and analyzed. It was found to consist of equal volumes of carbon dioxide (200 cc., 0.0083 mole) and carbon monoxide (200 cc., 0.0083 mole) by means of their absorption in potassium hydroxide and ammoniacal cuprous chloride solutions, respectively.

The solution from the decomposition reaction was filtered to remove a small amount of tarry polymer which could not be identified. Aliquot samples of the filtrate were treated at water-bath temperature with 2,4-dinitrophenylhydrazine reagent whereby an abundant red precipitate was formed only after prolonged heating. This was extracted with hot chloroform as before and the residue recrystallized from nitrobenzene and pyridine; m.p. 292–293°dec.; mixed m.p. with an authentic sample of bis-2,4-dinitrophenylhydrazone of methyl glyoxal gave no depression.

The remaining solution was extracted with ether in a continuous extraction apparatus. The ether extracts were dried over magnesium sulfate, fractionated and the fractions boiling at 40–57° and 58–65° collected and refractionated. From the low boiling fraction acetone was isolated, b.p. 56–57°; 2,4-dinitrophenylhydrazone, m.p. 125°; mixed m.p. with an authentic sample showed no depression.

Anal. Calcd. for $C_9H_{10}N_4O_4$: C, 45.37; H, 4.20; N, 23.53. Found: C, 45.20; H, 4.26; N, 23.50.

The high boiling fraction gave a strong aldehyde test with fuchsine reagent. It was fractionated twice to obtain a fraction of b.p. 63°. A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-water mixture; m.p. 187°. An authentic sample of this derivative was prepared from isobutyraldehyde and a mixed m.p. taken; there was no depression.

The decomposition was repeated several times using higher temperatures (100°) with essentially the same results. In one experiment the final aqueous sulfuric acid solution was steam distilled and the distillate which was strongly acidic was distilled to determine the Duclaux constants. These corresponded very closely to isobutyric acid.

Acknowledgment.—We are indebted to Lucidol Division of Wallace and Tiernan, Inc., for financial support of this investigation, to Rachel Keto, Mary A. Cleary and Phyllis Turransky for assistance in several of the experiments and separation of the products. For all the combustion analyses we wish to thank Dr. Nagy and his associates of this Institute.

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[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Preparation and Reactions of β-Chloroethyl- and γ-Chloropropylborane Derivatives

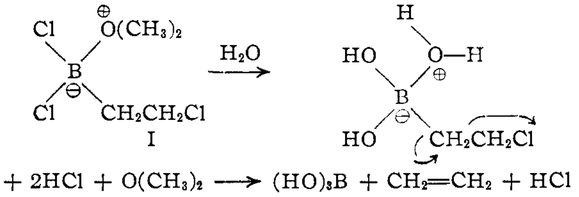
BY M. FREDERICK HAWTHORNE AND JOHN A. DUPONT

RECEIVED JUNE 16, 1958

Diborane has been found to add electrophilically to vinyl chloride in ethereal solvents to yield thermally unstable β-chloroethylborane derivatives. Crystalline β-chloroethylboron dichloride dimethyl etherate was obtained in this fashion. Similarly, allyl chloride reacts with diborane in diethyl ether to produce a mixture of tri-(γ-chloropropyl)-borane and di-(γ-chloropropyl)-boron chloride. Treatment of the β-chloroethyl and γ-chloropropyl derivatives with base results in the near quantitative formation of ethylene and cyclopropane, respectively.

Although the preparation and reactions of (chloroalkyl)-silane derivatives have been examined in some detail[1] the corresponding borane derivatives have remained unknown. It was therefore of interest to attempt the preparation of these novel materials by the method of Brown and Subba Rao,[2] a method which provides a direct path to trialkyl boranes by addition of diborane to the corresponding olefins.

Diglyme, tetrahydrofuran and diethyl ether solutions of vinyl chloride were found to react with diborane to produce thermally unstable product mixtures which defied separation. Dimethyl ether solutions of vinyl chloride were later employed in an attempt to simplify the separation of these reaction products. Vinyl chloride in dimethyl ether solution and at −80° smoothly absorbed diborane; however, on warming the product solution to room temperature violent exothermic decomposition often occurred and fires resulted on many occasions. In several instances the products survived this exothermic reaction and high boiling materials were obtained which were too unstable for fractional distillation and were not amenable to clean vacuum line separation at low temperatures. Vacuum line manipulation did allow the separation in very low yield, of a slightly volatile product which solidified and could be recrystallized from diethyl ether at low temperatures. This material melted at 54–56° and gave analyses which were in agreement with the empirical formula $C_4H_{10}BCl_3O$. Treatment of this material with water produced boric acid, hydrogen chloride and ethylene (contaminated with dimethyl ether) in the ratio 1:3:1, respectively. Ethylene was produced quantitatively if the assumption was made that the crystalline material was the dimethyl etherate of β-chloroethylboron dichloride (I). The production of ethylene from this material is reminiscent of the similar reaction of β-chloroethylalkylchlorosilanes with hydroxide ion observed by Sommer and co-workers.[3] The fact that dimethyl ether was retained in a coördination complex which was recrystallized unchanged from diethyl ether is interesting. Although exchange most likely occurred, the crystalline character of the dimethyl etherate would provide driving force for its separation. The violent exothermic decomposition of the crude reaction product might be interpreted in terms of the reaction sequence


