Hydroboration of β-bromostyrene with borane in tetrahydrofuran in a mole ratio of 2:1 utilized only 1 mole of the β-bromostyrene with the formation of 2-phenylethanol as the only alcohol with trace amounts of styrene and styrene oxide present.

Preparation of 4-*t*-Butyl-1-chlorocyclohexene.—The general procedure of Horner, Oediger, and Hoffmann was employed.[17] To a solution of triphenylphosphine (26.3 g, 0.1 mole) in 300 ml of dry benzene in a 500-ml three-necked flask equipped with a pressure-equalizing dropping funnel, stirring motor, and thermometer, was added 7.09 g (0.1 mole) of chlorine dissolved in 50 ml of carbon tetrachloride while maintaining the temperature of the reaction mixture below 6°. A fine precipitate was formed during the addition of the chlorine. To the triphenylphosphine dichloride solution was added 10.2 g (0.1 mole) of freshly distilled triethylamine in 20 ml of benzene followed by the addition of 15.3 g (0.1 mole) of 4-*t*-butylcyclohexanone in 20 ml of benzene. The addition funnel was replaced by a condensor and the reaction mixture was refluxed for 2 hr during which time the original precipitate disappeared with the formation of triethylamine hydrochloride. The reaction mixture was cooled and the solids were removed by filtration. The benzene was partially removed under reduced pressure during which time triphenylphosphine oxide precipitated. The triphenylphosphine oxide was removed by suction filtration, the crystals being washed several times with ether. The ether was removed from the filtrate and the residue was distilled under reduced pressure at 103° and 20 mm. The infrared spectrum of the distillate indicated the presence of some ketone. The distillate was separated by column chromatography on Florisil using hexane as the eluent. The final product showed no carbonyl absorption in the infrared and was distilled at 46° at 1 mm. The infrared spectrum (neat) displayed carbon–carbon double-bond absorption at 6.01 μ.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.53; H, 9.93; Cl, 20.54. Found: C, 69.46; H, 10.41; Cl, 20.48.

Hydroboration of 4-*t*-Butyl-1-chlorocyclohexene.—To 7.9 ml of 1.78 *M* borane in tetrahydrofuran (14 mmole) at 0° was added 1.2 g (7 mmole) of 4-*t*-butyl-1-chlorocyclohexene. After the initial reaction subsided, the reaction mixture was stirred at room temperature for 3 hr. The reaction mixture was then hydrolyzed, oxidized, and worked up as described for the hydroboration of β-bromostyrene. The crude residue was distilled at 110° (18 mm) giving 0.87 g (80%) of an alcohol mixture.

The alcohol mixture was dissolved in 5 ml of ether and 1 ml of acetic anhydride and 0.25 ml of pyridine were added and the reaction mixture allowed to stand for 24 hr. Direct analysis of the reaction mixture by glpc on a 30 ft Carbowax 20M column at 200° showed the presence of 6% *trans*-3-, and 15% *cis*-4-, 14% *cis*-3-, and 65% *trans*-4-*t*-butylcyclohexanol (the percentages were calculated using predetermined relative response ratios).

Preparation of 1-Chlorocycloheptene.—Cycloheptanone (11.2 g, 0.1 mole) was converted in moderate yield to the relatively unstable 1-chlorocycloheptene as described above for the preparation of 4-*t*-butyl-1-chlorocyclohexene. The material was purified by column chromatography on Florisil and finally by distillation at 59–62° (18 mm). The product was sufficiently unstable that no analysis could be obtained.

Hydroboration of 1-Chlorocycloheptene.—To 3.93 ml of 1.78 *M* borane in tetrahydrofuran (7 mmole) at 0° was added 0.62 g (4.75 mmole) of freshly distilled 1-chlorocycloheptene. After the initial reaction subsided, the reaction mixture was stirred at room temperature for 3 hr; the product was isolated as described above. Analysis of the product residue by gas–liquid partition chromatography on a 5-ft Carbowax 20M column at 150° showed the presence of cycloheptanol (57% yield) and less than 0.4% of a material that could have been cycloheptene or norcarane (the addition of authentic material far overshadowed the unknown peak so that unambiguous identification could not be accomplished).

Hydroboration of 2-Chloro-2-butene.—To 17.6 ml of 1.7 *M* borane in tetrahydrofuran (30 mmole) at 0° was added 2.71 g (30 mmole) of 2-chloro-2-butene producing a very exothermic reaction which could not be controlled if the chlorobutene were added too rapidly. After the initial reaction subsided the reaction mixture was stirred at room temperature for 5 hr and then was hydrolyzed and oxidized as described above. After oxidation the two-phase tetrahydrofuran–water system was saturated with potassium carbonate and the tetrahydrofuran layer was analyzed directly by glpc on a Carbowax 20M column showing only the presence of 2-butanol (80% yield) (no 1-butanol).

Hydroboration of 2-Bromo-2-butene.—To 16.6 ml of 1.2 *M* borane in tetrahydrofuran (20 mmole) at 0° was added 2.7 g (20 mmole) of 2-bromo-2-butene (highly exothermic). The reaction mixture was worked up and analyzed as described for 2-chloro-2-butene giving only 2-butanol (83.5% yield).

(17) L. Horner, H. Oediger, and H. Hoffmann, *Ann.*, **626**, 26 (1959).

Transfer Reactions Involving Boron. X. The Stereochemistry of Eliminations Involving β-Substituted Organoboranes[1,2]

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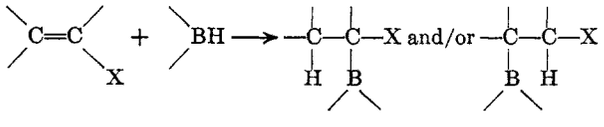
A series of β-substituted organoboranes have been prepared by the deuteroboration of *cis*-β-ethoxystyrene, *cis*-β-phenylmercaptostyrene, *trans*-β-benzylmercaptostyrene, *trans*-β-pyrolidinostyrene and 4-*t*-butyl-1-chlorocyclohexene. The stereochemistry of the uncatalyzed and acid- and base-catalyzed elimination reactions has been determined. The stereochemistry of the uncatalyzed eliminations involving β-alkoxyboranes is *cis*. The *trans*-β-chloroorganoborane derived from 4-*t*-butyl-1-chlorocyclohexene is stable in diethyl ether, but undergoes elimination in tetrahydrofuran solution giving 4-*t*-butylcyclohexene. This elimination is in all probability a base-catalyzed elimination, the tetrahydrofuran acting as the base. The β-aminoorganoborane derived from β-pyrolidinostyrene undergoes a *trans* elimination which is believed to be a self acid-catalyzed elimination. β-Aryl- and alkylmercaptoorganoboranes do not undergo uncatalyzed eliminations. The acid- and base-catalyzed eliminations involving β-substituted organoboranes have been found to be *trans* eliminations. The effect of the substituents bonded to the boron atom on the elimination mechanism has also been investigated and some of the factors controlling the competition between the elimination and transfer reactions have been deduced.

The hydroboration of a hetero-substituted olefin may result in the formation of α- and/or β-substituted organoboranes, the relative amounts of the two isomers depending on the structure of the carbon skeleton and the functional group X.



