Notes

Contribution from the Olin Research Center,
Chemicals Group, New Haven, Connecticut 06504

Icosahedral Carboranes. XVII. A Simplified Preparation of *o*-Carborane[1]

By Herbert Beall[2]

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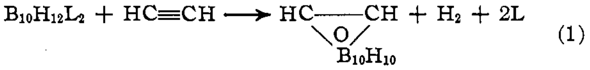
The usual preparation[3] of *o*-carborane (1,2-dicarba-*closo*-dodecaborane) involves the reaction at elevated temperature of acetylene with a solution of a compound of the type $B_{10}H_{12}L_2$ (eq 1). L may be any of a variety



$$B_{10}H_{12}L_2 + HC{\equiv}CH \longrightarrow \begin{array}{c} HC\text{——}CH \\ \diagdown O \diagup \\ B_{10}H_{10} \end{array} + H_2 + 2L \qquad (1)$$

of Lewis bases such as nitriles, sulfides, amines, and phosphines and the $B_{10}H_{12}L_2$ compound is prepared[4] by the reaction of $B_{10}H_{14}$ with the appropriate Lewis base according to

$$B_{10}H_{14} + 2L \longrightarrow B_{10}H_{12}L_2 + H_2 \qquad (2)$$

With the aim of developing a simpler procedure for the preparation of pure *o*-carborane, we have investigated the reaction of acetylene with $B_{10}H_{12}L_2$ compounds in the solid state. The reaction is successful with several $B_{10}H_{12}L_2$ compounds and the pure product is easily collected as it sublimes out of the reaction zone. The yield for this procedure (45–52%) is somewhat lower than that reported for the usual solution method (65–77% starting with 200 g of decaborane[3]). However, this one-step preparation of pure sublimed *o*-carborane from $B_{10}H_{12}L_2$ provides a very convenient route to this compound, particularly when relatively small amounts are needed.

Experimental Section

Reagents.—Chemicals were used as obtained from commercial sources except that the decaborane (Olin Corp.) was sublimed before reaction and the acetylene was purified as it was used by passage first through a tower containing granular alumina, then through a concentrated sulfuric acid scrubber, and finally through a tower containing sodium hydroxide pellets. The acetylene flow rate was determined by means of a tube flowmeter.

Preparation of $B_{10}H_{12}L_2$ Compounds.—The compounds which were prepared had L = acetonitrile, propionitrile, isobutyronitrile, diethyl sulfide, and triphenylphosphine. $B_{10}H_{12}(CH_3CN)_2$ was made according to the method of Schaeffer[4] and $B_{10}H_{12}((C_6H_5)_3P)_2$ according to the method of Hawthorne.[5] The other compounds were prepared by modifications of these procedures. The best results in the subsequent reaction with acetylene were obtained with $B_{10}H_{12}(CH_3CN)_2$ and $B_{10}H_{12}(CH_3CH_2CN)_2$. The detailed method of preparation of the latter compound is given below.

$B_{10}H_{12}(CH_3CH_2CN)_2$.—Ten grams (0.082 mol) of sublimed $B_{10}H_{14}$ was dissolved in 50 ml of propionitrile (Eastman White Label) in a round-bottom flask. To this a water condenser was fitted in reflux position and the mixture was refluxed for 50 min. The reaction mixture was cooled and the $B_{10}H_{12}(CH_3CH_2CN)_2$ was filtered off and dried overnight in a vacuum desiccator; mp 171° dec. *Anal.* Calcd: B, 46.9; H, 9.6; C, 31.3; N, 12.2. Found: B, 46.2; H, 10.0; C, 29.4; N, 12.1. The yield was 14.9 g (79%). It was noted that longer reflux times (or attempted recrystallization from CH_3CH_2CN) resulted in a darkening of the solution and a lower yield of the desired product.

***o*-Carborane.**—In all of the preparations the $B_{10}H_{12}L_2$ compound was mixed with 5 times its weight of dry sand to ensure even contact with the acetylene and placed in a reactor of one of two designs (Figure 1). In reactor A the dry mixture was placed in a U tube of 25-mm o.d. tubing and in reactor B the mixture was placed on a fritted-glass disk (coarse). Reactor A was found to be more convenient for the larger quantities of reactant. In each case the part of the reactor containing the dry reactant mixture was immersed in a heated oil bath, the purified acetylene was passed through the system, and the *o*-carborane which sublimed out of the reaction zone condensed on the walls of the vertical tube above. It was found to be desirable to place a loose glass wool plug in the top of the vertical condensing tube to minimize the amount of solid *o*-carborane which was blown out of the system. The 2 equiv of L which was liberated in reaction (eq 1) simply passed out of the system without condensing with the desired *o*-carborane product (except if L = $(C_6H_5)_3P$). Table I gives the conditions and results of some of the more informative experiments which were performed.

