of isopropylated and *n*-propylated products are in the ratio of ca. 20:1 for toluene, and ca. 10:1 for the xylenes. Interestingly, the isomeric composition of products is similar, except for a somewhat higher extent of ortho substitution for *n*-propylation.

(17) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 5935 (1972).

(18) J. L. Franklin in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer Ed., Wiley, New York, N.Y., 1968, p 77.

(19) For instance, in the case of toluene, $\Delta H^\circ \simeq -9$ kcal mol^{-1} for protonation, and -14 kcal mol^{-1} for hydride ion abstraction. For the protonation of xylenes, $\Delta H^\circ \simeq -12$ kcal mol^{-1} (cf. ref 20).

(20) Values arrived at calculating ΔH_f° of I from the ΔH_f° values of dimethylisopropylbenzenes, deduced from D. R. Stull, E. F. Westrum Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969, and using the gas-phase PA of xylenes, according to (a) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976), and (b) J. L. Devlin III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976). Isopropylation of toluene is estimated to be less exothermic by at least 6 kcal mol^{-1} with respect to that of *m*-xylene.

(21) Alkylation of cumene by i-$C_3H_7^+$ has been observed by M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **89**, 1047 (1967), in methane at 1 Torr.

(22) ΔH° for cumene protonation with CH_5^+ is ca. -53 kcal mol^{-1} and the excitation energy is of course distributed between the product, i.e., the arenium ion and CH_4.

(23) Theoretical and experimental data suggest that an additional methyl substituent increases appreciably the gas-phase proton affinity of an arene. In addition to ref 20b, *cf.* (a) S.-L. Chang and J. L. Franklin, *J. Am. Chem. Soc.*, **94**, 6630 (1972), and (b) J. L. Devlin III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976). On the relative instability of ipso-alkylated ions, cf. D. Heidrich, M. Grimmer, and B. Sommer, *Tetrahedron*, **32**, 2027 (1976).

(24) The activation energy for 1,2-hydrogen shifts in arenium ions is comparatively low, e.g., only 10–11 kcal mol^{-1} in methylbenzenium ions, as measured in acidic solutions by C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **34**, 165 (1962). See also, for gaseous cations, F. H. Field in "Ion-Molecule Reactions", Vol. 1, J. L. Franklin, Ed., Butterworths, London, 1972, p 283.

(25) The free energy of activation for 1,2-methyl group shifts in methylbenzenium ions, measured in HF-SbF$_5$ systems by D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 611 (1968) ranges from 15 to 22 kcal mol^{-1}. Consequently, the difference between the activation energies for the migration of the methyl and, respectively, the isopropyl group is necessarily much lower than the excitation energy of the arenium ions from the alkylation process 1.

(26) L. Friedman and A. T. Jurewicz, *J. Am. Chem. Soc.*, **91**, 1808 (1969).

(27) R. Nagane, O. Kurihora, and A. Takematsu, *J. Org. Chem.*, **36**, 2753 (1971).

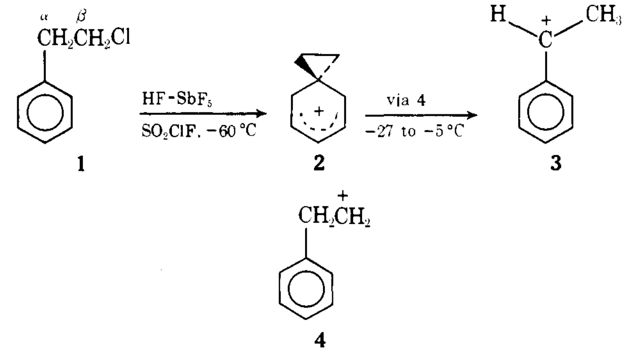
Rearrangement and Equilibria of Ions Formed from Side-Chain Substituted β-Phenylethyl Chlorides under Stable Ion Conditions[1]

George A. Olah,* Robert J. Spear,[2a] and David A. Forsyth[2b]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received August 23, 1976*

Abstract: Ionization of a series of β-arylethyl chlorides, substituted at C_α and/or C_β by methyl groups, with aryl = phenyl and *p*-methoxyphenyl, has been studied under stable ion conditions. The 1-aryl-2-chloropropanes and 3-aryl-2-chlorobutanes ionize exclusively to rearranged benzyl cations. Under these same conditions, neophyl chloride and 2-chloro-2-methyl-1-phenylpropane undergo competing ionization–rearrangement and protolytic cleavage reactions. The ethyl-*p*-methoxyphenyl carbenium ion (**9**) was found to be 8–10 kcal/mol more stable than the isomeric 1-*p*-methoxyphenyl-2-propyl cation (**10**) and this relatively small energy difference is regarded as strong support for π bridging in **10**. Benzylic and/or equilibrating cations are formed upon ionization of 3-aryl-2-chloro-2,3-dimethylbutanes. The relative stabilities are determined by the para substituent; methoxy exclusively forms the static benzyl cation, protonated methoxy (HO^+CH_3) the degenerate equilibrating β-phenylethyl cations, while the ion derived from the parent (phenyl) system is equilibrating with contributions from both benzyl and β-phenylethyl cations. There is no evidence for formation of σ-bridged ethylenearenium ions from any of the side-chain substituted β-phenylethyl systems studied.

Ionizations performed under "stable ion" conditions can potentially yield information unobtainable from normal solvolytic studies. Specifically, the exceedingly long ion lifetimes allow rearrangements which may be too slow to occur during solvolyses to be studied, thus experimental determination of energy differences between thermodynamically favored ions and their highly unstable transformation intermediates becomes feasible. Consider the recent study from our laboratories[3] where 2-chloroethylbenzene (**1**) was found to quantitatively ionize in fluoroantimonic acid (HF-SbF$_5$) to the ethylenebenzenium ion (**2**).[4] Subsequently, **2** was observed to rearrange to the methylphenylcarbenium ion (**3**) via the highly unstable intermediate **4**. This rearrangement has no solvolytic analogy;[5] the "hot" carbocations formed by deaminative acetolysis of 2-phenylethylamine, where 18% of products derive from **3**, do not rearrange via **2**.



