REACTION OF SOME HALOGEN DERIVATIVES OF PHOSPHORUS AND SULFUR WITH 1,2-BIS(HYDROXYMETHYL)-o-CARBORANE

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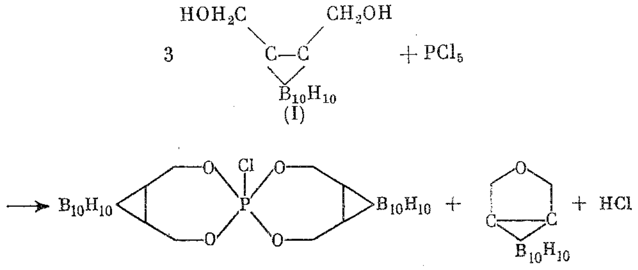
UDC 542.91:547.1'127

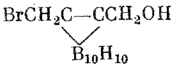
It was shown earlier in [1] that 1-chloromethyl-o-carborane is readily formed by the reaction of $SOCl_2$ with 1-hydroxymethyl-o-carborane. This paper reports a study of reactions of PCl_5, $(PhO)_3PCl_2$, $(PhO)_3PBr_2$, Ph_3PBr_2, and $SOCl_2$ with 1,2-bis(hydroxymethyl)-o-carborane (I) aimed at obtaining 1,2-bis(chloromethyl)- and 1,2-bis(bromomethyl)-o-carborane. It was shown that the reaction of the diol (I) with these reagents, which are widely used to replace the OH group in primary alcohols with a halogen atom, takes place in an unusual manner. Instead of the expected 1,2-bis(chloromethyl)-o-carborane (II), the reaction of (I) with PCl_5 results in a spiro derivative (III) and 3,4-(1',2'-o-carborano)oxolane (IV), according to the scheme



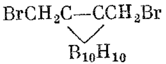
(III) (IV)

A compound analogous to compound (III) was obtained in [2] by reacting pyrocatechol with PCl_5. The spiro derivative (III) is stable in air on extended storage. When $(PhO)_3PCl_2$ and $(PhO)_3PBr_2$ react with (I), the OH group is not replaced by a halogen atom, but only compound (IV) is obtained with a high yield. The reaction takes place readily at 20°C.

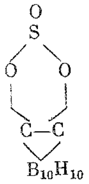
When (I) reacts with Ph_3PBr_2, either 1-bromomethyl-2-hydroxymethyl-o-carborane (V) or 1,2-bis(bromomethyl)-o-carborane (VI) is formed in a mixture with compound (IV), depending on the conditions:


$BrCH_2C{-}CCH_2OH$ ($B_{10}H_{10}$)

(V)


$BrCH_2C{-}CCH_2Br$ ($B_{10}H_{10}$)

(VI)



(VII)

The fact that the bromohydride (V) is obtained and that it is stable during the reaction of (I) with Ph_3PBr_2 indicates that it is not an intermediate product in the formation of (IV). The reaction of $SOCl_2$ with (I) in the presence of pyridine does not produce the dichloride (II), but rather a cyclic compound (VII) which is stable in air on extended storage.

Such an unusual course for the reaction of (I) with these phosphorus and sulfur halides is apparently explained by the ease with which rings form with inclusion of the o-carborane nucleus and by the electron-acceptor effect of the carboranyl group.

In the reaction of PCl_5 with 1-hydroxymethyl-o-carborane, as in its reaction with 1-hydroxymethyl-m-carborane [3], the products are 1-chloromethyl-o-carborane (VIII) and the o-carboranylmethyl ester of phosphoric acid (IX)

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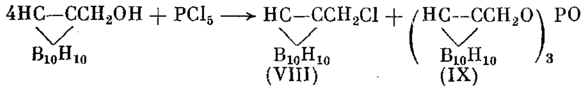

$$4\,\underset{B_{10}H_{10}}{HC{-}CCH_2OH} + PCl_5 \longrightarrow \underset{\underset{(VIII)}{B_{10}H_{10}}}{HC{-}CCH_2Cl} + \Big(\underset{\underset{(IX)}{B_{10}H_{10}}}{HC{-}CCH_2O}\Big)_3 PO$$

EXPERIMENTAL

1,2-Bis(hydroxymethyl)-o-carborane was prepared by a procedure in [4]. The PMR spectrum of the compound was obtained on a Hitachi–Perkin–Elmer R-20 instrument (60MHz).

