

SYNTHESIS OF ORGANOELEMENT DERIVATIVES OF BARENES
(CARBORANES)

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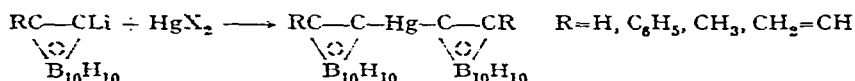
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The synthesis of mercury, silicon, tin and phosphorus derivatives of barenes by the reaction of lithium barenyls with organoelement halides was described in a recent note¹. American chemists²⁻⁴ have independently prepared a number of silicon and phosphorus derivatives of barenes (carboranes).

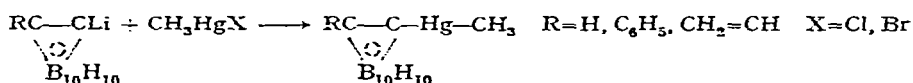
The detailed investigation of the organoelement derivatives of barene containing a direct bond between the element and the barene carbon atoms is particularly interesting owing to the unusual valency state of the carbon taking part in the formation of the barene system, the strong electron-withdrawing power of the system and pronounced steric hindrances.

It is possible to prepare a number of organoelement derivatives of barenes by alkylation (barenylation) of various mercury, silicon, germanium, tin, phosphorus, arsenic and antimony halides.

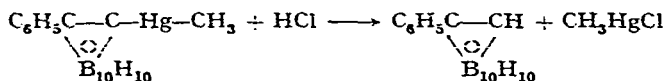
Steric hindrance was negligible in the alkylation of mercuric chloride because the system C-Hg-C is linear. The bis-barenyl derivatives of mercury were obtained in good yields:



The reaction between lithium barenyls and methylmercuric halides gives unsymmetrical derivatives of mercury:

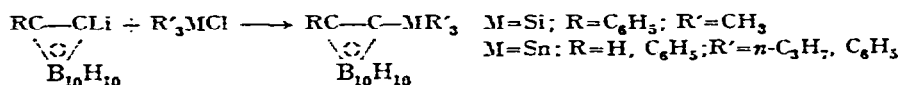


Compounds of this latter type are stable and have no tendency to disproportionation. When methyl(phenylbarenyl)mercury is treated with an alcoholic solution of hydrogen chloride the parent compounds, phenylbarene and methylmercury chloride, are formed as a result of the strong electron-withdrawing power of the barene system:

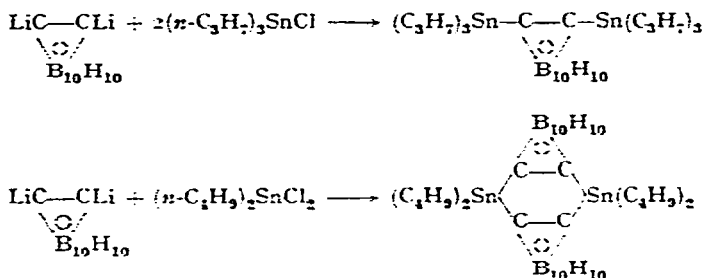


The majority of the barenyl derivatives of mercury are distinguished by remarkable thermal stability.

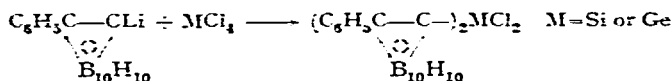
In the absence of steric hindrance the halides of IVB-group elements were found to undergo ready alkylation with lithium barenyls. For example, trimethylchlorosilane and tripropyl- and triphenyltin chlorides give the corresponding barenyl compounds:



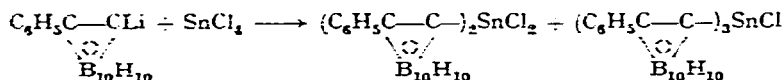
Barenylenedilithium reacts with tri- and dialkyltin chlorides to give compounds containing two tin atoms per molecule:



