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ORGANIC DERIVATIVES OF QUINQUEVALENT ANTIMONY
I. SYNTHESIS AND PROPERTIES OF ALKYLTETRAPHENYLANTIMONY COMPOUNDS

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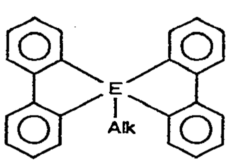
SUMMARY

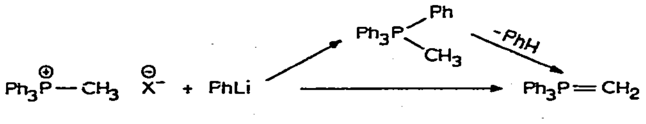
The reaction of AlkMgBr with Ph_4SbF gives Ph_4SbAlk (Alk$=CH_3$, C_2H_5). When treated with C_4H_9Li, PhLi, or RMgX, the Ph_4SbAlk compounds are "symmetrised" to produce Ph_5Sb and other products, the reaction occurring through the possible formation of derivatives of hexacovalent antimony. The action of HBr, $BF_3 \cdot O(C_2H_5)_2$, or mercury acetate results in the abstraction of phenyl, not alkyl. The reaction of Ph_3SbCH_3X ($X=I$ or BF_4) with PhLi also gives rise to methyltetraphenylantimony partially "symmetrised" *in situ*. Unlike the results reported by Henry and Wittig[15], Ph_4SbCH_3 heated with benzophenone yields no triphenylstibine while the benzophenone remains unaffected.

Wittig, Hellwinkel, and their co-workers[1-10] have described pentaaryl derivatives of the Group V elements. The alkyl tetraaryl compounds on the other hand have been reported from time to time by a number of workers, and belong to the type (I) where E is P or As[6,8,9].



(I)

Seyferth has shown that some phosphonium salts are transformed to the Wittig reagents through the intermediate formation of pentacovalent phosphorus compounds, $(C_6H_5)_4PAlk$ (II), these species eliminating benzene to produce the ylide[11-13].



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Antimony compounds of the same type may be anticipated to be more stable, since the abstraction of benzene would lead to the formation of the less favourable antimony ylide, in which the d–π π-overlap may be rather ineffective. In support of this suggestion, we have succeeded in isolating, and studying the reactions of methyl- and ethyltetraphenylantimony.

1. SYNTHESIS

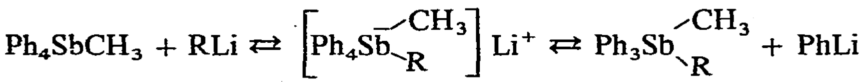
Phenylmagnesium bromide reacts with Ph_3SbX_2 (III; a, X=Br, b, X=Cl; c, X=F) to give a mixture of triphenylstibine and pentaphenylantimony if (IIIa) or (IIIb) are used. However, with the fluoride (IIIc) the pure pentaphenylantimony is produced in good yield, possibly because the fluoride is reduced less easily than other halides*. This synthesis seems to be more convenient than that reported earlier by Wittig[2]. Similarly, methyldiphenylstibine produces methyltetraphenylantimony (IVa).

$$Ph_2SbCH_3 \rightarrow Ph_2SbCH_3Cl_2 \xrightarrow{KF} Ph_2SbCH_3F_2 \xrightarrow{PhMgBr} Ph_4SbCH_3 \text{ (IVa)}$$

