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MIXED ORGANOMETALLIC COMPOUNDS OF GROUP V
I. SYNTHESIS OF TRIS(TRIMETHYL-GROUP-IV)STIBINES

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INTRODUCTION

Infrared and Raman spectra of trisilylphosphine[1,2] provide evidence that the PSi_3 skeleton is planar. It is suggested that similar compounds, such as trisilylarsine and trisilylstibine have a planar skeleton structure also.

It would be of interest to observe what the skeletal structure would be in compounds such as tris(tert-butyl)stibine, tris(trimethylsilyl)stibine, tris(trimethylgermyl)stibine and tris(trimethylstannyl)stibine in which antimony is the central atom. Since those compounds have, as yet, not been reported in the literature, we shall describe their synthesis.

These stibines were synthesized using the highly reactive trilithium stibine, Li_3Sb, prepared from the elements in liquid ammonia followed by a coupling reaction with a halide in diethyl ether:

$$3\,Li + Sb \xrightarrow{NH_3} Li_3Sb$$

$$Li_3Sb + 3\,(CH_3)_3E^{IV}X \rightarrow [(CH_3)_3E^{IV}]_3Sb + 3\,LiX$$

where E^{IV} is C, Si, Ge, Sn and X is Cl or Br.

Tris(tert-butyl)stibine is, at room temperature, a colorless liquid melting at −38°. At room temperature it has a vapor pressure lower than 0.1 mm Hg and its yield in the reaction is *ca.* 1%. The yields of the other stibines are in the order of 80 to 85%.

The silicon stibine, tris(trimethylsilyl)stibine is a colorless liquid at room temperature melting between −1° and 1°. It is the most reactive of these compounds and inflames on contact with air, especially if an inflamable substance such as ether is present. It is photosensitive.

The germanium stibine, tris(trimethylgermyl)stibine is also a colorless liquid at room temperature melting between 11° and 13°. On contact with air it rapidly turns to a white solid compound and on standing at room temperature, it turns yellow.

Tris(trimethylstannyl)stibine is a colorless crystalline solid which melts at 39°. On standing at room temperature it turns red. The substance can be purified by sublimation in high vacuum at 40° to 45°.

As mentioned, these stibine compounds are all somewhat sensitive to air, moisture and light. They start to decompose at temperatures above 60°. The overall sensitivity decreases from tris(trimethylsilyl)stibine to tris(trimethylstannyl)stibine.

The reactivity of these stibines required that all preparative work be done at temperatures below 55° in a high-vacuum system.

Infrared spectra from 33 cm^{-1} to 5000 cm^{-1} and Raman spectra have been obtained and will be the subject of a forthcoming communication.

Dipole moments suggest that the skeletal configuration is pyramidal.

EXPERIMENTAL

Synthesis of trilithium antimony[3,4,5]

Trilithium antimony was prepared according to Brauer[3]. A vacuum trap fitted with a standard taper joint and a stopcock was used as the reaction vessel. A bulb containing antimony powder is attached via the taper joint. Nitrogen gas can be passed, as required, into the vessel through the stopcock. Finely cut pieces of lithium are placed in the reaction vessel which is then completely evacuated. Ammonia is condensed onto the lithium (about 30 ml in the liquid phase) and allowed to warm to −50°, at which temperature antimony powder is added in small amounts to the continuously stirred solution of lithium in liquid ammonia. When formation of the trilithium antimony is complete, all the ammonia is allowed to distill off at −50°, continuous stirring being maintained. The vessel is warmed to room temperature and then heated to 80° under vacuum. The pumping was discontinued when no trace of ammonia was dectectable in an intermediate trap cooled with liquid nitrogen.

Remarks as to further experimental technique

All subsequent reactions were carried out in the vessel in which the trilithium antimony was produced. The Li_3Sb vessel was removed, in a nitrogen atmosphere, from the high vacuum line and diethyl ether added rapidly to the solid Li_3Sb. A solution of the reagent in diethyl ether is added rapidly to the suspension of Li_3Sb in ether. A reflux head fitted with a mercury valve is attached to the vessel and the system is warmed to boiling and stirred. All operations carried out outside of the high vacuum line were done under a nitrogen atmosphere.

Synthesis of tris(tert-butyl)stibine

A solution of 22.1 ml (228.7 mmole) tert-butyl chloride is added rapidly to a suspension of 76.23 mmole Li_3Sb in 25 ml diethyl ether. The reaction mixture is heated to reflux and stirred continuously for 100 h. The reaction vessel is allowed to cool to room temperature and attached to a high vacuum line, cooled to −196° and evacuated. After isolation from the high vacuum line, the reaction vessel is warmed to −60° and then the ether distilled off (pressure of the ether at −60° is 4 mm Hg). After removal of the ether, the reaction vessel is allowed to warm up to room temperature. The reaction mixture is allowed to pass through three traps (−15°, −40° and −196°), while open to a mercury diffusion pump (pressure of tert-butyl chloride at −15° is 5 mm Hg, at −40° 1.3 mm Hg). The stibine is found in the trap at −15°. The yield of the tris(tert-butyl)stibine is 0.2005 g corresponding to a yield of about 1%.

Tris(tert-butyl)stibine is a colorless liquid at room temperature having a very low pressure (the pressure could not be measured with a Hg manometer). The freezing point of the substance is −38°.