The energy of activation for the transformation of **2** to **3** was found to be only 13.0 kcal/mol.[3] This value, which must closely approximate the energy difference between **2** and **4**, encouraged us to examine some derivatives of **1** in the anticipation that relative energies of substituted ions derived from **2** to **4** could be elucidated. Accordingly, we chose derivatives of **1** substituted by groups able to stabilize these ions by electron donation, namely methyl groups at C_α and/or C_β, and a *p*-methoxy group on the aromatic ring. Although the energy of all ions corresponding to **2**, **3**, and **4** should thus be lowered, energy differences should still be experimentally detectable.

Previous studies of alkylated 2-phenylethyl systems under stable ion conditions were hampered by the formation of only benzylic ions (cf., **3**) or complex equilibria involving ions of type **3**, **4**, and possibly **2**.[5d] In the work we present in this study,

Table I. ^1H NMR Parameters[a] for Ions Derived from Substituted β-Phenylethyl Chlorides

Ion	Temp, °C	H(2), H(6)	H(3), H(5)	H_4 *or* OCH_3	^+CH	CH_2	CH_3
6[b]	−78	8.75-9.4 (m)	8.46 (t) $J = 8$ Hz	8.75-9.4 (m)	10.50 (t) $J = 8$ Hz	4.05 (m)	1.89 (t) $J = 7$ Hz
9[b]	−115	9.06 8.70	7.80	4.75	9.40	3.52	1.58
	−105	8.96 (d) 8.60 (d)	7.69 (t)	4.63	9.15 (t)	3.43 (m)	1.56 (t)
	−90	8.97	7.87	4.88	unobsd	unobsd	1.75
	−50	9.00	7.92	5.12	5.9 (br)	5.9 (br)	1.75
	−30	8.91	7.84	5.01	5.75 (br)	5.75 (br)	1.72 (q) $J = 4.8$ Hz
16[b]	−40	8.90 (d) $J = 8.5$ Hz	8.10 (t) $J = 8$ Hz	8.75 (t) $J = 8$ Hz		3.88 (q) $J = 8$ Hz	1.74 (t) $J = 8$ Hz
30[b]	−40	9.11 (d) $J = 9.5$ Hz	7.92 (d) $J = 9.5$ Hz	5.13		3.96 (q) $J = 7.5$ Hz	1.76 (t) $J = 7.5$ Hz
38[b]	−80	8.64	7.96	8.39			2.39
43[b,c]	−80	7.88	7.88	5.11 (d) $J = 4$ Hz			3.01

[a] Chemical shifts in parts per million from external (capillary) Me_4Si. Coupling constants are in hertz. Multiplicities, given in parentheses, are: s = singlet; d = doublet; t = triplet; q = quartet. [b] In $HF-SbF_5-SO_2ClF$. [c] ^+OH, δ 11.30 (q), $J = 4$ Hz.

Table II. ^{13}C NMR Parameters[a] for Ions Derived from Substituted β-Phenylethyl Chlorides

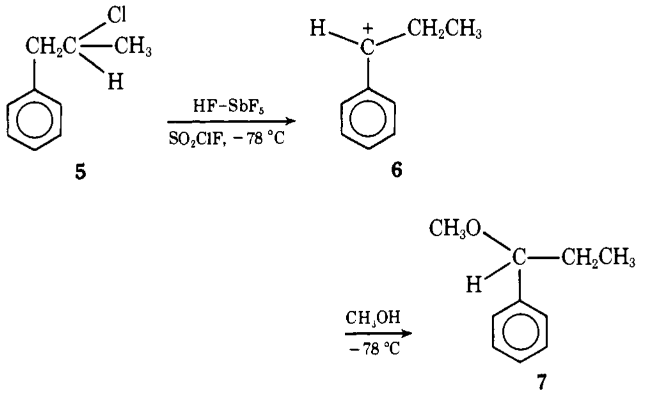
Ion	Temp, °C	C(1)	C(2), C(6)	C(3), C(5)	C(4)	C^+	Additional
2[b,c]	−70	68.8	171.8	133.4	155.4		CH_2, 60.7
3[b,c]	−70	142.4	C(2), 143.8 C(6), 155.3	134.3 133.9	162.0	229.8	CH_3, 27.2
6[c]	−75	140.4	C(2), 143.6 C(6), 155.0	133.8 133.6	161.3	234.4	CH_2, 34.7, $^1J_{CH} = 130.2$ CH_3, 12.1, $^1J_{CH} = 132.7$
9[c]	−90	134.65	C(2), 144.7 C(6), 155.7	119.1 121.9	183.9	203.0 (d) $^1J_{CH} = 157.7$	CH_2, 29.15 (t), $^1J_{CH} = 130.2$ CH_3, 11.85 (q), $^1J_{CH} = 129.9$; OCH_3, 60.85 (q), $^1J_{CH} = 152.3$
	−70	135.85	C(6), 156.1 (br) C(2), 146.0 (br)	120.3 (br)	180.3	212.8	CH_2, 31.45; CH_3, 12.1; OCH_3, 63.85
	−40	135.7	150.4 (br)	120.8	184.35	206.2 (q) $^1J_{CH} = 67.3$	CH_2, 30.0 (q), $^1J_{CH} = 87.8$; CH_3, 12.15 (q), $^1J_{CH} = 130.2$; OCH_3, 62.15 (q), $^1J_{CH} = 152.4$
16[c]	−40	139.5	140.9	132.8	155.5	259.8	CH_2, 39.9; CH_3, 31.3; 16.9
21[c]	−40					331.9	CH_2, 62.1; CH_3, 46.2
22[c]	−40					313.5	CH_2, 59.2; CH_3, 47.1, 10.5
30[c]	−60	133.3	144.0 145.2	118.4	164.8	270.2	CH_2, 42.8; OCH_3, 72.6 CH_3, 34.0, 17.0
38[d]	−115	135.2	141.0	131.7	147.6	unobsd	CH_3, 32.0
	−95	135.55	140.95	131.65	147.9	unobsd	CH_3, 32.0
	−80	136.1	141.0	131.75	148.25	164 (br)	CH_3, 32.1
	−60	136.35	140.95	131.8	148.4	164.3	CH_3, 32.3
	−40	136.65	141.0	132.0	148.6	164.55	CH_3, 32.6
43[c]	−70	141.7	131.1	120.1	152.8	199.3	CH_3, 35.9; OCH_3, 75.0

