distilled to give a single fraction: bp 79° (0.05 mm) (2.11 g, 50%); n^{23}_{D} 1.4361; ir (film) 3220 and 3450 (NH), and 1240 cm^{-1} (P→O); nmr (DCCl$_3$) δ 1.32 (OCH$_2$CH$_3$), two triplets at 1.85 and 2.15 (CH$_2$ adjacent to P→O, J_{HH} = 7 Hz and J_{PCH} = 18 Hz), two triplets at 3.04 and 3.13 (CH$_2$ adjacent to NH, J_{HH} = 7 Hz and J_{PCCH} = 13 Hz), 3.47 (s, NHOCH$_3$), and 4.08 (m, J = 7 Hz, OCH$_2$CH$_3$).

Anal. Calcd for $C_7H_{18}NO_4P$: P, 14.70; N, 6.63. Found: P, 14.61; N, 6.46.

Registry No.—**1**, 35212-68-1; **6**, 1445-84-7; **7**, 5324-30-1; **8**, 6326-73-4; **9**, 3958-23-4; **10**, 35212-72-7; **11**, 2658-24-4; tris(dipivalomethanato)europium(III), 15522-71-1.

Anisyl Neighboring-Group Participation in Carbonium Ion Formation in Antimony Pentafluoride and Sulfur Dioxide

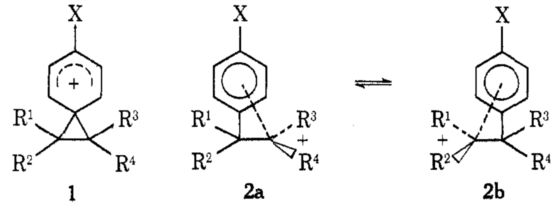
BRIAN G. RAMSEY,*[1,2] JAMES A. COOK, JR.,[3] AND JAMES A. MANNER[3]

Departments of Chemistry, University of Akron, Akron, Ohio 44304, and
California State University, San Francisco, California 94132

Received January 7, 1972[4]

A study by nmr spectroscopy of the carbonium ions formed in $SbF_5 \cdot SO_2$ at −60° from $p\text{-}CH_3OC_6H_4CR_2CR_2X$, $p\text{-}CH_3OC_6H_4CR_2(CH_2)_3X$, and $o\text{-}CH_3OC_6H_4CH_2CH_2X$ was carried out where each R was varied systematically from H to methyl and X was halogen, mesylate, or OH. Except for $p\text{-}CH_3OC_6H_4CH_2CH_2X$, only benzylic ion formation was observed. Where X left from a primary carbon at −60° anisyl migration occurred prior to benzylic ion formation. Where OH_2^+ (or $^+OHSbF_5^-$) leaves from a secondary carbon, D or CD_3 labeling established that less than 60% of the product ion formed could be derived from β-anisyl migration from a secondary or tertiary origin. It was suggested that β-anisylcarbonium ions formed without specific solvation at the carbonium ion center or anisyl participation probably rearrange to benzylic ions much faster than anisyl migration occurs. The activation energy (6 kcal/mol) for equilibration of all alkyl methyl groups in $p\text{-}CH_3OC_6H_4CMeCMe_3^+$ was determined. The o-anisylethyl chloride forms the corresponding oxonium ion in $SbF_5 \cdot SO_2$ rather than an ortho anisonium or benzylic ion. There is no evidence of anisyl participation in the formation of benzylic ions from $p\text{-}CH_3OC_6H_4(CH_2)_4X$ or $p\text{-}CH_3OC_6H_4CMe_2(CH_2)_3X$ in $SbF_5 \cdot SO_2$ at −60°.

Because of our previous success[5] in generating and studying simple alkoxycarbonium ions in strong acid solutions, we became interested in another group of alkoxy-stabilized carbonium ions more commonly known as anisonium ions, or methoxy-stabilized phenonium ions, **1** (X = OCH_3). Phenonium ions have been regarded[6] by many, though not all, as being intermediates in the normal solvolysis reactions of β-arylalkyl primary and secondary halides, tosylates, etc. The well-established[5,7] thermodynamic stability of alkoxycarbonium ions and ability of the p-anisyl group to enhance the solvolysis rates[6b,8] even in systems where anchimeric assistance by other β-aryl groups was contended, seemed when this work was initiated to make the anisyl system ideal for observing phenonium ions directly by spectroscopic means.



Further, it has been demonstrated[9] that apparent discrepancies between observed product ratios and titrimetric rates in β-arylalkyl solvolysis reactions disappear if the reaction rate is treated as a sum of the rates of a neighboring aryl-assisted reaction proceeding through a phenonium ion intermediate (rate constant k_Δ) and either a solvent-assisted rate (k_s) or alternatively[9d] simply unassisted ionization in secondary derivatives as originally proposed by Winstein. The observed rate constants then are k_Δ, corrected by a factor (F) for internal return, plus k_s, *i.e.*, $k_{tit} = Fk_\Delta + k_s$. The success of this treatment does not necessarily mean that k_Δ leads to a phenonium ion intermediate or transition state; a π complex ion (transition state), or ion pair, can yield the same rate expression.

Schleyer[10] argues that in the solvolysis of secondary alkyl tosylates, etc., participation by solvent in the ionization must be very strong and there is no "leakage" or conversion between phenonium ion and the solvent-complexed classical ion. This mechanism accounts for the much larger rate enhancements by β-aryl groups of solvolysis reactions in trifluoroacetic acid, a relatively weak nucleophilic solvent. *Extrapolating this solvent effect model to* $SbF_5 \cdot SO_2$ *would lead to the expectation that the process characterized by* k_Δ *would be the only significant ionization process in this solvent system.* Further, in $SbF_5 \cdot SO_2$ we can expect carbonium

---

[1] Department of Chemistry, California State University, San Francisco, Calif. 94132.

[2] Supported in part by the National Institute of Mental Health.

[3] (a) Taken in part from the Ph.D. theses of James A. Cook, Jr., and James A. Manner. (b) PPG Industries Fellows.

[4] Manuscript originally received by *J. Amer. Chem. Soc.*, Aug 1970.

[5] B. G. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 3058 (1966).

[6] (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965). (b) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968), suggested replacing phenonium ions in most cases by rapidly equilibrating π-bridged β-arylalkyl cations, or more recently ion pairs. (c) H. C. Brown and C. J. Kim, *ibid.*, **93**, 5765 (1971). (d) D. J. Cram, *ibid.*, **86**, 3767 (1964), summarizes the evidence for phenonium ions up to 1964. Numerous papers have appeared since. (e) C. J. Collins has shown that products observed from 3-phenyl-2-butyl tosylate are not inconsistent with rapidly equilibrating open carbonium ions: "Carbonium Ions," Vol. I, Wiley, New York, N. Y., 1968.

[7] H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlid, *Justus Liebigs Ann. Chem.*, **632**, 38 (1960).

[8] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Amer. Chem. Soc.*, **89**, 370 (1967).

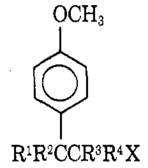
[9] (a) M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969); (b) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291, 4296 (1969); (c) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); (d) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4302 (1969), and leading references.

[10] P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297, 4300 (1969).

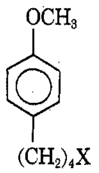
ion behavior to more closely approximate that of "free" unsolvated carbonium ions than that found for carbonium ions, or intimate ion pairs, in more normal solvents such as CH_3OH, acetic acid, etc.

The choice of β-anisylalkyl derivatives as carbonium ion precursors is also made attractive by the considerable amount of work previously reported[6b,8,11] by others on the solvolysis reactions of these systems.

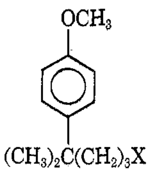
We, therefore, examined the ions produced in $SbF_5 \cdot SO_2$ in the temperature range −60 to −20° from the β-anisyl precursors **3a–g** below, where X is a suitable leaving group such as OH, halogen or mesylate. The formation and nmr spectrum of the parent anisonium ion[12] **1** ($X = OCH_3$, $R^1 = R^2 = R^3 = R^4 = H$) has already been reported and its structure as a static ion firmly[13] established by ^{13}C nmr. The ionization of **3h** (X = Cl) in $SbF_5 \cdot SO_2$ at −60° to give the 1-anisyl-1-propyl cation has also been published.[12] We wish to report here the results obtained for the remaining members of the series **3b–g**, and for **4**, **5**, and **6**, since ions **7**, **8**, and **9** have been postulated as intermediates[14] in the solvolysis of derivatives of **4**, **5**, and **6**.



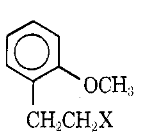
3a, $R^1 = R^2 = R^3 = R^4 = H$
b, $R^1 = Me$; $R^2 = R^3 = R^4 = H$
c, $R^1 = R^2 = Me$; $R^3 = R^4 = H$
d, $R^1 = R^3 = H$; $R^2 = R^4 = Me$
e, $R^1 = R^2 = R^4 = Me$; $R^3 = H$
f, $R^1 = R^2 = H$; $R^3 = R^4 = Me$
g, $R^1 = R^2 = R^3 = R^4 = Me$
h, $R^1 = R^2 = R^3 = H$; $R^4 = Me$



4

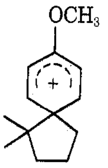


5

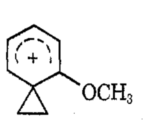


6

7



8



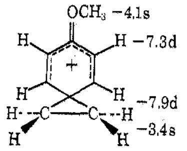
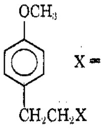
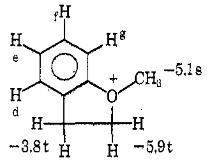
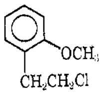
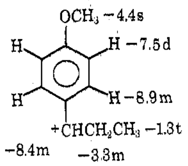
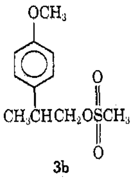
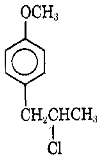
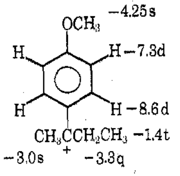
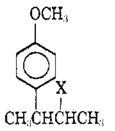
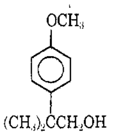
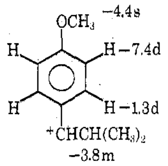
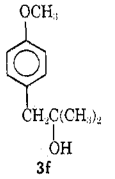
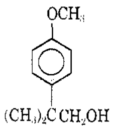
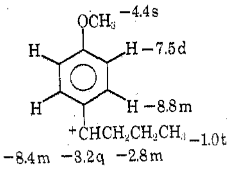
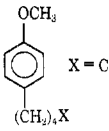
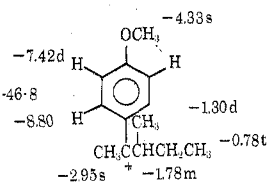
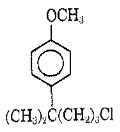
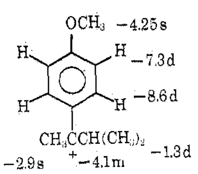
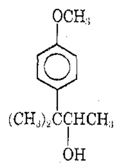
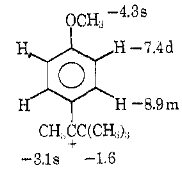
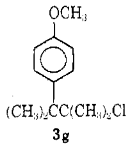
9

Results and Discussion

Some of the spectra presented here are of ions generated from β-anisylalkyl alcohols. Spectra obtained in this way are less clean than those obtained from ionization of corresponding halides or benzylic precursors. We have chosen, however, to present the spectra exactly as obtained rather than "cleaning" them up in any way by deleting peaks of side products. Where there could be any doubt about the presence or identity of any benzylic ion, that ion was also generated from benzylic halides or alcohols to obtain a better spectrum, and a criteria of exact correspondence between both spectra of the ions firmly established the identity of the benzylic ion produced. Chemical shifts, given in Table I, are taken from the best spectrum of the

TABLE I

CATION NMR CHEMICAL SHIFTS (δ) AND β-ANISYL PRECURSORS

Registry no.	Cation	Precursors in $SbF_5 \cdot SO_2$	
12312-28-6		 X = OH, Cl **3a**	
35144-41-3			
18207-34-6		 **3b**	 **3h**
35144-43-5		 **3d**, X = Cl, OH	 **3c** at −20°
35144-44-6		 **3f**	 **3c**
23002-63-3		 X = Cl, Br	
35144-46-8			
35144-47-9		 **3e**	
22666-69-9		 **3g**	

---

[11] C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4289 (1969).

