

Stable Carbonium Ions. LXXIII.¹

3-Aryl-2,3-dimethyl-2-butyl Cations and Factors Controlling Phenonium Ion-Phenethyl Cation-Benzyl Cation Equilibria

George A. Olah, Melvin B. Comisarow,² and C. J. Kim^{3,4}

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received June 20, 1968

Abstract: Ionization either of 3-*p*-X-phenyl-2,3-dimethyl-2-butyl chloride (1) or *p*-X-phenyl-*t*-butylmethylcarbonyl chloride (2) (X = H, CH₃, OCH₃, or CF₃) yields the same thermodynamically most stable carbonium ion(s). For X = H, the tetramethylethylenphenonium ion (3-H) is the most stable ion. For X = CH₃, the tetramethylethylene-*p*-toluonium ion (3-CH₃) and the *p*-tolylmethyl-*t*-butylcarbonium ion (7-CH₃) have comparable stability. For X = OCH₃, the *p*-anisyl-*t*-butylmethylcarbonium ion (7-OCH₃) is the most stable, and for X = CF₃, the 3-*p*-trifluoromethylphenyl-2,3-dimethyl-2-butyl cation (4-CF₃) is the most stable ion. The factors controlling these equilibria and the relationship between these ions and other systems where equilibrating ions and/or bridged ions may be important are discussed.

Continuing our investigation of stable, long-lived phenethyl cations⁵ and arylonium ions,⁶ we directed our attention to the investigation of the 3-aryl-2,3-dimethyl-2-butyl cation systems.

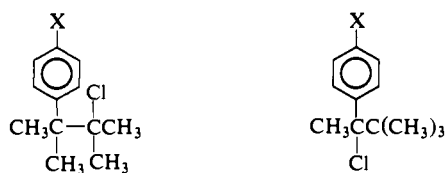
Our work was prompted by the original work of Cram and Knight^{7a} on tertiary phenonium ions and by the recent work of Brown and Kim^{7b} who conducted a comprehensive study of the carbonium ion chemistry of the 3-aryl-2,3-dimethyl-2-butyl system and concluded that this chemistry was most properly interpreted in terms of a rapidly equilibrating pair of π -bridged ions.^{7b} A study of the direct observation of 3-aryl-2,3-dimethyl-2-butyl cations was expected to furnish data of interest, supplementing previous kinetic and stereochemical studies.

In our previous preliminary study of the 3-phenyl-2,3-dimethyl-2-butyl cation, no clear differentiation between the bridged tetramethylethylenphenonium or the equilibrating open chain, classical 3-phenyl-2,3-dimethylbutyl cation pair was made. The position of the methyl nmr resonance absorption favored the former, but the non-descript phenyl proton region (at 60 MHz) could have also indicated the latter ion.

Results

The 3-Phenyl-2,3-dimethyl-2-butyl System. When 3-phenyl-2,3-dimethyl-2-butyl chloride (1-H) is treated with SbF₅-SO₂ at -78°, ionization takes place to yield a solution, the pmr spectrum of which is shown in Figure 1. The same ion may be obtained by ionization of 2-phenyl-2-chloro-3,3-dimethylbutane (2-H).

The aromatic region is considerably deshielded from that of the covalent starting material (dotted line in Figure 1 is the aromatic region of 1-H), indicating considerable



1-H, X = H
1-CH₃, X = CH₃
1-OCH₃, X = OCH₃
1-CF₃, X = CF₃

2-H, X = H
2-CH₃, X = CH₃
2-OCH₃, X = OCH₃
2-CF₃, X = CF₃

charge density on the aromatic ring. At 100 MHz the *ortho*, *meta*, and *para* protons are well separated permitting a first-order analysis of the spectrum. The spectrum also shows a single methyl peak at δ 2.31 which is deshielded from the methyl peaks of the covalent precursor 1-H (δ 1.25, 1.27). When a solution of this ion is quenched with cold methanol at low temperature and the product is analyzed by glpc and nmr, 3-phenyl-2,3-

Table I. Analysis of Methanolysis Products of Ions^a

X	Product, %			
H	82.2	10.2	7.6	Trace
H	62.5	26.6	10.2	0.7
H	66.5	22.6	10.0	0.9
CH ₃	56.6	1.0	43.5	1.0
CH ₃	54.9	4.2	39.0	1.9
CH ₃	62.3	1.0	37.7	1.0
OCH ₃	1.2	2.6	74.5	21.7
OCH ₃	1.0	0.4	98.4	0.2
CF ₃	77.0	23.0	<0.2	<0.2
CF ₃	87.0	13.0	<0.2	<0.2

^a Using an Aerograph Model HiFi 1200 gas chromatograph with 5% Carbowax on Aeropak (6 ft \times $\frac{1}{8}$ in.).

(1) Part LXXII: G. A. Olah, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **90**, 3882 (1968).

(2) Texaco Research Fellow, 1967-1968.

(3) Department of Chemistry, Purdue University, Lafayette, Ind.

(4) Purdue Research Foundation Fellow, 1966-1968.

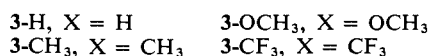
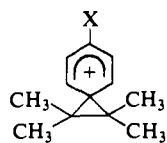
(5) G. A. Olah and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **87**, 3509 (1965).

(6) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *ibid.*, **89**, 5259 (1967).

(7) (a) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952); (b) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968).

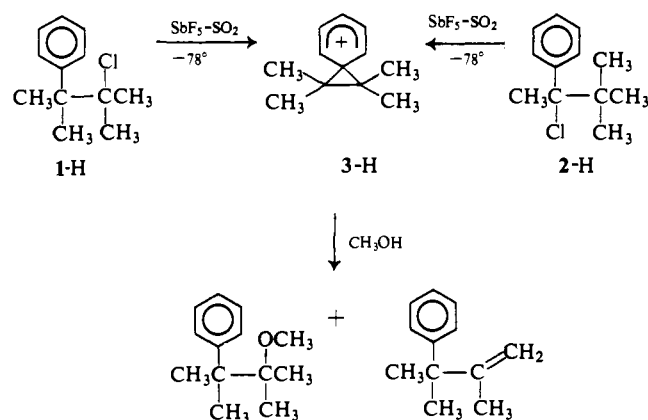
dimethyl-2-methoxybutane and 3-phenyl-2,3-dimethyl-1-butene are the predominant products. The complete gas chromatography (gc) analysis of the quenching products is shown in Table I.

Based on the spectral and solvolytic data, we conclude Figure 1 is the spectrum of the tetramethylethylenephonium ion (3-H). Ion 3-H is the first example of a

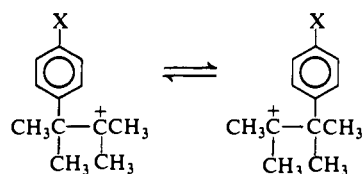


stable long-lived phenonium ion without any ring substituents. The chemistry of this system is summarized in Scheme I.

Scheme I



The spectrum of 3-H (Figure 1) deserves comment both with respect to the methyl groups and the aromatic ring. *A priori* (i.e., without recourse to model compounds) it would be very difficult to differentiate the tetramethylethylenephonium ion 3-H, from a rapidly equilibrating pair of open-chain phenethyl cations 4-H solely on the basis of the methyl group chemical shift. This is because



the methyl groups in both 3 and 4 would be expected to be moderately deshielded. In 4-H, the observed methyl shift would be an average of the slightly deshielded benzylic methyl groups and the greatly deshielded phenethyl methyl protons. Similarly the methyl groups in the phenonium ion 3-H would also be expected to be moderately deshielded. The cyclopropane hydrogens in the *p*-methoxyphenonium ion (5)⁶ are at δ 3.47, deshielded from the cyclopropane hydrogens in

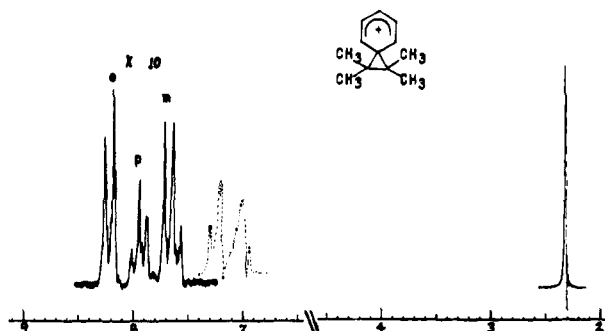


Figure 1. Spectrum (100 MHz) of the tetramethylethylenephonium ion, 3-H. Dotted line is the aromatic region of 1-H.

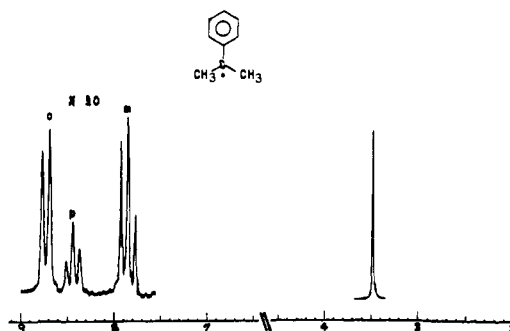
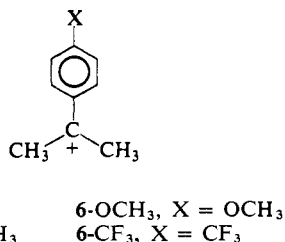


Figure 2. Spectrum (100 MHz) of the phenyldimethylcarbonium ion, 6-H.