[a] Chemical shifts are in parts per million from external (capillary) Me_4Si. Coupling constants are in hertz and multiplicities (in parentheses) are: t = triplet; q = quartet; d = doublet. [b] Data from ref 3. [c] In $HF-SbF_5-SO_2ClF$. [d] In $FSO_3H-SbF_5-SO_2ClF$.

a number of such rearrangements have also been observed. A number of interesting equilibrating systems have been detected, and data relating to energy differences between ions have thus been obtained. The structure and relative energies of substituted ions derived from **3** and **4** will be shown to follow a systematic, expected sequence according to substitution. Ions derived from **2** do not form from any 2-phenylethyl systems used in this study, and it would appear that only the parent chloride (**1**) and its ring-substituted derivatives require aryl participation for ionization under stable ion conditions (thus leading to **2** and ring-substituted derivatives).

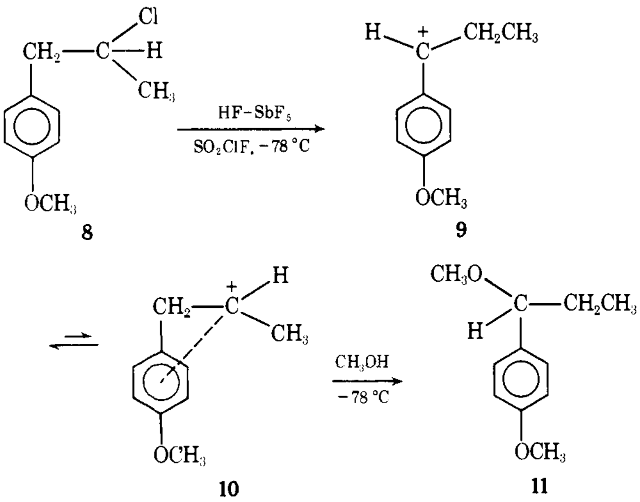
Results and Discussion

1-Aryl-2-propyl Systems. Ionization of 2-chloro-1-phenylpropane (**5**) in $HF-SbF_5-SO_2ClF$ at −78 °C affords a single



ion, readily identified from its ^{1}H and ^{13}C NMR data (Tables I and II) as the ethylphenylcarbenium ion (**6**). Quenching of the ion solution in methanol at −78 °C gave an almost quantitative yield of 1-methoxy-1-phenylpropane (**7**).

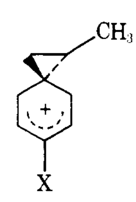
2-Chloro-1-(*p*-methoxyphenyl)propane (**8**) undergoes an analogous reaction in HF-SbF$_5$-SO$_2$ClF, yielding the ethyl-*p*-methoxyphenylcarbenium ion (**9**). However, the ^{1}H NMR spectrum of **9** (Table I) is markedly temperature dependent; at −40 °C, the methyl, δ 1.75, resonates as a quartet, $J = 4.8$ Hz, while the remaining three side-chain protons resonate as a broadened absorption at δ 5.75. Lowering the temperature to −105 °C results in a reversible change, leaving the methyl resonance now a triplet, $J = 7$ Hz, while the broadened δ 5.75 absorption separates into a triplet, intensity one proton, at δ 9.15, and a multiplet, intensity two protons, at δ 3.43. These observations are consistent with a rapid equilibration between **9** and the secondary ion **10** such that, at −40 °C, all three protons attached to C$_\alpha$ and C$_\beta$ are equivalent on the NMR time scale. At −105 °C, these rapid hydride shifts are frozen out, suggesting an energy barrier of 8-10 kcal/mol for the process. The concentration of **10** at equilibrium must, however, be exceedingly low, since quenching with methanol at −78 °C gave an almost quantitative yield of 1-methoxy-1-(*p*-methoxyphenyl)propane (**11**).



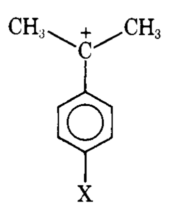
8 **9** **10** **11**

This conclusion is supported by the proton-decoupled ^{13}C NMR spectrum of $\mathbf{9} \rightleftharpoons \mathbf{10}$ (Table II), which although exhibiting small changes in resonance positions with temperature, is unquestionably that which would be expected were **9** the only species present (cf., **6**, Table II). The result of the fast hydride shifts can be seen in the proton-coupled ^{13}C NMR spectrum at −40 °C where *both* the "HC$^+$" and "CH$_2$" resonances are quartets of diminished coupling.

