Stable Carbonium Ions.
IX.[1] Methylbenzenonium Hexafluoroantimonates[2]

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Stable methylbenzenonium hexafluoroantimonate complexes derived from hexamethylbenzene, pentamethylbenzene, durene, isodurene, prehnitene, mesitylene, pseudocumene, hemimellitene, o-, m-, and p-xylene, as well as toluene were prepared by direct protonation of the methylbenzenes with $HF + SbF_5$ *or* $AgSbF_6 + HCl$ *and by metathetic reaction of bromocyclohexa-1,4-dienes with* $AgSbF_6$ *in sulfur dioxide solution. The* $HF + SbF_5$ *acid system was found to protonate even benzene at low temperature. The stable benzenonium hexafluoroantimonate salts were suitable for n.m.r. investigation in sulfur dioxide solution, e.g., under acid-free conditions where external hydrogen-exchange phenomena could be well eliminated. The proton magnetic resonance spectra fully substantiate the protonation on the ring and the suggested methylbenzenonium structures. The chemical reactivity of the benzenonium complexes was investigated and found generally to be a consequence of their strong protonating ability.*

Introduction

The protonation of methylbenzenes to form σ-complexes (or benzenonium ions according to the nomenclature suggested by Doering[3]) was first achieved by Lien and McCaulay.[4] By the use of HF and BF_3 using excess HF as solvent for xylenes, they observed complex formation upon introduction of BF_3, as evidenced by extraction experiments and by following the vapor pressure reduction of boron trifluoride. Olah and Kuhn reported[5] in 1956 the first isolation of stable alkylbenzenonium tetrafluoroborate complexes. Doering and collaborators isolated in 1958 heptamethylbenzenonium tetrachloroaluminate as a crystalline compound.[3]

Besides vapor pressure and conductivity measurements, the structure of the benzenonium ion type complexes was supported by chemical evidence in both the work of Lien and McCaulay[4] and Olah and Kuhn.[5] Vapor pressure measurements were used by Brown and co-workers[6] to substantiate benzenonium ion formation in alkylbenzene–aluminum (gallium) halide–hydrogen halide systems.

The first direct physical proof for the addition of the proton to a carbon atom forming an "aliphatic" CH_2 group was obtained by Gold and Tye[7] from observation of the electronic spectra of protonated anthracene. Reid[8] obtained similar data investigating alkylbenzenes.

Definite evidence in support of the benzenonium ion structures can be obtained from the n.m.r. spectra of the complexes. The first of these investigations as carried out by Doering and his collaborators[3] and by Mackor and co-workers.[9]

Using excess HF as solvent in the preparation of the conjugate acids of the aromatic hydrocarbons represents difficulties in the observation of their proton resonance spectra, as experienced in the work of Mackor and his co-workers.[9] Fast exchange with the solvent acid makes the observation of the fine structure of the spectra difficult. In subsequent work MacLean and Mackor succeeded by lowering the temperature to diminish the exchange sufficiently to obtain well-resolved spectra.[10] Besides $HF–BF_3$ they also used $BF_3 \cdot H_2O–CF_3CO_2H$ as the protonating media. Birchall and Gillespie in recent work[11] found that fluorosulfonic acid at low temperatures gives ring protonated benzenonium complexes from methylbenzenes, the spectra of which at the temperatures used (-40–$-90°$) were very well resolved.

MacLean and Mackor,[10] as well as Birchall and Gillespie[11] discussed the question of hydrogen exchange of the methylbenzenonium complexes.

Results and Discussion

Preparation of Methylbenzenonium Hexafluoroantimonate Complexes. a. Protonation of Aromatics. "Fluoride Method." The realization that $HF + SbF_5$ in the presence of suitable acceptor bases is an extremely strong conjugate acid[12] is supported by the investigations of Kilpatrick, Katz, and their co-workers[13] who established Hammett acidity functions for antimony pentafluoride in anhydrous hydrogen fluoride solution. A 3 *M* solution was found to have $H_0 = -15.2$; thus it is a 10^4 times stronger acid than 100% sulfuric acid and 10^5 time stronger than anhydrous HF itself.

In previous work relating stable carbonium ions, it was amply demonstrated that hexafluoroantimonate complexes show generally the highest stability of the investigated complex fluoro salts. It was therefore

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Table I. Thermal Decomposition Points of Methylbenzenonium Salts (°C.)

