methane or by slight warming in the case of dibromomethane), a mixture of *ca.* 0.25 mole of olefin and the remainder of the dihalomethane (0.35 mole total) was added dropwise over a period ranging from 0.5 to 2 hr. The reaction mixture was stirred at reflux for 20–30 hr. At the end of this time the reactions involving CH_2I_2 were a dark brown-purple while those run with CH_2Br_2 were a milky purple. The ether solution was then slowly decanted from the unchanged couple into a separatory funnel containing a mixture of ice and 1 *N* hydrochloric acid. (In the case of CH_2Br_2 reactions a moderate amount of gas evolution takes place upon hydrolysis.) The ethereal solution was separated, washed with a second portion of ice–hydrochloric acid, washed three times with water, and finally dried over potassium carbonate. The product was separated by the usual techniques.

Hydroboration of 1,4-Dihalo-2-alkenes

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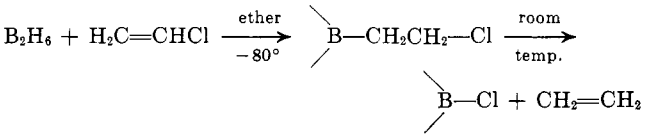
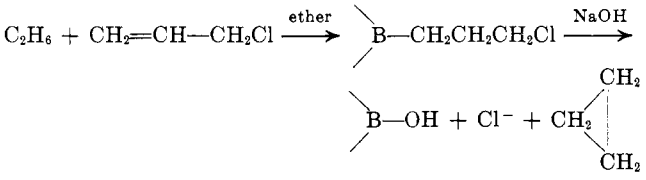
Hawthorne[2] observed that diborane added electrophilically to vinyl chloride in ethereal solvents at −80° to form β-chloroethylboranes that were thermally unstable and decomposed at room temperature to form ethylene. With vacuum line technique and in



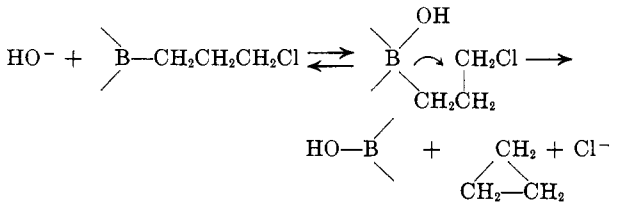
dimethyl ether as solvent, a low yield of crystalline β-chloroethylboron dichloride dimethyl etherate was isolated and found to hydrolyze and produce ethylene quantitatively.

$$Cl_2B{-}CH_2CH_2{-}Cl + 3H_2O \longrightarrow B(OH)_3 + 3HCl + CH_2{=}CH_2$$

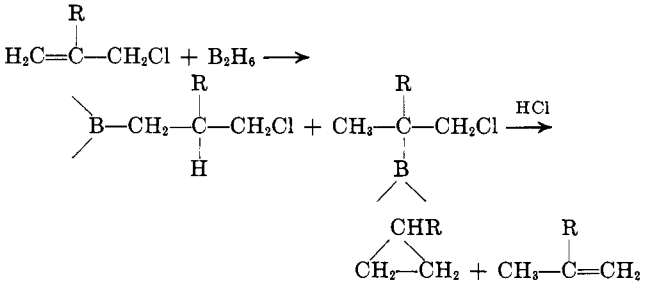
In contrast, the reaction of allyl chloride with diborane in ethyl ether was not hazardous and went smoothly at room temperature to give moderate yields of thermally stable γ-chloropropylboranes which were hydrolyzed to cyclopropanes by excess sodium hy-



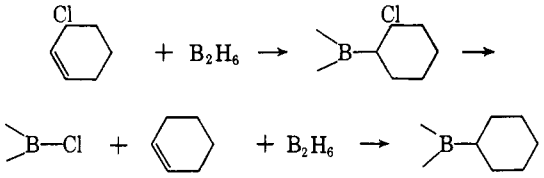
droxide. The almost quantitative cleavage to cyclopropane differed markedly from the rapid attack of water on β-chloroethyl derivatives and attempts to dehydrohalogenate with pyridine were unsuccessful. The reaction was also applied by Hawthorne[3] to β-alkylallyl and β-arylallyl chlorides to produce the corresponding substituted cyclopropanes. It was presumed that the base coordinated with boron to increase the carbanionic character of the boron–carbon bond and this novel basic hydrolysis was related to the similar cleavage of γ-chloropropyl groups from γ-chloropropyltrichlorosilane observed by Sommer.[4] The