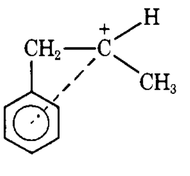
The formation of **6** and **9** upon ionization of **5** and **8**, respectively, can most readily be rationalized by a simple 1,2-hydride shift. The intermediacy of the σ-bridged ions **12-H** and **12-OMe**, as a reaction intermediate, can be discounted, since **12** would be expected to form the tertiary cations **13** in competition with formation of **6** and **9** and neither **13-H** nor **13-OMe** are observed.[6] It is interesting to note that the formation of **6** from **5** under conditions of Friedel-Crafts alkylation has recently been reported.[7]



12, X = H, OMe



13, X = H, OMe



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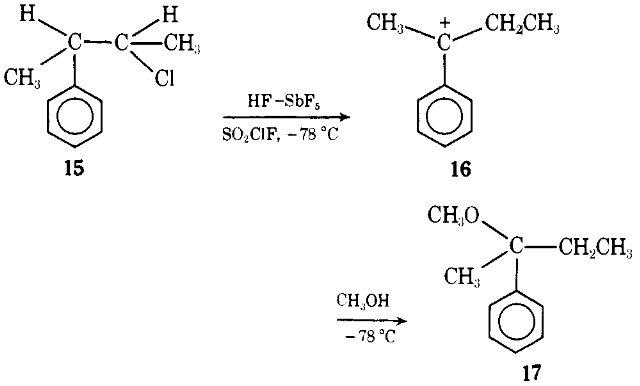
The energy barrier to the 1,2-hydride shifts in $\mathbf{9} \rightleftharpoons \mathbf{10}$, 8-10 kcal/mol, is lower than would be expected were **10** a simple secondary ion. Some interaction between the *p*-methoxyphenyl group and the secondary carbenium center must therefore stabilize **10**, and the obvious answer is π bridging.[5d,8] The transition state for the 1,2-hydride shift should thus also be stabilized, and the very low concentration of **10** at equilibrium suggests that **10** lies very close to the transition state on the energy profile.

The apparent inability to observe an analogous equilibration in **6**[9] is readily accommodated by the assumption that the energy of the 1-phenyl-2-propyl cation (**14**) and the transition state for the 1,2-hydride shift in $\mathbf{6} \rightleftharpoons \mathbf{14}$ are raised to an experimentally inaccessible value due to the diminished capability of the unsubstituted phenyl group to stabilize these intermediates.

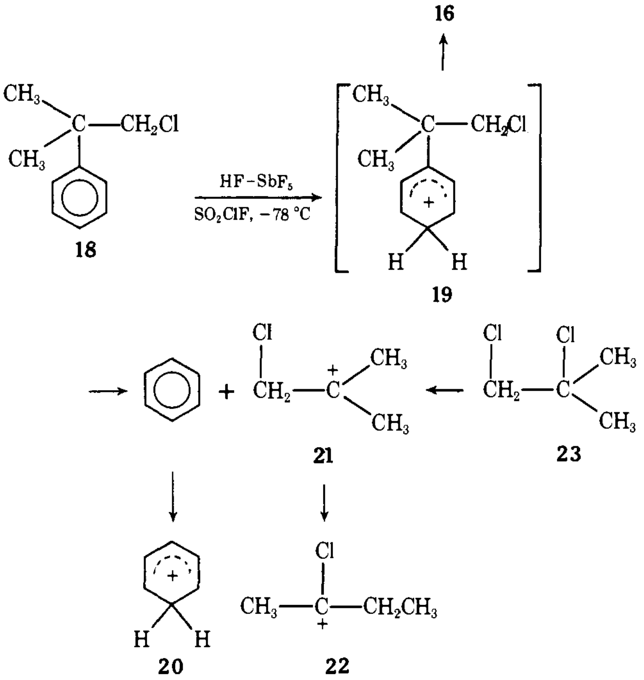
3-Aryl-2-butyl, Neophyl, and 1-Aryl-2-methyl-2-propyl Systems. The concept of σ-bridged ethylenearenium ions[4] originated from Cram's solvolytic studies of 3-aryl-2-butyl derivatives.[5] Several previous attempts[10-12] to observe ethylenearenium ions from molecules of this type under stable ion conditions were unsuccessful and only rearranged benzylic ions were detected. Dissolution of 2-chloro-3-phenylbutane (**15**, mixture of threo and erythro isomers) in HF-SbF$_5$-SO$_2$ClF at −78 °C parallels these earlier studies, with the 2-phenyl-2-butyl cation (**16**) being exclusively formed. Quenching the ion solution in methanol at −78 °C gave 2-methoxy-2-phenylbutane (**17**) in almost quantitative yield. Neither the ^{1}H nor ^{13}C NMR spectrum of **16** is temperature dependent (Tables I and II). The transformation of **15** to **16** was shown previously,[10] by deuterium labeling, to involve competing phenyl and hydride shifts; hydride shifts were only observed from the erythro isomer while phenyl shifts predominated in the threo isomer.



15 **16** **17**

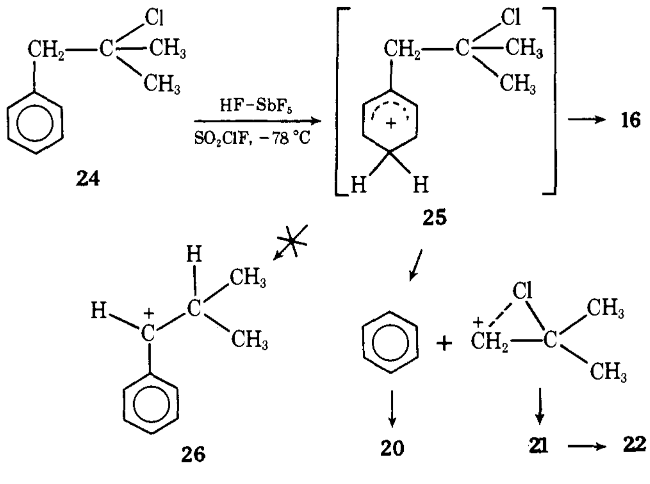
Ionization of the primary isomer, 1-chloro-2-methyl-2-phenylpropane (neophyl chloride, **18**), proceeds via two competing reactions. The benzenium ion **19** cannot be observed, but its intermediacy can be inferred from the products; deprotonation-ionization with a subsequent 1,2-methyl shift yields **16**, while proton migration followed by cleavage of the side chain gives benzene (which immediately protonates to the rapidly equilibrating benzenium ion **20**[13]) and the 1-chloro-2-methyl-2-propyl cation (**21**). This latter reaction is analogous to that observed for *tert*-butylbenzene under the same conditions.[13] It seems likely that **5** and **15** also initially protonate to benzenium ions (cf., **1**),[3] but do not subsequently undergo cleavage reactions. The reaction scheme is further complicated by rearrangement of **21** to the 2-chloro-2-butyl cation (**22**) which occurs, under these conditions, slowly at −78 °C and more rapidly at higher temperatures.[14] In a typical experiment, **16**, **20**, **21**, and **22** can all be observed (by ^{1}H or ^{13}C NMR spectroscopy, Tables I and II) in solution (Scheme I); about 65-75% of the reaction proceeds via the ionization route (to **16**), while the remainder produces cleavage to **20**, **21**, and subsequently **22**. The presence of **21** and **22** was confirmed by addition of 1,2-dichloro-2-methylpropane (**23**) and the concordance of the ^{1}H NMR spectra with previously reported values.[14] The presence of **20** was similarly confirmed by addition of benzene.

