camphor-9-sulfonate [(S)-(+)-4c·(−)-CSA]. The compound was prepared from (S)-(+)-4c·I⁻ and silver (−)-3-bromocamphor-9-sulfonate monohydrate as described for (S)-(+)-4c·(+)-CSA⁻. The crude solid was recrystallized twice from $Cl(CH_2)_2Cl$ to give colorless crystals: mp 179°; $[\alpha]^{20.5}D$ −25.2° (c 0.522, EtOH); ir (KBr) 3500 (s), 3450 (s), 1747 (s, C=O), 1649 (m), 1572 (m, thiazolium ring), ~1200 (s), and 1040 cm^{-1} (s, SO_2).

Anal. Calcd for $C_{22}H_{28}BrNS_2O_4$: C, 51.34; H, 5.48; N, 2.72; S, 12.46. Found: C, 51.11; H, 5.49; N, 2.78; S, 12.28.

Benzoin Condensation Catalyzed by Thiazolium Salts. The molar ratio of benzaldehyde:triethylamine:catalyst was 10:1:~0.95. The concentrations of the reaction mixtures ranged from 0.19 to 0.35 millimoles of catalyst/milliliters of solvent. In all reactions benzaldehyde was added to a solution of the catalyst in methanol (methanol-H_2O, 0.98:2.3 v/v) under nitrogen. A methanolic solution of triethylamine was added dropwise with stirring. After stirring for 24 hr at 30° the reaction mixture was evaporated to dryness and the residue was chromatographed on silicic acid with chloroform. After unreacted benzaldehyde, benzoin was eluted. When the initial separation of benzoin was incomplete, the overlapped portion was rechromatographed with chloroform–benzene (70:30).

Acknowledgment. Financial support for this study was provided by the Sloan Basic Research Fund. T. H. wishes to thank Teijin, Ltd., Tokyo, Japan, for partial financial support, and the Department of State for a Fulbright Travel Grant.

Registry No.—(R)-**2a**·½H_2SO_4, 51-62-7; (R)-(+)-**2b**, 3886-70-2; (S)-(−)-**2b**, 10420-89-0; (S)-**2c**, 2627-86-3; (R)-**3a**, 50486-64-1; (R)-(+)-**3b**, 50486-65-2; (S)-(−)-**3b**, 50486-66-3; (S)-**3c**, 50486-67-4; (R)-(−)-**4a**·BF_4^-, 50477-40-2; (R)-(−)-**4a**·Cl^-, 50486-68-5; (R)-(−)-**4b**·BF_4^-, 50477-41-3; (R)-(−)-**4b**·Br^-, 50486-69-6; (S)-(+)-**4b**·BF_4^-, 50477-42-4; (S)-(+)-**4b**·Br^-, 50486-70-9; (S)-(+)-**4c**·I^-, 50486-71-0; (S)-(+)-**4c**·(+)-CSA, 50486-72-1; (S)-(+)-**4c**·(−)-CSA, 51064-34-7.

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Stable Carbonium Ions from β-Arylalkyl Derivatives in SbF_5·SO_2. II. Ions Related to Mescaline[1,2]

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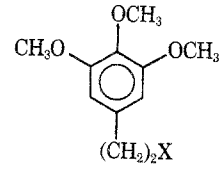
Received October 15, 1973

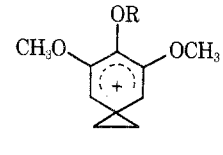
A study of carbonium ions formed from a series of β-di- and trimethoxyphenyl-1-chloroethanes and 2-(*o*-anisyl)-1-chloroethane in either SbF_5·SO_2 or SbF_5·SO_2·BF_3 was carried out. Methoxy-stabilized phenonium ions were generated only from BF_3 complexes of the di- and trimethoxyphenyl-1-chloroethanes in SbF_5·SO_2 wherein the number of ortho and para methoxy groups was greater than the number of meta "destabilizing" methoxys. The 2-(*o*-anisyl)-1-chloroethane gave the oxonium ion **14**, whereas its BF_3 complex gave phenonium ion **15**. In the reaction system SbF_5·SO_2·BF_3, the major reaction competing with phenonium ion formation appeared to be C-protonation by trace amounts of HF. The oxonium ion was obtained from 2-(2′,5′-dimethoxyphenyl)-1-chloroethane in $AgSbF_6$·SO_2 at −20°. No benzylic ion formation was observed in these systems, apparently because the stable ring carbon protonated ions will not readily undergo abstraction of Cl^- by SbF_5.