(1) Part IX: D. J. Pasto and Sr. R. Snyder, O.S.F., *J. Org. Chem.*, **31**, 2773 (1966).

(2) Taken from the Ph.D. Thesis of Sr. R. S., O.S.F. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant 1225-A1, 3.

These substituted organoboranes are generally quite reactive intermediates leading to α- and β-transfer reactions[1,3] and eliminations in the case of the β-substituted organoboranes.

Uncatalyzed eliminations in tetrahydrofuran have been reported for β-substituted organoboranes in which X is chlorine[4-6] and oxygen.[3c,6] Base-catalyzed eliminations have been reported for systems in which X is chlorine,[4,7] bromine,[7,8] certain oxygen derivatives,[6] and boron.[9] Acid-catalyzed eliminations have been reported for cases in which X is an oxygen derivative[3,10] and amino nitrogen.[11]

The stereochemistry of only a few of these eliminations reactions is known, generally through the use of cyclic substituted olefins in which the geometry of the borane adduct is restricted. The eliminations involving β-chloroorganoboranes appears to be spontaneous; however, the spontaneity of the elimination appears to be substrate and solvent dependent indicating that a more complex mechanism is operative. Cristol, Parungo, and Plorde[7] have reported the formation of stable β-haloorganoboranes by hydroboration of 2-chlorodibenzobicyclo[2.2.2]octatriene and bromo-*cis*-stilbene in diethyl ether. Elimination did not occur until the addition of water which allowed the subsequent isolation of the corresponding olefins. These eliminations must be *trans* and are catalyzed by the very weakly basic water molecule. Matteson and Liedtke[8] have reported that the *trans* elimination of the elements of $(RO)_2BBr$ from dibutyl 2,3-dibromo-2-butylboronate is also catalyzed by weak bases such as water.

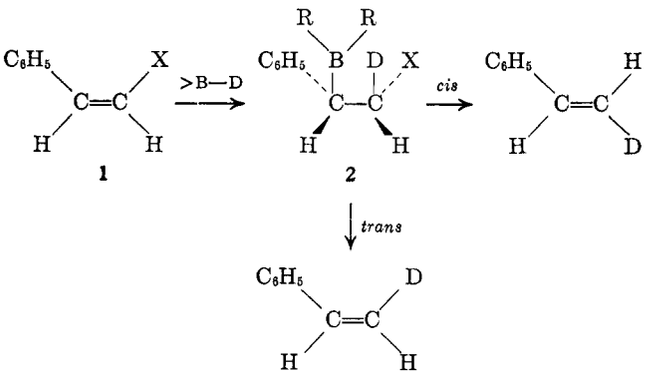
Acid-catalyzed eliminations in cyclic cases are *trans* when X is alkoxyl[3c] or amino,[11] but these results cannot be extrapolated to predict the stereochemistry of acid-catalyzed eliminations occurring in acryclic derivatives due to the possibility of acid-bridged transition states leading to a *cis* elimination.

The stereochemistry of the majority of uncatalyzed, acid- and base-catalyzed eliminations with various functional groups has not been determined. Furthermore, the effect of various functional groups bonded to boron on the course of the elimination reactions is not known. This article presents the results of a study of the stereochemistry of uncatalyzed and acid- and base-catalyzed eliminations involving a variety of substituents in the β position and on the boron atom. Unfortunately the hydroboration of a substituted olefin leads to α- and β-substituted organoboranes, the amounts of which vary greatly with the system. Although the results and conclusions drawn in this study involve reactions of only one of the hydroboration intermediates, the value of the data obtained with respect to the stereochemistry of the elimination reactions of β-substituted organoboranes is not reduced because of low yields or a multiplicity of other possible reactions. In the previous article in this series it was established that α-substituted organoboranes do not give rise to olefinic intermediates which would tend to destroy the utility of the present results. The synthesis of the desired β-substituted organoboranes in a pure stage cannot be accomplished using classical organic synthetic procedures thus necessitating the use of the hydroboration of substituted olefins to derive the desired intermediates.

Results and Discussion

A series of substituted olefins of known stereochemistry was required for this investigation. For a variety of reasons the β-substituted styrenes appeared to be ideal for this study. The stereochemistry of the β-substituted styrenes could be readily assigned on the basis of the size of the vicinal vinyl coupling constants, and the stereochemistry of the resulting β-deuteriostyrene could be assigned by nuclear magnetic resonance spectroscopy.

Addition of >B—D to a *cis*-β-substituted styrene (**1**) of known stereochemistry results in the formation of a β-substituted organoborane (**2**) (the presence of α-substituted organoboranes will be ignored) as illustrated below. A *cis* elimination of >B—X results in the formation of *trans*-β-deuteriostyrene, whereas a *trans* elimination would result in the formation of *cis*-β-

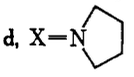


deuteriostyrene. The *cis*- and *trans*-β-deuteriostyrenes are readily distinguishable on the basis of their proton nmr spectra.[12,13]

The synthesis of the desired β-substituted styrenes were accomplished in the following manners. *cis*-β-ethoxystyrene (*cis*-**3a**) was prepared by the addition of ethoxide to phenylacetylene in refluxing ethanol. A mixture of *cis*- and *trans*-**3a** was obtained by equilibra-

$C_6H_5CH=CHX$

3a, $X=OC_2H_5$
b, $X=SC_6H_5$
c, $X=SCH_2C_6H_5$



tion over alumina and by irradiation. The observed coupling constants of the vinyl hydrogens are tabulated in Table I.

(3) (a) D. J. Pasto and J. L. Miesel, *J. Am. Chem. Soc.*, **84**, 4991 (1962); (b) D. J. Pasto and J. L. Miesel, *ibid.*, **85**, 2118 (1963); (c) D. J. Pasto and C. C. Cumbo, *ibid.*, **86**, 4343 (1964).

(4) M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).

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

(6) (a) H. C. Brown and K. A. Keblys, *J. Am. Chem. Soc.*, **86**, 1791 (1964); (b) H. C. Brown and O. J. Cope, *ibid.*, **86**, 1801 (1964).

(7) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965).

(8) D. S. Matteson and J. D. Liedtke, *ibid.*, **87**, 1526 (1965).

(9) D. J. Pasto, *ibid.*, **86**, 3039 (1964).

(10) L. Caglioti, G. Cainelli, G. Maina, and A. Selva, *Gazz. Chim. Ital.*, **92**, 309 (1962).

(11) J. W. Lewis and A. A. Pearce, *Tetrahedron Letters*, **No. 30**, 2039 (1964).

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 283–241.

(13) T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Am. Chem. Soc.*, **86**, 4670 (1964).

TABLE I
COUPLING CONSTANTS OF SUBSTITUTED STYRENES

Compd	J (calculated) trans	J (calculated) cis	J (observed) trans	J (observed) cis
3a	13.7	5.3	12.1	7.3
3b	16.7	8.9	14.4	11.0
3c	16.7	8.9	15.5	11.6
3d	15.4	7.3	14.9	...

cis-**3b** was prepared by the addition of thiophenoxide to phenylacetylene in ethanol.[3b] *cis*-**3b** proved to be quite stereochemically unstable, isomerizing to *trans*-**3b** on short exposure to sunlight. Precautions were taken to protect the sample from sunlight during the hydroboration experiments. The coupling constants for *cis*- and *trans*-**3b** are contained in Table I.