The interaction between silicon and germanium tetrachlorides and phenylbarenyllithium (2, 3 or 4 moles per mole of halide) resulted in the formation of only bis(phenylbarenyl)dichlorosilane and bis(phenylbarenyl)dichlorogermane, respectively:

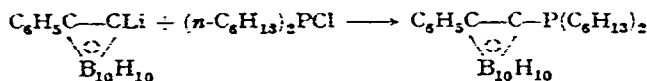


The reaction of stannic chloride with phenylbarenyllithium gives both di- and tri-substituted compounds. Attempts to prepare tetra(phenylbarenyl)tin failed:

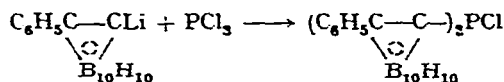


These results are due to the steric hindrance of the barene nucleus. The increase in the central atom radii in the order: Si, Ge, Sn, allows three barene substituents to be introduced.

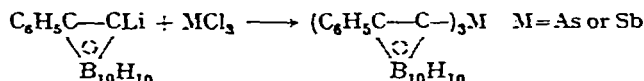
The alkylation of phosphorus halides is complicated by steric hindrance as with the silicon, germanium and tin compounds. (Phenylbarenyl)dihexylphosphine was obtained readily:



Nevertheless, in the case of phosphorus trichloride only two chloride atoms were substituted by phenylbarenyl species:



The increase in size of the arsenic and antimony atoms enables tris(phenylbarenyl)arsenic and tris(phenylbarenyl)antimony to be obtained:



EXPERIMENTAL

Bis(phenylbarenyl)mercury

To 50 ml of a stirred benzene solution of phenylbarenyllithium prepared from 4.4 g (0.02 mole) of phenylbarene, was added 30 ml of dry ether and 2.7 g (0.01 mole) of mercuric chloride. The temperature rose and the formation of a precipitate of lithium chloride was observed. The mixture was allowed to reflux for 10 h with stirring and after cooling was treated with 20 ml of dilute (1:4) hydrochloric acid. The water layer was separated and extracted with ether. The ether-benzene layer was dried over magnesium sulfate. The residue remaining after the removal of ether was recrystallized from benzene to yield 3.8 g (70 %) of bis(phenylbarenyl)mercury, m.p. 262–263°. (Found: C, 30.02; H, 4.80; B, 33.98; Hg, 31.00. $\text{C}_{16}\text{H}_{30}\text{B}_{20}\text{Hg}$ calcd.: C, 30.08; H, 4.72; B, 33.80; Hg, 31.40 %.)

Bis(vinylbarenyl)mercury

This compound was prepared by a procedure similar to that used for bis(phenylbarenyl)mercury. The product obtained from 0.02 mole of vinylbarenyllithium and 2.7 g (0.01 mole) of mercuric chloride was purified by recrystallization from cyclohexane to give 2.7 g (yield 51 %) of bis(vinylbarenyl)mercury, m.p. 153.5–154°. (Found: C, 17.15; H, 4.86; B, 39.74. $\text{C}_3\text{H}_{26}\text{B}_{20}\text{Hg}$ calcd.: C, 17.82; H, 4.86; B, 40.12 %.)

Bis(methylbarenyl)mercury

Similarly, treatment of mercuric chloride (2.7 g, 0.01 mole) with methylbarenyllithium (0.02 mole) gave 3.7 g (72 %) of bis(methylbarenyl)mercury, m.p. 255–256° (from cyclohexane). (Found: C, 14.60; H, 5.18; B, 41.80; Hg, 38.69. $\text{C}_6\text{H}_{26}\text{B}_{20}\text{Hg}$ calcd.: C, 13.98; H, 5.09; B, 42.00; Hg, 38.93 %.)

