Onium Ions. IV.[1] Dialkylaryloxonium Ions and Their Alkylating Ability

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Abstract: The reaction of methoxybenzenes with methyl or ethyl fluoroantimonate in SO_2ClF leads to the formation of the corresponding dialkylaryloxonium ions. Dialkylaryloxonium ions were shown to be stable onium ions at low temperature ($\sim -70°$). They are transformed into ring alkylated alkoxybenzenes when the temperatures are raised to 0°. Experimental evidence is provided which indicates that the alkylative transformation of the dimethylphenyloxonium ion proceeds *via* intermolecular nucleophilic displacement by uncomplexed (free) anisole on the oxonium ion, and not intramolecularly. The consequences of this observation concerning the substitution mechanism of anisole are discussed.

Meerwein's pioneering studies established trialkyloxonium ions as an important class of onium ions.[2] Nesmeyanov and his coworkers reported the preparation (although only in yields of 0.2% or less!) of triaryloxonium ions.[3] Alkylaryloxonium ions have been proposed as intermediates in the Friedel–Crafts alkylation of anisole to account for the unusual large amount of ortho product.[4] Recent evidence has been presented which suggests that the methylation of anisole proceeds by initial formation of the dimethylphenyloxonium ion followed by intermolecular rearrangement.[5] Furthermore, the acid-catalyzed rearrangement of alkyl aryl ethers has been studied extensively.[6] Recent evidence shows that the $AlBr_3$ catalyzed rearrangement of optically active *sec*-butyl phenyl ether proceeds by either an intramolecular or intermolecular methyl transfer depending on the reaction conditions.[7] The intermediate proposed for this rearrangement is of oxonium ion nature, with the acid complexed to the ether oxygen. The formation of a single aryldialkyloxonium ion, dimethylphenyloxonium hexachloroantimonate, by the reaction

$$C_6H_5\overset{H}{\underset{SbCl_6^-}{\overset{+}{O}}}CH_3 + CH_2N_2 \longrightarrow C_6H_5\overset{+}{O}(CH_3)_2SbCl_6^-$$

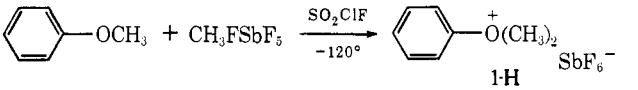
was reported by Klages and his coworkers.[8] However, no physical (spectroscopic) data were obtained or chemical studies reported.

We have now undertaken a study of dialkylaryloxonium ions based on their preparation by reacting anisole and substituted anisoles with methyl and ethyl fluoroantimonate in SO_2 or SO_2ClF solutions at low temperature.

(1) Part III: G. A. Olah and E. G. Melby, *J. Amer. Chem. Soc.*, **94**, 6220 (1972).
(2) H. Meerwein, "Methoden der Organischen Chemie," Vol. 6, No. 3, 1965, pp 325–365.
(3) A. N. Nesmeyanov and T. P. Tostaya, *Dokl. Akad. Nauk SSSR*, **117**, 626 (1957).
(4) P. Kovacic and J. J. Hiller, Jr., *J. Org. Chem.*, **30**, 1581 (1965).
(5) D. A. Simpson, S. G. Smith, and P. Beak, *J. Amer. Chem. Soc.*, **92**, 1071 (1970).
(6) M. J. S. Dewar in "Molecular Rearrangements," P. de Mayo, Ed., Wiley, New York, N. Y., pp 306–344, and references cited therein.
(7) P. A. Spanninger and J. L. von Rosenberg, *J. Amer. Chem. Soc.*, **94**, 1970, 1973 (1972).
(8) F. Klages, H. Meuresch, and W. Steppich, *Justus Liebigs Ann. Chem.*, **592**, 81 (1955).

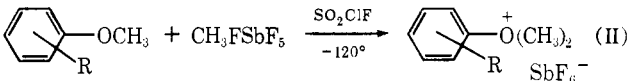
Results and Discussion

A. Preparation and Nmr Spectroscopic Study of Dialkylphenyloxonium Hexafluoroantimonates. When a solution of methyl fluoroantimonate in SO_2ClF is added to anisole in SO_2ClF at $-120°$, a clear solution results. The pmr spectrum of the solution shows in addition to excess methyl fluoroantimonate[9] a singlet at δ 4.95 and an aromatic absorption at δ 7.75, with a peak area ratio of 6:5, assigned to the dimethylphenyloxonium ion **1**. Methyl fluoroantimonate in SO_2ClF



(1)

solution is also O-methylating under similar conditions related substituted anisoles, giving the corresponding dimethylaryloxonium ions.



