tails of the gas chromatography trapping procedures. We also wish to thank the Esso Research and

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# Transfer Reactions Involving Boron. III. Hydroboration Studies with Enethiol Ethers[1]
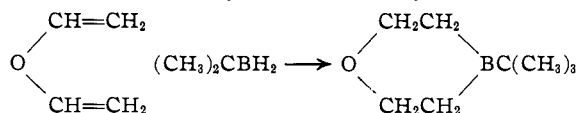
BY D. J. PASTO AND J. L. MIESEL[2]

A new rearrangement reaction of unstable substituted organoboranes is reported. Hydroboration of enethiol ethers gives both possible substituted organoboranes in which hydrogen and carbon undergo an intramolecular transfer from boron to carbon with the sulfur residue migrating from carbon to boron. The reactions are proposed to proceed via four-centered transition states.

Introduction

The reaction of diborane with unsaturated compounds has received much attention in the past few years. The vast majority of substrates investigated thus far have been non-functionally substituted olefins and acetylenes.[3] Several examples of addition of the B–H moiety to olefins have been reported in which a functional group was in a vinylic or allylic position. These include vinyltrimethylsilane,[4] allyltrimethyl- and allyltrichlorosilane,[5] dimethyldivinylsilane,[6] divinyl ethyl,[6] ethyl vinyl ether,[5] allyl methyl sulfide,[7] vinyl and allyl chlorides,[8] substituted allyl chlorides[9] and 3-chlorocyclohexene.[9] The substituted organoboranes derived from vinyl chloride and 3-chlorocyclohexene were unstable and underwent transfer of chlorine from carbon to boron with the elimination of the corresponding olefin. Hydroboration of allyl chloride led to the
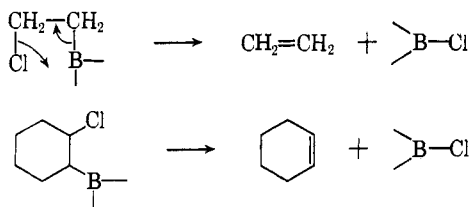
isolation of tri-(γ-chloropropyl)-borane, di-(γ-chloropropyl)-boron chloride and a product identified tentatively as γ-chloropropylboron dichloride. Hawthorne[8] suggests that the latter two products might arise by chlorine transfer from carbon to boron with the generation of cyclopropane which was not isolated. The addition of mono-t-butylborane to divinyl ether[6] led to the formation of 1-t-butyl-1-bora-4-oxacyclohexane. Ac-

cordingly, Brown[3] has divided substituted organoboranes into two divisions: (1) derivatives with relatively inert substituents and (2) derivatives with reactive (leading to unstable intermediate organoboranes) substituents.[10]

It is obvious that a systematic study is needed to determine the effects of substituents on the stability of organoboranes, the above few examples representing different types of structures from which little information can be gained as to the over-all picture. This article is part of an investigation on substituent effects and reports a new mode of reaction available for "unstable" organoboranes.

Results

Phenyl 1-Phenyl-1-propenyl Sulfide (I).—Treatment of I with diborane followed by hydrolysis and oxidation with hydrogen peroxide produced a volatile fraction which, when separated on Florisil, gave thioanisole (II) (50%) and an alcoholic fraction (26.5%). The alcohol fraction was shown to be 1-phenyl-1-propanol (III) and 1-phenyl-2-propanol (IV) in a ratio of 98:2. Careful analysis of the crude reaction mixture by gas–liquid chromatography (G.L.C.) showed that no n-propyl- or propenylbenzene was formed during the reaction.

The non-volatile fraction was separated by column chromatography on Florisil. The first fraction obtained was diphenyl disulfide (V). Immediately following V, a neutral sulfur-containing material, 9.4% ($C_{13}H_{16}S$) was eluted whose n.m.r. spectrum displayed a triplet at 9.13 τ (J of 7.7 c.p.s.) with an intensity of three protons, a multiplet at 8.10 τ corresponding to two protons, a four-peak pattern representing the A proton of an AB_2 system[11] at 6.02 τ, and aromatic protons at 2.87 τ (ten protons). The compound was identical spectrally with phenyl 1-phenylpropyl sulfide (VI), prepared by treating 1-phenyl-1-propyl chloride with sodium thiophenoxide, and gave a sulfone identical in melting point and mixture melting point with authentic sulfone. Elution with 40–50% benzene–petroleum ether provided a colorless viscous oil (1.6%) whose infrared spectrum showed the presence of a hydroxyl group (2.9 μ). The infrared and n.m.r. (two overlapping triplets at 9.40 and 9.32 τ representing six protons, a multiplet centered at 8.23 τ of four protons, a singlet at 8.16 τ (hydroxyl proton), a four-peak pattern for the A proton of an AB_2 system at 7.31 τ and aromatic protons at 3.09 τ) spectra were identical with those of 3,4-diphenyl-2-hexanol (VII), prepared by ethylation of desoxybenzoin[12] followed by treatment with ethylmagnesium iodide.[13]

(1) For previous articles in this series see: (a) D. J. Pasto, J. Am. Chem. Soc., **84**, 3777 (1962); (b) D. J. Pasto and J. L. Miesel, ibid., **84**, 4991 (1962).

(2) Taken in part from the Bachelor's Thesis of J. L. M.

(3) For an excellent book on the subject see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(4) D. Seyferth, J. Inorg. Nucl. Chem., **7**, 152 (1958).

(5) B. M. Mikhailov and T. A. Shchegoleva, Izvest. Akad. Nauk S.S.S.R., 546 (1959).

(6) M. F. Hawthorne, J. Am. Chem. Soc., **83**, 2541 (1961).

(7) H. C. Brown and K. Murray, ibid., **81**, 4108 (1959).

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

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

(10) The hydroboration of an enamine of cyclohexanone has been reported to give a stable substituted organoborane which on hydrolysis and oxidation gave a trans-2-substituted aminocyclohexanol (G. Stork, reported before the Organic Division at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 6, 1961.

(11) 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. 123–128.

(12) V. Meyer and L. Oelkers, Ber., **21**, 1299 (1888).

(13) G. Brownlee, F. C. Copp, W. M. Duffin and I. M. Tonkin, Biochem. J., **37**, 572 (1943).