A mixture of *cis*- and *trans*-**3c** was obtained by the addition of benzyl mercaptan to phenylacetylene.[3b] The *trans* isomer was isolated and purified by fractional recrystallization.

trans compound **3d** was prepared by the reaction of pyrolidine with phenylacetaldehyde in benzene. The *cis* isomer of **3d** was not prepared. The stereochemistry of *trans*-**3d** was assigned on the basis of the observed coupling constant and comparison with the calculated value (see the following paragraph).

The stereochemistry of the various β-substituted styrenes was assigned on the basis of the value of the coupling constant and by comparison of the observed coupling constants with calculated values using the equations of Banwell and Sheppard.[14] Although these equations were developed for monosubstituted olefins,

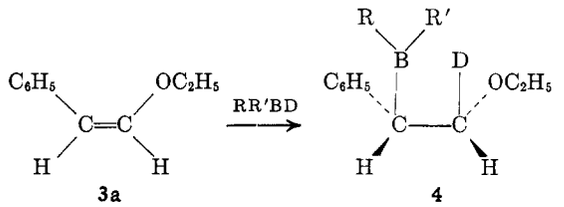
$$J_{trans} = 19 - 3.3\Delta E$$

$$J_{cis} = 11.7 - 4.0\Delta E$$

the electronegativity effects of more than one group appear to be reasonably additive. An electronegativity value for phenyl[15] of 2.5 was employed along with the atom electronegativities of the hetero atom of the X group bonded to the olefinic center. The calculated values are presented in Table I. The calculated values are consistently too large for the *trans* compounds and too small for the *cis* compounds. The deviations between the calculated and observed values are relatively small and are relatively consistent within each series.

The isolation of the deuteriostyrene formed in the eliminations presented certain problems. The hydroboration of the substituted styrenes proceeded generally only to the dialkylboron stage. Subsequent elimination would generate olefin in the presence of some residual >B—H which would result in destruction of the desired reaction product. For example, the hydroboration of **3a** in a ratio of 2 moles of olefin to 1 mole of borane resulted in only a 5% yield of styrene. Attempted hydroboration with disiamylborane did not result in hydroboration, apparently owing to the steric bulk of alkyl groups bonded to the boron. This problem was circumvented by the use of "di-*n*-propyldeuterioborane," 40% yields of deuteriostyrene being derived when employing this reagent with **3a**. Actually the deuteroboration reagent is an equilibrium mixture derived from 1 mole of deuterioborane and 2 moles of tri-*n*-propylborane. The composition of this equilibrium mixture was determined by quenching with *cis*-2-butene followed by glpc analysis indicating the presence of approximately 40% tri-*n*-propylboron, 38% di-*n*-propyldeuterioborane, 22% mono-*n*-propyldideuterioborane, and a trace of deuterioborane. This equilibrated mixture, hereafter referred to as "*n*-Pr_2BD," was employed in a 1:1 mole ratio with the substituted styrenes.

The deuterioboration of *cis*-**3a** with "*n*-Pr_2BD" at 0° and allowing the reaction mixture to stand at room temperature for 1 hr, followed by a typical oxidative work-up and isolation procedure, gave up to 40% yields of styrene. The nuclear magnetic resonance spectrum of the isolated styrene sample showed the presence of only *trans*-β-deuteriostyrene indicating a *cis* elimination



3a **4**

in **4** (R = R′ = *n*-Pr) had occurred. Control reactions were carried out demonstrating that the original *cis*-**3a** did not undergo isomerization in the presence of borane and that the styrene was formed prior to work-up. In fact, a hydroxide-catalyzed elimination of **4** (R = R′ = *n*-Pr) could not be realized.

Addition of *n*-butyllithium to **4** (R = R′ = *n*-Pr) at 0°, immediately after completion of the deuteroboration of **3a**, produced an exothermic reaction with the generation of styrene (35% yield) which, when analyzed by nuclear magnetic resonance spectroscopy, contained 90% *cis*-β-deuteriostyrene. The base-catalyzed elimination must be *trans;* the small amount of the *cis*-elimination product is believed to have been formed by some uncatalyzed elimination occurring prior to or during the addition of the *n*-butyllithium. The addition of sodium methoxide to **4** (R = R′ = *n*-Pr) did not result in a base-catalyzed elimination.

The addition of boron trifluoride etherate to **4** (R = R′ = *n*-Pr) at 0°, immediately after completion of the deuteroboration of **3a**, produced >90% stereochemically pure *cis*-β-deuteriostyrene (31% yield) again indicating a *trans* elimination.

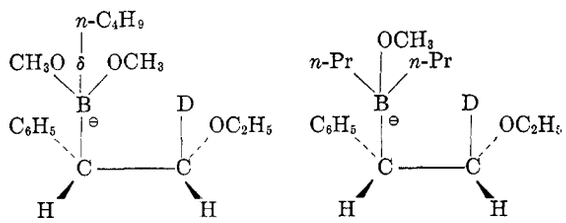
The effect of varying the substituents on the boron atom was also investigated. Intermediate **4** (R = R′ = D), formed in part by the deuteroboration of *cis*-**3a** in the presence of excess perdeuterioborane, underwent a much slower spontaneous *cis* elimination as indicated by the formation of *trans*-β-deuteriostyrene (4%). Extensive formation of transfer-type reaction products (15%) was evident.[3c] The difference in the mode of reaction of **4** (R = R′ = *n*-Pr) and **4** (R = R′ = D) may be due to steric factors or electronic effects on the Lewis acidity of the boron atoms. Extended Hückel calculations indicate that the charge density on the boron atom in monoalkylboranes average +0.64 ± 0.02 and in trialkylboron compounds +0.96. The increase in the positive charge on the boron atom in **4** (R = R′ = *n*-Pr) over that in **4** (R = R′ = D) should enhance the interaction between the boron and oxygen in **4** (R = R′ = *n*-Pr) leading to the transition state for

(14) C. N. Banwell and N. Sheppard, *Disc. Faraday Soc.*, **34**, 115 (1962).
(15) H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

elimination. We currently favor this explanation[16] over one involving steric factors.

The addition of *n*-butyllithium to **4** (R = R′ = D) at 0° produces *cis*-β-deuteriostyrene and extensive amounts of hydrogen-transfer products. The acid-catalyzed elimination of **4** (R = R′ = D) also gives *cis*-β-deuteriostyrene *via* a *trans* elimination.