(II)

R = CH_3, F, Cl, Br

The nmr parameters of the ions are summarized in Table I. The methyl protons are characteristically deshielded and occur at around δ 5.0. The fluorine-19 spectra of ions **2–6** show the expected deshielded shifts compared to their percursors and are also summarized in Table I, along with their pmr parameters. The pmr shifts of the dimethylaryloxonium ions compare well with those reported for methylphenyloxonium ions (O-protonated methoxybenzenes).[10]

When methyl fluoroantimonate in SO_2 solution is reacted with anisole and most substituted anisoles at $-78°$, complex spectra are obtained indicating sulfinylation and ring methylation. It is possible, however, to react fluoro-substituted anisoles with methyl fluoroantimonate in SO_2 solution to obtain the corresponding dialkylaryloxonium ions. Attempts to prepare the diphenylmethyloxonium ion from diphenyl ether and methyl fluoroantimonate in SO_2ClF at $-120°$ resulted only in methylation of the aromatic rings.

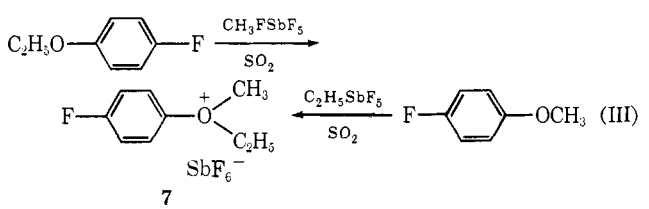
(9) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 156 (1972).
(10) D. M. Brouwer, E. L. Mackor, and C. Maclean, *Recl. Trav. Chim. Pays-Bas*, **85**, 109 114 (1966); G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 2212 (1973).

Table I. Pmr and Fmr Data of Dialkylaryloxonium Ions[a]

Ion		$O^+(CH_3)_n$	O^+CH_2	O^+CCH_3	CH_3	Aromatic	$\delta^{19}F$
$C_6H_5O^+(CH_3)_2$	(1)	4.95				7.75	
$2\text{-}FC_6H_4O^+(CH_3)_2$	(2)	5.15				7.5–8.0	+128.5
$3\text{-}FC_6H_4O^+(CH_3)_2$	(3)	5.05				7.3–7.9	+102.0
$4\text{-}FC_6H_4O^+(CH_3)_2$	(4)	5.00				7.3–7.9	+107.7
$2\text{-}FC_6H_4O^+(CH_3)(C_2H_5)$	(5)	5.17	5.90 (7.5)	1.70 (7.5)		7.6–8.1	+129.1
$3\text{-}FC_6H_4O^+(CH_3)(C_2H_5)$	(6)	5.05	5.60 (7.0)	1.70 (7.0)		7.3–7.9	+102.5
$4\text{-}FC_6H_4O^+(CH_3)(C_2H_5)$	(7)	4.97	5.35 (7.0)	1.66 (7.0)		7.4–7.9	+108.2
$C_6F_5O^+(CH_3)_2$	(8)	5.52					+157.5 +150.2 +147.0
$C_6F_5O^+(CH_3)(C_2H_5)$	(9)	5.42	5.98 (7.0)	1.84 (7.0)			+158.1 +149.1 +147.2
$4\text{-}FC_6H_4O^+(C_2H_5)_2$	(10)		5.30 (7.5)	1.72 (7.5)		7.3–7.8	+108.8
$2\text{-}CH_3C_6H_4O^+(CH_3)_2$	(11)	5.19			2.60	7.9–8.5	
$3\text{-}CH_3C_6H_4O^+(CH_3)_2$	(12)	5.18			2.90	7.7–8.6	
$4\text{-}CH_3C_6H_4O^+(CH_3)_2$	(13)	4.95			2.55	7.60	
$2\text{-}ClC_6H_4O^+(CH_3)_2$	(14)	5.23				7.9–8.4	
$3\text{-}ClC_6H_4O^+(CH_3)_2$	(15)	5.02				7.8–8.3	
$4\text{-}ClC_6H_4O^+(CH_3)_2$	(16)	5.00				7.75	
$2\text{-}ClC_6H_4O^+(CH_3)(C_2H_5)$	(17)	5.20	5.78 (7.0)	1.68 (7.0)		8.0–8.5	
$3\text{-}ClC_6H_4O^+(CH_3)(C_2H_5)$	(18)	5.10	5.60 (7.0)	1.65 (7.0)		7.7–8.3	
$4\text{-}ClC_6H_4O^+(CH_3)(C_2H_5)$	(19)	5.00	5.50 (7.5)	1.60 (7.5)		7.75	
$2\text{-}BrC_6H_4O^+(CH_3)_2$	(20)	5.19				7.6–8.5	
$3\text{-}BrC_6H_4O^+(CH_3)_2$	(21)	5.18				7.5–8.2	
$4\text{-}BrC_6H_4O^+(CH_3)_2$	(22)	5.01				7.8–8.1	
$4\text{-}CH_3BrC_6H_4O^+(CH_3)_2$	(23)	5.15			4.62	8.0–8.4	