A crystalline alcohol (12%) was eluted with 30–70% chloroform–benzene having a melting point of 138.0–138.8° and a molecular weight of 254. The n.m.r. spectrum displayed a triplet at 9.45 τ with J 6.3 c.p.s., a doublet at 9.12 τ, and multiplets at 8.71, 7.06, 6.36 and 2.94 τ. Chromic acid oxidation gave a crystalline ketone with melting point 127.2–128.0° and with infrared absorption at 5.80 μ (in carbon tetrachloride). The n.m.r. of the ketone displayed a triplet for three protons at 9.42 τ with J 6.6 c.p.s., a complex multiplet at 8.67 τ for two protons, a singlet for three protons at 8.29 τ, an eight peak group for the B portion of an A_2–B–X system at 6.78 τ, a doublet for one proton at 6.15 τ and aromatic protons at 2.78 and 2.68 τ (ten protons). The infrared and n.m.r. spectra of the ketone show that its structure must be that of 3,4-diphenyl-2-hexanone (VIII). Compound VIII has been prepared by Fross and co-workers[14] with a reported melting point of 127°. The alcohol is thus 3,4-diphenyl-2-hexanol (IX). Two other fractions of 1% or less were isolated but could not be identified. Neither of these fractions had spectral properties expected of 1-phenyl-1-thiophenyl-2-propanol (X) or propiophenone (XI). Hydrolysis of the reaction mixture of I and diborane with sodium deuteroxide in deuterium oxide, followed by oxidation with hydrogen peroxide, gave sulfide VI, in which deuterium had been incorporated only at the benzylic position as determined by n.m.r. analysis.
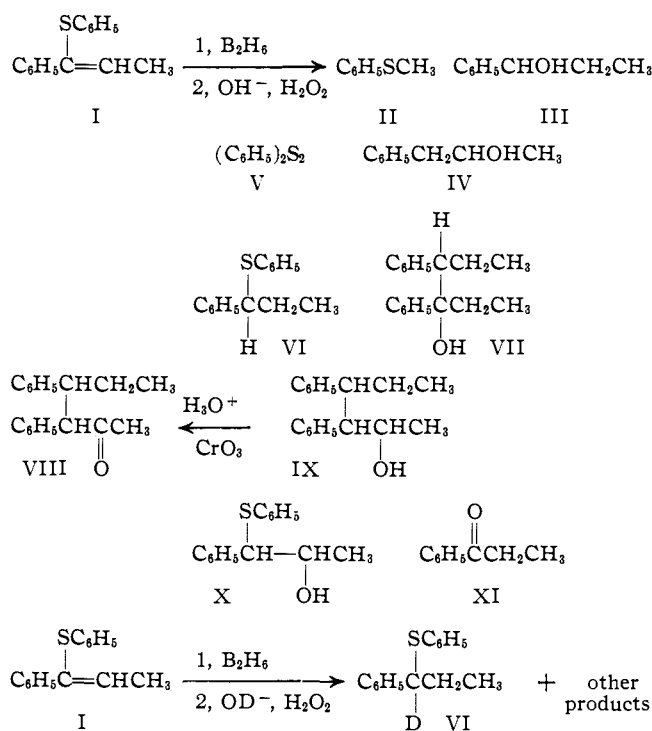

Phenyl Propenyl Sulfide (XII).—The volatile products, from the reaction of XII with diborane (mole ratio of 4:1.1) followed by basic hydrolysis and peroxide oxidation, were analyzed by G.L.C. showing the presence of 2-propanol (XIII) (3.9%), 1-propanol (XIV) (47.8%), 2-hexanol (XV) (1.9%), II (31%), thiophenetole (XVI) (14.4%) and phenyl propyl sulfide (XVII) (14.2%). Chromatographic separation of the residue on Florisil after removing most of the more volatile components under reduced pressure gave V (20.4%), a trace of XVII and a small amount of a hydroxylic material which could not be unambiguously identified.

(14) D. A. Fross, W. Freund and E. R. Stove, *J. Chem. Soc.*, 5038 (1952).
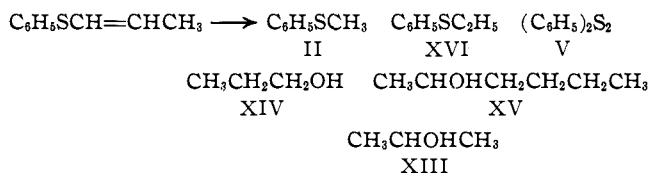
1-Phenyl-2-thiophenylethylene (XVIII).—Gas–liquid chromatographic analysis of the ether extract, from the treatment of either pure cis- or a mixture of cis- and trans-XVIII with diborane followed by the usual hydrolysis and oxidation, showed the presence of 57% II, a trace of XVI, 23.3% α-methylbenzyl alcohol (XIX) (yields are not corrected for recovered starting material) and 33.8% β-phenethyl alcohol (XX). After removal of the more volatile components under reduced pressure, the residue was chromatographed on Florisil giving 16.4% of trans-XVIII as identified by its infrared and n.m.r. spectra (see Experimental) and by conversion to the known sulfone, 1.8% phenyl β-phenethyl sulfide (XXI), 1.0% 1-phenyl-2-thiophenylethanol (XXII) as identified by infrared and n.m.r. spectral comparison with authentic material, and 7.9% of a viscous hydroxylic-containing material (apparently dimeric) which was not further separated.
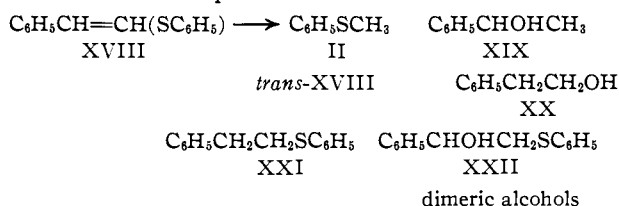
Hydrolysis and oxidation of the reaction after 10 minutes followed by G.L.C. analysis showed that 5.2% XIX and 20% XX had been formed.

trans-1-Phenyl-2-thiobenzylethylene (XXIII).—Analysis of the reaction product mixture from trans-XXIII with diborane in a mole ratio of 1:0.55 (using a mole ratio of 1:0.275 led to a 47% recovery of XXIII indicating that only a monoörganoborane was formed) as described for XVII showed the formation of 7.7% benzyl methyl sulfide (XXIV), 18.5% XIX, 38.6% XX, 57% bisbenzyl disulfide XXV, 0.6% benzyl β-phenethyl sulfide (XXVI), 6.6% 1-phenyl-2-thiobenzylethanol (XXVII) and 11.7% of a mixture of apparently dimeric alcohols which could not be separated.
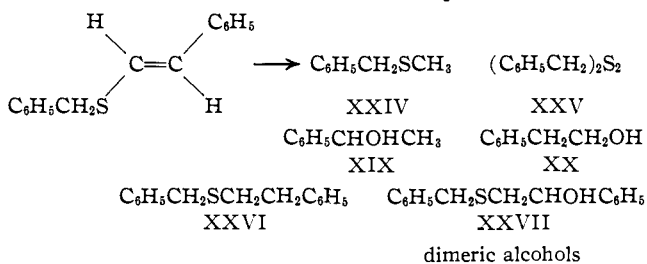

Allyl Phenyl Sulfide (XXVIII).—The reaction mixture of XXVIII and diborane in diglyme was allowed to stand at room temperature for three days. After hydrolysis and oxidation, G.L.C. analysis showed no XIII, 5.2% XIV, no hexanols and 8.1% II. Isolation of the hydroxysulfide fraction (55%) and analysis by n.m.r. showed it to contain 98% γ-hydroxypropyl phenyl sulfide (XXIX) and 2% β-hydroxypropyl phenyl sulfide (XXX). Maintaining the reaction mixture at 100° for 18 hours produced no XIII, 9.7% XIV, no hexanols and 21% II.