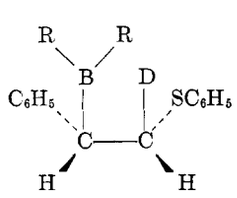
The addition of methanol to the adduct **4** (R = R′ = D) produces **4** (R = R′ = OCH_3) as determined by boron-11 magnetic resonance spectroscopy. Intermediate **4** (R = R′ = OCH_3) does not undergo an uncatalyzed elimination even in refluxing tetrahydrofuran (64°). The electron donating ability of the oxygens of the methoxyl groups bonded to the boron must reduce the electron deficiency on the boron atom thus reducing the tendency of the boron to interact with the oxygen of the ethoxyl group leading to elimination. The base-catalyzed elimination of **4** (R = R′ = OCH_3) cannot be affected by the addition of one molar equivalent of *n*-butyllithium. The adduct thus formed (**5**) would be nearly the same as that derived from **4** (R = R′ = *n*-Pr) with methoxide **6** which was also stable to elimination. The acid-catalyzed elimination with **4** (R = R′ = OCH_3) proceeds normally.



5 **6**

The addition of phenylthioborane[17] to *cis*-**3a** produces, in part, intermediate **4** (R = H; R′ = SC_6H_5) which undergoes a facile uncatalyzed elimination. The electron donation from sulfur to boron is apparently not sufficient to interfere with the interaction of the boron with the ethoxyl oxygen.

The addition of "$(n\text{-Pr})_2$BD" to *cis*-**3b** produces, in part, intermediate **7** (R = *n*-Pr) which does not undergo uncatalyzed or acid-catalyzed (BF_3) eliminations. It appears that the interaction between the



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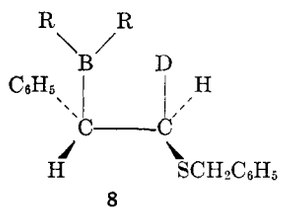
boron and sulfur is not sufficient to lead to a *cis* elimination. The inability to affect an acid-catalyzed elimination with boron trifluoride is also probably due to too weak an interaction between the sulfur and the boron trifluoride (see later mechanistic discussion). Intermediate **7** undergoes a facile *trans* elimination in the presence of *n*-butyllithium or aqueous base.

(16) A similar explanation is useful in rationalizing the relative rates of hydroboration by BH_3 *vs.* RBH_2 and the monomer ⇄ dimer equilibrium constants involving alkyl boranes (D. J. Pasto and P. Balasubramaniyan, unpublished observations).

(17) D. J. Pasto, C. C. Cumbo, and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **88**, 2187 (1966).

Deuterioboration of *trans*-**3c** with "$(n\text{-Pr})_2$BD" gave, in part, **8** (R = *n*-Pr) which does not undergo an uncatalyzed elimination. Treatment of **8** (R = *n*-Pr) with boron trifluoride however, produced *trans*-β-deuteriostyrene *via* a *trans* elimination. The difference in the reactivity of **7** (R = *n*-Pr) *vs.* **8** (R = *n*-Pr) must be due to the difference in the electronic effects of the groups bonded to the sulfur atom, the phenyl group being strongly electron-withdrawing, and hence reducing the electron density on the sulfur, whereas with the benzyl group the methylene shields the sulfur from this effect.[18] Treatment of **8** (R = *n*-Pr) with *n*-butyllithium or aqueous hydroxide results in a *trans* elimination.



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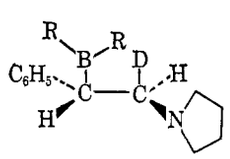
Deuteroboration of *trans*-**3d** with "$(n\text{-Pr})_2$BD" results in the formation of moderate quantities of **9** (R = *n*-Pr). Intermediate **9** (R = *n*-Pr) undergoes elimination with the production of *trans*-β-deuteriostyrene (14%) which must be formed *via* a *trans* elimination. This elimination is quite different from those involving **3a**, or other β-substituted organoboranes, in that **9** (R = *n*-Pr) contains a basic and an acidic functional group which may act to catalyze its own destruction. A choice must be made whether to describe the elimination involving **9** (R = *n*-Pr) as an acid-catalyzed or a base-catalyzed elimination. A self base-catalyzed elimination involving **9** (R = *n*-Pr) would require the expulsion of the pyrolidinyl anion, a process not expected to be favorable. In contrast, the self acid-catalyzed elimination in which R_2B^+ (R = *n*-Pr) is the leaving group (undoubtedly highly solvated by tetrahydrofuran) is very similar to the mechanisms proposed for the acid-catalyzed eliminations of β-alkoxyorganoboranes[3c] (see later discussion) and the reactions of epoxides with phenylthioborane[19] and perdeuterioborane[20] and is thus the mechanism of choice for the elimination involving **9** (R = *n*-Pr).



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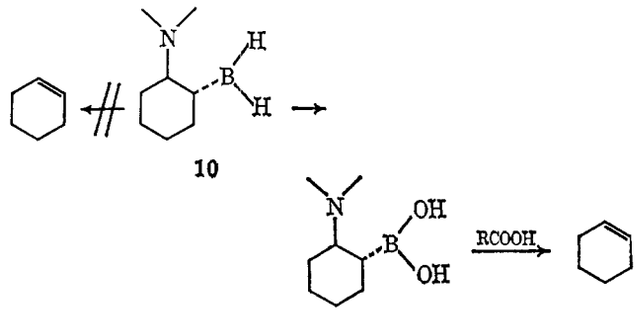
Hydroboration of **3d** with an excess of borane in tetrahydrofuran gives **9** (R = D) which does not undergo an uncatalyzed elimination, apparently due to the same reasons as outlined earlier for the differences between **4** (R = R′ = *n*-Pr) and **4** (R = R′ = D). Additional evidence supporting the above view is provided by the observation that the hydroboration product of the enamine of cyclohexanone (**10**) does not undergo a spontaneous elimination, but on conversion to the

(18) Similar differences have been noted in the properties of phenylthioborane *vs.* benzylthioborane.[17]

(19) D. J. Pasto, C. C. Cumbo, and J. Fraser, *ibid.*, **88**, 2194 (1966).

(20) D. J. Pasto, C. C. Cumbo, and J. Hickman, *ibid.*, **88**, 2201 (1966).



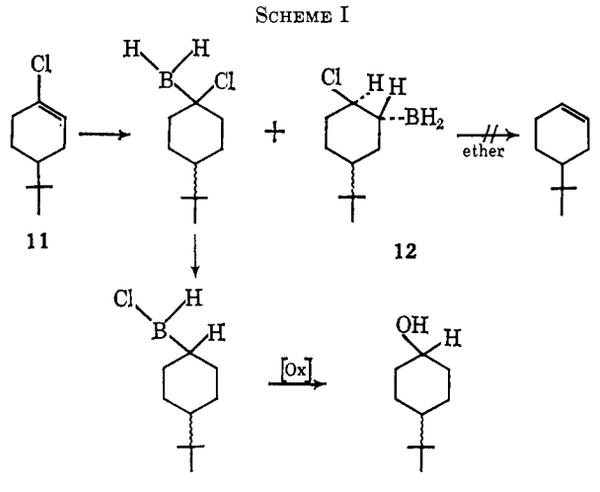
10

boronic acid followed by treatment with a carboxylic acid elimination occurs with the formation of cyclohexene.[11]