Scheme I



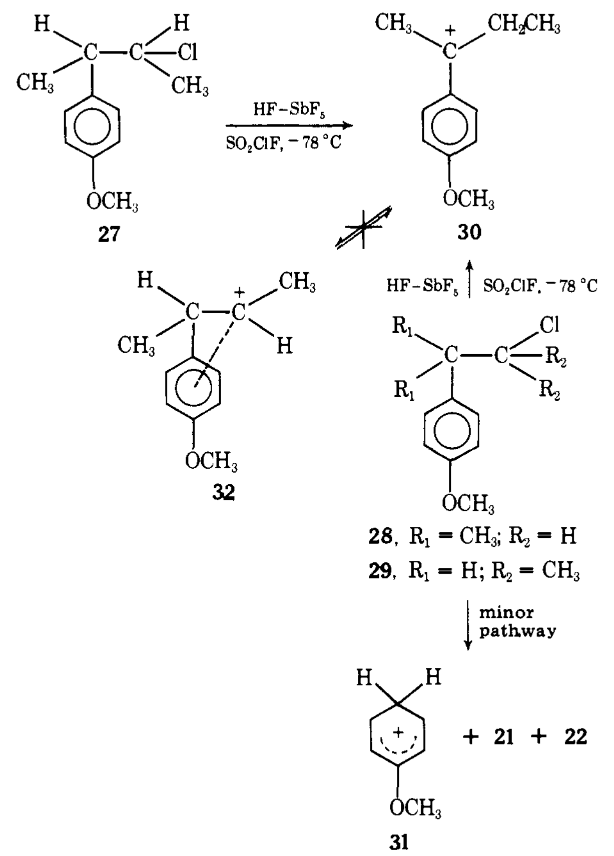
Surprisingly, dissolution of the tertiary isomer, 2-chloro-2-methyl-1-phenylpropane (**24**), in HF-SbF$_5$-SO$_2$ClF at −78 °C gave a solution of **16, 20, 21**, and **22** in ratios almost identical with **18** (Scheme II). The simple hydride shifted ion **26** is not observed, despite the necessity for concurrent phenyl and methyl shifts to generate **16**. The similarity of the results for **18** and **24** suggests that a common intermediate is involved, but this could not be verified experimentally. By analogy with the results for **18**, the reactions of **24** probably involve the initial intermediacy of the benzenium ion **25**.

Scheme II



The p-methoxy derivatives **27–29** all ionize in HF-SbF$_5$-SO$_2$ClF at −78 °C to the rearranged benzyl cation **30** (Tables I and II, Scheme III). The competing cleavage reaction from **28** and **29** constitutes only a very minor pathway, and the p-methoxybenzenium ion (**31**), **21**, and subsequently **22**, are observed in only very low concentrations. The ^{13}C and ^{1}H NMR spectra of **30** show no temperature dependence over the range −105 to −5 °C. This result is predictable from the foregoing, since the additional stabilization of the π-bridged 3-p-methoxyphenyl-2-butyl cation (**32**) over **10** will be smaller than the gain in energy by **30** relative to **9**. The energy required for the 1,2-hydride shift to equilibrate **30** with **32** has thus again been raised to an experimentally inaccessible value; **30** decomposes rapidly above −5 °C.

Scheme III



3-Aryl-2,3-dimethyl-2-butyl Systems. The parent chloride (**33-H**) and its para-substituted derivatives (**33-X**) have been intensely studied both under solvolytic[8b] and stable ion conditions.[12,15] There is a clear difference in conclusion with regard to the structure of the ions formed under these two experimental conditions. Brown[8b] has argued that the solvolytic data, including isotope scrambling, was consistent only with rapidly equilibrating, degenerate, π-bridged ions (**34**). In contrast, data obtained by ionization of **33-X** under stable ion conditions was interpreted to result from the presence of σ-bridged (**35**), benzylic (**36**), and rapidly equilibrating ions;[12,15] X = OCH$_3$ yielded **36-OCH$_3$** as the energy minimum, while it was suggested that X = H resulted in **35-H** being the most stable ion and X = Br or CF$_3$ existed as equilibrating ions with contributions from both **35-X** and the degenerate **34-X**. These differing conclusions will be discussed after presentation of our new data.

Dissolution of **33-H** in either HF-SbF$_5$ or FSO$_3$H-SbF$_5$ in SO$_2$ClF at −78 °C gave an ion (**38**) which is also formed from the isomeric chloride **37-H** under the same conditions. The ^{1}H NMR spectrum (Table I) displays separate ortho, para, and meta proton resonances, while the methyl protons resonate as a sharp singlet; no dependence with temperature is observed. Decomposition of **38** is rapid at temperatures above −30 °C.

