Notes

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Preparation and Properties of N-Haloalkylated Borazines[1]

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Although there has been considerable work reported on the preparation of N-alkylated borazines, there appears to have been no attempt to prepare materials containing N-haloalkylated groups. The present work was carried out in order to find out whether the presence of strongly electronegative groups would improve the thermal and hydrolytic stability of this class of materials. Since perfluoroalkyl and perchloroalkyl nitriles were available the reaction of these compounds with diborane seemed to be the best route to the borazines.

Results and Discussion

It was found that when perhalo nitriles were mixed with diborane at room temperature in the vapor phase the reaction was very slow. When the mixtures were heated to 90–100° the reaction proceeded much more rapidly, yielding the borazines and polymeric products. In the case of trichloroacetonitrile a number of violent explosions resulted from heating of the mixture in a sealed bulb.

In order to eliminate the danger of explosions it was found possible to carry out these reactions in ether solvents such as tetrahydrofuran and dimethoxyethane. The reaction of trichloroacetonitrile and diborane in dimethoxyethane yielded a crystalline sublimable solid with the empirical formula

$$2CCl_3CN + B_2H_6 \longrightarrow 2CCl_3C(H):NBH_2$$

The presence of two hydrolyzable hydrogen atoms was shown by gas evolution. In none of the reactions with perfluoroalkyl nitriles was an intermediate isolated. The attempted conversion of the trichloroacetimine-borane to the borazine by heating of the dry material resulted in several violent explosions which could have been caused by a dehydrohalogenation reaction that was autocatalytic. This was avoided by suspending the intermediate in an inert solvent and heating to the conversion temperature. The product separated on cooling.

The fluorinated borazines are either solids or high boiling liquids that do not readily hydrolyze in water, apparently due to their insolubility. This is indicated by their slow hydrolysis by atmospheric moisture and the rapid reaction with methanol to evolve hydrogen. The materials are soluble in benzene, chloroform, and carbon tetrachloride. The chlorinated compound N,N′,N″-tris(β,β,β-trichloroethyl)borazine was found to be insoluble in and unreactive with water and only slightly soluble in benzene and methanol. A detailed study of its reactivity was not made but it did not react with antimony trifluoride at 100°. Treatment with phenylmagnesium bromide in diethyl ether followed by hydrolysis yielded triphenylboroxine, indicating destruction of the ring.

As was noted by Eméleus and Wade[3] in the reaction of acetonitrile and diborane, a nonvolatile fraction was found in the reaction of the perfluoroalkyl nitriles and diborane. In the case of trifluoroacetonitrile, this fraction was a low melting solid. It was found to be soluble in benzene and chloroform and the infrared spectrum showed the presence of N–H, C–H, B–H, C–N, and CH_2 groups. One sample heated for 3 hr. at 200° under a nitrogen atmosphere increased in molecular weight from 832 to 1350. A comparison of the nuclear magnetic resonance spectrum of this material with that of the corresponding borazine showed that the materials had different structures. The borazine showed only the quadruplet splitting of the CH_2 group by the adjacent fluorine atoms but no quadruplet from the splitting of the hydride levels by B^{11}. The polymer showed different types of hydrogen although resolution was not good enough to distinguish their nature.

Borazines of this type were also prepared by the reaction of the α,α-dihydroperfluoroalkylamine and diborane which proceeded through the amine–borane adduct and split out hydrogen on heating to give the final product. In this case no polymeric materials were found.

Experimental

Reaction of Trifluoroacetonitrile and Diborane. (a) In Diethyl Ether.—A mixture of 3.90 mmoles of trifluoroacetonitrile and 1.76 mmoles of diborane was dissolved in 5 ml. of diethyl ether in a 50-ml. round-bottom flask, containing a magnetic stirrer bar, attached to a vacuum system. No reaction took place over a 1-hr. period at room temperature. However, when 1 ml. of dimethoxyethane was distilled into the reaction mixture a slow reaction took place at room temperature indicating that dissociation of the diborane is a necessary step in the reaction mechanism.

