

## Hydride Ion Abstraction with Antimony Pentachloride

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The hexachloroantimonate salts of several stable carbonium ions have been prepared by the reaction of antimony pentachloride with certain hydrocarbons.

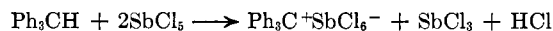
In connection with another problem it was observed that cycloheptatriene reacted with antimony pentachloride to produce tropylium hexachloroantimonate. This observation was not unexpected since there are several reported instances of analogous reactions of cycloheptatriene and strong Lewis acids. For example, phosphorus pentachloride,<sup>1</sup> stannic chloride,<sup>2</sup> and boron halides<sup>3</sup> each react with cycloheptatriene under various conditions to produce salts of the tropylium cation.

However, the present reaction with antimony pentachloride was intriguing in that the yields of tropylium salt appeared to be high and also because of the fact that the reaction could be carried out smoothly at ambient temperatures and in such inert solvents as dry carbon disulfide or benzene. These factors suggested that the method might be useful for the isolation of salts of other carbonium ions which have been observed to be stable for prolonged periods, but only in solutions which did not allow for their isolation, *e.g.*, the carbonium ions formed upon protonation of aromatic hydrocarbons in strong acids.<sup>4</sup> The results of several such attempts are discussed.

### Results and Discussion

The reaction of antimony pentachloride with cycloheptatriene in 2:1 molar ratio proceeds readily at 0° in solvents such as carbon disulfide and benzene to give a gray, crystalline precipitate of tropylium hexachloroantimonate and simultaneous formation of antimony trichloride and hydrogen chloride. In large scale preparations the salt formed is much darker and contains small amounts of polymeric material which possibly results from the impurity in the cycloheptatriene (~5%) or from other possible side reactions.

The reaction between triphenylmethane and antimony pentachloride in carbon disulfide followed a similar course<sup>5</sup> to produce yellow, crystalline triphenylmethyl hexachloroantimonate together with antimony trichloride, both in practically quantitative yields. The stoichiometry of the reaction is found to be as shown in the following equation.

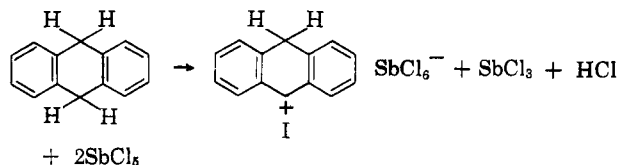


The triphenylmethyl salt obtained in this reaction is identical with that obtained from the reaction of

triphenylmethyl chloride and antimony pentachloride. It reacted immediately with water to produce triphenylmethanol and with cycloheptatriene to give tropylium hexachloroantimonate and triphenylmethane, a reaction typical of the triphenylmethyl cation.<sup>6</sup>

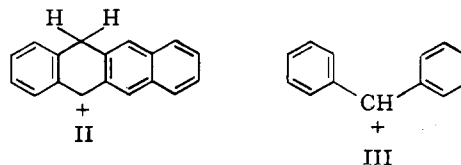
The antimony trichloride produced in these reactions was identified by conversion to the cesium chloride complex<sup>7</sup> and comparison of this with authentic material.

Utilizing the same reaction we have isolated the hexachloroantimonate salt of the 9-anthracenium  $\sigma$  complex (I). 9,10-Dihydroanthracene when treated with two moles of antimony pentachloride in cold anhydrous benzene produced a yellow, microcrystalline precipitate of the  $\text{SbCl}_6^-$  salt of I in yields of better than 95%. Quantitative amounts of antimony trichloride were formed and hydrogen chloride was again liberated. There can be little doubt that the reaction has taken the same course as indicated below. The isolation of quantitative amounts of antimony trichloride indicates that the salt is not an antimony pentachloride-hydrocarbon complex of the  $\sigma$  type or charge transfer type.<sup>8</sup>



The salt, I, rapidly decomposes on exposure to moist air. It reacts immediately with water to form anthracene. Solutions of the salt in nitromethane, when treated with cycloheptatriene, give rise to tropylium hexachloroantimonate.

In a similar manner, reaction of antimony pentachloride with dihydrotetracene gave a yellow precipitate to which addition of water produced tetracene. Although in this instance the yield of salt was less than the previous cases (25% based on recovered tetracene) it seems certain that the material involves the protonated tetracene  $\sigma$  complex II. The salt also rapidly decomposes on exposure to air.