2(2')-Chloro-5,6,5',6'-di(1",2"-o-carborano)-1,3,1',3',2,2'-spiro-2(2')-phosphorepane (III) and 3,4-(1',2'-o-carborano)oxolane (IV). We added 3.3 g (16 mmoles) of (I) in small portions to 10 g (48 mmoles) of PCl_5 in 30 ml anhydrous benzene with stirring at 20°C. The mixture was boiled 4 h until no more HCl was evolved, the solvent was distilled off, and the residue subjected to chromatography in a column filled with silica gel. The column was eluted with hexane. We obtained 0.72 g (24%) of compound (IV), mp 259-260°C (hexane); see [5]. Composition, percentage found: C 26.05; H 7.49; B 58.28. Percentage calculated as $C_4H_{14}B_{10}O$: C 25.79; H 7.58; B 58.04. PMR spectrum (δ, ppm in CCl_4): 2.03 (CH_2). We then eluted with benzene. We obtained 0.82 g (21.6%) of (III), mp 137-138°C (benzene–hexane). Composition, percentage found: C 20.50; H 5.99; Cl 8.39; P 6.48. Percentage calculated as $C_8H_{28}B_{20}ClO_4P$: C 20.40; H 5.99; Cl 7.53; P 6.58.

3,4-(1',2'-o-Carborano)oxolane (IV). a) We added 2.52 g (35 mmoles) of Cl_2 at 20°C with stirring to a solution of a mixture of 3.0 g (15 mmoles) of (I) and 11.0 g (35 mmoles) of $(PhO)_3P$ in 30 ml anhydrous CH_2Cl_2, stirred for another 5 h, separated the upper layer, distilled off the solvent, and sublimed the residue in vacuum (1 torr) at 80-90°C. We obtained 1.8 g (64%) of (IV).

b. We similarly obtained 2.4 g (86%) of (IV) from 3.0 g (I), 11.0 g (35 mmoles) of $(PhO)_3P$ in 30 ml anhydrous benzene, and 5.7 g (35 mmoles) of Br_2 contained in 10 ml benzene, after 5 h.

1,2-Bis(bromomethyl)-o-carborane (VI) and 3,4-(1',2'-o-Carborano)oxolane (IV). We added at 20°C, 7.3 g (46 mmoles) Br_2 in 10 ml benzene to a stirred solution of 2.0 g (10 mmoles) of (I) and 12.0 g (46 mmoles) of Ph_3P in 20 ml anhydrous benzene. We boiled the mixture 3 h, separated the upper layer, distilled off the solvent, and subjected the residue to chromatography in a column with stilica gel, using hexane as eluent. We obtained 1.2 g (36.4%) of (VI) and 0.5 g (26.9%) of (IV), identified by melting point and GLC and TLC data.

1-Bromomethyl-2-hydroxymethyl-o-carborane (V) and 3,4-(1',2'-o-Carborano)oxolane (IV). We similarly obtained 0.34 g (22%) of (IV) and 0.6 g (27%) of (V), mp 140-141°C (benzene–hexane) from the reaction of 1.7 g (8.3 mmoles) of (I), 6.0 g (23 mmoles) of Ph_3P, and 3.7 g (23 mmoles) of Br_2 in 30 ml anhydrous benzene. Composition, percentage found: C 18.53; H 5.75; B 40.34. Percentage calculated for $C_4H_{15}B_{10}BrO$: C 17.98; H 5.66; B 40.46. The IR spectrum of (V) contained a broad absorption band of the OH group in the 3400 cm^{-1} region.

2-Oxo-1,3-oxa-5,6-(1',2'-o-carborano)-2-thiaepane. We added 0.5 ml pyridine to a solution of 17.2 g (84 mmoles) of (I) in 75 ml anhydrous $CHCl_3$ and then 17.85 g (150 mmoles) of $SOCl_2$ while stirring and cooling with water. There was weak evolution of HCl, which became energetic on heating at 30°C. The mixture was warmed at that temperature for 0.5 h and then boiled 1 h. The solvent was distilled off and the residue recrystallized. We obtained 17.4 g (82.7%) of (VII), mp 52-53°C (from hexane). Composition, percentage found: C 19.97; H 5.62; B 42.92; S 12.73. Percentage calculated as $C_4H_{14}B_{10}O_3S$: C 19.19; H 5.64; B 43.19; S 12.81.

1-Chloromethyl-o-carborane (VIII) and o-Carboranylmethyl Ester of Phosphoric Acid (IX). We added 1.5 g (8.6 mmoles) of 1-hydroxymethyl-o-carborane to a solution of 2.5 g (12 mmoles) of PCl_5 in 20 ml anhydrous benzene while stirring at 20°C. The mixture was boiled 4 h, the solvent distilled off, and the residue subjected to chromatography in a column with silica gel. The column was first eluted with hexane. We obtained 0.66 g (39.9%) of (VIII), identified by GLC. The column was then eluted with benzene. We obtained 0.42 g (25.8%) of (IX), mp 247-248°C (benzene–hexane). Composition, percentage found: B 57.38; P 5.52. Percentage calculated for $C_9H_{39}B_{30}O_4P$: B 57.23; P 5.47.