A variety of ideas have been offered in attempts to correlate physiological activity and structure in mescaline (**1a**), amphetamines, and other hallucinogens.[4]

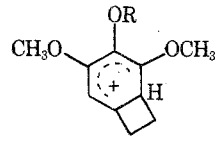
A report[5] that 2-(3′,4′,5′-trimethoxyphenyl)ethanol (**1b**) (a minor rat mescaline metabolite[6c]) or 3′,4′,5′-trimethoxyphenylacetaldehyde produced potent biological effects in rats at significantly lower doses than mescaline, coupled with the isolation of demethylated products[6] from *in vivo* mescaline metabolism [such as 3′,4′-dihydroxy-5′-methoxyphenylacetic acid and 2-(3′-hydroxy-4′,5′-dimethoxyphenyl)ethylamine], suggests the interesting possibility of the intervention of ions or ion pairs such as **2** or **3** at some stage in the biochemistry of mescaline. Such ions seem reasonable, since both alkoxycarbonium ions and the *p*-anisonium ion (**4**) are known to be exceptionally stable, and at least in the case of simple methoxy carbonium ions excellent methylating agents as well.[7,8] Further, Sung and Parker have recently observed a linear correlation between intermolecular charge transfer transition energies and biological activity in mescaline units for a series of psychoac-



1a, X = NH_2
b, X = OH



2
R = H, CH_3



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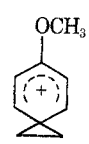
R = H, CH_3



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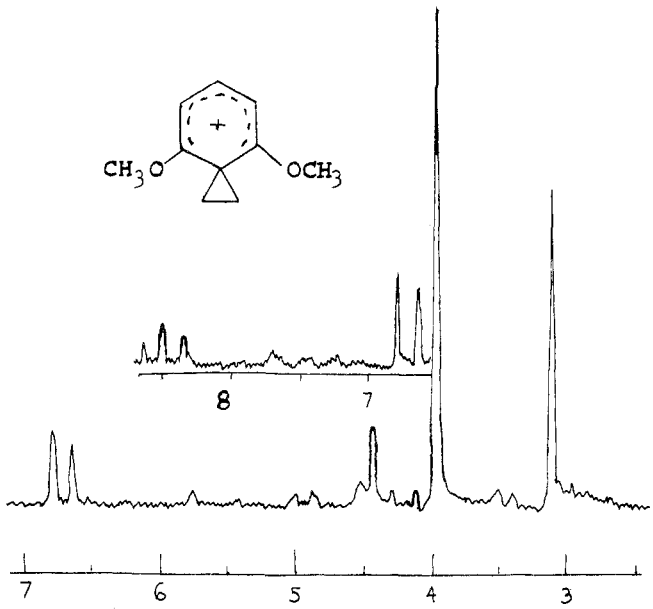


Figure 1. Nmr spectrum of the reaction mixture of 2-(2′,6′-dimethoxyphenyl)-1-chloroethane with BF_3 and SbF_5 in SO_2. Ionization at −70°, spectrum recorded at −30°.

tive methoxyamphetamines.[9] In view of the excellent correlation between charge transfer transition energies, or aryl group ionization potentials, and logarithms of solvolysis rate constants for β-arylalkyl derivatives,[10] this result would be very consistent with rate-determining formation of either phenonium ion or β-methoxyphenyl carbonium ion-like intermediates in the reactions responsible for hallucinogenic activity in mescaline and the amphetamines.

We report here a study of the formation of stable cations in SbF_5·SO_2 and similar solvents from methoxyphenethyl chloride precursors [$(CH_3O)_nC_6H_{5-n}CH_2CH_2Cl$, n = 2, 3] which could be expected to yield **2**, **3**, and analogous ions.

