Attack of Alkoxide Ions on Antimony in Tetraarylstibonium Salts[1]

William E. McEwen, George H. Briles, and Brandford E. Giddings

Contribution from the Chemistry Department of the University of Massachusetts, Amherst, Massachusetts 01002. *Received July 16, 1969*

Abstract: The reactions of tetraarylstibonium salts with sodium alkoxides have been studied. Treatment of tetraphenylstibonium bromide with sodium methoxide in methanol solution, for example, gives methoxytetraphenylantimony, a crystalline covalent compound, as the initial organic product. Further reaction produces dimethoxytriphenylantimony, another crystalline, covalent compound, plus benzene. That the mechanism of the latter reaction is an ionic one (unlike the decomposition of hydroxytetraphenylantimony to triphenylstibine oxide plus benzene which occurs by a radical process) is indicated by the following facts. (1) The rate of reaction shows a dependence on the concentration of methoxide ion. (2) With tetraarylstibonium salts having two different aryl groups bonded to antimony, the ease of departure of an aryl group parallels the stability of the corresponding aryl anion. (3) No products of a radical reaction, *e.g.*, a biaryl, are produced. Arguments are presented which indicate that an "ate" complex is formed as an intermediate in the reaction of an alkoxytetraarylantimony with a sodium alkoxide. A new, general method has been devised for the preparation of aryltriphenylstibonium fluoroborates.

In order to investigate the scope and mechanism of the reaction of sodium alkoxides with tetraarylstibonium salts, it was first necessary to develop reliable methods of synthesis of the stibonium compounds. The reaction of a triarylantimony dichloride or dibromide with an arylmagnesium halide represents a satisfactory method of preparation of salts such as tetraphenylstibonium halides[2] and tetra-*p*-tolylstibonium halides.[3] However, this method has proved to be unsatisfactory for the preparation of quaternary stibonium salts having two or more different aryl groups bonded to antimony, mainly because of the occurrence of exchange reactions between the Grignard reagent and the tetraarylstibonium cation. The procedure of Chatt and Mann[4] can be used to prepare tetraphenylstibonium halides in poor yields by reaction of triphenylantimony, bromobenzene, and aluminum chloride at 220–230°, but in this case too the reaction is of no use for the preparation of quaternary stibonium halides having different aryl groups bonded to antimony. Also, whereas Makarova and Nesmeyanov[5] found that the reaction of triphenylstibine with diphenyliodonium fluoroborate at an elevated temperature gave tetraphenylstibonium fluoroborate in good yield, we found that the reaction of di-*p*-tolylphenylstibine with diphenyliodonium fluoroborate was not satisfactory for the preparation of di-*p*-tolyldiphenylstibonium fluoroborate. There are a number of ways in which pentaphenylantimony can be converted to tetraphenylstibonium salts,[6–8] but these methods are of little use for the preparation of mixed tetraarylstibonium salts, since the mixed pentaarylantimony compounds which would be used as starting materials are unknown.

A convenient and general method of preparation of aryltriphenylstibonium fluoroborates was eventually developed, and this consisted of the reaction of aryldiazonium fluoroborates with triphenylstibine in nitrobenzene solution. The compounds prepared by this method are listed in Table I. The use of solvents other than nitrobenzene (ethanol, acetonitrile, dimethyl sulfoxide, methanol, and acetone) proved to be unsatisfactory except for the preparation of tetraphenylstibonium and *p*-nitrophenyltriphenylstibonium fluoroborates, which were formed in all of the solvents used.[9]

With suitable aryltriphenylstibonium salts available, we next undertook an investigation of their reactions with sodium alkoxides. Methoxytetraphenylantimony, $(C_6H_5)_4SbOMe$, mp 130–132°, was obtained in 68% yield when tetraphenlystibonium bromide was allowed to react with sodium methoxide in absolute methanol.[10,11] The nmr spectrum of the compound in carbon tetrachloride solution showed a singlet at δ 2.74 ppm (with reference to TMS) attributable to the methyl protons of the methoxyl group. Between δ 7.0 and 8.0 ppm there were two absorption regions. The first (and more strongly absorbing) region had its center at

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[1] A preliminary report of a portion of this work has been published: G. H. Briles and W. E. McEwen, *Tetrahedron Lett.*, 5191 (1966).

[2] H. H. Willard, L. R. Perkins, and F. F. Blicke, *J. Am. Chem. Soc.*, **70**, 737 (1940).

[3] K. W. Shen, W. E. McEwen, S. J. LaPlaca, W. C. Hamilton, and A. P. Wolf, *ibid.*, **90**, 1718 (1968).

[4] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1192 (1940).

[5] L. G. Makarova and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 617 (1945).

[6] G. Wittig and K. Clauss, *Ann.*, **577**, 26 (1952).

[7] G. Wittig and D. Hellwinkel, *Ber.*, **97**, 789 (1964).

[8] G. A. Razuvaev, N. A. Osanova, N. R. Shulaev, and B. M. Tsigin, *Zh. Obshch. Khim.*, **30**, 3234 (1960).

[9] The reason why nitrobenzene is a particularly favorable solvent for this reaction is not known. However, a hint as to the answer to this problem can perhaps be found in the observation that an aryldiazonium tetrafluoroborate can undergo decomposition in nitrobenzene by either an ionic or a radical mechanism, depending on the presence of other reagents. This dichotomy is not apparent when most other solvents are used: *cf.* F. Bell, *J. Chem. Soc.*, 835 (1934); G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2053 (1961); R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965).

