wax 20M on Chromosorb W column operated at 120° for hydrocarbon product and 190° for alcohol product. Hydrolysis of the product mixture was accomplished either by sealing the 40-ml centrifuge tube with the No-Air stopper and placing the sealed tube in an oil bath maintained at *ca.* 110° for 3 days or by adding 6 ml of 1.0 *N* aqueous sulfuric acid to the reaction mixture, and extracting the acidified solution with diethyl ether. The yield of alcohol as a function of the rate of addition of the alkylmercuric halide solution to the borohydride solution was determined by following these general procedures but varying the time involved in the addition of the mercurial solution to the solution of the borohydride. The effective stoichiometry of alcohol production with respect to borohydride ion was determined by following the general procedure but varying the starting amount of sodium borohydride.

Demercuration of Neophylmercuric Bromide (1) in the Presence of Oxygen and 2,6-Di-*tert*-butyl-4-methylphenol and Hydroquinone. The effects of these two inhibitors were determined by following the general procedure except that 0.1 mmol (20 mol % relative to **1**) of inhibitor (0.22 g of 2,6-di-*tert*-butyl-4-methylphenol or 0.11 g of hydroquinone) was dissolved in the mercurial solution before the latter was added to the oxygen-saturated solution of the reducing agent. Glpc analysis of the product mixture was carried out after 20 min. After this length of time the reactions carried out in the presence of inhibitor were not yet complete.

***O*-Neophyl-2,2,6,6-tetramethylpiperid-1-yl Oxide (19).** To 20 ml of a tetrahydrofuran solution of 0.3 *N* neophylmagnesium chloride (6.0 mmol) at −50° was added 10 ml of tetrahydrofuran containing 0.63 g (4 mmol) of 2,2,6,6-tetramethylpiperidoxyl. The resulting yellow solution was allowed to warm to room temperature overnight. The resulting light orange mixture was extracted with three 50-ml portions of chloroform. The combined organic phase was washed, dried, and concentrated. Glpc analysis (6-ft, 10% UC-W98 on Chromosorb W column temperature programmed from 100 to 230°) of the resulting red concentrate showed one major peak and several smaller peaks of long retention time, in addition to *tert*-butylbenzene. The major peak was assigned structure **19** on the basis of spectral data: ir (CCl_4) 3080 (w), 3052 (m), 2968 (s), 2930 (s), 2870 (s), 1944 (w), 1871 (w), 1801 (w), 1469 (m), 1372 (m), 1358 (m), 1255 (m), 1245 (m), 1048 (m), 968 (m), and 915 cm^{-1} (m); nmr (CCl_4) δ 7.3 (5 H, aromatic), 3.70 (2 H, CH_2O), 0.9–1.8 (24 H); mass spectrum (70 eV) *m/e* 289 (<1, M^+), 274 (<1), 177 (3), 157 (22), 143 (8), 142 (100), 91 (21).

Anal. Calcd for $C_{19}H_{31}HO$: mol wt, 289.2397. Found: mol wt, 289.2420.

Demercuration of Neophylmercuric Bromide (1) in the Presence of Oxygen and 2,2,6,6-Tetramethylpiperidoxyl. To a solution of 0.5 mmol of **1** and 0.5 mmol of *n*-pentadecane internal standard in 10 ml of DMF was added 0.76 g (4.85 mmol, 9.6-fold molar excess relative to **1**) of 2,2,6,6-tetramethylpiperidoxyl. This solution was added to the oxygen-saturated solution of 0.7 mmol of sodium borohydride in the usual manner. Elemental mercury was compacted by centrifugation after 30 min and the red supernatant solution was analyzed directly by glpc (6-ft, 10% on Chromosorb W column temperature programmed from 100 to 230° and an 8-ft, 15% Carbowax 20M on Chromosorb W column operated at 240°).

Demercuration of alkylmercuric bromides in the presence of oxygen and norbornadiene was carried out following the general procedure with 1.01 ml (10 mmol) of norbornadiene (a 20-fold molar excess of norbornadiene relative to alkylmercuric halide) added to the DMF solution of the mercurial before addition of the latter to the oxygen-saturated borohydride solution.

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Friedel–Crafts Chemistry. VIII.[1] Reaction of Benzene, Halobenzenes, and Alkylbenzenes with Antimony Pentafluoride. Oxidative Scholl Condensation and Friedel–Crafts Metalation, a New Route to Arylfluorostibines

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Abstract: Reaction of benzene or substituted benzenes with antimony pentafluoride gives, dependent on the aromatics and reaction conditions, diaryltrifluorostibines, triaryldifluorostibines, or polycondensed products. The mechanism of the Friedel–Crafts metalation reaction, a suitable new method for the preparation of arylantimony compounds, is discussed.

We recently observed the fluoroantimonic acid induced alkylation of benzene and substituted benzenes with alkanes.[3] We also studied previously the protonation of benzene and alkylbenzenes in the same acid.[4] In the course of our work it became obvious that antimony pentafluoride, always present in equilibrium in SbF_5 containing superacid systems, particularly when carrying out the reactions at or close to room temperature, itself reacts with aromatics. Due to the rather unique properties of antimony pentafluoride and depending on the aromatic and the reaction conditions, either Friedel–Crafts type substitution leading to metalated aromatics, *i.e.*, phenylfluorostibines, oxidative condensation, or complex formation occurs. Of these reactions the metalation reaction is of most interest as a preparative method to obtain phenyl-

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fluorostibines, whereas the oxidative condensation reactions are of interest not only in regard to the mechanism of Scholl-type condensations, but also concerning the general oxidizing ability of antimony pentafluoride toward π systems.

Triphenyldifluorostibine and its para-substituted derivatives are the only fluorinated pentavalent arylstibines described in the literature. Haszeldine[5] prepared triphenyldifluorostibine by reacting triphenylstibine with *N*-fluoroperfluoropiperidine. Glushkova, *et al.*,[6] obtained several ring-substituted triphenyldifluorostibines by the metathetic reaction of the corresponding triphenyldichlorostibines with potassium fluoride. We now report the Friedel-Crafts type, one-step preparation of arylfluoroantimony compounds which also represents a new general method for the preparation of arylstibines. There are several known methods[7] for the synthesis of arylstibines such as the reaction of arylmagnesium, lithium, cadmium, mercuri and silicon compounds with antimony tri- or pentachloride,[8] the reaction of aryldiazonium hexachloroantimonate(V) or tetrachloroantimonate(III) with cuprous chloride,[9] zinc or iron powder,[10] the reaction of arylhydrazines with antimony trichloride and cupric chloride,[11] the reaction of diaryliodonium chloroantimonates with metallic antimony,[12] and the reaction of halobenzenes and antimony trichloride with sodium.[13] A direct Friedel-Crafts type reaction of aromatics with antimony halides to give arylstibines was, however, unknown until now.

