example available of a methyl group replacing a hydrogen atom directly at the carbenium center (isopropyl cation vs. *tert*-butyl cation). The α effect of a methyl group on the carbenium center is +14.6 ppm as compared to +9.1 ppm for the alkanes.[13] The β effect of the methyl group through the carbenium center is −4.0 ppm compared to +9.4 ppm for the alkanes (Table III).[13]

In the second series (Table III), the methyl group is added β to the carbenium center. The α effect of 9.8 ppm is substantially decreased from the previously discussed one, while the β effect has increased to 0.8 ppm, which is quite small. The γ and γ' effects of −2.9 and −3.0 ppm on the carbenium center are close to the value of the corresponding alkanes of −2.5 ppm. It should be noted that the trend for substituent effects in this series is quite constant. Thus, there are not expected to be any large deviations by substitution in homologous cations. As in the case of alkanes, multiple substitution on the same carbon atom is expected to cause different effects and some corrections are necessary.

When a methyl replaces a hydrogen in the γ position from the carbenium center, the α effect increased slightly to 10.7 ppm. The β effect again increased to 6.7 ppm, and the γ effect on the carbenium center decreased by 1.1 to −1.8 ppm. The average effects show a higher deviation than above. This is partially due to the dimethylisobutylcarbenium ion ($(CH_3)_2C^+CH_2CH(CH_3)_2$), where two methyl groups are substituted γ from the carbenium center. This caused no significant deviation for the α effect, which is not unusual, but the β and γ effects would be 1.3 ppm larger and 0.6 ppm smaller, respectively, if this cation was excluded from the data.

In the case of the dimethyl-*n*-butyl- (**6**) and the dimethyl-*n*-pentyl- (**10**) carbenium ions, the methyl groups are substi-

Table I. ^{13}C Chemical Shifts of the Static C_3 to C_8 Alkyl Cations

Cation		1[a]	2	3	4	5	6	7	8
	1	51.5 (q)	320.6 (s)						
	2	47.5 (q)	335.2 (s)						
	3	44.6 (q)	335.4 (s)	57.5 (t)	9.3 (q)				
	4	41.9 (q)	336.4	54.5 (t)	8.9 (q)				
	5[b]	45.0 (q)	333.4	64.4 (t)	20.9 (t)	12.6 (q)			
	6	44.9 (q)	332.9 (s)	62.8 (t)	29.3 (t)	22.6 (t)	13.0 (q)		
	7	42.1 (q)	334.7 (s)	55.1 (t)	9.1 (q)	61.6 (t)	20.2 (t)	12.5 (q)	
	8	45.4 (q)	332.1 (s)	70.1 (t)	31.4 (d)	21.7 (q)			
	9		336.8 (s)	51.8 (t)	8.6 (q)				
	10	44.6 (q)	332.5 (s)	62.7 (t)	27.4 (t)	31.1 (t)	22.3 (t)	13.1 (q)	
	11		334.7 (s)	51.6 (t)	8.1 (q)	58.8 (t)	18.3 (t)	11.6 (q)	
	12	42.0 (q)	334.3 (s)	54.7 (t)	8.7 (q)	59.7 (t)	28.5 (t)	22.0 (t)	12.9 (q)
	13	42.1 (q)	332.8 (s)	61.9 (t)	19.7 (t)	12.1 (q)			

[a] All chemical shifts are measured from external Me_4Si. [b] The cations up to 5 have been previously measured by ^{13}C NMR.[4,31] The carbenium ion 4 and 5 have been measured only in a mixture of the two ions.

tuted δ and ε from the carbocation center, respectively. There is not much difference between these two ions, indicating that the carbocation center has little effect on the increasingly remote substituents. The farther away the methyl group is substituted from the carbenium center, the closer it approaches the values of the methyl substituent effects of alkanes. For example, the β effects in the last two cations are 8,4 and 8.5 ppm, respectively, which approaches the average value for the alkanes of 9.4 ppm. The γ effect is also slightly lower.

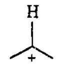
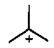
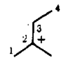
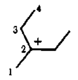
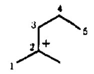
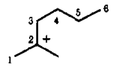
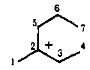
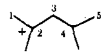
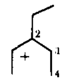
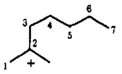
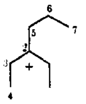
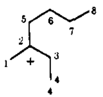
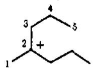
^{13}C NMR Chemical Shift Assignments for Equilibrating Carbocations. Several equilibrating alkylcarbenium ions (C_4 to C_8) have also been prepared in a manner similar to the static cations. Both the proton decoupled and coupled ^{13}C NMR spectra of these cations were obtained and are summarized in Tables IV and V. The equilibrating cations in Table IV undergo degenerate rearrangements and the ^{13}C spectra are temperature independent. The cations in Table V produce nondegenerate rearrangements and their ^{13}C spectra are temperature dependent. Such changes are not obviously seen from the ^{1}H NMR spectra, as from the ^{13}C spectra. This is due to the fact that the carbenium centers in the nonsymmetrical equilibrating cations are changing relative to one another. In the ^{13}C spectra this change is easily observed since the equilibrating carbenium centers are directly observed, while in the ^{1}H spectra only the average absorption of the proton shift is seen. The latter shift should not change very much with temperature since the hydrogen is always adjacent to a carbenium center at all times. The other groups are affected only slightly as shown by the ^{13}C shift data, but are unequivocally observed to change. Again these changes are not obvious from ^{1}H NMR spectra.

Specific assignments for the degenerate cations were made from the fully coupled spectra of these temperature independent equilibrating cations (**14–18**). These methods, as well as intensities of peaks and temperature dependent absorptions, were used to confirm the assignments for the nondegenerate equilibrating cations (**19–21**).

For example, the ethylisopropylmethylcarbenium ion ($(CH_3CH_2)(CH_3)C^+HC(CH_3)_2$, **19a**), which reversibly isomerizes to the dimethyl-2-butylcarbenium ion ($(CH_3)(CH_3CH_2)CH^+C(CH_3)_2$, **19b**), was assigned in the following manner. The barrier for isomerization must be low, as the cation rapidly equilibrates between the two tertiary structures on the NMR time scale. Thus, average signals are observed for **19a** and **19b** and the proton decoupled ^{13}C spectra showed only six absorptions for the equilibrating cation.

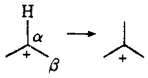
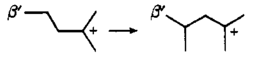
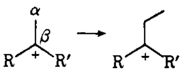
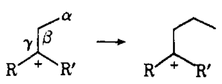
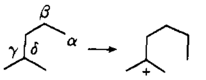
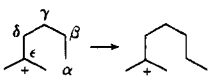
From the fully coupled experiments $\delta_{^{13}C}$ (Me_4Si) 31.7, 10.5, and 28.5 were assigned to the methyl groups and $\delta_{^{13}C}$ (Me_4Si) 43.1 to a methylene carbon, and $\delta_{^{13}C}$ (Me_4Si) 193.6 and 203.1 absorptions showed a doublet due to the methine carbons. Since C_4 is the only methylene carbon in the spectra its assignment was straightforward. In the proton decoupled ^{13}C

Table II. ^{13}C J_{C-H} Coupling Constants of the Static C_3 to C_8 Alkyl Cations

	1	2	3	4	5	6	7	8
	131.7[a]	171.3						
	130.8							
	131.8		127.4	130.8				
	131.7		124.8	129.6				
	132.1		126.6	131.8	129.1			
	131.4		126.7	131.4	127.5	126.2		
	131.5		124.0	128.8	119.2	126.2	123.9	
	131.6		124.7	137.2	124.1			
			123.2	129.8				
	131.4		127.2	~131	~131	133.1	126.4	
			121.6	130.3	121.1	125.6	124.3	
	132.5		~122	129.2	122.4			127.0
	132.0		126.2	132.5	129.5			

[a] All values are measured in hertz.