[10] An X-ray crystallographic study of methoxytetraphenylantimony has been carried out, and the results indicate that the compound adopts a trigonal bipyramidal configuration with the methoxyl group occupying an apical position: K. W. Shen, W. E. McEwen, S. J. LaPlaca, W. C. Hamilton, and A. P. Wolf, *J. Am. Chem. Soc.*, **90**, 1718 (1968). Hydroxytetraphenylantimony has been found to have a similar configuration: A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *ibid.*, **91**, 297 (1969).

[11] Doak, Long, and Freedman have reported a mp of 218–220° dec with softening near 130° for methoxytetraphenylantimony; yet their nmr data for the compound are in agreement with ours. We believe that their sample was converted to hydroxytetraphenylantimony, which is reported [H. E. Affstrung and H. E. May, *Anal. Chem.*, **32**, 1164 (1960)] to have a mp of 213–217°, sometime prior to the melting point determination. We have found that hydroxytetraphenylantimony is converted to methoxytetraphenylantimony on crystallization from methanol, and it is clear from the publication that the compound studied by Doak, Long, and Freedman was crystallized from this solvent just prior to the nmr determination: G. O. Doak, G. G. Long, and L. D. Freedman, *J. Organometal. Chem.*, **12**, 443 (1968).

Table I. Preparation of Aryltriphenylstibonium Fluoroborates

$Ar(C_6H_5)_3Sb^+ BF_4^-$ Ar	Mp, °C	Reaction solvent	Recrystallization solvent	% yield
p-Nitrophenyl[a]	191–192	Acetone	Acetone–ether	70
p-Nitrophenyl	191–192	Nitrobenzene	Acetone–ether	50
Phenyl[b]	275–276	Acetone	Acetone–ether	77
p-Tolyl[c]	138–139	Nitrobenzene	Ethyl acetate	22
m-Nitrophenyl[d]	198–200	Nitrobenzene	Acetone–ether	36
p-Bromophenyl[e]	160–162	Nitrobenzene	Acetone–ether	35
m-Bromophenyl[f]	157–159	Nitrobenzene	Ethyl acetate–ether	20
p-Anisyl[g]	136–138	Nitrobenzene	Ethyl acetate–ether	37

[a] *Anal.* Calcd for $C_{24}H_{19}SbO_2NBF_4$: C, 51.26; H, 3.38; N, 2.49. Found: C, 51.22; H, 3.35; N, 2.38. [b] Lit. mp 265° (A. N. Nesmeyanov, "Selected Works in Organic Chemistry," D. P. Gelfand, Ed., The Macmillan Co., New York, N. Y., 1963, p 748). [c] *Anal.* Calcd for $C_{25}H_{22}SbBF_4$: C, 56.59; H, 4.20; Sb, 22.90; B, 2.03; F, 14.30. Found: C, 56.75; H, 4.55; Sb, 23.21; B, 2.22; F, 13.60. [d] *Anal.* Calcd for $C_{24}H_{19}SbO_2NBF_3$: C, 51.26; H, 3.38; Sb, 21.71; N, 2.49. Found: C, 51.47; H, 3.51; Sb, 22.06; N, 2.46. [e] *Anal.* Calcd for $C_{24}H_{19}SbBrBF_4$: B, 1.82. Found: B, 1.94. [f] *Anal.* Calcd for $C_{24}H_{19}SbBrBF_4$: B, 1.82. Found: B, 1.73. [g] *Anal.* Calcd for $C_{25}H_{22}SbOBF_4$: C, 54.90; H, 4.03; Sb, 22.32. Found: C, 54.83; H, 4.10; Sb, 22.26. The nmr spectrum showed δ (ppm) 3.9 (singlet), 7.75 (multiplet); ratio 1:6.70 (calcd 1:6.33).

δ 7.26 ppm and the second at 7.55 ppm, these being attributable to the protons of the phenyl groups. An alkyl to aryl proton ratio of 3:21 was found by integration; the expected ratio for methoxytetraphenylantimony was 3:20. The same compound was obtained in 97% yield when pentaphenylantimony was refluxed in absolute methanol solution for 3.5 hr. Benzene was also isolated from this reaction mixture. This reaction is analogous to the known conversion of phenylbisbiphenyleneantimony to ethoxyphenyl-2-biphenylbiphenyleneantimony by the reaction of refluxing ethanol.[7]

The reaction between the tetraphenylstibonium cation and methoxide ion is evidently a rapid one inasmuch as the nmr spectrum of a fresh solution of equivalent amounts of tetraphenylstibonium bromide and sodium methoxide in methanol is identical with that of a methanol solution of preformed methoxytetraphenylantimony. A solution of tetraphenylstibonium bromide in methanol gives a completely different spectrum.

It should be pointed out that, whereas a carbon tetrachloride solution of methoxytetraphenylantimony has a sharp singlet absorption peak at δ 2.74 ppm in its nmr spectrum, this peak is absent in the spectrum of a methanol solution of methoxytetraphenylantimony. The absorption patterns in the aromatic region with the two different solvents are very similar, but not identical. A carbon tetrachloride solution has absorption areas with centers at δ 7.26 and 7.55 ppm compared with δ 7.38 and 7.60 ppm for a methanol solution. These results can be explained by the assumption that equilibria such as the following exist in methanol solution.

$$\begin{tikzcd}
(C_6H_5)_4Sb^+(OMe)'^- + MeOH \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left] & (C_6H_5)_4Sb^+OMe^- + (MeOH)' \arrow[d, shift left] \\
(C_6H_5)_4Sb(OMe)' + MeOH \arrow[r, phantom, "\rightleftharpoons"] \arrow[u, shift left] & (C_6H_5)_4SbOMe + (MeOH)' \arrow[u, shift left]
\end{tikzcd}$$

If one or more of these exchange reactions are very rapid, the lack of any absorption at δ 2.74 ppm is understandable; rapid chemical exchange would cause the appearance of a single peak which is a weighted average of the chemical shifts of methanol and the methoxy group bonded to antimony. At the same time, the nature of the absorption in the aromatic region indicated that the equilibrium favors the covalent form of the molecule even in methanol solution.