[12] G. A. Olah, E. Namanworth, M. B. Comisarow, and B. Ramsey, *ibid.*, **89**, 711 (1967); **89**, 5259 (1967).

[13] G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

[14] (a) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

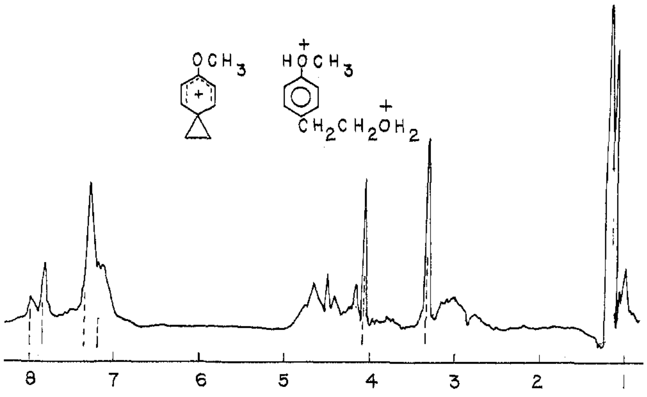


Figure 1.—Nmr spectrum of the reaction mixture from reacting 2-(4-methoxyphenyl)ethanol; chemical shifts for anisonium ion generated from 2-anisyl-1-chloroethane (- - -) with SbF_5 in SO_2 at −70°.

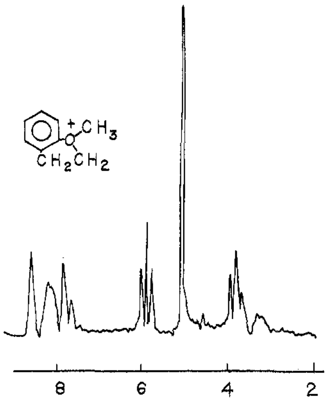


Figure 2.—Nmr spectrum of the reaction mixture of 2-(2-methoxyphenyl)-1-chloroethane and SbF_5 in SO_2. Ionization at −70°, spectrum recorded at −10°.

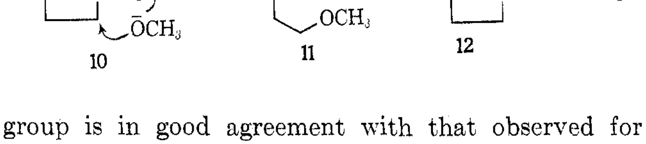
ion available. We will now present the results for each system individually.

The 2-*p*-Anisylethyl System (3a).—The formation of the *p*-anisonium ion from 2-*p*-anisyl-1-chloroethane in $SbF_5 \cdot SO_2$ at −70° has already been reported.[12] We also find, however, that the *p*-anisonium ion can be generated under the same conditions from the alcohol (**3a**, X = OH) with some minor formation of what appears to be the diprotonated ion[12] (Figure 1). This result is important with regard to the study of other systems such as 2-*p*-anisyl-2-methylpropanol, where we were unable to prepare unrearranged derivatives of the alcohol and therefore used the alcohol directly to generate the ions. The "diprotonated ion" itself is stable at −70° and does not convert at any appreciable rate to anisonium ion.

The spectrum of the anisonium ion generated from the alcohol (Figure 1) is certainly not as clean as that previously reported[12] in which the anisonium ion is generated from the chloride, but the simple expedient of overlaying a clean spectrum of the anisonium ion generated from 2-*p*-anisylethyl chloride over the spectrum of Figure 1 is sufficient to remove doubts over the identity of the anisonium ion. Quenching results confirm this conclusion. Figure 1 is provided to enable the reader to compare the kind of spectra which may be obtained from alcohols with those of the same ion generated from alkyl chlorides and also that reported elsewhere.[12]

The 2-(2-Methoxyphenyl)-1-ethyl System (6).—The nmr spectrum of the ion generated from 2-(2-methoxyphenyl)-1-chloroethane in $SbF_5 \cdot SO_2$ (Figure 2) is stable over the temperature range −70 to −10° and is most consistent with the formation of the oxonium ion **10** (Scheme I). The chemical shift (δ 5.1) of the CH_3O group is in good agreement with that observed for other methyloxonium ions such as O-protonated anisylethanol (δ 5.0). The appearance of two triplets, one of which, at δ 5.9, is at lower field than the CH_3O resonance, is also in good agreement with the structure assigned.

SCHEME I



The nmr spectra of quenching products of **10** indicated the major product to be 2-(2-methoxyphenyl)-1-ethyl methyl ether (**11**); however, a 5% yield, based on starting material (20% based on recovered neutral product), of dihydrobenzofuran (**12**) was also obtained. The formation of **12** would appear to require ion **10** as a logical precursor. The products are presumed to have formed in the reactions indicated in Scheme I. Oxonium ions are known[5] to be excellent alkylating agents.

On the basis of similar solvolysis rates and activation parameters, Winstein originally concluded[14a] that both 2-(2-methoxyphenyl)- and 2-(*p*-anisyl)ethyl tosylates solvolyze by a similar mechanism involving formation of a phenonium ion. No product study was made by Winstein in this case. Later, however, Winstein[15] found substantial amounts of furans from the solvolysis of 2-(2-methoxyphenyl)-2-methylpropyl tosylate and proposed an intermediate oxonium ion analogous to cation **10**. Probably, therefore, ion **10** does correspond to the intermediate in the solvolysis reactions. However, the formation of **10** may also be the result of a very low activation energy in $SbF_5 \cdot SO_2$ such that ground-state geometry is the controlling factor over ring or methoxyl participation.

The 2-(*p*-Anisyl)-1-propyl System (3b).—Because considerable difficulty was met in attempts to prepare 2-(4-methoxyphenyl)-1-propyl halides from the alcohol without rearrangement, the mesylate **13** was ionized in $SbF_5 \cdot SO_2$ to give the ion **15**, whose nmr spectrum[12] has previously been published. Phenyl followed by hydride migration (Scheme II) as the route to ion **15** rather than methyl migration was established by nmr observation of the ion **16** from 2-(4-methoxyphenyl)-*2*-*d*-propyl methanesulfonate. The aliphatic methyl group of **16** appears as a doublet centered at δ 1.34.

The 1-(*p*-anisyl)-*1*-*d*-propyl cation **17** was obtained from the corresponding carbinol in $SbF_5 \cdot SO_2$. After periods at −60° of 20 min and at −40° of 20 min, the spectrum gave *no* sign of extensive exchange of D. This rules out ion **17** as a precursor to **16** under the conditions of the experiment. After 45 min at −20°, however, equilibration between D and CH_2 hydrogens

---

[15] R. Heck, E. Corse, E. Greenwald, and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3278 (1957).

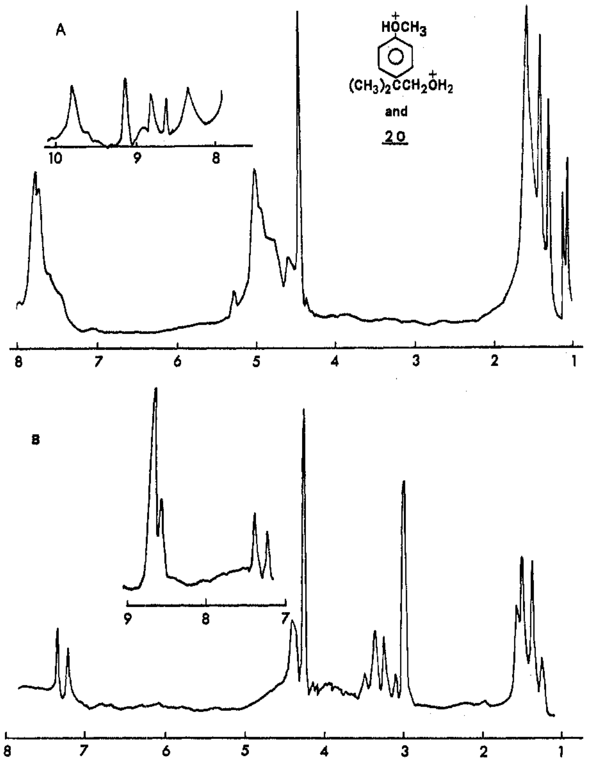
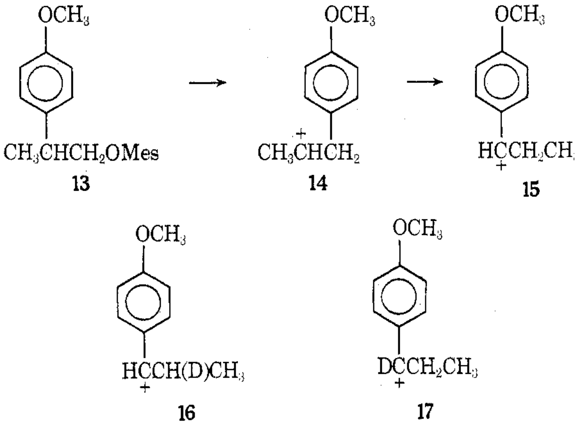


Figure 3.—(A) Nmr spectrum of the reaction mixture of 2-(4-methoxyphenyl)-2-methylpropanol and SbF_5 in SO_2. Ionization at −70°. (B) At −20°.

SCHEME II



was complete. The ortho protons of **17** remain nonequivalent (Δδ 0.4 ppm) even at −20°, demonstrating significant restriction of anisyl ring rotation about the carbonium ion σ bond.