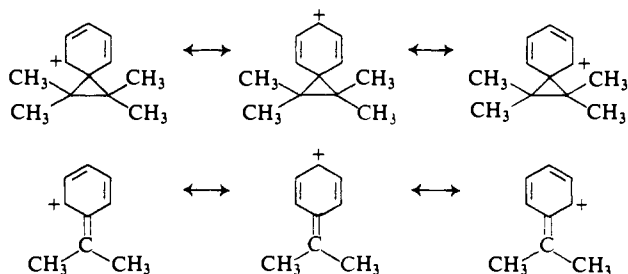
p-anisylcyclopropane, and it is therefore reasonable to expect that the methyl groups in 3-H would also be deshielded from the covalent precursors. However, in 4-H the positive charge would be (time-averaged) delocalized over only the four methyl groups, whereas in 3-H the phenyl ring would be expected to carry the major portion of the positive charge. Thus the methyl shift in 3-H would be expected to be of high field of the methyl shift in 4-H. There are suitable model compounds available for comparison with the expected spectra of 3-H and 4-H. In particular, the equilibrating 3-*p*-trifluoromethylphenyl-2,3-dimethyl-2-butyl cation, 4-CF₃ (*vide infra*), has its methyl absorption at δ 2.82. Since the ion in Figure 1 has its methyl absorption significantly upfield from this value at δ 2.31, the ion in Figure 1 must be considered the phenonium ion 3-H.

The aromatic region of the ion in Figure 1 is also consistent with 3-H but inconsistent with 4-H. In the equilibrating ion 4-H, the positive charge rests on the side chain and not on the aromatic ring. Except for a possible small inductive or field effect from the positive charge to the ring, the aromatic spectrum of 4-H would be expected to be very similar to that of 3-phenyl-2,3-dimethyl-2-chlorobutane (1-H). As the aromatic spectrum of 1-H (dotted line in Figure 1) is upfield from that of the ion, the ion in Figure 1 cannot be the equilibrating ion 4-H,

but must be the phenonium ion 3-H. Moreover, models are also available for the aromatic region of a phenonium ion such as 3-H. In particular the phenyldimethylcarbonium ion 6-H would be expected to have an aromatic ring pattern similar to that of the phenonium ion 3-H. That this is the case is evident from consideration of the various resonance forms of 6-H and 3-H shown in Scheme II. Comparison of the nmr spectrum of 3-H



Scheme II



(Figure 1) with that of 6-H (Figure 2) shows the expected similarities. Both ions have aromatic regions which are considerably deshielded from their covalent precursors and, as expected, from Scheme II, the *ortho* and *para* protons in both ions are to low field of the *meta* protons.

Phenylcarbonium ions are well known.⁸ Farnum in a recent paper⁹ discussed the nmr spectra of a number of phenylcarbonium ions including that of 6-H and concluded that the *para* (but not the *meta* or *ortho*) proton shift was a reasonably accurate measure of the positive charge density on the *para* carbon atom. Inspection of Figures 1 and 2 shows that the *para* proton in 3-H is upfield (δ 7.92) from the *para* proton in 6-H (δ 8.42) indicating a lower charge density on the ring¹⁰ in 3-H than in 6-H. There are several possible explanations for this observation.

(a) In the phenonium ion 3-H, the cyclopropane ring carries an appreciable portion of the positive charge, thus lowering the charge density on the aromatic ring. The ability of a cyclopropane ring to stabilize an α positive charge is well known.^{11,12}

(b) The ion in Figure 1 is a rapidly equilibrating mixture of the phenonium ion 3-H and the phenethyl cation 4-H, with the proportions of 3-H and 4-H such that the spectrum in Figure 1 results.¹³

(8) G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 932 (1964); D. G. Farnum, *ibid.*, **86**, 934 (1964).

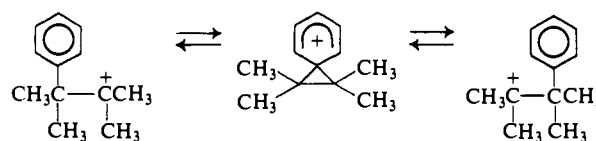
(9) D. G. Farnum, *ibid.*, **89**, 2970 (1967).

(10) The *ortho* and *meta* protons in 3-H are also upfield from their counterparts in 6-H, but because of Farnum's conclusions we are centering the discussion on the *para* shift.

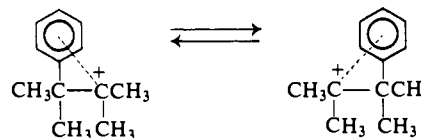
(11) H. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, **81**, 320 (1959).

(12) For a recent relevant example of this phenomenon, see H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).

(13) According to this argument, the pure phenonium ion 3-H would have an aromatic spectrum which is as deshielded as that of 6-H and the phenethyl cation would have an aromatic spectrum like 1-H.



(c) The ion in Figure 1 is a rapidly equilibrating pair of π -bridged ions. In these π -bridged ions the positive charge is partially delocalized into the aromatic ring and



is partially on the β -carbon atom. A π -bridged ion may be considered intermediate in structure between an open-chain phenethyl cation and a symmetrically bridged phenonium ion. In their studies of the solvolytic behavior of the 3-phenyl-2,3-dimethyl-2-butyl system, Brown and Kim⁷ postulated that the transition state in solvolysis of 1-H and 1-OCH₃ had a π -bridged structure and by using the Hammond postulate they concluded that the intermediate also had an unsymmetrical π -bridged structure.

Distinguishing among these alternative explanations is difficult but we feel that explanation a is preferred, based on the following reasoning. Consider the differences in behavior between a primary system such as the *p*-methoxyphenethyl system and a tertiary system such as 3-phenyl-2,3-dimethyl-2-butyl. If explanation b were valid, then the proportion of phenethyl cation would be much greater in the case of the tertiary system. If explanation c were valid, then the structure of the π -bridged ion would be less symmetrical for the tertiary system (*i.e.*, more like a phenethyl cation and less like a phenonium ion) than for the primary system. Thus if explanation b or c is correct, the observed aromatic region of the nmr spectra of the ions would be more deshielded for the primary system than for the tertiary system. Inspection of the appropriate spectra shows this to not be the case. The relevant chemical shifts are summarized in Table II.

Table II. Comparison of Chemical Shifts^a of Primary and Tertiary Phenethyl Cation Systems

Ion	Phenethyl system	Benzylic system	$\Delta\delta^b$
Primary 5	8.15 <i>ortho</i>	6-OCH ₃ 8.74 <i>ortho</i>	+0.59
	7.50 <i>meta</i>	7.40 <i>meta</i>	-0.10
Tertiary 3-H	8.21 <i>ortho</i>	6-H 8.73 <i>ortho</i>	+0.52
	7.62 <i>meta</i>	7.82 <i>meta</i>	+0.20
	7.92 <i>para</i>	8.42 <i>para</i>	+0.50

^a δ in parts per million (ppm) from external TMS. ^b This column gives the difference in positional chemical shift between the benzylic system and the phenethyl system.

In Table II, the chemical shifts of a primary phenethyl system and a tertiary phenethyl system (3-H) are compared with the chemical shifts of the appropriate aryl-dimethylcarbonium ions. The $\Delta\delta$ column gives the difference in positional chemical shifts between the phenethyl and benzylic systems. As can be seen, the