Results and Discussion

In order to study the *reaction of antimony pentafluoride with benzenoid aromatics* we carried out an investigation of its reactions with benzene, halo-, and methylbenzenes. In the case of parent benzene the mechanistic aspects of the formation of phenylfluorostibines by the Friedel-Crafts reaction were also studied in detail and are discussed.

Reaction with Benzene. When antimony pentafluoride is added to benzene, a vigorous, strongly exothermic reaction occurs with immediate formation of a dark colored viscous tar, accompanied by evolution of HF and dark (purple to greenish) fumes. When this heterogeneous reaction mixture is worked up, separation into three components can be achieved, as is summarized in Table I. A polyphenyl polymer which is insoluble in nonpolar, as well as in polar solvents, was obtained in a yield of about 9% (independent of the reaction time), diphenyltrifluorostibine which gives the water-soluble monohydrate **8** in yields up to 20% (dependent on the reaction time) and triphenyldifluorostibine **9**, soluble in nonpolar solvents, in about 4% yield. By varying the reaction time from 5 min to 4 hr and quenching the reaction mixtures with pyridine the yield of polymeric material remains constant at about 9% whereas the amount of diphenyltrifluorostibine, which forms the pyridinium salt of diphenyltetrafluoroantimony acid **6** (indicating that the HF which is formed during the reaction is bound to diphenyltrifluorostibine), increased from 5 to 11%. When the reaction mixture is carefully neutralized with KOH or $NaOCH_3$ in methanol, the corresponding potassium or sodium salt is obtained, which on treatment with diluted sulfuric acid are transformed to the monohydrate **8**. The corresponding diphenyltrichlorostibine monohydrate was previously obtained by Schmidt[14] when he dissolved diphenylstibinic acid $(C_6H_5)_2SbO_2H$ in dilute HCl. Carrying out the reaction in nonpolar solvents, such as Freon 113 (CCl_2FCClF_2) or cyclohexane, the amount of polymer could be reduced to about 4%. Triphenyldifluorostibine **9** was not formed within 12 hr under these conditions. When $HF-SbF_5$ (1:1 v/v) was used (instead of neat SbF_5), the formation of polymeric material was entirely repressed. Upon addition of $HF-SbF_5$ to benzene white crystalline, very hygroscopic diphenyltetrafluoroantimonic acid (**5**) precipitated, which on treatment with pyridine gave the pyridinium salt **6**. When AsF_3 is used as solvent (for benzene as well as for SbF_5, which forms a AsF_3 soluble AsF_3-SbF_5 1:1 adduct[15]), a 15% yield of triphenyldifluorostibine **9** could be obtained. Substituting these lower polarity solvents by solvents with strong n-donor ability, such as acetonitrile, nitromethane, nitrobenzene, or pyridine (addition of benzene to SbF_5 dissolved in excess pyridine precipitates the pyridine-SbF_5 1:1 complex from its solution), the formation of phenylfluorostibines is entirely repressed or the yields are very low (1-2%).

Reactions with Halobenzenes. When halobenzenes were reacted with antimony pentafluoride only fluoro- and chlorobenzene gave the corresponding di(4-fluorophenyl)- and di(4-chlorophenyl)trifluorostibine hydrates in yields of 10-12% or in the case of fluorobenzene tri(4-fluorophenyl)difluorostibine in about 5% yield,

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Table I. Reaction of Benzene and Substituted Benzenes with Antimony Pentafluoride at Room Temperature

Substrate	Reactant	Solvent	Reaction time, hr	Reaction products, %[a]				
					$(4\text{-}RC_6H_4)_2SbF_3 \cdot H_2O$	$(4\text{-}RC_6H_4)_3SbF_2$	Polymer	Miscellaneous
Benzene	SbF_5	Benzene	12	R = H	11.0	3.7	7.6	
	SbF_5	Benzene	24		20.5	3.9	8.6	
	SbF_5	CCl_2FCCF_2	12		8.7		3.3	
	SbF_5	Cyclohexane	12		11.6		3.4	
	SbF_5	AsF_3	16		9.2	12.1	2.5	
	SbF_5	AsF_3	48			15.2	3.7	
	SbF_5	Benzene	5 min				8.9	5.5 $C_5H_5NH^+[(C_6H_5)_2SbF_4]^-$ [b]
	SbF_5	Benzene	2				9.2	6.7 $C_5H_5NH^+[(C_6H_5)_2SbF_4]^-$ [b]
	SbF_5	Benzene	4				8.6	10.6 $C_5H_5NH^+[(C_6H_5)_2SbF_4]^-$ [b]
	SbF_5	CCl_4	6					15.8 benzophenone + C_6H_5Cl
	SbF_5	Benzene	16			3.4	9.4	14.3 $K^+[(C_6H_5)_2SbF_4]^-$ [c]
	SbF_5	Benzene	16			3.0	8.4	12.3 $Na^+[(C_6H_5)_2SbF_4]^-$ [d]
	$HF\text{-}SbF_5$	Benzene	4		15.2	2.3		
Fluorobenzene	SbF_5	Fluorobenzene	16	R = F	7.7	4.8	6.5	
	SbF_5	AsF_3	16		12.1		3.2	
	$HF\text{-}SbF_5$	Fluorobenzene	6		11.2			
	$HF\text{-}SbF_5$	Fluorobenzene	2					12.9 $C_5H_5NH^+[(4\text{-}FC_6H_4)_2SbF_4]^-$
Chlorobenzene	SbF_5	Chlorobenzene	3	R = Cl	7.7		9.2	
	$HF\text{-}SbF_5$	Chlorobenzene	5		9.2			
	$HF\text{-}SbF_5$	Chlorobenzene	2					20.1 $C_5H_5NH^+[(4\text{-}ClC_6H_4)_2SbF_4]^-$
Bromobenzene	SbF_5	Bromobenzene	3	R = H	5.5		10.1	+ dibromobenzenes
	SbF_5	CCl_2FCClF_2	12		2.5		14.4	+ dibromobenzenes
	$HF\text{-}SbF_5$	Bromobenzene	15		10.2		4.2	+ dibromobenzenes
o-Difluorobenzene	$HF\text{-}SbF_5$	*o*-$F_2C_6H_4$	2					6.5 $C_5H_5NH^+[(3,4\text{-}F_2C_6H_3)_2SbF_4]^-$
o-Dichlorobenzene	$HF\text{-}SbF_5$	*o*-$Cl_2C_6H_4$	2					1.2 $C_5H_5NH^+[(3,4\text{-}Cl_2C_6H_3)_2SbF_4]^-$
o-Dibromobenzene	$HF\text{-}SbF_5$	*o*-$Br_2C_6H_4$	2				15.0	4.0 1,3,5-tribromobenzene
Toluene	SbF_5	Toluene	1	R = CH_3		8.2		0.6 dimer
	$HF\text{-}SbF_5$	Toluene	30 min		8.8	3.5		
	$HF\text{-}SbF_5$	Toluene	15 min			2.8		4.2 $C_5H_5NH^+[(4\text{-}CH_3C_6C_4)_2SbF_4]^-$
o-Fluorotoluene	$HF\text{-}SbF_5$	*o*-Fluorotoluene	2			12.0		3.0 $C_5H_5NH^+[(3\text{-}F\text{-}4\text{-}CH_3C_6H_3)_2SbF_4]^-$
m-Fluorotoluene	$HF\text{-}SbF_5$	*m*-Fluorotoluene	2					No reaction
p-Fluorotoluene	$HF\text{-}SbF_5$	*p*-Fluorotoluene	2					No reaction
Mesitylene	SbF_5	Mesitylene	60				1.5	1.3 dimer
Hexamethylbenzene	SbF_5	AsF_3 or C_6F_6	15 min					HMB–SbF_5 complex
Naphthalene	$HF\text{-}SbF_5$	CCl_2FCClF_2	1					Only polymer[e]
Biphenyl	SbF_5	CCl_2FCClF_2	1					Only polymer
	$HF\text{-}SbF_5$	CCl_2FCClF_2	1					Only polymer
Benzene	$SbCl_5\text{-}SbF_5$	Benzene	2					Only chlorobenzene[f]
	$AlBr_3\text{-}SbF_5$	Benzene	10					Only bromobenzene[f]
	$SiCl_4\text{-}SbF_5$	Benzene	10					Only chlorobenzene[f]
	$TiCl_4\text{-}SbF_5$	Benzene	5					Only chlorobenzene[f]
	$AlF_3\text{-}SbF_5$	Benzene	24		16.1	2.8	*g*	