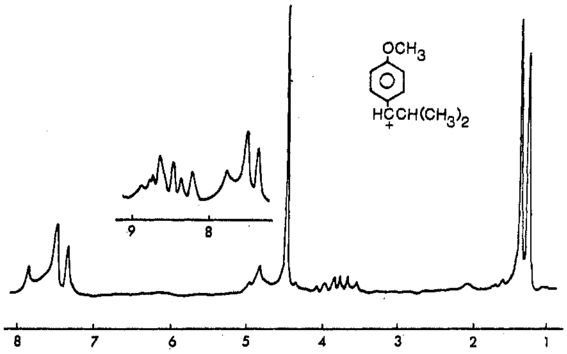


Figure 4.—Nmr spectrum of the reaction mixture of 1-(4-methoxyphenyl)-2-methyl-2-propanol and SbF_5 in SO_2. Spectrum recorded at −40°.

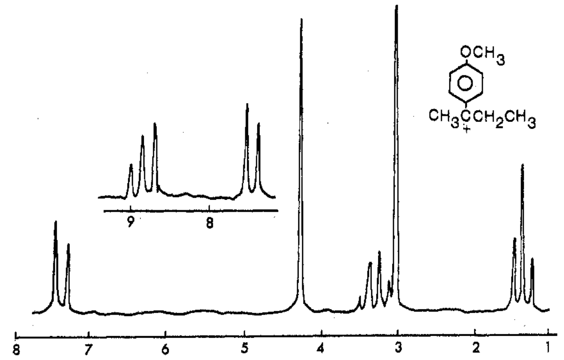
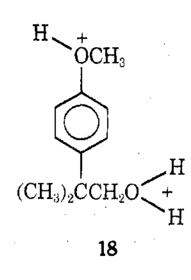
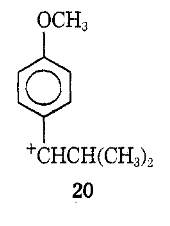


Figure 5.—Nmr spectrum of the reaction mixture of 2-(4-methoxyphenyl)-2-butanol and SbF_5 in SO_2. Spectrum recorded at −20°.

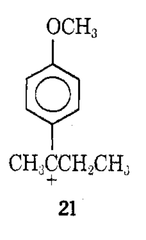
The 2-(*p*-Anisyl)-2-methyl-1-propyl System (3c).—Because we were unable to prepare a pure unrearranged halide or mesylate derivative, 2-(*p*-anisyl)-2-methyl-1-propanol was allowed to react with $SbF_5 \cdot SO_2$ under those conditions previously found to be successful in generating the anisonium ion from *p*-anisylethanol. At −70° the expected product of anisyl migration, 1-(*p*-anisyl)-2-methyl-1-propyl cation **20**, is clearly observed by careful comparison of the spectrum of Figure 3a with that of the ion **20** generated from 1-(*p*-anisyl)-2-methyl-2-propanol (Figure 4). The major species present appears to be the diprotonated alcohol **18**. (It is also possible that OH and OCH_3 may be complexed with SbF_5 rather than H^+.) When the solution is warmed to −20°, species **18** disappears and the principal ion obtained is the 2-*p*-anisyl-2-butyl cation **21**, as determined from careful comparison of Figure 3b with the nmr spectrum of 2-(*p*-anisyl)-2-butanol (**19**) in $SbF_5 \cdot SO_2$ (Figure 5). Since an $SbF_5 \cdot SO_2$ solution of the 1-(*p*-anisyl)-2-methyl-1-propyl cation **20** can be held at −20° for over 1 hr without detectable appearance in its nmr spectrum of ion **21**, the ion **21** must be formed from acid-complexed [OH_2^+ or $^+O(H)SbF_5^-$] *p*-methoxyneophyl alcohol directly at −20°, not through rearrangement of ion **20**, and by methyl rather than anisyl migration. If one assumes initial formation at −20° of a very reactive primary carbonium ion (or ion pair), there are several possible explanations for subsequent preferred methyl over anisyl migration. Statistically, methyl migration is preferred over anisyl migration. Furthermore, a migrating anisyl ring must assume a sterically unfavorable geometry, because of the adjacent methyl groups in which the ring is perpendicular to the plane of the incipient phenonium ion three-membered ring. The stability of **18** (or analogous SbF_5 complex) at −70° also suggests deactivation of the anisyl ring toward



18



20



21

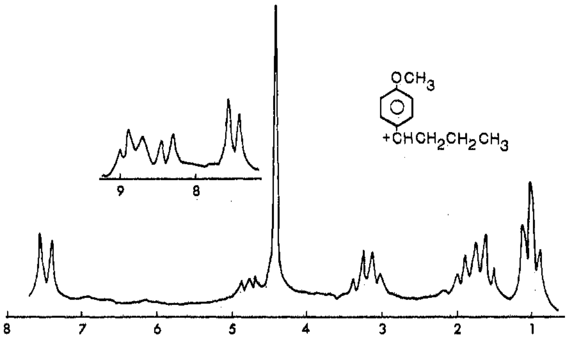


Figure 6.—Nmr spectrum of the reaction mixture of 4-(4-methoxyphenyl)-1-chlorobutane and SbF_5 in SO_2 at −70°.

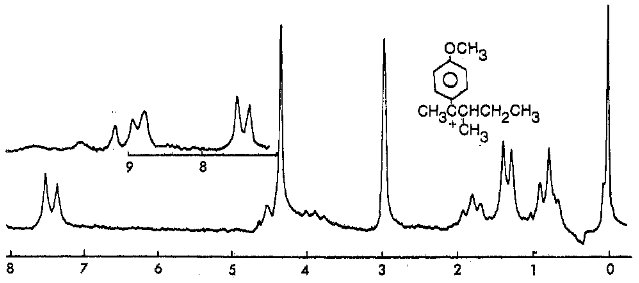


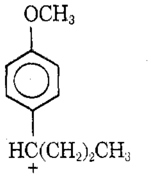
Figure 7.—Nmr spectrum of the 2-*p*-anisyl-3-methyl-2-pentyl cation in $SbF_5 \cdot SO_2$ at −70°.

neighboring group participation and a resultant decreased migration aptitude at −20°.

A scheme in which a primary carbonium ion pair at −20° is in rapid preequilibrium with the anisyl-*tert*-butyl cation (anisonium ion optional) may be ruled out by the absence of the formation of ion **21** from ionization of 1-(4-methoxyphenyl)-2-methyl-2-propanol, which yields ion **20** exclusively.

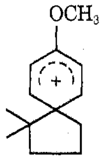
The 4-(*p*-Anisyl)-1-butyl Halides (4) and 4-(*p*-Anisyl)-4-methyl-1-chloropentane (5).—Since observation of the simple anisonium ion, but not phenonium ions, with alkyl substitution of the cyclopropyl ring, could be explained by the presence of the strained three-membered ring, and because of the ease with which this cyclopropyl ring could open to secondary or tertiary carbonium ions, it was hoped that ions **7** and **8**, where one or both of these factors were absent, might be observed by nmr.

The 4-(*p*-anisyl)-1-butyl halides in $SbF_5 \cdot SO_2$ at −60°, however, did not give the desired phenonium ion **7**. The chloride (and bromide only by using 7 molar excess of SbF_5) could be ionized to the 1-(*p*-anisyl)-1-butyl cation **22**, whose nmr spectrum (Figure 6) was confirmed by generating the ion from the corresponding benzylic methyl ether in $SbF_5 \cdot SO_2$. Although the *tert*-butyl cation is easily generated[3] even from *n*-butyl iodide, all attempts to generate **22** from 4-anisylbutyl iodide (or the alcohol) failed. The anisyl group appears to deactivate the *n*-butyl halide, perhaps by an electron-withdrawing inductive effect of a benzyl group on the initial formation of a protonated cyclopropyl cation intermediate.



22

7

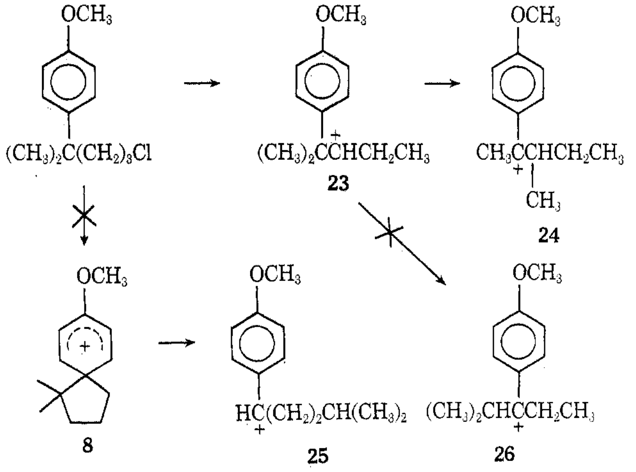


8

The failure to observe ion **7** from the 4-*p*-anisylbutyl halides in $SbF_5 \cdot SO_2$ does not rule out the intervention of ion **7** in the route to **22**, but, in view of previous success with the parent anisonium ion and the expected stability of **7**, had it been formed, it should have been easily detected at −70°. Opening the ion **7** requires at best formation of a π-complexed primary ion, and this should require prohibitive activation energy.

These conclusions are greatly strengthened by the formation of ion **24** from 4-(*p*-anisyl)-4-methyl-1-chloropentane in $SbF_5 \cdot SO_2$ at −70° (Scheme III).

SCHEME III

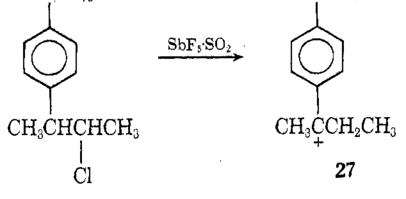


The spectrum of ion **24** (Figure 7) was also obtained from 2-*p*-anisyl-2-methoxy-3-methylpentane in $SbF_5 \cdot SO_2$. There was in the nmr spectrum (Figure 7) no evidence of **8**, **25**, or other ions which would be expected products of anisyl participation in the ionization.

The observed product ion **24** can be arrived at from ion **8** only if we postulate either a long series of hydride and methyl shifts which *must* at some time require the formation of a *primary* carbonium ion, or, even less likely, the preferential opening of **8** to a primary ion. We, therefore, conclude that the formation of ion **24** took place without participation by the anisyl group.

If we make the reasonable assumption that the formation of **24** proceeds through ion **23**, whose presence was not, however, experimentally observed, the absence of ion **26** becomes significant. The implication is that in $SbF_5 \cdot SO_2$ migration of methyl groups from a tertiary center to a "preformed" secondary carbonium ion center is much more rapid than anisyl migration.

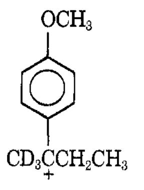
The 3-(*p*-Anisyl)-2-butyl System (3d).—The 2-(*p*-anisyl)-2-butyl cation **27** is obtained from ionization



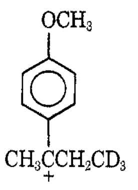
3d, X = Cl **27**

of either 3-(*p*-anisyl)-2-chlorobutane or 2-(*p*-anisyl)-2-butanol (Figure 5). The structure of the ion is established by the appearance of a typical ethyl group triplet (δ 1.3) and quartet (δ 3.3), a singlet methyl adjacent to a positive charge (δ 3.0), and the large downfield shift of the ortho and meta ring protons. There is no change in the spectrum over the temperature range −60 to −20°.