(b) **In Dimethoxyethane.**—In a 500-ml. three-necked flask equipped with a stirrer, two gas inlet tubes, and a Dry Ice cooled reflux condenser was placed 100 ml. of anhydrous dimethoxyethane. The flask was flushed with dry nitrogen and the trifluoroacetonitrile and diborane fed into the solution in a 2:1 ratio as measured by rotameters. The reaction mixture grew warm as the gases were added and in a 3-hr. period 33 g. of

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[2] Arthur D. Little, Inc., Cambridge, Mass.

[3] H. J. Eméleus and K. Wade, *J. Chem. Soc.*, 2614 (1960).

trifluoroacetonitrile was added. At the conclusion of the reaction, the system was purged with nitrogen and the solvent removed by distillation. The remaining liquid was transferred to a micro distillation apparatus and the final traces of solvent were removed at atmospheric pressure. The remaining liquid was then distilled under reduced pressure to yield the fractions shown in Table I.

TABLE I

Fraction	B.p., °C. (mm.)	Amount, g.
I	90	2.8
II	55–106 (92)	1.5
III	106–111 (92)	6.5
IV	100 (32)	2.0

Fractions I and II were solvent while III was the borazine which crystallized on cooling. Fraction IV was contaminated borazine and there remained an oily residue that slowly became viscous on cooling.

Anal. Calcd. for $(CF_3CH_2NBH)_3$: C, 22.10; H, 2.76; N, 12.90; F, 52.5; B, 9.98; mol. wt., 327. Found: C, 21.36; H, 2.20; N, 12.08; F, 53.67; B, 9.77; mol. wt. (boiling point elevation in benzene), 332. The material is slowly hydrolyzed by moisture although not soluble in water.

Anal. Found for residue: C, 19.11; H, 3.18; N, 9.72; B, 9.89. The material slowly changed to a white powder on standing, indicating the formation of boric oxide. Not enough was available to determine decomposition products.

An attempt was made to determine the number of hydridic hydrogen atoms per unit structure of the residue by methanolysis in a sealed tube. A sample weighing 0.1272 g. was heated with excess methanol for 3 hr. on a steam bath and 0.45 mmole of hydrogen was evolved. If the basic structure is $(CF_3CHBNH)_n$, 1.17 mmoles of hydrogen would have been evolved, indicating either incomplete reaction or less hydridic hydrogen in the structure. A second sample weighing 0.1690 g. was pyrolyzed at 300° for 16 hr. and only 0.40 mmole of hydrogen was evolved. This also indicated less B–H bonding than theoretically expected.

Reaction of Trichloroacetonitrile and Diborane. (a) Vapor Phase.—The reactions were carried out in 500-ml. sealed bulbs equipped with breakers. In a typical reaction 1.1037 g. (7.65 mmoles) of trichloroacetonitrile and 3.22 mmoles of diborane were mixed at room temperature with no noticeable reaction and then heated to 85° for 15 hr. After cooling, crystals were deposited over the surface of the bulb. The bulb was opened to the vacuum system and 0.38 mmole of noncondensable gas was measured plus 0.10 mmole of unreacted diborane, giving a reaction ratio of trichloroacetonitrile to diborane of 2.38. Other runs gave ratios of 2.38 to 2.75 and in some cases a liquid was also present that reacted rapidly with methanol. Sublimation of the solid product at 130° under vacuum yielded a crystalline white powder, m.p. 202–203°.

Anal. Calcd. for $(CCl_3CH_2NBH)_3$: C, 15.15; H, 1.89; N, 8.85; Cl, 67.30; B, 6.85; mol. wt., 478. Found: C, 15.21; H, 2.01; N, 8.61; Cl, 67.16; B, 7.00; mol. wt., 477.

(b) In Dimethoxyethane.—In a 500 ml. three-necked flask fitted with gas inlet tube, stirrer, and condenser was placed 57 g. (0.392 mole) of trichloroacetonitrile and 200 ml. of dimethoxyethane. The flask was purged with dry nitrogen and diborane was added at a rate of 30 ml./min. until a calculated excess was present. The system was again purged with nitrogen and the solvent was removed under water aspirator vacuum. The remaining slurry was washed with 30–60° petroleum ether to remove the last traces of ether and to leave a fine powder (38 g.). This material, m.p. 116°, could be sublimed at 110–120° under vacuum and was the intermediate, $CCl_3CH{:}NBH_2$.