[a] Yields based on the amount of overall SbF_5. [b] By quenching with pyridine. [c] By quenching with KOH in methanol. [d] By quenching with $NaOCH_3$ in methanol. [e] Was not isolated. [f] Determined by glc; approximately 80% yield based on the amount Lewis acid used. [g] Was not determined.

besides polymeric products. On quenching with pyridine, 13% pyridinium di(4-fluorophenyl)tetrafluoroantimonate and 20% pyridinium di(4-chlorophenyl)-tetrafluoroantimonate could be obtained. Bromobenzene disproportionates during the reaction with SbF_5, giving on quenching with water diphenyltrifluorostibine monohydrate and a rather large amount of polymeric material, besides isomeric dibromobenzenes, the major reaction products. From the *dihalobenzenes* investigated only *o*-difluoro- and *o*-dichlorobenzene gave pyridinium di(3,4-difluorophenyl)tetrafluoroantimonate (7%), tri(3,4-difluorophenyl)difluorostibine, and pyridinium di(3,4-dichlorophenyl)tetrafluoroantimonate (2%), when they were reacted with $HF\text{-}SbF_5$ and subsequently quenched with pyridine. *o*-Dibromobenzene only gave polymeric material under the same reaction conditions together with 4% of 1,3,5-tribromobenzene formed by transbromination–isomerization processes. With *hexafluorobenzene* antimony pentafluoride is miscible in all proportions without undergoing any substitution reaction. The ^{19}F nmr spectra of the solution indicate that the polymeric character of SbF_5 is maintained. There are several published ^{19}F nmr spectroscopic investigations of SbF_5. Jolly[16a] studied the spectrum of neat SbF_5, Moss[16b] investigated solutions of SbF_5 in AsF_3, and Gillespie[16c] undertook a very detailed study of SbF_5 dissolved in 1,1,2-trichlorotrifluoroethane (Freon 113). Similar to these solvents, SbF_5 in hexafluorobenzene at room temperature shows a three multiplet spectrum with relative peak intensities of 1:2:2 (due to the three kinds of nonequivalent fluorine atoms in polymeric SbF_5 arranged octahedrally around antimony). The signals[17] are found at ϕ 94.8 (intensity 1, F-bridges), 115.2 (2), and 130.8 (2). The ^{19}F shift of hexafluorobenzene in the presence of excess

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SbF_5 is only deshielded by 1.3 ppm (neat HFB has its ^{19}F shift at ϕ 166.6) indicating a weak interaction between HFB and SbF_5.

Reactions with Methylbenzenes. *Toluene* which has a much higher σ basicity[18] than benzene reacts rapidly with antimony pentafluoride to give tri-*p*-tolyldifluorostibine (8%). Except for some dimerization products only a small amount of polymer is formed when neat SbF_5 is used. Using HF-SbF_5 the formation of the polymer was repressed, but the dimer is still formed. On quenching the reaction mixture with water or pyridine after a short reaction period (15 min) the corresponding di-*p*-tolyltrifluorostibine monohydrate (9%) and pyridinium di-*p*-tolyltetrafluoroantimonate (4%) could be isolated. Interestingly no ortho isomers of the tolylfluorostibines are formed. In our investigations of the three isomeric *fluorotoluenes* (these were used, because they do not readily undergo Friedel-Crafts isomerization) it could be shown that the exclusive formation of para-substituted arylfluorostibines is probably due to considerable steric hindrance caused by the bulky SbF_5, which prevents the formation of an ortho σ complex. Only *o*-fluorotoluene reacted with SbF_5 or HF-SbF_5 to give tri(3-fluoro-4-methylphenyl)-difluorostibine in 12% yield and pyridinium di(3-fluoro-4-methylphenyl)tetrafluoroantimonate in 3% yield, respectively, on quenching with pyridine. *m*- and *p*-fluorotoluene did not react, probably since in the former case the position para to the methyl group is also ortho to a fluorine atom and in the latter it is blocked by fluorine. This shows that by blocking the para position the electrophile cannot enter the position ortho to the methyl group. Further evidence that steric hindrance plays an important role is found in the case of *mesitylene*, which has a σ basicity much higher than toluene.[18] Even after reacting 60 hr with SbF_5, mesitylene was recovered nearly unreacted except for 2% polymeric material and 1% of the dimer (2,4,6,2′,4′,6′-hexamethyldiphenyl). The reason for failing to obtain mesitylfluorostibines can in all probability be found in the fact that only relatively hindered ortho positions would be available for the substitution reaction. When adding SbF_5 to neat mesitylene or combining Freon 113 solutions of both SbF_5 and mesitylene, the precipitation of a mesitylene-SbF_5 complex is observed (the complex is extremely hygroscopic and could not be isolated in pure form). *Hexamethylbenzene* which cannot readily undergo ring substitution (the methyl group being a poor leaving group) is a good model substance to study the interaction between SbF_5 and methylbenzenes leading to π- or σ-complex formation. σ-Complexes are readily formed in the case of the protonation,[19] methylation,[20] nitration, and chlorination[21] of hexamethylbenzene under stable ion conditions. In neat SbF_5 hexamethylbenzene shows good solubility giving, at room temperature, a purple solution. The ^1H nmr spectrum of this solution exhibits a single signal for the methyl protons[17] at δ 3.1, deshielded only by 0.4 ppm from the precursor dissolved in CCl_4 (δ 2.7), thus indicating only formation of a π complex. (At higher temperatures and in hexafluorobenzene, SO_3ClF, or AsF_3 solution more complex reactions, including formation of the pentamethylbenzyl cation, also take place.)