I

$$+ 2HCl + O(CH_3)_2 \longrightarrow (HO)_3B + CH_2{=}CH_2 + HCl$$

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(1) See P. D. George, M. Prober and J. K. Elliot, *Chem. Revs.*, **56**, 1065 (1956).

(2) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

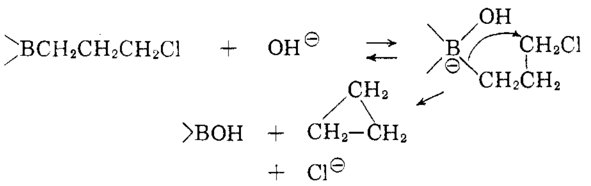
(3) L. H. Sommer, G. M. Goldberg, J. R. Gould and F. C. Whitmore, THIS JOURNAL, **68**, 1083 (1946).

$$B(CH_2CH_2Cl)_3 \longrightarrow ClB(CH_2CH_2Cl)_2 + CH_2{=}CH_2 \longrightarrow Cl_2BCH_2CH_2Cl + CH_2{=}CH_2$$

In contrast to the rather hazardous reaction of diborane with vinyl chloride, allyl chloride in diethyl ether was found to add diborane smoothly at room temperature to produce thermally stable reaction products in moderate yields. In this manner there was obtained a mixture of two major components which inflamed on contact with cloth in the air and which could be separated by fractional distillation at low pressures. The higher boiling of these materials was found to be tri-(γ-chloropropyl)-borane (II) while the lower boiling fraction was shown to be di-(γ-chloropropyl)-boron chloride (III). Minor amounts of a more volatile and unidentified material were obtained and it has been designated tentatively as impure γ-chloropropylboron dichloride. The yields of all components varied somewhat from run to run.

Tri-(γ-chloropropyl)-borane (II, b.p. 118°, 1 mm.) was isolated in approximately 36% yield and was characterized by carbon and hydrogen analyses and the following data: Hydrolysis of II with excess aqueous sodium hydroxide solution released three equivalents of chloride ion per mole of reactant. Vacuum line manipulation of the hydrolysis reaction products afforded 2.80 moles of cyclopropane (pure by infrared and mass spectrum) per mole of reactant. The nuclear magnetic proton resonance spectrum of II was in agreement with that predicted for the γ-chloropropyl group (see Experimental).

The facile basic hydrolysis of II to yield pure cyclopropane in nearly quantitative yield is novel and undoubtedly is related to the similar cleavage of γ-chloropropyl groups from γ-chloropropyltrichlorosilane which was observed by Sommer and co-workers.[4] Mechanistically this process most likely proceeds by the repetition of the reaction sequence.



The cleavage of II also was effected by the bases phenyllithium (84% yield of cyclopropane) and by water (100° for one week). In the latter case the yield of cyclopropane was only 45%. This latter result contrasts strongly with the rapid attack of water upon the β-chloroethyl derivative described above.

Attempts to dehydrohalogenate II cleanly with pyridine were unsuccessful. A complex mixture of high boiling materials was formed which could not be separated. The infrared spectrum of the crude product mixture exhibited carbon–carbon double bond stretching absorption in the infrared and alcoholic silver nitrate produced silver metal and no chloride silver. It thus appears as though olefinic boranes were formed but suffered subsequent polymerization.

The reaction of II with silver trifluoroacetate in diethyl ether solvent was equally unrewarding although silver chloride was produced.

Heating II with aluminum chloride in carbon disulfide solution at reflux produced extensive decomposition without the formation of cyclopropane.

Di-(γ-chloropropyl)-boron dichloride (III, b.p. 76° (1 mm.)) was isolated in approximately 12% yield and characterized in the same fashion as was II. Hydrolysis with aqueous base afforded 1.90 moles of pure cyclopropane and exactly 3.0 equivalents of chloride ion per mole of reactant. The nuclear magnetic proton resonance spectrum was nearly identical with that of II except for intensity (see Experimental).

Water reacted vigorously with III to produce hydrogen chloride but no cyclopropane. Methanolysis of III afforded methyl di-(γ-chloropropyl)-boronite (IV) in 65% yield as a colorless high boiling liquid, a result which again illustrates the requirement of strong base for cleavage of the γ-chloropropyl group.