ArH	$ArH_2^+BF_4^{-a}$	$ArH_2^+PF_6^-$	$ArH_2^+SbF_6^-$
1,3-$(CH_3)_2C_6H_4$	−55	−24	+37
1,3,5-$(CH_3)_3C_6H_3$	−15	+ 8	+51
1,2,4,5-$(CH_3)_4C_6H_2$			+62
1,2,3,5-$(CH_3)_4C_6H_2$	−10		
$(CH_3)_5C_6H$		+10	+57
$(CH_3)_6C_6$		+13	+95

[a] See ref. 5.

Table II. Proton Magnetic Resonance of Methylbenzenonium Hexafluoroantimonate Complexes in Sulfur Dioxide Solution[a]

$ArH \cdot H^+SbF_6^+$ ArH	Temp., °C.	Conjugated CH^+	Aliphatic CH_2 or CH_3	p-CH_3 (relative to aliphatic CH_2)	o-CH_3 (relative to aliphatic CH_2)	m-CH_3 (relative to aliphatic CH_2)	$H \atop C<$ CH_3
Benzene	−68	−8.8, 7.5, −7.2	(−3.6)				
Toluene	−68	−8.8, −7.6	−3.8	−2.6	−2.4		
o-Xylene	−70	−8.3, −7.6	−4.4		−2.4	−2.2	
m-Xylene	−71	−8.4, −7.8	−4.6		−2.9	−2.7	
p-Xylene	−65	−8.2, −7.8, −7.6	−4.7		−2.4	−2.2	
Hemimellitene (1,2,3-)	−62	−8.3, −7.6	−4.6	−2.6	−2.2	−2.0	
Pseudocumene (1,2,4-)	−65	−8.3, −7.8	−4.6	−2.6	−2.3	−2.1	
Mesitylene (1,3,5-)	−80	−7.7	−4.6	−2.9	−2.8		
Isodurene (1,2,3,5-)	−66	−7.4	−4.4	−2.7	−2.5	−2.2	
Prehnitene (1,2,3,4-)	−63	−7.9	−4.4		−2.4	−2.2	
Durene (1,2,4,5-)	−68	−7.8	−4.7		−2.8	−2.5	
Pentamethylbenzene	−68		−4.3	−2.5	−2.4	−2.1	
Hexamethylbenzene	−65		−4.2	−3	−2.8	−2.6	−1.9

[a] δ p.p.m. from external tetramethylsilane

felt a logical extension of previous work on benzenonium tetrafluoroborates[5] to investigate the protonation of methylbenzenes with HF + SbF_5 in an attempt to prepare expectedly stable methylbenzenonium hexafluoroantimonate complexes.

The protonation of methylbenzenes, including toluene, the isomeric xylenes, trimethyl- and tetramethylbenzenes, pentamethylbenzene, and hexamethylbenzene with equimolar HF + SbF_5 was successfully carried out and stable, well-defined complexes with substantial thermal stability could be isolated from the sulfur dioxide or fluorochloroalkane solutions in which the complex formation was preferentially performed. In certain cases the complexes were effectively isolated as crystalline compounds. In other cases, the sulfur dioxide solutions were used, without isolation of the complexes, to record their spectra and investigate their chemical reactivity. Table I summarizes the thermal decomposition points of isolated methylbenzenonium hexafluoroantimonate complexes (for sake of comparison, similar data of previously reported tetrafluoroborate and related new hexafluorophosphate complexes are also included). As uncomplexed antimony pentafluoride reacts quite vigorously with alkylbenzenes, it is advantageous to mix the pentafluoride first with HF and then to add a solution of the conjugate acid ($HSbF_6$) to the alkylbenzenes.

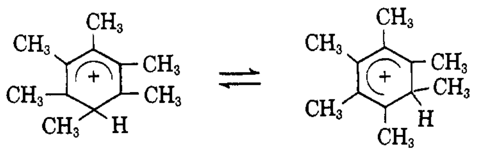
In the course of these investigations it was also observed that HF + SbF_5 is a sufficiently strong acid to protonate even benzene and toluene. These complexes, however, were stable only in solution and at low temperature and could not be isolated.

b. "Silver Salt Method." Instead of HF + SbF_5 it was also found suitable to use anhydrous $AgSbF_6$ + HCl (or HBr) as the source of the protonating acid.

$$ArH + AgSbF_6 + HCl = ArH_2^+SbF_6^- + AgCl$$

Proton Magnetic Resonance Investigations. The best evidence concerning the arenonium ion structure of protonated aromatic hydrocarbons can be obtained by proton magnetic resonance spectra.