It has also been established that *p*-nitrophenyltriphenylstibonium fluoroborate undergoes facile reaction with sodium methoxide in methanol solution to give methoxy-*p*-nitrophenyltriphenylantimony, mp 127–129°. This compound showed no signs of decomposition even after several months exposure to the air. On the other hand, methoxy-*p*-anisyltriphenylantimony, prepared by the reaction of *p*-anisyltriphenylstibonium fluoroborate with sodium methoxide, was isolated as an oil only with difficulty, and it rapidly underwent reaction with moisture in the air to form hydroxy-*p*-anisyltriphenylantimony. It had been anticipated that the presence of an electron-donating substituent would increase the ease of dissociation of the methoxytetraarylantimony compound and thus facilitate reaction with water.

When methoxytetraphenylantimony was heated under reflux in absolute methanol for a period of 5 weeks, dimethoxytriphenylantimony,[12] mp 100–102°, and benzene were obtained in 81% yield. It was also found that the rate of this reaction is dependent on methoxide ion concentration. In essentially qualitative experiments, equal amounts of tetraphenylstibonium bromide were dissolved in equal volumes of methanol containing varying concentrations of sodium methoxide. As mentioned before, examination of nmr spectra revealed very rapid formation of methoxytetraphenylantimony. The solutions were refluxed, and, after convenient periods of time, samples were withdrawn from the reaction mixtures and nmr spectra taken. Since the absorption peak of benzene, which appears at δ 7.27 ppm, is sufficiently well separated from the absorption regions of the aromatic protons of methoxytetraphenylantimony (δ 7.38 and 7.60 ppm) and of the tetraphenylstibonium cation (δ 7.95 ppm) in methanol solution, it was possible to observe the increase in benzene concentration as the reactions progressed. In this way it was convincingly demonstrated that benzene was produced more rapidly as the concentration of methoxide ion was increased.

As a prelude to a study of substituent effects in the reactions of tetraarylstibonium fluoroborates with sodium methoxide in methanol solution, it was first of interest to determine whether an anion effect was also operative. Thus, the reaction of tetraphenylstibonium fluoroborate with sodium methoxide was investigated. The products proved to be the same as those produced in the reaction of the corresponding bromide salt, but the rate was distinctly less. The decrease in rate is probably

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(12) An X-ray crystallographic study of dimethoxytriphenylantimony has been carried out,[10] and the results indicate that the compound adopts a trigonal bipyramidal configuration with the methoxyl groups occupying apical positions.

attributable, at least in part, to a slow, competing solvolysis of the tetrafluoroborate ion, which brings about a decrease in the concentration of methoxide ion.[13]

Each of the triphenylarylstibonium fluoroborate salts listed in Table I was then subjected to reaction with sodium methoxide in refluxing methanol solution for 188 hr, and the volatile products were subjected to vapor phase chromatographic analysis. The results are summarized in Table II. Since *p*-tolyltriphenylstibonium and *p*-anisyltriphenylstibonium fluoroborates had undergone reaction to the stage of formation of aromatic hydrocarbons only to the extent of less than 2%, a second series of reactions of each of these fluoroborate salts with sodium *n*-butoxide in *n*-butyl alcohol at 117° for 188 hr was carried out and the volatile products were analyzed. These results are also summarized in Table II. From a combination of the results of the two series of experiments it is clear that the order of relative rates of formation of benzene or monosubstituted benzenes is $C_6H_5NO_2 > C_6H_5Br > C_6H_6 > C_6H_5CH_3, C_6H_5OCH_3$. Since this parallels the order of stabilities of the respective aryl anions, and since there is no evidence of formation of biaryls or other products to be expected of a radical reaction,[14,15] this constitutes valid evidence that these reactions are of an ionic nature.[16]

Table II. Aromatic Compounds Produced by Reactions of Aryltriphenylstibonium Fluoroborates with Sodium Alkoxides

$Ar(C_6H_5)_3Sb^+$ BF_4^-Ar	Sodium alkoxide	Solvent	Temp, °C	Products	Yield, %
Phenyl	NaOMe	MeOH	65	Benzene	16
Phenyl	NaOBu	BuOH	117	Benzene	49
p-Tolyl	NaOMe	MeOH	65	Benzene	<1
				Toluene	<1
p-Tolyl	NaOBu	BuOH	117	Benzene	15
				Toluene	<1
p-Anisyl	NaOMe	MeOH	65	Benzene	<1
				Anisole	<1
p-Anisyl	NaOBu	BuOH	117	Benzene	4
				Anisole	<1
p-Nitrophenyl	NaOMe	MeOH	65	Benzene	<1
				Nitrobenzene	43
m-Nitrophenyl	NaOMe	MeOH	65	Benzene	<1
				Nitrobenzene	46
p-Bromophenyl	NaOMe	MeOH	65	Benzene	6
				Bromobenzene	32

