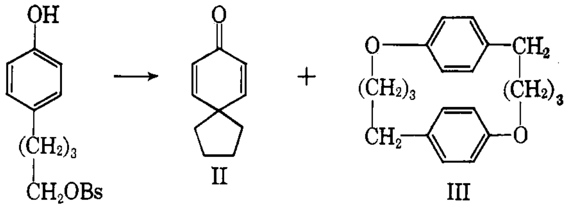
(I). The solvolysis of I and the isolation and characterization of the principal product (II) has been previously described.[3]

The neutral products from the solvolysis of I were chromatographed on a column of grade I basic alumina rather than distilled as previously described. Elution with benzene–pentane (1:9) gave a solid (III). Continued elution with benzene–pentane (2:3) gave II. The minor product (III) is clearly a dimer (osmometric molecular weight 294, calculated for III 296.4).[4] The infrared spectrum of III shows no hydroxyl absorption. The ultraviolet spectrum (λ_{max} 223, 277, and 285 mμ) is comparable with that of 4-methylanisole (223, 279, and 286 mμ).[5] The nuclear magnetic resonance spectrum of III shows eight aromatic protons as a pair of superimposed A_2B_2 patterns centered at τ 3.48, four protons as an unsymmetric triplet at 6.08 ($-CH_2-O-$), four protons as a similar triplet at 7.58 (benzylic methylene protons), and eight protons as a broad multiplet at 8.52 (remaining methylene protons).

Structure III is confirmed by the following chemical evidence. Refluxing constant boiling hydriodic acid converts III to 4-(4-iodobutyl)phenol (IV). Immediate reduction of IV using 5% palladium on sodium carbonate as catalyst gives 4-*n*-butylphenol (V) identified by its spectral properties[6] and the crystalline phenylcarbamate, m.p. 114–115°.



I II III

The preparation of III by dimerization of I points to a useful synthetic method for heteroatom substituted paracyclophanes. Although the solvolysis reaction was run in this study at twice the original[3] concentration, the results imply that solvolysis of I in still more concentrated solutions should favor higher yields of 1,12-dioxa[5.5]paracyclophane.

Experimental

General Procedure.—A solution containing 14.5 g. of 4-(*p*-hydroxyphenyl)butyl brosylate (I) in 950 ml. of 0.025 *N* potassium *t*-butoxide in *t*-butyl alcohol was heated in a constant temperature bath at 54.8 ± 0.1° for 7 hr. The work-up of the reaction mixture was identical with that of Baird and Winstein[3] except the crude residue (usually 4–4.5 g.) was not distilled, but carefullly chromatographed on Woelm grade I basic alumina using increasing concentrations of benzene in pentane.

Elution with benzene in pentane (1:9) gave III (5–7% yield, m.p. 123–126°). One recrystallization from cyclohexane gave pure III, m.p. 132–132.5°. The infrared spectrum (KBr) of III showed bands at 3.30, 3.42, 3.51, 6.22, 6.33, 6.65, 6.92, 7.72, 8.15, 12.05, 12.20, 12.50, and 12.91 μ. In the ultraviolet, III showed $\lambda_{max}^{95\%\ EtOH}$ 223 mμ (ε 14,000), 277 (2320), and 285 (1710).

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 80.97; H, 8.16; mol. wt., 296.4. Found: C, 80.90; H, 7.93; mol. wt., 294 (osmometric).

Elution (2:3 benzene–pentane) provided nearly pure II as determined by ultraviolet analysis, $\lambda_{max}^{95\%\ EtOH}$ 242 mμ (ε 14,500).[3] For complete purity, the liquid was distilled[7] giving a product that was solid at room temperature.

Degradation of 1,12-Dioxa[5.5]paracyclophane (III) to 4-*n*-Butylphenol (V).—A solution containing 400 mg. of III in 7 ml. of constant boiling hydriodic acid was heated under reflux for 5 hr., at which time all but a very small amount of III had gone into solution. The cooled reaction mixture was diluted with 25 ml. of water and extracted with three 15-ml. portions of ether. The combined ether fractions were dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, a semisolid, reddish residue was obtained that showed hydroxyl absorption in the infrared. The residue was immediately dissolved in 10 ml. of 5% ethanolic potassium hydroxide. A small quantity of solid would not dissolve and was filtered off. After the addition of 5% palladium on sodium carbonate (400 mg.), the ethanolic solution was hydrogenated at atmospheric pressure. The solution absorbed 23.5 ml. (60.5 ml. theory) of hydrogen. After removal of the catalyst by filtration, the solution was diluted with 50 ml. of water and extracted with four 15-ml. portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. Removal of the ether under reduced pressure left 310 mg. of a yellow oil. The oil was chromatographed on a silicic acid column (15 × 300 mm.) providing 153 mg. of 4-*n*-butylphenol (V). The infrared spectrum (CCl_4) of V showed bands at 3.00, 3.32, 3.43, 3.50, 6.21, 6.62, 8.08, 12.12, and 12.42 μ. A concentrated solution of V in CCl_4 showed absorption at 5.33 and 5.70 μ.[6]

The reaction of V with phenyl isocyanate gave 4-*n*-butylphenyl phenylcarbamate, m.p. 114–115°, lit.[8] m.p. 115°.