Scheme III

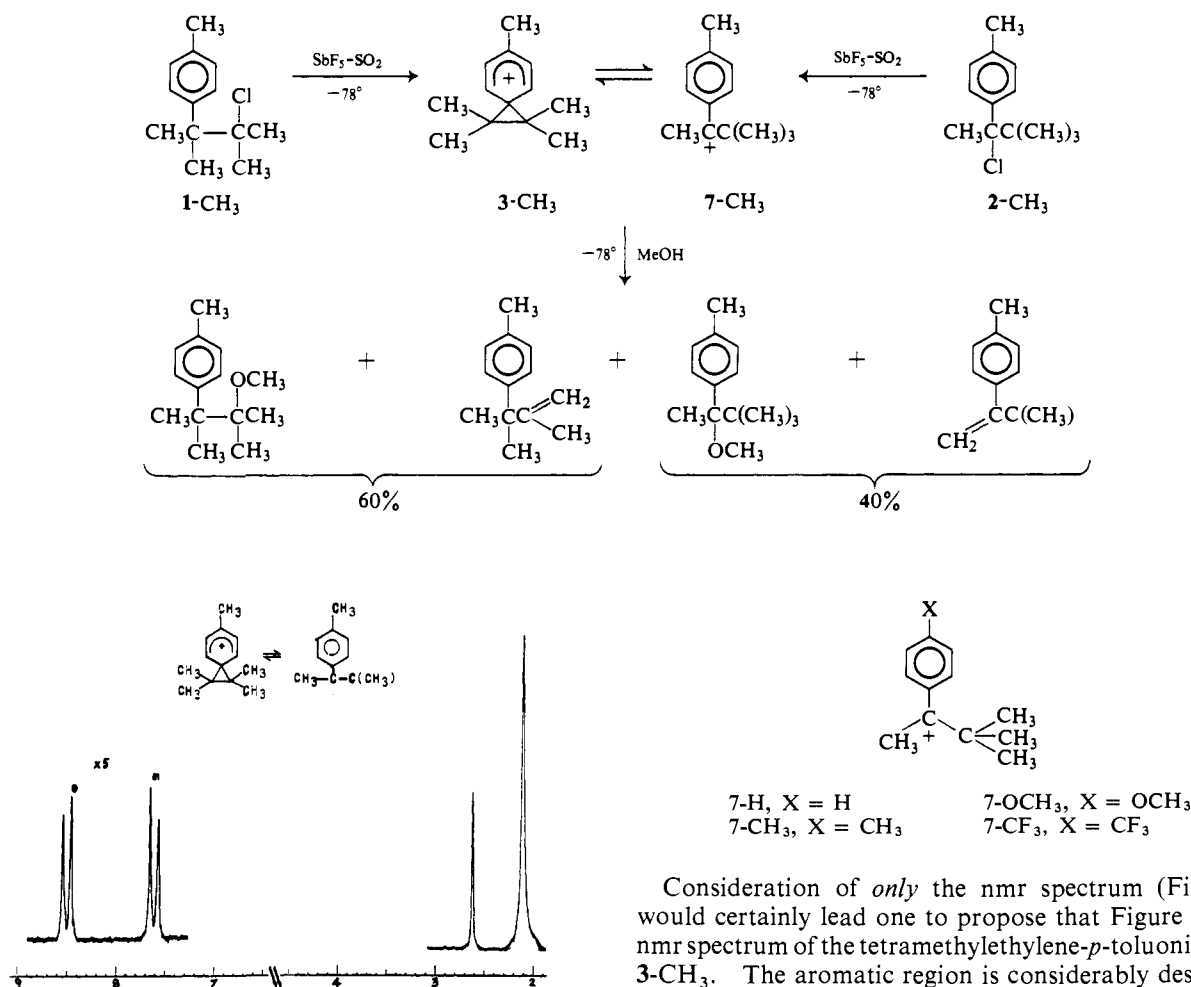


Figure 3. Spectrum (100 MHz) of the rapidly equilibrating mixture of 3-CH₃ and 7-CH₃ (approximately 60:40), see text.

ortho-shift differences (0.59 and 0.52) are very similar as are the *meta*-shift differences (-0.10 and +0.20). We feel that these similar differences are most consistent with explanation a.¹⁴

In summary, the structure proof for 3-H (Figure 1) is based on: (1) the quenching results, (2) the large deshielding of 3-H relative to 1-H, (3) the difference between the methyl shifts in 3-H and 4-CF₃.

The *p*-Tolyl-2,3-dimethyl-2-butyl System. When 3-*p*-tolyl-2,3-dimethyl-2-chlorobutane (1-CH₃) is treated with SbF₅ at -78° in SO₂, ionization takes place to yield the ion whose pmr spectrum is shown in Figure 3. The same ion is formed by ionization of 2-*p*-tolyl-2-chloro-3,3-dimethylbutane (2-CH₃). When a solution of this ion is quenched with methanol at low temperature, a mixture of products indicative of significant amounts of both α and β ions is formed. We believe that the nmr spectrum and the quenching results are most consistent with a rapidly equilibrating mixture of the tetramethylethylene-*p*-toluonium ion, 3-CH₃, and the benzylic *p*-tolylmethyl-*t*-butylcarbonium ion, 7-CH₃. The chemistry of this system is summarized in Scheme III.

(14) It is fully recognized that the accuracy of this analysis is dependent on the degree to which chemical shift parallels charge density and on the degree to which charge density implies structure.

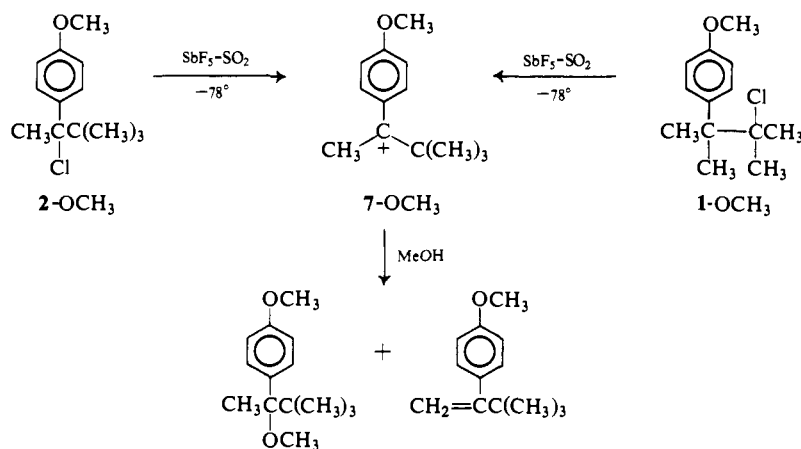
Consideration of *only* the nmr spectrum (Figure 3) would certainly lead one to propose that Figure 3 is the nmr spectrum of the tetramethylethylene-*p*-toluonium ion, 3-CH₃. The aromatic region is considerably deshielded from that of the covalent precursor 1-CH₃ and the tetramethyl groups and the tolyl methyl group are also deshielded relative to the corresponding groups in 1-CH₃. Comparison of Figure 3 with the spectrum of the *p*-tolyl-dimethylcarbonium ion, 6-CH₃ (Figure 4), shows the expected similarities. The charge density on the aromatic ring is higher in 6-CH₃ and thus the *ortho* (δ 8.75) and *meta* (δ 7.86) protons are to lower field of those in 3-CH₃. This phenomenon was discussed above in relation to ions 3-H and 6-H.

Table III. Pmr Shifts of *p*-X-Phenyldimethylcarbonium Ions

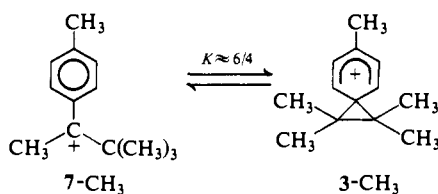
Ion	<i>o</i>	<i>m</i>	X	CH ₃
6-H	8.73	7.82	8.42	3.48
6-CH ₃	8.75	7.86	2.84	3.45
6-OCH ₃	8.72	7.40	4.37	3.12
6-CF ₃	8.90	8.08	φ + 66.0	3.71

Comparison of the spectra of 6-H and 6-CH₃ (Figures 2 and 4, Table III) shows that the benzylic methyl groups, the *ortho* protons, and the *meta* protons all have very similar chemical shifts in both ions. Thus it is reasonable to expect the *ortho*, *meta*, and tetramethyl shifts in 3-H (Figure 1) and 3-CH₃ to be very similar. Examination of the shifts in Figure 3 shows that these shifts are considerably different from those in 3-H (Figure 1). This is difficult to explain if Figure 3 is the spectrum of only the phenonium ion, 3-CH₃.

Scheme IV



A benzylic ion such as 7-CH₃ would be expected to show an aromatic ring pattern which would be deshielded from its precursor 2-CH₃. If the benzylic ion was in rapid equilibrium with a phenonium ion, a symmetrical deshielded ring pattern would result. Similarly a single moderately deshielded tetramethyl peak would result from time averaging of the methyls in 3-CH₃ and methyls in 7-CH₃. Assuming a rapidly equilibrating 60:40 mixture (from the quenching results) of 3-CH₃ and 7-CH₃ one can calculate an average tetramethyl shift of δ 2.09 for this mixture. This is based on assuming δ 2.31 (from 3-H) for the tetramethyl shift in 3-CH₃ and assuming δ 3.45¹⁵ for the methyl and δ 1.50 (from 7-OCH₃; *vide infra*) for the *t*-butyl shifts, respectively, in 7-CH₃. This calculated value is in excellent agreement with the observed value of δ 2.11. Thus the suggestion of an equilibrium between 3-CH₃ and 7-CH₃ must be considered completely consistent with Figure 3 and indeed is demanded by the quenching results.^{16,17}

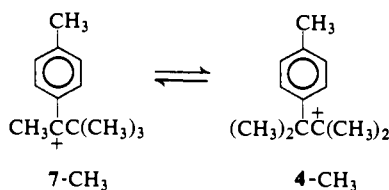


The *p*-tolyl-2,3-dimethyl-2-butyl system illustrates the

(15) This shift was arrived at by an upfield shift of 0.16 from the benzylic methyl shift of 6-CH₃; 0.16 is the difference in the benzylic methyl shifts of 6-OCH₃ and 7-OCH₃.

(16) The possibility that Figure 3 is the spectrum of 3-CH₃ and that isomerization takes place during quenching to yield a mixture of α and β products is considered and rejected in the Discussion.

(17) The following equilibrium would also account for the quenching results but would be inconsistent with the tetramethyl shift.



Assuming a 40:60 mixture of 7-CH₃ and 4-CH₃ a time-averaged tetramethyl shift of δ 2.49 is calculated. This is based on assuming the shifts in 7-CH₃ are δ 3.45 (CH₃ based on 6-CH₃) and 1.50 (*t*-butyl based on 7-OCH₃; *vide infra*) and assuming the average tetramethyl shift in 4-CH₃ is 2.82 (based on 4-CF₃; *vide infra*).

importance of (1) careful analysis of the spectra of homologous members of a series; (2) carrying out quantitative quenching experiments when analyzing the nmr spectra of carbonium ions.