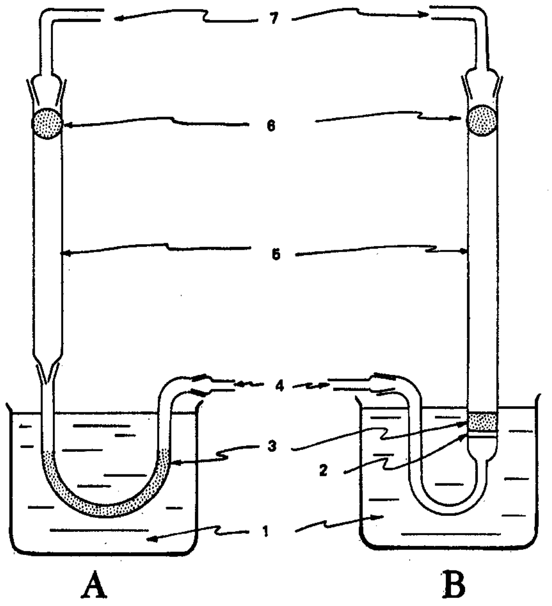


Figure 1.—Two reactors used in the nonsolution preparation of *o*-carborane: (1) oil bath, (2) fritted-glass disk, (3) reactant, (4) acetylene inlet, (5) condensing tube, ~30-mm o.d. × 800-mm length, (6) loose glass wool plug, (7) acetylene outlet.

Examination of Table I shows that best results were obtained using CH_3CH_2CN as L. The optimum temperature range for the oil bath was found to be 92–96° and an acetylene flow of 50 cm^3/min or less was satisfactory. During the course of the longer reactions, it was found to be advantageous and convenient to interrupt the reaction every 12–24 hr and remove the product which had condensed on the walls of the vertical tube. In all reactions the *o*-carborane product was identified by its infrared spectrum and the purity was ascertained by vapor-phase chromatography.

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[1] Preceding communication: K. O. Knollmueller, R. N. Scott, H. Kwasnik, and J. F. Sieckhaus, *J. Polym. Sci., Part A-1*, **9**, 1071 (1971).

[2] Address correspondence to Department of Chemistry, Worcester Polytechnic Institute, Worcester, Mass. 01609.

[3] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

[4] R. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 1006 (1957).

[5] M. F. Hawthorne and O. R. Pitochelli, *ibid.*, **80**, 6685 (1958).

TABLE I

L	Wt of $B_{10}H_{12}L_2$, g	Reactor	Temp, °C	Time, hr	HCCH flow, cm³/min	Yield, %[a]
Et_2S	1.0	B	100	6	250	Trace
Et_2S	3.0	B	70	3	250	Trace
$(C_6H_5)_3P$	2.0	B	150	17	50	0.0
$(C_6H_5)_3P$	3.0	B	195	3	50	Trace[b]
CH_3CN	5.0	B	100	5	100	20.4
CH_3CN	3.0	B	96	144	96	33.1
CH_3CH_2CN	3.0	B	96	46	50	41.5
CH_3CH_2CN	3.0	B	96	58	50	45.2
CH_3CH_2CN	3.0	B	96	82	50	45.7
CH_3CH_2CN	10.0	A	92	7	25	20.7
CH_3CH_2CN	10.0	A	92	72	25	44.0
CH_3CH_2CN	10.0	A	93	120	50	52.7
$CH_3CH(CH_3)CN$	3.0	B	92	21	50	2.4

[a] Yield based on $B_{10}H_{12}L_2$. [b] Product contaminated with $(C_6H_5)_3P$.

Results and Discussion

A displacement series for Lewis bases, L, in $B_{10}H_{12}L_2$ has been established by Hawthorne[5] and expanded by Zakharkin.[6] The solution preparation of *o*-carborane is most successful when L in eq 1 is one of the bases which is most easily displaced. The low yield for the nonsolution preparation of *o*-carborane when L = $(C_6H_5)_3P$ is in agreement with this generalization. When $B_{10}H_{12}(Et_2S)_2$ was allowed to react in the nonsolution system, softening of the reactant was observed even below its normal melting point and the low yield of product may be due to inefficient contact between this melt and the acetylene. The difference in yield of *o*-carborane for the various nitriles tested is not easily explained.

Higher yields might be realized by changes in the apparatus design. In particular, the use of a fluidized bed of $B_{10}H_{12}L_2$ has been suggested.[7] However, the apparatus described above is easy to assemble and provides a satisfactory yield.