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(1) (a) National Institutes of Health Predoctoral Fellow, 1961–1963. Portions of this manuscript were abstracted from a thesis submitted by A. A. Griswold to the faculty of Iowa State University of Science and Technology, 1963. (b) Research Department, Chemicals Co., Union Carbide Corp., South Charleston, W. Va.

(2) The nomenclature used is that proposed by D. J. Cram and J. Abell, *J. Am. Chem. Soc.*, **77**, 1179 (1955).

(3) R. Baird and S. Winstein, *ibid.*, **84**, 788 (1962).

(4) This determination was made by Mr. T. A. Rettig.

(5) "Organic Electronic Spectral Data," Vol. I, M. J. Kamlet, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 210.

(6) D. D. Shrewsbury, *Spectrochim. Acta*, **16**, 1294 (1960); P. Montigny and G. Bichet, *Compt. rend.*, **237**, 820 (1954).

(7) Decomposition of II during distillation can be reduced by pretreating the glassware with dilute base.

(8) J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, **117**, 103 (1920).

Cyclopropanes from an Easily Prepared, Highly Active Zinc–Copper Couple, Dibromomethane, and Olefins

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The general reaction developed by Simmons and Smith for the preparation of cyclopropanes[1] from olefins, diiodomethane, and zinc–copper couple has proven to be exceedingly useful. The single drawback of their procedure, the inconvenience of preparing an active zinc–copper couple, was alleviated somewhat by the findings of Shank and Shechter[2] that a more conveniently prepared zinc–copper couple described by Hennion and Sheehan[3] will take part in the Simmons–Smith reaction. The couples described by these various groups may require several hours of tedious manipulations to prepare, may vary in activity from batch to batch, frequently requiring activation by iodine, and will react only with the expensive diiodomethane and chloroiodomethane. Reported here is a vastly simplified preparation of a *highly active* zinc–copper couple which, in the presence of olefins and without the use of

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(1) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(2) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(3) G. F. Hennion and J. C. Sheehan, *J. Am. Chem. Soc.*, **71**, 1964 (1949).

TABLE I

Olefin (mole)	Polyhalomethane (mole)	Granular Zn–Cu, mole	Reaction time, hr.	Product	% yield[b]
Cyclooctene (0.26)	CH_2I_2 (0.31)	0.47	20	Bicyclo[6.1.0]nonane	82
Cyclooctene (0.26)	CH_2Br_2 (0.35)	0.47	30	Bicyclo[6.1.0]nonane	56
Cyclooctene (0.26)	CH_2Br_2 (0.35)	0.47	40	Bicyclo[6.1.0]nonane	43[c]
Cyclooctene (0.26)	$CHBr_3$ (0.35)	0.47	25	. . .	0
Cyclooctene (0.26)	$CHBrCl_2$ (0.40)	0.5[a]	20	. . .	0
Cyclooctene (0.26)	$PhCHCl_2$ (0.40)	0.54	20	. . .	0
Cyclohexane (0.29)	CH_2Br_2 (0.44)	0.47	25	Norcarane	61[d,e]

[a] Zinc–copper couple prepared from zinc dust. The granular couple proved unreactive. [b] Yields were obtained from gas chromatographic analysis. Only a limited amount of effort was made to maximize these yields. [c] Preparative gas chromatographic isolation afforded a 28% yield of a colorless liquid, $n^{25}\text{D}$ 1.4671; A. C. Cope and C. L. Woo [*J. Am. Chem. Soc.*, **85**, 3601 (1963)] give $n^{25.5}\text{D}$ 1.4668. [d] Distillation through a spinning band column gave a 38% yield of a colorless liquid, b.p. 115–116°, $n^{25}\text{D}$ 1.4542; lit.[2] b.p. 116°, $n^{25}\text{D}$ 1.4542. [e] This 61% yield, which is somewhat better than the 50% yield obtained by Shank and Shechter,[2] fell to 40% in the case of diiodomethane and 2% in the case of dibromomethane when zinc–copper dust was used in place of the granular couple.

iodine activation, forms cyclopropanes, not only with diiodomethane, but also with dibromomethane.