The *p*-Anisyl-2,3-dimethyl-2-butyl System. When 3-*p*-anisyl-2,3-dimethyl-2-chlorobutane (1-OCH₃) is treated with SbF₅-SO₂ at -78°, ionization takes place to yield the ion whose spectrum is shown in Figure 5. The same ion is obtained by ionization of 2-*p*-anisyl-2-chloro-3,3-dimethylbutane (2-OCH₃). When solutions of this ion are quenched with methanol at low temperature, 2-*p*-anisyl-2-methoxy-3,3-dimethylbutane and 1-*p*-anisyl-1-*t*-butylethylene are formed as the predominant products (see Table I). The data indicate the ion in Figure 5 to be the *p*-anisyl-*t*-butylmethylcarbonium ion, 7-OCH₃. The chemistry of 7-OCH₃ is summarized in Scheme IV.

The nmr spectrum of 7-OCH₃ (Figure 5) shows the deshielded aromatic pattern characteristic of benzylic cations and, in addition, the nonequivalence of the *ortho* (and to a lesser extent, *meta*) protons characteristic of benzyl cations with two different α substituents.^{6,18} The methoxyl group (δ 4.11) is deshielded from the methoxyl position in 2-OCH₃ (δ 3.48) indicating considerable positive charge density on the methoxyl oxygen and, as expected, the benzylic groups are also to low field of their counterparts in 2-OCH₃. It is interesting to compare the spectra of 7-OCH₃ (Figure 5) with that of the *p*-anisyl-dimethylcarbonium ion, 6-OCH₃ (Figure 6). The interesting feature which becomes apparent on comparison of these spectra is the difference in the methoxyl shifts. The methoxyl group in 7-OCH₃ (δ 4.11) is to high field of the methoxyl in 6-OCH₃ (δ 4.37). Since Farnum⁹ found that the *para* proton shift in unsubstituted phenylcarbonium ions was a quantitative measure of the *para* charge density, it is reasonable to expect a similar relationship to hold for *para* substituents in general, thus indicating a lower charge density on the ring in 7-OCH₃ than in 6-OCH₃. Interestingly enough, support for this explanation is available from solvolytic studies. Brown and coworkers¹⁹ found that 2-*H* solvolyzed many times slower than did α -cumyl chloride and suggested that steric inhibition of resonance in 7-H was responsible.

When solutions of 7-OCH₃ are warmed to -30°,

(18) J. M. Bollinger, M. B. Comisarow, C. A. Cupas, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 5687 (1967).

(19) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965).

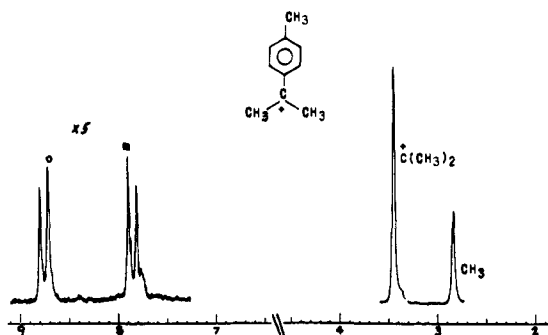


Figure 4. Spectrum (100 MHz) of the *p*-tolyldimethylcarbonium ion, 6-CH₃.

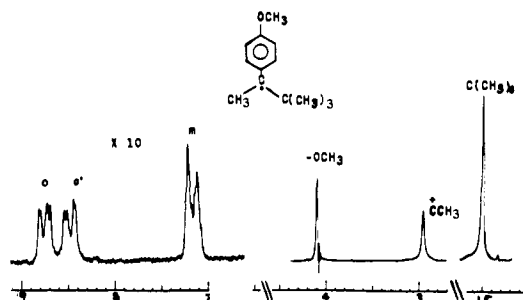
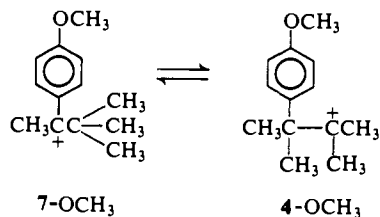


Figure 5. Spectrum (100 MHz) of the *p*-anisyl-*t*-butylmethylcarbonium ion, 7-OCH₃.

changes take place in the nmr spectrum which indicate that equilibration of the alkyl methyl groups and equilibration between the two *ortho* and two *meta* protons is occurring. The *ortho* protons start to become a simple doublet and the methyl and *t*-butyl groups are broadened. This broadening is especially marked for the methyl group. The methoxyl peak, however, remains sharp. That this change is reversible can be shown by cooling the sample down to -75° . These changes indicate that at -30° the following equilibrium takes place.



The equilibration between the methyl groups arises because of free rotation about the C_α-C_β bond in 4-OCH₃. The equilibration between the *ortho* and between the *meta* protons takes place because of free rotation about the C_{arom}-C_α bond in 4-OCH₃ and/or because of the equilibrium

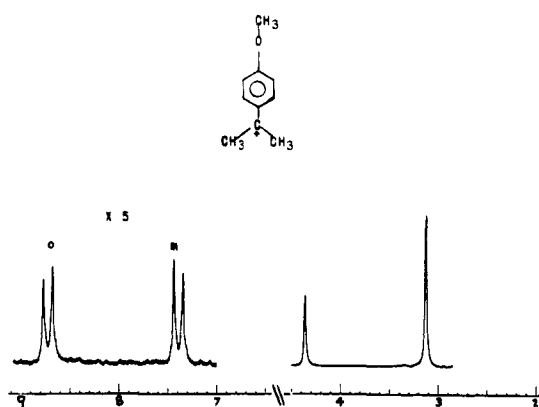
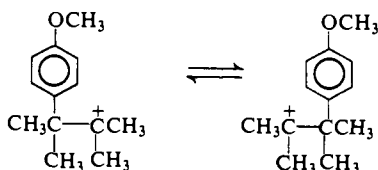


Figure 6. Spectrum (100 MHz) of the *p*-anisylidimethylcarbonium ion, 6-OCH₃.

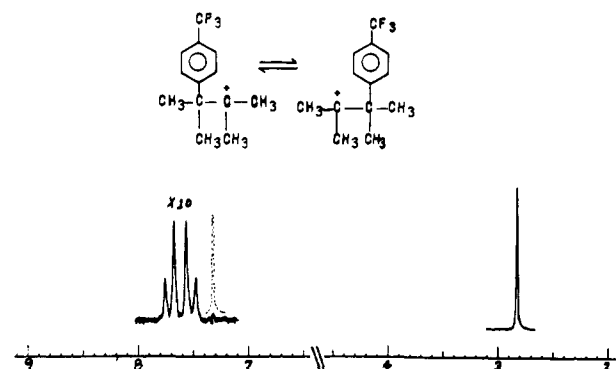


Figure 7. Spectrum (100 MHz) of the rapidly equilibrating *p*-(trifluoromethyl)phenyl-2,3-dimethyl-2-butyl cation, 4-CF₃. Dotted line is the aromatic region of 1-CF₃.

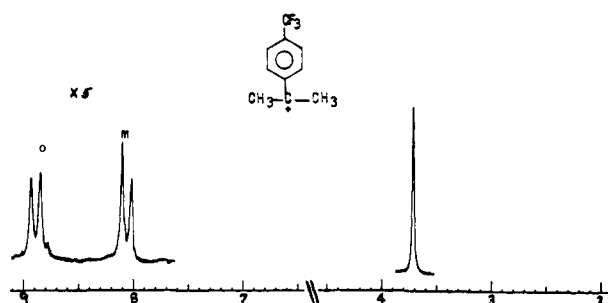
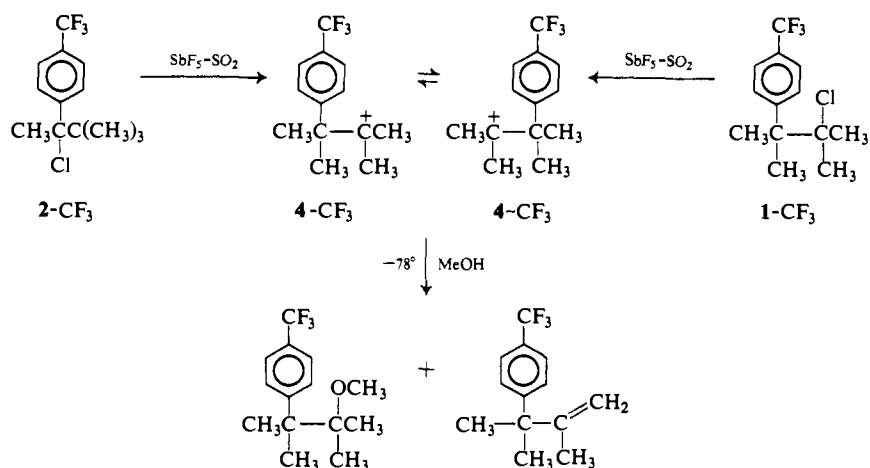


Figure 8. Spectrum (100 MHz) of the *p*-trifluoromethylphenyl-dimethylcarbonium ion, 6-CF₃.