Table III. Effects (ppm) of Methyl Substituents on Carbenium Ions

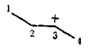
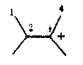
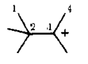
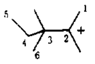
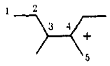
	Expt	α	β	β'	γ[a]	γ'	δ	δ'	ε	ζ	CH_3[b]
	1	14.6	−4.0								α
	6	9.8 ± 0.3	0.8 ± 0.6		−2.9 ± 0.2	−3.0 ± 0.4	−0.8 ± 1.1	1.0	−0.5 ± 0.4	−0.1	β
	5	10.7 ± 1.0	6.7 ± 1.0	9.1	−1.8 ± 0.5		+0.3 ± 0.2	−0.1 ± 0.1	−0.3 ± 0.2	−0.4	γ
	1	10.0	8.4		−1.6		−0.5		−0.1		δ
	1	9.3	8.5		−1.9		−0.1		−0.4	−0.3	ε

[a] The γ through ζ are chosen to be longer chain while the shorter chain was chosen for γ' and δ'. [b] The position of the methyl group in relevance to the carbenium center.

spectra the resonance at $\delta_{^{13}C}$ (Me_4Si) 31.7 is twice as intense as the adjacent methyl group and was assigned to C_1. It is expected that C_1 and C_6 would have similar resonances. Therefore C_6 was assigned to the absorption at $\delta_{^{13}C}$ (Me_4Si) 28.5. The remaining methyl (C_5) assigned to the $\delta_{^{13}C}$ (Me_4Si) 10.5 peak should be relatively shielded, since it is not adjacent to a positive charge.

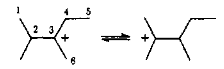
Since the remaining resonances show doublets in the fully coupled experiment, C_2 and C_3 cannot be assigned in a straightforward manner by the above methods. The positions of these carbons can be inferred by correlating them with the temperature dependent absorptions, which were unequivocally assigned. Using Table V it can be observed that the C_1 shift becomes deshielded at a lower temperature. This indicates a

Table IV. ^{13}C Chemical Shifts and J_{C-H} Coupling Constants for Temperature-Independent Equilibrating Alkyl Cations, J_{CH}

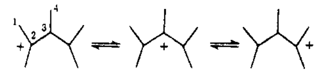
	14	1,4[a] 21.0	2,3 171.6			1,4 130.7	2,3 66.7
	**15**	1,4 32.1	2,3 197.8			132.2	67.5
	**16**	1,4 33.6	2,3 197.3			131.5	
	17	1,6 31.3	2,3 199.4	4 48.0	5 9.4		
	18	1 10.7	2 42.8	3,4 199.1	5 28.3		

[a] All chemical shifts are measured from external Me_4Si.

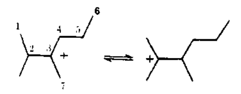
Table V. ^{13}C Chemical Shifts for the Temperature-Dependent Equilibrating Alkyl Cations


19a **19b**

°C	1(q)[a]	2(d)	3(d)	4 (+)	5(q)	6(q)
−129	29.9	175.6	221.2	43.9	10.0	30.7
−120	30.5	180.4	216.5	43.8	10.2	29.5
−110	30.8	184.1	212.5	43.4	10.3	29.1
−98	31.3	188.7	208.0	43.3	10.5	28.9
−90	31.4	191.4	205.3	43.1	10.4	28.6
−81	31.7	193.6	203.1	43.0	10.5	28.5
−72	31.9	195.5	201.0	42.9	10.6	28.4
−62	32.1	197.1	199.4	42.8	10.7	28.3
−51	32.1	198.6	197.9	42.7	10.8	28.2


20a **20b** **20c**

°C	1(q)	2	3	4(q)
−123	30.7	174.4	97.4	15.7
−116	30.6	173.3	100.3	16.4
−107	30.4	171.1	104.2	16.7
−101	30.3	169.9	106.3	17.0
−92	30.2	168.7	108.8	17.3
−85	30.1	167.0	112.2	17.8


21a **21b**

°C	1(q)	2(d)	3(d)	4(+)	5(+)	6(q)	7(q)
−119	36.1	252.9	140.5	46.6	22.1	12.8	22.1
−112	35.9	250.1	143.0	46.7	22.0	12.7	22.4
−104	35.7	247.9	145.2	46.9	22.0	12.7	22.7
−97	35.5	245.2	147.8	47.1	22.0	12.7	23.0
−85	35.3	241.5	151.3	47.4	22.0	12.7	23.4
−79	35.1	239.9	152.8	47.5	22.0	12.7	23.6
−72	35.0	237.8	154.8	47.8	22.1	12.8	24.0
−65	34.8	235.6	157.3		22.1	12.7	24.2

[a] All values measured from Me_4Si.

decrease in the carbenium ion character of the adjacent carbon.[18] The opposite trend is seen with C_4 and C_6, which signifies that there is an increase in charge at the adjacent carbenium center. It is expected that C_2 and C_3 should follow the same trend of decreasing and increasing carbenium ion character, respectively. Thus, carbons 2 and 3 were assigned values of $\delta_{^{13}C}$ (Me_4Si) 193.6 and 203.1, respectively. The two other temperature dependent equilibrating cations (**20** and **21**) were assigned using similar techniques.

Discussion

Application of Methyl Substituent Effects to Equilibrating Cations. The substituent effects summarized in Table III are remarkably constant for methyl groups, which are substituted either β or γ from the carbenium center. However, the two sets of methyl substituent effects have quite different values. The values for the methyl substituent effects are clearly dependent on their position related to the carbenium center. This is not unexpected in view of the fact that the carbenium ion center itself affects the ^{13}C NMR chemical shifts, as the effect becomes different for each of the carbon positions.[18] The consistency of the β- and γ-methyl substituent effects on the ^{13}C NMR chemical shift indicates the same degree of charge delocalization by these groups in the static carbocations. In Table III there is only one example for each methyl substituent effect, which is the α, β, and ϵ position, respectively, from the carbocationic center. Therefore, in the latter cases there is only an indication of the constancy of the methyl substituent effects from these positions owing to an insufficient number of examples.

Besides using these substituent effects for estimating the ^{13}C shifts of yet unknown carbocations, it is also possible to calculate the ^{13}C shifts of equilibrating carbocations. The calculated (uncorrected) ^{13}C NMR shifts of the equilibrating cations **14–18,** which were derived from the methyl substituents listed in Table III, are tabulated in Table VI. Since some of the substituents could not be estimated from known carbocation models, the values computed by Grant and Paul[13] for neutral alkanes were used. These values were chosen because the carbocation center is appreciably distant from the substituent. Thus, the actual value for the cation approaches those observed for the alkanes. The average ^{13}C shifts are listed in the right column of Table VI. The calculated ^{13}C shifts for the temperature independent equilibrating cations compare well with the actual observed average shifts except in the case of the *sec*-butyl cation. The large deviation for this ion will be discussed later.

The static tertiary C_5 to C_8 carbocations, which can be derived by substitution of methyl groups on the *tert*-butyl cation, represent straight chains with branching only at the carbenium center.[19] When a methyl group is substituted β from the carbenium center of static cations, it results in an equilibrating cation since the barrier is low for its rearrangement to an isomeric tertiary ion. The methyl substituent effects in Table III were determined for straight-chained alkyl groups based on their comparison to the *tert*-butyl cation, while the values for branched carbocations could not be determined since they are equilibrating systems.

It is known from two previous substituent effect studies on alkanes by Grant and Paul[13] and Lindeman and Adams[14] that corrections are needed to reproduce the ^{13}C shifts of the secondary, tertiary, and quaternary carbons of alkanes. In fact, in Lindeman and Adam's study of alkanes, these differences are not considered as corrections but as typical of that specific type of carbon, which is the basis of their empirical study.

The α-methyl substituent effect decreases in value on proceeding from a primary to a secondary to a tertiary to a quaternary carbon. When the actual and calculated values of the ^{13}C shifts of the carbenium center and the adjacent equilibrating carbon were compared between the dimethylisopropylcarbinyl cation ($(CH_3)_2CH^+C(CH_3)_2$, **15**)[7,4,20,21] and the dimethyl-*tert*-butylcarbinyl cation ($(CH_3)_3C^+C(CH_3)_2$, **16**),[7,4,22] the calculated value increased and the actual values remained relatively constant. This indicates that the value for the methyl substituent effect is too large in the calculated ^{13}C shifts in the tertiary and quaternary carbons of **15** and **16.** As in the case of the alkanes some corrections must be made for the methyl substituent effect in the tertiary and quaternary cases.

Since none of the static forms are known experimentally for the alkyl equilibrating ions,[4] estimates were chosen for the corrections. These were based on the qualitative relationship with the values for the corresponding alkanes, and they reproduce the actual values for ^{13}C shifts of the degenerate equilibrating cations **15** and **16.** These corrected values (Table VI) were used in the corrected calculations of ^{13}C NMR shifts for the alicyclic equilibrating carbocations.