Anal. Calcd. for $CCl_3CH{:}NBH_2$: C, 15.15; H, 1.89; N, 8.85; Cl, 67.30; B, 6.85. Found: C, 15.00; H, 1.87; N, 8.61; Cl, 67.03; B, 6.55.

In order to determine the number of hydridic hydrogens per molecule a freshly prepared sample of intermediate was treated with methanol and the hydrogen measured. A sample of 0.1735 g. (1.20 mmoles) of trichloroacetonitrile in 5 ml. of dimethoxyethane was allowed to react with 1.625 mmoles of diborane in a 50-ml. flask attached to the vacuum system. After the reaction was complete all of the volatile materials were removed by pumping and excess methanol condensed onto the product. This yielded 2.275 mmoles of hydrogen as measured in the Toepler pump giving a H_2/CCl_3CN ratio of 1.895, establishing the presence of two hydridic atoms per molecule.

The intermediate was conveniently converted into the borazine by heating in an inert solvent. A sample of 20.9 g. of intermediate was suspended in mineral spirits at 140° for 2 hr., the mixture was cooled, and the product was filtered off to yield 11.4 g. (54.5%). Several explosions resulted from heating the dry intermediate.

Reaction of N,N′,N′′-Tris(β,β,β-trichloroethyl)borazine with Antimony Trifluoride.—A mixture of 4 g. of the borazine and 12 g. of antimony trifluoride was suspended in 30 ml. of toluene and heated to 110° for 3 hr. The mixture was cooled to room temperature and the antimony salt filtered off. Evaporation of the toluene left the unreacted starting borazine.

Reaction of N,N′,N′′-Tris(β,β,β-trichloroethyl)borazine with Phenylmagnesium Bromide.—A solution of phenylmagnesium bromide was prepared in a 500-ml. three-necked flask equipped with a stirrer, condenser, and addition funnel by treating 3.3 g. of magnesium with 14 ml. of bromobenzene in 150 ml. of anhydrous diethyl ether in a nitrogen atmosphere. To this was added 4 g. of the solid borazine in small amounts and the mixture was allowed to stir overnight. The resultant product was hydrolyzed, hydrochloric acid was added to dissolve the magnesium hydroxide, and the ether solution was separated. It was washed with water, the ether was evaporated, and the residue was crystallized from carbon tetrachloride. The product was a light tan solid, m.p. 228–230°, and was identified as triphenylboroxine.

Anal. Calcd. for $(C_6H_5BO)_3$: C, 69.4; H, 4.82; B, 10.35; mol. wt., 311.4. Found: C, 68.63; H, 4.75; B, 10.61; N, 0.35; Cl, 0.45; mol. wt., 319.5.

Reaction of β,β,β-Trifluoroethylamine and Diborane.—Trifluoroethylamine was prepared from trifluoroacetic acid by known methods.[4] The amine–borane adduct was formed from 10 g. of the amine and 1.5 l. (STP) of diborane in diethyl ether. The ether was evaporated and the adduct held at 140° overnight in a long tube in a nitrogen atmosphere. The residue was sublimed *in vacuo* to yield the borazine, m.p. 40–41°.

Anal. Calcd. for $(CF_3CH_2NBH)_3$: N, 12.90; B, 9.98. Found: N, 12.70; B, 9.30.

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(4) E. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1256 (1959).

CONTRIBUTION FROM THE NATIONAL LEAD COMPANY
TITANIUM ALLOY MANUFACTURING DIVISION,
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Crystalline Hydrous Zirconia

BY A. CLEARFIELD

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X-Ray diffraction studies[1,2] have shown that the zirconyl ion in the zirconyl halides is a tetramer, $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}$, and that this species also exists in aqueous solution. Addition of base to zirconyl halide solutions results in further polymerization and eventual precipitation of a gelatinous, amorphous,

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(1) A. Clearfield and P. A. Vaughan, *Acta Cryst.*, **9**, 555 (1956).

(2) G. M. Muha and P. A. Vaughan, *J. Chem. Phys.*, **33**, 194 (1960).