Mackor and his co-workers observed[9,10] for pentamethylbenzene in HF–BF_3 a rather broad line at room temperature due to the CH_2 group. For hexamethylbenzene, durene, prehnitene, mesitylene, and *m*-xylene, it was necessary to obtain the spectra at low temperatures in order to observe the resonance of the aliphatic CH_2 groups. The authors have attributed this finding to the exchange of the CH_2 protons by one of three exchange processes: (a) exchange with the acidic solvent, (b) intermolecular exchange between aromatic hydrocarbons and their conjugate acids (the benzenonium complexes), or (c) intramolecular exchange of the proton between positions of equal proton affinity on the same benzenonium ion, for example



From the results of their proton magnetic resonance studies in HF–BF_3 systems, *e.g.*, in a strong proton acid, MacLean and Mackor[10] concluded that in the case of hexamethylbenzene, durene, and prehnitene the exchange proceeds *via* c; in the case of mesitylene, *via* b and a; in the case of *m*-xylene, *via* b; while in the case of pentamethylbenzene they observed no exchange.

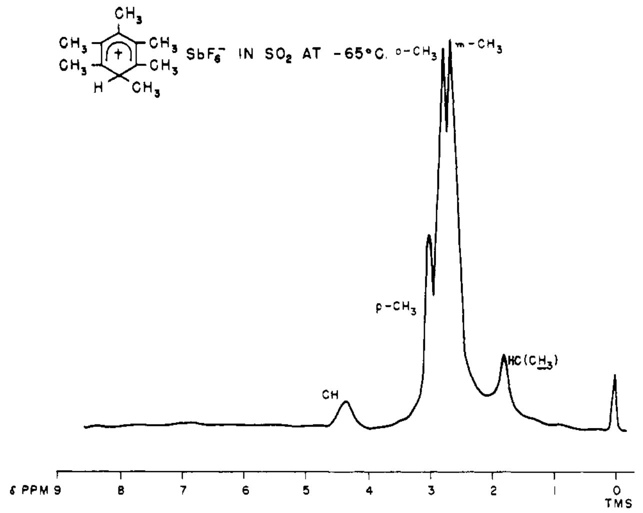


Figure 1. Proton magnetic resonance spectrum of the hexamethylarenonium hexafluoroantimonate complex at 65°.

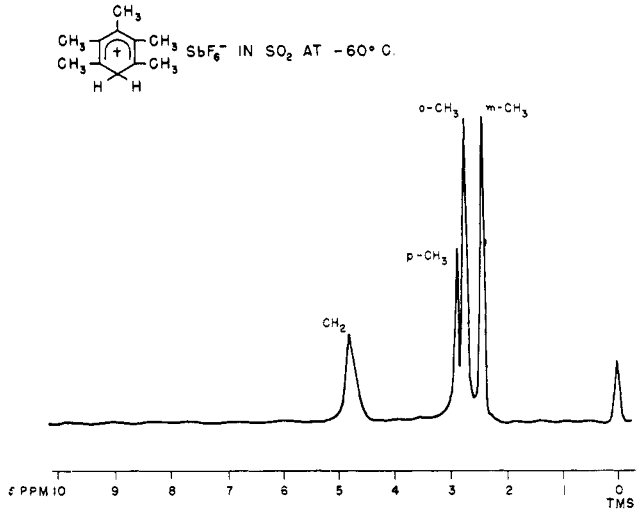


Figure 2. Proton magnetic resonance spectrum of the pentamethylarenonium hexafluoroantimonate complex at 60°.

Birchall and Gillespie made similar n.m.r. studies of the same aromatic hydrocarbons in solutions in fluorosulfuric acid at temperatures down to $-90°$.[11] In contrast to MacLean and Mackor they found that the observed spectra may in all cases be interpreted in terms of exchange by process a, *e.g.*, intermolecular exchange with the acidic solvent.

$$ArH_2^+ + S^- \rightleftharpoons ArH + HS$$

The high stability of the arenonium hexafluoroantimonate complexes, as compared with the tetrafluoroborate and hexafluorophosphate complexes (see Table I), allowed their nuclear magnetic proton resonance investigation in aprotonic solvents such as sulfur dioxide. Under these conditions exchange with the acidic solvent, a major factor in the n.m.r. investigations of MacLean and Mackor and Birchall and Gillespie, can be avoided. The exchange phenomena to be considered are reduced to the possibility of intramolecular proton exchange between positions of equal proton affinity and intermolecular exchange between the benzenonium ions and their parent hydrocarbon precursors *via* deprotonation–protonation equilibrium.