The occurrence of II and III in the reaction mixture suggests that III arises from II by the elimination of cyclopropane and the formation of a B–Cl bond, perhaps in a concerted fashion.

Other systems which may provide useful cyclopropane derivatives are under examination.

Acknowledgment.—The authors wish to thank Dr. Keith McCallum and Mrs. Carolyn Haney for n.m.r. spectra and their interpretation.

Experimental

Diborane.—This material was generated in approximately 0.067-mole quantities by the method of Brown and Subba Rao.[2] The gas was passed directly from the generator to the reaction vessel. The entire apparatus was flushed with dry nitrogen before and after the generation of diborane. The reactor exit gases were passed through acetone.

Reaction of Diborane with Vinyl Chloride.—Approximately 30 g. (0.5 mole) of vinyl chloride was condensed in a flask equipped with a Dry Ice reflux condenser and gas inlet tube. The flask was cooled to −70° with a Dry Ice and acetone-bath to effect condensation. Approximately 100 ml. of dimethyl ether was condensed in the reaction vessel, the system flushed with nitrogen and diborane slowly admitted as the reaction zone was cooled to −70°. Following the diborane addition the coolant in the Dry Ice condenser was allowed to evaporate and the contents of the reaction flask slowly warmed to room temperature in a stream of nitrogen. As the last portion of dimethyl ether was removed the reaction mixture often gassed violently with the evolution of heat and ignited if air entered the system. In several cases this was avoided by judiciously applied cooling and a heavy colorless oil resulted.

The oily residue was transferred via a dry-box to the vacuum line and the product pumped through a trap maintained at 0° at high vacuum. After several hours about 5 g. of material was observed in the trap. This material was quickly dissolved in an equal volume of diethyl ether and cooled overnight at −70°. Large white crystals (I) were deposited and these were removed by filtration with the vacuum line filtration apparatus.

A small sample (321 mg.) of the crystalline solid was weighed and hydrolyzed in the dry-box with water. Potentiometric titration with standard sodium hydroxide solution afforded 4.85 meq. of strong acid (HCl) and 1.46 mmoles of boric acid. Assuming that three moles of HCl are produced per mole of reactant a molecular weight of 200 is obtained (theor. for $(CH_3)_2O{\cdot}BCl_2CH_2CH_2Cl$, 191).

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[4] L. H. Sommer, R. E. v. Strien and F. C. Whitmore, THIS JOURNAL, 71, 3056 (1949).

Hydrolysis of 370 mg. of the same material in a sealed bulb afforded after pumping through a −80° trap into a calibrated volume 2.2 mmoles of gas which analyzed approximately 90% ethylene and 10% dimethyl ether by mass spectrometer. Assuming one mole of ethylene arises from the hydrolysis of one mole of reactant a molecular weight of 186 is obtained.

Anal. Calcd. for $C_4H_{10}BCl_3O$: C, 24.72; H, 5.19. Found: C, 25.11; H, 5.19.

Reaction of Diborane with Allyl Chloride.—To 30.0 g. (0.39 mole) of allyl chloride dissolved in 100 ml. of dry ether was added 0.13 mole of diborane at room temperature. After the addition, the apparatus was swept with dry nitrogen and the product mixture freed of ether solvent by pumping on the vacuum line. The residual oil was fractionated with a 30 theoretical plate spinning band distillation column at a pressure of 1 mm. Three fractions were obtained: A, b.p. 30–40°, wt. 1.0 g.; B, b.p. 76°, wt. 3.1 g.; and C, b.p. 115–118°, wt. 11.3 g.

Fractions A and B reacted violently with water and all three fractions inflamed in the air when placed on cloth or paper. Fraction A was probably a mixture of materials containing γ-chloropropylboron dichloride, but could not be sufficiently purified to give reliable analytical data. Cyclopropane was produced on treating A with aqueous base.

Di-(γ-chloropropyl)-boron Chloride (III).—Fraction B (III, 405 mg.) was hydrolyzed with 10% sodium hydroxide solution in a sealed bulb or the vacuum line to produce 85.4 ml. (S.T.P.) of pure cyclopropane which was identified by infrared and mass spectrometry. The theoretical volume of cyclopropane for the reaction

$$\mathrm{ClB(CH_2CH_2CH_2Cl)_2} \xrightarrow[\mathrm{OH^{\ominus}}]{\mathrm{H_2O}} 2\mathrm{C_3H_6} + 3\mathrm{HCl} + \mathrm{(HO)_3B}$$

was 90 ml. (S.T.P.).

Anal. Calcd. for $C_6H_{12}BCl_3$: C, 35.79; H, 6.01; Cl, 52.83. Found: C, 35.46; H, 5.89; Cl, 53.0.

The nuclear magnetic proton resonance spectrum of fraction B was in agreement with the predicted spectrum of the γ-chloropropyl group. The yield of III based upon diborane was 12%.