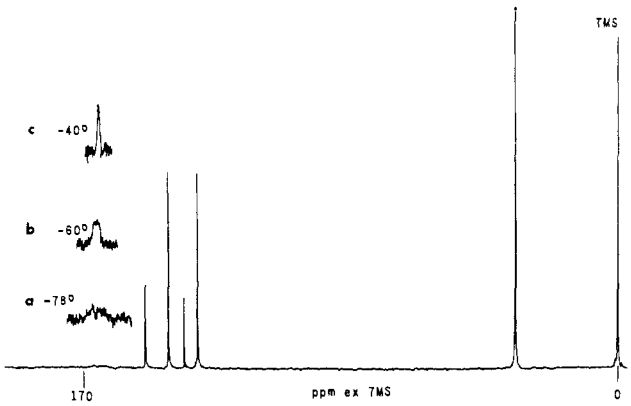
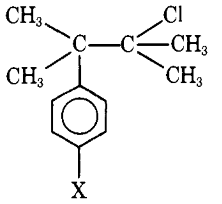


Figure 1. The ^{13}C NMR spectrum of the ion **38**, formed by ionization of 2-chloro-2,3-dimethyl-3-phenylbutane (**33-H**) in FSO_3H-SbF_5-SO_2ClF at −78 °C. The lower spectrum was recorded at −90 °C, while the inserts (a)-(c) depict changes in the carbon resonance at approximately δ 164 as the temperature was raised to −78, −60, and −40 °C, respectively.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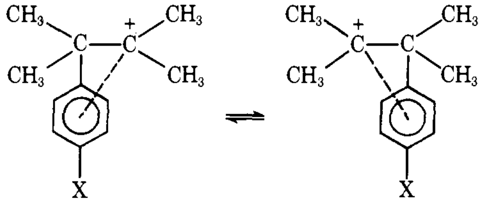
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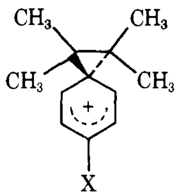
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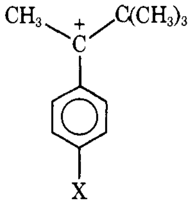
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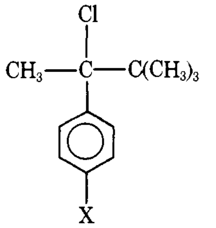
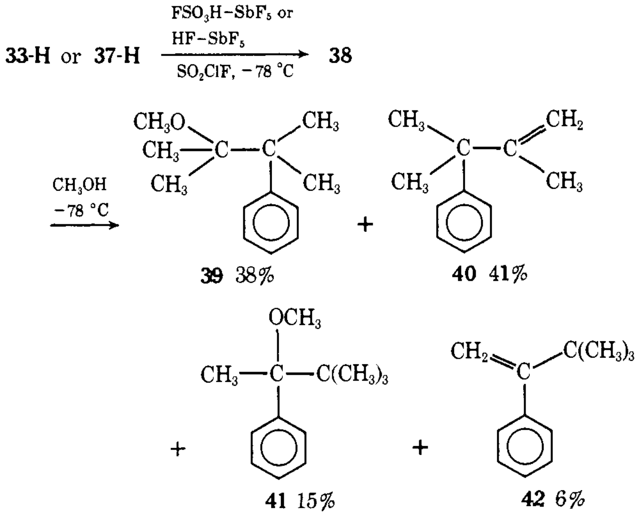

37

The ^{13}C NMR spectrum (Table II), however, exhibits a rather unusual temperature dependence, as shown in Figure 1. At −115 °C there is a missing peak which appears as a very broad singlet, approximately δ 164, at −78 °C, then sharpens as the temperature is raised to −60 °C then −40 °C. This process is completely reversible and the resonances for the other carbon atoms show no sharpening with increased temperature, although their resonance positions show small dependencies in some cases, but none in others (Table II).

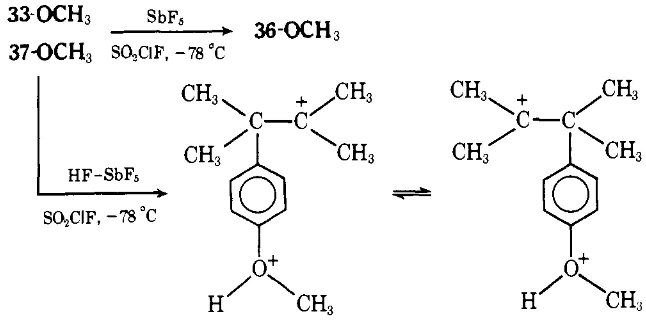
The ^{13}C FT NMR spectrum of **38** is not consistent with structure **35-H** which was assigned previously based on INDOR and limited FT data.[12,15,16] The ^{13}C shift of C(1) in **35-H**, due to its approximately tetrahedral hybridization, would be expected at a maximum of δ 100, by analogy with the shielded position of C(1) in **2** (Table II).[18] The resonance position observed experimentally for C(1), δ 135.2-136.65, is typical of ipso carbons in phenyl carbenium ions[20] (cf., also, to the corresponding shifts in **3-30** in Table II). It has also been noted previously that a cyclopropyl group strongly deshields the directly attached carbon atoms[3,21] and thus, by analogy with **2**, C(2) = C(6) in **35-H** would be strongly deshielded relative to C(4), and this is not observed for **38** (Table II). Quenching of **38** with methanol at −78 °C gave **39-42** in the percentages shown in Scheme IV.

Scheme IV



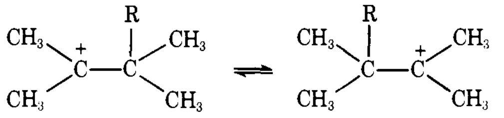
39 38% **40** 41% **41** 15% **42** 6%

The product from ionization of **33-OCH$_3$** or **37-OCH$_3$** is dependent upon the superacid used. SbF_5 in SO_2ClF at −78 °C affords, from both precursors, the static benzylic ion **36-OCH$_3$**,[12,15] while HF-SbF_5 in SO_2ClF at −78 °C yields an ion (**43**) whose ^1H and ^{13}C NMR parameters are shown in Tables I and II, respectively. The ^1H NMR spectrum of **43** shows the equivalent methyl protons substantially deshielded from **38**, while the methoxy methyl group, a doublet, with the corresponding quartet at δ 11.30, shows the methoxy group to be protonated, as shown on **43** below.[22] The equivalent meta and ortho protons resonate at a position normally observed for meta protons in phenyl carbenium ions (cf., data for **6-30** in Table I) and indicate minimal charge localization in the aromatic ring except by inductive electron withdrawal. This conclusion is confirmed by the ^{13}C NMR shifts for the ortho and meta carbons, which are only slightly deshielded from neutral benzene derivatives.[19,20] In contrast to **38**, the ^{13}C NMR spectrum of **43** shows no temperature dependence.