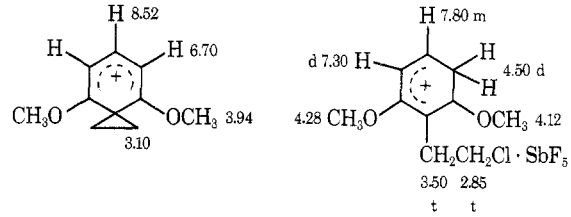
Results and Discussion

Initial attempts to ionize di- and trimethoxyphenethyl chlorides in SbF_5·SO_2 at −70° produced dark, viscous solutions with nmr spectra having only broad and unresolved bands. Since similar problems were not encountered in earlier studies of β-anisylalkyl derivatives,[1] we attributed these complications to increased reactivity of the di- and trimethoxy-substituted phenyl ring toward sulfination, polymerization, and protonation. We decided, therefore, to block one or more of the methoxyl groups by initial complexing with BF_3 in the hope that this would deactivate the aryl ring toward undesirable side reactions but would not prevent phenonium ion formation. This approach has met with modest success.

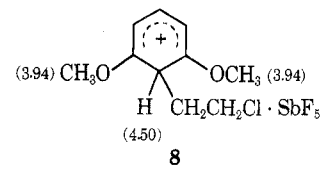
Proton nmr chemical shifts (−δ) (d or t is doublet or triplet) for the ions observed are indicated next to the appropriate hydrogens in the text structures. Chemical shifts in parentheses should be regarded as tentative in assignment.

2-(2′,6′-Dimethoxyphenyl)-1-chloroethane (5). Ionization of the BF_3 complex of **5** in SbF_5·SO_2 at −70° produces, after warming to −30°, a solution whose nmr spectrum is given in Figure 1. Quenching of the −70° solution in methanol yields 30–40% of 2-(2′,6′-dimethoxyphenyl)-ethyl methyl ether and 60–70% of unreacted chloride. The nmr spectrum (Figure 1) is easily assigned to the expected dimethoxyphenonium ion **6**. The sharp singlet at δ 3.10 (relative area 4.0) for the cyclopropyl hydrogens (compared to δ 3.47 for the parent *p*-anisonium ion) is a clear signal of phenonium ion formation. The two methoxyls appear at δ 3.94 (relative area 6.2) and ring protons are displayed very nicely as a doublet (δ 6.70) and triplet (δ 8.25) with relative areas of 1.8 and 1.0.

At −70°, nmr spectra[11] of SbF_5·SO_2 solutions of **5** indicate only very little, if any, phenonium ion formation. Comparisons of the −70° spectra with proton chemical shifts and spectra recently reported[12] for carbon-protonated di- and trimethoxybenzenes in similar solvents strongly support the formation of ions **7** (major) and **8** (minor), which then account for the recovered starting material. There is no evidence of benzylic ion formation from **5** either in the solution nmr spectra, where a strong characteristic $RCHCH_3^+$ methyl *doublet*[8b] would be expected near δ 3.0, or in the quenching products which normally provide benzylic methyl ethers from benzylic ions.[1]

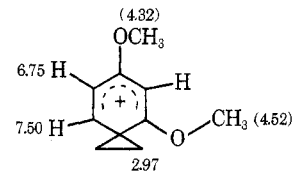


6 **7**



8

2-(2′,4′-Dimethoxyphenyl)-1-chloroethane (9). Acetolysis of 2-(2′,4′-dimethoxyphenyl)ethyl brosylate is about 20 times faster than that of the *p*-anisylethyl brosylate,[13] and easy formation of a phenonium ion from **9** was anticipated. Ionization of BF_3 complexes in SbF_5·SO_2, however, produced only complex spectra. Ionization at −60° of the mono-BF_3 complex of **9** in SOClF, however, produced a simple spectrum in which the presence of the expected dimethoxy phenonium ion **10** was clearly indicated by a sharp singlet of cyclopropyl protons (δ 2.97) and two singlet methoxyl resonances (at δ 4.32 and 4.52) in relative 4:3:3 areas.[11] The indicated assignment, **10**, was made on the basis of the chemical shift of the ortho anisonium ion (CH_3O δ 4.62) compared with that of the para anisonium ion (CH_3O δ 4.25),[8] although any cyclopropyl ring anisotropic effect should produce[14] an *upfield* shift of the ortho CH_3O relative to para CH_3O groups; it is possible that these assignments should be reversed.