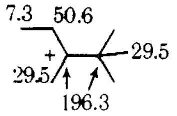
If the calculated and experimentally observed ^{13}C shifts are compared for the *tert*-amylethylmethylcarbenium ion ($(CH_3CH_2)(CH_3)_2CH^+C(CH_2CH_3)(CH_3)$, **18**), the calculated values are too low for the methylene and methyl carbon shifts and the values for the equilibrating carbenium center and the adjacent carbon are too high. The actual and corrected values for **17** and **18** show practically no difference. The methylene carbon shift is still too low, but that of the methyl adjacent to the equilibrating center is closer to the experimental value. The discrepancy for the calculated methylene carbon shift is probably due to being adjacent to a secondary and tertiary carbon center. No corrections were made for these effects since it was assumed that they would be small. Contrary to these cases the shift of the methylene carbon in the ethylmethylisopropylcarbenium ion ($(CH_3)_2CH^+C(CH_3)$-(CH_2CH_3), **19**)[7] was estimated accurately. This ion will be discussed subsequently.

The four absorptions in the ^{13}C spectra of *tert*-amyldimethylcarbenium ion (**17**)[23] correspond to the carbons shown in equilibration of **17a–d.** If the equilibration were only between **17a** and **17b,** which is exclusively methyl migration, there would be six absorptions in the ^{13}C NMR spectra. These two extra absorptions would correspond to two different equilibrating carbenium centers and two kinds of methyl groups, whereas only one equilibrating cation center and one kind of methyl are actually observed in the spectrum for this ion. Four absorptions would be observed if the equilibration were only between **17b** and **17c,** which is exclusively ethyl migration, but this was excluded by a comparison of the calculations of the equilibration between **17a–d** and **17b** and **17c.**

The ^{13}C calculation for the exclusive equilibration between **17b** and **17c** (Table VI) shows a deviation of 9.1 and 3.0 ppm between the observed and corrected values of the shifts for the methylene and methyl groups, respectively. These deviations are larger than those for the calculation of **17a–d** and indicate that both methyl and ethyl migrations are taking place rather than an exclusive methyl or ethyl migration.

Even though the stabilization for a methyl group and an ethyl group is expected to be different, the evidence from the ^{13}C spectra indicated the above equilibration (**17a–d**). Thus, the calculations of the ^{13}C shifts for **17** are based on the assumption that ethyl and methyl migrate at the same rate (Table VI). Both the calculated and corrected ^{13}C shifts reasonably reproduce the observed shifts. The largest error appears in the calculation of the methylene group. The difference between the corrected and observed shift is 4.8 ppm. Again this could be due to different substituent effects when a carbon is multiply substituted.

An alternative explanation is that the populations are such as to increase the percentage contribution of **17a** and **17d** relative to **17b** and **17c.** Cation **17a** could be thermodynamically more stable than **17b** as found in **19a** and **19b** (discussed subsequently). However, in **19** methyl and ethyl migration are much slower in comparison to hydrogen migration.[22] In **17** it is expected that methyl and ethyl stabilization would be different, but methyl and ethyl migration rates would not. An extreme example of equilibration between **17a** and **17d** excluding contributions of **17b** and **17c** in the ^{13}C NMR chemical shifts would allow equilibration through **17b** and **17c** and would show four absorptions in the ^{13}C NMR spectrum. Calculations on **17** for equilibration between **17a** and **17d** gave the following calculated ^{13}C NMR chemical shifts. The primary differences in the calculations of the equilibration between **17a** and **17d** and that of **17a–d** occur in the methylene carbon and the carbenium center. The deviation in the calculated methylene carbon is in the same direction as that actually observed. There is an observed deviation in ^{13}C NMR chemical shift of the carbenium center as calculated above by a few parts per million. A balance of the contributions of **17a** and **17b** relative to **17b** and **17c** would give a satisfactory fit of the observed ^{13}C NMR chemical shifts. Contrary to this argument one might expect that the ^{13}C NMR spectrum of **17** would be temperature dependent. However, only a slight temperature dependence is observed, where the chemical shift varies less than 1 ppm over a 40 °C temperature range.



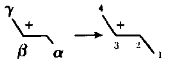
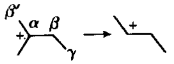
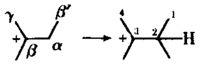
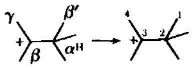
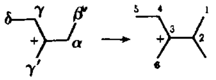
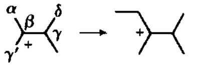
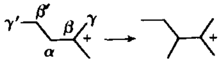
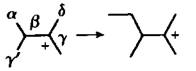
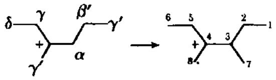
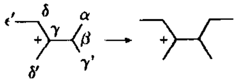
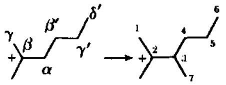
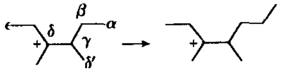
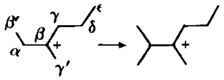
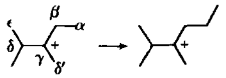
17a and **17d**

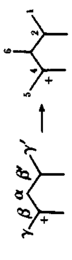
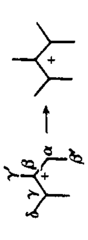
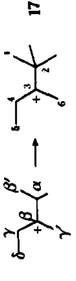
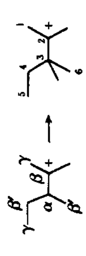
The use of methyl substituents to estimate the ^{13}C shifts of symmetrical equilibrating tertiary cations is in good agreement with the experimental values. Only minor corrections were necessary to reproduce the actual values. These corrections were applied to the other temperature independent equilibrating carbocations also and showed an improvement in the calculation of the ^{13}C shifts.

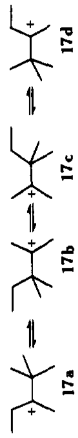
Since the method worked well with the symmetrical equilibrating cations, we considered it to be applicable also to unsymmetrical cations **19, 20,** and **21** (Table V). In the symmetrical equilibrating cations the Wagner–Meerwein rearrangements are degenerate so that the ^{13}C shifts can be calculated by averaging the absorption of the carbenium ion center and the adjacent methine carbon. The symmetrical equilibrating cations display one ^{13}C NMR absorption for the equilibrating carbenium center, while the unsymmetrical carbocations show two distinct peaks in this region. The unsymmetrical equilibrating carbocations show the average ^{13}C shift of two distinct tertiary cations, e.g., the ethylisopropylmethylcarbenium ion (**19a**) and the *sec*-butyldimethylcarbenium ion (**19b**). The ^{13}C shift of one equilibrating carbenium center results from the averaging of the carbenium center of one tertiary cation (**19a**) with the corresponding methine carbon of the tertiary carbocation (**19b**) and vice versa for the other equilibrating center.

In the case of the symmetrical equilibrating cations the Wagner–Meerwein shift produces the same cation. Thus, the ^{13}C NMR spectra are independent of temperature. The ^{13}C spectra of the unsymmetrical equilibrating cations are temperature dependent, since each Wagner–Meerwein rearrangement results in a distinct tertiary cation, which has a

Table VI. Estimation of ^{13}C Shifts for Equilibrating Alkyl Cations from Methyl Substituent Effects of Static Alkyl Cations

	1	2	3	4	5	6	7	8		$C_{1,4}$		$C_{2,3}$		
	11.8[d]	61.3	321.4	48.6						30.2 21.0		191.4 (calcd)[a] 171.6 (obsd)		
	11.8[d]	61.4	320.8	48.6						30.2		191.1 (calcd)		
	18.7[d]	67.2	336.2	41.7						30.2		201.7 (calcd)		
										32.1		197.8 (actual)		
	cor α = 2.0, β = 0.8, γ = −1.9, β′ = 12.2													
	21.5	59.4	336.2	42.7						32.1		197.8 (cor)[b]		
	28.1[d]	77.0	337.0	38.8						32.4		207.0 (calcd)		
										33.6		197.3 (actual)		
	cor α = −1.8, β = 0.8, γ = −1.9, β′ = 7.3													
	28.8	57.6	337.0	40.8										
	18.3[d]	64.3	337.2	51.6	8.1	38.9			1	2	3	4	5	6
	20.8	56.5	337.2	42.4	8.1	39.7								
	42.0	334.2	74.2	30.3[d]	10.1[d]	16.2			30.2	199.3	205.7	41.0	9.1 (calcd)	27.6
									31.9	195.5	201.0	42.9	10.6	28.4
	43.0	334.4	66.1	32.2	10.1[d]	19.0						(actual) −72 °C		
									31.9	195.5	201.6	42.4	9.1 (cor)	29.4
	10.0[d]	29.6[d]	71.4	335.5	52.1	8.3	15.2	39.1	1,6	2,5	3,4	7,8		
									9.2	40.9	203.5	27.2	(calcd)	
	10.0[d]	29.0	63.2	335.2	52.8	7.8	18.3	39.5	10.7	42.8	199.1	28.3	(actual)	
									8.9	40.9	199.2	28.9	(cor)	
	42.2	333.7	72.6	38.7[d]	20.1[d]	13.3[d]		16.5 (calcd)						
	42.7	334.0	64.5	40.6[d]	20.1[d]	13.3[d]		19.3 (cor)						
	18.5[d]	64.8	335.5	58.7	19.4	12.0		39.0 (calcd)						
	20.5	56.8	335.2	59.2	18.8	12.0		39.5 (cor)						