43

What processes are responsible for the equivalence of C_α and C_β and their attached methyl groups in **43**? The discussion presented above for **38**, when applied to the data for **43**, rules out participation from σ-bridged ions and the HO^+CH_3 group would be expected to severely destabilize the benzylic species **36-HO$^+$CH$_3$**. An important clue is the chemical shift of C_α=C_β, δ_C 199.3, which lies between the corresponding shifts for the equilibrating 2,3,3-trimethyl-2-butenyl (**44**, δ_C 205.3)[17,23] and 2,3-dimethyl-2-butenyl (**45**, δ_C 197.2)[17,23] cations.



44, R = CH_3
45, R = H

The shift of $C_\alpha{=}C_\beta$, combined with the conclusion that virtually no charge is localized into the aromatic ring, leads only to **43** being the degenerate equilibrating ions as shown above. Any π delocalization (cf., **34**) must be minimal. Curiously, quenching of **43** with methanol at −78 °C gives products predominantly derived from **36-OCH$_3$**, but this is understandable since the lowered acidity initially leads to deprotonation of **43**, which rearranges to **36-OCH$_3$** and then reacts with methanol.

We have therefore determined the two limiting cases; OCH_3 is the most stabilizing substituent we can study under these conditions and leads exclusively to the static benzylic ion **36-OCH$_3$**, while HO^+CH_3 is the most destabilizing substituent and results in the degenerate equilibrating ion **43**, where there is no detectable charge delocalization into the aromatic ring.

But what of the parent ion **38**? The quenching data, to yield **39–42**, suggest that both benzylic and equilibrating ions contribute to the total ion structure.[24] Sorenson[25] has recently reported the ^{13}C NMR spectrum of the interconverting 2,3-*endo*-dimethyl and 2,3-*exo*-dimethyl-2-norbornyl cations, and a similar broadening and eventual disappearance of the carbenium carbon resonance to that shown in Figure 1 was observed, as well as minor changes to other carbon resonances. This interconversion, which proceeds via two Wagner-Meerwein and one 6,2-hydride shifts,[25] suggests by analogy that several processes may contribute to the equilibrium in **38**. Certainly any process which would rapidly exchange the methyl groups, and C_α and C_β, in **36-H** must involve **34-H** ions as intermediates.

The combined evidence shows that **38** is a rapidly equilibrating ion where both **34-H** and **36-H** contribute; as discussed above, the presence of **35-H** should be detectable from the ^{13}C NMR shifts, if present in significant concentration. It must be concluded that **35-H** is only a transition state or present in low concentration in the degenerate interconversion of **34-H** and is not a detectable intermediate.

The inability to freeze out the equilibration processes in **38**, even at temperatures as low as −120 °C, prevents an accurate determination of the relative populations of **34-H** and **36-H** and hence their relative energy levels. The lack of separate chemical shift data for the two ion types also prevents an accurate line-shape treatment of the data to determine the energy barriers in the interconversion processes. However, rough estimates of these quantities can be made by using model compounds to predict the relevant chemical shifts.

The averaged chemical shift for C_α and C_β, δ_C 164, which is evident at −78 °C and above, indicates that **36-H** predominates over **34-H** in the equilibrating ion **38**. A shift closer to the δ_C 199.3 observed for **43** would be expected if **34-H** predominated. In **36-H**, an estimate of δ_C 260 for C_α is reasonable, based on C^+ in **16**, and an estimate of δ_C 60 is reasonable for C_β, based on the shift for CH_2 in **16** plus 20 ppm for the effect of two additional methyl groups. The averaged C_α–C_β shift would then be δ_C 160, close to the observed value. The para carbon shift of **38**, δ_C 148.6, indicates only a moderate degree[20] of charge delocalization into the phenyl ring; however, the delocalization could be decreased in **36-H** due to nonplanarity caused by steric interaction between the phenyl and *tert*-butyl groups.

For the purpose of gaining a rough estimate of the energy barriers involved in the equilibration process, ion **38** can thus be considered as **36-H** with δ_C 260 for C_α and δ_C 60 for C_β. Rapid exchange of two singlet peaks separated by 200 ppm (5032 Hz) requires a rate of $1.12 \times 10^4\ s^{-1}$ at the coalescence point.[27] The exact coalescence point cannot be determined precisely in the experimental spectra because of the extreme broadness of the small peak at that point, but the spectrum at −95 °C is a reasonable choice. Using −95 °C as the temperature in the Eyring equation, the coalescence rate translates into a free energy of activation of 5.3 kcal/mol at −95 °C for the interconversion of ions **36-H**. The signal for the methyl carbons shows no temperature dependence because the methyl chemical shifts in **36-H** probably differ by no more than 10 ppm and thus would give a coalesced signal at a much lower temperature.

Although our stable ion data indicate an approximate maximum barrier of only 5 kcal/mol for interconversion processes involving **36-H** and **34-H**, the solvolytic data for **33-X**[8b] indicate **34-X** to be the only intermediates, since no products derived from **36-X** were detected.[28] Solvation differences undoubtedly account for the discrepancy between the solvolytic and stable ion studies, with the delicate energy balance swung in favor of **34-X** in the solvolytic system.