Dibarenylmercury

n-Butyllithium (0.05 mole) in 50 ml of ether was added at 0° to a solution of 7.2 g (0.05 mole) of barene in 50 ml of dry ether. Mercuric chloride (6.75 g, 0.025 mole) was added to the stirred solution. The mixture was treated with water and the ether layer separated and dried over magnesium sulfate. The ether was removed. Dibarenylmercury (6.4 g) was obtained in 53% yield and did not melt below 400°. (Found:

C, 9.62; H, 4.38; B, 44.72; Hg, 40.86. $C_4H_{22}B_{20}Hg$ calcd.: C, 9.86; H, 4.55; B, 44.41; Hg, 41.17%.)

Methyl(phenylbarenyl)mercury

To a stirred suspension of methylmercuric bromide (5.9 g, 0.02 mole) in dry benzene was added 50 ml of a benzene solution of phenylbarenyllithium prepared from 4.4 g (0.02 mole) of phenylbarene. The mixture was allowed to reflux for 3 h with stirring and after cooling was filtered. The residue remaining after the removal of benzene was recrystallized from cyclohexane to yield 5.3 g (62%) of methyl(phenylbarenyl)mercury, m.p. 159–160°. (Found: C, 24.82; H, 4.44; B, 24.74. $C_9H_{13}B_{10}Hg$ calcd.: C, 24.85; H, 4.16; B, 24.87%.)

Methyl(vinylbarenyl)mercury

To 50 ml of a stirred benzene solution of vinylbarenyllithium prepared from 5.1 g (0.03 mole) of vinylbarene was added 30 ml of dry ether and then 7.5 g (0.03 mole) of methylmercuric chloride. The mixture was allowed to reflux for 3 h with stirring and after cooling was filtered and the solvent removed. Methyl(vinylbarenyl)mercury (5.8 g) was obtained in 51% yield after recrystallization from *n*-hexane, m.p. 100–100.5°. (Found: C, 15.40; H, 4.16; B, 28.05; Hg, 51.66. $C_3H_{16}B_{10}Hg$ calcd.: C, 15.60; H, 4.19; B, 28.10; Hg, 52.11%.)

Methylbarenylmercury

Methylmercuric chloride (7.5 g, 0.03 mole) was added to 50 ml of a stirred ether solution of barenyllithium prepared from 4.3 g (0.03 mole) of barene. After heating for 3 h the mixture was cooled and filtered and the ether removed. Methylbarenylmercury (5.5 g) was obtained in 51% yield after recrystallization from benzene, m.p. 200–201°. (Found: C, 10.11; H, 3.78; B, 29.50; Hg, 56.05. $C_3H_{14}B_{10}Hg$ calcd.: C, 10.04; H, 3.93; B, 30.14; Hg, 55.89%.)

Trimethyl(phenylbarenyl)silane

Trimethylchlorosilane (3.6 g, 0.034 mole) was added dropwise to 50 ml of a stirred benzene solution of phenylbarenyllithium prepared from 7.5 g (0.034 mole) of phenylbarene. The reaction was accompanied by precipitation of lithium chloride. The mixture was refluxed for 3 h, cooled, filtered, and the solvent removed. Trimethyl(phenylbarenyl)silane (6.0 g) was obtained in 61% yield after recrystallization from *n*-hexane, m.p. 105–106°. (Found: C, 45.32; H, 8.32; B, 36.98; Si, 9.34. $C_{11}H_{24}B_{10}Si$ calcd.: C, 45.15; H, 8.27; B, 36.98; Si, 9.60%.)

Triphenyl(phenylbarenyl)tin

Similarly, treatment of triphenyltin chloride (3.85 g, 0.01 mole) with phenylbarenyllithium (0.01 mole) gave 4.8 g (yield 84%) of triphenyl(phenylbarenyl)tin which melted at 186–187° after recrystallization from cyclohexane. (Found: C, 54.94; H, 5.60. $C_{26}H_{20}B_{10}Sn$ calcd.: C, 54.86; H, 5.39%.)