The hydroboration of *trans*-β-bromostyrene does not lead to the formation of styrene, the predominant adduct formed being the α-bromoorganoborane.[1] Evidence concerning the stereochemistry of eliminations involving β-haloorganoboranes is, however, provided by the results obtained in the hydroboration of 4-*t*-butyl-1-chlorocyclohexene (**11**) and the results reported by Cristol, Parungo, and Plorde.[7] The hydroboration of 2-chlorodibenzobicyclo[2.2.2]octatriene and bromo-*cis*-stilbene in diethyl ether is reported to give stable β-haloorganoboranes which on further treatment with water produced the dehalogenated olefins.[7] Hydroboration of the same olefins in tetrahydrofuran resulted in an immediate elimination producing olefins. Similar results have been observed with 4-*t*-butyl-1-chlorocyclohexene.[1]

The hydroboration of 4-*t*-butyl-1-chlorocyclohexene introduces approximately 40% of the boron at the 2-position to give 5-*t*-butyl-*trans*-2-chlorocyclohexylborane **12**.[1] In tetrahydrofuran this adduct undergoes an immediate *trans* elimination giving 4-*t*-butylcyclohexene which undergoes subsequent hydroboration to give approximately a 50:50 mixture of the 3- and 4-cyclohexyl derivatives. Hydroboration of **11** in diethyl ether, followed by the oxidative procedure of Cristol, Parungo, and Plorde[7] employing a per acid in chloroform, produced as the only simple alcohols the *cis*- and *trans*-4-*t*-butylcyclohexanols in the *t*-butylcyclohexanol fraction. These two products are formed by an α-transfer reaction which appears to an uncatalyzed reaction. No attempts were made to characterize the oxidation products of **12**. (See Scheme I.)

SCHEME I



The *trans*-β-chloroorganoborane **12** does not undergo elimination in diethyl either to give 4-*t*-butylcyclohexene as evidenced by the lack of the 3-*t*-butylcyclohexanols (intermediate **12** cannot undergo a β transfer owing to the stereochemistry of the system). The difference in the reactivity of **12** in tetrahydrofuran relative to diethyl ether must be due to the greater basicity of tetrahydrofuran[21] which is capable of affecting a base-catalyzed elimination of the β-haloorganoboranes.

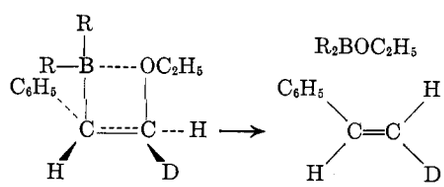
Unfortunately we have not been able to determine the stereochemistry of the elimination reactions involving acyclic β-haloorganoboranes. Attempts to isolate the 2-butenes and stilbenes that might be formed by the elimination reactions involving the β-haloorganoboranes derived from the 2-bromo- and 2-chloro-2-butenes and bromo- and chloro-*cis*-stilbenes, respectively, have met with failure. The olefins formed in the elimination are more reactive toward hydroboration than are the starting vinyl halides and are thus destroyed essentially as fast as they are formed.

The observation that β-ethoxyorganoboranes undergo uncatalyzed eliminations, whereas β-aryl- and alkylmercaptoorganoboranes do not, might lead one to expect that acyclic β-chloro- and bromoorganoboranes should not undergo uncatalyzed eliminations. This would appear to be the case with the intermediate derived from bromo-*cis*-stilbene reported by Cristol, Parungo, and Plorde.[7,22] Stable β-bromo- and chloroorganoboranes have been prepared by Hawthorne and Dupont[4] and Matteson and Liedtke[8] although strong electron-donating groups were present on the boron atom.

Summary

The results of the various eliminations are tabulated in Table II.

The mechanism of the uncatalyzed elimination involving intermediates **4** may be pictured as follows.



Similar reasonable transition states can be written for other oxygen containing functional groups, such as acetate, benzoate, hydroxyl, etc. No definitive results are available concerning the stereochemistry of such eliminations although one might expect these to be *cis* also. The occurrence of such uncatalyzed *cis* eliminations is highly dependent on the substituents bonded to the boron atom, and apparently on the heteroatom X although information is available only on oxygen, sulfur, chlorine and bromine containing systems.

The mechanism of the acid-catalyzed eliminations is pictured as follows.

(21) J. F. Deters, P. A. McCusker, and R. C. Pilger, Abstracts of the 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964, p 6V.

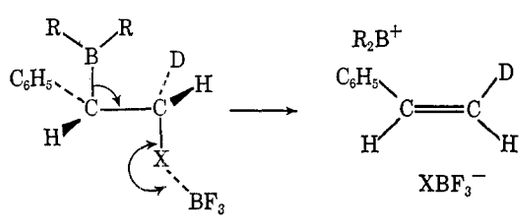
(22) We were unable to detect any stilbene formation with bromo- and chloro-*cis*-stilbene in diethyl ether under a variety of conditions even though extensive hydroboration had occurred. Cristol, Parungo, and Plorde did not report the conditions for the hydroboration of bromo-*cis*-stilbene and our inability to isolate stilbene in our experiments may be due to a difference in reaction conditions.

TABLE II

ELIMINATION REACTIONS INVOLVING $C_6H_5CH(RR'B)-CH_2X$

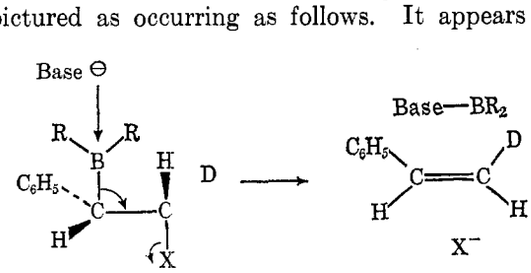
R	R'	X	Catalyst	Stereochemistry of elimination
n-C_3H_7	n-C_3H_7	OC_2H_5	None	*cis*
n-C_3H_7	n-C_3H_7	OC_2H_5	BF_3	*trans*
n-C_3H_7	n-C_3H_7	OC_2H_5	n-BuLi	*trans*
OCH_3	OCH_3	OC_2H_5	None	No elimination
OCH_3	OCH_3	OC_2H_5	BF_3	*trans*[a]
OCH_3	OCH_3	OC_2H_5	n-BuLi[b]	No elimination
SC_6H_5	H	OC_2H_5	None	*cis*[a]
H	H	OC_2H_5	None	*cis*[c]
n-C_3H_7	n-C_3H_7	SC_6H_5	None	No elimination
n-C_3H_7	n-C_3H_7	$SCH_2C_6H_5$	None	No elimination
n-C_3H_7	n-C_3H_7	SC_6H_5	BF_3	No elimination
n-C_3H_7	n-C_3H_7	$SCH_2C_6H_5$	BF_3	*trans*
n-C_3H_7	n-C_3H_7	SC_6H_5	n-BuLi	*trans*
n-C_3H_7	n-C_3H_7	$SCH_2C_6H_5$	n-BuLi	*trans*
n-C_3H_7	n-C_3H_7		None	*trans*
H	H[d]		None	No elimination

[a] Assumed to be *trans* by analogy with other acid-catalyzed eliminations, deuterium labeling experiments were not run. [b] Employed in a 1:1 mole ratio of n-BuLi to organoborane. [c] This elimination appears to be much slower. The liberated styrene could not be isolated owing to subsequent hydroboration of the styrene. [d] The stage to which the hydroboration proceeded is not known. Hydrogen evolution studies are not diagnostic.