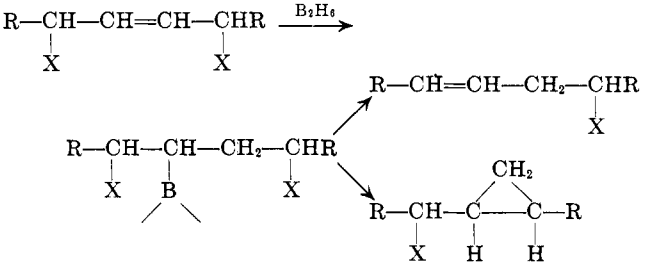
less than quantitative yields of cyclopropanes were attributed to side reactions such as hydroboration at the secondary carbon which was more important with β-alkyl and β-aryl substituents and may have led to β-elimination and olefin formation. Binger and



Köster[5] similarly observed that 3-chlorocyclohexene underwent elimination to form cyclohexene which reacted with diborane to form cyclohexylborane.



In this study, olefin and cyclopropane formation were compared by hydroboration of 1,4-dihalo-2-alkenes which could then undergo β- or γ-elimination to form a 4-halo-2-alkene or α-halocyclopropane, respectively.



Olefin formation by elimination is both kinetically and stereochemically favored and occurs spontaneously on warming to room temperature with water whereas cyclopropane formation requires treatment with aqueous sodium hydroxide.

The three 1,4-dihalo-2-alkenes studied underwent the expected β-elimination to form 4-halo-1-alkenes. Hydroboration of 1,4-dichloro-2-butene at room temperature produced a mixture of products which were

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(5) P. Binger and R. Köster, *Tetrahedron Letters*, **No. 4**, 156 (1961).

presumed to be formed from further hydroboration of 4-chloro-1-butene. This was prevented by hydroborating at −25 to −30° over 12 hr. and hydrolysis of the reaction mixture before warming to room temperature. Under identical conditions, 2,5-dichloro-2,5-dimethyl-3-hexene gave 5-chloro-2,5-dimethyl-2-hexene while 3,6-dibromocyclohexene was transformed to 4-bromocyclohexene. The relatively lower yield (12%) of the latter olefin may be attributed to the fact that bromine is a better leaving group than chlorine and may undergo more elimination during hydroboration.

Experimental

4-Chloro-1-butene.—Diborane was generated by adding over 5 hr. 3.1 g. (0.076 mole) of sodium borohydride (Callery Chemical) in 50 ml. of diglyme (purified by distillation over sodium) to 27.0 g. (0.20 mole) of redistilled Eastman boron trifluoride in 25 ml. of diglyme. It was fed through a delivery tube to a reaction flask, previously flushed with nitrogen, which was kept at −30° and contained 18.6 g (0.15 mole) of the 55–55° (20 mm.) fraction of Eastman 1,4-dichloro-2-butene dissolved in 50 ml. of diglyme. After borohydride addition was complete, the generator was warmed for 10 min. at 70° and the reaction mixture kept at −25 to −30° for 7 hr. and then hydrolyzed with 25 ml. of water followed by 25 ml. of 1.0 *M* aqueous sodium bicarbonate. After the mixture had come to room temperature, the upper layer was separated, dried over anhydrous sodium sulfate, and distilled at 74–75° (761 mm.) through a Vigreux column to give 4.5 g. of a liquid that was identified by its b.p. of 74–75°, d^{20}_4 0.918, n^{20}_D 1.4192° (lit.[6] b.p. 75°, d^{20}_4 0.9211, n^{20}_D 1.4205°), mol. wt. by Dumas 93.0 (calcd. 90.5), and infrared spectrum with peaks at 6.1 (C=C stretching), 7.1 (terminal C=C), and 15.5 μ (C—Cl stretching). Hydroboration followed by oxidation gave 4-chloro-1-butanol which formed a phenylurethane, m.p. 56°, lit.[7] 54°.