Of various, conceivable, ionic mechanisms for the conversion of an alkoxytetraarylantimony to a dialkoxytriarylantimony by the action of sodium alkoxide, only one seems to be worthy of serious consideration.[17] This consists of the addition of the sodium alkoxide to the alkoxytetraarylantimony to give $Na^+[(RO)_2SbAr_4]^-$, which then ejects a sodium aryl. Thus, a complete mechanism of reaction is as follows[18]

$$Ar_4Sb^+X^- + Na^+OR^- \rightleftharpoons NaX + Ar_4SbOR \quad (1)$$

$$Ar_4Sb(OR) + Na^+OR^- \longrightarrow Na^+[Ar_4Sb(OR)_2]^- \quad (2)$$

$$Na^+[Ar_4Sb(OR)_2]^- \longrightarrow Na^+Ar^- + Ar_3Sb(OR)_2 \quad (3)$$

$$Na^+Ar^- + ROH \longrightarrow ArH + Na^+OR^- \quad (4)$$

The most attractive feature of this mechanism is that the negative charge of the "ate" ion, $[Ar_4Sb(OR)_2]^-$, aids the departure of Ar^-. Also, it is obvious that a more stable aryl anion, *e.g.*, $O_2NC_6H_4^-$, would depart more readily than a less stable one, *e.g.*, $C_6H_5^-$, and this accommodates the order of elimination of aryl groups cited previously. That "ate" ions of antimony are readily formed is evident from the preparation and isolation of $Li^+ Sb(C_6H_5)_6^-$ by the reaction of tetraphenylstibonium halides with phenyllithium.[6]

There is no conclusive experimental evidence available to indicate whether or not step 2 of the mechanism cited above is reversible.[19] However, since an alkoxide ion is a weaker base than an aryl anion, it is highly probable that both the forward and reverse reactions of step 2 are fast compared to step 3. Furthermore, there is no chance for reversal of step 3 because the alcohol used as solvent reacts with the aryl anion (step 4) as soon as it is formed. Thus, this argument leads to the conclusion that step 3 is the rate-limiting step.

Although there is some formal similarity between the reactions of quaternary phosphonium salts with sodium alkoxides[20,21] and those of quaternary stibonium salts with the same reagents, entirely different sets of products are formed, and fundamentally different mechanisms are operative. An explanation for these differences encompasses two major points. (1) The formation of the unusually strong P=O bond represents a major driving force in many reactions of organophosphorus compounds, but there is no convincing evidence that the same holds true with respect to formation of the Sb=O bond. Thus, SN2 attack of OR^- on the primary carbon atom of the R group of $(RO)_2PR'_3$ (or $ROP^+R'_3$) takes place readily to give ROR plus

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(13) Such a solvolysis reaction of BF_4^- in alkaline medium has been observed: A. Gonard, *Bull. Soc. Chim. Fr.*, [5] **9**, 917 (1942).

(14) There is convincing evidence available that hydroxytetraarylantimony compounds undergo decomposition to triarylstibine oxides plus aromatic hydrocarbons by a radical mechanism: F. Chupka and W. E. McEwen, unpublished results.

(15) Biaryls, aromatic hydrocarbons, diaryl sulfides, alkyl aryl ethers, and aldehydes (or ketones) are produced in free-radical reactions of triarylsulfonium halides with sodium alkoxides in alcohol solution: (a) J. W. Knapczyk, G. H. Wiegand, and W. E. McEwen, *Tetrahedron Lett.*, 2971 (1965); (b) G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968); (c) J. W. Knapczyk and W. E. McEwen, *J. Am. Chem. Soc.*, **91**, 145 (1969).

(16) Quaternary phosphonium alkoxides and hydroxides undergo decomposition by an ionic mechanism, and the order of ease of formation of the hydrocarbons parallels the order of stabilities of the conjugate bases: W. E. McEwen, G. Axelrad, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **87**, 3948 (1965), and references cited therein.

(17) A synchronous (SN2 type) attack of OR^- on $ROSbAr_4$ to give $(RO)_2SbAr_3$ plus Ar^- is unattractive because it involves the direct displacement of a stronger base (Ar^-) by weaker one (OR^-). A prior ionization of $ROSbAr_4$ to give $(ROSbAr_3)^+$ and Ar^- (SN1 type) and subsequent addition of OR^- to $(ROSbAr_3)^+$ is also relatively unattractive in view of the strongly basic nature of the anion Ar^-. Of course, dissociation of $ROSbAr_4$ to Ar_4Sb^+ and OR^- undoubtedly does occur on the basis of the nmr evidence presented previously, but this does not lead to the formation of ArH plus $(RO)_2SbAr_3$.

(18) In the reaction of *p*-nitrophenyltriphenylstibonium fluoroborate with sodium *n*-butoxide in *n*-butyl alcohol at 117° for 188 hr, 1 equiv of nitrobenzene (which is destroyed by the reagent) and nearly 1 equiv of benzene are produced. Thus, it is evident that reaction can proceed beyond the stage of formation of di-*n*-butoxytriphenylantimony under these conditions.

$$(C_6H_5)_3Sb(OC_4H_9)_2 + Na^+OC_4H_9^- \rightleftharpoons Na^+[(C_6H_5)_3Sb(OC_4H_9)_3]^- \longrightarrow NaC_6H_5 + (C_6H_5)_2Sb(OC_4H_9)_3$$

$$NaC_6H_5 + C_4H_9OH \longrightarrow C_6H_6 + C_4H_9ONa$$

(19) Evidence based on tracer experiments indicates that the formation of $Li^+(C_6H_5)_6Sb^-$ from $(C_6H_5)_5Sb$ and LiC_6H_5 is not reversible, at least in ether: (a) K. W. Shen, W. E. McEwen, and A. P. Wolf, *J. Am. Chem. Soc.*, **91**, 1283 (1969); (b) H. Daniel and J. Paetsch, *Chem. Ber.*, **101**, 1451 (1968).

(20) M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960).

(21) C. B. Parisek, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **82**, 5503 (1960).