The nmr spectra of 4,4,4-trideuterio-3-(*p*-anisyl)-2-butanol in $SbF_5 \cdot SO_2$ at −60° and after warming to −20° are given in Figures 8A and 8B. At −20° the spectrum is unchanged after 1.5 hr. The relative amounts of ions **28** and **29** were determined by integration of the singlet at δ 3.05 for CH_3C^+, and the methyl triplet at δ 1.31 for CH_2CH_3. At −60°, the ratio of ion **28** to **29** is greater than 10:1. Thus, at −60° neither prior equilibrium with an anisonium ion nor rapidly equilibrating β-anisylcarbonium ion pairs can be of significant importance, and hydride ion migration must be about ten times faster than net anisyl migration to a carbonium ion center. The resonances at δ 1.55–1.80, 4.75, 4.95, and 7.7 present at −60° disappear on warming to −20°, and integration of the spectrum (Figure 8B) then gives 80% of cation **28** from net hydrogen migration and 20% of cation **29** from net anisyl migration.

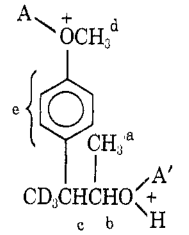


28

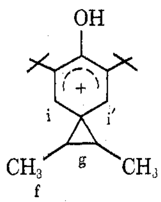


29

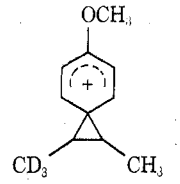
If the intermediate present at −60° which disappears at −20° is assumed to be the acid-complexed alcohol **30**, where A is H or SbF_5, the following assignments can be made: δ 1.55–1.80 (a and c), 4.75 (b), 4.95 (d), and 7.7 (e). These assignments are in good agreement with resonances observed for corresponding hydrogens of protonated alcohols, 2-(*p*-anisyl)-2-methyl-1-propanol and 2-*p*-anisylethanol. It is not obvious, however, why at −20° ion **30** should give **29**, whereas the comparable ion **18** did *not* give the anisyl migration product **20** under similar conditions. It may be that the primary protonated alcohol **18** is in rapid equilibrium at −20° with the SbF_5 complex, which in turn ionizes at −20° without the anisyl assistance which it required at −60°. The ion **30** (A′ = H), on the other hand, may ionize with anisyl participation at some temperature between −60 and −20°, since it yields the more easily formed secondary ion.



30



31



32

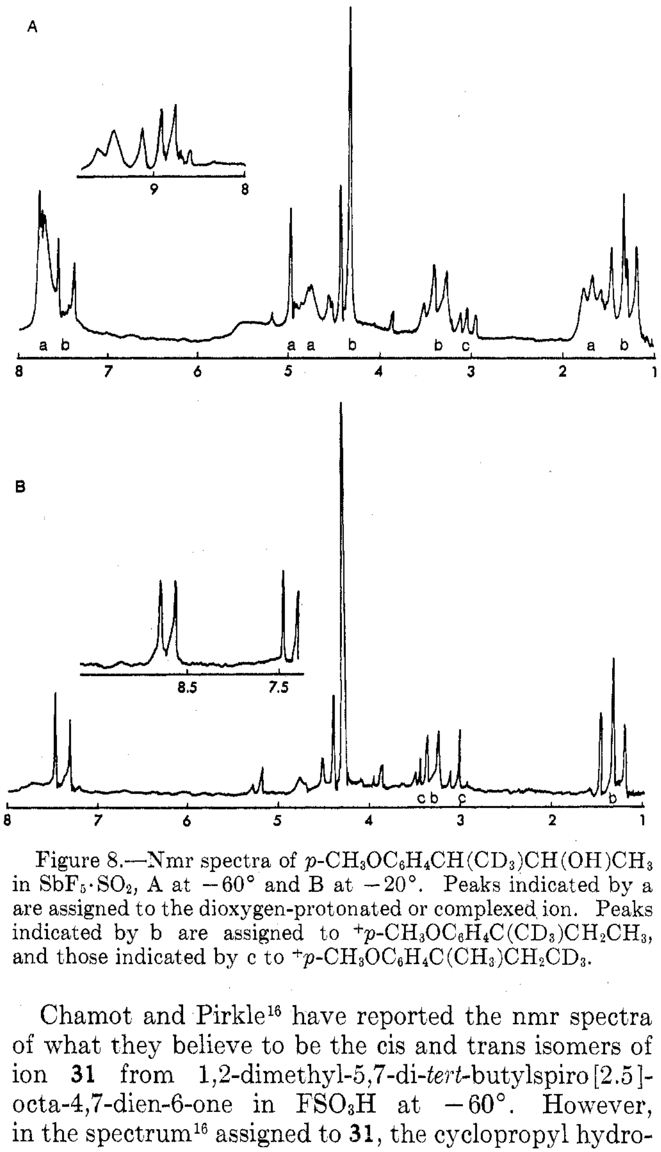
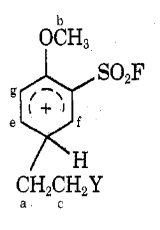


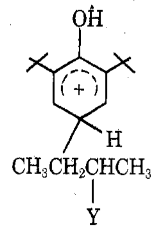
Figure 8.—Nmr spectra of $p\text{-}CH_3OC_6H_4CH(CD_3)CH(OH)CH_3$ in $SbF_5 \cdot SO_2$, A at −60° and B at −20°. Peaks indicated by a are assigned to the dioxygen-protonated or complexed ion. Peaks indicated by b are assigned to $^+p\text{-}CH_3OC_6H_4C(CD_3)CH_2CH_3$, and those indicated by c to $^+p\text{-}CH_3OC_6H_4C(CH_3)CH_2CD_3$.

Chamot and Pirkle[16] have reported the nmr spectra of what they believe to be the cis and trans isomers of ion **31** from 1,2-dimethyl-5,7-di-*tert*-butylspiro[2.5]-octa-4,7-dien-6-one in FSO_3H at −60°. However, in the spectrum[16] assigned to **31**, the cyclopropyl hydrogens are more than 1 ppm further downfield than their position (δ 3.5) in the anisonium ion. In fact, the chemical shifts reported for **31** seem quite close to those observed[17] by us for *p*-anisylethanol in fluorosulfonic or sulfuric acid at −60°, and eventually assigned to a species such as **33**, with resonances at δ 3.10 (a), 3.90 (b), 4.71 (c), 7.19 (g), and 7.75 (e,f). An analogous ion from the dienone might be an ion such as **34**. Moreover, since we can find no nmr evidence of ions analogous to **32** or **30** from 2-(*p*-anisyl)-3-chlorobutane in $SbF_5 \cdot SO_2$ at −70°, in spite of repeated attempts, we prefer at this time to interpret the nmr of the 3-(*p*-anisyl)-2-butyl alcohols in $SbF_5 \cdot SO_2$ in terms of ions



Y = $^+OH_2$, OSO_3H, OSO_2F

33



Y = $^+OH_2$, OSO_3H, OSO_2F

34

---

[16] D. Chamot and W. H. Pirkle, *J. Amer. Chem. Soc.*, **91**, 1570 (1969).

[17] B. Ramsey, unpublished results.

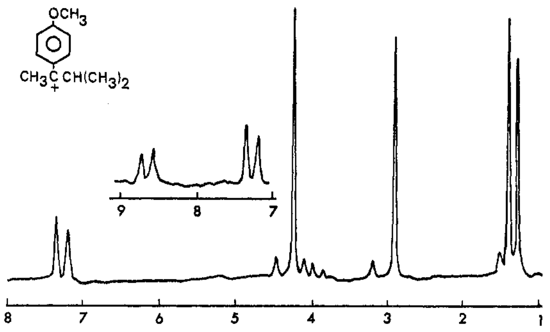
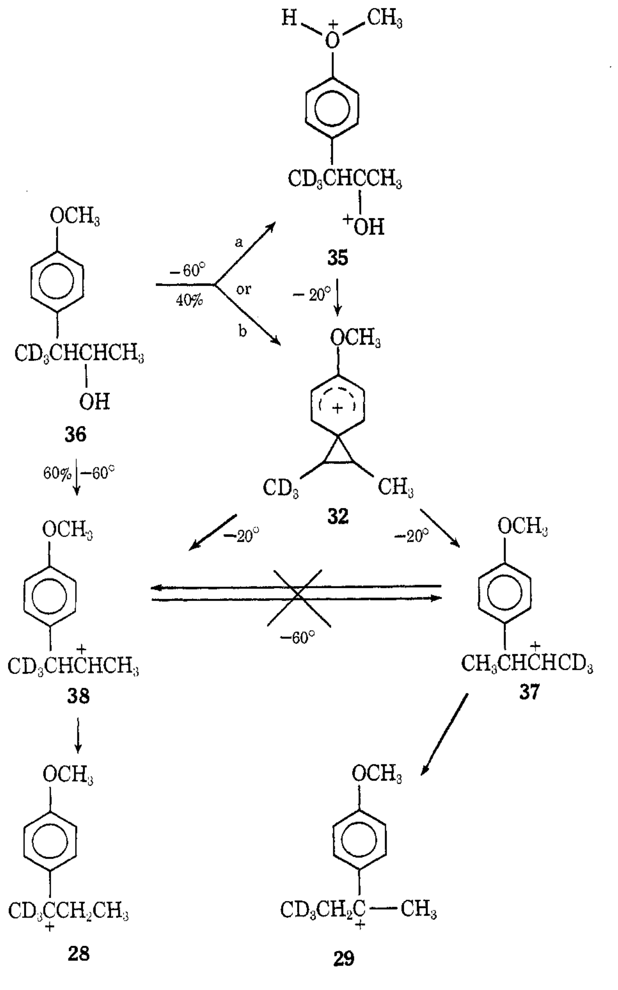


Figure 9.—Nmr spectrum of the reaction mixture of 2-(4-methoxyphenyl)-2-methyl-3-butanol and SbF_5 in SO_2 at −60°.

27, 28, 29, 30, or 35 rather than an anisonium ion 32, *in which case hydride migration is at least ten times faster than either net anisyl migration or anisonium ion formation at −60°.*

Scheme IV is suggested for an ionization in $SbF_5 \cdot SO_2$ of 36 which proceeds through intermediates[18] 38, 32, and 35. (A final choice between alternatives a and b at −60° awaits a more detailed report of Chamot and Pirkle on proposed ion 31.)

SCHEME IV



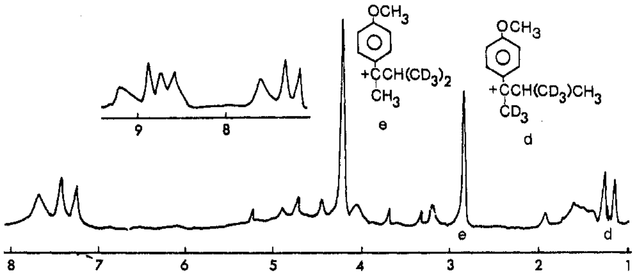
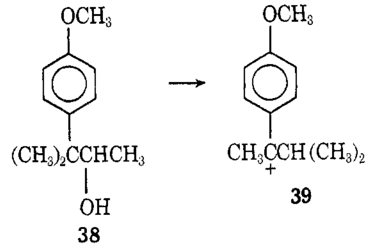


Figure 10.—Nmr spectrum of $p\text{-}CH_3OC_6H_4C(CD_3)_2CH(OH)CH_3$ in $SbF_5 \cdot SO_2$ at −60°.