Unfortunately quantitative study of these spectral changes is prohibited by the fact that, in SbF₅-SO₂ solution, the ion slowly decomposes at or above -30° .

The 3-*p*-Trifluoromethylphenyl-2,3-dimethyl-2-butyl System. When 3-*p*-trifluoromethylphenyl-2,3-dimethyl-2-chlorobutane (1-CF₃) is treated with SbF₅-SO₂ at -78° , the ion whose spectrum is shown in Figure 7 is obtained. The same ion is obtained by ionization of 2-*p*-trifluoromethylphenyl-2-chloro-3,3-dimethylbutane (2-CF₃). When this ion is quenched with methanol at low temperature, 3-*p*-trifluoromethylphenyl-2,3-dimethyl-2-methoxybutane and 3-*p*-trifluoromethylphenyl-2,3-di-

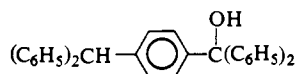
Scheme V



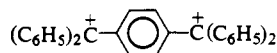
methyl-1-butene are formed as the predominant products (see Table I). The nmr spectrum of the ion shows an AA'BB' pattern which is only slightly deshielded from that of the covalent precursor 1-CF₃ (dotted line in Figure 7). The data indicate that the ion in Figure 7 is the rapidly equilibrating phenethyl cation 4-CF₃. Ion 4-CF₃ is considered the first well-established example of a stable, long-lived rapidly equilibrating phenethyl cation.²⁰ The chemistry of this ion is summarized in Scheme V.

Comparison of spectrum 4-CF₃ (Figure 7) with the spectrum of the *p*-trifluoromethylphenyldimethylcarbonium ion 6-CF₃ (Figure 8) shows the expected differences. The aromatic spectrum of 6-CF₃ is similar to that of 6-CH₃ (Figure 4) and 6-OCH₃ (Figure 6). All of these ions have the deshielded patterns characteristic of phenyl-carbonium ions. The ion in Figure 7 however has a ring pattern which is only very slightly deshielded²³ from that

(20) We had thought in a previous publication that such a case was obtained in the study of the pentaphenylethyl cation, generated through ionization of alleged pentaphenylethanol in the strong acid system, FSO₃H-SbF₅-SO₂. Reinvestigation of the preparation of the starting "pentaphenylethanol," however, showed that although it had the correct analytical data and molecular weight and is a tertiary aryl alcohol, it is indeed the compound



The work of Tomboulian and Stehower²¹ on the attempted preparation of pentaphenylethanol resulted in the same observation and was of great help to clarify this problem. Ionization can then give a dicarbonium ion with four equivalent deshielded phenyl groups adjacent to charged carbon and an A₂B₂ quartet for the *p*-phenylene group



which, however, is underlying at 60 MHz the terminal phenyl group absorptions, giving rise to the previously claimed "equivalence" of all five phenyl groups. Integration of the peak area was not sufficiently accurate to differentiate between the presence of 24 or 25 ring protons. The dication, incidentally, was reported independently by Volz and Hart.²² Thus clearly a reinvestigation of the pentaphenylethyl cation is needed and attempts are being made to this effect.

(21) P. Tomboulian and K. Stehower, personal communication, to be published.

(22) (a) A. Volz and M. J. Volz de Leces, *Tetrahedron Lett.*, 1871 (1964); (b) H. Hart, T. Sulzberg, and R. R. Rufus, *J. Amer. Chem. Soc.*, **85**, 1800 (1963).

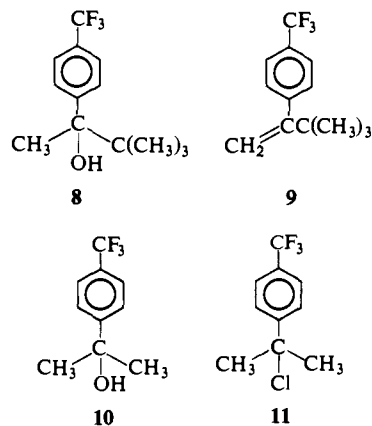
(23) The slight deshielding which is observed in 4-CF₃ may be regarded as a result of the inductive (field) effect of the β positive charge on the phenyl ring.

of 1-CF₃ (dotted line in Figure 7). Comparison of the methyl shifts in 3-CH₃ (Figure 1) and 4-CF₃ (Figure 7) shows the methyl shift in the equilibrating ion to be to low field of the methyl shift in the phenonium ion. We feel there is no internally consistent explanation for the differences between the spectrum in Figure 1 and the spectrum in Figure 7 (in both the aromatic and methyl regions) except to assign Figure 1 to the phenonium ion 3-H and Figure 7 to the rapidly equilibrating phenethyl cation 4-CF₃.

Further evidence for the assignment of Figure 7 to the rapidly equilibrating phenethyl cation comes from the study of its ¹⁹F chemical shift. Typical *p*-alkylbenzotrifluorides have ¹⁹F chemical shifts of φ + 63.²⁴ From the point of view of the CF₃ group, 4-CF₃ is a normal *p*-alkylbenzotrifluoride and indeed its ¹⁹F chemical shift is at φ + 62.6. In contrast the ¹⁹F shift in the benzyl cation 6-CF₃ is at φ + 66.0.²⁵

The spectra of the *p*-X-phenyldimethylcarbonium ions have been discussed above with reference to the appropriate phenethyl systems, but it is worthwhile to compare these cations among themselves. 6-H and 6-CH₃ have virtually identical chemical shifts for their *ortho* and *meta* protons, but in addition they have virtually the same methyl shifts. In contrast in 6-OCH₃ the methyl shift

(24) For instance, 1-CF₃, φ + 63.23; 2-CF₃, φ + 63.17; 8, φ + 63.30; 9, φ + 63.16; 10, φ + 63.21; 11, φ + 63.63.

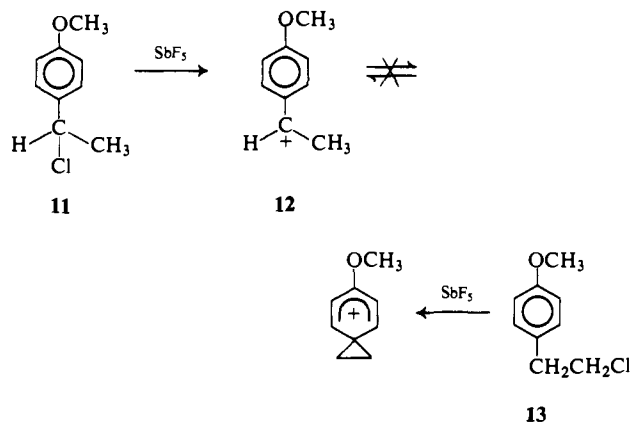


(25) This upfield shift upon ionization is expected. For instance, the 1,1,1-trifluoroethane ¹⁹F shifts move upfield with increasing electronegativity of the β-carbon atom: J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Pergamon Press, New York, N. Y., 1966, pp 883-884.

(δ 3.12) is well upfield from that in *p*-H and *p*-CH₃ compounds indicating substantial charge delocalization onto the methoxyl oxygen. In 6-CF₃ the methyl shift (δ 3.71) is to low field of that in the *p*-H and *p*-CH₃ ions indicating a small contribution from the *p*-quinoidal form and a consequent higher charge density on the methyl groups. The *ortho* protons of 6-CF₃ (δ 8.90) are also to low field of the *ortho* proton of the other ions indicating a larger contribution from the resonance form which places the positive charge at the *ortho* carbon atoms. The nmr parameters of *p*-X-phenyldimethylcarbonium ions (cumyl cations) are summarized in Table III. The variation in methyl shifts in the cumyl ions 6 suggests the possibility that the proton (or ¹³C) shifts of the methyl groups could be used to derive substituent constants for the *para* substituents. Constants derived in this manner would complement the kinetic σ^+ constants derived from solvolysis of α -cumyl chlorides.²⁶ This possibility is presently being tested.

Discussion

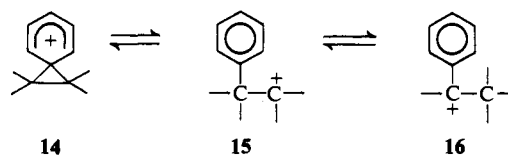
It should be pointed out that in the strong acid system (SbF₅-SO₂) the anion possesses a very low nucleophilicity and thus cations, once formed, are not trapped by a nucleophile. Because trapping of the cations is not an important process, a cation may rearrange to a thermodynamically more stable isomeric ion, if one exists. The 3-aryl-2,3-dimethyl-2-butyl system possesses three isomeric tertiary or highly delocalized ions: the tertiary phenethyl cation 4, the phenonium ion 3, and the benzylic ion 7. The observation that for each case X = H, CH₃, OCH₃, CF₃, the same ion was formed from either the phenethyl precursor 1 or the benzylic precursor 2 (Schemes I, III-V) conclusively proves that in all cases the observed ion is the most stable one. In our previous studies on phenonium ions,⁶ it was shown that benzylic precursors such as 11 could be ionized to the corresponding benzylic ion 12 and that phenethyl precursors such as 13 could be ionized to the phenonium ion 5, but equilibration between the benzylic ions and the phenonium ions does not take place.²⁷ The fact that the systems studied in the



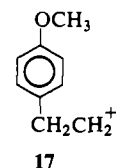
(26) For a review, see L. Stork and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 35 (1963).