*Tri-*n*-propylbarenyltin*

Similarly, treatment of tri-*n*-propyltin chloride (5.6 g, 0.02 mole) with an ether solution of barenyllithium (0.02 mole) gave a product which was distilled to give

2.7 g (35 %) of tri-*n*-propylbarenyltin, b.p. 148–150° at 1 mm, n_D^{20} , 1.5470. (Found: C, 34.03; H, 8.05; B, 27.42. $C_{11}H_{32}B_{10}Sn$ calcd.: C, 33.77; H, 8.24; B, 27.65 %.)

Bis(phenylbarenyl)tin dichloride and tris(phenylbarenyl)tin chloride

Dry ether (30 ml) and then 2.6 g (0.01 mole) of stannic chloride were added at 5–10° to a stirred benzene solution of phenylbarenyllithium prepared from 8.8 g (0.04 mole) of phenylbarene. The reaction was accompanied by the formation of a precipitate. The mixture was refluxed for 3 h, cooled and treated with 50 ml of dilute (1:4) hydrochloric acid. The precipitate, which was insoluble in water and an ether-benzene mixture, was separated and dried to give tris(phenylbarenyl)tin chloride (2 g, yield 25 %), m.p. 287–289°. (Found: C, 35.40; H, 5.80; Cl, 4.92. $C_{24}H_{45}B_{30}Cl_3Sn$ calcd.: C, 35.48; H, 5.58; Cl, 4.36 %.)

The ether-benzene layer was separated, dried over magnesium sulfate, and the solvent removed. After recrystallization from 1,2-dichloroethane, bis(phenylbarenyl)tin dichloride (2.3 g) was obtained in 37 % yield, m.p. 216.5–217.5°. (Found: C, 30.91; H, 5.01; B, 34.46; Cl, 11.32. $C_{16}H_{30}B_{20}Cl_2Sn$ calcd.: C, 30.58; H, 4.81; B, 34.44; Cl, 11.28 %.)

*Barenylenebis(tri-*n*-propyltin)*

Tri-*n*-propyltin chloride (6.1 g, 0.021 mole) in 30 ml of dry ether was added to 50 ml of a stirred ether-benzene solution of barenylenedilithium prepared from 1.6 g (0.011 mole) of barene. The mixture was refluxed for 8 h, cooled and treated with water. The ether-benzene solution was separated, dried over magnesium sulfate, and the solvent removed. The residue was distilled at 140–143° (2×10^{-3} mm) to yield 2 g (30 %) of barenylenebis(tri-*n*-propyltin), m.p. 42–43°. (Found: C, 38.23; H, 8.56; B, 16.70. $C_{20}H_{52}B_{10}Sn_2$ calcd.: C, 37.64; H, 8.21; B, 16.95 %.)

Dimeric dibutylbarenylenetin

This was prepared by essentially the same procedure from dibutyltin dichloride (6 g, 0.02 mole) and barenylenedilithium (0.02 mole). Recrystallization from isooctane gave 5 g (66 %) of dimeric dibutylbarenylenetin, m.p. 186–186.5°. (Found: C, 32.47; H, 7.60; B, 28.60; mol. wt., 785. $C_{20}H_{56}B_{20}Sn_2$ calcd.: C, 32.01; H, 7.52; B, 28.84 %; mol. wt., 750.)

Bis(phenylbarenyl)dichlorosilane

Silicon tetrachloride (3.4 g, 0.02 mole) in 20 ml of dry ether was added at 5–10° to 50 ml of a stirred benzene solution of phenylbarenyllithium prepared from 8.8 g (0.04 mole) of phenylbarene. The mixture was refluxed for 8 h, cooled, filtered, and the solvent removed. Bis(phenylbarenyl)dichlorosilane (6.8 g) was obtained in 64 % yield after recrystallization from 1,2-dichloroethane, m.p. 179–179.5°. (Found: C, 35.98; H, 5.84; B, 39.96; Cl, 13.10; Si, 5.20. $C_{16}H_{30}B_{20}Cl_2Si$ calcd.: C, 35.73; H, 5.62; B, 40.24; Cl, 13.19; Si, 5.22 %.)