Although R_2B^+ is pictured as the cationic leaving group, this is undoubtedly highly solvated by the solvent tetrahydrofuran. Miller and Muetterties have reported the existence of cationic borane complexes of the type $H_2B(base)_2^+$ in which the (base) is a tertiary amine, phosphine, arsine, or dialkyl sulfide.[23] Similar R_2B^+ species, where R = H, n-Pr, OCH_3 or H and C_6H_5S, have been previously postulated in the reactions of epoxides with phenylthioborane[19] and borane.[20] Substituents X which have been found to undergo such acid-catalyzed eliminations include alkoxy, alkylthio (but not arylthio), and amino.

The mechanism of the base-catalyzed eliminations is pictured as occurring as follows. It appears that



the only requirement governing this reaction is that of the base strength of the added base.

(23) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

Experimental Section

Preparation of *cis*-β-Ethoxystyrene.—To a refluxing solution of sodium ethoxide in ethanol, prepared by dissolving 23 g of sodium in 300 ml of absolute ethanol, in a 1-l. three-necked flask equipped with a pressure-equalizing addition funnel and a condenser, was added 20.4 g (0.2 mole) of phenylacetylene. After refluxing the reaction mixture for 14 hr the reaction mixture was poured into 20 ml of water, which after cooling separated into two layers. The aqueous phase was extracted with two 50-ml portions of ether and combined with the organic layer. The solvent was removed under reduced pressure and the residue was distilled at 62° at 0.2 mm (87%).

The nuclear magnetic resonance spectrum displayed the following absorption patterns: triplet at −75.5 cps (relative to tetramethylsilane), quartet at −229.8 cps, AX doublets at −305 and −361 cps with J 7.3 cps, and phenyl hydrogen absorption at −437 cps.

Isomerization of *cis*-β-Ethoxystyrene.—A. A solution of 2 ml of *cis*-β-ethoxystyrene in 90% Skelly B-10% benzene was placed on a Woelm activity I alumina column and was allowed to stand for 12 hr at room temperature. Elution with the same solvent system produced a mixture of *cis*- and *trans*-β-ethoxystyrene as was evidenced by the gas–liquid partition chromatogram and the nuclear magnetic resonance spectrum which displayed two sets of AX doublets in the vinyl region at −305 and −359 cps, with J 7.2 cps and at −339 and −412 cps with J 12.1 cps.

B. A solution of 1 ml of *cis*-β-ethoxystyrene in 150 ml of ether was irradiated for 16 hr with a 250-w Hanovia immersion lamp. Analysis of the mixture showed the presence of *cis*- and *trans*-β-ethoxystyrene.

Preparation of "Di-*n*-propyldeuterioborane."—To a solution of perdeuterioborane in tetrahydrofuran, external generation of perdeuterioborane from lithium aluminum deuteride in diglyme with boron trifluoride etherate, was added tri-*n*-propylboron in a 1:2 mole ratio of perdeuterioborane:tri-*n*-propylboron. The solution was allowed to stand at room temperature for 24 hr. An aliquot of the solution was quenched by the addition of an excess of *cis*-2-butene in tetrahydrofuran. Gas–liquid partition chromatographic analysis of the quenched mixture on a silicone oil column revealed the presence of 40% tri-*n*-propylboron, 38% di-*n*-propyl-*sec*-butylboron, 22% mono-*n*-propyl-di-*sec*-butylboron, and a trace of tri-*sec*-butylboron.

Deuterioboration of *cis*-β-Ethoxystyrene with "(n-C_3H_7)$_2$BD." Noncatalyzed Elimination Studies.—To a solution of 9.3 mmoles of "(n-C_3H_7)$_2$BD" in about 10 ml of tetrahydrofuran at 0° was added 1.37 g (9.3 mmoles) of *cis*-β-ethoxystyrene. The reaction mixture was stirred at room temperature for 1 hr. The reaction mixture was hydrolyzed with a 20% excess of sodium hydroxide and oxidized by the addition of a 20% excess of 30% hydrogen peroxide. The reaction mixture was extracted with ether, the extract dried over magnesium sulfate and the solvent removed by distillation. The residue was distilled under reduced pressure into a flask immersed in a Dry Ice–acetone bath. Gas–liquid partition chromatographic analysis of the distillate showed the presence of styrene (up to 42%) and some solvent peaks. The nuclear magnetic resonance spectrum of the distillate displayed two doublets at −339 and −398 cps, with J 17.8 cps, the latter doublet further split into three lines with J_{HD} 1.5 cps.

Control experiments were carried out showing that the starting olefin was not isomerized in the presence of borane prior to hydroboration, and that the styrene was formed prior to work-up. The addition of an excess of *cis*-β-ethoxystyrene to borane in tetrahydrofuran, followed by recovery of the excess starting material and analysis by nuclear magnetic resonance, showed that no isomerization had occurred. That the styrene is formed prior to work up was shown in the following manner. Methanol was added to the hydroboration reaction mixture and the solvent was carefully removed by distillation. The remaining residue was subjected to vacuum distillation at room temperature, the distillate being collected in a flask immersed in a Dry Ice–acetone bath. Gas–liquid partition chromatographic analysis showed the presence of styrene.

Acid-Catalyzed Elimination.—To 9.3 mmoles of "(n-C_3H_7)BD" in 10 ml of tetrahydrofuran at 0° was added 1.37 g (9.3 mmoles) of *cis*-β-ethoxystyrene. The reaction mixture was stirred at 0° for 20 min and 1.32 g (9.3 mmoles) of boron trifluoride etherate was added maintaining the temperature of the reaction mixture below 5°. The mixture was hydrolyzed and oxidized, and the product was isolated as described above. The nuclear magnetic

resonance spectrum of the distillate displayed doublets at −309 cps (J 12.2 cps) and −340 cps (J 17.9 cps) (in an area ratio slightly greater than 5:1), and a doublet each line of which was further split into three equally intense lines at −399 cps with J_{HH} 12.2 cps and J_{HD} 2.8 cps.

Base-Catalyzed Elimination.—To 7.5 mmoles of "(n-C_3H_7)$_2$BD" in 10 ml of tetrahydrofuran at 0° was added 1.11 g (7.5 mmoles) of *cis*-β-ethoxystyrene. The reaction mixture was stirred at 0° for 20 min and 4.6 ml of 1.6 N n-butyllithium (7.5 mmoles) was added maintaining the temperature below 5°. The product was isolated as described above. The nuclear magnetic resonance spectrum of the product showed doublets at −309 and −340 cps (J 11.5 and 17.3 cps, respectively) in an area ratio of 9:1, and a doublet, each line of which is further divided into three lines, at −397 cps., with J_{HH} 11.5 cps and J_{HD} 2.7 cps.

Preparation and Eliminations Involving Dimethyl 2-Ethoxy-1-phenylethylboronate.—To 5.6 ml of 1.78 M perdeuterioborane in tetrahydrofuran (10 mmoles) at 0° was added 0.74 g (5 mmoles) of *cis*-β-ethoxystyrene. Immediately after the addition of the ethoxystyrene 0.96 g (30 mmoles) ofm ethanol was added to the reaction mixture. The boron-11 magnetic resonance spectrum of the reaction mixture showed peaks at −18.9 ppm (relative to internal capillary boron trifluoride etherate) for trimethyl borate and at −31.7 ppm for dimethyl 2-ethoxy-1-phenylethylboronate.