Rapid equilibration between 37 and 38, clearly absent at −60°, can probably also be ruled out at −20° since $\Delta S^{\neq}$ for anisyl migration is more negative than for hydride migration, and an increase in temperature should favor benzylic ion formation. Provided that the *relative* migration aptitudes of anisyl and CH_3 groups are not reduced by H^+ or SbF_5 coordination to the methoxy group, the absence of an equilibration between ions 37 and 38, which is faster than benzylic ion formation in $SbF_5 \cdot SO_2$, suggests that similar rapidly equilibrating β-anisyl ions are not important intermediates in the solvolysis of 2-anisyl-3-butyl derivatives in more normal solvents such as acetic acid, formic acid, etc., where benzylic products are not found. It may also be significant that the deaminative acetolysis of 3-phenyl-2-butylamine (which would not proceed through an ion pair intermediate) yields a substantial amount of benzylic products,[19] whereas solvolysis of the tosylate[20] does not.



The 3-(p-Anisyl)-3-methyl-2-butyl System (3e).—Ionization of 3-(p-anisyl)-3-methyl-2-butanol in $SbF_5 \cdot SO_2$ at −60° gave the ion 39, whose nmr spectrum (Figure 9) is characterized by the doublet of the isopropyl-methyl group at δ 1.3 and the large downfield shift of the ortho (δ 8.6) and meta (δ 7.3) ring protons. The spectrum of the ion shows no change on warming to −20°.

As expected on the basis of relief of steric strain, anisyl migration is more important from a tertiary carbon than from a secondary carbon. When 4,4,4-trideuterio-3-trideuteriomethyl-3-(p-anisyl)-2-butanol is ionized at −60° in $SbF_5 \cdot SO_2$, a mixture of ions 43 (42%) and 41 (58%) is obtained (based on the integration of the nmr spectrum in Figure 10). After 15 min at −20°, the ratio changes to 46:54 and, after 70 min reaches a ratio 60:40, which corresponds to $K_H/K_D = 1.3$.

Ions 41 and 43 do not interconvert at −60° at an appreciable rate; therefore they must be formed in competing processes (Scheme Va or b). Since opening of the anisonium ion to 40, a tertiary ion, should be much more rapid than opening to 42, a secondary ion,

---

[18] Formation of 28 without intervention of 38 requires that an assisted ionization of the alcohol with simultaneous migration of the neighboring groups is more important for the hydride than the anisyl. This is contrary to previous experience.

[19] D. J. Cram and J. F. McCarty, *J. Amer. Chem. Soc.*, **79**, 2866 (1957).

[20] S. Winstein and R. Baker, *ibid.*, **86**, 2091 (1964).

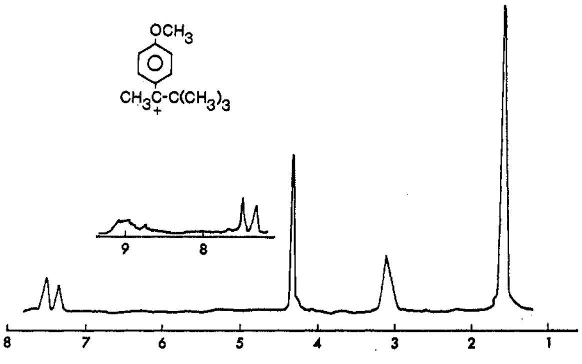
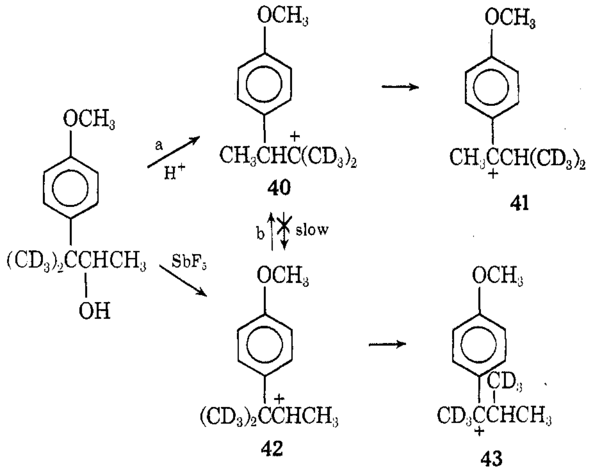


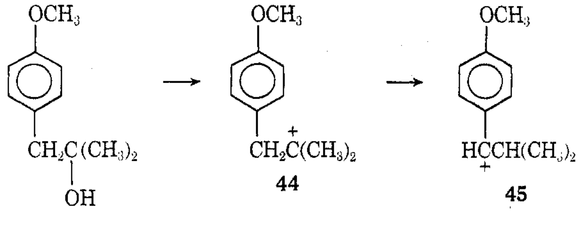
Figure 11.—Nmr spectrum of 2-(4-methoxyphenyl)-2,3-dimethyl-3-butanol in $SbF_5 \cdot SO_2$ at −70°.

Scheme V



either a common anisonium ion intermediate or migration of the anisyl group concurrent with ionization to form **40** should lead to ion **41** as the exclusive product. Ion **43** must then arise directly from methyl migration to the secondary carbonium ion center of **42**. Formation of **41** by way of **42** (Scheme Vb) cannot be ruled out, but the apparent absence of similar anisyl migrations in ion **23** from the ionization of 4-anisyl-4-methyl-1-chloropentane, and in ion **38** of Scheme IV, suggest that an alternative interpretation such as Scheme Va should be found. This alternative is simply based on the postulate that in secondary alcohols $-OH_2^+$ ionization may take place provided aryl assistance is available, but $-OSbF_5^+$ ionization proceeds without aryl assistance.

The 3-(4-Methoxyphenyl)-2-methyl-2-propyl System (3f).—The ionization of 1-(4-methoxyphenyl)-2-methyl-2-propanol gave only the anisyl isopropylcarbonium ion **45** (Figure 4). It seems safe to assume that the reaction below proceeds without anisyl migration. No



change in the spectrum was observed between −70 and −15°.

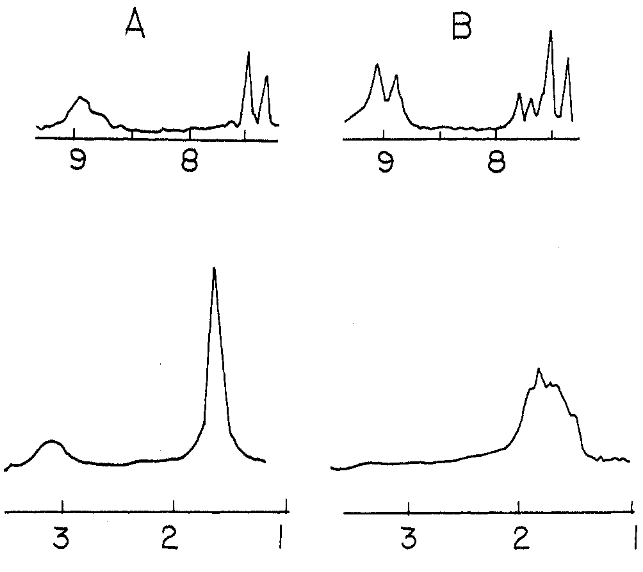
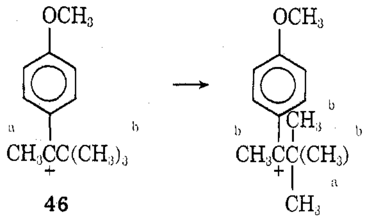


Figure 12.—Nmr spectrum of 2-(4-methoxyphenyl)-2,3-dimethyl-3-butanol in $SbF_5 \cdot SO_2$, A at −50°, B at −20°.

The 3-(4-Methoxyphenyl)-2,3-dimethyl-2-butyl System (3g).—The nmr spectrum (Figure 11) of 3-(4-methoxyphenyl)-2,3-dimethyl-2-butanol in $SbF_5 \cdot SO_2$ at −70° is clearly that of the *p*-anisyl *tert*-butyl methyl carbonium ion **46**. Complete scrambling of methyl groups is found when the methyl-deuterated analog of ion **47** is generated at −70° from 1,1,1-trideuterio-2-trideuteriomethyl-3-(*p*-anisyl)-3-methyl-2-butanol. At −50° the broadening of the methyl resonances is quite pronounced, and the collapse of the methyl resonances is observed at −20° (Figure 12). If the exchange process is written according to eq 1, and P_{ab}



(1)

$$P_{ab} = \frac{3\pi\sqrt{\delta^2 - \Delta\nu^2}}{4\sqrt{2}} \tag{2}$$

is the transition probability for the benzylic methyl group a, eq 2 may be derived as the relation between P_{ab}, $\Delta\nu$ (the chemical shift difference between methyl a and b and δ (the methyl a and b limiting chemical shift difference) in hertz. The value of δ was obtained as 91 cps at −70°. Chemical shift differences ($\Delta\nu$) were obtained at −60° (90 Hz), −50° (88 Hz), and −30° (83 Hz).

An Arrhenius activation energy (E_a = 6.5 kcal/mol) was obtained from a plot of log P_{ab} as calculated from eq 2 *vs.* $1/T$. The enthalpy and entropy of activation are $\Delta H^{\ddagger}$ = 6.1 kcal/mol and $\Delta S^{\ddagger}$ = −12 eu. If the rate determined from the collapse temperature, which is the least accurate measurement, is omitted, an activation energy of only 5.0 kcal/mol is obtained. (The Varian variable-temperature probe used is reliable only to ±1°. In addition there are also temperature gradients within the sample tube. This leads to estimated errors of as much as ±3 kcal/mol in E_a and ±12

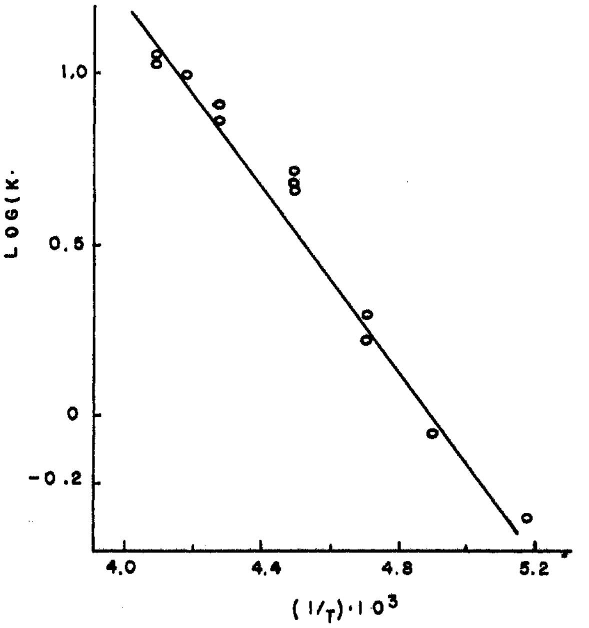
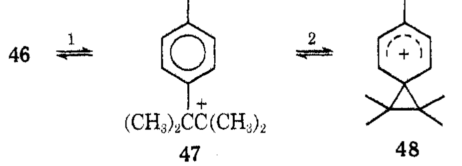


Figure 13.—Log k (based on excess line broadening) for CH_3 exchanging of ^+p-$CH_3OC_6H_4CH(CH_3)C(CH_3)_3$ *vs.* $1/T$.

eu in $\Delta S^{\ddagger}$, which are probably more realistic than standard deviations commonly reported.)