$R'_3P{=}O$, but no similar reaction takes place between RO^- and $(RO)_2SbR'_3$. (2) Some pentacovalent antimony compounds form "ate" ions readily by attack of sufficiently strong bases,[6,22–24] and, as mentioned previously, this provides a driving force for step 3 of the mechanism cited above. Pentavalent phosphorus compounds, on the other hand, have less tendency[25,26] to form "ate" complexes than do pentavalent antimony compounds, and consequently intermediates of the type $(RO)_2PR'_3$ are formed in reactions of quaternary phosphonium salts with sodium alkoxides by a mechanism[20,21] which is probably different from that operative in the antimony case.

It is clear from the data summarized in Table II that the presence of an electron-donating substituent in the tetraarylstibonium salt causes a marked decrease in the rate of the over-all reaction with a sodium alkoxide, while the presence of an electron-withdrawing substituent produces a marked increase in rate. These facts are readily explained in terms of the mechanism shown previously. With *p*-anisyltriphenylstibonium fluoroborate and sodium methoxide, for example, the concentrations of methoxy-*p*-anisyltriphenylantimony and the corresponding "ate" complex are small as against the unsubstituted case, and this concentration effect, together with the presence of one poor leaving group, causes the over-all rate to be low. With the *p*-nitro compound, on the other hand, the concentrations of the pentavalent intermediate and the "ate" complex are relatively large as against the unsubstituted case, and a good leaving group is present; thus, the over-all rate in this case is relatively large.

Dimethoxytriphenylantimony was also prepared by treatment of triphenylantimony dibromide[27] with sodium methoxide in absolute methanol. Furthermore, dimethoxytriphenylantimony was hydrolyzed to methanol plus triphenylantimony oxide by the action of an equivalent amount of water dissolved in acetone. The nmr spectra of the compound in both carbon tetrachloride and methanol solution show a singlet at δ 3.03 ppm, although the singlet is somewhat broader when methanol is used as the solvent than when carbon tetrachloride is used. Integration shows the correct ratio of methoxyl hydrogens to aromatic hydrogens.

Several new triarylstibines were prepared in the course of this work. They included tri-*m*-chlorophenylstibine, phenyl-di-*p*-tolylstibine, phenyl-di-*p*-fluorophenylstibine, phenyl-di-*p*-anisylstibine, and phenyl-di-*p*-chlorophenylstibine. The preparation and properties of these compounds are described in the Experimental Section.

Experimental Section

General. All melting points and boiling points are uncorrected. The procedure of Potratz and Rosen[28] was used in the preparation of cobaltous ammonium thiocyanate solution, which was used to detect the presence of the various quaternary stibonium ions in solution.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Tetraphenylstibonium Bromide. An adaptation of the method of Willard, Perkins, and Blicke[2] was used. A solution of 25.4 g (0.06 mol) of triphenylstibine dichloride[27] in a mixture of 200 ml of ether and 70 ml of benzene was added slowly with stirring to a solution of 0.18 mol of phenylmagnesium bromide in 200 ml of ether, the mixture being maintained under a nitrogen atmosphere. Heat was evolved, and a brown solution resulted. The mixture was allowed to stand at room temperature for 3 days. A small amount of crystalline product had precipitated during this period. To the mixture was added slowly and with stirring 20 ml of 48% hydrobromic acid.[29] The ether–benzene layer was separated from the aqueous layer, and the solvents were removed by distillation. A brown gum which remained was extracted ten times with 200-ml portions of hot water. The combined aqueous extract was concentrated to 200 ml and 25 g of sodium bromide was added to the hot mixture. The mixture was cooled in a refrigerator for 12 hr, and the solid which had formed was collected by filtration. After recrystallization (charcoal treatment) from water–ethanol (9:1) the tetraphenylstibonium bromide weighed 16.2 g (53%) and had a mp of 214–216° (lit.[29] mp 210–215°).

Preparation of Aryltriphenylstibonium Fluoroborates. To a stirred solution of 1.78 g (0.005 mol) of triphenylstibine in 50 ml of nitrobenzene was slowly added 0.005 mol of the solid aryldiazonium fluoroborate[30] while the mixture was maintained at a temperature of 85–100°. At first the evolution of nitrogen was slow, but it soon became rapid. Within 2 hr, the reaction mixture rather suddenly became black, and, when tested with cobaltous ammonium thiocyanate solution,[28] gave a positive indication of the presence of a quaternary stibonium salt. The mixture was heated at 85–100° with stirring for 12 hr. The black reaction mixture was cooled in an ice bath, and an excess of Skelly F solvent was added to cause separation of a dense, dark oil. The dark oil was induced to solidify by washing it with about 400 ml of Skelly F solvent and then with 100 ml of ether. The brown powder which resulted was crystallized from ethyl acetate (charcoal treatment) to give the aryltriphenylstibonium fluoroborate. Yields, melting points of the salts, and analyses are summarized in Table I.

Reaction of Tetraphenylstibonium Bromide with Sodium Methoxide. Slightly more than 0.6 g (0.25 g-atom) of sodium was converted to sodium methoxide by being added to 30 ml of anhydrous methanol, and the solution was cooled to room temperature. To this solution was added 12.5 g (0.025 mol) of tetraphenylstibonium bromide, and the mixture was refluxed until the solid dissolved (about 30 min), the mixture being protected against moisture of the air by use of a calcium chloride drying tube. The mixture was allowed to cool to room temperature, and the flask was connected to a trap immersed in a Dry Ice–acetone bath. The system was evacuated by use of a vacuum pump and then closed off. The methanol was allowed to distill into the trap with no external heating. The white solid residue was shaken for 5 min with 30 ml of petroleum ether of bp 30–60°, and the mixture was filtered. The solid was extracted three more times in the same manner, care being taken to minimize access of moist air to the system. The combined petroleum ether solution was concentrated to 20 ml in a closed system. A colorless, crystalline solid precipitated during the evaporation process. The mixture was cooled in a Dry Ice–acetone bath, and the solvent was decanted from the solid. The flask containing the solid was quickly evacuated to remove the small amount of remaining liquid by evaporation. The amount of methoxytetraphenylantimony, mp 128–131°, so obtained was 6.8 g (68%). After recrystallization from petroleum ether it had a mp of 130–132°.