10

Even −60° SO_2ClF solutions deteriorated rapidly, however, and methanolic quenching yielded only 15% of the dimethoxyphenyl methyl ether by glc analysis.

2-(2′,3′,6′-Trimethoxyphenyl)-1-chloroethane (11). Ionization of the tris-BF_3 complex of **11** at −70° in SbF_5·SO_2 produced a green solution with a complex nmr spectrum[11] containing at least six different CH_3O resonances between δ 3.60 and 4.50. A very strong isolated singlet at δ 2.98 in the nmr spectrum again, however, is indicative of the formation of ion **12**, and peak areas are in agreement with the indicated assignments. Further, methanolic quenching of solutions provided the expected methyl ether from **12**. The overall complexity, however, of the nmr spectrum suggests the presence of other ions

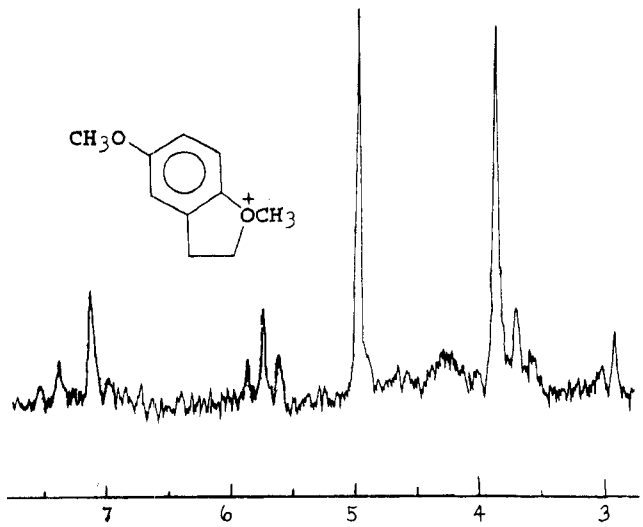
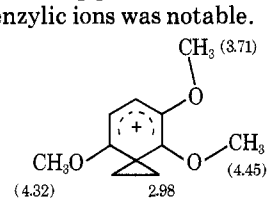


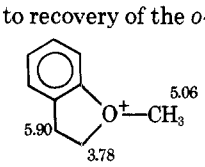
Figure 2. Nmr spectrum of the reaction mixture of 2-(2′,5′-dimethoxyphenyl)-1-chloroethane with $AgSbF_6$ in SO_2. Ionization at −70°, spectrum recorded at −20°.

formed by 1′ and 3′ ring protonation. As in previous cases, the absence of benzylic ions was notable.



12

2-(*o*-Anisyl)-1-chloroethane (13). Since we reported earlier[1] that the ionization of *o*-anisylethyl chloride in SbF_5·SO_2 at −70° produced the oxonium ion 14 rather than the *o*-anisonium ion **15**, we have reinvestigated the ionization of the BF_3 complex under the conditions reported here. In addition to nmr resonances previously identified[1] with **14**, the nmr spectra of BF_3 complexes of 13 in SbF_5·SO_2 at −20° exhibit additional strong singlet resonances at δ 3.00 and 4.62 which may be assigned to the *o*-anisonium ion **15**. Methanolic quenching of 14 and **15** lead to recovery of the *o*-anisylethyl methyl ether.



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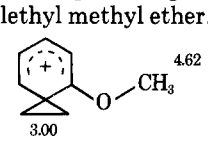
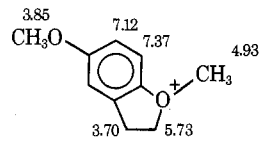


15

2-(2′,5′-Dimethoxyphenyl)-1-chloroethane (16). In the case of **16**, the 5′-methoxyl is in a position which actually leads to inductive destabilization of the phenonium ion which would normally result from aryl participation in the ionization. For example, the acetolysis rate of 2-(*m*-anisyl)-ethyl brosylate is roughly 80 times slower than that of the *p*-anisyl derivative, and even slightly slower than that of the parent 2-phenylethyl brosylate.[13] Attempts to generate a recognizable ion from **16** in SbF_5·SO_2·BF_3, SbF_5·SO_2, or SbF_5·SO_2ClF by previous procedures were without success. A change, however, from the "superacid" system SbF_5·SO_2 to $AgSbF_6$·SO_2 produced a green solution of the oxonium ion **17** from precursor **16**. The ^1H nmr spectrum of **17** at −20° is given in Figure 2.