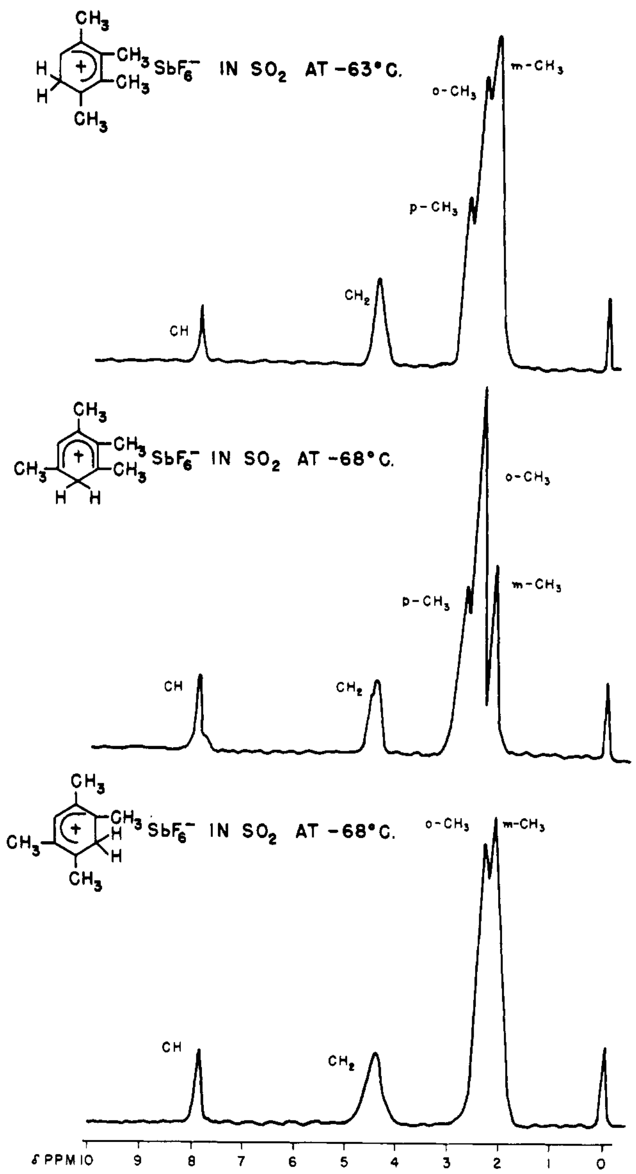


Figure 3. P.m.r. spectra of tetramethylbenzenonium hexafluoroantimonates.

The chemical shifts in the proton magnetic resonance spectra of the methylarenonium hexafluoroantimonate complexes (in p.p.m. from external $Si(CH_3)_4$ contained in a sealed capillary tube centered in the middle of the sample tubes) are summarized in Table II. The spectra themselves showing the assignment of the protons are displayed in Figures 1–5.

The spectra are well resolved when obtained at sufficiently low temperatures (-60–$-80°$). With increasing temperature, however, exchange phenomena are becoming more predominant. For example, the spectrum of the 1,3,5-trimethylbenzenonium ion shows the *o*- and *p*-methyl groups resolved at $-78°$, whereas at higher temperatures, owing to exchange of the extra proton between positions of equal proton affinity, the spectrum shows all the methyl groups equivalent.

Whether the proton exchange is intramolecular or a very fast intermolecular deprotonation–protonation process cannot be unequivocally decided from the present data, although the first possibility must be preferred.