Allyl Benzyl Sulfide (XXXI).—Analysis by G.L.C. of the crude product from XXXI and diborane, with a reaction time of 3 days at room temperature, showed no XIII, no XIV and no XXIV. The n.m.r. spectrum of

the hydroxysulfide fraction (56%) isolated by distillation indicated a composition of 13% benzyl β-hydroxypropyl benzyl sulfide (XXXII) and 87% γ-hydroxypropyl benzyl sulfide (XXXIII). Maintaining the reaction temperature at 100° for 24 hours produced a trace of XIII, 2.1% XIV and 1.7% XXIV. The hydroxysulfide fraction (60%) contained 92% benzyl γ-hydroxypropyl sulfide (XXXIII) and 8% benzyl β-hydroxypropyl sulfide (XXXII).

1,1-Diphenyl-2-thiophenylethylene (XXXIV).—The reaction product from XXXIV and diborane (mole ratio of 1:0.55) when analyzed by G.L.C. on a GE SF-96 column at 238° showed the presence of 2,2-diphenylethanol (XXXV) and 1,1-diphenylethanol (XXXVI). No 1,2-diphenylethanol (XXXVII) was present. As a further check for XXXVII a portion of the crude product was carefully oxidized with acidic dichromate giving diphenylacetic acid and a neutral fraction which did not contain desoxybenzoin when analyzed by n.m.r. or treated with 2,4-dinitrophenylhydrazine. Compounds XXXV and XXXVI were formed in yields of 60 and 4%, respectively.
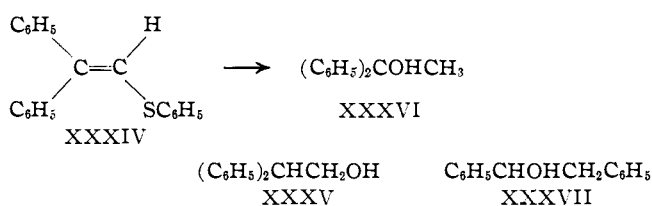

Discussion

From the results presented in the previous section it is evident that three basically different reactions have occurred in addition to simple hydration of the double bond. They are: (1) the removal of the substituted sulfur and replacement by hydrogen and substituted carbon residues, (2) the subsequent alkylation of the sulfur residue, and (3) reduction of the double bond.

Several pieces of evidence indicate that the reaction proceeds by addition of B–H to the double bond, for example the isolation of the β-hydroxysulfides XXII and XXVII from XVIII and XXIII. An alternate possibility is that borane could complex with the sulfur atom followed by a displacement of the vinyl sulfur group by hydrogen. That this does not occur is supported by the fact that in the treatment of I with diborane no propenylbenzene could be detected during the reaction, and secondly that the ratio of III to IV (98:2) is significantly different from that observed in the hydroboration of propenylbenzene (85:15).[3] (This latter fact also demonstrates that an insignificant amount of the intermediate organoborane XXXVIII underwent elimination to produce propenylbenzene, which then underwent hydroboration, and a sulfur-boron bonded species.)

The intermediate organoborane to give rise to the saturated sulfides, by a base-catalyzed reductive dealkylation,[15] was shown to be only XXXIX by deuterium studies. Deuterolysis of a reaction mixture of I with sodium deuteroxide in deuterium oxide gave VI in which deuterium had been incorporated only in the benzylic position. The above combined evidence shows that B–H adds to the double bond in both

(15) A. J. Weinheimer and W. E. Marsico, *J. Org. Chem.*, **27**, 1926 (1962), and references cited therein. The reaction proceeds with retention of configuration and has been proposed to proceed by the following mechanism where the carbon bonded to boron can sustain a negative charge.

SCHEME 1
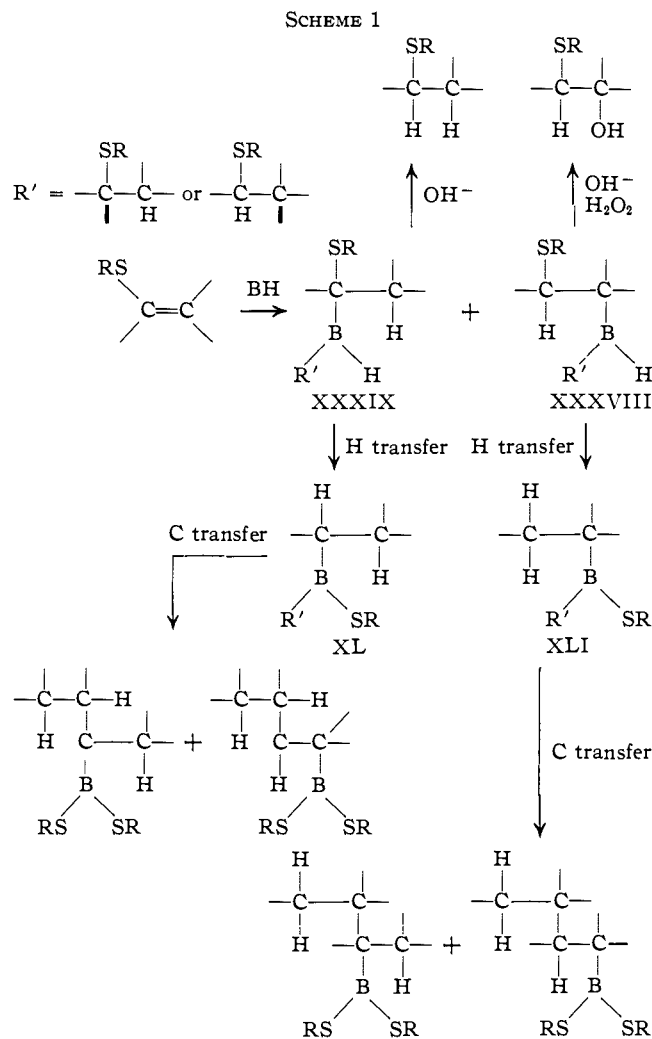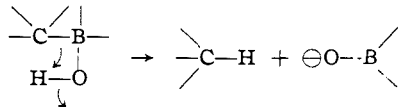
directions giving the intermediate organoboranes XXXVIII and XXXIX.

It is now necessary to explain the formation of the remaining products after having established the intermediacy of both possible addition products. If a hydrogen is bonded to boron in either XXXVIII or XXXIX, a transfer reaction occurs in which hydrogen is transferred from boron to carbon while the sulfur residue is transferred from carbon to boron (designated as H transfer). This type of transfer occurs when both sulfur and boron are geminal (designated as an α-transfer) as in XXXIX or vicinal (designated as a β-transfer) as in XXXVIII. Interruption of the reaction at this point by hydrolysis and oxidation would give the "desulfurized monomeric" alcohols. A similar explanation, with certain reservations to be discussed in the following paragraphs, can account for the observed replacement of the sulfur group by substituted carbon (designated as C transfer).

