$BH_2(NH_3)_2BH_4$ was prepared[6] in a 25 × 300 mm. circular tube. To the tube was added 3 mmoles of $NaC{\equiv}CH$[7] under an atmosphere of dry nitrogen. The system then was evacuated and 15 ml. of liquid ammonia was distilled into the tube. The solution then was stirred, by means of a solenoid actuated spiral, for approximately 1 hr. at −78°. The appearance of ammonia-insoluble BH_2NH_2 was immediate. There seemed to be no slow induction period preceding the formation of this material. Ammonia then was distilled from the mixture onto sodium metal. The presence of $HC{\equiv}CH$ in the ammonia was demonstrated through the formation of $NaC{\equiv}CH$, which was identified through its X-ray powder diffraction pattern. The presence of $B_3H_6N_3H_6$, $NaBH_4$, and ammonia-insoluble BH_2NH_2 remaining in the reaction tube also was demonstrated through X-ray powder analysis. Cyclotriborazane was isolated from this reaction mixture through a sublimation procedure *in vacuo* at 120°. The yield of $B_3H_6N_3H_6$ was 15% of theory.

Anal. Calcd. for $B_3H_6N_3H_6$: B, 37.6; N, 48.6; H (hydridic), 7.00. Found: B, 37.9; N, 49.8; H (hydridic), 7.01.

Preparation of $B_3H_6N_3H_6$ from $B_3H_3N_3H_3$.—In order to obtain sufficiently large samples for the molecular weight studies, $B_3H_6N_3H_6$ was prepared through modification of the procedure of Dahl and Schaeffer.[2] $B_3H_3Cl_3N_3H_6$ was formed by bubbling excess HCl into a solution containing 10 moles of borazine[8] in diethyl ether at −78°. The ether was distilled away, leaving behind the solid hydrochloride adduct to which 35 mmoles of $LiBH_4$ was added. About 50 ml. of anhydrous ether, containing 5 ml. of glyme, was distilled into the flask. The system then was stirred at room temperature until B_2H_6 evolution ceased. Volatile materials then were distilled away, leaving behind the dry ether-free residue, which was placed on a frit and washed with ice-cold water. Cyclotriborazane is insoluble in water, and is unaffected by ice-cold water, *provided ether is absent*. A 90% yield of crude cyclotriborazane was obtained. It was purified for the molecular weight studies through extraction with liquid ammonia at −75°.

Molecular Weight Studies.—Molecular weights were determined cryoscopically. The apparatus used has been described briefly elsewhere.[9] Each molecular weight reported in Table II represents an average of eight separate cooling curves; four cooling curves were taken from the freshly prepared solutions and four curves were taken from the solutions which were aged at −45°.

Acknowledgment.—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation.

[6] R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

[7] K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, **2**, 75 (1946).

[8] G. Dahl and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **12**, 380 (1960).

[9] B. Z. Egan and S. G. Shore, *J. Am. Chem. Soc.*, **83**, 4717 (1961).

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A New Type of Boron–Nitrogen Heterocycle

BY ROY M. ADAMS AND FRANK D. POHOLSKY

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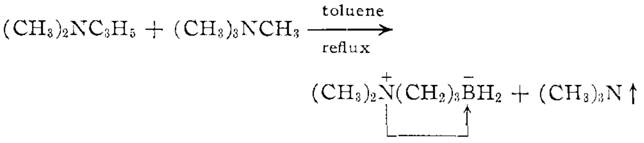
A recent review[1] on heterocyclic boron compounds includes no mention of a five-membered ring with one boron and one nitrogen. Initial attempts to prepare this type of heterocycle by the hydroboration[2] of allylamine resulted in polymer formation. Such a compound has now been prepared from N,N-dimethylallylamine.

The synthesis was successfully carried out by refluxing dimethylallylamine with trimethylamineborane in toluene.[3]



$$(CH_3)_2NC_3H_5 + (CH_3)_3NCH_3 \xrightarrow[\text{reflux}]{\text{toluene}} (CH_3)_2\overset{+}{N}(CH_2)_3\overset{-}{B}H_2 + (CH_3)_3N\uparrow$$

The toluene was removed at atmospheric pressure and the residue was distilled under vacuum. The fraction collected between 80 and 100° at 25 mm. was redistilled to give approximately 25% yields of 1,1-dimethyl-1,2-azaborolidine or cyclo-(N-B)-dimethylaminopropylborane; b.p. 85° (25 mm.).