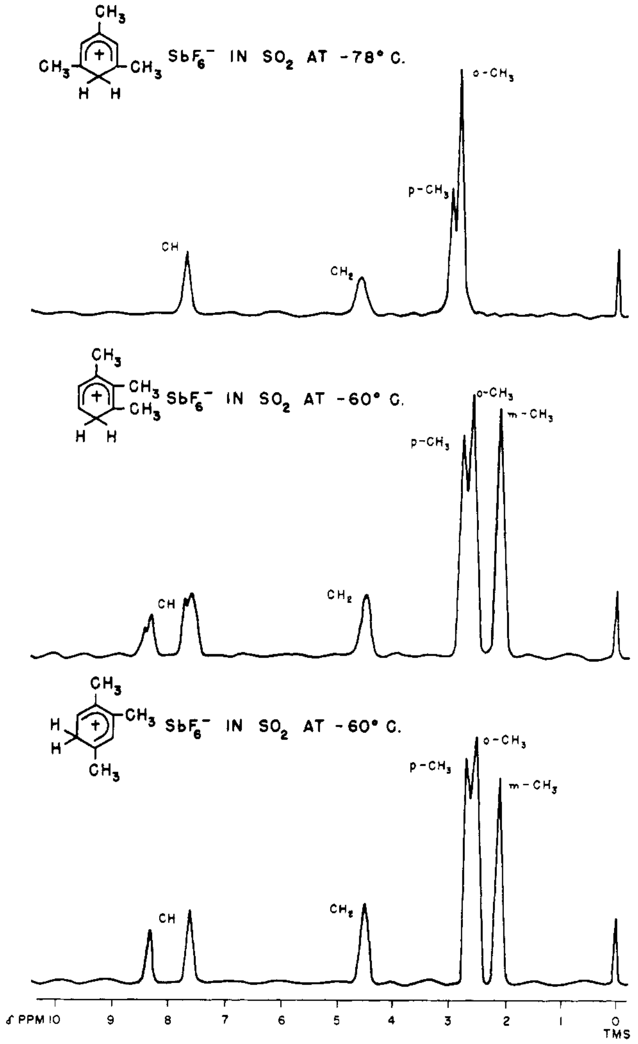


Figure 4. P.m.r. spectra of trimethylbenzenonium hexafluoroantimonates.

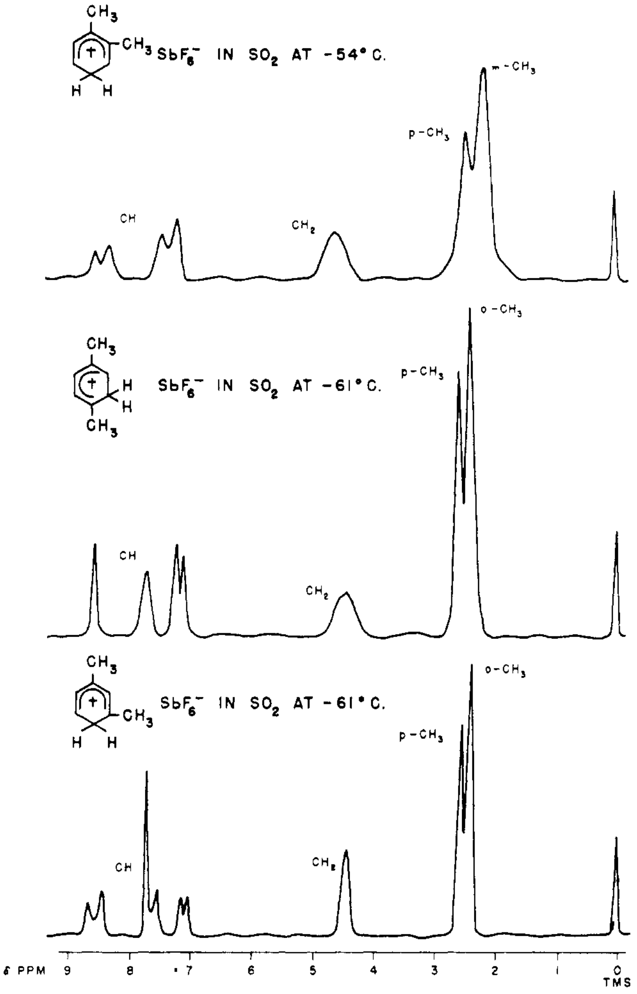
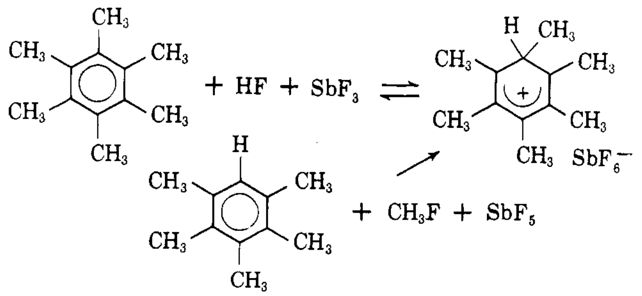


Figure 5. P.m.r. spectra of dimethylbenzenonium hexafluoroantimonates.