Attempted Noncatalyzed Elimination.—One-fourth of the reaction mixture was allowed to stand at room temperature for 8 hr; a portion was worked up as described above. No styrene was detected by gas–liquid partition chromatography. The remaining portion was refluxed in tetrahydrofuran for 30 min. No styrene was detected after work-up.

Acid-Catalyzed Elimination.—One-fourth of the original reaction mixture was treated with 0.2 ml of boron trifluoride etherate. Analysis, following the usual work-up, showed the presence of mostly styrene in the gas–liquid partition chromatography.

Attempted Base-Catalyzed Elimination.—To one-fourth of the original reaction mixture was added an equivalent amount of n-butyl lithium. The reaction was worked up as above and analyzed showing only a trace of styrene, the predominant product being 1-phenyl-2-ethoxyethanol.

Hydroboration of *cis*-β-Ethoxystyrene with Phenylthioborane.—To a solution of phenylthioborane in tetrahydrofuran at 25° was added an equimolar amount of *cis*-β-ethoxystyrene. The reaction mixture was allowed to stir at room temperature for 3 hr. Gas–liquid partition chromatographic analysis of the product mixture, following the usual work-up, produced mostly 2-phenylethanol and 1-phenylethanol in a ratio slightly larger than 4:1 indicating the intermediacy of styrene.

Preparation of *cis*-β-Phenylmercaptostyrene.—*cis*-β-Phenylmercaptostyrene was prepared by the addition of thiophenoxide to phenylacetylene in absolute ethanol. The nuclear magnetic resonance spectrum of the product in carbon tetrachloride displayed AB doublets at −381 and −387 with J 10.8 cps.

Isomerization of *cis*-β-Phenylmercaptostyrene.—The nuclear magnetic resonance sample tube was exposed to moderate sunlight for 1 hr. The nuclear magnetic resonance spectrum showed a new, and more intense band than the *cis* AB doublets, AB system at −396 and −405 cps with J 15.8 cps.

Deuteroboration of *cis*-β-Phenylmercaptostyrene with "(n-C_3H_7)$_2$BD." Attempted Noncatalyzed Elimination.—To 12 mmoles of "(n-C_3H_7)$_2$BD" in tetrahydrofuran at 0° in a flask protected from sunlight was added 2.12 g of *cis*-β-phenylmercaptostyrene. The reaction mixture was stirred at room temperature for 24 hr. Aliquots removed during this time showed no styrene when analyzed by ultraviolet spectroscopy. An excess of methanol was added to the reaction mixture and the volatile materials distilled under reduced pressure into a flask immersed in a Dry Ice–acetone bath. Analysis of the distillate by gas–liquid partition chromatography showed that no styrene was present. Analysis of the nuclear magnetic resonance spectrum of the original hydroboration mixture also showed the absence of styrene.

Attempted Acid-Catalyzed Elimination.—A portion of an original deuterioboration mixture formed from *cis*-β-phenylmercaptostyrene and "(n-C_3H_7)$_2$BD" was mixed with an equimolar amount of boron trifluoride etherate in a nuclear magnetic resonance tube and the spectrum was then recorded. The spectrum showed no peaks characteristic of a β-deuteriostyrene.

Base-Catalyzed Elimination.—A portion of an original deuterioboration mixture from *cis*-β-phenylmercaptostyrene and "(n-C_3H_7)$_2$BD" was mixed with an equimolar amount of n-butyllithium producing a fine precipitate. The precipitate was allowed to settle and the supernatant liquid was removed and the nuclear magnetic resonance spectrum of the sample was recorded showing a doublet at −305 cps with J 10.6 cps. No absorption was observed in the −340 cps region.

Preparation of *trans*-β-Benzylmercaptostyrene.—A mixture of 24.6 g (0.2 mole) of benzylmercaptan and 20.4 g (0.20 mole) of phenylacetylene was heated at 110° under nitrogen for 10 hr. The reaction mixture was poured into water and extracted with ether. The extract was washed with aqueous sodium hydroxide, water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was distilled at 185° at 2 mm. Fractional recrystallization from petroleum ether gave 12 g of the *trans* isomer, mp 67.5–68°.[21] The nuclear magnetic resonance spectrum showed AB doublets at −384 and −395 cps with J 15.5 cps.

Deuteroboration of *trans*-β-Benzylmercaptostyrene with "(n-C_3H_7)$_2$BD." Attempted Noncatalyzed Elimination.—To 15 mmoles of "(n-C_3H_7)$_2$BD" in tetrahydrofuran at 0° was added 15 mmoles of *trans*-β-benzylmercaptostyrene. The reaction mixture was stirred at room temperature for 24 hr and the reaction mixture was quenched by the addition of methanol. The volatile components of the quenched mixture were distilled under reduced pressure into a flask immersed in a Dry Ice–acetone bath. Analysis of the distillate by gas–liquid partition chromatography showed no styrene.

Acid-Catalyzed Elimination.—*trans*-β-Benzylmercaptostyrene (2.26 g, 10 mmole) was deuteroborated with 10 mmoles of "(n-C_3H_7)$_2$BD" in tetrahydrofuran at 0°. After allowing the reaction mixture to stir at room temperature for 18 hr, one-third of the reaction mixture was removed, boron trifluoride etherate was added, and the reaction mixture was then quenched with methanol. The volatile materials were then removed by distillation under reduced pressure into a collection flask immersed in a Dry Ice–acetone bath. The nuclear magnetic resonance spectrum showed peaks corresponding to only *trans*-β-deuteriostyrene.

Base-Catalyzed Elimination.—One-third of the foregoing deuterioboration mixture was treated with an equimolar amount of n-butyllithium. The reaction mixture was quenched by the addition of methanol and the volatiles isolated as indicated above. The nuclear magnetic resonance spectrum of the distillate showed the presence of only *trans*-β-deuteriostyrene.

Preparation of *trans*-β-Pyrolidinostyrene.—To a solution of 30 g (0.25 mole) of phenylacetaldehyde in 150 ml of benzene in a round bottom flask equipped with a Dean-Stark trap and condenser was cautiously added 23.3 g (0.37 mole) of freshly distilled pyrolidine in the presence of a trace of p-toluenesulfonic acid. After the initial exothermic reaction subsided, the reaction mixture was refluxed until no more water was collected in the trap. The benzene and pyrolidine were removed by distillation and the residue was distilled under reduced pressure at 131° at 0.6 mm. The pyrolidinostyrene rapidly turns brown on exposure to air and light. The nuclear magnetic resonance spectrum showed an X portion of an AX system at −301.2 cps with J 14.9 cps with the A portion buried under the phenyl hydrogen absorption region.

Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.09. Found: C, 83.16; H, 8.65; N, 8.18.