Naphthalene and biphenyl which have much lower ionization potentials than benzene and the halobenzenes[22] give only polymeric material when treated with SbF_5. The intermediates are probably radical cations, similar to the stable species obtained when these aromatics are treated with $SbCl_5$ in methylene chloride.[23] Arenium ion formation of naphthalene with HF-SbF_5 was recently studied and reported.[24]

Mechanism. From the results of our investigation of the reactions of SbF_5 with benzene and substituted benzenes it seems to be established that two different mechanisms can be suggested for the formation of fluorophenylstibines and polyphenylenic polymers. This suggestion is based on the fact that polymer is only formed in the absence of HF (the polymer formation stops when HF is formed as the condensation proceeds) whereas the metalation reaction can be carried out either with neat SbF_5 or with HF-SbF_5 (1:1). Using neat SbF_5 it can be shown by product analysis that the metalation of benzene starts when the condensation reaction to give polyphenyl ceases. (The polymeric material is formed immediately upon addition of SbF_5 and reaches a time independent value of about 9%, whereas the metalation reaction proceeds slower and the amount of pyridinium diphenyltetrafluoroantimonates **6** increase from 5.5% after 5 min to 10.6% after 4 hr.)

For the *metalation* reaction a mechanism can be assumed proceeding through initial π- followed by σ-complex formation between SbF_5 and benzene to give phenyltetrafluorostibine (**3**) as the primary reaction product, which, however, cannot be isolated (Scheme I). Attempts to trap this intermediate by quenching the reaction mixture with pyridine, even after only very short reaction times, failed. This seems to indicate that **3** is also a strong electrophile and reacts further with benzene to give diphenyltrifluorostibine (**4**). The latter on quenching with water gives the monohydrate **8** or by quenching the corresponding diphenyltetrafluoroantimonic acid (**5**) giving with pyridine, sodium methoxide, or potassium hydroxide, the pyridinium **6**, sodium, or potassium salt **7**. Since **4** still has Lewis acid character it will react further with benzene (in a rather slow reaction) to give the neutral triphenyldifluorostibine (**9**). Further reaction to give pentaphenylantimony (**10**) is not possible under the reaction conditions as **10** gives **9** when it is treated with HF in benzene, as it was shown in control experiments. Further evidence that SbF_5 is involved as an electrophile is found in the exclusive formation of para-substituted arylfluorostibines as reaction products with substituted benzenes, indicating a

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(19) For a review, see D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 837.

(20) W. v. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wodley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

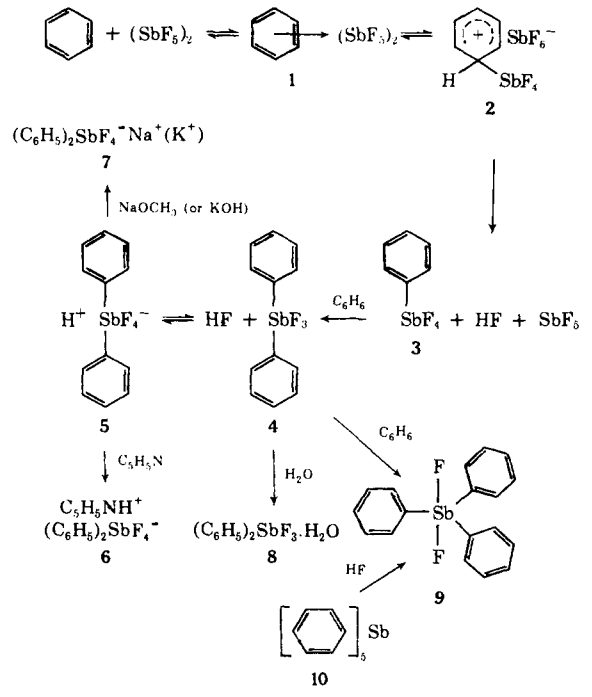
(21) G. A. Olah, H. C. Lin, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3667 (1972).

(22) (a) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960); (b) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc., Ser. A*, **258**, 459 (1960); (c) C. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962). For comparison, biphenyl has an ionization potential 0.77 eV lower than that of benzene.

(23) (a) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965); (b) J. R. Atkinson, T. P. Jones, and E. C. Baughan, *J. Chem. Soc.*, 5808 (1964); (c) W. I. J. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *ibid.*, 3055 (1959).

(24) G. A. Olah, Gh.D. Mateescu, and Y. K. Mo, *J. Amer. Chem. Soc.*, **95**, 1865 (1973).

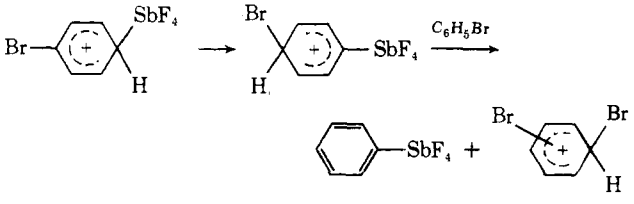
Scheme I



selective electrophilic substitution involving a bulky electrophile. In addition to high positional selectivity, high substrate selectivity is thus also observed in this Friedel-Crafts metalation reaction. When an equimolar mixture of benzene and fluorobenzene or benzene and toluene is used, only pyridinium diphenyltetrafluoroantimonate is formed upon quenching the reaction mixtures with pyridine (within the experimental error of the observation by means of pmr spectroscopy) in 19.5% yield after 2 hr in the former case and only tri-*p*-tolyldifluorostibine in 10% yield after 1 hr of reaction time in the latter case.