(1) (a) D. N. Kursanov and M. E. Volpin, *Dokl. Akad. Nauk, SSSR*, **113**, 339 (1957); (b) D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1339 (1962).

(2) Unpublished work of H. J. Dauben and K. M. Harmon (personal communication). Cycloheptatriene also forms tropylium salts when treated with stannic chloride and *t*-butyl chloride [D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 2320 (1961)]; whether this reaction involves hydride abstraction by stannic chloride is not clear.

(3) K. M. Harmon, A. B. Harmon, and F. E. Cummings, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

(4) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

(5) The isolation of a complex from this reaction was first reported by S. Hilpert and L. Wolf [*Ber.*, **46**, 2218 (1913)] but the nature of the material was not then discussed.

(6) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

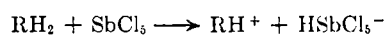
(7) G. W. Watt, *Inorg. Syn.*, **4**, 6 (1953).

(8) W. I. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3055 (1959).

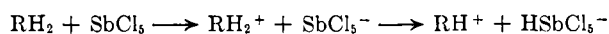
In view of the stability of the protonated anthracene cation attempts were made to prepare the chloroantimonate salt of the diphenylmethyl cation (III) in a similar manner from diphenylmethane and antimony pentachloride. Although copious amounts of hydrogen chloride were liberated, the reaction did not lead to the separation of a solid salt. However, it seems most likely that a salt of the cation III is formed to some extent at least. The ultraviolet spectrum of a solution of diphenylmethane in methylene chloride containing antimony pentachloride shows a strong absorption at  $451\text{ m}\mu$ ; this same peak appears in the spectrum of the hexachloroantimonate salt of III prepared as described later. Gold and Tye<sup>4</sup> report that the cation displays a strong broad absorption peak at  $446\text{ m}\mu$  when dissolved in concentrated sulfuric acid.

The hexachloroantimonate salt of III is easily prepared by treatment of antimony pentachloride with diphenylchloromethane in an inert solvent such as carbon disulfide.<sup>9</sup> The yellow salt is fairly stable when kept in an inert atmosphere; when treated with water it forms bisdiphenylmethyl ether and it reacts with cycloheptatriene to give tropylium hexachloroantimonate and diphenylmethane.

As yet we have no evidence for any mechanism which might apply in the reactions just described. A direct hydride ion abstraction seems to be the simplest explanation.



However, in view of the charge transfer reactions known to occur between aromatic hydrocarbons and strong Lewis acids,<sup>8</sup> a possible alternative for the first step in this sequence is indicated.



It should be noted that Harmon and co-workers<sup>3</sup> have shown, in the case of cycloheptatriene at least, that such a direct hydride abstraction is not the mechanism common to all Lewis acids.

### Experimental

**Tropylium Hexachloroantimonate.**—A solution of antimony pentachloride (30.0 g.) in carbon disulfide (30 ml.) was added dropwise with stirring to a solution of cycloheptatriene (5.2 g.) in carbon disulfide (100 ml.) contained in an ice-water bath. After the addition, the mixture was stirred for 10 min. and the brown precipitate of tropylium hexachloroantimonate (22.0 g.) was filtered. The pure salt was obtained as pale yellow prisms, m.p.  $190^\circ$ , from nitromethane.<sup>10</sup>

*Anal.* Calcd. for  $\text{C}_7\text{H}_7\text{SbCl}_6$ : C, 19.72; Cl, 50.00; H, 1.64. Found: C, 20.01; Cl, 49.99; H, 1.44.

In a separate experiment on 0.2 the preceding scale the mother liquors from the initial reaction gave, upon evaporation, 2.3 g. of antimony trichloride. This was converted to the  $(\text{C}_7\text{H}_7)_3(\text{SbCl}_3)_2$  complex in the manner described. The X-ray powder pattern of this material was identical to that of an authentic sample.<sup>11</sup>

(9) This same salt of III has also been prepared by an identical method by H. J. Dauben and co-workers (personal communication from H. J. Dauben). These workers also found that III abstracts hydride ion from cycloheptatriene.

(10) The melting point appears to vary as much as  $10^\circ$  depending on the rate of heating.

(11) We thank Mr. David Butler for providing the X-ray data.