The new zinc–copper couple is readily prepared by treating either zinc granules or zinc dust with a hot acetic acid solution of cupric acetate monohydrate, then washing with acetic acid and ether.[4] The couple prepared from zinc dust is more reactive[5] than granular zinc couple and can be used in reactions involving unreactive polyhalomethanes. The granular zinc–copper couple has the advantage of giving a smoother, more easily controlled reaction. The couple reacts spontaneously with both diiodomethane and dibromomethane. When an olefin is present both dihalomethanes give cyclopropanes. Compared to diiodomethane only a small sacrifice in yield was encountered when dibromomethane is used as a source of the elements of methylene.

A convenient procedure for carrying out the Simmons–Smith reaction involves slow addition of a mixture of the olefin and dihalomethane to a warm, rapidly stirred suspension of the couple in ether. The reaction will start faster if a small portion of the dihalomethane is added first to the ether–couple suspension to initiate the reaction before addition of the olefin–dihalomethane mixture. An attempt to improve on this procedure by adding dibromomethane to a mixture of cyclooctene and couple in ether gave a lower yield.

Bromoform, carbon tetrabromide, 2,2-dibromopropane, and benzal chloride also react readily with this zinc–copper couple. However, no cyclopropane derivatives have yet been detected when the reactions are carried out in the presence of an olefin. Instead, gas chromatographic analysis indicates that the olefin is essentially unchanged, while the polyhalomethanes have been consumed to give a number of high boiling products, probably as a result of intermolecular condensation. Iodoform also reacts readily with this couple, but chloroform, dichloromethane, and 2,2-dichloropropane have proven unreactive.

Other zinc couples of somewhat less reactivity have been formed by variations in solvents as well as metal salts. Thus, a moderately reactive zinc–copper couple can be prepared by treating zinc with a hot solution of anhydrous cupric chloride in tetrahydrofuran. Couples derived from zinc and other metals are easily prepared by treating zinc with an appropriate metal salt in acetic acid. In this way zinc–silver, zinc–platinum, and zinc–palladium couples were obtained from acetic acid solutions of silver acetate, chloroplatinic acid, and hydrated palladium chloride. Although these four couples spontaneously reacted with diiodomethane, they were relatively sluggish compared to the cupric acetate derived couple. Thus, their use in the preparation of cyclopropanes was not investigated. All of these couples will no doubt prove useful in other dehalogenation reactions.

Experimental

Materials.—The granular zinc was Baker's 30-mesh reagent grade, while Fisher's zinc dust, both the 97% reagent grade and the technical grade, was used. The cupric acetate monohydrate was Fisher's reagent grade. The organic compounds were the best grade obtainable, usually Eastman's White Label grade. The cyclooctene was part of a generous sample supplied by Cities Service Research and Development Co.

Preparation of Granular Zinc–Copper Couple.—To a hot (nearly refluxing) solution of 0.5 g. of cupric acetate monohydrate in 50 ml. of glacial acetic acid was added 30–35 g. (*ca.* 0.5 mole) of granular zinc (30 mesh). The mixture was shaken for 1 to 3 min., keeping it hot during this period to prevent precipitation of zinc acetate. The acetic acid was decanted and the zinc–copper couple was washed with a 50-ml. portion of glacial acetic acid, then with three 50-ml. portions of ether.[6] The couple was shaken with each washing for 0.5–1 min. At this point the ether-moistened couple is ready for use as is or it can be freed of ether by passing a stream of nitrogen through it.

Preparation of Zinc–Copper Dust.—To a hot, rapidly stirred solution of 2.0 g. of cupric acetate monohydrate in 50 ml. of glacial acetic acid was added 35 g. of zinc dust. After about 0.5 min. all of the copper had deposited on the zinc. The couple was allowed to settle for 0.5–1 min., then as much of the acetic acid as possible was decanted taking care not to lose the silt-like couple. The dark reddish gray couple was then washed with one 50-ml. portion of acetic acid followed by three 100-ml. portions of ether.[6] The moist couple was ready for use.

Synthesis of Cyclopropanes.—The general procedure used for the synthesis of norcarane and bicyclo[6.1.0]nonane (Table I) was as follows. The erlenmeyer flask used for the preparation of the zinc–copper couple and containing *ca.* 0.5 mole of the couple was fitted with a condenser, dropping funnel, and magnetic stirrer. The solvent, 100 ml. of ether, was added followed by a few milliliters of the dihalomethane.[7] If the reaction does not start immediately (as indicated by bubbles rising from the couple) brief warming will initiate it. While the stirred suspension was kept at gentle reflux (either by the heat of reaction in the case of diiodo-

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(4) In early preparations a few absolute ethanol washings were made before the ether washings. These ethanol washings were found to be unnecessary. They also decreased the reactivity of the couple.