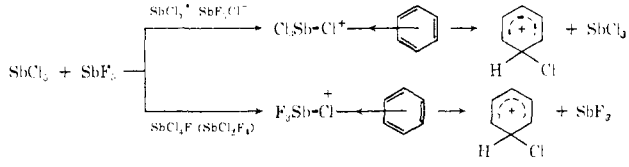
For the reaction of SbF_5 with bromobenzene giving diphenyltrifluorostibine monohydrate instead of the expected para-substituted bromo derivative (besides polymeric materials) it is difficult to decide, if the cleavage of "Br^+" occurs in the σ complex **11** or if SbF_5 reacts with benzene formed by the HF-SbF_5 catalyzed disproportionation of bromobenzene. In the case, since SbF_5 was shown to be a highly selective electrophile, high substrate selectivity would be expected ($C_6H_6 \gg C_6H_5Br$) with SbF_5 preferentially attacking benzene.

In a model experiment *p*-bromotoluene was used for bromobenzene with a blocked para position and found not to react with SbF_5. The failure to obtain any *p*-tolylfluorostibines (which would have indicated a preceding disproportionation reaction to toluene and dibromotoluenes and subsequent reaction of SbF_5 with toluene) seems to favor the mechanism in which the σ complex **11** *via* intramolecular rearrangement to **12** acts as an transbrominating agent.



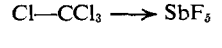
For the formation of the *polymeric* material when benzene is treated with neat SbF_5, a mechanism can be assumed involving radical cation formation, since SbF_5 should have a oxidation potential which is comparable (if not higher) to that of $SbCl_5$. Recently Brouwer[25] succeeded in the preparation of the dications of anthracene, naphthacene, and related polynuclear aromatics by reacting them with antimony pentafluoride in SO_2 or SO_2ClF. The mechanism of the formation of these cations is assumed to involve a two-electron oxidation of the aromatics by SbF_5. Under present reaction conditions, with benzene in excess, condensation to biphenyl is the preferred reaction. Biphenyl, due to its higher σ basicity and lower ionization potential,[22] then is subsequently reacting much faster with SbF_5 to give polymeric products. The inhibition of the polymerization in the presence of HF also indicates that radical species are involved. Simmons[26] studied the reaction of benzene with oxygen in the presence of HF and oxygen carriers such as As_2O_3, MoO_3, Fe_2O_3, or Ag_2O and found up to 100% phenol and only traces of polymeric material.

Reaction of Benzene with Lewis Acids in the Presence of Antimony Pentafluoride. In an attempt to prepare triphenyldichlorostibine by the SbF_5 catalyzed reaction of benzene and $SbCl_5$, chlorobenzene was obtained in about 80% yield, instead of triphenyldichlorostibine. The ability of $SbCl_5$ to act as a chlorinating agent for aromatics was extensively investigated by Kovacic.[27] When $SbCl_5$ is brought into contact with SbF_5, the ionization of $SbCl_5$ to $SbCl_4^+$ and SbF_5Cl^- (and probably other mixed chlorofluorides) can take place.[28] $SbCl_4^+$ can subsequently cause ionic chlorination of benzene. On the other hand, $SbCl_5$ can also react further with SbF_5 in an halogen exchange reaction forming $SbClF_4$ or $SbCl_2F_3$ which are stronger chlorinating agents than $SbCl_5$.



We have also investigated the behavior of other Lewis acid halides such as $SiCl_4$, $TiCl_4$, and $AlBr_3$ with benzene in the presence of SbF_5. In all cases only halobenzenes were formed. The reactions are similar to that of $SbCl_5$, involving halogen exchange between the Lewis acids and SbF_5. The antimony chloride (bromide)-fluorides then act as halogenating agents.

When CCl_4 is reacted with benzene in the presence of SbF_5, the major reaction product upon work-up is benzophenone (due to hydrolysis of the intermediately formed diphenylchlorocarbenium ion). There is, however, also some dichlorobenzene formed indicating that CCl_4 also acts as chlorinating agent, with the CCl_3 group acting as a pseudohalide.



(25) D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, **91**, 1110 (1972).
(26) J. H. Simmons and R. E: McArthur, *Ind. Eng. Chem.*, **35**, (3), 364 (1947).
(27) A. Kovacic and A. K. Sparks, *J. Amer. Chem. Soc.*, 82, 5740 (1960); *J. Org. Chem.*, 28, 972 (1963); P. Kovacic and A. K. Sparks, *ibid.*, **26**, 2541 (1961).
(28) N. E. Aubrey and J. R. van Wazer, *J. Inorg. Nucl. Chem.*, 27, 1761 (1965).

It was not possible to prepare arylsilanes through the reaction of benzene with $SiCl_4$ in the presence of SbF_5. The reason is, as shown in control experiments, that arylsilanes, such as triphenylfluorosilane, react even at −50° in Freon 113 solution with SbF_5 to give through transarylation processes triphenyldifluoro- and diphenyltrifluorostibine (isolated as monohydrate after quenching with water) in high yield; SiF_4 escapes during the reaction from the solution.

Experimental Section

The melting points were determined on a Mettler automatic melting point apparatus. The ir spectra were obtained on a Beckman IR-10 spectrometer. The nmr spectra were recorded on a Varian Associate A-56/60-A spectrometer. The gas chromatographic analyses were performed on a Perkin-Elmer 226 chromatograph. Reagents used were of highest commercially available purity and were not further purified. SbF_5 (Allied Chemical Co.) was freshly distilled and kept in a dry atmosphere. Elemental analyses were carried out by Crobaugh Laboratories, Cleveland, Ohio.

Reaction of Benzene. SbF_5 (21.7 g, 0.1 mol) was added in a very fine stream into 200 ml of benzene with good stirring and cooling (ice–water). After the addition was completed, the ice bath was removed and the dark reaction mixture was allowed to react at room temperature for several hours (see Table I) [the reaction has to be carried out in a good working hood since an appreciable amount of HF is formed]. At the end of the reaction the mixture was either quenched by water, pyridine, or KOH or $NaOCH_3$ in methanol.

