Journal of Organometallic Chemistry, 295 (1985) 29–32
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SYNTHESIS OF 1,6-DISTIBATRIPTYCENE (5,10-*o*-BENZENOSTIBANTHRENE), $Sb_2(C_6H_4)_3$

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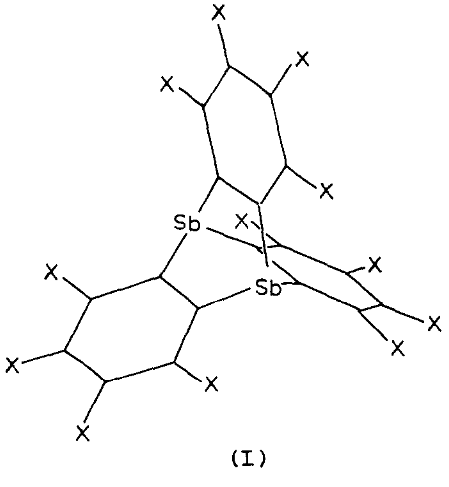
(Received June 3rd, 1985)

Summary

1,6-Distibatriptycene has been synthesised by heating a mixture of antimony powder with *ortho*-phenylenemercury trimer in a sealed evacuated tube.

Introduction

Although 1,6-diaza-, 1,6-diphospha-, and 1,6-diarsa-triptycenes are well known, 1,6-distibatriptycene (I, X = H) has not previously been described in the literature. On the other hand, the perfluoro- and perchloro-distibatriptycenes (I, X = F, Cl) can be made simply by heating antimony with the corresponding 1,2-diiodotetrahalobenzene [1]; when antimony was heated with a mixture of $1,2\text{-}I_2C_6F_4$ and $1,2\text{-}I_2C_6H_4$ three products were formed: $Sb_2(C_6F_4)_{3-n}(C_6H_4)_n$ where $n = 0$, 1 and 2 [2]. This showed that the distiba-triptycene structure must be stable when at least partial substitution of halogen for hydrogen occurs. Consequently we have expended considerable effort in trying to make the fully hydrogen-substituted species $Sb_2(C_6H_4)_3$. This note describes some of our unsuccessful attempts before we finally managed to isolate the compound in low yield.

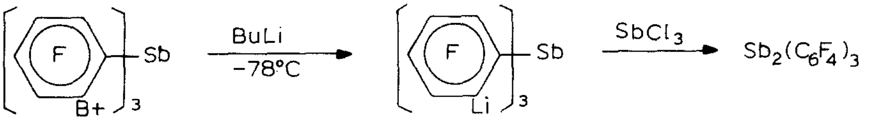


(I)

Results and discussion

1,6-Diphospha- [3] and 1,6-diarsa-triptycene [4] have been made by direct synthesis from 1,2-dihalobenzenes and either phosphorus or arsenic, so our first experiments involved heating 1,2-dibromobenzene, 2-chloroiodobenzene and 1,2-diiodobenzene with antimony powder in sealed, evacuated tubes at a variety of temperatures; however, the only product sometimes isolated was triphenylene. It is noteworthy that in the "mixed" synthesis mentioned above, $Sb_2(C_6H_4)_3$ was entirely missing from amongst the products.

In the perfluoro-triptycene series we made [5] eight derivatives, including $Sb_2(C_6F_4)_3$, by lithiating $M(2\text{-}BrC_6F_4)_3$ [M = P, As, Sb, Bi, SiMe] with butyllithium and then adding a Group V trichloride; e.g.:



However, the corresponding $M(2\text{-}BrC_6H_4)_3$ intermediates could not be prepared from 1,2-dibromobenzene even at very low temperatures. When attempts were made to dilithiate benzene by adding 2 mol of LiBu · TMEDA (TMEDA = tetramethylethylene diamine) to 1,2-dibromobenzene, followed by the addition of antimony trichloride, no $Sb_2(C_6H_4)_3$ was formed. By adding LiBu · TMEDA to 2-chloroiodobenzene it was found possible to make tris(2-chlorophenyl)antimony in high yield [6] but all attempts to lithiate the 2-chlorine atoms, and carry out a reaction similar to that in the above equation, were unsuccesful when BuLi, BuLi · TMEDA, or Li metal were employed. This was probably due either to the occurrence of metallation *ortho* to the chlorine atoms or to cleavage of chlorophenyl groups from the antimony.