The exchange rate as a function of temperature was also obtained by measuring the exchange line broadening of the $(CH_3)_3C$ methyl peak and using the line width of the CH_3O peak at each temperature to approximate the natural line width of $(CH_3)_3C$ in the absence of exchange. As may be seen from Figure 13, the results of plotting log k *vs.* $1/T$ are reasonably good and the calculated E_a (6.0 kcal/mol), $\Delta H^{\ddagger}$ (5.6 kcal/mol), and $\Delta S^{\ddagger}$ (-27 eu) are in agreement with those previously calculated from chemical shift differences by eq 2, within experimental error.

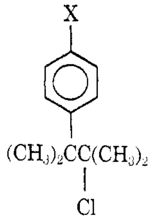
In view of the zero to slightly positive entropy of activation found for the rate-determining methide shift in equilibration of the *tert*-amyl cation methyl groups[21] and also for the rate-determining hydride shift[22] in the isopropyl cation, we would like to modify an earlier conclusion[23] and suggest that a negative (-12 to -27 eu) activation entropy for methyl of equilibration of ion **46** is best explained by a transition state leading to a phenonium ion; *i.e.*, step 2 of eq 3 may be rate determining.



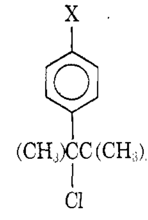
(3)

Brown and Kim[6b] reported the results of CD_3-labeled scrambling of the compounds p-$RC_6H_4C(CH_3)_2C(CD_3)_2X$ (R is H or OCH_3) in a variety of reactions normally regarded as proceeding by carbonium ion, S_N1, mechanisms. Based on the small rate enhancement caused by the anisyl relative to phenyl, and the observed 100% CD_3 scrambling in the reactions of p-$CH_3OC_6H_4C(CH_3)_2C(CD_3)_2X$ (*except* dehydration of the alcohol over alumina and reaction of the sodium alkoxide with bromoform), Brown and Kim concluded that carbonium ion reactions of p-$CH_3OC_6H_4C(CH_3)_2C(CH_3)_2OH$ derivatives proceeded through rapidly equilibrating 3-anisyl-2,3-dimethyl-2-butyl cations. Benzylic ion products were less than 5%. It is very difficult to reconcile Brown's model with our results, since we have concluded (eq 3) that in $SbF_5 \cdot SO_2$ benzylic ion formation is not only competitive with but faster than anisyl migration. The difference may lie either in the ability of SbF_5 to complex the anisyl methoxyl group, or, if the equilibrating 2-butyl cations are in fact ion pairs in more normal solvents, the absence of the closely associated anion in $SbF_5 \cdot SO_2$ may result in faster benzylic ion formation. There is after all no *a priori* reason why relative free energies or rates of interconversion of carbonium ion ion pairs (or highly solvated ions) should parallel those of the dissociated "nonsolvated" cations expected in $SbF_5 \cdot SO_2$.

The activation energy and entropy determined for the equilibration of methyl groups in the p-anisyl methyl *tert*-butyl carbonium ion has some bearing on conclusions reached by Olah, *et al.*,[24a] on the identity of the carbonium ions present when **49** or **50** are dissolved in $SbF_5 \cdot SO_2$.



49



50

X = H, CH_3, or OCH_3

Where X = CH_3, the spectrum was assigned to equilibrating benzylic (**51**) and phenonium ions (**53**), for X = H, to **53**, the phenonium ion, and to **52** where X = CF_3. Considerations outlined below, however, suggest an alternative interpretation of these data for X = CH_3 and H.

The relative free energies of formation, $\delta\Delta G$, for the di- and triaryl carbonium ions $(p$-$XC_6H_4)_{3-n}C^+H_n$ (n = 0, 1) in sulfuric acid have been reported.[25] The p-methyl and methoxyl ions are about 4 and 10 kcal/mol, respectively, more stable than the unsubstituted aryl carbonium ions. The gas-phase relative ionization potentials[26] of the benzyl, p-methyl-, and p-methoxyl benzyl radicals (0.0, -7, and -18.7 kcal/mol, respectively) may be used to estimate an upper limit on the ability of these para substituents to stabilize a benzylic cation, since electron demands on the substituent would be much smaller in solution.

Clearly, the activation energy (6 kcal/mol) for the exchange of methyl groups in ion **46** is very close to that expected for the relative difference in energies of the p-methyl- and p-methoxy-substituted ions and of the same order of magnitude as the unsubstituted phenyl methyl *tert*-butyl carbonium ion. Since the energies

---

[21] M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

[22] M. Saunders and E. L. Hagen, *ibid.*, **90**, 6881 (1968).

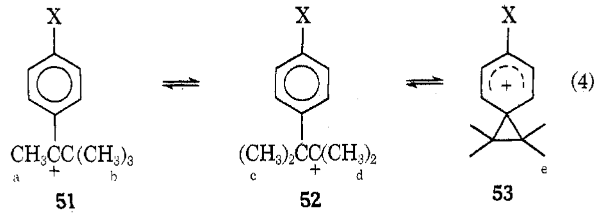
[23] B. G. Ramsey and J. Cook, *Tetrahedron Lett.*, 535 (1969).

[24] (a) G. Olah, M. B. Comisarow, and C. J. Kim, *J. Amer. Chem. Soc.*, **91**, 1458 (1969); (b) G. Olah and R. Porter, *ibid.*, **93**, 6877 (1971).

[25] N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).

[26] J. L. Franklin, "Carbonium Ions," Vol. 1, Wiley, New York N. Y., 1968, p 105.

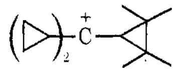
of the tertiary carbonium ions **52** should be relatively insensitive to substituent X, the energies of the benzylic ion **51** and tertiary ion **52** may be expected on the basis of the above relative energies to be very similar (within 1 kcal) where X is CH_3 (eq 4) and comparable even



51 **52** **53**

where X is H. This may be more easily realized graphically from Figure 14, which indicates estimated ΔG substitution and experimental $\Delta G^{\ddagger}$ for exchange for the benzylic and alkyl cations. Certainly where X is CH_3 and possibly where X is H, the activation energy for the equilibration of ions **51** and **52** or even all three ions **51**, **52**, and **53** may be less than 3 or 4 kcal/mol, and the absence of line broadening in the nmr spectra of these systems even at −120° should not be regarded[24a] as conclusive evidence for the presence of only a single major species.

Fundamental to Olah's assignment[24a] *of the proton nmr spectrum of the parent phenonium ion (X = H) is assigning a chemical shift of δ 2.3 to methyl groups of phenonium ion* **53** *(X = H).* This may be too far downfield in view of the methyl chemical shifts of δ 1.25 obtained by Deno[27] for ion **54** or even δ 1.9 for ion **31**, which is itself suspected.



54

If perhaps a more reasonable choice of δ 1.6 is made for the chemical shift of methyls e, and if the remaining methyl chemical shifts are estimated [for methyls a, δ 3.2 on the assumption that the benzylic methyl chemical shift differences between $p\text{-}CH_3C_6H_4C(CH_3)_2^+$ (δ 3.45) and $p\text{-}CH_3C_6H_4CCH_3C(CH_3)_3^+$ (estimated Δδ 0.21 ppm) should be slightly greater than the difference of 0.16 observed[24] for the corresponding $p\text{-}CH_3O$ substituted ions because of an expected smaller para substituent effect in the *tert*-butyl substituted benzylic ions, resulting from *tert*-butyl steric hindrance to phenyl ring stabilization of the positive charge [for methyls b δ 1.5 from ion **46** ($X = CH_3O$); the average of methyls c and d δ 2.8 from ion **52** ($X = CF_3$)]; these chemical shifts will satisfy both observed alkyl methyl nmr chemical shifts within 0.1 ppm and drowning product ratios provided the ratios of the concentrations of ions **51**, **52**, and **53** are taken as 4:3:3 where X is methyl or 1:5:4 where X is H. The 4:3:3 ratio of ions **51**, **52**, and **53** ($X = CH_3$) also satisfactorily predicts the chemical shift of the $p\text{-}CH_3$ if the chemical shifts are taken as δ 2.8 (**51**), 2.3 (**52**), and 2.4–2.5 (**53**). Qualitatively it is easily seen that ring proton chemical shifts and the ortho–meta chemical shift differences may be accounted for by equilibrating ions **51**, **52**, and **53**. Chemical shifts of ring protons will be much more sensitive to the nature of X and the amount of ring to carbonium ion π bonding in ion **52**; therefore, adequate models for these protons are not available. Still, the above-suggested approximate ratios of ions also predict the average ring proton chemical shifts within 0.2 ppm, where the average ring ortho and meta hydrogen chemical shifts of contributing ions are taken from anisonium ion, **51**, $X = OCH_3$, and **52**, $X = CF_3$.

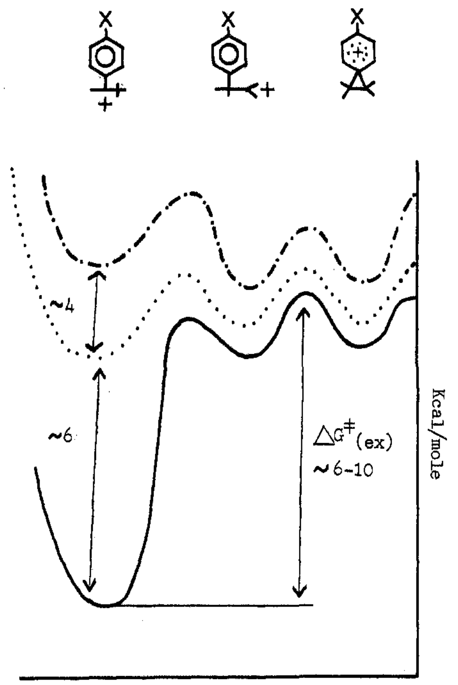


Figure 14.—A suggested qualitative free energy surface for the relative free energies of $^+p\text{-}XC_6H_4CMeCMe_3$, $^+p\text{-}XC_6H_4CMe_2CMe_2$, and p-X-phenonium ion; $X = CH_3O$ (——), CH_3 (·····), H (—·—·).

We have not in any way tried to optimize all of the parameters, and better agreement could undoubtedly be obtained by slightly different equilibrium ion concentrations, allowing for increased downfield shift in a through d in ions **51** and **52** as one proceeds from CH_3O to CH_3 to H, *and by recognizing that ratios of drowning products may themselves only reflect approximate equilibrium ratios of ions.*

If the interpretation of a negative and apparently large activation entropy in equilibration of CH_3 groups in the $p\text{-}CH_3OC_6H_4C(CH_3)C(CH_3)_3^+$ ion is correct in its conclusion that the highest energy transition state is that for step 2, eq 3, anisonium ion **48** must be very nearly equal to if not higher in energy than the β-anisyl alkyl cation **47**, and replacement of CH_3O by CH_3 or H should not lead to a system in which the anisonium ion is the most stable ion present.