**Triphenylmethyl Hexachloroantimonate.**—Antimony pentachloride (18.0 g.) in carbon disulfide (20 ml.) was added slowly to a solution of triphenylmethane (7.3 g.) in carbon disulfide (100 ml.) and the mixture was stirred at room temperature for 1 hr. The yellow crystals of triphenylmethyl hexachloroantimonate were collected (17.0 g.); evaporation of the mother liquors afforded white prisms of antimony trichloride (6.1 g.). The salt crystallized from nitromethane in yellow prisms, m.p.  $218^\circ$ .<sup>10</sup>

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{15}\text{SbCl}_6$ : C, 39.45; H, 2.60; Cl, 36.85. Found: C, 39.58; H, 2.57; Cl, 36.73.

The same salt was obtained in quantitative yield upon vigorous shaking of equimolar amounts of triphenylmethyl chloride and antimony pentachloride in carbon tetrachloride.

Reaction of the salt (5.0 g.) in dry nitromethane (20 ml.) with cycloheptatriene (1.0 g.), followed by addition of dry ether, gave tropylium hexachloroantimonate (3.5 g.) and, upon evaporation of the solvent, triphenylmethane (2.0 g.).

**9-Anthracenium Hexachloroantimonate.**—Antimony pentachloride (6.0 g.) in carbon disulfide (20 ml.) was added to a stirred solution of 9,10-dihydroanthracene (1.8 g.) in dry carbon disulfide (100 ml.) at  $0^\circ$ . The yellow precipitate was collected upon a pad of Celite under nitrogen, then washed several times with dry carbon disulfide and benzene. Evaporation of the mother liquors gave antimony trichloride (2.3 g.). The salt, together with the Celite, was immediately shaken with a mixture of benzene and dilute hydrochloric acid. The benzene layer, after drying and treatment with decolorizing charcoal, gave, upon evaporation of the solvent, anthracene (1.7 g.).

The salt had a  $\lambda_{\text{max}}$  at  $448\text{ m}\mu$  ( $\log \epsilon$ , 4.0).<sup>12</sup> When treated with cycloheptatriene in nitromethane in the usual manner the material gave tropylium hexachloroantimonate.

**9-Tetracenium Hexachloroantimonate.**—Dihydrotetracene (0.40 g.) in dry benzene (75 ml.) was treated with antimony pentachloride (1.5 g.) in the usual way. The yellow material which separated was collected on Celite, washed several times with benzene, then shaken with a mixture of benzene and dilute hydrochloric acid. The residue obtained after evaporation of the benzene and trituration with hot ethanol was tetracene (0.10 g.), identified by means of its characteristic ultraviolet absorption spectrum and comparison with that of an authentic specimen.

**Diphenylmethyl Hexachloroantimonate.**—Antimony pentachloride (8.0 g.) in carbon disulfide (50 ml.) was added with stirring to diphenylchloromethane (5.0 g.) in carbon disulfide (150 ml.). The yellow precipitate was collected under nitrogen, washed several times with dry carbon disulfide, then transferred to a flask, and the excess solvent removed under reduced pressure. The yield of salt is quantitative; m.p.  $98\text{--}99^\circ$ ;  $\lambda_{\text{max}}$ ,  $451\text{ m}\mu$  ( $\log \epsilon$  4.6).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{11}\text{SbCl}_6$ : C, 31.11; H, 2.19. Found: C, 31.02; H, 2.62.

The salt derived from 5.0 g. of diphenylchloromethane was added at  $-10^\circ$  to nitromethane (30 ml.) containing cycloheptatriene (2.5 g.). The mixture was allowed to warm to  $10^\circ$  and dry ether (300 ml.) then added. Tropylium hexachloroantimonate (4.4 g.) separated and was collected. The mother liquors were washed several times with water and dilute hydrochloric acid; removal of the solvent followed by chromatography of the residue on alumina and elution with pentane gave diphenylmethane (1.1 g.) identified by a comparison of its infrared spectrum and v.p.c. retention time with that of an authentic sample.

In a separate experiment, the salt derived from 5.0 g. of diphenylmethyl chloride was shaken vigorously with a mixture of benzene and water. Evaporation of the organic layer and recrystallization of the residue from ethanol afforded bisdiphenylmethyl ether (1.6 g.), m.p.  $109\text{--}110^\circ$ .

**Acknowledgment.**—We thank the Robert A. Welch Foundation and the Alfred P. Sloan Foundation for financial assistance.

(12) The spectra were determined in methylene chloride. The salt decomposes slowly in this solvent and the  $\log \epsilon$  values quoted were obtained by extrapolation to zero time. Solutions in methylene chloride containing 1% antimony pentachloride are much more stable.