	19.2[d]	40.8[d]	79.9	332.9	42.9	13.7 (calcd)
	19.2[d]	43.6	72.1	332.9	43.5	13.7 (cor)
	17.2[d]	61.4	338.0	61.4	17.5	35.9 (calcd)
	20.3[d]	54.5	337.8	54.6	20.0	37.8 (cor)
 17a	27.4[d]	74.1	338.0	48.7	7.3	35.9 (calcd)
	28.1	54.7	337.8	50.6	7.3	37.8 (cor)
 17b	39.1[d]	335.0	84.0	39.7[d]	7.6[d]	25.6 (calcd)
	41.1	335.2	64.3	39.5	7.6[d]	26.1 (cor)



17a ⇌ 17b ⇌ 17c ⇌ 17d

1[c]	2	3	4	5	6
31.4	208.4	208.4	42.7	7.5	31.4 (calcd)
32.6	198.6	198.6	43.2	7.5	32.6 (cor)

17b ⇌ 17c

1,6	2,3	4	5	
32.4	209.5	39.7	7.6	(calcd)
33.6	199.8	39.5	7.6	(cor)

---

[a] The appropriate methyl substituent values in Table III were used to calculate the ^{13}C shifts for the static carbenium ions. [b] The corrected methyl substituent values determined for 15 and 16 were used throughout the remaining calculations to estimate the corrected ^{13}C shifts. [c] The average ^{13}C shifts for 17a–d assume equal migration of ethyl and methyl groups. [d] The substituent effects for alkanes were used for the estimations of these shifts, because they cannot be determined from the static alkyl cations.

different thermodynamic stability (**19a** and **19b**). This difference in stability results in unequal populations of the two carbocations in the equilibrating system. As the temperature is changed, the thermodynamically controlled equilibrium changes, which results in an alternation of the populations. The new populations of the equilibrating cations account for the change in the ^{13}C spectra with temperature.

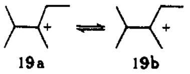
The application of methyl substituent effects to unsymmetrical equilibrating carbocations can be demonstrated generally in the following way. The ^{13}C shifts of the two static cations, which equilibrate, were calculated using the methyl substituent effects in Table III and the corrected methyl substituent effect in Table VI. Since the averaging method will only produce the ^{13}C shifts for an equal contribution from each cation and worked well for the symmetrical equilibrating cations, especially for the equilibrating carbenium centers, the experimental ^{13}C shifts were used in comparison with the calculated values, including the corrected one, to determine the numerical contribution of each cation in equilibrium. The method of simultaneous equations was used to determine the percentage of each cation, e.g., **19a** and **19b**. Then the percentages of ions were used to calculate the remaining ^{13}C shifts. As seen in Table VII the trends approximate well the observed shifts in Table V, supporting the assignments of the central carbons in the unsymmetrical equilibrating carbocations.

The percentages of ion compositions can be used to determine the equilibrium constants for the unsymmetrical equilibrating carbocations. Thus, the small energy differences can be estimated between the two different tertiary cations. The ΔS is expected to be important in these systems. Using the thermodynamic relationship $\Delta G = \Delta H - T\Delta S$, the values for ΔH, ΔS, and ΔG were calculated from the plot of the natural logarithm of the two tertiary cations equilibrium constant vs. the corresponding inverse temperature. All plots gave high correlation constants indicating no deviation from a straight line. The slope of the lines and the Y intercept were interpreted to be ΔH and ΔS, respectively. The values of ΔG can be determined from either ΔH or ΔS or from the equilibrium constant. The former method was chosen and values for all the calculated thermodynamic properties are summarized in Table VIII.

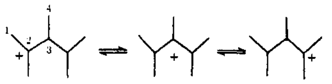
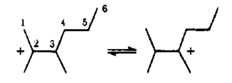
These results directly reflect the stability of the substituents on a carbenium center. In the nondegenerate equilibrating carbocation **19** it appears superficially to represent methyl vs. ethyl stabilization, whereas **19a** is really stabilized by a methyl, ethyl, and isopropyl group and **19b** by two methyls and a *sec*-butyl group. From the temperature dependent data of this carbocation it can be concluded that with decreasing temperature an ethyl and an isopropyl group are better at stabilizing a positive charge than a methyl and a *sec*-butyl group. By analyzing other temperature dependent equilibrating carbocations in the same manner, it would be possible to set up a quantitative thermodynamic scale and to define the stability of groups vs. one another in solution. Presently, there are insufficient examples known to determine an unequivocal quantitative order, but it is possible to set up a qualitative order from our data.

The order of alkyl substituents on the stabilities between equilibrating carbocations **19** and **21** appears to be in the opposite direction. This seeming discrepancy can be rationalized using the thermodynamic values from Table VIII and the preceding discussion. By taking the differences between the corrected thermodynamic properties of **19** and **21** a ΔH of -616 cal/mol and a ΔS of -1.74 cal/mol K can be estimated for the unknown equilibrating cation **22.** The differences predict that ion **22b** is thermodynamically more stable than **22a** as the temperature decreases. Thus an ethyl and a 2-pentyl group are better stabilizing substituents of a carbenium center than a propyl and a *sec*-butyl group.

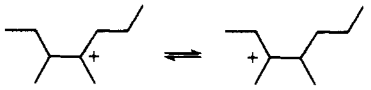
Table VII. Estimation of ^{13}C NMR Shifts of Temperature-Dependent Equilibrating Cations



19a **19b**

°C	1[a]	2	3	4	5	6		
−129	27.9	176.3	221.3	41.8	8.8	28.7		calcd
−120	28.3	180.6	216.7	41.4	8.8	28.3		
−110	28.6	184.3	212.7	41.1	8.7	28.0		
−98	29.0	188.8	207.9	40.6	8.9	27.5		
−90	29.2	191.5	205.2	40.4	8.9	27.3		
−81	29.4	193.7	203.2	40.3	8.9	27.1		
−74	29.5	195.5	201.0	40.1	9.0	27.0		
−62	29.7	197.1	199.4	40.0	8.9	26.8		
−51	29.8	198.7	197.8	39.8	9.0	26.6		
−129	30.3	175.4	221.1	43.8	8.9	30.8		cor
−120	30.7	180.5	216.5	43.5	9.0	30.5		
−110	31.0	184.1	212.6	43.2	9.0	30.2		
−98	31.4	188.8	208.1	42.8	9.0	29.8		
−90	31.6	191.5	205.3	42.6	9.1	29.6		
−81	31.7	193.8	203.2	42.5	9.1	29.5		
−74	31.9	195.6	201.5	42.2	9.1	29.3		
−62	32.0	197.0	199.2	42.1	9.1	29.1		
−51	32.1	198.7	197.9	42.1	9.1	29.0		
 **20a** **20b** **20c**								
−123	29.5	174.6	97.5	15.0	calcd			
−116	29.3	173.4	100.4	15.2				
−107	29.2	171.2	104.4	15.8				
−101	29.0	169.9	106.3	15.9				
−92	28.8	168.6	108.9	16.0				
−85	28.7	166.8	112.3	16.3				
−123	30.1	174.5	97.6	16.1	cor			
−116	30.1	173.4	100.3	16.2				
−107	29.9	171.2	104.2	16.6				
−101	29.7	169.8	106.1	16.7				
−92	29.6	168.8	108.8	17.1				
−85	29.6	167.3	112.1	17.3				
 **21a** **21b**								
−119	34.7	252.8	140.5	42.9	19.4	12.6	22.0	calcd
−112	34.5	250.2	143.1	43.1	19.4	12.6	22.3	
−104	34.3	248.0	145.2	43.3	19.3	12.6	22.5	
−97	34.0	245.3	147.8	43.5	19.3	12.5	22.7	
−85	33.7	241.6	151.5	43.8	19.3	12.5	23.0	
−79	33.6	239.9	152.8	43.9	19.3	12.6	23.1	
−72	33.3	237.7	154.9	44.0	19.3	12.5	23.2	
−65	33.2	235.6	157.3	44.2	19.3	12.5	23.5	
−119	36.1	252.9	140.6	45.6	19.6	12.8	24.9	cor
−112	35.8	250.0	143.0	45.7	19.5	12.8	25.0	
−104	35.7	247.8	145.2	45.9	19.5	12.8	25.2	
−97	35.5	245.1	147.8	46.0	19.5	12.8	25.3	
−85	35.1	241.4	151.4	46.2	19.5	12.8	25.7	
−79	35.0	239.7	152.6	46.3	19.5	12.7	25.8	
−72	34.9	237.9	154.8	46.5	19.5	12.7	25.9	
−65	34.7	235.7	157.3	46.7	19.5	12.7	26.1	

[a] The experimental ^{13}C shifts of C_2 and C_3 for **19**, 20, and **21** in Table V are used to estimate the relative amounts for each of the equilibrating isomers. The relative amounts were used to calculate the ^{13}C shift in this table. Therefore, the values for C_2 and C_3 are the same in the experimental and estimated, while the remaining carbon's shifts depend on the relative amounts. The latter values are comparable with the experimental ones.