At this point it is necessary to discusss why these transfer reactions occur and the reason why only certain products are formed. Summation of the bond energies[16] involved indicates that H transfer is favored over C transfer by at least 5 kcal./mole and in fact it is probably more like 15–20 kcal./mole. Therefore, if XXXVIII and XXXIX are actually diorganoboranes (R' being one of the two possible organic residues formed by BH addition), competition between H and C transfer would exist with H transfer predominantly occurring first. The resulting products XL and XLI

(16) Although adequate values for bond energies in systems similar to these are not available it is possible to set reasonable limits for the necessary bond energies.

then contain one desulfurized organic residue and one original organic residue still containing sulfur. The only possible rearrangement left is now a C transfer leading to "dimeric" products. In support of this sequence of events is the fact that the "dimeric" products found do not contain sulfur.

Hydrolysis and oxidation of a reaction mixture of XVIII after 10 minutes showed that α-transfer occurred only slightly faster than β-transfer (5.2% and 20%, respectively). If the relative rates of α-C and β-C transfer are also competitive, and since the addition of BH can occur in either direction, the diorganoboranes (except in the case of XXXIV which probably forms only monoörganoboranes as intermediates) may contain organic residues which are bonded to boron by the same or different carbon atoms and there will be no great selectivity in the transfer of H, or secondly C, with either of the two possible organic residues. The net result would be the formation of four possible "dimeric" alcohols. If addition of B–H occurs predominantly in one direction, as in the case of I, then only one or two "dimeric" alcohols will predominate and separation is made easier (it is thought that the two non-identified products produced in very low yield might be the two remaining "dimeric" alcohols in the case of I), whereas with XVIII and XXIII a complex mixture of the four possible "dimeric" alcohols is obtained which is difficult to separate.

The mechanism proposed for these transfer reactions involves an intramolecular transfer of hydrogen or substituted carbon from boron to carbon, with the sulfur going from carbon to boron, *via* a four-centered transition state. The transition states for these transfer reactions resemble bicyclic [1.1.0] and [1.1.1] systems as (no stereochemistry is implied in the outline shown).

α-transfer   (R = H or substituted carbon)
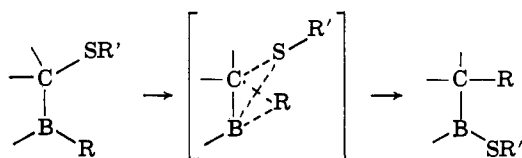
β-transfer   (R = H or substituted carbon)
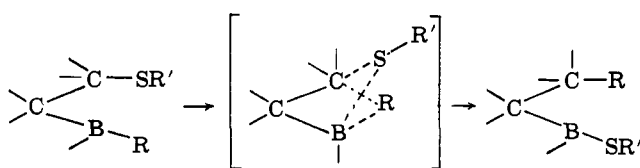
It does not seem possible for an intermolecular transfer to occur due to the steric crowding of such a transition state and by the fact that γ-transfer (see below) occurs only very slowly if at all. The transfer reactions proceed with no rearrangement of the carbon skeleton of the original olefin as shown in the case XXXIV which gives XXXV and XXXVI but no 1,2-diphenylethanol. This indicates that carbonium ions, formed by complete transfer of the sulfur before H or C transfer, in which phenyl migration is possible, are not formed, and that phenyl does not participate in any way during the transfer.

An investigation of the stereochemistry of this transfer reaction is in progress to determine whether the sulfur is replaced with retention or inversion.

As α- and β-transfer reactions have been demonstrated to occur, it was of interest to see if transfer reactions of a higher order than β would occur. Treatment of XXVIII with diborane and allowing the reaction mixture to stand at room temperature for 3 days produced a low yield of XIV and II and no detectable
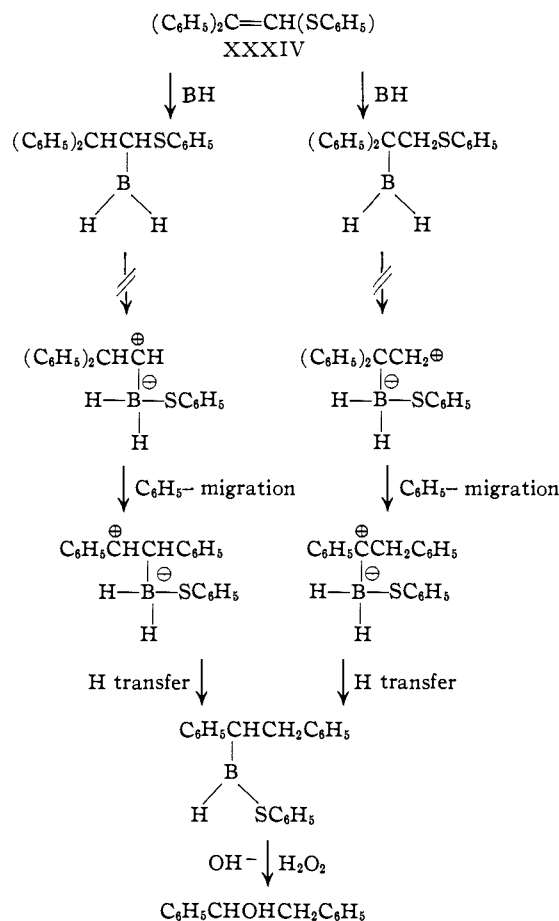

XIII or hexanols. The total amount of transfer reaction occurring can be determined quite readily by the amount of II formed, since the alkyl transfer from oxygen to sulfur is faster than the rate of intramolecular transfer. At these temperatures the hydroxysulfide fraction contained a small amount of XXX indicating BH addition had occurred in both directions. Heating the above reaction of XXVIII at 100° for 18 hours still produced no XIII or hexanols. Under the same conditions XXXI gave a low yield of XIV and XXIV but no XIII or hexanols (XXXI with diborane underwent essentially no transfer at about 25°).

The above experimental results suggest that a γ-transfer might occur, but certain of the evidence provides a possible alternate path for deriving the products. For example, the isolation of 1-propanol (XIV) from room temperature reactions would indicate that a γ-transfer had occurred. The inability to detect any XIII is surprising as some β-hydroxysulfides were found as products. It is difficult to visualize rearrangement of internal organoboranes such as XL and XLI to the terminal isomers at about 25°.

The attempted transfer reactions at 100°, which produced greater yields of sulfur transfer products, tend to add to the confusion. The isolation of significant amounts of XXXII was unexpected since under these conditions the terminal organoborane is expected almost exclusively,[3] although it must be pointed out that the systems used in this study are quite different. An alternate explanation of the results would involve an equilibrium shown in Scheme 2. Labeling experiments appear to be one of the few ways in which this can be clarified. If indeed γ-transfer is occurring, the drastically decreased rates and lack of formation of "dimeric" products are probably due to entropy factors involved in the thermodynamics of formation of the bicyclic transition states and are in the expected order.