17

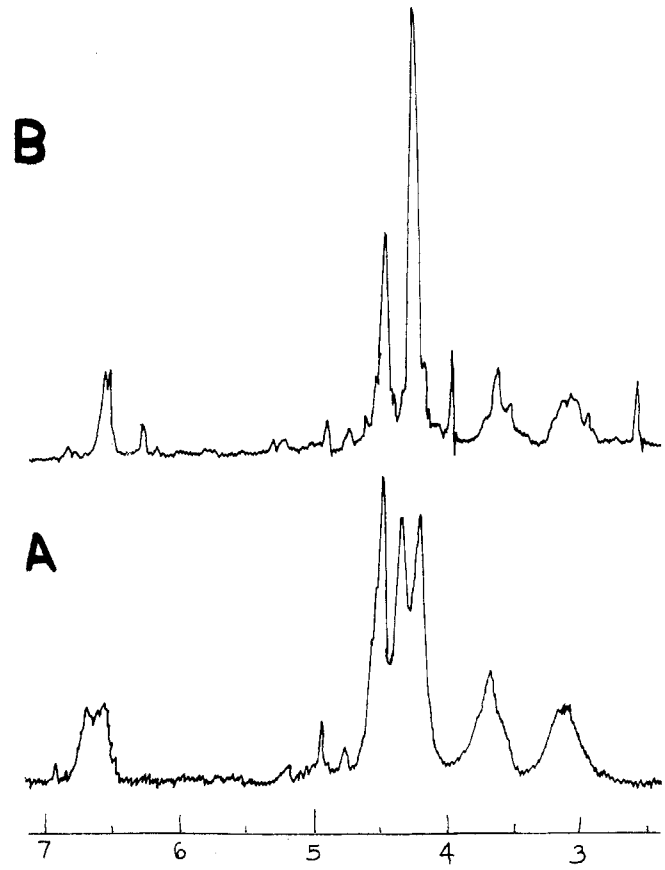
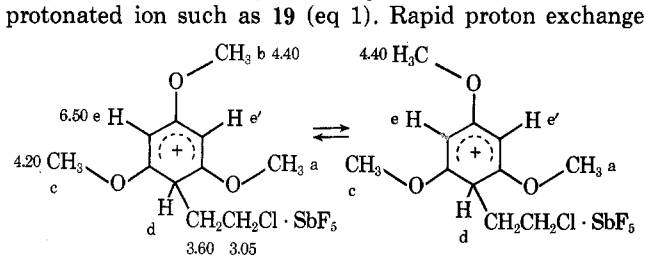


Figure 3. Nmr spectrum of the reaction mixture of 2-(2′,4′,6′-trimethoxyphenyl)-1-chloroethane with SbF_5 in SO_2, ionization at −70°: (A) spectrum at −60°; (B) spectrum at −20°.

2-(2′,4′,6′-Trimethoxyphenyl)-1-chloroethane (18). Ionization of either the mono-BF_3 complex of **18** or the free chloride in SbF_5·SO_2 at −70° and subsequent warming to −20° produced solutions whose nmr spectra gave no sign of any major benzylic phenonium ion formation (Figure 3). The spectrum (Figure 3) of **18** in SbF_5·SO_2 is most simply explained by equilibrating conformers of a carbon-protonated ion such as **19** (eq 1). Rapid proton exchange



19 (1)

at e and e′ in **19** would collapse the δ 4.40 singlet as methoxyls a and c became equivalent and may be excluded. The absence of a sharp two-proton singlet near δ 4.00 as found[12] for monoprotonated 1,3,5-trimethoxybenzene also rules out protonation at positions e or e′ at −20°. At −60° (Figure 3a) equilibration between conformers (eq 1) is sufficiently slow that the different CH_3O groups (a or c) begin to be resolved into a doublet centered about δ 4.30, and the three nonequivalent methoxyls of **19** may now be seen. The proton d is unobserved as a weak or buried triplet. This interpretation is supported by relative areas of 6:3 for the δ 4.30 doublet and 4.50 singlet at −60° and the δ 4.20 and 4.40 singlets at −20°. Steric models appear to preclude easy rotation of methoxyls a and c to form other rotational conformers.