22a **22b**

Using the preceding examples and the data from the diisopropylmethylcarbenium ion (**20b**), the relative order of stability for some simple alkyl groups can be determined qualitatively in the following way. Since the stabilization by isopropyl, *sec*-butyl, 3-methyl-2-butyl, and 2-pentyl groups is approximately the same, they were equated. Thus an ethyl group is a better stabilizer than a methyl group in **19**, and a methyl is better than an isopropyl in **20** and a propyl in **21**. The order of alkyl substituents which stabilize a carbenium center is ethyl > methyl > propyl and isopropyl. Again it is noted that the order is not the one expected from solution chemistry.[24]

Considering gaseous ions[25] and their studies by theoretical quantum mechanical calculations,[26] the order of stabilities for substituents attached to carbenium centers is isopropyl > ethyl > methyl. This is attributed to a better inductive stabilizing ability of the substituents. In ordinary solution chemistry the order is reversed and it is expected that a methyl is a better stabilizing group than an ethyl. This reversal has been originally attributed to the so-called Baker-Nathan effect,[27] on the basis of different stability due to hyperconjugation effects. Recently, it has been shown that the Baker-Nathan order results basically as a consequence of decreasing solvation ability with increasing steric requirement of an alkyl group, i.e., CH_3 > CH_3CH_2 > $(CH_3)_2CH$ > $(CH_3)_3C$.[28,29] Our results are contrary to both of these sequences. They can be considered to be intermediate between the gas-phase and regular solution behavior. Solvent SO_2ClF used in our solution work has a low nucleophilicity and therefore is not strongly interacting with the carbocations. Thus, the carbocations in SO_2ClF solutions approach gas-phase behavior and reflect little stabilization due to nucleophilic solvation.

Of course our assumption that the stability differences of the isopropyl, *sec*-butyl, 3-methyl-2-butyl, and 2-pentyl groups are equivalent might not be strictly true as pointed out in the discussion of **19** and **21**. A slightly different stability could be caused by these groups, which affects the above qualitative order or stability.

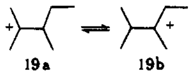
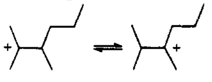
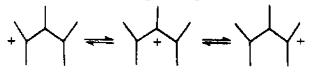
Methyl substituent effects, as shown, are quite effective in calculating individual carbon shifts for the various carbocations and these calculated shifts can be used to estimate the ^{13}C shifts of symmetrical and unsymmetrical equilibrating carbocations. Additionally, in the unsymmetrical equilibrating carbocations the equilibrium constants can be computed from the ^{13}C shifts. From the equilibrium constant the thermodynamic values ΔH, ΔS, and ΔG can be determined for the difference between the equilibrating carbocations.

The calculated ^{13}C shifts of the equilibrating cation are the averaged shifts of a trivalent tertiary carbenium center with its corresponding methine or quaternary carbon. Since the averaging method works well for analyzing the equilibrating cations **15**–**21**, these cations can be considered as typical classical carbenium ions. As the tertiary to tertiary carbenium ion rearrangements can be well accounted for by the use of methyl substituent effects, they can also be applied to secondary to secondary carbenium ion rearrangements.

There is, so far, only one static aliphatic secondary carbenium ion known, the isopropyl cation.[4] Other secondary cations obtainable under stable ion conditions are stabilized by relatively rich electron substituents, which can delocalize the charge significantly away from the carbenium ion center. Therefore, these carbocations cannot be used in our study as typical secondary carbenium ions, because of the presence of strong electron-delocalizing groups. Since the isopropyl and *tert*-butyl cations are static, they can represent the methyl substituent effect for a classical secondary carbocation to the related classical tertiary carbocation.

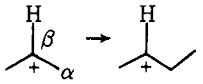
There are two ways to estimate the ^{13}C shifts of the *sec*-butyl cation from methyl substituents. The first involves substituting

Table VIII. Comparison of Thermodynamic Properties of Temperature-Dependent Equilibrating Alkyl Cations

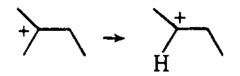
ΔH, cal/mol[a]	ΔS, cal/mol K[a]	r^2 [a]	ΔG, cal/mol[b]	Temp, °C	Rel amounts 19a	 19b	ΔG, cal/mol[c]
			 19a 19b				
−293 ± 9[d]	−1.45 ± 0.05[d]	0.993 (calcd)	−84 ± 8[e]	−129	0.419	0.564	−85 ± 4[f]
			+29 ± 3	−51	0.503	0.476	24 ± 3
			+139 ± 12	25			
−280 ± 10	−1.39 ± 0.05	0.993 (cor)					
			−80 ± 7	−129	0.428	0.572	−83 ± 4
			+29 ± 3	−51	0.512	0.487	+27 ± 3
			+134 ± 12	25			
			 21a 21b				
+360 ± 8	+0.40 ± 0.04	0.997 (calcd)			21a	21b	
			+299 ± 42	−119	0.706	0.266	+298 ± 22
			+277 ± 39	−65	0.642	0.330	+274 ± 20
			+241 ± 34	25			
+336 ± 8	+0.35 ± 0.04	0.997 (cor)					
			+282 ± 44	−119	0.709	0.283	+280 ± 21
			+263 ± 41	−65	0.647	0.345	+259 ± 19
			+232 ± 36	25			
			 20a 20b 20c				
					20a + 20c	20b	
+939 ± 35	1.28 ± 0.21	0.994 (calcd)	+747 ± 191	−123	0.910	0.073	+749 ± 166
			+698 ± 149	−85	0.850	0.131	+696 ± 73
			+557 ± 116	25			
+751 ± 27	0.59 ± 0.16	0.994 (cor)					
			+663 ± 217	−123	0.898	0.097	+661 ± 104
			+640 ± 206	−85	0.843	0.152	+638 ± 63
			+575 ± 182	25			

[a] These values were determined from the calculated (corrected) K_{eq} values with the corresponding inverse temperature using a linear least-square regression program (HP-65 calculator). [b] These ΔG values were determined from $\Delta G = \Delta H - T\Delta S$. [c] These ΔG values were determined from $\Delta G = -RT \ln K$. [d] Standard calculated error of method. [e] Sum of standard error using $\Delta G = \Delta H - T\Delta S$; the deviation in K was estimated to be ±3 K. [f] Sum of standard error using $\Delta G = -RT \ln K$ for individual measurements; the deviation in K was estimated to be ±3 K and the deviation in K_{eq} was the difference between (calcd) and (cor) K_{eq} values.

a methyl group β from the carbenium center in the isopropyl cation



and using the appropriate substituent effects in Table III (Table IV) to estimate the ^{13}C shifts. The second involves removing a methyl group adjacent from the carbenium center in the *tert*-amyl cation.



It can be seen that both estimations in Table VI result in the same ^{13}C shifts for the static and equilibrating *sec*-butyl cation. But a comparison of the experimental and calculated values show deviations of 9.2 and 19.8 ppm per carbon for the methyls and the equilibrating carbocation centers, respectively.

The experimental NMR shifts are shielded as compared to the above estimated shifts. There is no precedent for the use of corrections in the calculated shifts for the *sec*-butyl cation, since in the first estimate (Table VI) the isopropyl cation to *sec*-butyl cation's transformation involved a straight chain and in the second one the *tert*-amyl to *sec*-butyl cation's transformation used the methyl substituent values between the isopropyl cation and *tert*-butyl cation.

The fact that both estimations produce the same ^{13}C shifts indicates some reliability of the method. The deviation from additivity in the case of *sec*-butyl cation cannot be accounted for by the estimated values from the methyl substituent effects.