(27) Ionization of 13 at higher temperatures leads to irreversible formation of 12. High-temperature ionization of 11 also yields 12. This proves that 12 is more stable than 5.

present work do equilibrate at -78° to yield the thermodynamically most stable ion is considered a direct consequence of the fact that these phenethyl cation systems are tertiary. Consider the following equilibrium



For the phenonium ion 14 to rearrange to the benzylic ion 16 a structure approximating the open-chain phenethyl cation 15 must first be formed. In the case of the present work 15 is the tertiary ion 4, whereas in our prior work⁶ 15 is the primary ion 17. Since the energy of the open-chain



phenethyl cation 15 represents the barrier to the interconversion $14 \rightleftharpoons 16$ it is easy to see why this interconversion readily takes place in the tertiary cases, but does not take place in the primary case.

The factors controlling the stability of the various ions in the present work merit some discussion. In the unsubstituted 3-phenyl-2,3-dimethyl-2-butyl system the phenonium ion 3-H is the most stable; in the *p*-CH₃ system the phenonium ion 3-CH₃ and the benzylic ion 7-CH₃ have comparable stability; in the *p*-OCH₃ system the benzylic ion 7-OCH₃ is the most stable ion; and in the *p*-CF₃ system the equilibrating phenethyl cation 4-CH₃ is the most stable. Since the changes in the relative stability of the ions are brought about solely by changing the *para* substituents, it is difficult to see how steric effects could have major importance. Electronic effects must therefore be responsible for these changes.

Let us consider the electronic effects expected to be important in determining the relative stability of the phenethyl cation 4-H, the phenonium ion 3-H, and the benzylic ion 7-H. In the ion 4-H, the charge is localized at the β -carbon atom and is only stabilized by the β -alkyl substituents. Transforming 4-H into the phenonium ion 3-H involves delocalizing the positive charge into the phenyl and cyclopropane rings with a resultant lowering of the potential energy of the ion. Provided that this loss of potential energy is greater than the strain energy of the cyclopropane ring and the loss in resonance energy of the phenyl group, the phenonium ion will be expected to be more stable than the open-chain phenethyl cation. Similarly transforming 4-H into 7-H involves delocalizing the positive charge into the ring with a consequent lowering of potential energy. Provided that this lowering of the potential energy is greater than the loss in resonance energy of the phenyl group and the possible strain energy in the benzylic group, the benzylic ion 7-H could be expected to be more stable than the open-chain phenethyl cation 4-H. Electropositive substituents will stabilize and electronegative substituents will destabilize 3 and 7 relative to 4, which would be expected to be more or less insensitive to ring substitution. Because of the electro-

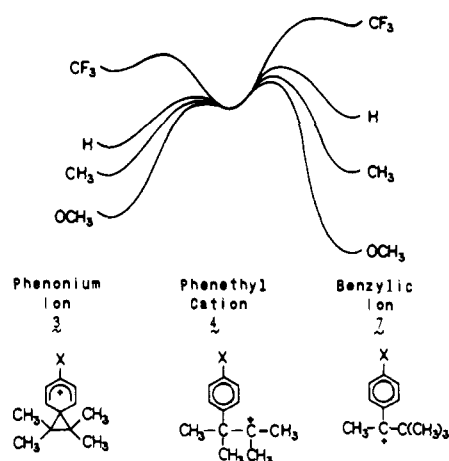
Free Energy Diagram for Phenyl Dimethyl
Butyl Cations

Figure 9.

positive nature of the spirocyclopropane ring in the phenonium ion 3, and because of some steric inhibition of resonance in the arylmethyl-*t*-butylcarbonium ion 7, the stability of both 3 and 7 would be expected to be less sensitive to ring substitution than is the cumyl cation 6. The relative importance of these effects is difficult to predict beforehand, but the empirical fact (*vide infra*) is that the stability of the phenonium ion 3 is less sensitive to ring substitution than is the benzylic ion 7.

These comments can conveniently be displayed on a free energy diagram, shown in Figure 9. In this diagram the energies of the phenethyl cations 4-H, 4-CH₃, 4-OCH₃, 4-CF₃ have been set equal to 0. In the unsubstituted system the phenonium ion is more stable than the benzylic ion, because of the additional charge delocalization into the cyclopropane ring. Substitution of a *para* methyl group stabilizes both the phenonium ion and the benzylic ion relative to the unsubstituted case, but the benzylic ion is stabilized more, resulting in approximate equal stability for both ions. Similarly substitution of a *p*-OCH₃ group lowers the free energy of the phenonium ion and the benzylic ion, with the lowering being greater for the benzylic ion. The *p*-CF₃ group destabilizes both the phenonium and benzylic ions, with the destabilization being greater for the latter.²⁸

Although it does not follow directly from the results of this work, it has been assumed in the construction of Figure 9 that the barrier to the phenonium ion-phenethyl cation rearrangement is lower than for the phenethyl cation-benzylic cation rearrangement, where a 1,2-methyl shift is involved. The activation energy for the phenethyl cation-phenonium ion rearrangement may even be zero for the H, CH₃, and OCH₃ systems.

In the case of the rapidly equilibrating phenethyl cation 4-CF₃, it is interesting to speculate as to why this ion equilibrates at all and why it is not a static phenethyl cation. This ion may equilibrate either *via* phenyl or

(28) From the behavior of the H, CH₃, and OCH₃ systems, it is concluded that the energy of the benzylic ion 7 is more sensitive to ring substitution than is the energy of the phenonium ion 3. Therefore by extrapolation 7-CF₃ is less stable than 3-CF₃.

methyl shifts. In the methyl shift mechanism a rapid equilibration between 4-CF₃ and a very small (but finite) amount of 7-CF₃ would give a spectrum like the one in

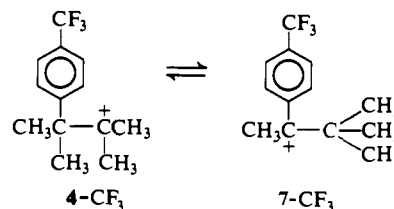
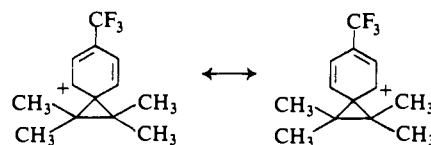


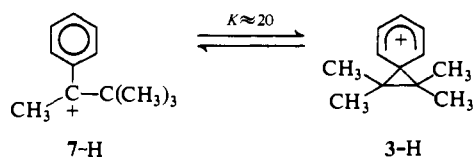
Figure 7. This mechanism is rendered unlikely by the instability of 7-CF₃ relative to 3-CF₃ (Figure 9).²⁶ Therefore it is concluded that phenyl bridging is the mechanism by which the above equilibration takes place. The energy gap between 3-CF₃ and 4-CF₃ is small enough such that this equilibration is rapid on the nmr time scale, indicating that considerable energy stabilization accrues from the resonance forms which place the positive charge at the *ortho* positions. It is not clear if the phenonium ion



is an intermediate for this equilibration or if it is the transition state. Experiments are presently in progress to determine if substituents which are more electronegative than *p*-CF₃ will permit this equilibration to be slowed to a rate measurable by nmr spectroscopy.

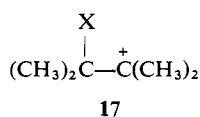
In the Results, it was stated that provided the quenching products (Table I) are a valid indication of the structure of their precursor ions, the *p*-CH₃ system must be a rapidly equilibrating mixture of the phenonium ion 3-CH₃ and the benzylic ion 7-CH₃ in the approximate ratio 60:40. That this indeed is the case can be substantiated now by the following reasoning. If a rearrangement of a phenonium ion to a benzylic ion takes place during quenching, the barrier to this rearrangement may be represented by the energy of the open-chain phenethyl cation. Inspection of Figure 9 shows that this barrier is higher for the *p*-CH₃ system than for the *p*-H system. Thus if rearrangement occurs in the *p*-CH₃ system even more rearrangement must occur in the *p*-H system. However, the quenching results of the *p*-H system (Table I) show lesser amounts of α products than do the quenching results of the *p*-CH₃ system. Therefore we conclude that rearrangement does not take place to any significant degree during quenching. In the case of the *p*-OCH₃ system, it is possible to determine the "error" in quenching since the spectrum of the system (Figure 5) shows only the static benzylic cation 7-OCH₃. Quenching of this ion yields about 3.5% of the β products characteristic of the phenonium or phenethyl cations. Therefore for this system, the quenching error (*i.e.*, amount of rearrangement during quenching) is no more than 3.5%. Because of the factors discussed above more rearrangement and thus a somewhat greater error may be expected for the *p*-CH₃ and *p*-H systems. The *p*-H ion (Figure 1) yields on quenching about 10% of the products characteristic of the benzylic cation. This could result from a greater amount of rearrangement during quenching than in the *p*-OCH₃ system. Alternatively,

it could be concluded that the quenching error is, say, 4% and that the ion in Figure 1 is really a rapidly equilibrating mixture of the phenonium ion 3-H and the benzylic ion 7-H, in a ratio of about 20:1. The present data do not



permit us to distinguish between these two possibilities, and for simplicity, the ion in Figure 1 is referred to simply as 3-H.²⁹