The absence of significant phenonium ion formation from solutions of **18** in SbF_5·SO_2 could reflect the unusual

thermodynamic stability of the C-protonated species **19**, since 1,3,5-trimethoxybenzene protonates readily in 70% perchloric acid.[15]

Quenching of various $SbF_5 \cdot SO_2$ solutions of **15** in cold methanol and sodium ethoxide gave 2-(2′,4′,6′-trimethoxyphenyl)ethyl methyl ether in yields ranging from 35% (from BF_3 complex) to 15–20%. This suggests either that the C-protonated species may be in rapid equilibrium at quenching temperatures with the desired trimethoxyphenonium ion, or that SN2 attack at $-CH_2Cl \cdot SbF_5$ is favorable in this case. Phenonium ion concentrations of the order of 20% are consistent with the singlets at δ 2.55 (assigned to cyclopropyl) and 3.90 (CH_3O) (Figure 3b).

2-(3′,4′,5′-Trimethoxyphenyl)-1-chloroethane (20). Protonation of 1,2,3-trimethoxybenzene in strong acid occurs at the 4 position,[12] and one might expect analogous protonation of mescaline or the chloroethane **20**. However, the 4′ methoxy group of mescaline is easily and selectively hydrolyzed by 20% hydrochloric acid.[16] This is easily rationalized only by ring protonation at the 1′ position of mescaline in dilute aqueous acid, since 2′ protonation should produce hydrolysis of the 3′ (and 5′) methoxyl groups. Low-temperature nmr spectra at −70° of **20** in $SbF_5 \cdot SO_2$ are consistent at least with protonation at both 1′ and 2′ ring positions.

Only the starting chloride could be recovered when these solutions were quenched in cold methanol, and on this basis and the nmr spectra, formation of both benzylic and phenonium ions as major products may be ruled out.

2-(3′,4′- and 2′,3′-Dimethoxyphenyl)-1-chloroethane (21 and 22). Precursors **21** and **22** under the conditions reported here produced only unstable solutions whose nmr spectra contained no recognizable ions.

Conclusions

Except in the case of 2′,4′,6′-trimethoxyphenyl-1-chloroethane, provided that the number of ortho and para methoxy groups exceeded the number of meta "destabilizing" methoxyls, methoxy-stabilized phenonium ions could be generated from BF_3 complexes of di- and trimethoxyphenyl-1-chloroethanes in $SbF_5 \cdot SO_2$. Where ortho methoxy groups are available, unless these groups are coordinated to BF_3, our results here and those reported previously for *o*-anisylethyl chloride[1] suggest that, at least in $SbF_5 \cdot SO_2$, ortho oxygen participation to form an oxonium ion is favored over phenonium ion formation. In the reaction system reported here ($BF_3 \cdot SO_2 \cdot SbF_5$), the major reaction competing with phenonium ion formation appears to be C-protonation by trace amounts of HF. In fact, in the case of 2-(2′,4′,6′-trimethoxyphenyl)-1-chloroethane, our results seem to indicate that the C-protonated ion may be thermodynamically more stable than the corresponding trimethoxyphenonium ion, since the 2′,6′-dimethoxy-3′-C-protonated ion **7** is converted to a dimethoxyphenonium ion **6** at higher temperatures.

Benzylic ion formation is common[1] in $SbF_5 \cdot SO_2$ solutions of p-$CH_3OC_6H_5CR_2CR_2X$ (R = H or CH_3; X = OH or Cl) and the absence of benzylic ion formation in the polymethoxyphenethyl chloride systems investigated here is interesting. We have been unable to prepare $SbF_5 \cdot SO_2$ solutions free of the HF which results from hydrolysis of SbF_5 by trace amounts of water, and the increased basicity of polymethoxy-substituted phenyl rings clearly favors formation of thermodynamically stable ring-protonated ions such as **7** and **19**. Ionization of the primary carbon-chlorine bond in these ions with subsequent or concurrent hydride migration to form a benzylic ion is effectively prohibited by the positively charged protonated ring.

With regard to any proposed metabolic mechanism for *in vivo* activity or demethylation of mescaline, our results do demonstate the stability of polymethoxy-stabilized phenonium ions and encourage us to believe that the ions **2** and/or **3** could be obtained in suitable systems either free of protonic acids or with suitable steric requirements. These ions **2** and/or **3**, or similar ion pairs, remain reasonable intermediates in the *in vivo* reactions of mescaline derivatives.