SCHEME 2
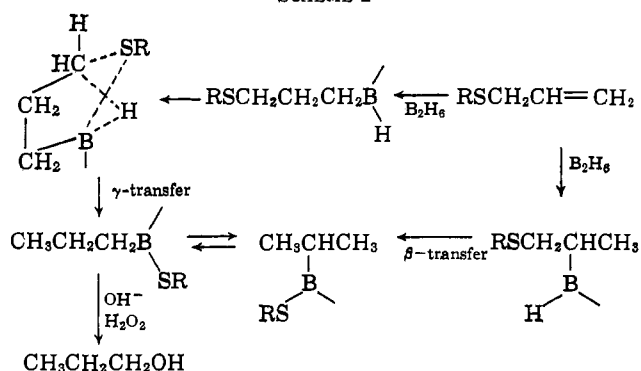
The formation of II and XXIV occurs by an alkyl transfer (methyl) from the solvent ether diglyme to sulfur which is bonded to boron.[1a] The disulfides V and XXV arise by peroxide oxidation of the free mercaptides generated during the hydrolysis of the sulfur–boron bonded species.

Conclusions

The results reported in this paper have presented a new reaction of "unstable" substituted organoboranes. From these and the previous results it is possible to define more specifically the conditions giving rise to "unstable" substituted organoboranes. Two requirements are readily apparent. First, the hetero atom must have one or more pairs of non-bonded electrons capable of entering into a complexing interaction with boron and, secondly, the stereochemistry must be such that intramolecular complexing is possible. The stability of the substituted organoboranes derived from vinyltrimethylsilane[4] and allyltrimethyl- and allyltrichlorosilane[5] can be attributed to the fact that silicon has no non-bonded electron pairs for interaction. On the other hand, the chlorine atom in the organoboranes derived from vinyl[8] and the substituted allyl chlorides[8,9] may interact with the boron leading to the "instability." Steric factors may be attributed to the "stability" of 1-t-butyl-1-bora-4-oxacyclohexane and the organoborane derived from the enamine of cyclohexanone; in the former a 1,4-interaction should not exist to any appreciable extent and in the latter the required interaction between $trans$-1,2-substituents on a cyclohexane ring is unfavorable.

In support of the above statements several new pieces of information can be cited. For example, in a preliminary report on the hydroboration of ω-ethoxystyrene[1b] it has been shown that the substituted organoboranes formed are unstable and undergo transfer reactions similar to those presented in this article. In addition to the transfer reaction a competing elimination was observed giving rise to styrene. We are currently studying the hydroboration of various substituted olefins (acyclic, cyclic and exocyclic) to determine the dependency of the type of reaction (elimination $vs.$ rearrangement) on the substituent and to determine the stereochemical requirements necessary for these reactions to occur.

Experimental

All m.p.'s are uncorrected. Microanalyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of Phenyl 1-Phenyl-1-propenyl Sulfide (I) with Diborane.—To a solution of 13.5 g. (0.060 mole) of phenyl 1-phenyl-1-propenyl sulfide[17] (I) in 100 ml. of diglyme at 0° was added 1.26 g. of sodium borohydride and 6.4 g. of boron trifluoride etherate (equivalent to 0.045 mole of diborane, 50% excess above the ratio of olefin to diborane of 4:1). The reaction mixture was stirred at room temperature for 18 hr., after which time the mixture was cooled to 0° and 15 ml. of 30% sodium hydroxide

and 10 ml. of 30% hydrogen peroxide were added dropwise. Considerable foaming occurred. The hydrolyzed mixture was stirred 1 hr. and poured into 500 ml. of water and was extracted with two 200-ml. portions of ether. The ether layers were combined and washed several times with water and the extract was then dried over sodium sulfate. Removal of the solvent under reduced pressure gave 14.5 g. of a vile smelling liquid. Partial distillation of the crude product gave 8.0 g. of material with a boiling range of 45–70° at 1.0 mm. A portion of the distillate was separated chromatographically on Florisil giving a sulfur-containing material with 10% benzene–petroleum ether and an alcohol with 60% chloroform–benzene. The n.m.r. spectrum of the sulfur-containing material showed only aromatic protons and a singlet at 7.82 τ (ratio of 5:3). The infrared spectrum was identical with the spectrum of thioanisole. Oxidation with potassium permanganate in acetic acid gave the sulfone, m.p. 87.5–88.0° (lit.[18] 88°). The infrared spectrum of the alcohol was identical with that of 1-phenyl-1-propanol. The n.m.r. spectrum showed in addition to the peaks of 1-phenyl-1-propanol weak peaks (2%) corresponding to 1-phenyl-2-propanol. Gas–liquid chromatographic analysis on a 10-ft. Carbowax column at 180° showed the original distillate to contain 3.72 g. of thioanisole (50%) and 2.20 g. of the alcohol mixture (26.5% yield of 1-phenyl-1-propanol and 0.3% yield of 1-phenyl-2-propanol).

The pot residue (6.5 g.) from the distillation was chromatographed on a 30 × 2.5 cm. Florisil column. Elution with 5–10% benzene–petroleum ether gave 1.43 g. (22%) of colorless crystalline material. Recrystallization from petroleum ether gave m.p. and m.m.p. with authentic diphenyl disulfide of 60.0–60.3°. Fractions eluted with 10–15% benzene–petroleum ether appeared as pale yellow, viscous oils which were combined and separated on alumina giving 1.51 g. of diphenyl disulfide (44.7% total yield) and a pale yellow liquid. Fractions eluted from the Florisil column with 15–35% benzene–petroleum ether were combined with the yellow oil recovered from alumina above, giving 1.28 g. (9.4%)[19] of material identified as phenyl 1-phenylpropyl sulfide. The n.m.r. spectrum of the oil showed a triplet at 9.13 τ with J 7.7 c.p.s., multiplet at 8.10 τ, four peaks centered at 6.02 τ and a multiplet at 2.87 τ. Oxidation with aqueous potassium permanganate in acetic acid produced the sulfone, m.p. and m.m.p. of 99.5–100.0° and 99.3–100.0° with authentic sulfone.

Elution with 40–50% benzene–petroleum ether gave 0.12 g. (1.6%) of a viscous material which showed a peak in the infrared at 2.9 μ. The infrared and n.m.r. (triplets at 9.40 and 9.32 τ, multiplet at 8.23 τ with an overlapping singlet at 8.16 τ, four peaks centered at 7.31 τ and a multiplet at 3.09 τ) spectra were identical with those of 3,4-diphenyl-2-hexanol prepared by ethylation of desoxybenzoin[12] followed by treatment with ethylmagnesium iodide.[13]

Fractions eluted with 60–70% benzene–petroleum ether (0.05 g.) and 85–95% benzene–petroleum ether (0.10 g.) showed hydroxyl absorption in the infrared, but the n.m.r. spectra could not satisfactorily be interpreted.

Fractions eluted with 30–90% chloroform–benzene (0.91 g., 12%) were crystalline, m.p. 138.0–138.8° after recrystallization from petroleum ether. The infrared spectrum showed absorption at 2.9 μ and the n.m.r. spectrum showed a triplet at 9.45 τ, doublet at 9.12 τ, and multiplets at 8.71, 7.06, 6.36 and 2.94 τ.