This compound may be also obtained from tetraphenylstibonium fluoride and methylmagnesium bromide,

$$Ph_3SbCl_2 \xrightarrow{KF} Ph_3SbF_2 \xrightarrow{PhMgBr} Ph_5Sb \xrightarrow{HBr} Ph_4SbBr \xrightarrow{KF}$$
$$\longrightarrow Ph_4SbF \xrightarrow{CH_3MgBr} Ph_4SbCH_3$$

this method of preparation being preferred in that triphenylstibine is easier to synthesise than methyldiphenylstibine. Ethyltetraphenylantimony (IVb) has been synthesised in the same way. The use of stibonium fluoride in these syntheses is essential, since the use of the bromide or the chloride results in the "symmetrisation" of species (IV) with the organomagnesium compound, and this results in appreciable amounts of Ph_5Sb. In the absence of Grignard reagent alkyltetraphenylantimony is not "symmetrised", while its addition leads to the slow formation of Ph_5Sb, and of other products which have not been isolated. Ph_4SbF reacts with AlkMgBr much faster than the chloride or the bromide, and for this reason the formation of (IV) outpaces its "symmetrisation". It should be emphasised that organolithium compounds such as PhLi or C_4H_9Li accelerate the "symmetrisation" of (IV) to an even greater extent. The compound (IVa) when treated with butyllithium, and then with benzophenone, produces noticeable amounts of pentaphenylantimony and triphenylcarbinol. This reaction, and the existence of the Ph_6SbLi compounds found by Wittig[2], enables the following mechanism to be suggested for "symmetrisation" process.



$$Ph_4SbCH_3 + RLi \rightleftarrows \left[Ph_4Sb\begin{smallmatrix}\nearrow CH_3\\ \searrow R\end{smallmatrix}\right]Li^+ \rightleftarrows Ph_3Sb\begin{smallmatrix}\nearrow CH_3\\ \searrow R\end{smallmatrix} + PhLi \quad (1)$$

$$Ph_4SbCH_3 + PhLi \rightleftarrows [Ph_5\overset{-}{Sb}CH_3]Li^+ \rightleftarrows Ph_5Sb + CH_3Li \quad (2)$$

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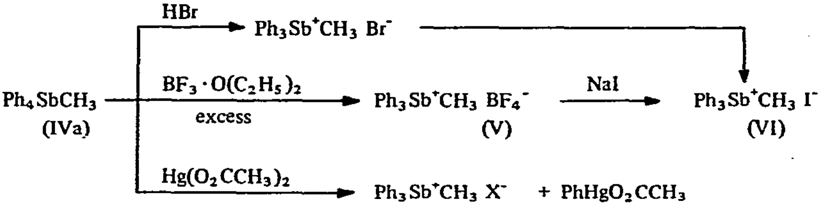
* The preparation of Ph_4SbBr has been reported[14] by treating (IIIb) with PhMgBr and then with HBr. Apparently, a mixture of Ph_3Sb and Ph_5Sb was initially formed which after treatment with HBr yielded the reported product.

$$Ph_2C{=}O + PhLi \rightarrow Ph_3COH \tag{3}$$

We have no proof, of course, that an uncomplexed PhLi entity is formed, since the complexes may react directly with benzophenone; also, the transfer of PhLi does not necessarily imply that it exists as a free species. The action of Grignard reagents on (IV) may be governed by a similar mechanism.

2. PROPERTIES

Methyl- and ethyltetraphenylantimony are crystalline compounds fairly soluble in organic solvents. The compound (IVa) reacts with hydrogen bromide, boron trifluoride etherate (in ether), or mercury acetate to give the expected products following phenyl abstraction.



With boron trifluoride etherate stibonium tetrafluoroborate (V) is obtained and further treatment with NaI yields the iodide (VI) described by Wittig and Henry[15]. Mercury acetate caused Ph–M bond rupture similar to that which occurs with Ar-HgAlk on treatment with $^{203}HgX_2$ (ref. 16) or with $TlCl_3$ (ref. 17). It is probable that these reactions are facilitated by the formation of an intermediate π-complex. Henry and Wittig[15] reported that the ylide was formed from the iodide (VI) on treatment of the latter with phenyllithium; the ylide was further claimed to react with benzophenone to give triphenylstibine and 1,1-diphenylethylene epoxide in a good yield (the epoxide rearranged *in situ* to diphenylacetaldehyde). On attempting to repeat these experiments using either the iodide (VI) or the tetrafluoroborate (V), we found that benzophenone is recovered almost entirely and neither triphenylstibine nor 1,1-diphenylacetaldehyde are apparently formed. Furthermore, treatment of (V) or (VI) with phenyllithium yielded (IVa) which was partially "symmetrised", the reaction mixture containing quite appreciable amounts of pentaphenylantimony. This latter compound may be isolated, or the reaction mixture may be further treated with mercury acetate to give PhHgX, Ph_4SbX (which can only be derived from Ph_5Sb) and Ph_3SbCH_3X, probably formed from (IVa). In an attempt to avoid the above "symmetrisation" a pure sample of (IVa) was heated with benzophenone at 60 to 80°, the benzophenone remaining unchanged while (IVa) eliminated benzene (GLC) and produced a mixture whose composition is at present being investigated. The same mixture is formed in the absence of benzophenone.