Acknowledgment.—The author is grateful to Drs. H. A. Schroeder and T. L. Heying for useful discussions and to the Office of Naval Research for support of this work.

(6) L. I. Zakharkin, V. I. Stanko, and A. I. Klimova, *Izv. Akad. Nauk SSSR, Ser. Khim*, 917 (1964).

(7) T. L. Heying, personal communication.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF VERMONT, BURLINGTON, VERMONT 05401,
AND MASSACHUSETTS STATE COLLEGE AT NORTH ADAMS,
NORTH ADAMS, MASSACHUSETTS 01247

Gold(III)-Gold(II) and Silver(II)-Silver(III) Equilibria with the *N*,*N*-Di-*n*-butyldithiocarbamate Ligand

BY TIMOTHY J. BERGENDAHL* AND ESTERINA M. BERGENDAHL

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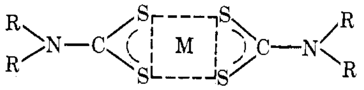
In 1959 Vänngard and Åkerström[1] reported that they had observed electron spin resonance spectra when gold(I) and silver(I) complexes containing the *N*,*N*-diethyldithiocarbamate ligand were allowed to react with tetraethylthiuram disulfide in benzene solution. The electron spin resonance spectra were presumably due to divalent complexes having structure I (R = C_2H_5, M = Au, Ag). These workers also reported the observation of an electron spin resonance spectrum when tris(*N*,*N*-diethyldithiocarbamato)gold(III) was dissolved in benzene. The origin of the signal was attributed to equilibrium reaction 1 (R = C_2H_5, M = Au).



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$$[R_2NCS_2]_3M \rightleftharpoons [R_2NCS_2]_2M + 0.5[R_2NCS_2]_2 \qquad (1)$$

It was of interest to investigate the possibility of generating an equilibrium reaction similar to (1) with silver as the metal. If such an equilibrium could be identified, it would be in support of a complex of silver(III) containing a sulfur-donor ligand. The *N*,*N*-di-*n*-butyldithiocarbamate ligand was chosen for the study.

Experimental Section

General Information.—Tetrahydrofuran was distilled from lithium aluminum hydride and collected under nitrogen. Electron spin resonance spectra were obtained on a Varian V-4502-13 instrument. The standard for esr measurements was 1,1-diphenylpicrylhydrazyl.

Preparation of Reactants.—Tetra-*n*-butylammonium tetrabromoaurate(III)[2] and silver(I) *N*,*N*-di-*n*-butyldithiocarbamate[3] were prepared according to the published methods.

Stock solutions containing the *N*,*N*-di-*n*-butyldithiocarbamate ligand and tetra-*n*-butylthiuram disulfide were prepared by methods similar to those reported in the literature.[3] Lithium methoxide was used as the base and tetrahydrofuran was the solvent.

Gold Reactions.—For all reactions involving gold 20 ml of a ligand stock solution containing 0.0039 mol of lithium *N*,*N*-di-*n*-butyldithiocarbamate and where appropriate tetra-*n*-butylthiuram disulfide was allowed to react with a solution consisting of 0.0013 mol of tetra-*n*-butylammonium tetrabromoaurate(III) in 30 ml of tetrahydrofuran.

Electron spin resonance spectra were obtained under identical conditions for all gold experiments.

Silver Reactions.—For all reactions involving silver 0.0004 mol of silver(I) *N*,*N*-di-*n*-butyldithiocarbamate in 5 ml of tetrahydrofuran was allowed to react with 10 ml of a stock solution containing the appropriate amount of tetra-*n*-butylthiuram disulfide.

Electron spin resonance spectra were obtained under identical conditions for all silver experiments.

Apparatus.—All vacuum-line experiments were conducted in an apparatus consisting of two reactant vessels, one of which contained an esr tube.

The gold- or silver-containing reactant was placed in one reactant vessel and the ligand stock solution or the disulfide stock solution was placed in the other along with a small stirring bar. Both solutions were degassed three times before they were mixed. The pressure in the apparatus was maintained at 1 μ.

After the reactants were mixed, the reaction solution was stirred for 5 min. The esr tube was filled and sealed with a propane torch. All esr spectra were recorded 21 min after the reactants were allowed to mix.

Results and Discussion

When tetra-*n*-butylammonium tetrabromoaurate(III) was allowed to react with 3 molar equiv of lithium *N*,*N*-di-*n*-butyldithiocarbamate, in tetrahydrofuran,

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* To whom correspondence should be addressed at Massachusetts State College at North Adams.

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