When pentamethylbenzene was treated with CH_3F–SbF_5 in sulfur dioxide solution, a hexamethylbenzenonium ion complex identical with that of the protonation of hexamethylbenzene with HF + SbF_5 was obtained.

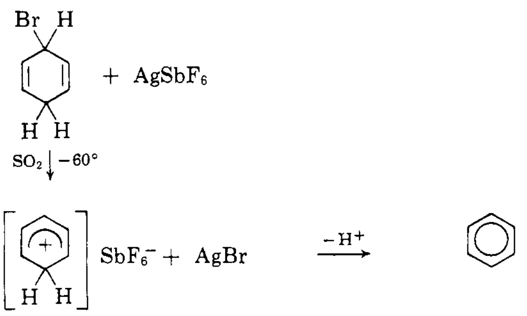


Methylation, like protonation, thus occurs at the only unsubstituted ring position. By raising the temperature, increasing proton exchange between the equivalent ring position occurs, but no evidence of methyl migration, *e.g.*, formation of geminal dimethyl group, was observed. Reaction with excess methyl fluoride gives the heptamethylbenzenonium ion described previously by Doering.[3]

The protonation of benzene can be effected only at low temperature, and the exchange phenomena in this case cannot be slowed down entirely even at −78°. The absence of methyl groups capable of conjugative stabilization is obviously responsible for the substantially increased proton exchange. The spectrum shows only a small, substantially broadened peak in the aliphatic methylene proton region, the peak area being less than the theoretical equivalent for two aliphatic protons. The conjugated ring protons show a 1:2:2 peak area ratio and also substantial deshielding from the position of the benzene ring protons.

Protonation of toluene yields a mixture of 2- and 4-methylbenzenonium ions. Proton peaks at −2.6 and −2.4 p.p.m. are attributed to nonequivalent methyl groups in the mixture of isomers. The unequal heights of the methyl peaks may be attributed to unresolved spin–spin coupling causing a greater broadening of one peak than the other. The relative amounts of the two isomers are unknown and their unequal ratio can also be a major contributing factor. The aliphatic methylene protons are at −3.8 p.p.m. (broadened). The conjugated ring protons show an AB quartet at −7.6 p.p.m. and an asymmetric doublet at −8.8 p.p.m. (partially superimposed).

The benzenonium hexafluoroantimonate complex could also be obtained by the metathetic reaction of bromocyclohexa-1,4-diene with anhydrous silver hexafluoroantimonate, the reaction carried out preferen-



tially in sulfur dioxide solution at low temperature. If the complex was deprotonated by addition of cold alcohol, benzene was obtained.

Chemical Reactivity. The isolation of stable arenonium complexes has allowed an investigation of their chemical reactivity.

It was found in qualitative experiments that the arenonium hexafluoroantimonate complexes react in sulfur dioxide solution with a number of reagents such as alkyl (and aralkyl) halides, acyl halides, acid anhydrides, olefins, carbon monoxide, ketene, etc. No attempt was made to find out optimum reaction conditions. The reagents were added to the solution of the arenonium salt at temperatures ranging from −15 to −50° and allowed to react for an average reaction time of 1 hr.; the mixture was than worked up and analyzed.

$$ArH_2SbF_6^- + RF \longrightarrow ArHR^+SbF_6^- + HF \longrightarrow ArR + SbF_5 + HF$$

$$ArH_2^+SbF_6^- + RCOF \longrightarrow ArHCOR^+SbF_6^- + HF \longrightarrow ArCOR + HF + SbF_5$$