Quenching with Water. The reaction mixture was diluted with 200 ml of methanol; insoluble polymeric materials were filtered off. The clear solution was evaporated *in vacuo*, diluted again with a small amount of methanol, and poured into water. The insoluble oily material dissolved in CCl_4 or CH_2Cl_2 and separated from the aqueous solution. The organic phase was dried ($MgSO_4$) and evaporated to dryness *in vacuo*. The remaining transparent yellow oil was dissolved in a small amount of hot methanol and on standing overnight *triphenyldifluorostibine* crystallized. It was recrystallized from methanol (mp 114–115°). The ir and nmr spectra were identical with those obtained from the authentic material prepared by halogen exchange of triphenyldichlorostibine.

The aqueous solution was evaporated *in vacuo* until white needles separated from the mother liquor. After cooling the solution the precipitate was filtered off and dissolved in acetone. $MgSO_4$ was added and the solution stirred for 1 hr. After the solvent was removed, the residue was recrystallized from acetone–ether or acetone–CCl_4, mp 140–145° (for the yield, see Table I).

Diphenyltrifluorostibine Monohydrate ($C_{12}H_{12}F_3OSb$). *Anal.* Calcd: C, 41.05; H, 3.43; F, 16.25; Sb, 34.71. Found: C, 40.80; H, 3.58; F, 16.83; Sb, 35.12.

Quenching with Pyridine. To a typical reaction mixture 50 ml of pyridine was added under stirring and cooling and diluted with 100 ml of CCl_4. The precipitate (A) was filtered off and washed with CCl_4. The filtrate was evaporated and the oily residue was dissolved in a small amount of methanol. Overnight, *triphenyldifluorostibine* crystallized from the solution. The precipitate (A) was stirred with 300 ml of acetone and the insoluble polymeric material was filtered off. The filtrate was evaporated to dryness *in vacuo* and 20 ml of acetone added. The crystals were filtered and recrystallized from acetone–ether or acetone–water, mp 180–185° (for yield, see Table I).

Pyridinium diphenyltetrafluoroantimonate ($C_{17}H_{16}F_4NSb$). *Anal.* Calcd: C, 47.25; H, 3.71; F, 17.60; N, 3.24; Sb, 28.20. Found: C, 47.20; H, 3.77; F, 17.97; N, 3.35; Sb, 27.38. The water-soluble pyridinium hexafluoroantimonate remains in the mother liquor.

Quenching with KOH or $NaOCH_3$. The reaction mixture was diluted with 290 ml of methanol and neutralized with a methanolic solution of KOH or $NaOCH_3$. The polymeric material was filtered off and the filtrate was partly evaporated. By adding excess of ether a white precipitate separated which was filtered. This mixture of potassium (sodium) diphenyltetrafluoroantimonate and potassium (sodium) hexafluoroantimonate showed no melting point below 350°. Redissolving the salt and adding diluted H_2SO_4 resulted in the formation of the monohydrate which separated when the aqueous solution was partially evaporated. Triphenyldifluorostilbine was obtained from the ether filtrate in the usual way.

Reaction of Benzene in Different Solvents. SbF_5 (10.8 g, 0.05 mol) was dissolved in 50 ml of solvent (CCl_2FCClF_2, CH_3CN, $C_5H_5NO_2$, CH_3NO_2, C_5H_5N) and 20 ml of benzene was added; 10.8 g (0.05 mol) of SbF_5 was dissolved in 10 ml of AsF_3 and added to 5 g (0.065 mol) of benzene dissolved in 20 ml of AsF_3. In the case of cyclohexane and carbon tetrachloride 50 ml of benzene was diluted with 50 ml of the solvent and 10.8 g (0.05 mol) of SbF_5 was added in a fine stream. The work-up of the reaction mixtures after quenching with water or pyridine were similar to the procedures described earlier.

Benzophenone which was obtained from the reaction in CCl_4 was distilled under reduced pressure and identified by comparison with the ir and nmr spectra of the authentic material.

Reaction of Halobenzenes. Fluorobenzene. SbF_5 (10.9 g, 0.05 mol) or 12 g (0.05 mol) of HF–SbF_5 was added to 20 ml of fluorobenzene (or 10.9 g of SbF_5 dissolved in 10 ml of AsF_3 was added to 5 ml of fluorobenzene in 20 ml of AsF_3) and stirred at room temperature. The work-up after quenching with water or pyridine was the same as described with benzene.

Tri(4-fluorophenyl)difluorostibine ($C_{18}H_{12}F_5Sb$) was recrystallized from methanol, mp 77–78°. *Anal.* Calcd: C, 48.57; H, 2.70; F, 21.36; Sb, 27.37. Found: C, 48.53; H, 2.85; F, 21.70; Sb, 26.95.

Di(4-fluorophenyl)trifluorostibine monohydrate ($C_{12}H_{10}F_5OSb$) was recrystallized from acetone–ether, mp 150–153°. *Anal.* Calcd: C, 37.23; H, 2.59; F, 24.56; Sb, 31.48. Found: C, 37.77; H, 2.99; F, 24.61; Sb, 30.60.

Pyridinium di(4-fluorophenyl)tetrafluoroantimonate ($C_{17}H_{10}F_6NSb$) was recrystallized from acetone–ether or water, mp 155–158°. *Anal.* Calcd: C, 43.99; H, 2.16; F, 24.58; N, 3.02; Sb, 26.25. Found: C, 43.10; H, 2.85; F, 24.80; N, 2.98; Sb, 25.76.

Chlorobenzene. SbF_5 (10.9 g, 0.05 mol) or 12 g (0.05 mol) of HF–SbF_5 was added to 20 ml of chlorobenzene and stirred at room temperature. The work-up of the reaction mixture after quenching with water or pyridine was the same as described with benzene.

Di(4-chlorophenyl)trifluorostibine monohydrate ($C_{12}H_{10}Cl_2F_3OSb$) was recrystallized from acetone–ether, mp 189–192°. *Anal.* Calcd: C, 34.37, H, 2.38; F, 13.58; Cl, 16.90; Sb, 29.01. Found: C, 33.65; H, 2.50; F, 13.48; Cl, 16.38; Sb, 27.65.

Pyridinium di(4-chlorophenyl)tetrafluoroantimonate ($C_{17}H_{10}Cl_2F_4NSb$) was recrystallized from acetone–ether or water, mp 167–172°. *Anal.* Calcd: C, 41.08; H, 2.01; F, 15.30; Cl, 14.28; N, 2.82; Sb, 24.51. Found: C, 40.48; H, 3.02; F, 15.4; Cl, 14.53; N, 2.76; Sb, 24.07.