If antimony is heated in sealed tubes with perfluoro-*ortho*-phenylenemercury trimer, $Sb_2(C_6F_4)_3$ is formed [2]. When this synthesis was repeated at 260°C with finely ground antimony powder intimately mixed with *ortho*-phenylenemercury trimer, about a 5% yield of 1,6-distibatriptycene was isolated on extraction of the residues with 60–80°C petroleum ether or hexane. A series of repeat mass spectra verified the homogeneity of the sample, the identity of which was confirmed by accurate mass measurements of the three antimony isotopomers present in the parent ion: $C_{18}H_{12}{}^{121}Sb_2$, obs. 469.900 (calcd. 469.901 m.u.); $C_{18}H_{12}{}^{121}Sb^{123}Sb$, obs. 471.899 (calcd. 471.902 m.u.); $C_{18}H_{12}{}^{123}Sb_2$, obs. 473.906 (calcd. 473.902 m.u.). Mass measurements on the ^{13}C satellites of these peaks also gave excellent agreement between the observed and calculated values.

Experimental

The direct syntheses, and reactions with mercurials, were carried out in sealed, evacuated pyrex tubes which had been thoroughly baked out under vacuum (10^{-4} mmHg) before use to remove any traces of adsorbed moisture. A dry nitrogen atmosphere was provided for those reactions involving the use of butyllithium. *Ortho*-phenylenemercury trimer was prepared, in about a 2% yield, as previously described [7].

Reaction of 1,2-diiodobenzene with antimony

1,2-Diiodobenzene (0.5 g) and antimony (0.2 g) were heated in a sealed tube at 300°C for 48 h. The tube was then cooled and opened, and the contents were extracted with ether. The ether extract was shaken with aqueous sodium thiosulphate then dried over anhydrous magnesium sulphate; removal of the solvent gave a tiny amount of pale yellow solid, which was shown to be mainly triphenylene from its mass spectrum.

Under the same conditions [4] arsenic and 1,2-diiodobenzene gave a 30% yield of 1,6-diarsatriptycene, m.p. 296–298°C (ref. 8: 295–296°C).

No 1,6-distibatriptycene resulted when 1,2-bromobenzene and antimony were heated at 300°C for 96 h; much unchanged starting material was present in the tube.

Attempts at lithiation of tris(2-chlorophenyl)antimony

In either ether or tetrahydrofuran no lithiation of the chlorine atoms could be detected at temperatures from −90°C to the reflux point of ether using BuLi, BuLi · TMEDA or Li chips. Only unidentified oils resulted when antimony trichloride was added to the solutions and the products worked up.

Reaction of ortho-phenylenemercury trimer with antimony

Powdered antimony was ground as fine as possible in an agate mortar before *ortho*-phenylenemercury was added to the mortar and the two ground carefully to an intimate mixture prior to being loaded into a reaction tube. The sealed, evacuated tube was heated to 260°C (i.e. below the m.p. of the mercurial) for 2 h when mercury droplets were visible on the inside. After cooling, the tube was cut open, the contents extracted with boiling hexane and the filtered solution evaporated to small volume. Tiny amounts of colourless crystals of $Sb_2(C_6H_4)_3$ separated out overnight; the mother liquor was decanted off and crystals quickly washed with cold 40–60°C petroleum ether before being dried in the open air, m.p. 254–255°C. (Found: C, 48.9, 49.35; H, 3.5, 3.6%; $Sb_2(C_6H_4)_3 \cdot 0.5$hexane calcd.: C, 48.9; H, 3.7%). The main antimony-containing ions in the mass spectrum were $Sb_2(C_6H_4)_3^+$ (34% for the major peak in the ion cluster), $Sb(C_6H_4)_2^+$ (43%), $SbC_6H_4^+$ (52%) and Sb^+ (13%) (the corresponding fluoro ions also give prominent peaks in the spectrum of $Sb_2(C_6F_4)_3$). The base peak was due to the ion $C_{18}H_{12}^+$, presumably ionized triphenylene; TLC of the mass spectral sample showed the compound to consist of a single component with a different R_f value to triphenylene. A mixture of $Sb_2(C_6H_4)_3$ and triphenylene showed two spots on the TLC plate – hence the ion $C_{18}H_{12}^+$ must arise, via a fragmentation process, from the $Sb_2(C_6H_4)_3$ sample. Again, in the spectrum of $Sb_2(C_6F_4)_3$ there is a fairly intense peak due to $C_{18}F_{12}^+$. Infrared spectrum (Nujol mull): 3038w; 3010w; 3005w; 1423m; 1415msh; 1249s; 1244wsh; 1158w; 1072s; 1019w; 936w; 869vw; 741vs; 736vs; 678vw; 416s; 360s; 297sh; 291m; 267w; 258m; 250sh; 245sh.

Acknowledgement

Mrs. Al-Jabar gratefully thanks the University of Salah Al-ddine (Iraq), for a scholarship.

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