Anal. Calcd for $C_{25}H_{24}SbO$: C, 65.09; H, 5.03; Sb, 26.41 Found: C, 65.45; H, 4.87; Sb, 26.64.

Reaction of Pentaphenylantimony with Methanol. A suspension of 5.01 g of pentaphenylantimony[6] in 10 ml of anhydrous methanol was heated under reflux for 3.5 hr, the system being protected from moisture in the air by use of a calcium chloride tube.[31] The color-

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[27] W. J. Lile and R. C. Menzies, *J. Chem. Soc.*, 617 (1950).

[28] H. A. Potratz and J. M. Rosen, *Anal. Chem.*, **21**, 1276 (1949).

[29] Wittig and Clauss[6] have reported that tetraphenylstibonium bromide reacts with concentrated hydrobromic acid to give benzene and triphenylantimony dibromide. However, no such reaction was apparent under the conditions described here.

[30] A. I. Vogel, "Practical Organic Chemistry," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1962, p 612.

[31] This precaution is probably unnecessary. Crystallization of either methoxytetraphenylantimony or hydroxytetraphenylantimony from ordinary methanol or even slightly aqueous methanol gives pure, crystalline methoxytetraphenylantimony. However, in petroleum ether solution, methoxytetraphenylantimony rapidly undergoes hydrolysis to hydroxytetraphenylantimony in contact with moist air.

Table III

Methoxyaryltriphenylantimony, Ar	δ (ppm) relative to TMS Aromatic H	 Methoxyl H	Ratio of Arom H:aliph H Calcd	 Found
p-Anisyl	6.8–7.5 (m)	3.0 (s), 3.82 (s)	19:6	21.6:6
m-Nitrophenyl	7.2–8.0 (m)	2.90 (s)	19:3	19.5:3
p-Bromophenyl	7.0–7.8 (m)	2.85 (s)	19:3	19.8:3
p-Tolyl	7.0–8.0 (m)	2.6 (s), 2.8 (s)	19:6	18.6:6

less solution was cooled to room temperature, and the solvent was evaporated *in vacuo* in a closed system, the vapor being condensed in a trap immersed in a Dry Ice–acetone bath. The residue consisted of 4.45 g (96%) of methoxytetraphenylantimony, mp 130–132°, also in admixture with the sample described above.

Benzene (0.8 ml when melted) crystallized from the distillate which had been collected in the Dry Ice–acetone trap.

Methoxy-*p*-nitrophenylantimony. This compound, mp 127–129° after recrystallization from methanol, was obtained in 72% yield by reaction of *p*-nitrophenyltriphenylstibonium fluoroborate with sodium methoxide in absolute methanol solution. It crystallized directly from the reaction mixture during a 4-hr reflux period.

Anal. Calcd for $C_{24}H_{22}SbNO_3$: C, 59.29; H, 4.33; N, 2.79. Found: C, 59.02; H, 4.54; N, 2.93.

An nmr spectrum of the compound taken in deuteriochloroform solution showed a singlet at δ 3.92 ppm (relative to TMS) and a multiplet at δ 7.4–8.2 ppm. Integration revealed that the ratio of aromatic to aliphatic protons was approximately that required by the formula—18.4:3 (calcd 19:3).

Spectral Evidence for the Formation of Other Methoxyaryltriphenylantimony Compounds. In each case, the aryltriphenylstibonium fluoroborate was heated under reflux with 1 equiv of sodium methoxide in absolute methanol solution for 4 hr, the methanol evaporated *in vacuo*, the residue extracted with boiling pentane, and the pentane extract concentrated to dryness to give an oil. The oil was then dissolved in deuteriochloroform and its nmr spectrum taken. The results are summarized in Table III.

Dimethoxytriphenylantimony. To a cold solution of 0.10 mol of sodium methoxide (prepared by reaction of the metal with methanol) in 100 ml of absolute methanol was added slowly with stirring a solution of 25.6 g (0.05 mol) of triphenylantimony dibromide in 100 ml of benzene. The mixture was stirred for 1 hr at room temperature, and then the solvent was evaporated *in vacuo*, a trap immersed in a Dry Ice–acetone bath being used to condense the vapors. To the residual, colorless gum was added 60 ml of anhydrous benzene, and the mixture was shaken for 5 min, and then filtered. The precipitate consisted of 9.5 g (92%) of sodium bromide. The solvent was evaporated from the filtrate, again a closed system being used. The residue consisted of 19.5 g (95%) of dimethoxytriphenylantimony, mp 97–100°. Purification of the compound was achieved by sublimation at 0.1 mm and at a bath temperature of 110–130°. There was obtained 18.2 g (89%) of sublimate of mp 100–102°.

Anal. Calcd for $C_{20}H_{19}SbO_2$: C, 57.87; H, 5.10; Sb, 29.34. Found: C, 57.77; H, 5.00; Sb, 29.49.

The nmr spectrum of the compound was taken in carbon tetrachloride solution and showed a singlet at δ 3.03 ppm (relative to TMS) and two multiplets in the 7.0–8.20-ppm region, one centered at δ 7.3 ppm and the other at δ 7.9 ppm.