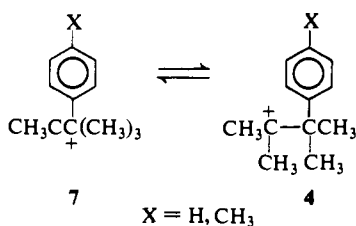
Finally, some comments seem to be warranted relating to the factors controlling equilibrating and bridged tetramethylethyl cations. The following stable, long-lived 2-substituted tetramethylethyl cations **17** all show a single methyl resonance in their nmr spectra. This observation,



X = C₆H₅,³⁰ *p*-CF₃C₆H₄,³⁰ F,³¹ Cl,³¹ Br,³¹ I,³¹ H,³² CH₃,³²

per se, is consistent with either a rapidly equilibrating pair of tetramethylethyl cations **18**

(29) One of the referees has suggested that the spectra in Figures 1 and 3 could be interpreted in terms of the equilibrium



with the deshielded aromatic regions resulting from the presence of 7. In the chart below, column A gives calculated amounts of 7 and 4 which fit the observed tetramethyl shifts in Figures 1 and 3. For these calculations we have assumed that the alkyl methyl shifts in 7-H and 7-CH₃ are the same (since the methyl shifts in 6-H and 6-CH₃ are virtually the same) and that the average tetramethyl shifts in 4-CH₃ and 4-H are the same. The methyl shifts in 4-CH₃ and 7-CH₃ are derived in footnote 15. Column B gives the ratio of α to β products obtained

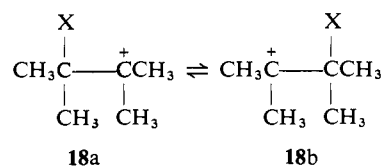
	A	B	C
	7:4	α : β	7:3
H	59:41	10:90	0:100
CH ₃	88:12	40:60	40:60

on quenching. Comparison of columns A and B shows that if the column A interpretation of the nmr spectra is correct, then the quenching results are not a valid indicator of the precursor ion mixture. The possible reason for this (suggested by the referee) is that the less stable ions (which are present in lower concentration) react faster on quenching. Applying this principle to this system it seems reasonable to suggest that 4-CH₃ and 4-H have virtually identical stabilities and quenching rates. Ion 7-H should be less stable than ion 7-CH₃ and therefore should quench faster. However, the amount of α compound decreases on quenching by a factor of 6 for the *p*-H system and by a factor of 2 for the *p*-CH₃ system, opposite to what is predicted. Therefore we conclude ground-state stabilities cannot explain these anomalous quenching results. In contrast, the interpretation of the nmr spectra as given in the body of this paper (column C) easily fits the quenching results and it is for this reason that the data are interpreted along these lines.

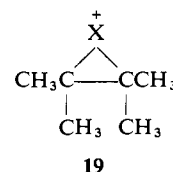
(30) This work.

(31) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967).

(32) G. A. Olah and J. Lukas, *ibid.*, **89**, 4734 (1967).



or with the bridged ion **19**.³³



The chemical shifts of the ions together with their covalent precursors are summarized in Table IV. The first four ions in Table IV (X = C₆H₅, Cl, Br, I) have the bridged structure **19** and the next two ions (*p*-CF₃C₆H₄, F) have the open-chain equilibrating structure **18**. In the absence of the other effects, the absolute methyl shift in the bridged ion **19** would be at higher field than the absolute methyl shift in the equilibrating ion **18**. Inspection of Table IV shows that these other effects (C-X bond anisotropy and/or steric effects) are important and thus the absolute methyl shift cannot be used as a criterion for proving the structure of the ion. In an attempt to minimize these extraneous effects, the chemical shifts of the ions relative to their chloride precursors are given in Table IV ($\Delta\delta$ column). As can be seen, the four bridged ions are deshielded δ 0.90 to 1.04 from their precursors while the equilibrating ions are deshielded δ 1.55 from their precursors.

Table IV. Nmr Chemical Shift Data for 2-Substituted Tetramethylethyl Cations

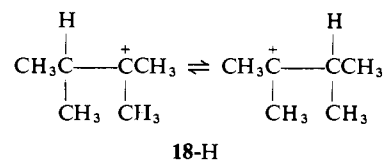
Substituent X	Methyl shift precursor ^{a,b} SO ₂		Methyl shift ^c ion SO ₂	$\Delta\delta$
	CH ₃ CX	CH ₃ CCl		
C ₆ H ₅	1.27	1.25	2.31	-1.04
Cl	1.52	1.52	2.47	-0.95
Br	1.71	1.58 ^d	2.61	-0.90
I	1.91	1.65	2.80	-0.89
<i>p</i> -CF ₃ C ₆ H ₄	1.27	1.26	2.82	-1.55
F	1.29	1.32	2.85	-1.56
H	0.71	1.26	2.62	-1.91
CH ₃	0.75	1.29	2.40	-1.65

^a Chemical shifts of the 2-substituted tetramethylethyl chloride.

^b External (capillary) TMS, SO₂ solvent. ^c Difference between the shift in SO₂ of the ion and the shift in SO₂ of the CH₃CX group.

^d Estimated.

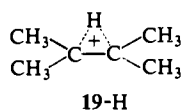
The nmr spectrum of the *t*-hexyl ion (17-H) consists of a methyl doublet at δ 2.62 ($J = 4.5$ Hz) and a 13-line methine multiplet at δ 4.13. The methyl relative shift (1.91, Table IV) is consistent with this ion being the equilibrating ion **18-H**. The position of the methine multiplet is also consistent with structure **18-H**. The



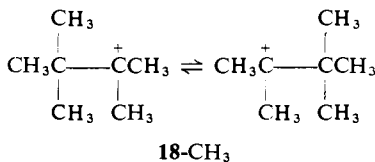
(33) This does apply to 17-CH₃. See subsequent discussion.

methine hydrogen in the isopropyl cation which is α to a positive charge resonates at δ 13.5. Thus at first consideration, the observed methine shift of δ 4.13 for the *t*-hexyl ion **17-H** seems to be at remarkably high field for a bridged structure like **19-H**.

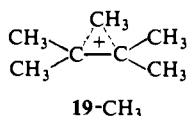
The bridged structure **19-H** cannot be, however, completely eliminated on this argument alone. It is not clear what chemical shift is to be expected for the methyl groups in **19-H**. Bridging hydrogen might be expected to be less able to carry a possible charge than the bridging groups discussed above and thus in the bridged ion **19-H**, the methyl groups might be expected to be substantially deshielded.



As with the *t*-hexyl ion **17-H**, no final decision can be made as to the structure of the *t*-heptyl ion **17-CH₃** based on the position of the observed methyl resonance absorption. Using the α - and β -methyl shifts in the *t*-amyl³⁴ cation (δ 3.97 and 1.72) as models, one can calculate the estimated average chemical shift for the equilibrating ion



18-CH₃ to be δ 2.62. This is slightly to low field of the observed chemical shift (δ 2.40). **17-CH₃** shows a relative deshielding of the methyl chemical shift ($\Delta\delta$, Table IV) of δ 1.65. This value is to low field of the $\Delta\delta$ values of the ions known to be equilibrating. The observed singlet methyl peak (even at -120°) eliminates the bridged ion **19-CH₃** as the sole structure of the ion, since **19-CH₃** would show two kinds of methyl shifts in the ratio of 3:12. If **19-CH₃** were, however, in rapid equilibration with a very small (but finite) amount of **18-CH₃**, a single methyl peak would result whose chemical shift would be the statistical average of those in **19-CH₃**. Definitively



proving or eliminating **19-CH₃** as the most stable isomer of **17-CH₃** is precluded by the difficulty of predicting the chemical shift of the bridging methyl group.

A comprehensive study of the stable *t*-hexyl and *t*-heptyl cations by laser Raman spectroscopy (a substantially faster physical method than nmr spectroscopy) is in progress in our laboratories.^{35,36}

Experimental Section

General. Melting points were determined on a Mettler automatic melting point apparatus and are uncorrected. All new compounds except **2-CH₃** gave correct elemental analysis. At room tempera-

(34) G. A. Olah *et al.*, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

(35) NOTE ADDED IN PROOF. These studies (with A. Commeyras) have now been completed and are in complete agreement with the equilibrating classical structure of the ions.

Table V. Nmr Shifts of 3-*p*-X-Phenylmethyl-*t*-butylcarbinols^a

X	Aromatic	Me	<i>t</i> -Bu	X	Bp, °C (mm)
H	7.30 (m)	1.50	0.88	...	95.5 (4.5)
CH ₃	7.25, 6.98	1.48	0.87	2.29	98 (2.5)
CF ₃	7.52	1.57	0.92	ϕ +63.30	85 (1.7)

^a CCl₄.

Table VI. Nmr Shifts of 3-*p*-X-Phenylmethyl-*t*-butylcarbiny Chlorides^a

X	Aromatic	Me	<i>t</i> -Bu	X
H ^b	7.30 (m) ^d	2.00	1.02	...
CH ₃	7.35, 7.03	1.98	1.01	2.33
OCH ₃ ^c	7.37, 6.72	1.96	1.01	3.72
CF ₃	7.62, 7.55	2.02	1.04	ϕ +63.23

^a CCl₄. ^b Bp 65° (0.6 mm). ^c Mp 44° (from hexane). ^d m = multiplet.

ture. **2-CH₃** slowly eliminates HCl. By nmr, **2-CH₃** is pure when freshly prepared and only freshly prepared samples were used for carbonium ion formation. For the compounds which could be distilled (crystallized) the analytical samples were distilled (crystallized) a second time.