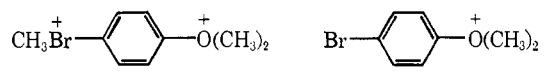
[a] Proton chemical shifts are recorded from TMS in external capillary tube. Fluorine chemical shifts are from external $CFCl_3$. Spectra were recorded at −70° in SO_2ClF or SO_2 solution. Coupling constants are shown in parentheses.

Reaction of 4-fluoroanisole with ethyl fluoroantimonate in SO_2 at −78° gives the ethylmethyl-4-fluorophenyloxonium ion (**7**). Ion **7** was also obtained by methylation of 4-fluorophenetole with methyl fluoroantimonate. The fact that **7** can be formed from two pathways is further proof of the structure of dialkylphenyloxonium ions. Decomposition of ion **7** occurs above −50° giving a pmr spectrum indicating disproportionation and ring substitution. Reaction of 4-fluorophenetole with ethyl fluoroantimonate in SO_2 solution resulted in the formation of the 4-fluorodiethylphenyloxonium ion (**10**). When alkylation of other alkyl phenyl ethers was attempted with ethyl fluoroantimonate in either SO_2 or SO_2ClF solution, the formation of the corresponding oxonium ions was observed only with halogen substituted alkyl phenyl ethers.



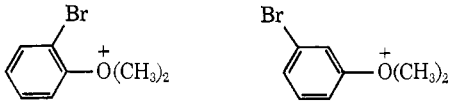
7

Reaction of 4-bromoanisole with excess methyl fluoroantimonate at −78° resulted in a mixture of monomethylated and dimethylated onium ions in a ratio of 1:4.4, respectively. Ion **23** is the first example of a mixed halonium, oxonium dication. Upon heating



23 22

of the solution of the ions to −15°, the ratio of **23**:**22** decreases. Cooling of the solution back to −80° reverses the process giving the same ratio of ions. This observation is analogous to the methylation of *p*-dibromobenzene reported previously.[11] Methylation of *o*- and *m*-bromoanisoles resulted only in formation of the mono-O-methylated oxonium ions, **20** and **21**. These results show that oxygen has a greater affinity for the incipient methyl cation than bromine.

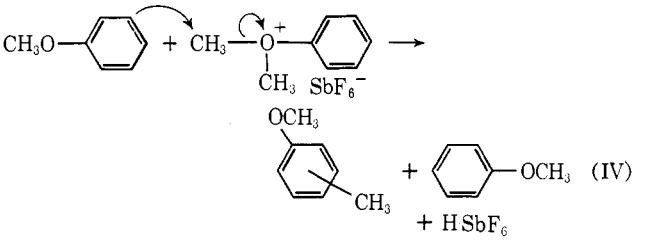


20 21

Reaction of *o*-, *m*-, or *p*-iodoanisole with methyl fluoroantimonate in SO_2 or SO_2ClF solution gave solutions with complicated pmr spectra, indicating mixtures of methylated products. The fact that iodoanisoles behave differently than the other haloanisoles in methylation may be related to the Reverdin rearrangement[12] where the migration of iodine is known to occur during nitration of *p*-iodoanisole.