It is apparent that the averaging of the estimated ^{13}C shifts for the *sec*-butyl cation cannot alone explain the observed ^{13}C shifts. They do not exclude equilibration between **14a** and **14b**, but only indicate that some additional effect may be causing the discrepancy. Two possible reasons are either that β C–C hyperconjugation participates much more strongly than C–H hyperconjugation or the hydrogen bridged intermediate is involved in the equilibration. It is not possible to distinguish between these two suggestions by the methyl substituent effect method, since there are no stable model alkyl cations available, which can be suitably applied in these cases for estimating the ^{13}C shifts.

It has been shown by MO calculations that C–C hyperconjugation is more effective than C–H hyperconjugation in substituted ethyl cations.[26] But they also showed that the substituent effects observed in the primary cations were only slightly diminished in the cases of secondary and tertiary cations. On this basis, the methyl substituent effect studies in tertiary cations should be also applicable to secondary carbocations, since the C–C hyperconjugation should be about the same in both cases. Thus C–C hyperconjugation should not be primarily responsible for the differences in the calculated and observed ^{13}C NMR shifts in the *sec*-butyl cation.

The NMR results exclude a static hydrogen bridged intermediate. The static hydrogen bridged *sec*-butyl cation would show two absorptions in the proton decoupled ^{13}C experiment, but the fully coupled spectra are expected to show a doublet

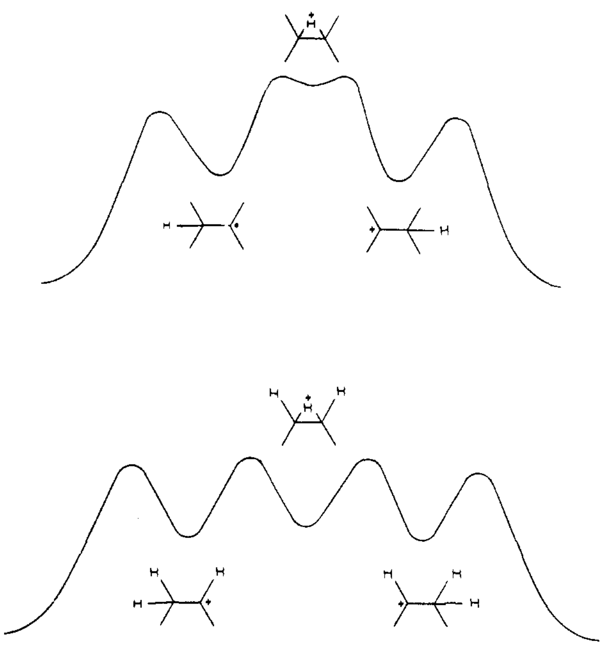


Figure 1. Energy profiles of the equilibrating carbocations, dimethylisopropyl and *sec*-butyl cations.

of doublets and quartet for the hydrogen bridged carbons and the methyl carbons, respectively. This is not consistent with the two quartets experimentally observed for both absorptions, but it can be consistent with a rapidly equilibrating system involving bridged species. If the three hydrogen attached to central carbons of the hydrogen bridged *sec*-butyl cations were exchanging rapidly on the NMR time scale, the fully coupled ^{13}C spectra would show a quartet for these central carbons as well as a quartet for the methyl groups.

There is no way to accurately estimate the ^{13}C shifts of an equilibrating, hydrogen bridged *sec*-butyl cation. It is expected, however, that they should be more shielded than the experimentally observed values, if they are comparable to the ^{13}C NMR shifts in bridged ethylene halonium ions, used as rough models.[30] Thus, the equilibrating hydrogen bridged *sec*-butyl cation does not fit the observed ^{13}C NMR data.

If the hydrogen bridged *sec*-butyl cation's thermodynamic stability is similar to that of the two degenerate open chain secondary carbocations, both intermediates would contribute to average ^{13}C NMR shifts. The ^{13}C NMR shifts and the coupled spectra are compatible with this assumption, but the percentage of contributors cannot be calculated, owing to lack of accurate models, to estimate the ^{13}C NMR shifts of the hydrogen bridged *sec*-butyl cation. The deviations from calculated and experimental ^{13}C NMR shifts, however, indicate that the *sec*-butyl cation is best represented as equilibrating between the intermediates **14a, 14b,** and **14c** (Figure 1), whereas in the dimethylisopropylcarbenium ion (**15**), the hydrogen bridged intermediate contributes very little or none to the ^{13}C shifts and is best represented as an tertiary–tertiary equilibrating carbocation.

Attempts to prepare the ethyl cation from ethyl fluoride with SbF_5 in SO_2ClF or SO_2F_2 resulted in the formation of *tert*-butyl and *tert*-hexyl cations, rather than a long-lived ethyl cation. The formation of the latter cations can be attributed to the deprotonation of the intermediately formed ethyl cation to ethylene. An excess of the ethyl cation ethylates ethylene to account for the observed tertiary carbocations.

By analogy from **15** to **14** to the ethyl cation and its discussed behavior, it is reasonable to assume that in the ethyl cation too there is a significant contribution from the hydrogen bridged form, accounting for the low barrier for deprotonation. Ab initio calculations of the ethyl cation support this conclusion. The hydrogen bridged form differs by 1–2 kcal from the open chain classical ethyl cation structure.[32]

From the consideration of estimated methyl substituent effects and comparison with experimentally found data it is possible to demonstrate that the equilibrating cations, which undergo methyl or hydrogen migration from a tertiary to tertiary carbenium center, can be represented best as classical carbenium ions with the two-electron three-center bonded bridged nonclassical ion as a higher lying metastable state, which does not contribute to the ^{13}C NMR shifts. The migrations from a secondary to secondary and a primary to primary carbenium center, however, proceed from classical through nonclassical bridged carbocation intermediates. Bridged nonclassical ions cannot be described by using two-electron two-center Lewis bonds, but involve a two-electron three-center bonded structures, with the empty orbital of a carbenium center overlapping with the electron pair of the interacting bond.

Study of the Mechanism of Rearrangement of Some Carbocations. In our present study attempts to prepare pure isomeric ions undergoing equilibration resulted frequently, even at very low temperatures, in equilibration with isomeric carbocations themselves undergoing equilibration or in rearrangement to their more stable isomeric ions as the temperature was raised. Since these rearrangements involved equilibrating cations and were not the main interest of our study no equilibrium constants were measured for the mixtures. The rearrangement temperature, at which the new carbocations are formed, was limited to the temperature range of the ^{13}C measurements for the equilibrating carbocations. Generally, these rearrangements can be best explained as proceeding through protonated cyclopropanes and secondary carbocations. Before their discussion, a brief summary of the energies of hydrogen and alkyl bridged carbocations with relation to their corresponding open-chain tertiary, secondary, and primary alkly cations is necessary and will aid in deciding the most probable mechanism for these rearrangements.

Based on Saunders' discussion of protonated cyclopropanes,[33] the energies can be estimated for several bridged intermediates. Figure 2 shows these structures together with their open-chain alkylcarbenium ions and their thermodynamically more stable isomers. The upper and lower limits for the activation energies of the dimethylisopropylcarbenium ion (**15**) were estimated on the basis that the barrier for the degenerate 1,2-hydrogen and methyl migration, respectively. In these open-chain cations they could not be measured directly by using NMR methods, as these processes are not "frozen" out even at the lowest temperatures (∼−160 °C).