(5) Caution should be exercised in handling the zinc dust couple. The unchanged zinc residue from one preparation charred some paper which was in contact with it. Careful addition of cold water to the used couple seems to deactivate it.

(6) To prevent violent boiling of the ether it may be necessary to cool the couple in ice–water.

(7) Adding all of the dihalomethane to the couple as is usually done[1,2] may cause the reaction mixture to erupt violently from the flask. This is especially true when zinc–copper dust and diiodomethane are used.

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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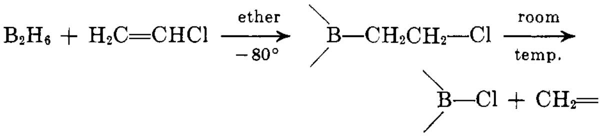
Received July 8, 1963

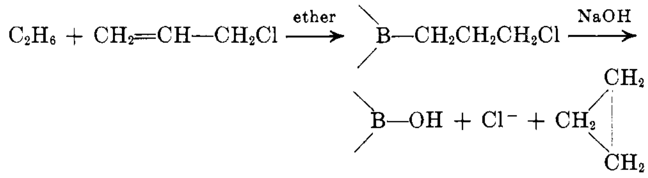
Hawthorne[2] observed that diborane added electrophilically to vinyl chloride in ethereal solvents at −80° to form β-chloroethylboranes that were thermally unstable and decomposed at room temperature to form ethylene.



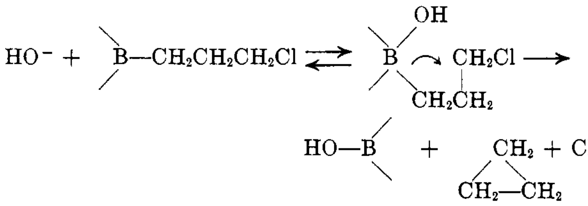
With vacuum line technique and in dimethyl ether as solvent, a low yield of crystalline β-chloroethylboron dichloride dimethyl etherate was isolated and found to hydrolyze and produce ethylene quantitatively.

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

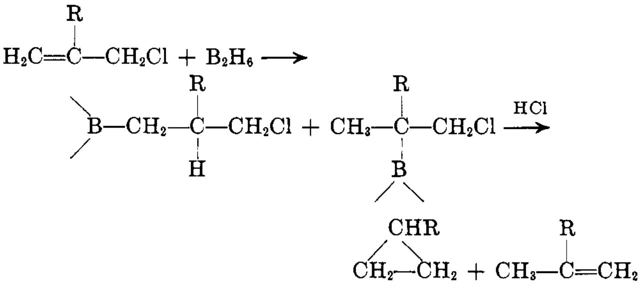
In contrast, the reaction of allyl chloride with diborane in ethyl ether was not hazardous and went smoothly at room temperature to give moderate yields of thermally stable γ-chloropropylboranes which were hydrolyzed to cyclopropanes by excess sodium hydroxide.



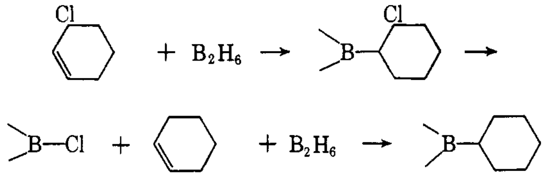
The almost quantitative cleavage to cyclopropane differed markedly from the rapid attack of water on β-chloroethyl derivatives and attempts to dehydrohalogenate with pyridine were unsuccessful. The reaction was also applied by Hawthorne[3] to β-alkylallyl and β-arylallyl chlorides to produce the corresponding 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]



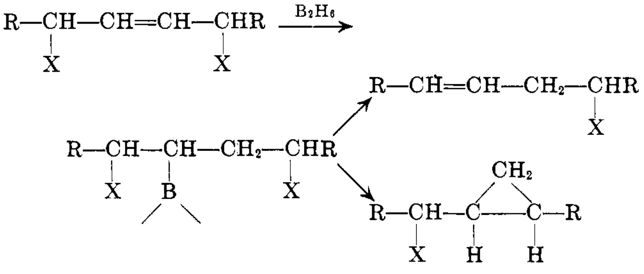
The less than quantitative yields of cyclopropanes were attributed to side reactions such as hydroboration at the secondary carbon which was more important with β-alkyl and β-aryl substituents and may have led to β-elimination and olefin formation.



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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[1] From a thesis submitted by S. H. Pohl in partial fulfillment of the requirements for the M.A. degree, Sept., 1963; Cities Service University Fellow, 1961–1962.

[2] M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

[3] M. F. Hawthorne, *ibid.*, **82**, 1886 (1960).

[4] L. H. Sommer, R. E. von Strien, and F. C. Whitmore, *ibid.*, **71**, 3056 (1949).

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