Other alkylating agents were also reacted with anisole at low temperature to see if oxonium ion formation is a general process in its Friedel–Crafts alkylations. When CH_3F–BF_3, CH_3F–PF_5, CH_3Cl–$SbCl_5$, or CH_3Br–$AlBr_3$ was added to anisole dissolved in SO_2ClF at −78°, neither ring alkylation nor oxonium ion formation was observed. However, pmr spectra of the solutions indicated that the Lewis acid catalyst is transferred to the oxygen atom of anisole. Likewise, when anisole was dissolved in neat methyl fluorosulfate at room temperature neither ring alkylation nor alkylation of the methoxy substituent was observed. Recent work shows that the reaction of anisole with methyl fluorosulfate at 100° for 12 hr results in methyl *p*-methoxybenzenesulfonate.[13] When solutions of dimethylbromonium hexafluoroantimonate or dimethylchloronium hexafluoroantimonate in SO_2ClF were added to anisole at −120°, the pmr spectra of the solutions indicated formation of the dimethylphenyloxonium ion (**1**). However, since the dimethylhalonium ions are rather insoluble in SO_2ClF at low temperatures, this method is less suitable than the use of methyl fluoroantimonate as the methylating agent.

B. Properties. All of the dimethylphenyloxonium ions studied were stable to −10°, as shown by pmr. When a solution of the dimethylphenyloxonium ion (**1**) in SO_2ClF, prepared without excess anisole or excess methyl fluorantimonate, was allowed to stand overnight in a sealed tube at room temperature, no appreciable transformation or decomposition had taken place. After 5 days, the pmr spectrum indicated that the ion had essentially rearranged into a mixture of ring methylated products. When a solution of **1** in SO_2ClF is allowed to stand overnight in the presence of a small excess of anisole, complete transformation of **1** occurs with the formation of ring alkylated products. Thus, the dimethylphenyloxonium ion appears to be reasonably stable in the absence of free anisole. The fact that the oxonium ion rearranges more readily in the presence of anisole indicates that the rearrangement of **1** occurs *via* a nucleophilic displacement by

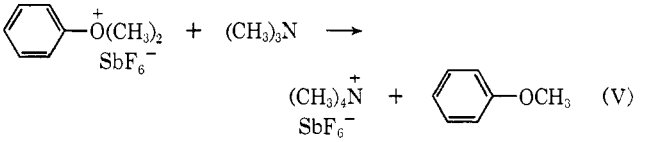


(IV)

the aromatic π system on the oxonium ion. In the reaction besides methylanisole, an equimolar amount of anisole is formed, which can in turn be alkylated (thus the reaction is autocatalytic). Termination of the reaction will occur when all of the oxonium ion is used up. This observation is analogous to the recently reported intermolecular rearrangement of the methylphenylbromonium ion.[1]

Since dialkylphenyloxonium ions are quite stable in solution, we also attempted isolating them as salts. A solution of dimethylphenyloxonium hexafluoroantimonate (**1**) was prepared. Evaporation of solvent SO_2ClF at room temperature yielded a dark colored somewhat sticky solid, which when redissolved in SO_2ClF gives a pmr spectrum identical with that of the starting ion except for traces of uncomplexed anisole and methanol. The salt is very hygroscopic and exposure to atmospheric moisture leads to immediate hydrolysis. The salt is stable only when kept in an inert atmosphere in a freezer. In an analogous fashion, dimethyl-4-fluorophenyloxonium hexafluoroantimonate (**2**) was isolated as a dark colored solid. Likewise, **2** is very hygroscopic and is hydrolyzed when exposed to moisture. However, this salt is more stable than the parent oxonium ion salt and can be stored at room temperature in an inert atmosphere for several days without decomposition.

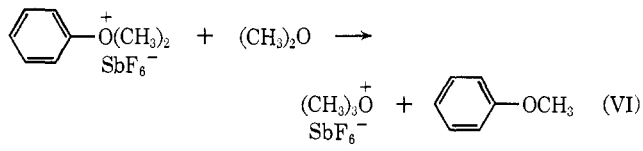
C. Alkylating Ability. Trialkyloxonium ions,[2] dialkylhalonium ions,[14] and alkylarylhalonium ions[1] have been shown to be versatile alkylating agents, capable of alkylating various n-, π-, or σ-donor bases. Therefore, it should be expected that dialkylphenyloxonium ions should have similar capabilities as alkylating agents. When trimethylamine is added to a solution of **1**, in SO_2ClF at −78°, an immediate reaction occurred to give the tetramethylammonium ion.