Dimethoxytriphenylantimony was found to be very soluble in benzene, methanol, and petroleum ether, but it could not be recrystallized from any of these solvents.

Solvolysis of Methoxytetraphenylantimony in Methanol. A solution of 5.1 g (0.012 mol) of methoxytetraphenylantimony in 10 ml of absolute methanol was refluxed for 5 weeks. The solvent was distilled *in vacuo* in a closed system, the distillate being collected in a trap immersed in a Dry Ice–acetone bath. The residue consisted of 4.92 g (99%) of crude dimethoxytriphenylantimony in the form of a gum. Sublimation of this material under the conditions described previously gave 4.01 g (80.5%) of the compound, mp 100–102°, also in admixture with the sample prepared by the reaction of triphenylantimony dibromide with sodium methoxide.

The distillate which had condensed in the trap was found to contain a crystalline solid. This was collected in the cold and then allowed to melt to give 0.76 ml (76%) of pure benzene, as shown by glpc analysis.

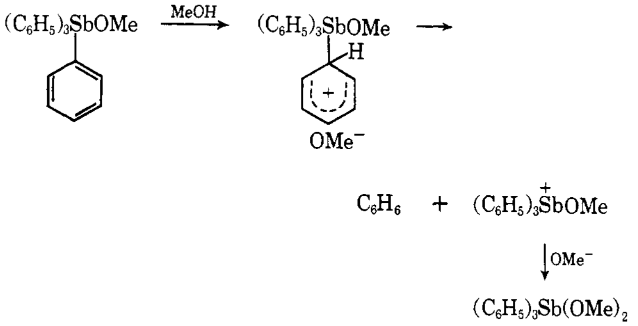
When a solution of 2.50 g of methoxytetraphenylantimony in 10 ml of a petroleum ether fraction of bp 55–65° was heated under reflux for 18 days, not less than 1.93 g of the starting compound could be recovered unchanged by evaporation of the solvent and recrystallization of the residue.[32]

Demonstration of Methoxide Ion Catalysis of the Solvolysis Reaction. Three separate solutions of 0.05 mol of tetraphenylstibonium bromide in 100 ml of absolute methanol containing varying amounts of sodium methoxide were heated under reflux. After 2 days, the nmr spectra of aliquots of all three solutions showed a new peak, a sharp singlet at δ 7.27 ppm (relative to TMS), attributable to benzene. Additional aliquots were removed at intervals, and the relative peak heights of the absorption attributable to benzene are shown in Table IV, the peak height for the solution containing equimolar amounts of reagents being used as the basis of comparison for each set of results.

Table IV

NaOMe, mol	Relative benzene peak heights after *x* days 4	 6	 14	 29
0.045	0.60	0.63	0.66	0.65
0.050	1.00	1.00	1.00	1.00
0.055	1.08	1.11	1.26	1.56

The apparent acceleration of reaction with increase of time of reaction in the reaction mixture in which 0.055 mol of sodium methoxide was used simply reflects the fact that, as the initially formed methoxytetraphenylantimony is consumed with formation of benzene and dimethoxytriphenylantimony, the molar ratio of excess sodium methoxide to remaining methoxytetraphenylantimony increases. This is not the case when equivalent amounts of tetraphenylstibonium cation and methoxide ion are employed as reagents or when there is a relative deficiency of methoxide ion. The data indicate that there is an unmistakable dependence of the rate of reaction on the concentration of methoxide ion.[33]



Prolonged Reactions of Aryltriphenylstibonium Fluoroborates with Sodium Methoxide. The aryltriphenylstibonium fluoroborate, 0.02 mol, was added to a solution prepared from 10 ml of anhydrous methanol and 0.04 g-atom of sodium. The resulting mixture was stirred and heated under reflux for 188 hr. The reaction mixture was then cooled and a 5-μl sample was directly injected into an F & M Model 609 vapor phase fractometer equipped with either an

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(32) Doak, Long, and Freedman[11] reported that their sample of methoxytetraphenylantimony, mp 218–220° dec, underwent decomposition at an elevated temperature in a hydrocarbon solvent to give benzene as one of the products. If their compound were actually hydroxytetraphenylantimony (as we suspect), benzene and triphenylstibine oxide would have been formed, as previously reported: G. H. Briles and W. E. McEwen, *Tetrahedron Lett.*, 5299 (1966).

(33) This clearly rules out a conceivable mechanism in which a conjugate acid of methoxytetraphenylantimony is formed as an intermediate in the production of benzene and dimethoxytriphenylantimony.

Apiezon L or a fluorosilicone column. A quantitative determination of the volatile products was made by comparing retention times and peak areas of the products with those of series of standard solutions. The results are summarized in Table II.

In control experiments, it was demonstrated that no significant changes in concentration of nitrobenzene or bromobenzene occurred when these compounds were subjected to the reactions cited above.

Reactions of Aryltriphenylstibonium Fluoroborates with Sodium *n*-Butoxide. Clean sodium, 0.002 g-atom, was allowed to react with 7.5 ml of anhydrous *n*-butyl alcohol contained in a glass tube sealed at one end, and the resulting sodium *n*-butoxide solution was cooled in an ice bath. The aryltriphenylsulfonium fluoroborate, 0.001 mol, was added to the solution and the tube sealed. It was placed in an oil bath maintained at about 120° for 188 hr, the tube and its contents being shaken at least once every day. At the end of the reaction period the tube was cooled in an ice bath, opened, and a 5-μl sample subjected to vpc analysis as described previously. The results are summarized in Table II.