Experimental Section

The nmr spectra were obtained on a Varian Model A-60 spectrometer with a variable-temperature probe. All synthesized compounds and isolated products from the quenching of ion solutions had nmr and infrared spectra consistent with the assigned structure. The nmr spectra of ions were obtained using internal capillary reference tetramethylsilane (TMS), and chemical shifts (δ, parts per million downfield from TMS) are indicated next to the appropriate hydrogens in the text structures.

Preparation of Ions. The complexing of the various methoxyphenylethyl chlorides with BF_3 was accomplished by first dissolving these compounds in SO_2. To the solution calculated amounts of BF_3 were transferred by means of a vacuum line. The reaction flask containing SO_2 and the BF_3–methoxyphenylethyl chloride complex was then removed from the vacuum line and equipped with a three-necked head containing two liquid nitrogen cold fingers with the center neck covered with a rubber septum. This assembly was then placed in a Dry Ice–acetone bath. A previously prepared $SbF_5 \cdot SO_2$ or $SbF_5 \cdot SO_2ClF$ solution was then rapidly injected into the reactor by means of the rubber septum adapter, with vigorous stirring during addition. In some cases the $SbF_5 \cdot SO_2$ or $SbF_5 \cdot SO_2ClF$ was frozen in liquid nitrogen and added at a slower rate as the solution warmed up.

The oxonium ion **17** was prepared by the dropwise addition of 2-(2′,5′-dimethoxyphenyl)-1-chloroethane (2 mmol) from a syringe (equipped with a 25-gauge needle) to a rapidly stirred solution of $AgSbF_6$ (4 mmol) in excess SO_2 (5–7 ml), following the general procedure of Olah.[17] After the solution had stood for 1 hr without stirring, a sample was withdrawn and the nmr spectrum was determined at −20° (Figure 2).

Drowning of the ions was accomplished by pouring the ion solution into methanol or methanol and sodium methoxide at −70°. The mixture was warmed to room temperature, poured into ether, and washed first with 5% sodium bicarbonate and finally with saturated sodium bicarbonate. The etheral solution was washed with water, dried, and evaporated to leave a crude residue, which was chromatographed on neutral alumina. The products were identified by infrared and nmr, and by comparison of glc retention times and peak enhancement with authentic compounds.

Synthesis of Arylethyl Alcohols and Chlorides. Details of the synthesis and physical properties of the alcohols 2-(2′,6′-dimethoxyphenyl)ethanol, 2-(2′,4′-dimethoxyphenyl)ethanol, 2-(2′,4′,6′-trimethyoxyphenyl)ethanol, and 2-(2′,5′-dimethoxyphenyl)ethanol as well as their corresponding chlorides are given[11] as supplementary material.

Registry No.—**5** BF_3 complex, 51016-46-7; **6**, 50986-73-7; **9** mono-BF_3 complex, 50987-63-8; **10**, 50986-72-6; **11** tris-BF_3 complex, 51016-48-9; **12**, 50986-71-5; **13** BF_3 complex, 51016-49-0; **14**, 35144-41-3; **15**, 50986-70-4; **16** BF_3, 51016-51-4; **17**, 50987-64-9; **18**, 832-86-0; **18** mono-BF_3 complex, 50987-65-0; **19**, 50986-69-1; **20**, 50987-66-1; SbF_5, 7783-70-2; SO_2, 7446-09-5; SOClF, 13637-84-8; $AgSbF_6$, 26042-64-8.

Supplementary Material Available. Full nmr spectra will appear following these pages in the microfilm edition of this volume of the journal for the following reaction mixtures as figures with comments: 2-(2′,6′-dimethoxyphenyl)-1-chloroethane with BF_3 and SbF_5 in SO_2 at −70°; 2-(2′,4′-dimethoxyphenyl)-1-chloroethane with BF_3 and SbF_5 in SO_2ClF, ionization at −70°, spectrum recorded at −20°; 2-(2′,3′,6′-trimethoxyphenyl)-1-chloroethane with BF_3 and SbF_5 in SO_2, ionization at −70°, spectrum recorded at −20° after 1 hr at −20° (peaks indicated by a are assigned to ion **12**). 2-(*o*-anisyl)-1-chloroethane with BF_3 and SbF_5 in SO_2, ionization at −70°, spectrum recorded at −20°; 2-(3′,4′,5′-trimethoxyphenyl)-1-chloroethane with SbF_5 in SO_2 at −70°. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-1199.