Deuteroboration of *trans*-β-Pyrolidinostyrene.—To 10.8 mmoles of "(n-C_3H_7)$_2$BD" in tetrahydrofuran at 0° was added 1.73 g (10 mmoles) of *trans*-β-pyrolidinostyrene. The reaction mixture was stirred for 24 hr at room temperature and was then quenched by the addition of a slight excess of methanol. The volatile materials were distilled under reduced pressure into a flask immersed in a Dry Ice–acetone bath. Gas–liquid partition chromatographic analysis showed the presence of styrene (13.5%). The nuclear magnetic resonance spectrum of the distillate showed only doublets at −337 and −399 cps, with J 17.5 cps, in the vinyl region, with the latter doublet further split into three lines with J_{HD} 1.5 cps.

Hydroboration of *trans*-β-Pyrolidinostyrene.—Hydroboration of *trans*-β-pyrolidinostyrene with borane in tetrahydrofuran in a mole ratio of 1:2 at 0° did not produce any styrene (or any of the phenylethanols) when analyzed as above (or oxidized and analyzed after work-up). The products of the reaction were not identified.

Hydroboration of 4-*t*-Butyl-1-chlorocyclohexene in Diethyl Ether Followed by Per Acid Oxidation.—A solution of 1 g (5.8 mmoles) of 4-*t*-butyl-1-chlorocyclohexene in 50 ml of freshly dried

diethyl ether was cooled at 0° and a 100% excess of diborane, generated externally from sodium borohydride and boron trifluoride etherate, was bubbled into the solution with a stream of nitrogen. The reaction mixture was allowed to stand at room temperature for 4 hr and most of the ether and excess diborane were removed by distillation under nitrogen. The residue was dissolved in 50 ml of dry chloroform and a 20% excess of *m*-chloroperbenzoic acid was added and allowed to stand for 24 hr. The solution was washed with several small portions of acidified 5% ferrous ammonium sulfate. The chloroform was removed under reduced pressure. The residue was dissolved in 30 ml of ether and 5 ml of pyridine and 10 ml of acetic anhydride was added and allowed to stand at room temperature for 16 hr. Direct analysis of the mixture by gas–liquid partition chromatography on a 30-ft 20% Carbowax 20M on firebrick column showed the presence of *cis*- and *trans*-4-*t*-butylcyclohexyl acetate in approximately a 65:35 ratio. No *cis*- or *trans*-3-*t*-butylcyclohexyl acetate was present.

A New Synthesis of Tetracyanocyclopropanes

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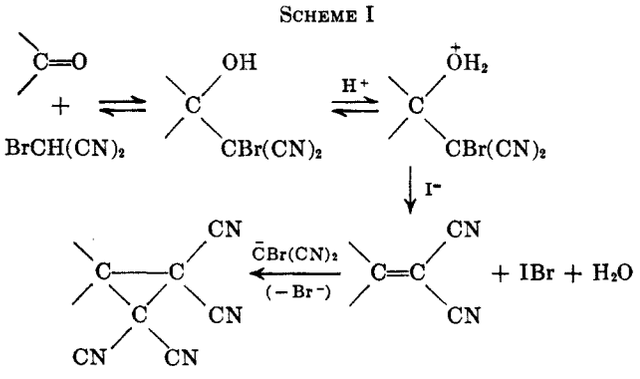
Alkylidenemalononitriles ($R_1R_2C{=}C(CN)_2$) are shown to react at room temperature with bromomalononitrile in aqueous ethanol to produce tetracyanocyclopropanes in good yields. Examples include $R_1 = CH_3$; $R_2 = CH_3$, C_2H_5, *n*- and *i*-C_3H_7, *n*-C_5H_{11}, aryl; and $R_1 = C_2H_5$; $R_2 = C_2H_5$, C_6H_5; $R_1 = R_2$ = cyclopropyl. Spirocyclopropanes were obtained from cycloalkylidenemalononitriles with 5-, 6-, 10-, 12-, and 15-membered rings. In many instances this method provides a better route to tetracyanocyclopropanes than the Wideqvist reaction (carbonyl compound, bromomalononitrile, and iodide ion), which either fails altogether or, in the case of aryl methyl ketones, gives low yields. It probably represents the final stage of the Wideqvist reaction. The present reaction seems sensitive to steric factors, either proceeding poorly or failing altogether when R_1 and/or R_2 are long chains or highly branched. In two instances (2,3-benzocyclohexylidenemalononitrile and 2,3-benzocyclopentylidenemalononitrile) the substrate underwent bromination rather than cyclopropanization, although with the former the direction could be controlled by relatively minor changes in solvent polarity. Bromomalononitrile reacts with aqueous ethanol, either on prolonged standing or on reflux, to give 1,1-dicyano-2-amino-2-ethoxyethene.

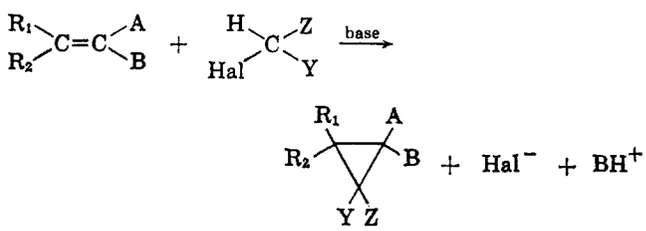
Wideqvist and Ramberg showed[1] that certain carbonyl compounds react with bromomalononitrile and iodide ion to produce tetracyanocyclopropanes. The reaction, now referred to as the Wideqvist reaction,[2] is fairly general,[3,4] although certain limitations were encountered which will be described in more detail below. It was suggested[3] that the Wideqvist reaction follows the scheme shown, the function of the iodide ion being to bring about an elimination reaction to form alkylidenemalononitrile. (See Scheme I.)

SCHEME I



In order to test the last step in this scheme, we have prepared a number of alkylidenemalononitriles and allowed them to react with bromomalononitrile in the absence of iodide ion. In many cases tetracyanocyclopropanes were formed quickly and in high yield; indeed, this procedure allows the preparation of a number of tetracyanocyclopropanes which cannot be obtained directly by the Wideqvist reaction, presumably because under the conditions normally used for that reaction the first equilibria shown in the scheme may be unfavorable.

It should be pointed out that the literature abounds in examples of syntheses of polyfunctional cyclopropanes by the base-catalyzed condensation of activated α,β-unsaturated systems with α-halo esters, ketones, nitriles, etc., followed by intramolecular dehydrohalogenation.[5-10] The present work involves a similar



(A, B, Y, and Z are generally electron-withdrawing groups)

type of reaction except that base is omitted, because bromomalononitrile is a reasonably strong acid[11] which can furnish a sufficient concentration of bromodicyanocarbanion for reaction.[12]

(1) L. Ramberg and S. Wideqvist, *Arkiv. Kemi*, **12A**, No 22 (1937); S. Wideqvist, *ibid.*, **20B**, No 4 (1945).

(2) H. Hart and F. Freeman, *J. Am. Chem. Soc.*, **85**, 1161 (1963).

(3) H. Hart and F. Freeman, *J. Org. Chem.*, **28**, 1220 (1963).

(4) R. M. Scribner, G. N. Sausen, and W. W. Prichard, *ibid.*, **25**, 1440 (1960).

(5) O. Widman, *Ber.*, **51**, 533, 907 (1918).

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