EXPERIMENTAL

(1).*Methyldiphenylstibine difluoride*

A solution of 8 g of KF in 20 ml water was added to a solution of 5 g of methyldiphenylstibine dichloride in 20 ml dimethylformamide. The mixture was heated for 2 to 3 min, diluted, and cooled to give 4.4 g (97 %) of the crude product and 3.7 g (81 %) of the pure material after crystallisation from heptane; m.p. 98–99°. (Found: C, 46.84; H, 3.82. $C_{13}H_{13}F_2Sb$ calcd.: C, 47.46; H, 3.98 %.)

Triphenylstibine difluoride was obtained in the same way. The yield was 95 % (76 % after crystallisation).

(2) *Pentaphenylantimony*

Ph_3SbF_2 (30 g, 0.076 mole, ref. 18) dissolved in 100 ml benzene was added over a period of 10 min to PhMgBr (ca. 0.18 mole) dissolved in 300 ml ether. The mixture was stirred for 2 h, left overnight, and diluted with 50 ml water and cooled. The organic layer was decanted and the residue twice stirred with benzene. The combined extracts were washed with water and dried over $CaCl_2$. The solvent was evaporated until the volume of the solution was approximately 40 ml, when 150 ml of ligroin were added yielding a precipitate of pentaphenylantimony, 29 g (75 %); m.p. 169–170° (acetonitrile). The IR spectrum of this material was identical to that expected for the pure compound[3].

(3). *Methyltetraphenylantimony*

Method A. $Ph_2SbCH_3F_2$ (23 mmole) dissolved in 50 ml ether was added to a solution of PhMgBr (ca. 48 mmole in 50 ml ether) over a period of 5 min in a dry argon atmosphere. The mixture was stirred at 0° for 20 min*, diluted with 15 ml water at 0°, and the ether layer decanted and dried over $CaCl_2$. The ether was evaporated *in vacuo* to give (IVa) 7.5 g (74 %), m.p. 110° (ether, −40°). (Found: C, 66.76; H, 5.25; Sb, 27.35. $C_{25}H_{23}Sb$ calcd.: C, 67.44; H, 5.27; Sb, 27.21 %.) PMR δ 7.2 (singlet, phenyl, 20 H), 1.62 (singlet, methyl, 3H).

Method B. Ph_4SbF (5 g, 11.1 mmole) was added to a stirred solution of CH_3MgBr (13 mmole) in 75 ml ether at 0°. After 20 min the mixture was treated with 20 ml water, the ether layer removed and the water layer washed twice with ether. The combined ether extracts were washed with water, dried over $CaCl_2$, and the ether removed by evaporation *in vacuo* to give 3.5 g (69 %) of the product; m.p. 107–108°; m.p. 110° after crystallisation from ether*.

(4) *Ethyltetraphenylantimony*

This compound was prepared using method (3*B*) above. The yield was 79 %; m.p. 105–106°; 107–108° (ether, −40°). (Found: C, 68.00; H, 5.49. $C_{26}H_{25}Sb$ calcd.: C, 68.21; H, 5.48 %.) PMR: δ 7.2 (singlet, phenyl, 20 H), 2.30 (quartet, methylene, 2H), 1.25 (triplet, methyl, 3H).