$Anal.$ Calcd. for $C_{12}H_{22}O$: C, 84.97; H, 8.72; mol. wt., 254. Found: C, 85.29; H, 8.60; mol. wt., 254.

Oxidation of Alcohol IX.—A solution of 0.38 g. of IX in 20 ml. of acetone was treated with 0.22 g. of sodium dichromate dihydrate (50% excess) in 2 ml. of acetic acid with 4 drops of sulfuric acid and 0.5 ml. of water. The reaction mixture was stirred at room temperature for 1 hr. and methanol was added dropwise to decompose the excess oxidizing agent. The mixture was poured into water and extracted with two 75-ml. portions of ether. The extract was washed with dilute bicarbonate and dried over sodium sulfate. Removal of the solvent under reduced pressure gave 0.25 g. of colorless crystals which on recrystallization from petroleum ether gave colorless needles, m.p. 127.2–128.0° (lit.[14] 127°). The infrared spectrum showed a carbonyl maximum at 5.80 μ in carbon tetrachloride. The n.m.r. spectrum showed a triplet at 9.42 τ, multiplet at 8.67 τ, singlet at 8.29 τ, eight peaks centered at 6.78 τ, doublet at 6.11 τ and two broad bands at 2.78 and 2.68 τ.

$Anal.$ Calcd. for $C_{12}H_{20}O$: C, 85.66; H, 7.90. Found: C, 85.62; H, 8.11.

Phenyl 1-Phenylpropyl Sulfide (VI).—To a solution of 1.8 g. (0.0783 mole) of sodium and 8.6 g. (0.0783 mole) of thiophenol in

(17) E. Campaigne and J. R. Lead, $J. Am. Chem. Soc.$, **76**, 1272 (1954).

(18) N. D. Cheronis and J. B. Entriken, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p. 699.

(19) The total yield of sulfur-containing products was slightly greater than 100% due to a small amount of thiophenol which was in the starting material.

75 ml. of absolute ethanol was added 6.0 g. (0.0391 mole) of 1-phenyl-1-propyl chloride. The reaction mixture was allowed to stand overnight at room temperature. The ethanol was removed under reduced pressure and 150 ml. of water was added. The aqueous mixture was extracted with 100 ml. of ether. The extract was dried over magnesium sulfate and the solvent was removed under reduced pressure. Distillation at 109° at 0.20 mm. gave a pale yellow liquid which solidified on standing; m.p. 37.5–38.5°. The n.m.r. spectrum showed a triplet at 9.13 τ, multiplet at 8.10 τ, four peaks centered at 6.02 τ and a multiplet at 2.87 τ.

Anal. Calcd. for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 78.71; H, 6.96.

Sulfoxide.—A solution of 1.0 g. of VI in 40 ml. of chloroform at 0° was treated with an equivalent amount of perbenzoic acid. The reaction mixture was allowed to stand at room temperature for 3 hr. and was then extracted with dilute base. The chloroform solution was dried over sodium sulfate and the solvent removed *in vacuo*. The residue was recrystallized from benzene-petroleum ether; m.p. 140.1–144.4°.

Anal. Calcd. for $C_{15}H_{16}OS$: C, 73.73; H, 6.60; S, 13.12. Found: C, 73.45; H, 6.55; S, 13.28.

Sulfone.—A solution of 0.5 g. of VI in 15 ml. of acetic acid was treated with an excess of aqueous potassium permanganate. The excess oxidizing agent was decomposed by addition of sodium bisulfite. The reaction mixture was poured over cracked ice and the crystals collected by filtration. Recrystallization from ether-petroleum ether gave colorless crystals, m.p. 99.5–100.0°. The n.m.r. spectrum showed a triplet at 9.12 τ, complex multiplet at 7.73 τ, four peaks centered at 6.61 τ and multiplets at 2.91 and 2.57 τ.

Anal. Calcd. for $C_{15}H_{16}O_2S$: C, 69.19; H, 6.20; S, 12.32. Found: C, 69.47; H, 6.49; S, 12.64.

Phenyl Propenyl Sulfide (XII) with Diborane.—The crude reaction mixture, from 0.1 mole of XII[20] with 0.0275 mole of diborane followed by hydrolysis and oxidation as described for I, was diluted directly with 100 ml. of ether. The solids were removed by filtration. A portion of this solution was analyzed by G.L.C. techniques[21] on a 10-ft. Carbowax column at 148° and 168° showing the presence of XIII (3.9%), XIV (47.8%), XV (1.9%), II (31%), XVI (14.4%)[22] and XVII[23] (14.2%).

The more volatile components were removed by fractional vacuum distillation. The pot residue on chromatographic separation on Florisil gave diphenyl disulfide (20.4%), a small amount of phenyl propyl sulfide and 0.30 g. of a hydroxylic material which did not give a resolvable 3,5-dinitrobenzoate.

1-Phenyl-2-thiophenylethylene (XVIII) with Diborane.—The crude reaction mixture (15.8 g.) from 19.2 g. (0.091 mole) of 1-phenyl-2-thiophenylethylene,[24] following the procedure for I, was analyzed by G.L.C. on a Carbowax column at 210° showing the presence of a trace of XVI, XIX (23.3%) and XX (33.8%).[25]

The more volatile components were removed by fractional distillation at 0.5 mm. and the pot residue was chromatographed on Florisil. Elution with 0 to 10% benzene-petroleum ether gave 3.15 g. (16.4%) of *trans*-XVIII identified by infrared and n.m.r. spectra comparison and conversion to the known *trans*-XVIII sulfone, m.p. 73.5–74.5° (lit.[26] 73.5–74.5°). Elution with 20 to 40% benzene-petroleum ether gave 0.35 g. (1.8%) of XXI[27] identified by infrared comparison with authentic material. An unidentified material, 0.20 g., was eluted with 60 to 100% benzene–petroleum ether. Elution with 0 to 40% chloro-

form–benzene gave 0.20 g. (1.0%) of XXII identified by infrared and n.m.r. (unsymmetrical multiplet at 7.00 τ (two protons), singlet at 6.41 τ (hydroxyl proton) and two doublets centered at 5.49 and 5.37 τ (one proton)) spectral comparison with authentic material.[28] Elution with 40 to 100% chloroform–benzene gave 0.85 g. (7.9%) of apparently dimeric alcohols (by infrared) which were not separated.

1-Phenyl-2-thiobenzylethylene (XXIII).—A mixture of 24.6 g. (0.20 mole) of benzyl mercaptan and 20.4 g. (0.20 mole) of phenylacetylene was heated under nitrogen at 110° overnight. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with aqueous sodium hydroxide and water and was dried over magnesium sulfate. The solvent was removed and the product was distilled at 160° (0.3 mm.) giving 29.0 g. (65%) of a pale yellow liquid which partially crystallized on standing. Fractional recrystallization from petroleum ether gave 11 g. of *trans*-XXIII, m.p. 67.5–68.5°. The infrared spectrum showed a peak at 10.27 μ indicative of a *trans* disubstituted olefin.[29] The n.m.r. spectrum showed a singlet at 4.20 τ, AB doublets at 3.59 and 3.49 τ with J 15.5 c.p.s. and aromatic multiplets at 2.94 and 2.85 τ.