Anal. Calcd. for $(CH_3)_2N(CH_2)_3BH_2$: C, 60.6; H, 14.2; N, 14.2; B, 11.0. Found: C, 60.6, H, 14.3; N, 14.6; B, 11.1.

The product is a colorless liquid with a boiling point of 185° at 745 mm. and a calculated heat of vaporization of 112 cal./g., indicating very strong intermolecular forces. Molecular weight determinations in benzene, cyclohexanol, and camphene indicated extensive association. This has been found to be characteristic of amineboranes and is attributed to the high dipole moments of such substances due to the formal charges on the nitrogen and boron.[4] However, the mass spectrum shows a cut-off at mass number 99 and the largest peak at mass number 98 which is in good agreement with the formula weight of 98.98. The infrared spectrum indicates a N–B bond and absence of C–C double bonds. The density at 25° is 0.8161 g./ml. and the index of refraction at 25° is 1.4538, leading to a molar refractivity of 32.84. This leads to a calculated value for the atomic refractivity of quaternary boron of 2.5, a value which has not been available previously. The freezing point is approximately −25°. The product is immiscible with water and miscible with ether and with toluene.

Attempts to carry out the hydroboration by the direct reaction of diborane with the amine in ethyl ether resulted in the initial formation of a colorless solid, which we were unable to isolate and purify and which we assume is the amineborane. When the ether was evaporated and the product warmed to approximately 120°, an uncontrolled reaction occurred which we believe involved internal hydroboration. Bennett and Skinner[5] have shown that the hydroboration reaction is very exothermic, evolving 136 kcal./mole of

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[1] P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962).

[2] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1961.

[3] E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4991 (1959).

[4] H. Noth and H. Beyer, *Chem. Ber.*, **93**, 928 (1960). A referee has pointed out that the cyclic aminoborane trimers behave normally by cryoscopy (*cf.* T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 3481 (1955); G. W. Campbell and L. Johnson, *ibid.*, **81**, 3800 (1959). These also have nitrogen and boron carrying formal charges, but due to symmetry have no net dipole moment such as would be expected for our compound.

[5] J. E. Bennett and H. A. Skinner, *J. Chem. Soc.*, 2472 (1961).

olefin compared to a heat of vaporization of 11.1 kcal./mole for the product.

$$42B_2H_6 + (CH_3)_2NC_3H_5 \xrightarrow[\text{ethyl ether}]{25°} \underset{\text{white solid}}{(CH_3)_2C_3H_5N:BH_3} \xrightarrow[\text{no solvent}]{120°} \text{uncontrolled reaction}$$

An attempt to carry out the same reaction by the addition of boron trifluoride ethyl etherate to a solution of sodium borohydride and the amine in tetraethylene glycol dimethyl ether resulted in the formation of a dark polymer and no material more volatile than the solvent.

Acknowledgment.—We wish to thank the National Science Foundation Undergraduate Research Program for partial support of this work and Callery Chemical Company for the chemical and spectral analyses and for samples of sodium borohydride and trimethylamine-borane.

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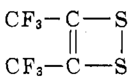
Organosulfur Derivatives of the Metal Carbonyls. III. The Reaction between Molybdenum Hexacarbonyl and Bis-(trifluoromethyl)-dithietene[1]

BY R. B. KING[2]

Received October 25, 1962

Recently the novel heterocyclic sulfur compound bis-(trifluoromethyl)-dithietene (I) was reported as being formed in good yield in the reaction between hexafluorobutyne-2 and sulfur under appropriate conditions.[3] In an attempt to prepare unusual organometallic compounds the reactions between bis-(trifluoromethyl)-dithietene and a variety of metal carbonyl derivatives were investigated. This note describes a novel compound obtained in the reaction between bis-(trifluoromethyl)-dithietene and molybdenum hexacarbonyl.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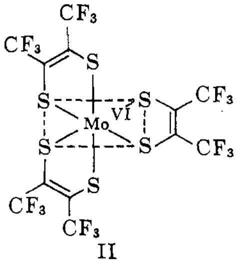
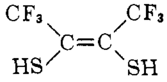


II


III

Experimental

Molybdenum hexacarbonyl was purchased from Climax Molybdenum Company. Bis-(trifluoromethyl)-dithietene was prepared by the method of Krespan and McKusick.[3] The infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Infracord machine.