In Saunders' work on the *tert*-amyl cation, the scrambling of the methyl groups was found to have an activation barrier of 15.3 kcal/mol. The mechanism proposed for this rearrangement involves the formation of a secondary cation followed by methyl migration through the methyl bridged intermediate (three-corner protonated 1,2-dimethylcyclopropane, **23**). A second process with an activation energy of 3.5 kcal/mol, which is 18.8 kcal/mol higher in energy than the static *tert*-amyl cation,[34,35] interchanges the methylene hydrogens with the methyl's hydrogens. The mechanism needed to explain this observation involves the formation of the methyl bridged intermediate (two-corner protonated 1,1-dimethylcyclopropane **25**) from the *tert*-amyl cation, followed by corner to edge to corner proton migration and ring opening to the *tert*-amyl cation, which would interchange the hydrogens of the ethyl group in the tertiary carbocation. This mechanism coupled with the methyl migration explains the hydrogen scrambling throughout the entire cation. From these considerations (Figure 2) the methylisopropylcarbenium ion **24** and two-corner protonated 1,2-dimethylcyclopropane **23** are more stable than the two-corner protonated 1,1-dimethylcyclopro-

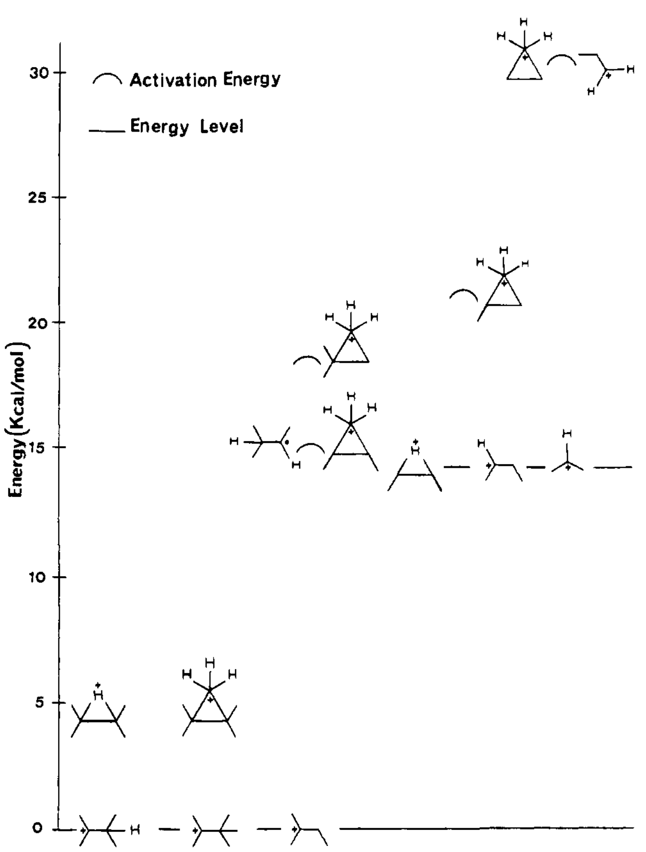
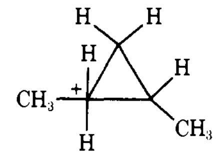


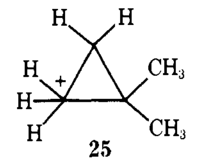
Figure 2. Schematic representation of the relative stabilities of carbocations.



23


$(CH_3)_2CH\overset{+}{C}H(CH_3)$

24



25

pane 25.

Methylpropylisopropyl- (21), Diethylisopropyl- (26), and 2-Butylethylmethylcarbenium (18) Ions. Attempts to prepare 26 ($(CH_3)_2CH^+C(CH_2CH_3)_2$) from its corresponding tertiary chloride precursor in $SbF_5/SO_2ClF/SO_2F_2$ at −130 °C resulted in the exclusive formation of 21 ($(CH_3)_2CH^+C(CH_3)(CH_2CH_2CH_3)$). After the solution is allowed to rise to −100 °C the formation of a small amount of ion 18 ($(CH_3)_2(CH_2CH_3)CH^+C(CH_3)(CH_2CH_3)$) is observed. When the chloride of 18 is ionized under similar conditions a mixture of both 18 and 21 is formed with larger amount of 18 present at −110 °C. None of 26 is ever observed in the solutions. It appears that 18, 26, and 21 are in equilibrium and 26 is less stable by more than 1 kcal than 18 and 21; thus 26 is not observed in the ^{13}C spectrum.

A reasonable mechanism for these rearrangements is shown in Figure 3 with the corresponding approximate energy profile. The equilibrating cation 21 ring closes to the 3-protonated 3-ethyl-1,1,2-trimethylcyclopropane 21c. This carbonium ion

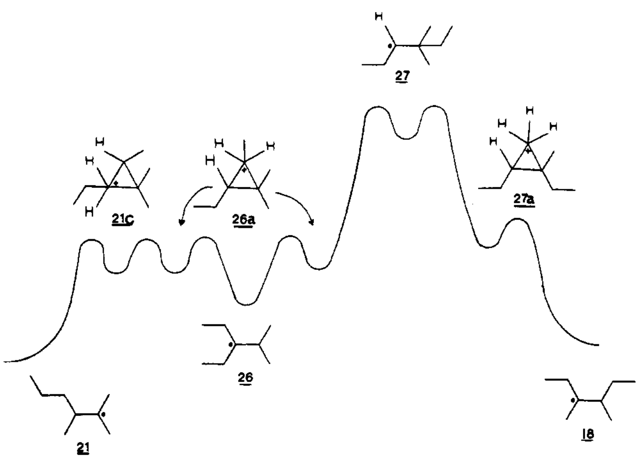
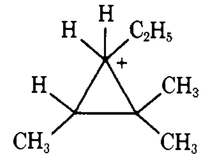
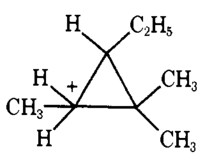


Figure 3. Reaction coordinate profile of the proposed intermediates in the equilibrium of 21, 26, and 18.

25



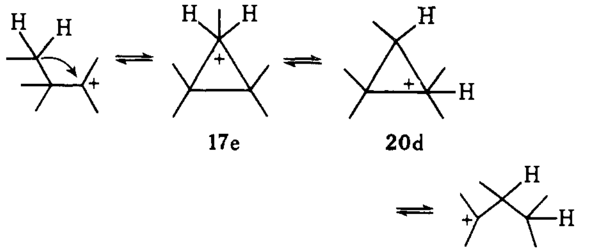
21c



26a

can rearrange by hydrogen migration to the isomeric 2-protonated 3-ethyl-1,1,2-trimethylcyclopropane 26a, which can ring open to 26. According to the energy diagram in Figure 2 the activation energies to form 26a and 21c are about 7–10 kcal above those of the tertiary cations. Since the formation of 18 takes place only at higher temperature, the barrier for its formation must be higher than that involved in rearrangement to 21 and 26. The rearrangement of 26 or 26a to 18 involves the formation of a secondary cation 27 followed by methyl migration through 27a to 18. An analogous mechanism was used by Saunders to explain the methyl migrations in the deuteriomethyl derivatives of the dimethylisopropylcarbenium ion (15).

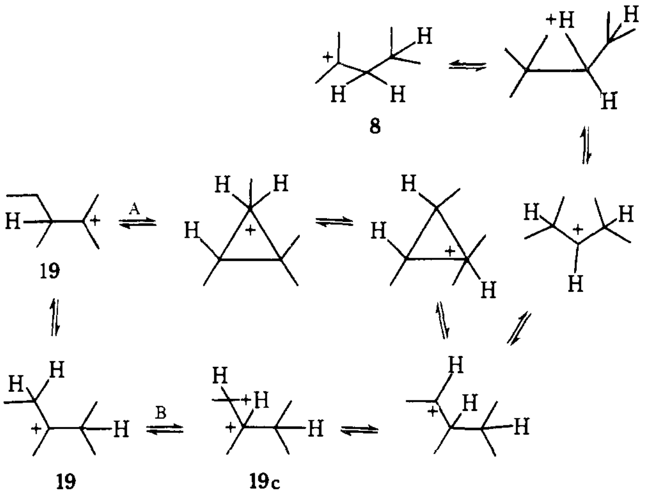
The Dimethyl-2-methyl-2-butyl- (17) and Diisopropylmethylcarbenium (20) Ions. Ionization of the corresponding tertiary chloride of either 17 or 20 at −130 °C resulted in an equilibrium mixture of the two carbocations. Since the barrier is again low, a mechanism involving protonated cyclopropanes is most probable. This process through 17e should have a low



(1)

activation barrier, similar to the case of *tert*-butyldimethylcarbenium ion (16) and 20d is expected to be less stable than 17e by a few kilocalories. The barrier between 17e and 20d should be between 5 and 10 kcal for corner to corner proton migration, which is less than the corresponding secondary cation.

The Ethylisopropylmethyl- (19) and Isobutyldimethylcarbenium (8) Ion. The equilibration between **19** and **8** has been observed by Saunders[37] in studying ion **8** ($(CH_3)_2CHCH_2{}^+C(CH_3)_2$),[36] where the formation of **19** ($(CH_3)(CH_3CH_2)CH^+C(CH_3)_2$) was regarded as an impurity. In our temperature dependent ^{13}C NMR study of **19** and **8** we found that these ions equilibrate at about −80 °C with **19** predominating in the equilibrium mixture. Two mechanisms are consistent with these observations. One (path A) proceeds through protonated cyclopropane, followed by ring opening to a secondary cation ($CH_3{}^+CHCH(CH_3)CH(CH_3)_2$, **19c**), which is a common intermediate in both mechanisms. The secondary cation undergoes a hydrogen shift to **8**. The other way (path B) proceeds through a direct hydrogen transfer to the identical secondary cation (**19c**) and from here the same mechanism is followed to **8** as above.