Conclusion

Under stable ion conditions, σ-bridged ethylenearenium ions are formed only from 2-chloroethylbenzene (**1**)[3] and its ring-substituted derivatives. Substitution at C_α and/or C_β leads, upon ionization, to rearranged benzylic and/or equilibrating β-phenylethyl cations. There is no evidence for ethylenearenium ion intermediates in these rearrangements. It follows that ionization of **1** under stable ion conditions must proceed with phenyl participation (to **2**) else the initially formed intermediate **4** would immediately rearrange to **3**, a result observed subsequently from **2**.

Ionization of 1-aryl-2-chloropropanes (**5** and **8**) and 3-aryl-2-chlorobutanes (**15** and **27**) or their isomers (**18**, **24**, **28**, and **29**) yielded only rearranged benzyl cations. Experimental determination of the energy difference between the thermodynamically favored benzylic ions and their isomeric β-phenylethyl cations was only possible for the equilibrating ethyl-*p*-methoxyphenyl carbenium ion (**9**) and 1-*p*-methoxyphenyl-2-propyl cation (**10**), where **10** was found to be 8–10 kcal/mol higher in energy. This relatively small energy difference provides strong support for the concept of π bridging,[5b,8] which lowers the energy of **10** from that of a static 1-aryl-2-propyl cation.

3-Aryl-2-chloro-2,3-dimethylbutanes (**33-X**) form both benzylic and equilibrating ions upon ionization. The benzylic ions are destabilized due to the severe steric crowding in the planar conformation necessary for optimal charge delocalization, and only a *p*-methoxy substituent can swing the delicate balance between the equilibrating π-bridged ions (**34-OCH$_3$**) and benzylic **36-OCH$_3$** to exclusively favor the latter species. In contrast, the extremely destabilizing substituent *p*-HO^+CH_3 exclusively favors the degenerate equilibrating ion **43**, but the ring is now so deactivated that π bridging is undetectably small. The ion derived from the parent chloride (**38**) exists as an equilibrating ion where both the degenerate π-bridged **34-H** and benzylic **36-H** contribute. The energy difference between **34-H** and **36-H** must be <5 kcal/mol. Comparison of data for **38** with data published previously for ions derived from **33-CH$_3$**, **-Br**, and **-CF$_3$**[12,15] shows that these ions must also be equilibrating between **34-X** and **36-X**, and not **35-X**.

Clearly, these results are different from those obtained in solvolytic studies[5] and illustrate the strong effects of solvation and diminished ion lifetimes under nucleophilic conditions. Although studies of β-arylalkyl systems under stable ion conditions cannot, therefore, answer the questions relating to the still controversial solvolytic reactions, the ability to observe thermodynamically favored ions, and in some cases to relate the energy of these ions to less stable species on the energy profile, are in no way less valuable than conventional solvolytic studies.

Finally attention must be called to the obvious similiarities between β-phenylethyl and β-haloethyl systems[29,30] in their ability to form bridged or equilibrating open-chain (partially bridged) ions. The parent primary systems are examples of the former and the tertiary-tertiary tetramethyl-substituted systems for the latter.

Experimental Section

Materials. The substituted β-phenylethyl chlorides used in this study were either available from previous studies (**8**, **33-H**, **33-OCH3**),[12,15] commercial sources (**18**), or were synthesized from the corresponding alcohols using $SOCl_2$ at −40 °C.[6] The alcohols were themselves either commercially available or were synthesized via standard reduction or Grignard reactions on appropriate ketones and esters.

All chlorides were purified by distillation or recrystallization before use. $HF\text{-}SbF_5$ refers to an equimolar solution prepared by addition of anhydrous HF to triply distilled SbF_5. FSO_3H was doubly distilled and $FSO_3H\text{-}SbF_5$ refers to an equimolar solution.

Preparation of Ions. Every ion described in this study was prepared by the following general procedure with the exception of **38**, where $FSO_3H\text{-}SbF_5$ was used in place of $HF\text{-}SbF_5$. Although **38** is also formed in $HF\text{-}SbF_5$, the stability at higher temperatures is markedly reduced in comparison with $FSO_3H\text{-}SbF_5$. A solution of the chloride (300 mg) in SO_2ClF (1.0 mL) at −78 °C was added dropwise, in portions, to a 1:1 (by volume) solution of $HF\text{-}SbF_5$ in SO_2ClF (total volume 2.5 mL) at −78 °C. After vigorous shaking (Vortex mixer) and cooling, the ion solution was transferred by precooled pipette to a precooled NMR tube for study.

Quenching of Ions. The ion solution was added dropwise to methanol at −78 °C while vigorous stirring was maintained. After complete addition, the solution was allowed to warm to 0 °C and was then poured onto ice. The organic products were recovered by extraction into ether.

Product mixtures were analyzed by gas liquid chromatography and ^1H NMR spectroscopy. The identity of each component was confirmed by comparison with authentic samples prepared by standard literature methods.

Nuclear Magnetic Resonance Spectra. ^1H NMR spectra were obtained using a Varian Associates Model A56/60 spectrometer equipped with a variable temperature probe. Probe temperatures were determined by direct insertion of a precalibrated thermometer. Chemical shifts were measured from external (capillary) Me_4Si. ^{13}C NMR spectra were obtained using a Varian Associates Model XL-100 spectrometer equipped with a broad band decoupler, variable temperature probe, and interfaced with a Varian 620-L computer operating with 8192 digital points. Chemical shifts were measured from the ^{13}C signal of 5% ^{13}C-enriched Me_4Si contained in a 1.75-mm tube held concentrically inside the standard 12-mm sample tube. Coupling constants were obtained directly from the spectra recorded in the gyro-gate mode.

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(17) Converted to parts per million from Me_4Si using $\delta_{Me_4Si}{}^{CS_2}$ = 193.8 ppm.

(18) The β-substituent effect[19] produced by the four methyl groups will deshield C(1) in **35-H** relative to **2**, but a maximum shift of 100.0 ppm would be a reasonable estimate.

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