The Reaction between Molybdenum Hexacarbonyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 2.4 g. (9.1 mmoles) of molybdenum hexacarbonyl, 2 ml. (~3.2 g., ~14 mmoles) of bis-(trifluoromethyl)-dithietene, and 50 ml. of methylcyclohexane was refluxed 18 hr. under nitrogen with magnetic stirring, the reaction mixture turning black. After cooling to room temperature and then in a −78° bath, the black crystals were filtered and product was isolated from them by sublimation at 185–190° (0.2 mm.) for 24 hr. to give 1.96 g. (55% yield) of glistening purple crystals of $Mo(C_4F_6S_2)_3$, m.p. > 245°.

Anal. Calcd. for $C_{12}F_{18}S_6Mo$: C, 18.6; H, 0.0; F, 44.2; S, 24.8; Mo, 12.4; mol. wt., 774. Found: C, 18.8; H, 0.0; F, 43.5; S, 24.9; Mo, 12.9; mol. wt., 685 (isopiestic in tetrahydrofuran).

Infrared Spectrum.—C=C band at 1451 (w) cm.$^{-1}$; C–F bands at 1258 (s), 1214 (vs), 1176 (s), and 1148 (s) cm.$^{-1}$; other bands at 859 (w), 730 (m), 699 (m), and 692 (vw, sh) cm.$^{-1}$.

F^{19} N.m.r. Spectrum.—Single sharp peak at −316 cycles relative to internal $(CFCl_2)_2$.

Properties of $Mo(C_4F_6S_2)_3$.—This new molybdenum complex is a glistening purple solid sparingly soluble in organic solvents, giving intense blue-violet solutions. It was necessary to use the excellent solvent tetrahydrofuran in order to obtain solutions of sufficient concentration for n.m.r. and molecular weight studies. Both the solutions and the solid compounds seem to be extremely stable to air oxidation. The compound is also very stable to thermal decomposition as indicated by its isolation in 55% yield after a sublimation at 185–190° (0.1 mm.).

Discussion

The infrared spectrum and the analytical data of $Mo(C_4F_6S_2)_3$ indicate complete absence of carbonyl groups in the product. The F^{19} n.m.r. spectrum of a solution of the complex in tetrahydrofuran shows only a single sharp CF_3 peak, indicating the compound to be diamagnetic and all $C_4F_6S_2$ residues to be equivalent. On this basis, structure II is proposed for the complex, which may be regarded as a hexavalent molybdenum derivative of the as yet unknown dithiol III. It bears a formal analogy to molybdenum hexafluoride. Instead of six fluorine atoms, three chelating bidentate residues derived from bis-(trifluoromethyl)-dithietene surround the hexavalent molybdenum atom.

The formation of the hexavalent molybdenum derivative $Mo(C_4F_6S_2)_3$ from the zerovalent molybdenum derivative $Mo(CO)_6$ may be regarded as an oxidation–reduction reaction with the zerovalent molybdenum atom being oxidized to the hexavalent oxidation state by three equivalents of bis-(trifluoromethyl)-dithietene which are in turn reduced to the dianion formed by the loss of two protons from the dithiol III. The isolation of $Mo(C_4F_6S_2)_3$ from this reaction is believed to be the first example of the preparation of an organosulfur derivative of molybdenum by the reaction between molybdenum hexacarbonyl and an organosulfur derivative. On the other hand, numerous organosulfur derivatives of iron have been prepared by the reactions be-

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[1] Part II: R. B. King, *Inorg. Chem.*, **2**, 326 (1963).

[2] Mellon Institute, Pittsburgh 13, Pennsylvania.

[3] C. G. Krespan and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 3434 (1961).