3-Aryl-2,3-dimethyl-2-chlorobutanes. The *p*-H, *p*-CH₃, and *p*-OCH₃ compounds were described earlier.⁷ The synthesis of the *p*-CF₃ compound is given below. Its nmr (CCl₄) spectrum shows resonances at δ 7.55 (4), 1.58 (6), and 1.52 (6); ¹⁹F ϕ 63.17.

***p*-X-Phenyl-*t*-butylmethylcarbinols** were prepared by reaction of the appropriate arylmagnesium bromide and pinacolone. The yields are usually 30–40%. The nmr spectra and boiling points are given in Table V. The *p*-H compound was described earlier.¹⁷

Anal. Calcd for C₁₃H₂₀O (*p*-CH₃): C, 81.19; H, 10.48. Found: C, 80.82; H, 10.30.

Anal. Calcd for C₁₃H₁₇OF₃ (*p*-CF₃): C, 63.39; H, 6.95. Found: C, 63.88; H, 6.87.

The *p*-OCH₃ compound was prepared in the same manner, but dehydrated on distillation to give **1-*p*-anisyl-1-*t*-butylethylene**, bp 63° (0.6 mm); nmr (CCl₄) δ 6.98 (2), 6.68 (2), 5.10 (1), 4.70 (1), 3.70 (3), and 1.12 (9).

Anal. Calcd for C₁₃H₁₈O: C, 82.05; H, 9.53. Found: C, 81.80; H, 9.35.

3-*p*-X-Phenyl-*t*-butylmethylcarbiny Chlorides. The *p*-H and *p*-CH₃ compounds were prepared by chlorination of the corresponding carbinols with HCl at 0°. The *p*-CH₃ compound was prepared by chlorination of the olefin with anhydrous HCl in CH₂Cl₂ at -30° . The *p*-CF₃ carbinol is inert to HCl for at least 3 hr at 27°. Chlorination of the *p*-CF₃ carbinol with Lucas reagent (45 g of ZnCl₂ in 75 ml of HCl) for 2 hr at 25° yields a 90:10 mixture of **1-CF₃** and **2-CF₃**. Pure **2-CF₃** can be prepared by chlorination of the olefin (*vide infra*) with anhydrous HCl in CH₂Cl₂ at -40° . The nmr spectra are listed in Table VI.

Anal. Calcd for C₁₃H₁₉ClO (*p*-OCH₃): C, 68.84; H, 8.44; Cl, 15.65. Found: C, 69.04; H, 8.50; Cl, 15.85.

***p*-X-Phenyldimethylcarbinols**²⁶ were prepared by reaction of methyl Grignard with the appropriate *para*-substituted aceto-

(36) NOTE ADDED IN PROOF. ¹³C magnetic resonance spectra of a number of the ions described above have now been obtained in our laboratories (with Dr. A. M. White). It has been established that this technique enables a clear distinction to be made between bridged and equilibrating ions due to the considerably enhanced ¹³C chemical-shift differences encountered as compared to proton nmr. The results in all the examples so far studied confirm the conclusions reached above; thus the *t*-hexyl cation (**17-H**) and the *t*-heptyl cation (**17-CH₃**) are both equilibrating ions while the tetramethylethylenecarbonium ion (**17-Cl**) is bridged. In addition, the ethylene-*p*-anisonium ion (**5**) has been demonstrated by ¹³C nmr to have the bridged structure, the results being incompatible with either a pair of rapidly equilibrating primary or π -bridged carbonium ions.

Table VII. Nmr Shifts of *p*-X-Phenyldimethylcarbinols^a

X	Aromatic	Me	X	Bp, °C (mm)
H	7.25 (m) ^c	1.43	...	51 (1)
CH ₃	7.25, 6.95	1.45	2.28	48 (0.3)
OCH ₃	7.25, 6.68	1.43	3.68	80 (0.03)
CF ₃ ^b	7.55	1.52	φ + 63.21	57 (0.9)

^aCCl₄. ^bMp 42°. ^cm = multiplet.

phenone. The nmr spectra and boiling points are listed in Table VII.

p-X-Phenyldimethylcarbinyl chlorides²⁶ were prepared by reaction of the appropriate carbinol with HCl at 0° (H, CH₃, OCH₃) or with Lucas reagent (CF₃) at 20°. Their nmr spectra are listed in Table VIII.

2,3-Dimethyl-2-chlorobutane was prepared by chlorination of tetramethylethylene with anhydrous HCl at 0° in CH₂Cl₂; nmr (CCl₄) septuplet (*J* = 6.3 Hz) δ 1.88 (1), singlet 1.51 (6), and doublet (*J* = 6.3 Hz) 1.05 (6).

1-*p*-CF₃-Phenyl-1-*t*-butylethylene. Five grams of *p*-CF₃-phenyl-*t*-butylmethylcarbinol was stirred overnight with a mixture of 50 ml of ether and 50 ml of thionyl chloride. Evaporation of the solvent and excess thionyl chloride yielded a foul-smelling residue which had no hydroxyl in the ir and nmr chemical shifts which were very similar to those of the starting alcohol. Distillation at 2.5 mm yielded the title compound, bp 75° (7 mm); nmr (CCl₄) δ 7.52 (2), 7.22 (2), 5.21 (1), 4.76 (1), and 1.12 (9); ¹⁹F φ 63.16.

Anal. Calcd for C₁₃H₁₈: C, 82.05; H, 9.53. Found: C, 81.80; H, 9.35.

2,3,3-Trimethyl-2-chlorobutane was obtained from Aldrich.

Nmr spectra were obtained on Varian Associates Model HA 100 (¹H) and A56-60A (¹⁹F) nmr spectrometers. Unless otherwise indicated, all proton shifts are in SO₂ solvent from external (capillary) TMS. Shifts in CCl₄ (internal TMS) may be converted to SO₂ (external TMS) by an upfield shift of 0.25 ppm. For the

Table VIII. Nmr Shifts of *p*-X-Phenyldimethylcarbinyl Chlorides^a

X	Aromatic	Me	X
H	7.40 (m) ^b	1.97	...
CH ₃	7.38, 7.07	1.92	2.31
OCH ₃	7.40, 6.75	1.95	3.75
CF ₃	7.68	1.99	φ + 63.63

^aCCl₄. ^bm = multiplet.

compounds in this paper, the maximum error in this procedure is δ 0.03. ¹⁹F shifts are from CCl₃F in a separate tube (ions) or from internal CCl₃F as solvent (covalent precursors).

Preparation of the Ions. SbF₅ (0.075 ml) was dissolved in 0.5 ml of SO₂ at -10°. The solution was then cooled to -78° causing most of the SbF₅ to precipitate out of solution. The organic chloride (50 mg) was then carefully added to the surface of the SO₂ solution. After standing for 3 min to allow the organic precursor to cool to -78°, the solution was then stirred at -78° until the insolubles dissolved. Generally 5 min was required for the benzylic chlorides and 15-20 min for the tertiary chlorides. As the ion is quite soluble in SO₂ at this temperature, but SbF₅ and organic chlorides are almost insoluble, ionization proceeds at a moderate rate.

Quenching experiments with methanol were carried out as described previously.⁶ In preparative scale runs with analysis by nmr the yields were over 75%.

Acknowledgment. Support of the work by grants of the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged. Texaco, Inc., is thanked for a graduate fellowship (M. B. C.). Professor H. C. Brown is thanked for critical discussions.

Polar Additions to the Styrene and 2-Butene Systems.¹ I. Distribution and Stereochemistry of Bromination Products in Acetic Acid

John H. Rolston² and Keith Yates

Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada. Received October 5, 1968

Abstract: The products of bromine addition in acetic acid have been investigated for a series of ten ring- and side-chain-substituted styrenes and for *cis*- and *trans*-2-butenes. The styrenes generally give substantial amounts of acetoxy bromides as well as the expected 1,2-dibromides, but the butenes give almost exclusively dibromide under the same conditions. The acetoxy bromides isolated are shown to be the 1-acetoxy-2-bromo derivatives, with one exception. The additions to the styrenes are nonstereospecific, although *trans* addition is favored, whereas additions to *cis*- and *trans*-2-butenes are completely stereospecific and *trans*. Acetoxy bromide formation was found to be more stereoselective than dibromide formation. The results are taken as evidence that the intermediates formed in the styrene reactions resemble open α-phenylcarbonium ions more than bromonium ions.

It is widely accepted that the electrophilic addition of bromine to olefins in polar solvents proceeds stereospecifically and *trans*. Further, it is generally held that

this stereospecificity results from the formation of cyclic bromonium ion intermediates of the type originally postulated by Roberts and Kimball.³ However despite their long-standing acceptance the evidence on which these intermediates is based can hardly be considered

(1) Presented in part at the 50th Canadian Chemical Conference, Toronto, June 1967.

(2) Department of Chemistry, King's College, University of London, London.

(3) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).