A control experiment demonstrated that nitrobenzene was completely destroyed when subjected to the reaction conditions described above for as little as 10 min.

Tri-*m*-chlorophenylstibine. To a solution of 0.1 mol of *m*-chlorophenylmagnesium bromide in 100 ml of ether was added slowly a solution of 7.75 g (0.034 mol) of antimony trichloride in 50 ml of ether. A vigorous reaction occurred, and a steady reflux was maintained during the addition of the antimony trichloride and for 1 hr thereafter. The mixture was cooled and poured into 1000 ml of an ice-cold, saturated, aqueous solution of ammonium chloride. The organic layer was separated from the aqueous layer, and the latter was extracted with ether. The combined organic solution was concentrated to dryness, and the residual oil was induced to crystallize from 95% ethanol. There was obtained 10 g (65%) of tri-*m*-chlorophenylstibine, mp 53–54°.

Anal. Calcd for $C_{18}H_{12}Cl_3Sb$: C, 47.65; H, 2.63; Cl, 23.30. Found: C, 47.46; H, 2.65; Cl, 23.19.

Phenyldi-*p*-tolylstibine. To a Grignard reagent prepared from 0.2 mol of *p*-bromotoluene and 0.2 g-atom of magnesium in 175 ml of ether was added a suspension of 0.1 mol of phenyldichlorostibine[34] in 200 ml of ether over a period of 30 min. The mixture was refluxed for 5 hr, then cooled and added to a mixture of 200 ml of saturated ammonium chloride solution and 200 g of ice. The colorless organic layer was separated from the aqueous layer, which was washed thoroughly with warm benzene. Evaporation of the combined organic layer and benzene wash solution gave a viscous, colorless residue which was induced to crystallize from 95% ethanol to give 12.0 g (33%) of phenyldi-*p*-tolylstibine, mp 71–73°.

Anal. Calcd for $C_{20}H_{19}Sb$: C, 63.0; H, 5.0. Found: C, 62.6; H, 4.8.

Phenyldi-*p*-fluorophenylstibine. Prepared in essentially the same manner as described above for phenyldi-*p*-tolylstibine, the fluoro compound had a mp of 66–67° and was obtained in 52% yield.

Anal. Calcd for $C_{18}H_{13}SbF_2$: C, 55.3; H, 3.3; F, 9.7. Found: C, 55.5; H, 3.4; F, 9.6.

Phenyldi-*p*-anisylstibine. This compound, mp 109–110°, was obtained in 45% yield by the same general procedure as described above.

Anal. Calcd for $C_{20}H_{19}SbO_2$: C, 58.2; H, 4.6. Found: C, 58.1; H, 4.6.

Phenyldi-*p*-chlorophenylstibine. A 56% yield of the compound, mp 82–84°, was obtained.

Anal. Calcd for $C_{18}H_{13}SbCl_2$: C, 51.1; H, 3.1; Cl, 16.8. Found: C, 51.3; H, 3.1; Cl, 17.0.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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(34) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **72**, 3027 (1950).

Oxidation of Organic Compounds with Cerium(IV). X. Oxidation of 1,3,5-Cycloheptatriene[1]

Walter S. Trahanovsky, L. Brewster Young,[1d] and M. Dwight Robbins[1e]

Contribution from the Department of Chemistry,
Iowa State University of Science and Technology, Ames, Iowa 50010.

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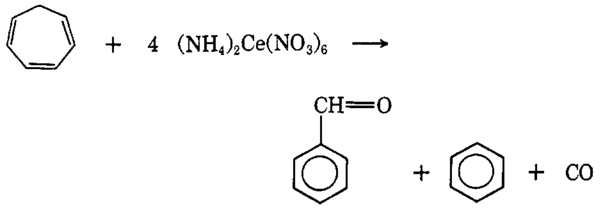
Abstract: The facile oxidation of 1,3,5-cycloheptatriene by 4 equiv of ceric ammonium nitrate in aqueous acetic acid and other solvents is shown to lead to benzaldehyde, benzene, and carbon monoxide. The results of three sets of experiments are presented which strongly support the tropylium ion an an intermediate in this oxidation. Evidence is presented which establishes that the oxygen of the benzaldehyde produced by the ceric ammonium nitrate oxidation of cycloheptatriene in anhydrous acetonitrile comes from the nitrate ion. A mechanism is proposed which is consistent with these and other experimental findings.

We have found that 4 equiv of ceric ammonium nitrate (CAN) in aqueous acetic acid and other solvents smoothly oxidizes 1,3,5-cycloheptatriene (CHT) to a high yield of benzaldehyde, benzene, and carbon monoxide. The reaction is quite facile (a few minutes at 90° in most solvents used), being more rapid in 50% aqueous acetic acid than the oxidation of benzyl alcohol.[2] CHT and substituted cycloheptatrienes[1g] have



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(1) (a) For Part IX, see W. S. Trahanovsky, M. G. Young, and P. M. Nave, *Tetrahedron Lett.*, 2501 (1969). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences. The mass spectrometer was purchased with funds from the National Science Foundation Grant GP 1715 and a grant from the Iowa State Alumni Research Foundation. We thank these organizations for their support. (c) Based on work by L. B. Y. and M. D. R. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University. (d) U. S. Public Health Service Fellow, 1966–1967. (e) National Science Foundation Trainee, 1967–1969. (f) Preliminary Communication: Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., September, 1966, p 52 S. (g) All cycloheptatrienes mentioned in this paper are 1,3,5-cycloheptatrienes.

(2) W. S. Trahanovsky, L. B. Young, and G. L. Brown, *J. Org. Chem.*, **32**, 3865 (1967).