Bromobenzene. SbF_5 (10.9 g, 0.05 mol) or 12 g (0.05 mol) of HF–SbF_5 1:1 was added to 20 ml of bromobenzene and stirred at room temperature. After quenching with water excess of bromobenzene was removed by steam distillation. The dibromobenzenes which were found in the distillate were analyzed by glc. The isolation of diphenyltrifluorostilbine monohydrate was accomplished as described for benzene.

***o*-Difluorobenzene.** HF–SbF_5 1:1 (12 g, 0.05 mol) was added to 20 ml of *o*-difluorobenzene and stirred at room temperature. The reaction mixture was quenched with pyridine, excess CCl_4 was added, and the pyridinium salts were filtered off. The filtrate was evaporated to dryness and the residue purified by column chromatography on silica gel (80–200 mesh, CCl_4 and $CHCl_3$ as eluents).

Tri(3,4-difluorophenyl)difluorostibine. It could not be obtained in crystalline form and was identified by ^1H and ^{19}F nmr spectroscopy.

The pyridinium salts were dissolved in hot water; the solution was filtered and evaporated *in vacuo* until most of the tetraantimonate crystallized from the solution. The salt after drying was recrystallized from acetone–ether, mp 165–170°.

Pyridinium di(3,4-difluorophenyl)tetrafluoroantimonate ($C_{17}H_{12}F_8NSb$). *Anal.* Calcd: C, 40.50, H, 2.38, F, 30.17; N, 2.78; Sb, 24.17. Found: C, 40.86; H, 2.72; F, 29.65; N, 2.60; Sb, 25.44.

***o*-Dichlorobenzene.** HF–SbF_5 1:1 (12 g, 0.05 mol) was added to 30 ml of *o*-dichlorobenzene and stirred at room temperature. The work-up of the reaction mixture after quenching with pyridine was carried out as described with *o*-difluorobenzene. The excess of *o*-dichlorobenzene was removed by vacuum distillation.

Pyridinium di(3,4-dichlorophenyl)tetrafluoroantimonate ($C_{17}H_{12}Cl_4F_4NSb$) was recrystallized from acetone–ether, mp 187–192°. *Anal.* Calcd: C, 35.82; H, 2.11; F, 13.34; N, 2.46; Sb, 21.37. Found: C, 35.80; H, 2.22; F, 13.53; N, 2.40; Sb, 22.10.

***o*-Dibromobenzene.** HF–SbF_5 1:1 (12 g, 0.05 ml) was added to 20 ml of *o*-dibromobenzene, stirred at room temperature, and quenched with pyridine. The reaction mixture was diluted with CCl_4 and the polymeric material filtered off. The filtrate was

Table II. ^1H Chemical Shifts of Triaryldifluorostibines, Diaryltrifluorostibine Pyridine Monohydrates and Pyridinium Diaryltetrafluoroantimonates at 30°[a,b]

Aryl	$C_5H_5NH^+Ar_2SbF_4^-$[c,f]					$Ar_2SbF_3 \cdot H_2O$[c]				Ar_3SbF_2[d]				Precursor	
	H_2	H_3	H_4	H_5	H_6	CH_3	H_2	H_3	H_4	H_6	CH_3	H_2	H_3	H_4	H_5	H_6	CH_3	In CCl_4	In acetone	In CCl_4	In acetone
C_6H_5	8.25	7.78	7.78	7.78	8.25		7.93	7.40	7.40	7.40	7.93	8.55	7.85	7.85	7.85	8.55		7.73		7.12, 7.62[e]	
4-$CH_3C_6H_4$	7.73	6.97		6.97	7.73	2.15	7.96	7.30		7.30	7.96	2.17	8.48	7.72		7.72	8.48	2.82	7.53, 2.78		7.01, 2.12	
3-F-4-$CH_3C_6H_3$	7.70			6.92	7.92	2.18							8.39			7.60	8.45	2.81	7.36–7.58, 2.70		6.80–7.10, 2.08	
4-FC_6H_4	7.90	6.98		6.98	7.90		7.95	7.13		7.13	7.95		8.52	7.60		7.60	8.52		7.30–7.85		6.73–7.23	
3,4-$F_2C_6H_3$	7.68			7.15	7.54								8.33			7.82	8.53		7.45–7.55		6.95–7.05	
4-ClC_6H_4	7.86	7.25		7.52	7.86		7.95	7.40		7.40	7.95								7.70		7.20	
3,4-$Cl_2C_6H_3$	8.10			7.68	7.98														7.45–7.90		7.10–7.52	

[a] TMS was used as external standard. [b] The spectra are mostly multiplets, no attempt was made to determine the H–H or F–H coupling constants. [c] In acetone or acetone-d_6. [d] In CCl_4. [e] In DMSO. [f] The proton signals of the pyridinium cation are unaffected by the anion and found at 13.0 (1), 8.7 (2), 8.5 (1), and 8.0 (2).

evaporated and the residue steam distilled *in vacuo*. The remaining solid was recrystallized from acetone. It was identified as 1,3,5-tribromobenzene by nmr spectroscopy and the mixture melting point with an authentic material showed no depression.

Reaction of Substituted Benzenes. Toluene. SbF_5 (10.9 g, 0.05 mol) or 12 g (0.05 mol) of HF–SbF_5 1:1 was added to 50–100 ml of toluene and stirred at room temperature. After different reaction times (see Table I) the mixtures were quenched with water or pyridine. The products soluble in CCl_4 were separated by column chromatography or silica gel (80–200 mesh, CCl_4 and $CHCl_3$ as eluents). The dimers were identified by glc and nmr spectroscopy.

Tri-*p*-tolyldifluorostibine could not be obtained in crystalline form; it was identified by comparison of the ir and nmr spectra obtained in this compound and an authentic sample prepared by the reaction of the corresponding dichloride with KF in methanol.[3]

Di-*p*-tolyltrifluorostibine monohydrate ($C_{14}H_{16}F_3OSb$) was recrystallized from acetone–water, mp 120–123°. *Anal.* Calcd: C, 44.36; H, 4.22; F, 15.05; Sb, 32.15. Found: C, 42.60; H, 4.73; F, 14.71; Sb, 32.76.

Pyridinium di-*p*-tolyltetrafluoroantimonate ($C_{19}H_{20}F_4NSb$) was recrystallized from acetone–water, mp 162–165°. *Anal.* Calcd: C, 49.59; H, 4.35; F, 16.53; N, 3.05; Sb, 26.48. Found: C, 49.12; H, 4.58; F, 16.90; N, 2.99; Sb, 27.12.