Anal. Calcd. for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found: C, 79.85; H, 6.25.

The corresponding sulfone was prepared by hydrogen peroxide oxidation in acetic acid followed by recrystallization from ether-acetone, giving colorless plates, m.p. 145.4–146.0° (10.27 μ).

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.61; H, 5.41; S, 12.14.

The mother liquid from isolation of *trans*-XXIII contained predominantly *cis*-1-phenyl-2-thiobenzylethylene with infrared absorption at 12.91 μ[27] and an n.m.r. spectrum showing a singlet at 4.24 τ, AB doublets at 3.96 and 3.74 τ and J 11.6 c.p.s. with aromatic multiplets at 2.81 τ. This material was identical with that obtained by the addition of benzyl mercaptide to phenylacetylene.

The *cis*-XXIII sulfoxide was prepared by hydrogen peroxide oxidation in acetic acid at 0°, giving colorless needles from acetone-ether; m.p. 76.0–76.6°.

Anal. Calcd. for $C_{15}H_{14}OS$: C, 74.34; H, 5.82; S, 13.23. Found: C, 74.42; H, 6.06; S, 13.38.

The *cis*-XXIII sulfone was prepared by hydrogen peroxide oxidation in acetic acid at steam-bath temperature, giving colorless needles from benzene; m.p. 125–126° (12.66 μ).

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.84; H, 5.47; S, 12.70.

Reaction of *trans*-1-Phenyl-1-thiobenzylethylene (XXIII) with Diborane.—The reaction mixture from 0.0398 mole of *trans*-XXIII and 0.022 mole of diborane[30] in diglyme, as described for I, was analyzed by G.L.C. on a Carbowax column at 210° showing the presence of XXIV (7.7%),[31] XIX (18.5%) and XX (38.6%).

The volatile components were removed and the residue was chromatographed on Florisil. Elution with 10 to 40% benzene-petroleum ether gave XXV (57%), m.p. 70.0–70.7° from petroleum ether (lit. 71°).[32] Following XXV, XXVI (0.6%) was eluted which was identified by infrared comparison with authentic material.[33] Elution with 20 to 60% chloroform–benzene gave 6.6% colorless crystals, m.p. 46–47° from petroleum ether-ether. The n.m.r. spectrum of this material in carbon tetrachloride was identical with that of authentic 1-phenyl-2-thiobenzylethanol. Elution with 60 to 100% chloroform–benzene gave a viscous material, 11.7%, which was probably a mixture of dimeric alcohols which were not separated.

1-Phenyl-2-thiobenzylethanol (XXVII).—To a solution of 1.27 g. (0.055 mole) of sodium in 100 ml. of absolute ethanol was added 6.2 g. (0.050 mole) of benzyl mercaptan. The mixture was cooled, 6.0 g. (0.050 mole) of styrene oxide was added and the reaction mixture was allowed to stand 2 days at room temperature. The ethanol was partially removed under reduced pressure. Water was added to the residue and the mixture was extracted with ether. The ether extract was washed with water and dried over magnesium sulfate. The solvent was removed, leaving 8.5 g. of a pale yellow semicrystalline mass. Recrystallization from petroleum ether–diethyl ether gave colorless crystals, m.p. 46.2–46.9°. The n.m.r. spectrum of XXVII in carbon

(20) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

(21) The peaks were identified by retention time comparisons and by the addition of authentic compounds. Quantitative measurements were made by the addition of known quantities of one component and calculating the amount present using individually determined area: weight ratios.

(22) This peak had an identical retention time with that of thiophenetole but was not isolated for unambiguous identification. It is unusual that thiophenetole should be formed by an alkyl transfer from ethyl ether, added as the boron trifluoride etherate, as it has been shown elsewhere that methyl transfer is much more highly favored (see ref. 1a).

(23) An authentic sample was prepared for comparison by the procedure of V. N. Ipatieff, H. Pines and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938).

(24) The starting material was prepared both by the addition of thiophenol to phenylacetylene giving a mixture of *cis* (12.88 μ, AB doublets centered at 3.59 τ with $\Delta\delta$ 1.1 c.p.s. and J. 11.0 c.p.s.) and *trans* (10.57 μ, AB doublets centered at 3.33 τ with $\Delta\delta$ 2.2 c.p.s. and J 14.4 c.p.s.) isomers (W. E. Truce, H. E. Hill and M. M. Boudakian, *ibid.*, **78**, 2760 (1956)) and by thiophenoxide addition to phenylacetylene giving the pure *cis* isomer. Both the *cis*, *trans* mixture and pure *cis* gave the same results.

(25) Work-up of a mixture after standing for 10 min. at 0° showed the formation of 5.2% α-methylbenzyl alcohol and 20% β-phenethyl alcohol.

(26) L. I. Smith and H. R. Davis, Jr., *J. Org. Chem.*, **15**, 824 (1950); W. E. Truce, J. A. Simms and H. E. Hill, *J. Am. Chem. Soc.*, **75**, 5411 (1953).

(27) J. Braun and K. Weissback, *Ber.*, **62B**, 2416 (1929).

(28) Prepared by thiophenoxide addition to styrene oxide in a related study; D. J. Pasto and J. Fraser, unpublished results.

(29) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

(30) Treatment of XXIII with diborane in a molar ratio of 4:1 led to recovery of 47% starting material after 18 hours, indicating that only a monoalkyl borane was formed.

(31) F. Krollpfeiffer and H. Hartmann, *Ber.*, **83**, 90 (1950).

(32) R. Kempf and F. Kutter, "Schmelzpunktstabellen," Braunschweig. Friedr. Vieweg Sohn Akt-Ges., 1928, p. 78.

(33) R. Brown, W. E. Jones and A. R. Pinder, *J. Chem. Soc.*, 3315 (1951).

tetrachloride showed a B_2 multiplet of an AB_2 system at 7.47 τ, a doublet at 6.84 τ (hydroxyl proton), a singlet at 6.37 τ (benzyl protons), a multiplet at 5.50 τ and aromatic protons at 2.81 τ.

Anal. Calcd. for $C_{15}H_{16}OS$: C, 73.73; H, 6.60; S, 13.12. Found: C, 73.55; H, 6.29; S, 12.96.