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Aromatic Substitution. XXXII.[1] Aluminum Chloride Catalyzed Arenesulfinylation of Benzene and Toluene with Benzenesulfinyl and Substituted Benzenesulfinyl Chlorides in Nitromethane Solution

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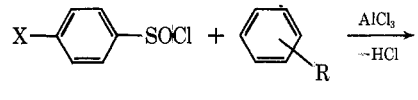
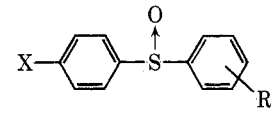
Aluminum chloride catalyzed arenesulfinylation of benzene and polymethylbenzene with substituted benzenesulfinyl chlorides in nitromethane showed that the reaction is of high selectivity. The linear correlation between logarithms of k_{tol}/k_{benz} values and Brown σ^+ substituent constants gives a positive ρ value. These data contrast with previously reported data of sulfonylation and indicate the differing nature of the reactions. The mechanism of the reaction is discussed based on experimental data.

Our preceding work has proved in the case of a series of studied reactions that the transition state of electrophilic aromatic substitutions is not rigidly fixed, resembling the Wheland intermediates (σ complex), but frequently represents a much earlier state on the reaction coordinate resembling starting aromatics (*i.e.*, being of the π-complex character).[3] It was possible to vary in a systematic way the electrophilicity of reagents, such as alkylating agents, by introducing suitable substituents. Thus, a regular change of the transition state of highest energy can be observed from σ-complex to π-complex nature corresponding to the "late" or "early" position of the transition state along the reaction coordinate.

Reactions studied included the titanium tetrachloride catalyzed benzylation of benzene and toluene with substituted benzyl chlorides, giving k_T/k_B rate ratios varying between 2.5 and 136.0 and a correspondingly significant change of the ortho/para isomer ratio.[4] The results of benzoylation of benzene and toluene with substituted benzoyl halides further proved the importance of substituents in the electrophilic substituting agent influencing both substrate and positional selectivity.[5] Aryl thiolcarboxylation also showed the same substituent effect on k_T/k_B and isomer ratio.[6]

Related to these carbocationic reactions, arenesulfonylation of aromatics was also investigated with arenesulfonyl halides.[7] In spite of the fact that the sulfonylation reaction is regarded as an analog of the acylation reaction, it is interesting that the para-substituent effects in arenesulfonyl chlorides on both substrate and positional selectivity show closer similarity to those found in benzylation than in benzoylation reactions. Therefore, from a mechanistic point of view, Friedel–Crafts sulfonylation cannot be considered as a simple analog of the acylation reaction. In order to further study the possible scope and implication of this observation, we undertook a study of the aluminum chloride catalyzed arenesulfinylation of aromatics with benzenesulfinyl and substituted benzenesulfinyl chlorides in which the electron-deficient center of the electrophilic reagent is also on sulfur.





Arenesulfinylation of aromatics giving diaryl sulfoxides was so far little studied. The literature contains but a single report[8] of the preparation of aryl sulfoxides by this reaction. The reaction was found in our hands to be of general utility and allowed us to study the mechanism of arenesulfinylation, including the effect of substituents in the arenesulfinylating agent on the reaction.

Results and Discussion

In order to study the inter- and intramolecular selectivities of Friedel–Crafts arenesulfinylation reactions, we determined, by the use of the competititve method, the relative rates (compared to benzene) of the *p*-toluenesulfinylation of a series of polymethylbenzenes, as well as the related isomer distributions of the alkyl and aryl sulfoxides formed. Data obtained are summarized in Table I.

The results summarized in Table I show that the sulfinylating agent obviously is a very weak electrophile, giving reactions of high selectivity with the aromatic substrates. Data of Table I in comparison with known σ basicities[9] (against $HF-BF_3$ as determined by equilibrium studies by Mackor) show good correlation, indicating that the transi-