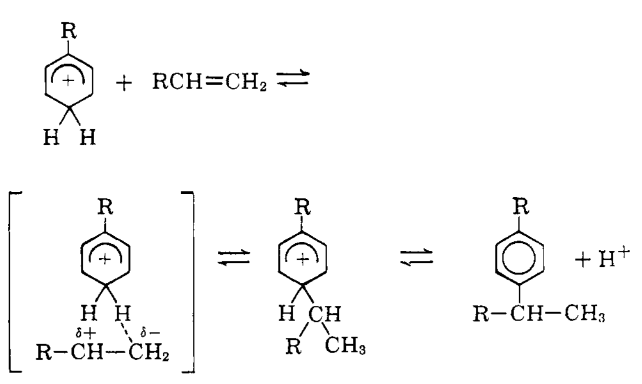
$$ArH_2^+SbF_6^- + (RCO)_2O \longrightarrow ArHCOR^+SbF_6^- + RCO_2H \longrightarrow ArCOR + HF + SbF_5$$

$$ArH_2^+SbF_6^- + RCH{=}CH_2 \longrightarrow ArHCHRCH_3^+SbF_6^- \longrightarrow ArCHRCH_3 + HF + SbF_5$$

$$ArH_2^+SbF_6^- + CO \longrightarrow ArHCHO^+SbF_6^- \longrightarrow ArCHO + HF + SbF_5$$

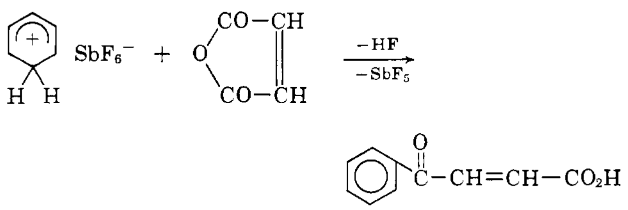
$$ArH_2^+SbF_6^- + CH_2{=}C{=}O \longrightarrow ArHCOCH_3^+SbF_6^- \longrightarrow ArCOCH_3 + HF + SbF_5$$

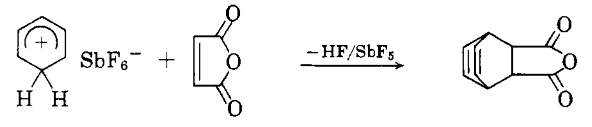
Concerning the reaction mechanism of the interactions of alkylbenzenonium salts, it is suggested that they act as strong protonating agents forming with the reagents new electrophilic species which in turn substitute the ring. The reactions can be interpreted then as simple electrophilic substitutions. However, it is not necessary to consider complete heterolysis before the interaction with the electrophilic reagent begins, as a polarized intermediate can even more likely be the real reaction intermediate in a concerted mechanism.

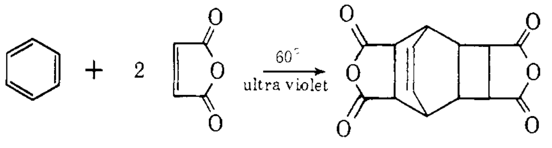


All the previously discussed reactions of arenonium complexes take place as a consequence of the strong conjugate acid nature of the compounds. Attempts were made to find out if the conjugate π-electron system itself has any chemical reactivity. The obvious choice for these investigations was to attempt a Diels–Alder reaction.

Attempted Diels–Alder addition of $C_6H_7^+SbF_6^-$ with maleic anhydride (in liquid HF and SO_2 solutions) gave preferentially the Friedel–Crafts acylation product: β-benzoylacrylic acid. However, a small amount (less than 5% of over-all products) of a 1:1 adduct of benzene with maleic anhydride was also isolated which based on spectroscopic data (see Experimental part) is considered to be a 1,4-adduct. The isolation of the benzene–maleic anhydride adduct through the reaction of benzenonium hexafluoroantimonate with maleic anhydride can be considered as an example of the Friedel–Crafts catalyzed Diels–Alder addition of aromatics, observed by Yates and Eaton[14] and Robinson and Fray.[15] The mechanism may be that of intermediate deprotonation of the benzenonium ion or a concerted mechanism. Although the acid-catalyzed Diels–Alder addition was so far reported only for more reactive aromatic hydrocarbons than benzene, the photochemical addition of maleic anhydride to benzene, yielding a diadduct, is known.[16]







Experimental

Materials. Benzene and alkylbenzenes were the purest available commercial products (Phillips Petroleum research grade, American Petroleum Institute standards, Eastman research grade). When needed they were further purified by preparative g.l.c. using an F and M Model 770 preparative gas chromatograph. The average purity, as analyzed by analytical g.l.c., was better than 99.5%. Anhydrous hydrogen fluoride (minimum purity 99.5%) was used without further purification. Antimony pentafluoride (Allied Chemical Corp., General Chemical Division) was twice distilled before use. Anhydrous $AgSbF_6$ was prepared as described.[17]

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Procedure for Preparation of $ArH_2^+SbF_6^-$ Complexes. a. "Fluoride Method." An equimolar sulfur dioxide solution of HF + SbF_5 was mixed with a sulfur dioxide solution of the aromatic hydrocarbon at temperatures ranging from −15 to −78°. The addition of the reagents was carried out in a closed system with exclusion of atmospheric moisture. After stirring the solution for 10–15 min. (Teflon-coated magnetic stirrer), the solvent (SO_2) was pumped off and the remaining complex recrystallized from sulfur dioxide.