(V)

Likewise, the addition of dimethyl ether to a SO_2ClF solution of **1** results in the immediate formation of the trimethyloxonium ion.

(11) G. A. Olah, Y. K. Mo, E. G. Melby, and H. C. Lin, *J. Org. Chem.*, **38**, 367 (1973).
(12) F. Reverdin, *Ber.*, **29**, 1000 (1896).
(13) T. Kametani, K. Takahashi, and K. Ogasawara, *Synthesis*, **4**, 473 (1972).
(14) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 2562 (1970).



(VI)

However, when anisole is added to a SO_2ClF solution of either trimethyloxonium hexafluorophosphate or triethyloxonium hexafluorophosphate[15] at 0°, no reaction occurs. This indicates that oxonium ion **1** is a stronger alkylating agent than the trialkyloxonium ions and reaction VI is not rapidly reversible under the experimental conditions employed. When methyl bromide or methyl chloride is added to a SO_2ClF solution of **1**, no reaction is observed. As we previously stated, the dimethylbromonium and dimethylchloronium ions are capable of alkylating anisole at low temperatures to give ion **1**. This result is consistent with our previous studies where dialkylhalonium ions were shown to alkylate dimethyl ether.[14] As we indicated earlier, the dimethylphenyloxonium ion **1** is capable of alkylating anisole in an intermolecular reaction (eq IV). Likewise, if benzene or toluene is added to a solution of ion **1** at −78°, the pmr spectrum indicates the formation of a mixture of ring alkylated products. These results demonstrate that the oxonium ion **1** is capable of alkylating both π- and n-donor bases. Although the alkylating ability is greater than that of the trialkyloxonium ions, it is somewhat less than that of the dialkylhalonium ions. In each case, the alkylation reaction can be visualized to proceed *via* a nucleophilic displacement by either the n- or π-donor bases on the dimethylphenyloxonium ion to give alkylated products.

D. Products of Ring Alkylative Transformation of Dimethylphenyloxonium Hexafluoroantimonate. To further establish the possible role of dialkylaryloxonium ions in Friedel–Crafts alkylations, the products isolated from the ring alkylative transformation of **1** were analyzed. The reactions were carried out under conditions as described in the Experimental Section. In experiment I, **1** was refluxed in SO_2ClF–CH_2Cl_2 for only 15 min, in contrast to II where refluxing was continued for 18 hr. In experiment III, **1** was refluxed in the presence of excess anisole for 15 min. As a comparison, methylation of anisole was carried out with methyl fluoroantimonate in SO_2ClF at 0°, where, as shown by pmr spectroscopy, ring methylation of anisole competes with oxonium ion formation (expt IV). The composition of the CH_2Cl_2 extracts (obtained by gas chromatography) for each experiment is given in Table II, together with reported literature data of conventional Friedel–Crafts alkylation and metathetic silver ion catalyzed alkylation of anisole.

The fact that there is a lower percentage of C-methylated products obtained in experiment I as compared to experiment II is due to the difference in reaction times. In experiment I, the transformation was carried out for a much shorter period of time, during which the oxonium ion **1** may have not rearranged completely. Quenching of this reaction mixture gives 93% of anisole (indicative of unreacted dimethylphenyloxonium ion) and only 7% methylanisoles, the formed ring methylated products. In experiment III, where an excess of anisole was added and the mixture refluxed for only 15 min, the CH_2Cl_2 extract contains a much larger percentage (45%) of methylated products than that obtained in either experiments I or II. Therefore, alkylative transformation of the oxonium ion **1** is much faster and more complete, giving a larger percentage of ring methylated products when excess anisole is present. This further substantiates our earlier conclusion that the transalkylation of **1** proceeds basically by an intermolecular nucleophilic displacement mechanism (eq IV). Since an equimolar amount of anisole is generated as the reaction proceeds, it is only necessary to have a small initial concentration of uncomplexed anisole, always present in equilibrium under Friedel–Crafts conditions. As the isomer distribution is the same for experiments I, II, and III, the intermolecular displacement mechanism may be operating in all three cases.