(5) *Tetraphenylstibonium fluoride*

Aqueous hydrobromic acid (150 ml, 48 %) was added to crude pentaphenylantimony obtained from 93 g of triphenylstibine difluoride (*Method* 2). The mixture was refluxed for 2 to 3 min, the crystalline precipitate dissolved in 1.5 litre hot water, the solution filtered, and a solution of $KF \cdot 2H_2O$ (100 g) in 300 ml water added to

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* At higher temperatures, or if the reaction mixture is allowed to stand for a long period, the yield of (IVa) falls through the process of "symmetrisation".

the hot filtrate. The fluoride separated from the warm solution. The yield was 77 g (73 %); m.p. 162–163° (benzene).

(6) *Methyltriphenylstibonium salts*

(*a*). *Methyltriphenylstibonium tetrafluoroborate* (*V*). (IVa) (5g) was mixed with 15 ml of $BF_3 \cdot O(C_2H_5)_2$ and 30 ml abs. ether. The mixture was diluted with 200 ml ether and the resulting precipitate crystallised from isopropanol to give 3.6 g (70 %) of the product; m.p. 133–134° (lit.[15] 133–134°).

(*b*). *Tetraphenylstibonium tetrafluoroborate*. This was obtained from Ph_5Sb using the procedure described above. The yield was 79 %; m.p. 270–271° (methanol/water). (Found: C, 56.70; H, 3.94. $C_{24}H_{20}BF_4Sb$ calcd.: C, 55.76, H, 3.90 %.)

(*c*). *Methyltriphenylstibonium iodide*. Sodium iodide (30 g), dissolved in water, was added to a solution of the tetrafluoroborate (V) (5 g) and sodium iodide (30 g) in 30 ml of 50 % aqueous methanol. The mixture was maintained at 0° for half an hour and the resulting precipitate washed with water to give 76 % of (VI). The yield was 70 % after crystallisation from chloroform/ether; m.p. 109–110° (dec.) (lit.[5] 124.5–125.5°). When stored over a period of time, or heated, (VI) decomposed to give methyl iodide and triphenylstibine. (Found: C, 46.68; H, 3.53. $C_{19}H_{18}Sb$ calcd.: C,46.10; H, 3.66 %.)

(7). *Pentavalent antimony compounds and mercury acetate*

(*a*). *Methyltetraphenylantimony*. A solution of (IVa) (2.0 g, 4.5 mmole) in 20 ml CCl_4 was heated with mercury acetate (1.44 g, 4.5 mmole) for 5 min. The hot mixture was filtered, cooled, and the precipitate washed with ether to give 0.98 g (68 %) of phenylmercury acetate; m.p. 147–148°; m.p. 149° (ethanol). The IR spectrum of the compound was found to be identical to that expected for the pure material. The filtrate which remained after phenylmercury acetate had been filtered off was washed with several 20 ml portions of water, and the water solution was treated with 7 g of $NaBF_4$. The precipiitate (V) was washed with either. The yield was 73 %; m.p. 131–133°.

(*b*). *Ethyltetraphenylantimony* under the same conditions as (7*a*) gave phenylmercury acetate (yield 70%) and ethyltriphenylstibonium tetrafluoroborate (yield 72%); m.p. 112° (isopropanol). (Found: C, 51.24; H, 4.32. $C_{20}H_{20}BF_4Sb$ calcd.: C, 51.21; H, 4.30%.)

(*c*). *Pentaphenylantimony* treated in the same manner produced phenylmercury acetate (yield 70%) and Ph_4SbBF_4 (yield 62%, *cf*. 6*b*).

(8). "*Symmetrisation*" *of methyltetraphenylantimony*.

(*a*). (*IVa*) *and the Grignard reagent*. Ph_4SbCH_3 (10 g, 22 mmole) was added to a solution of CH_3MgBr (26 mmole) in 100 ml ether, the mixture stirred at 20° for 2 h, and then treated with 20 ml water. The ether layer was removed and the water layer washed twice with ether. The combined ether extracts were dried over $CaCl_2$, the ether removed, and the residue dissolved in 10 ml ether. Crystals of pentaphenylantimony separated from the solution on cooling the latter to −40°. The yield was 2.1 g (4.14 mmole)*.