5-Chloro-2,5-dimethyl-2-hexene.—2,5-Dimethyl-2,4-hexadiene (Tennessee Eastman) was purified by distillation and then treated with an equimolar amount of chlorine by the method of Skvarchenko[8] to form 2,5-dichloro-2,5-dimethyl-3-hexene. An 18.5-g. (0.10 mole) sample of the latter was hydroborated by the procedure described above and the product distilled to give 4.1 g. of a liquid, b.p. 67–68° (25 mm.) which was identified as 5-chloro-2,5-dimethyl-2-hexene by the 0.5 min. required for reaction with alcoholic silver nitrate as compared with immediate precipitation with 2,5-dichloro-2,5-dimethyl-2-hexene, infrared peaks at 6.1 (C=C stretching) and medium intensity at 14 μ (C—Cl stretching), and its formation of a Grignard reagent which was hydrolyzed to 2,5-dimethyl-2-hexene, b.p. 110–111°, d^{20}_4 0.7244, n^{20}_D 1.4133 (lit.[8] b.p. 112.2°, d^{20}_4 0.720, n^{20}_D 1.4140).

Anal. Calcd. for $C_8H_{15}Cl$: C, 65.6; H, 10.2; Cl, 24.2. Found: C, 65.2; H, 9.93; Cl, 24.4.

4-Bromocyclohexene.—Wohl–Zeigler[9] bromination of cyclohexene gave 3-bromocyclohexene which was dehydrohalogenated with quinoline to 1,3-cyclohexadiene. Addition of an equimolar amount of bromine to this diolefin by the method of Crossley and Haas[10] gave 3,6-dibromocyclohexene; 25.0 g. (0.10 mole) of this product was hydroborated by the procedure above. Hydrolysis and separation of the reaction product gave 1.9 g. of 4-bromocyclohexene, b.p. 53–55° (15 mm.), d^{20}_4 1.3772, n^{21}_D 1.5188 (lit.[11] b.p. 48° (12 mm.), d^{20}_4 1.3779, n^{20}_D 1.5168).

Anal. Calcd. for C_6H_9Br: Br, 49.5. Found: Br, 49.9.

Acknowledgment.—The authors wish to express their thanks to the Cities Service Research and Development Corporation for their support of this work with a University Fellowship Grant to S. H. P.

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An Improved Laboratory Method for the Preparation of Diacetylene

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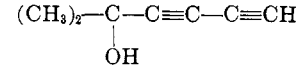
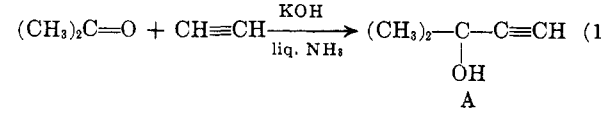
Diacetylene is a highly reactive bifunctional building block for the synthesis of a variety of polyacetylenic derivatives.[1,2] However, due to its instability, it has never been deliberately prepared on a commercial scale, and is consequently not readily available as a synthesis intermediate. It polymerizes rapidly above 0°, and in the presence of air can be readily detonated in vapor concentrations of 20–25% by a suitable ignition source.

The presently accepted method of preparing free diacetylene at the bench-scale level is the dehydrohalogenation of 1,4-dichlorobut-2-yne with either sodium hydroxide[3,4] or with sodamide in liquid ammonia. The latter method utilizes 3 moles of sodamide/mole of dichloride and forms the disodium diacetylide *in situ*, while the former method yields free diacetylene in 60% conversion

Although the base-catalyzed cleavage of 1,4-acetylenic diols[5] to acetylene is well known, the analogous cleavage of 1,3-diyne-1,6-diols to diacetylene and ketone has been studied only by Zalkind and Aizikovich.[6] In their cursory investigation, they employed large amounts of base (alkali metal carbonates and alkaline earth hydroxides) and obtained from 2,7-dimethylocta-3,5-diyne-2,7-diol low conversions to diacetylene, besides the semicleavage product, 2-methylhexa-3,5-diyn-2-ol.



During the course of work at this laboratory it was necessary conveniently to prepare free diacetylene as a starting material. Consequently, the above diynediol (B), readily available from acetone and acetylene *via* the following catalytic reactions,[1,2,7] was considered an excellent starting material for diacetylene preparation. Under optimum conditions the conversions to A and B, respectively, average 95–100%.



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