It is also possible to carry out the complex formation in 1,1,2-trifluorotrichloroethane (Freon 113) or difluorodichloromethane (Freon 12) solution.

The stoichiometry of the isolated complexes was established by the use of neutron activation analysis in analyzing fluorine and antimony, together with conventional C–H determinations in cases where the thermal stability allowed these analyses. The infrared spectra of the complexes show the SbF_6^- ion as the characteristic strong absorption band at 660 cm.$^{-1}$. F^{19} magnetic resonance investigation revealed also the presence of the anion, showing all fluorine atoms equivalent.

b. "Silver Salt Method." Anhydrous silver hexafluoroantimonate (0.2 mole) and 0.2 mole of the corresponding methylbenzene were dissolved in 200 ml. of sulfur dioxide at −15°. The cold solution was then saturated with dry HCl (or HBr). Silver halide precipitated. After filtering the silver halide (closed system), the benzenonium complexes were isolated by pumping off the solvent or the solutions were directly used to record the spectra. The n.m.r. spectra were obtained on a Varian Model A60 spectrograph with a low temperature probe. Dr. E. B. Baker is thanked for F^{19} spectra.

Formation of Benzenonium Hexafluoroantimonate from Bromocyclohexa-1,4-diene and Anhydrous Silver Hexafluoroantimonate. Monobromocyclohexa-1,4-diene was prepared according to the adaptation[18] of the procedure of Wibaut and Haak,[19] based on the N-bromosuccinimide bromination of cyclohexa-1,4-diene.

To a solution of 0.02 mole of bromocyclohexa-1,4-diene in 25 ml. of sulfur dioxide, kept at −50°, a solution of 0.02 mole of anhydrous $AgSbF_6$ in 25 ml. of sulfur dioxide was added. The reaction was carried out in a closed system to avoid atmospheric moisture. The mixture was stirred for 30 min. and filtered through a glass filter attached to an arm of the reaction vessel, and the sulfur dioxide solution was used directly to record the n.m.r. spectrum.

Reactions of Methylbenzenonium Hexafluoroantimonates. Into a cold (−25–−50°) solution of 0.1 mole of the corresponding methylbenzenonium hexafluoroantimonate complexes (as prepared according to "fluoride" or "silver salt" method) was added 0.15 mole of isopropyl or *sec*-butyl fluoride, acetyl or propionyl fluoride, acetic anhydride, ketene, butene-1, or isobutylene, and the reaction mixture was stirred for 1 hr. The temperature was then slowly raised to −15° and the mixture stirred for another hour. After quenching with ice–water, the organic layer was separated, washed acid free, dried, and worked up. Products were analyzed by gas chromotography and identified by preparative scale separation from the gas chromatograph, followed by infrared and n.m.r. analyses.

Reaction of Benzenonium Hexafluorantimonate with Maleic Anhydride. The benzenonium hexafluoroantimonate complex (0.1 mole) in sulfur dioxide or anhydrous HF solution was allowed to react with 0.1 mole of maleic anhydride in the same solvent. The reaction mixture was kept at −60° for 24 hr. Thereafter the temperature was raised to −10° for 2 hr., the solvent pumped off, and the residue recrystallized. The main reaction product (besides recovered benzene and maleic acid) was β-benzoylacrylic acid (m.p. 97°). From the mother liquid, however, in 5% of the product, there was isolated a crystalline material, m.p. 186°. *Anal.* Calcd. for $C_{10}H_8O_3$: C, 68.2; H, 4.55. Found: C, 67.25; H, 4.57. Infrared analysis shows characteristic anhydride bands at 1805 (vs) and at 1680 (s) cm.$^{-1}$; n.m.r. chemical shifts (in p.p.m. from TMS, sulfur dioxide solution, relative peak areas in parentheses) −2.92 (2), −4.2 (2), and −5.53 (4).

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