Bis(phenylbarenyl)germanium dichloride

This was prepared by the same procedure from germanium tetrachloride (2.14 g, 0.01 mole) and phenylbarenyllithium (0.02 mole). Recrystallization from isooctane gave 3.1 g (59 %) of bis(phenylbarenyl)germanium dichloride; m.p. 205.5–206°. (Found: C, 33.38; H, 5.36. $C_{16}H_{30}B_{20}Cl_2Ge$ calcd.: C, 33.00; H, 5.19 %.)

Bis(phenylbarenyl)tin dibromide

Similarly, bis(phenylbarenyl)tin dibromide (4.4 g) was obtained from tin tetrabromide (4.3 g, 0.01 mole) and phenylbarenyllithium (0.02 mole) in 61% yield, m.p. 203–204° (from 1,2-dichloroethane). (Found: C, 26.85; H, 4.20; B, 30.26; Br, 22.36. $C_{16}H_{30}B_{20}Br_2Sn$ calcd.: C, 26.79; H, 4.21; B, 30.17; Br, 22.28%.)

Di-n-hexyl(phenylbarenyl)phosphine

Di-n-hexylchlorophosphine (4.2 g, 0.0175 mole) was added to 50 ml of a stirred benzene solution of phenylbarenyllithium (0.0175 mole). The mixture was refluxed for 3 h, cooled, filtered from the precipitate of lithium chloride, and the solvent removed. Recrystallization from n-hexane gave 3.9 g (52%) di-n-hexyl(phenylbarenyl)phosphine, m.p. 9–10°. (Found: C, 57.77; H, 9.97; B, 24.80; P, 6.60. $C_{20}H_{41}B_{10}P$ calcd.: C, 57.10; H, 9.82; B, 25.72; P, 7.36%.)

Bis(phenylbarenyl)chlorophosphine

Phosphorus trichloride (1.4 g, 0.01 mole) in 30 ml of dry ether was added at 5–10° to 50 ml of a stirred benzene solution of phenylbarenyllithium (0.03 mole). The mixture was refluxed for 8 h, cooled and treated with water. The ether-benzene solution was separated, dried over magnesium sulfate, and the solvent removed. Recrystallization from 1,2-dichloroethane gave 2.64 g (52%) of bis(phenylbarenyl)chlorophosphine, m.p. 226–227°. (Found: C, 38.08; H, 6.02; B, 42.48; Cl, 7.68; P, 6.02. $C_{16}H_{30}B_{20}ClP$ calcd.: C, 38.04; H, 5.98; B, 42.83; Cl, 7.02; P, 6.13%.)

Tris(phenylbarenyl)arsine

This was prepared by the same procedure from arsenic trichloride (1.8 g, 0.01 mole) and phenylbarenyllithium (0.03 mole). Tris(phenylbarenyl)arsine (4.1 g) was obtained in 55% yield, m.p. 175–176°. (Found: C, 39.25; H, 6.50; $C_{24}H_{45}B_{30}As$ calcd.: C, 39.32; H, 6.19%.)

Tris(phenylbarenyl)antimony

Similarly, tris(phenylbarenyl)antimony (5.3 g) was obtained from antimony trichloride (2.8 g, 0.012 mole) and phenylbarenyllithium (0.036 mole) in 57% yield, m.p. 313–316° (decomp.). (Found: C, 37.18; H, 6.02; $C_{24}H_{45}B_{30}Sb$ calcd.: C, 36.95; H, 5.82%.)

SUMMARY

The preparation of organoelement derivatives of barenes by alkylation (barenylation) of various mercury, silicon, germanium, tin, phosphorus, arsenic and antimony halides is described. Attempts to prepare the tetrabarenyltin and tribarenylphosphine compounds failed because of steric hindrance. The increase in size of the arsenic and antimony atoms allowed the tri-substituted compounds to be prepared.

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