CONCLUSIONS

1. In the reaction of PCl_5 with 1,2-bis(hydroxymethyl)-o-carborane, the OH group is not replaced by chlorine, but 2(2')-chloro-5,6,5',6'-di(1",2"-o-carborano)-1,3,1',3'-tetraoxa-2,2'-spiro-2(2')-phosphorepane and 3,4-(1',2'-o-carborano)oxolane are formed.

2. The reaction of $(C_6H_5O)_3PX_2$ (X=Cl, Br) with 1,2-bis(hydroxymethyl)-o-carborane produces 3,4-(1',2'-o-carborano)oxolane.

3. The reaction of $SOCl_2$ with 1,2-bis(hydroxymethyl)-o-carborane in the presence of pyridine gives 2-oxo-1,3-oxa -5,6-(1',2'-o-carborano)-2-thiaepane.

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OXIDATIVE INSERTION OF TIN(II) ACETYLACETONATE INTO MERCURY CARBONYL DERIVATIVES

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UDC 542.91 : 547.1'127

The carbenoid type of $Sn(acac)_2$ insertion which, at the first stage, leads to the formation of bimetallic compounds has only been observed in the case of organomercury compounds [1] and carboranyl derivatives of Tl [2]. In the present work this reaction has been extended to symmetric and asymmetric mercury derivatives of carboranes in which the reaction site is a B–Hg bond.

The reaction between the symmetric di(o-carboranyl-9)-mercury(I) and $Sn(acac)_2$ in a mixture of benzene and THF (10:1) leads to the formation of the bimetallic derivative (II):

$$\underset{(I)}{C_2H_2B_{10}H_9HgB_{10}H_9C_2H_2} \xrightarrow{Sn(acac)_2} \underset{(II)}{C_2H_2B_{10}H_9}\text{—}Hg\text{—}Sn(acac)_2B_{10}H_9C_2H_2$$

In the presence of a twofold excess of $Sn(acac)_2$ in a mixture of benzene and THF (1:10), the reaction with di-(m-carboranyl-9)mercury(II), judging from the data obtained from elemental analysis, leads to the double insertion product (IV):

$$\underset{(III)}{C_2H_2B_{10}H_9HgB_{10}H_9C_2H_2} \xrightarrow{2Sn(acac)_2} \left| \begin{array}{l} \rightarrow C_2H_2B_{10}H_9\text{—}Sn(acac)_2\text{—}Hg\text{—}Sn(acac)_2\text{—}B_{10}H_9C_2H_2 \\ \rightarrow C_2H_2B_{10}H_9Hg\text{—}Sn(acac)_2\text{—}Sn(acac)_2\text{—}B_{10}H_9C_2H_2 \end{array} \right. \quad (IV)$$

This reaction is the first example of a double insertion of $Sn(acac)_2$ into a Hg–element bond. The reaction apparently takes place stepwise with an insertion into each B–Hg bond, but the possibility cannot be excluded of an insertion of a second molecule of $Sn(acac)_2$ into the Sn–Hg bond which has been formed, much like as described in [3], with the formation of an asymmetric chain –Sn–Sn–Hg–.

The reaction of B-carboranylmercury halides with $Sn(acac)_2$ in a mixture of benzene and THF (10:1) also leads to the formation of bimetallic carborane derivatives:

$$\underset{(V)}{C_2H_2B_{10}H_9HgCl} \xrightarrow{Sn(acac)_2} \left| \begin{array}{l} \rightarrow C_2H_2B_{10}H_9\text{—}Hg\text{—}Sn(acac)_2Cl \\ \rightarrow C_2H_2B_{10}H_9\text{—}Sn(acac)_2\text{—}HgCl \end{array} \right. \quad (VI)$$

In the case of the carboranylmercury halides, insertion may occur either into the B–Hg bond or into the Hg–halogen bond. It has been established that the C-carboranyl derivatives of mercury are also capable of entering into a similar reaction with $Sn(acac)_2$.

It should be noted that all the bimetallic compounds prepared in THF and other polar solvents undergo demercuration at 20°C over a period of several days, and after several hours, when boiled. In analogy with [4], it might be expected that compounds with a B–Sn bond would be formed as a result of demercuration. However, it has not been possible to isolate these compounds in an analytically pure form up to now. The bimetallic com-

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1606-1607, July, 1982. Original article submitted November 28, 1981.