Figure 14 represents our interpretation of the relative free energies of benzylic $p\text{-}XC_6H_4CMe_2CMe_2^+$ and phenonium ions as a function of X. *The only systems where phenonium ions are firmly established as the only major species present in strong acid remain those in which the phenonium ion cyclopropyl ring does not possess substituents capable of stablizing positive charge.*

In the time interval since the original submission of this manuscript in substantially its present content,[4] Olah and coworkers[24b] have published conclusions in general agreement with those arrived at here, although it is still maintained by Olah and coworkers on the basis of ^{13}C nmr that the major species is benzylic ion **51** when X is CH_3 and phenonium ion **53** when X is H.

---

[27] N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

Summary of Conclusions.—The carbonium ions and their precursors reported in this paper are summarized in Table I with their proton chemical shifts.

There are at least two acids present in $SbF_5 \cdot SO_2$ solutions, SbF_5 itself and unavoidable small amounts of HF, and this tends to complicate the results obtained in ionization of alcohols. In terms of the theory of hard and soft acids we would expect the OH group to lie somewhere between Cl and F in its effectiveness as a leaving group when attacked by $SbF_5(Sb_2F_{10})$. At $-60°$ our results with the primary alcohols agree well with the idea that $^+p\text{-}CH_3OC_6H_4CH(CH_3)CH_2OHSbF_5^-$ and $^+p\text{-}CH_3OC_6H_4C(CH_3)_2CH_2OHSbF_5^-$ ionizations proceed with anisyl participation *via* phenonium ions, but that the alkyl OH_2^+ does not leave from a primary carbon at any appreciable rate at $-60°$. The β-anisylethanol does not form the anisonium ion in $FSO_3H \cdot SbF_5$, a H^+ superacid, at $-60°$.

It is pertinent to this point that we have confirmed[3] that, although *n*-propyl fluoride gives an isopropyl ion in $SbF_5 \cdot SO_2$, the chlorides and bromides do not. Apparently, ionization of primary halides other than fluoride requires at least some anchimeric assistance, if only from neighboring alkyl groups. Products at $-60°$ are then determined by competition between $SbF_5 \cdot SO_2$ and $HF \cdot SbF_5$ for the alkyl OH group. This appears to carry over also to secondary alcohols but with a new twist.

Ionization of OH from a secondary carbon when attacked by SbF_5 seems to proceed by a mechanism in which the β-anisylalkyl cation is formed without assistance from the anisyl group, or presumably neighboring alkyl, hydride, or solvent. Strong evidence, we believe, indicates that at $-60°$ hydride migration is at least ten times faster than anisyl migration for the ion $^+p\text{-}CH_3OC_6H_4CH(CH_3)CHCH_3$, and methyl migration is at least nearly as fast as anisyl migration in the ion $^+p\text{-}CH_3OC_6H_4C(CH_3)_2CHCH_3$ at $-60°$. An additional term, k_E, the overall rate constant for eq 5, could be introduced into a generalized formulation for the observed solvolytic rate as in eq 6. In eq 6 k_Δ and k_s represent nucleophilic participation by neighboring groups and solvent, respectively, but k_E is a rate constant for what is essentially electrophilic substitution on X. The $(AXR)^n$ is either a transition state or intermediate which ionizes without aryl assistance.

$$A^{n+} + XR \xrightarrow{\text{slow}} (AXR)^{n+} \xrightarrow{\text{fast}} (AX)^{n-1} + R^+ \qquad (5)$$

$$k_{\text{obsd}} = Fk_\Delta + k_s + k_E \qquad (6)$$

The fate of the protonated secondary alcohol apparently reflects the increased ease with which a secondary carbonium ion may be formed over a primary one, since during the process of warming to -20 from $-60°$ disappearance of the protonated alcohol $p\text{-}CH_3OC_6H_4CH(CH_3)CH(CH_3)OH_2^+$ is accompanied by the appearance of product ions of anisyl group migration or anisonium ion formation. Our results seem at least consistent with the idea that protonated secondary alcohols will ionize in $SbF_5 \cdot SO_2$ at temperatures between -60 and $-20°$ *with* anisyl participation. To reconcile this with the behavior of $p\text{-}CH_3OC_6H_4C(CH_3)_2CH_2OH_2^+$ at $-20°$, we suggest that this ion may convert rapidly to the $OH \cdot SbF_5$ complex, which at $-20°$ then ionizes without anisyl participation to a primary ion or ion pair precursor of **21**.

The consequences of the previous arguments are apparent in Scheme V, for example, with the assumption that the reaction represented by eq 5 is important where A is SbF_5 but not where A is HF, $HFSb_2F_{10}$, etc.

In the ionization of secondary alcohols in $SbF_5 \cdot SO_2$, we have observed an unexpected decrease in migratory aptitude of anisyl groups toward a carbonium ion center relative to CH_3 or H migration. The unique properties of the $SbF_5 \cdot SO_2$ solvent system offer at least two basically different explanations for this result.

First of all, rapid initial coordination of the anisyl CH_3O group by SbF_5 may destroy the ability of the anisyl group to provide anchimeric assistance to ionization, or, even if such assistance is not required, the migration aptitude of the anisyl group toward a preformed carbonium ion center is reduced to such an extent that CH_3 or H migration rates are comparable to or greater than that of anisyl. The first step in the reaction schemes presented previously would be formation of $^+CH_3O(A)C_6H_5CR_2CR'X$ (A is SbF_5 or H^+), and all anisyl alkyl cations such as **23**, **38**, **40**, etc., in Schemes III–V should be written with complexed methoxy groups $[CH_3O^+(A)-]$. We have some objections to this mechanism, however, in that we have recently[17] found that prior coordination of CH_3O to BF_3 in the case of $(CH_3O)_2C_6H_5CH_2CH_2X$ followed by addition of SbF_5 produces the *o,o*-2,6-dimethoxyphenonium ion, not the oxonium ion analog of **10**. This in turn implies that under the conditions reported here the oxonium ion **10** was formed from uncomplexed $o\text{-}CH_3OC_6H_5CH_2CH_2Cl$ precursor in $SbF_5 \cdot SO_2$. It also demonstrates that Lewis acid coordination of anisyl CH_3O group will not necessarily prevent anisonium ion formation.

A variation of the above mechanism assumes competitive formation of two intermediates, $^+p\text{-}CH_3O(A)\text{-}C_6H_5CR_2CH(CH_3)OH$ and either the anisonium ion or $p\text{-}CH_3OC_6H_5CR_2CHCH_3^+$. The first of these gives only products of R migration, whereas the latter two produce products of anisyl migration (or anisonium ion formation). This mechanism seems most satisfactory to us for the case of initial formation of anisonium ion rather than $p\text{-}CH_3OC_6H_5CR_2CHCH_3^+$, since it more readily accounts for the greater anisyl migration where R_2 is CH_3, CH_3 than where R_2 is CH_3, H. In this case in Scheme V, for example, ion **42** should be written with $^+CH_3O(A)-$, ion **40** should be left as is or replaced with an anisonium ion, and the methoxyls of **38** (Scheme IV) and **23** (Scheme III) indicated as SbF_5 complexed. We are not satisfied with this mechanism, however, since it requires fortuitiously comparable rates for SbF_5 coordination to CH_3O and for anisonium ion formation.

At this time we prefer the following alternative explanation for our results in the secondary alcohol series. Very recently Brown and Kim[6c] and Ramsey and Das,[28] have independently suggested that the solvolysis of secondary alkylaryl derivatives in solvents such as acetic and formic acid proceeded through intimate ion pair intermediates. Brown and Kim reached this conclusion from a general consideration of solvolysis rates and activation parameters; Ramsey and Das based their conclusion on correlation of the logarithm of titrimetric rate constants with aryl group

---

[28] B. G. Ramsey and N. K. Das, *J. Amer. Chem. Soc.*, in press.

ionization potential. We suggest here then that the essential difference between the $SbF_5 \cdot SO_2$ solvent system and acetic acid, formic acid solvent systems, etc., is the combined absence of the intimate ion pair in $SbF_5 \cdot SO_2$ and significant solvent stabilization of the cation center. In other words, we suggest that in a "free" poorly solvated β-arylalkyl carbonium ion alkyl or hydride shift to form a benzylic ion may be faster than phenonium ion formation or net aryl migration. Some brief speculations as to why this might be the case are given below.

In an intimate ion pair ($R^+ \cdots XS_n^-$) the leaving group X, which it is reasonable to assume is at least partially solvated, should have a greater effect in stabilization of the β-anisylalkyl cation ($^+AnCR_2CR'_2$-$X\bar{S}_n$) than the benzylic ion ($^+AnCRCRR'_2X\bar{S}_n$), in which the positive charge is largely delocalized into the anisyl ring. There are steric considerations also, for in the free β-anisyl cation migration of R to form the benzylic ion may take place from either side of the plane of the carbonium ion. In the ion pair, however, R migration would be expected only from the more restricted geometry in which the migrating R (H or CH_3) is coplanar with and on the opposite side of the anion of the ion pair. This geometry would also introduce significant steric interactions between the anisyl group and the partially solvated leaving group XS_n^-. We would not, therefore, be surprised to find that conversion of β-arylalkyl carbonium ion ion pairs to benzylic ions (or ion pairs) is slower than the rate of formation of benzylic ions from the "free" alkyl cation. Dissociation of intimate ion pairs may be faster in $SbF_5 \cdot SO_2$ than other solvents because SbF_5 is polymeric and an anion transport mechanism similar to that for H^+ and OH^- ions in water is available. Further, since coordination of CH_3O by SbF_5 should reduce not only the ease of phenonium ion formation, but also benzylic ion formation, *relative* competitive rates of anisyl (or anisonium ion formation) and alkyl or hydride migration may be insensitive to whether the CH_3O group is acid complexed or not in $SbF_5 \cdot SO_2$.

Experimental Section

All compounds had nmr and infrared spectra consistent with the assigned structure. Physical properties agreed with those reported in the literature.

2-(*o*-Anisyl)-1-chloroethane.—Lithium aluminum hydride reduction of *o*-anisylacetic acid gave the alcohol, which was converted to the chloride in 66% yield by reaction with excess thionyl chloride in pyridine. The chloride was purified by distillation at 67–68° (0.4 mm), $n^{28}D$ 1.5321.

Anal. Calcd for $C_9H_{11}OCl$: C, 63.34; H, 6.50. Found: C, 63.18; H, 6.46.

2,3-Dihydrobenzofuran.—Atmospheric hydrogenation of benzofuran in ethanol using 5% Pd on C gave dihydrobenzofuran.

4-(*p*-Anisyl)-1-chlorobutane.—Reaction of 4-(*p*-anisyl)-1-butanol, obtained from lithium aluminum hydride reduction of the acid, with excess thionylchloride in pyridine gave the title compound in 76% yield after distillation, $n^{27}D$ 1.5215. Gas chromatography on Carbowax 20M indicated a purity of ≥99%.

Anal. Calcd for $C_{11}H_{15}OCl$: C, 66.48; H, 7.61. Found: C, 66.63; H, 7.80.