Table II. Composition of Products Isolated from the Alkylative Transformation of Dimethylphenyloxonium Hexafluoroantimonate[a,b] and Methylation Products of Anisole[c]

No.	Anisole, %	Methylanisoles, %	Other,[d] %	Ortho	Meta	Para	Ortho/para
I	93	7	<1	17	3	80	0.21
II	66	23	10	20	2	78	0.26
III	55	32	13	17	2	81	0.21
IV	89	11	<1	38	15	47	0.81
V		24		35	5	70	0.58
VI				56	12	32	1.75

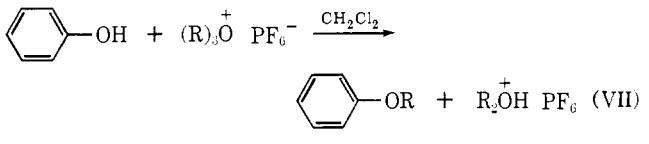
[a] The ortho, meta, and para ratios are the values for the methylanisoles. [b] The percentages given are based on the relative amounts of anisole, methylanisoles, and other products found present in the CH_2Cl_2 extracts. [c] The values for V and VI are literature reported values given in ref 5 and 4, respectively. [d] These products are mainly a mixture of dimethylated anisoles.

The isomer distribution resulting from the alkylative transformation of the dimethylphenyloxonium ion is clearly different from that resulting from the methylation of anisole with methyl fluoroantimonate at 0°, where direct methylation of the aromatic ring competes with oxonium ion formation. In the methylation of anisole with methyl chloroformate and silver hexafluoroantimonate (eq V), intermolecular methyl transfer from the intermediate dimethylphenyloxonium ion was demonstrated by isotopic labeling.[6] In this experiment, some direct alkylation of the aromatic ring competing with the intermolecular oxonium ion mechanism was not excluded. This may account for the fact that the ortho/para ratio for the metathetic reaction is higher than our results (experiments I, II, and III) where methylated products are formed exclusively from the transformation of the oxonium ion **1**. In fact, the values for the metathetic reaction are close to those obtained for our experiment IV, where direct alkylation of the ring is competing with the oxonium ion pathway. The reported methylation of anisole with CH_3Br–$AlCl_3$ in nitromethane[4] gives a higher ortho/para ratio than either our results or the results for the silver ion catalyzed reaction. This could be explained by assuming that in this case the direct alkylation of the aromatic ring may be proceeding to an even greater extent.

As a further comparison, anisole was also reacted with trimethyloxonium hexafluorophosphate in re-

(15) For the preparation and advantages of trialkyloxonium hexafluorophosphates over the more widely used tetrafluoroborates, see G. A. Olah, J. A. Olah, and J. J. Svoboda, *Synthesis*, in press.

fluxing CH_2Cl_2. After 3 days, however, no ring methylated products had formed. Therefore, the only interaction that may have occurred is a reversible O-alkylation of the methoxy group. O-Alkylation is indeed the case when phenol is reacted with either trimethyl- or triethyloxonium hexafluorophosphate where a good yield of anisole or phenetole is obtained.



$R = CH_3$, 45% yield
$R = C_2H_5$, 57% yield

When phenetole is similarly reacted with trimethyloxonium hexafluorophosphate, no reaction is observed. When anisole is reacted with triethyloxonium hexafluorophosphate in CH_2Cl_2, a small yield of phenetole (4%) is obtained.

Conclusion

Results obtained indicate that when the dimethylphenyloxonium ion is involved in the electrophilic methylation of anisole, the preferred pathway to subsequent ring substitution is by intermolecular methyl transfer rather than intramolecular rearrangement. In our experiments using different alkylating agents, aryldialkyloxonium ion formation from anisole was observed only with powerful alkylating agents, such as methyl fluoroantimonate or dimethylhalonium ions. Apparently, with these rather unselective reagents, there is competition between C-methylation of the aromatic ring and O-methylation of the methoxy substituent. When methylation of anisole is carried out at temperatures higher than $-70°$, rapid, irreversible ring alkylation occurs and no dimethylphenyloxonium ion is observed. At lower temperatures ring alkylation becomes slow and O-alkylation giving the stable oxonium ion is becoming predominant. With other alkylating agents such as CH_3Br–$AlBr_3$, electrophilic methylation of anisole may be also proceeding *via* direct alkylation of the aromatic ring without intervention of the oxonium ion, resulting in substantially different isomeric ratios. It has often been proposed that the high ortho/para ratios in these reactions are due to intramolecular rearrangement of the oxonium ion. We find, however, that the alkylative transformation of the oxonium ion, **1**, results in quite low ortho/para ratios. The different positional selectivities observed can be probably due to the differing nature of the transition states.[16] A highly reactive electrophile will interact in a exothermic reaction resulting in an early transition state of π-complex nature, favoring ortho substitution. This may be the case with CH_3Br–$AlBr_3$, where direct attack of the aromatic ring by the powerful electrophile results *via* an early transition state and gives a high ortho/para ratio. In cases where initially the oxonium ion **1** is formed, it acts as a weaker electrophile and ring alkylation instead proceeds by an intermolecular nucleophilic displacement, in a selective reaction of "late" transition nature giving a much increased amount of para substitution. The greater amount of para substitution may be also due to steric factors.