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* Ph_5Sb was identified in this and subsequent preparations through its melting point and IR spectrum.

(*b*). (*IVa*) *and phenyllithium.* A solution of (IVa) (2.26 mmole) and phenyllithium (2.5 mmole) in 2 ml ether was maintained in a sealed ampoule under argon at 20° for 12 h. The resulting suspension was treated with 20 ml benzene, cooled, and treated with 10 ml water. The organic layer was removed and washed with water, dried over $CaCl_2$, and the solvent removed *in vacuo*. The residual oil was treated with 10 ml ligroin yielding 1.08 mmole (0.55 g) of pentaphenylantimony.

(*c*). (*IVa*) *and butyllithium.* A solution of (IVa) (2 g, 4.5 mmole) and butyllithium (2.5 mmole) in 2.5 ml ether was maintained in a sealed ampoule under argon at 20° for 12 h. The mixture was cooled, and treated with 5 ml water. The ether solution was washed with water, dried over $CaCl_2$, and the ether distilled off. The ether distillate contained benzene (GLC). The residue was treated with ligroin yielding 0.30 g (0.59 mmole) of pentaphenylantimony.

(*d*). (*IVa*) *and butyllithium.* The reaction mixture, obtained as above following the use of 4.5 mmole C_4H_9Li, was treated with benzophenone (4.5 mmole) and the resulting mixture left overnight. It was then treated with 20 ml benzene and 10 ml water and the benzene/ether solution "worked up" to give 0.77 g (2.9 mmole) of triphenylmethanol; m.p. 161° (CCl_4). The IR spectrum was found to be identical to that expected for the pure compound.

(9). *Methyltriphenylstibonium salts and phenyllithium.*

A solution of phenyllithium (3 mmole) in ether was added to a solution of (VI) (1.5 g, 3 mmole) in 40 ml ether at 0° in an argon atmosphere. The mixture was stirred at 0° for 20 min and then treated with 10 ml water. The ether layer was separated, washed with water, and dried over $CaCl_2$. Evaporation of the ether was followed by treatment of the residue with 15 ml CCl_4 and 0.97 g (3 mmole) of mercury acetate. The resulting mixture was heated for 5 min, the hot solution decanted and cooled to give a precipitate of phenylmercury acetate, 0.70 g (2.1 mmole); m.p. 149°. The solvent was removed from the filtrate and the residue was treated with a solution of sodium tetrafluoroborate in water. The resulting precipitate was filtered off, washed with water, dried, and heated with 15 ml isopropanol. The insoluble residue obtained was found to be tetraphenylstibonium tetrafluoroborate (0.39 g, 0.75 mmole); m.p. 271° (ethanol/water). The isopropanol solution was cooled yielding crystals of (V), 0.24 g (0.53 mmole); m.p. 134° Similar results were obtained with (V).

(10). *Reaction of methyltriphenylstibonium iodide with phenyllithium and benzophenone*

A mixture of (VI) (2 g, 4 mmole) and phenyllithium (3 ml, 4 mmole) dissolved in ether was shaken in a Schlenk tube at 20° in an argon atmosphere for 12 h. A solution of benzophenone (0.75 g, 4 mmole) in 10 ml ether was then added to the mixture and the latter heated at 60° for 12 h. It was then treated with 10 ml of 6 *N* HCl, the ether layer washed with water, and the aqueous solution treated with ammonium tetrafluoroborate to give 1.1 g of the mixture of tetrafluoroborates whose separation has been described above. From this mixture tetraphenylstibonium tetrafluoroborate (0.52 g, 1.0 mmole) and 0.37 g of (V) (0.8 mmole) were obtained. The ether solution was subjected to chromatographic separation on alumina allowing the recovery of 0.62 g (81 %) of the initial benzophenone.

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