4-(*p*-Anisyl)-1-bromobutane.—The bromide was obtained from reaction of the corresponding alcohol with thionyl bromide. Distillation at 0.07 mm (bp 112°) gave a product which was 75% bromide, 11% chloride, and 12% alcohol (by gas chromatography).

1-(*p*-Anisyl)-1-methoxybutane.—The benzylic alcohol was prepared in 92% yield by adding 4-methoxybenzaldehyde to *n*-propylmagnesium bromide in ether. The crude alcohol was treated with a mixture of excess sodium hydride in dimethyl sulfoxide followed by addition of methyl iodide. The reaction was hydrolyzed by cautious addition of water, and the mixture was poured into a large volume of water and extracted with pentane. The pentane solution was washed with water, dried, and evaporated to give a quantitative yield of the crude ether. Distillation at 0.09 mm (bp 65°) yielded the product.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.29; H, 9.30.

4-(*p*-Anisyl)-4-methyl-1-chloropentane.—The Grignard reaction of methylmagnesium iodide with butyrolactone gave 2-methyl-2,5-pentanediol in 43% yield after distillation, bp 74–79° (0.15 mm). Reaction of the diol with 3 equiv of anhydrous aluminum chloride and 0.5 equiv of anisole in CS_2 under typical Friedel–Crafts conditions gave, after work-up and vacuum distillation, the alcohol 4-(*p*-anisyl)-4-methylpentanol, bp 113–115° (0.3 mm). The alcohol was converted in 50% yield to 4-(*p*-anisyl)-4-methyl-1-chloropentane by refluxing in carbon tetrachloride with an equimolar amount of triphenylphosphine, according to the method of Lee and Downie.[29] The 4-(*p*-anisyl)-4-methylpentyl chloride was obtained as a 70:30 mixture of the ortho and para isomers by distillation (bp 88–94°) at 0.2 mm. A second distillation provided a product whose nmr spectrum in the region of δ 7.0 indicated only para substitution.

2-(*p*-Anisyl)-2-methoxy-3-methylpentane.—The Grignard reaction of *p*-anisylmagnesium bromide with 3-methyl-2-pentanone gave 2-(*p*-anisyl)-3-methylpentan-2-ol. The crude alcohol was allowed to react first with a 2 molar excess of sodium hydride in dimethyl sulfoxide followed by 4 equiv of methyl iodide. Hydrolysis with water followed by petroleum ether (bp 30–60°) extraction and vacuum distillation at 0.2 mm (bp 84–90°) gave the title compound (86%) contaminated with 11% of 2-(*p*-anisyl)-3-methyl-2-pentene (structure based on positive Br_2 and permanganate tests for olefin, absence of vinyl hydrogens in nmr, and analysis.)

2-(*p*-Anisyl)-1-propyl Methanesulfonate.—Crude 2-(*p*-anisyl)-propionic acid was prepared in 100% yield by analogy to the method of Hauser,[30] from *p*-anisylacetic acid, potassium amide in liquid ammonia, and methyl iodide. Lithium aluminum hydride reduction of the acid gave the propanol, which was converted by excess methanesulfonyl chloride in pyridine to 2-(*p*-anisyl)-1-propyl methanesulfonate mp 48–49°.

Anal. Calcd for $C_{11}H_{16}O_4S$: C, 54.08; H, 6.60. Found: C, 53.85; H, 6.52.

2-(*p*-Anisyl)-*2-d*-1-propyl Methanesulfonate.—An ether solution of the 2-*p*-anisylpropionic acid dicarbanion, prepared from reaction of the acid with 2 equiv of KNH_2 in liquid ammonia, was drowned in D_2O. The resultant 2-deuterated acid was reduced to the alcohol with lithium aluminum hydride, and the title mesylate was prepared as above for the nondeuterated compound. Only 55% deuteration was achieved; however, the nmr spectrum of the nondeuterated ion was easily subtracted from the spectrum of the mixture in $SbF_5 \cdot SO_2$.

2-(*p*-Anisyl)-2-methylpropanol.—The methylation of 2-(*p*-anisyl)propionic acid was carried out first by reaction with 2 equiv of $NaNH_2$ in liquid ammonia and then addition of methyl iodide. Work-up and recrystallization from hexane gave 2-*p*-anisyl-2-methylpropionic acid (67% yield), mp 82–83.5°, which was reduced to the desired propanol in 92% yield with lithium aluminum hydride.

3-(*p*-Anisyl)-2-chlorobutane.—Treatment of 1-(*p*-anisyl)-2-propanone with $NaNH_2$ in liquid ammonia, followed by addition of methyl iodide, gave 2-(*p*-anisyl)-3-butanone in 60% yield after distillation, bp 72–75° (0.1 mm). A mixture of erythro and threo isomers was obtained after lithium aluminum hydride reduction of the ketone to the alcohol, bp 66° (0.05 mm). Reaction of 3-*p*-anisyl-2-butanol with thionyl chloride in pyridine followed by short-path distillation at 86° (0.1 mm) gave a liquid, $n^{19.5}D$ 1.5273, which was a mixture of *erythro*- and *threo*-3-*p*-anisyl-2-chlorobutanes.

Anal. Calcd for $C_{11}H_{15}OCl$: C, 66.45; H, 7.61. Found: 66.53; H, 7.60.

4,4,4-Trideuterio-3-(*p*-anisyl)-2-butanol.—The title compound was prepared as above from 1-*p*-anisyl-2-propanone, $NaNH_2$,

---

[29] J. B. Lee and I. M. Downie, *Tetrahedron*, **23**, 359 (1967).

[30] C. R. Hauser and W. J. Chambers, *J. Amer. Chem. Soc.*, **78**, 4942 (1967).

and CD_3I followed by reduction of the methylated ketone with $LiAlH_4$ to the alcohol. The nmr spectra indicated greater than 98% deuteration in the desired compound; overall glc purity was 95%.

2-(*p*-Anisyl)-2-methyl-3-butanol.—The corresponding ketone was prepared by successive methylation of 1-(*p*-anisyl)-2-propanone with methyl iodide and sodium amide in liquid ammonia. Lithium aluminum hydride reduction of the ketone gave the desired alcohol in 87% yield, bp 83° (0.03 mm).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.17; H, 9.34. Found: C, 74.31; H, 9.33.

4,4,4-Trideuterio-3-tridueteriomethyl-3-(*p*-anisyl)-2-butanol.—The title compound was prepared as above for 2-(*p*-anisyl)-2-methyl-3-butanol, using CD_3I in methylation of 1-(*p*-anisyl)-2-propanone. Within experimental error integration of nmr spectra of the title compound indicated greater than 98% theoretical deuteration in the desired position.

1-(*p*-Anisyl)-2-methyl-2-propanol.—The Grignard reaction of methyl iodide and ethyl *p*-anisylacetate gave the title compound in 94% yield.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.59; H, 8.94.

2-(*p*-Anisyl)-2,3-dimethyl-3-butanol.—The ethyl ester of 2-(*p*-anisyl)-2-methylpropionic acid was converted to the title alcohol by reaction for 15 hr at room temperature with methylmagnesium iodide in ether. Work-up followed by distillation (0.08 mm) gave the alcohol, bp 85–90°, in 50% yield.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.10; H, 9.66.

1,1,1-Trideuterio-2-tridueteriomethyl-3-(*p*-anisyl)-3-methyl-2-butanol.—The Grignard reaction of methyl-d_3-magnesium iodide in ether with the ethyl ester of 2-(*p*-anisyl)-2-methylpropionic acid gave the desired title alcohol after work-up in the usual fashion. Nmr spectra indicated greater than 98% deuteration in the desired position.

Preparations of Ions.—The ions were prepared by adding the substrate (0.02 mol) dropwise from a syringe equipped with a 25-gauge needle to a rapidly stirred solution of distilled SbF_5 (0.07 mol) in excess SO_2 (5–7 ml), following the general procedure of Olah.[31]

In general, a 3:1 molar ratio of SbF_5 to substrate was found necessary to obtain complete ionization of the substrate. The reactions were run under dry nitrogen.

The nmr spectra was taken on a Varian Associates Model A-60 spectrometer equipped with a variable-temperature probe and improved to give a signal-to-noise ratio of 15:1. The spectra were obtained using internal capillary reference tetramethylsilane (TMS) which was calibrated against tetramethylammonium ion (chloride in $SbF_5 \cdot SO_2$ solution, δ 2.95 ppm). Chemical shifts are reported as parts per million downfield from TMS. The chemical shifts for all ions reported here are computed in Table I.

Quenching of Ions.—Quenching of the ions was accomplished by pouring the ion solution into dry methanol or methanol and sodium methoxide at −70°. After stirring for 1 hr, the mixture was evaporated to dryness on a rotary evaporator, and the residue was taken up in water and pentane. The aqueous phase was extracted with fresh pentane and the pentane solution was dried ($MgSO_4$) and evaporated. Identification of the products was by glc analysis, by comparison, and by retention times and peak enhancement. Sometimes products were also trapped as they were eluted from the glc and were identified by comparing their infrared or nmr spectra to those of authentic materials.

Quenched $SbF_5 \cdot SO_2$ solutions of 2-*p*-anisylethanol yielded 45% 2-(*p*-anisyl)-1-methoxyethane and 41% of the starting alcohol.

Quenched solutions of 2-(*o*-anisyl)-1-chloroethane, after extraction of pentane with aqueous Na_2SO_3, gave 20% 1,2-dihydrobenzofuran (per cent yield of neutral product).

The 4-(*p*-anisyl)-1-chlorobutane $SbF_5 \cdot SO_2$ solutions after quenching gave a crude product whose nmr spectrum agreed with that of authentic 1-(*p*-anisyl)-1-methoxybutane.

Registry No.—2-(*o*-Anisyl)-1-chloroethane, 35144-25-3; 4-(*p*-anisyl)-1-chlorobutane, 23002-61-1; 4-(*p*-anisyl)-1-bromobutane, 35191-43-6; 1-(*p*-anisyl)-1-methoxybutane, 35144-27-5; 4-(*p*-anisyl)-4-methyl-1-chloropentane, 35144-28-6; 4-(*o*-anisyl)-4-methyl-1-chloropentane, 35144-29-7; 4-(*p*-anisyl)-4-methylpentanol, 26315-95-7; 2-(*p*-anisyl)-2-methoxy-3-methylpentane, 35144-31-1; 2-(*p*-anisyl)-1-propyl methanesulfonate, 35144-32-2; 2-(*p*-anisyl)-3-methylpropionic acid, 2955-46-6; 2-(*p*-anisyl)-3-butanone (erythro), 35144-34-4; 2-(*p*-anisyl)-3-butanone (threo), 35144-35-5; 3-(*p*-anisyl)-2-chlorobutane (erythro), 26348-35-6; 3-(*p*-anisyl)-2-chlorobutane (threo), 26348-36-7; 2-(*p*-anisyl)-2-methyl-3-butanol, 14614-79-0; 1-(*p*-anisyl)-2-methyl-2-propanol, 35144-39-9; 2-(*p*-anisyl)-2,3-dimethyl-3-butanol, 23002-62-2.

---

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