***o*-, *m*-, and *p*-Fluorotoluene.** HF–SbF_5 1:1 (12 g, 0.05 mol) was added to 15–20 ml of each isomer and stirred at room temperature. The work-up after quenching with pyridine was the same as described previously.

Pyridinium di(3-fluoro-4-methylphenyl)tetrafluoroantimonate ($C_{19}H_{18}F_6NSb$) was recrystallized from acetone–water, mp 174–178°. *Anal.* Calcd: C, 45.99; H, 3.64; F, 22.99; N, 2.82; Sb, 24.56. Found: C, 45.52; H, 3.81; F, 22.89; N, 2.69; Sb, 24.27.

Tri(3-fluoro-4-methylphenyl)difluorostibine could not be obtained in crystalline form and was identified by ^1H and ^{19}F nmr spectroscopy.

Reaction of Benzene in the Presence of Different Lewis Acids. Five millimoles of the corresponding Lewis acid ($SbCl_5$, $AlBr_3$, $TiCl_4$, $SnCl_4$, AlF_4, $SiCl_4$) was dissolved or suspended in 50 ml of benzene and under ice cooling and stirring 5 mmol of SbF_5 was slowly added. The reaction mixture was kept at room temperature for several hours, and after quenching with ice–water the benzene layer was analyzed by glc.

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Appendix

Nmr Spectroscopic Study of Arylfluoroantimony Compounds. A survey of the literature of arylhaloantimony compounds shows that little work has been done on their nmr spectroscopic study. Only a few spectra of compounds of the type Ar_3SbX_2 (X = halogen) were reported.[29] It therefore seems of value to summarize the results of the nmr spectroscopic studies which we undertook in connection with the investigation of arylfluoroantimony compounds reported in the present paper. Data of pmr and fmr studies are summarized in Tables II and III, respectively.

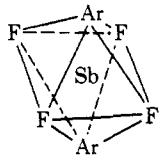
Pyridinium Diaryltetrafluoroantimonates. The octahedral diaryltetrafluoroantimonates can exist as two isomers, I and II. From the ^{19}F chemical shift of the fluorine atoms bonded to antimony [ϕ, 105 (see Table III)] it cannot be decided whether the studied anions had structure I or II. The observation of simple AA'XX' patterns (which often resemble AB quartets) in the aromatic pmr region of the spectra show the generally para-disubstituted nature of the aryl ligands. Compared to the parent aromatics the protons ortho to the SbF_4 group are generally deshielded by 0.7–1.0 ppm, whereas the protons in the meta positions are nearly

(29) (a) E. L. Muetterties, W. Mahler, K. J. Pocker, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964); (b) R. L. McKenney and H. Sisler, *ibid.*, **6**, 1178 (1967).

Table III. ^{19}F Chemical Shifts of Triaryldifluorostibines, Diaryltrifluorostibine Monohydrates, and Pyridinium Diaryltetrafluoroantimonates at 30° [a,b]

Aryl	$C_5H_5NH^+Ar_2SbF_4^-$ [c] Sb–F	C–F	$Ar_2SbF_3 \cdot H_2O$ [c] Sb–F	C–F	Ar_3SbF_2 [d] Sb–F	C–F
C_6H_5	102.7[e]		114.2		153.0	
4-$CH_3C_6H_4$	105.2		116.1		154.7	
3-F-4-$CH_3C_6H_3$	103.9	118.4			152.3	101.3
4-FC_6H_4	104.0	113.4	115.9	110.8	149.8	105.7
3,4-$F_2C_6H_3$	105.2 139.5	141.2			150.1 129.2	133.1
4-ClC_6H_4	105.0		115.2			
3,4-$Cl_2C_6H_3$	105.6					

[a] CCl_3F was used as external standard. [b] The signals for the fluorines bound to carbon are all multiplets, the signals for the fluorines attached to antimony are relatively broad singlets. [c] In acetone. [d] In CCl_4. [e] In DMSO.



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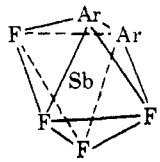

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unaffected by this substituent. The fluorine atoms in meta and para positions are deshielded by 0.5–1.3 ppm.

Diaryltrifluorostibine Monohydrates. Due to the fact that diaryltrifluorostibines themselves act as Lewis acids, they coordinate with 1 mol of water when the reaction mixtures of studied aromatics with SbF_5 are quenched with water. As mentioned the structure of the corresponding diphenyltrichlorostibine monohydrate was determined by X-ray crystallography. It is octahedral with the two chlorine atoms in the apical positions.

The ^{19}F shifts of the fluorine atoms attached to antimony are found at around ϕ 115. Thus substituting a fluorine ligand by a less electronegative oxygen causes a shielding of 10 ppm for the remaining fluorine atoms (substitution of a fluorine atom by chlorine in the triaryldifluorides causes a shielding of 15 ppm).[29] The observation of relatively broad singlets at room temperature indicates a rapid intramolecular fluorine exchange process between the apical and the equatorial positions. Recently the ^{19}F nmr spectrum of the parent monohydrate $SbF_5 \cdot H_2O$ in sulfur dioxide was obtained by Gillespie[30] and the shifts of the equatorial fluorine atoms were found at ϕ 110.5 (−85°). This is in good agreement with present data and shows that the substitution of two fluorine atoms by aryl groups has little influence on the shifts of the fluorine atoms attached to antimony (if we consider the differences in temperature and in the solvent systems). The shifts of the para fluorine atoms in the aromatic ring are deshielded by 4.1 ppm. The pmr spectrum shows the ortho protons deshielded by 0.75–0.95 ppm and the meta protons deshielded by 0.15–0.30 ppm.

Triaryldifluorostibines. Dihalotriarylstibines generally have trigonal bipyramidal structures with the halides occupying the apical positions. ^{19}F nmr data are in accordance with these structures. In contrast to diphenyltrifluorostibine hydrates, the ^{19}F shifts corresponding to fluorine on antimony are found at much higher field, at around ϕ 150–154. This can be attributed to the higher covalent nature of these compounds compared with the more polarized tetra- and trifluoro compounds. The fluorines attached to the aromatic ring are deshielded by 6–10 ppm, thus showing an increased deshielding with decreasing number of fluorine atoms attached to antimony. In the pmr spectrum, the protons in the ortho position to the SbF_2 group are deshielded by 0.8–1.0 ppm, and the meta protons are deshielded by 0.15 ppm.

(30) P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, **91**, 7264 (1969).