Energetically, the C–C and C–H bond delocalization (path A or B) can be similar in this system and there is no possibility of differentiating between them. In fact, both paths could be involved in the rearrangement.

From the above observations it is reasonable to propose protonated cyclopropanes as intermediates in the rearrangements, i.e., *β* C–C bond delocalization via a bridged, pentacoordinated carbonium ion, but this is not always the case. For example, in the C_7 alkyl cation series, the triethylcarbenium ion (**9**) was prepared from its corresponding tertiary chloride precursor at −100 °C. When the temperature was raised to −80 °C, two other cations, the dimethylbutyl- (**6**) and the ethylmethylpropyl- (**7**) carbenium ion, dominate the spectra, with only a small amount of the triethylcarbenium ion observable. No other isomeric C_7 carbenium ions are formed at −80 °C. The most reasonable mechanism to explain the formation of **6** and **7** involves the exclusive intermediacy of secondary cations. If protonated cyclopropanes were involved, additional isomers would also be found in the mixture.

Conclusions

Our studies showed that ^{13}C NMR methyl substituent effects can be applied in a systematic way to alkyl cations. Since they were found to be constant and additive, they can be successfully used to estimate the ^{13}C shifts of static alkyl cations, as well as symmetrical or unsymmetrical equilibrating carbocations. From the study of substituent effects it was possible to demonstrate that equilibrating aliphatic tertiary–tertiary carbocations show little or no contribution to the hydrogen or methyl bridged structures. Thus they are best represented as equilibrating tertiary carbenium ions. From the experimental data it was possible to calculate ΔG, ΔH, and ΔS for the difference between the tertiary carbenium ions of the unsymmetrical equilibrating carbocation systems. The application of these methods to secondary-secondary equilibrating carbocations, such as the *sec*-butyl cation, showed significant deviations of the estimated from the experimental values. A comparison of the experimental and calculated ^{13}C shifts of the secondary alkyl cations indicates the contribution of partial hydrogen bridging of the *sec*-butyl cation. The application of the empirical additivity technique has significant use in estimating ^{13}C NMR shifts and determination of the structural nature of the carbocation.

From the structural identification of the carbocations formed in the studied systems it was possible to suggest the most realistic mechanistic paths from the initially observed carbocation(s) to the subsequently found rearranged ion(s). These paths are based on the energy difference of the various carbocations. Owing to stabilization by the neighboring methyl groups, the order of stabilities for the open-chain carbocations is tertiary > secondary > primary and the order of stabilities for the bridged carbonium ions also increases with the number of stabilizing methyl groups. Depending on their thermodynamic stability, a bridged nonclassical carbonium ion can be more stable than the corresponding open-chain classical carbenium ions (Figure 3). The observable intermediates could be examined for their relative stability and a mechanistic path could be chosen to proceed through the lowest lying intermediate(s).

Alkyl cations are of fundamental significance as reaction intermediates of electrophilic chemical and biological alkylations. The latter are of increased importance since the realization of the possible action mechanism of certain chemical carcinogens through electrophilic alkylation of nucleic acids.[38] Regardless of whether real alkyl cations can be involved in such processes, which is most improbable in systems which would give rise to primary cations (such as *N*,*N*-dimethylnitrosamine[39]), a better knowledge of the de facto alkyl cations and their formation mechanism, as well as of possible alternative pathways leading to reactive alkylating agents,[39] is of great interest. We are continuing our in vitro studies in these directions.

Experimental Section

Starting Materials. Isopropyl, *tert*-butyl, *sec*-butyl, and *tert*-amyl chlorides were commercially available and the highest purity of the alcohol precursors **4–21** was used. The alkyl alcohols were converted to the alkyl chlorides by concentrated hydrogen chloride at 0 °C and worked up and purified by standard methods. It was found that some of the tertiary alkyl chlorides started to decompose after a few days. This is probably due to the autocatalytic effect of hydrogen chloride. Consequently, these alkyl chlorides were freshly prepared and used within a day to avoid decomposition. No rearrangements were observed in the formation from precursor alkyl chlorides of cations 4–13 and they were ionized to the expected alkyl cations.

As in the case of equilibrating cations **17–21**, proton, methyl, or ethyl migration is possible; the same equilibrating carbocation would form despite any possible rearrangements of the precursors and these chlorides were not purified specifically to avoid isomers. In fact, it has been demonstrated from carbon labeling and product identification studies that some rearrangements do take place under similar or the same conditions as used in the conversion of the precursor alcohol to chloride. However, there is no evidence for chain lengthening or shortening in the conversion of any tertiary alcohols to chlorides, as shown in the case of alcohols of **21**, **28**, and **18**. The ^{13}C NMR of the alcohols and chlorides for each isomer displayed similar spectra indicating no carbon backbone rearrangement. Thus, there is no evidence for prior rearrangement of the alkyl chloride before ionization by antimony pentafluoride.

The chlorides were used in preference to the corresponding alcohols in carbocation formation, as they have distinct advantages. The chlorides are soluble in SO_2ClF at low temperature (−80 °C), whereas the alcohols tend to crystallize out of solution at this temperature. Thus, the solution of alcohols must be warmed until the alcohols dissolve in the solution. The higher temperatures needed for dissolving alcohols has caused some decomposition and rearrangements, which is probably due to local heating. These problems have been eliminated by the use of the alkyl chlorides.

Preparation of Alkyl Cations. The carbocations **1–3** were prepared at −78 °C (dry ice/acetone bath). The chlorides of **1–3** (~0.5 g) were dissolved in SO_2ClF (~1.0 g) and these solutions were carefully added to a well-stirred solution of SbF_5 (~2.5 g)/SO_2ClF (~4.0 g) at the same temperature. The alkyl chloride to antimony pentafluoride ratio was kept at 1:4, respectively. The ratio of alkyl chloride to sulfuryl chloride fluoride was between 1:20 and 1:30. The prepared solutions were either colorless or slightly yellow. All solutions were homogeneous with no precipitated solids.

The same method was also used for the preparation of **14** from its chloride and **15** and **16** from their alcohols. Cation **14** was cooled in a liquid N_2/ethanol bath after its formation, since it slowly rearranges to the *tert*-butyl cation at −80 °C. When the chlorides and alcohols of **4–13** and **17–21** were ionized by antimony pentafluoride using the above method (−80 °C), besides forming the corresponding alkyl cation, a mixture of isomeric carbocations was also observed.

It was found that lowering the temperature for preparation of the ions to about −130 to −135 °C in a liquid N_2/ethanol slush bath and adding SO_2F_2 (~1.5 g) to the SbF_5/SO_2ClF solution to reduce the viscosity of the solution resulted in the formation of only the corresponding parent carbocation from the chloride precursor of **19**, **21**, and **4–13.** The same technique as for preparing cations at −80 °C was used at −130 °C except that the $SbF_5/SO_2ClF/SO_2F_2$ solution was cooled to −130 °C. Only in the case of **17**, **18–20**, and **27** were any rearrangements observed (see Discussion).

Carbon-13 nuclear magnetic resonance spectroscopic studies were performed on a Varian XL-100-15 NMR spectrometer equipped with proton decoupling, a variable temperature unit, and a 620i computer with 16K data points. The instrument was operated in the Fourier transform pulse mode with either proton decoupling or the gyrogate experiment (gives fully coupled spectra with some nuclear Overhauser effect). The pulse width (H_1 field) in typical experiments was 2–15 μs, where a 42-μs pulse is equivalent to a 90° pulse. Acquisition times were between 0.3 and 0.8 s with pulse delays of 0–9 s depending on the experiment. The total number of transients for suitable S/N for each absorption varied from 100 to 7000 passes. The radiofrequency was 25.16 MHz with the absorption referenced from external Me_4Si in CCl_3F.

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$$CH_3CH_2^+ \xrightarrow{CH_4} CH_3\overset{+}{C}H\mathit{CH_3} \qquad \alpha^+ + \beta = 53.6 \tag{1}$$

$$(CH_3)_2CH^+ \xrightarrow{CH_4} (CH_3)_2\overset{+}{C}\mathit{CH_3} \qquad \alpha^+ + 2\beta = 49.6 \tag{2}$$

$$\beta = -4.0,\ \alpha^+ = 57.6$$

From the above equation (1) the effect of the ethyl cation (a carbenium center α^+ and a methyl group β) forming the isopropyl cation on methane's ^{13}C shift can be calculated. A similar equation (2) can be set up for the isopropyl cation forming the *tert*-butyl cation. From these results it can be shown that the carbenium center produces a 57.6-ppm deshielding on the adjacent methyl group.

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