Quantitative analysis of antimony was carried out by pyrolysis of the stibine at 300–400° at which temperature an antimony mirror is formed. (Found: C, 48.09; H, 9.17; Sb, 42.32; mol.wt. cryoscopic in benzene, 282.13. $C_{12}H_{27}Sb$ calcd.: C, 49.16; H, 9.28; Sb, 41.54%; mol.wt., 293.10.)

A colorless liquid whose analytical data gave a composition of 84.10% C and 14.56% H, that is a 98.66% hydrocarbon, was found in the −40° trap. It is, perhaps, not free of the stibine. Gas chromatography proved this liquid to consist of two components in the ratio of 1:2.3 and with a retention time difference of 1.85 minutes. A Perkin Elmer gas chromatograph type 116 H, He gas a 1.5 ml/min, a type "C" column substance and 180° block temperature were used. Molecular weight determinations (osmometric in benzene) on the mixture gave a value of 238.

Synthesis of tris(trimethylsilyl)stibine[6]

A solution of 15 ml diethyl ether and 14.28 ml (112.9 mmole) trimethylsilyl chloride is added rapidly to a suspension of 37.63 mmole Li_3Sb in 15 ml diethyl ether. The reaction mixture is heated to reflux and stirred continuously for 70 h. The reaction vessel is allowed to cool to room temperature and attached to a high-vacuum line, cooled to −196° and evacuated. After isolation from the high-vacuum line, the reaction vessel is warmed to −60° and then the ether distilled off (pressure of the ether at −60° is 4 mm Hg). After removal of the ether, the reaction vessel is allowed to warm up to room temperature. The reaction mixture is allowed to pass through two traps (−62° and −196°) while open to a mercury diffusion pump (pressure of trimethylsilyl chloride at −62.8° is 1 mm Hg). The silicon stibine is found in the trap at −62°. The yield of the tris(trimethylsilyl)stibine is 10.3 g which corresponds to a 80% yield.

This stibine is a liquid at room temperature melting between −1° and 1° and is soluble in benzene and cyclohexane. Its pressure, at room temperature, is too low to be measured with a Hg manometer. (Found: C, 28.78; H, 8.17; mol.wt. cryoscopic in benzene, 320. $C_9H_{27}SbSi_3$ calcd.: C, 31.67; H, 7.97%; mol.wt., 341.34.) The dipole moment, measured in benzene at 25°, gave a value of 1.50 Debye units.

Synthesis of tris(trimethylgermyl)stibine[6]

A solution of 15 ml diethyl ether and 14.08 ml (110.6 mmole) trimethylgermyl bromide is added rapidly to a suspension of 36.88 mmole Li_3Sb and 15 ml diethyl ether. The reaction mixture is heated to reflux and stirred continuously for 70 h. The reaction vessel is allowed to cool to room temperature and attached to a high-vacuum line, cooled to −196° and evacuated. After isolation from the high-vacuum line, the reaction vessel is warmed to −60° and then the ether distilled off (pressure of the ether at −60° is 4 mm Hg). After removal of the ether, the reaction mixture is allowed to warm up to room temperature. The reaction mixture is allowed to pass through two traps (−20° and −196°) while open to a mercury diffusion pump (pressure of trimethylgermyl bromide at −25° is 0.1 mm Hg). The germanium stibine is found in the trap at −20°. The yield of tris(trimethylgermyl)stibine is of 14.95 g corresponding to a 85% yield.

At room temperature this stibine is a colorless liquid which melts between 11° and 13° and is soluble in benzene and cyclohexane. On exposure to air, it turns rapidly to a white solid substance, probably the stibine oxide. (Found: C, 21.64; H, 5.62; Ge+Sb, 69.4; mol.wt. cryoscopic in benzene, 454.2. $C_9H_{27}Ge_3Sb$ calcd.: C, 22.76;

H, 5.73; Ge+Sb, 71.50%; mol.wt., 474.87.) The germanium plus antimony analysis were determined by the pyrolysis of a sample at 300°–400° and measuring the weight of the mirror produced. The dipole moment in benzene at 25° gave a value of 1.378 Debye units.

Synthesis of tris(trimethylstannyl)stibine[6]

A solution of 50 ml diethyl ether and 7.76 g (38.94 mmole) trimethylstannyl chloride is added rapidly to a suspension of 12.96 mmole Li_3Sb and 20 ml diethyl ether. The reaction mixture is heated to reflux and stirred continuously for 70 h. The reaction vessel is allowed to cool to room temperature and 50 ml diethyl ether were added. The reaction mixture is filtered. After filtration, the ether was removed at −60° under vacuum, and the solid material sublimed until the stibine is free of trimethylstannyl chloride. The yield of the chloride-free tris(trimethylstannyl)stibine was 6.36 g corresponding to a 80% yield.

This tin stibine is a colorless crystalline solid melting at 39°. (Found: C, 17.64; H, 4.68; Sb, 19.4; Sn, 57.64; mol.wt. cryoscopic in benzene, 583.2. $C_9H_{27}SbSn_3$ calcd.: C, 17.63; H, 4.43; Sb, 19.85; Sn, 58.06%; mol.wt., 613.7.) The substance was destroyed in fuming nitric acid. Tin was determined as SnO_2, antimony as Sb_2S_3. The observed dipole moment in benzene at 25° was ~1.7 Debye units.

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SUMMARY

The synthesis of tris(tert-butyl)stibine, tris(trimethylsilyl)stibine, tris(trimethylgermyl)stibine and tris(trimethylstannyl)stibine by a coupling reaction between Li_3Sb and the appropiate trimethyl halogen derivative of the Group IV element is described.

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