Methyl Di-(γ-chloropropyl)-boronite (IV).—To 6.2 g. (0.031 mole) of III contained in a 50-ml. round-bottom flask equipped with a magnetic stirrer, dropping funnel and inert atmosphere was added dropwise with ice-bath cooling 25 ml. of anhydrous methanol. Hydrogen chloride was evolved and after 0.5 hour the methanol was removed on the vacuum line and the residual oil was distilled at reduced pressure, b.p. 68–72° (0.6 mm.), wt. 4.0 g. (65%).

Anal. Calcd. for $C_7H_{15}BOCl_2$: C, 42.70; H, 7.68; Cl, 36.01. Found: C, 42,30; H, 8.02; Cl, 36.09.

Tri-(γ-chloropropyl)-borane (II).—Fraction C (II, 364 mg.) gave 93 ml. (S.T.P.) of pure cyclopropane when hydrolyzed with aqueous 10% sodium hydroxide in the vacuum system; theoretical yield of cyclopropane for the reaction

$$\mathrm{B(CH_2CH_2CH_2Cl)_3} \xrightarrow[\mathrm{OH^{\ominus}}]{\mathrm{H_2O}} 3\mathrm{C_3H_6} + 3\mathrm{HCl} + \mathrm{(HO)_3B}$$

was 100 ml. (S.T.P.).

Anal. Calcd. for $C_9H_{18}BCl_3$: C, 44.40; H, 7.45; Cl, 43.6. Found C, 44.40; H, 7.45; Cl, 43.7

The nuclear magnetic proton resonance spectrum of II was identical to but more intense than that of III.

Cleavage of II by excess 1.0 *M* phenyllithium produced an 84% yield of cyclopropane while heating with water at 100° in a sealed bulb for one week gave only 45% of the theoretical amount although all of the oily II had dissolved.

Treatment of II with three equivalents of silver trifluoroacetate in an inert atmosphere and in diethyl ether at the reflux temperature produced silver chloride but no other isolatable products. Cyclopropane may have been produced and lost from the reaction system. The yield of II was 36% based upon diborane.

N.m.r. **Proton Spectra.**—Compounds II and III were examined as neat liquids using Varian Model V-4300B nuclear magnetic resonance spectrometer equipped with a 40 megacycle probe. Both II and III exhibited a symmetrical triplet centered at 40 c.p.s. higher field strength than the reference water and a large series of peaks (probably nine or more) centered at 108 c.p.s. higher field strength than water. The triplet represents the hydrogens of the terminal chloromethyl group.

HUNTSVILLE, ALA.

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUÍMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO AND THE INSTITUTO TECNOLÓGICO DE AERONÁUTICA]

The Action of Raney Nickel upon Sulfur Compounds. VI.[1] Formation of Biphenyl Derivatives

BY HEINRICH HAUPTMANN, WOLFGANG FERDINAND WALTER[2] AND CYRO MARINO[3]

RECEIVED APRIL 29, 1958

Aromatic thioethers, disulfides, thioesters and thiols yield biphenyl derivatives when heated at 220° with degassed Raney nickel or nickel prepared after Sabatier.

Aromatic disulfides,[4] thioesters and thiols[5] have been found to be transformed into thioethers when refluxed in xylene solution in the presence of Raney nickel degassed at 200°.[4,5] A biphenyl derivative was obtained in these experiments only with 4,4′-dimethoxydiphenyl disulfide, from which a small amount of 4,4′-dimethoxybiphenyl was isolated.[5]

It already has been reported briefly[6] that all the types of sulfur compounds mentioned above as well as aromatic thioethers yield biphenyl derivatives when the reaction is performed at higher temperature. Heating at 220° for 15 hours in the presence of Raney nickel degassed at 200° was found to be suitable for this purpose, but even at 180° biphenyl was an important reaction product, often accompanied by considerable amounts of diphenyl sulfide, especially when phenyl thiobenzoate was the starting material.

Compounds like diphenyl disulfide, diphenyl sulfide and phenyl thiobenzoate which contain only

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[1] Part V, THIS JOURNAL, **77**, 4929 (1955).

[2] Extracted in part from the thesis presented in 1955 to the Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo by W. F. Walter in partial fulfillment of the requirements for the obtention of the degree of Dr. em Ciências.

[3] Experiments to be included in a thesis to be presented to the Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo by C. Marino, in partial fulfillment of the requirements for the obtention of the degree of Dr. em Ciências.

[4] H. Hauptmann and B. Wladislaw, THIS JOURNAL, **72**, 707, 710 (1950).

[5] H. Hauptmann, B. Wladislaw, L. L. Nazario and W. F. Walter, *Ann.*, **576**, 45 (1952).

[6] Comm. to the XIV Intern. Congress of Pure and Applied Chemistry, Zürich, July, 1955.