(16) G. A. Olah, *Accounts Chem. Res.*, 4, 240 (1971).

The results described in the present paper do not completely rule out the possibility that a small amount of intramolecular rearrangement occurs simultaneous to the intermolecular reaction. As mentioned earlier, intramolecular rearrangements have been substantiated in the $AlBr_3$ catalyzed rearrangement of *sec*-butyl phenyl ethers.[7] In this system in which free, excess ether was present, an intramolecular mechanism was demonstrated under conditions where the ether was added to $AlBr_3$, *i.e.*, the catalyst was in excess. For the latter path a tight ion pair mechanism seems reasonable, which collapses giving preferential ortho substitution. This path is more favorable for the *sec*-butyl cation than would be for the incipient methyl (or ethyl) cation in our present studies. Thus it is not surprising that the two systems show different behavior reflecting the differing stability of the related ions. Primary methyl and ethyl cations are improbable to be formed in any "free" state: thus alkylations with their precursor oxonium ions take place only through SN2 like intermolecular displacement. SN1 like ion-pair mechanism may be possible with much more stable secondary or tertiary systems.

The results reported relating the alkylating ability of the dimethylphenyloxonium ion *via* intermolecular displacement mechanism raise the possibility that other aromatic substitution reactions also occur by similar mechanism.

Experimental Section

All of the substituted anisoles used in this study were commercially available materials and used without purification. The preparation of methyl (ethyl) fluoroantimonate in SO_2 or SO_2ClF solutions has been described previously.[9] Alkylation of fluorine substituted anisoles was achieved when excess methyl (ethyl) fluoroantimonate in SO_2 was added to the aromatic reagent at $-78°$. The mixtures were stirred vigorously until clear solutions were formed. All other alkylations were carried out in the same fashion at $-120°$ with SO_2ClF solvent.

The dimethylphenyloxonium hexafluoroantimonate used for studies of alkylative transformations (I, II, and III) was prepared by the reaction of 0.028 mol of anisole and 0.028 mol of methyl fluoroantimonate (excess CH_3F) in 15 ml of SO_2ClF solvent at $-120°$. Pmr indicated that all anisole was methylated and that no excess methyl fluoroantimonate remained. The resulting solution was divided into three equal portions for experiments I, II, and III. Experiment I was carried out by allowing **1** to stand at 0° in SO_2ClF solution for 2 hr, whereupon 50 ml of CH_2Cl_2 was added and the mixture refluxed for 15 min. In experiment II, **1** was allowed to stand at 0° in SO_2ClF for 2 hr and then refluxed for 18 hr with 50 ml CH_2Cl_2. In experiment III, an additional amount of anisole (0.25 g, 0.0019 mol) was added to the solution of **1** at low temperature. The resulting mixture was subjected to the same experimental conditions as used in experiment I. Experiment IV was carried out by reacting 0.018 mol of anisole and 0.018 mol of methyl fluoroantimonate at 0° in 10 ml of SO_2ClF for 2 hr and then refluxing with 50 ml of CH_2Cl_2 for 2 hr. In each experiment, the products were isolated by extracting the mixtures with 50 ml of saturated aqueous $NaHCO_3$. The CH_2Cl_2 extracts were subsequently analyzed by gas chromatography under standard conditions using a 10-ft column packed with 5% silicon oil, DC 200, and 5% Bentone 34 on Chromosorb W. Trimethyloxonium hexafluorophosphate and triethyloxonium hexafluorophosphate[15] were commercial materials donated by Cationics, Inc. Nmr spectra were obtained on a Varian Associates Model A-56/60A nmr spectrometer equipped with a variable-temperature probe. Proton chemical shifts are referred to external TMS. Fluorine chemical shifts are referred to external $CFCl_3$.

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