Allyl Phenyl Sulfide XXVIII with Diborane.—Analyses of the reaction mixture of XXVIII[34] with diborane, carried out by the procedure described for XII except with a reaction time of 72 hr., on Carbowax, Theed and GE SF-96 columns at 110°, 90°, and 150°, respectively, showed the presence of 5.2% XIV, no XIII, no hexanols and 8.1% II. The ether solution was then repeatedly washed with water and dried and the solvent was removed under reduced pressure. The residue was distilled at 111° at 0.45 mm., giving a viscous colorless liquid (55%). N.m.r. analysis indicated the product was a mixture of γ-hydroxypropyl phenyl sulfide[35] and β-hydroxypropyl phenyl sulfide.[34]

Maintaining the reaction mixture of XXVIII with diborane in diglyme at 100° for 18 hr., followed by the work-up and analysis described above, showed the formation of 9.7% XIV, no XIII, no hexanols and 21% II.

Reaction of Allyl Benzyl Sulfide (XXXI) with Diborane. A.—The reaction mixture from 0.1 mole of XXXI[23] and diborane was allowed to stand for 3 days. The reaction mixture was hydrolyzed (considerable hydrogen evolution), oxidized and diluted with ether as described for XII. An aliquot of the ethereal solution was dried over magnesium sulfate. Analysis by G.L.C. on a Carbowax 20 M column at 100° showed no XIII or XIV. Analysis at 160° showed the presence of no XXIV.

The original ether solution was washed repeatedly with water and dried over magnesium sulfate. Removal of the solvent and distillation of the residue at 129° at 0.2 mm. gave 10.1 g. (56%) of a mixture of XXXII[36] (13%) and XXXIII[36] (87%) as analyzed by n.m.r.

B.—The reaction mixture from 0.1 mole of XXXI and diborane in diglyme was maintained at 100° for 24 hours. Analysis by the procedure above showed a trace of XIII, 2.1% XIV and 1.7% II.

The ether solution was washed repeatedly with water, dried and the solvent was removed under reduced pressure. The residue was distilled at 105–108° (0.35 mm.), giving a viscous colorless liquid (60%). The n.m.r. spectrum of the distillate indicated the product to be a mixture of XXXIII (92%) and XXXII (8%).

1,1-Diphenyl-2-thiophenylethylene (XXXIV).—A solution of 50.8 g. (0.33 mole) of phenacyl chloride in 300 ml. of absolute ethanol was added to 0.36 mole of sodium thiophenoxide in 300 ml. of absolute ethanol and allowed to stand for 3 hr. at room temperature and finally 1 hr. on a steam-bath. The ethanol was removed under reduced pressure and the residue poured into water and extracted with ether. The ether was evaporated and the material was recrystallized from benzene–petroleum ether to give 57.5 g. of colorless plates, m.p. 44–46°.

(34) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **72**, 3356 (1950).
(35) By comparison with authentic materials (M. A. Kim and R. D. Schuetz, *ibid.*, **74**, 5102 (1952)).
(36) E. Rothstein, *J. Chem. Soc.*, 686 (1934).

A solution of 57 g. of ketosulfide in 400 ml. of ether was slowly added to a 20% excess of phenyllithium in 500 ml. of ether. The reaction mixture was stirred overnight and was then hydrolyzed with 100 ml. of 10% sulfuric acid. The ether layer was removed and washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on 2 lb. of Merck activated alumina. Elution with 0 to 37.5% benzene–petroleum ether gave 15 g. of starting material. Elution with 37.5 to 75% benzene–petroleum ether gave 8.5 g. of a mixture of starting material and product alcohol. Elution with 75% benzene–petroleum ether to 37.5% chloroform–benzene gave 25.5 g. of 1,1-diphenyl-2-thiophenylethanol as colorless needles, m.p. 74.6–75.0° from petroleum ether.

A mixture of 16 g. of 1,1-diphenyl-2-thiophenylethanol and 0.5 g. of *p*-toluenesulfonic acid was heated at 169° under aspirator vacuum until the reaction mixture was clear. The mixture was cooled, dissolved in ether and the ether phase was washed with water and dried over magesium sulfate. The solvent was removed under reduced pressure. The residue was recrystallized four times from petroleum ether and finally twice from ethanol, giving 8.0 g. of very fine colorless needles, m.p. 71.1–71.5°.[37]

Anal. Calcd. for $C_{20}H_{16}S$: C, 83.29; H, 5.59. Found: C, 83.08; H, 5.75.

1,1-Diphenyl-2-thiophenylethylene (XXXIV) with Diborane.—The crude reaction product (2.55 g.) from 4.5 g. of XXXIV and 0.55 molar equivalent of diborane was analyzed by G.L.C. on a GE SF-96 column at 238° showing the presence of XXXV (60%) and XXXVI (4%). No 1,2-diphenylethanol (XXXVII) was detected.

As a further check for the presence of XXXVII, 0.50 g. of crude product was dissolved in 30 ml. of acetone and dichromate in 30% sulfuric acid was added until an excess was present. The mixture was stirred for 15 min. at room temperature and methanol was added to decompose the excess oxidizing agent. The mixture was poured into 200 ml. of water and extracted with ether. Extraction of the ether layer with 5% sodium hydroxide, followed by acidification and extraction with ether, gave 0.27 g. of diphenylacetic acid, m.p. 137.8–148.5° (lit.[38] 148°). The original ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure leaving 0.16 g. of neutral material. Although the infrared spectrum showed a weak carbonyl peak at approximately 6.0 μ the n.m.r. spectrum showed no peak for the methylene group of desoxybenzoin. Treatment of the neutral fraction with 2,4-dinitrophenylhydrazine reagent gave a small amount of a derivative, m.p. (crude) 233–237° (2,4-dinitrophenylhydrazone of desoxybenzoin m.p. 204°).[39]

(37) It was necessary to recrystallize the material repeatedly to remove a small amount of 1,2-diphenyl-1-thiophenyl ethylene, formed by thiophenyl and phenyl migration, which would lead to erroneous results and interpretations.
(38) Reference 17, p. 560.
(39) Reference 17, p. 666.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Polarographic Oxidation Potentials of Aromatic Compounds

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The oxidation half-wave potentials of fifty-three organic compounds have been determined in acetonitrile at a rotating platinum electrode. These values are correlated with ionization potentials, with interaction energies of charge-transfer complexes with trinitrofluorenone, with Hückel coefficients of the resonance integral in the expression for the highest occupied molecular orbital energy level, and with p-absorption band spectra. The correlations yield linear relations for alternant hydrocarbons. On the basis of these correlations, the values of the oxidation half-wave potentials are applied to calculate ionization potentials for aromatic hydrocarbons and to verify the values of molecular orbital calculations.

Introduction

Polarographic oxidation half-wave potentials of organic compounds are, within certain limits, directly related to ionization potentials, charge-transfer spectra, absorption spectra and molecular orbital energy levels.[2] Ionization potentials of large organic molecules

(1) Fellow of the Alfred P. Sloan Foundation.
(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," J. Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

are difficult to determine. Although ionization potentials have been calculated through study of charge-transfer spectra, it would be useful to have another easily accessible experimental measure of relative ionization potentials. Polarographic half-wave potentials can also provide, in some cases, an experimental measure to check various molecular orbital calculations. Considering the potential usefulness of polarographic oxidation potentials, very few experimental measure-