

olefins is a 10-ft. squalene on acid treated Chromosorb (42/60 mesh). A 10-ft. column of 1/1 in. o.d. stainless steel was used at 40° with a helium flow rate of 60 cc./min. and a chart speed of 15 in./hr. The average precision of the rate constant for the 25 olefins reported here is $\pm 5\%$ of the absolute number value. Bromination of diethyl ketone was carried out as outlined in reference 1d. The pseudo-first-order rate constant under the conditions noted is $1.33 \times 10^{-3} \pm 0.13 \text{ sec.}^{-1}$.

Acknowledgment.—The authors are grateful to Dr. W. Bartok for the calculation of the resonance energies and to Professors W. von E. Doering and H. C. Brown for helpful discussions. We also wish to thank the Esso Research and Engineering Company for permission to publish this research.

[CONTRIBUTION FROM ESSO RESEARCH AND ENGINEERING COMPANY, LINDEN, N. J.]

Anionic Activation of C–H Bonds in Olefins. VI. Intramolecular Nature and Kinetic Isotope Effect of Base-Catalyzed Olefin Isomerization¹

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The relative rates of double bond migration and of deuterium exchange of perdeuterio-1-pentene with unlabeled 2-methyl-1-pentene and solvent have been determined at 55° in the system potassium *tert*-butoxide–dimethyl sulfoxide. It was found that isomerization is 16 times faster than exchange. The base-catalyzed prototropic migration is thus shown to be intramolecular. The relative rates of isomerization, activation enthalpies and entropies of 1-pentene and perdeuterio-1-pentene were obtained. These values are compared with the values calculated for a primary isotope effect. The good agreement indicates that the carbon to hydrogen bond cleavage is largely complete in the transition state. These results are interpreted on the basis of a tightly bound ion pair.

Anionic reactions of relatively weak organic acids ($\text{p}K_a$ 10–20) are well known. Recently, the anionic prototropic shifts of still weaker acids, *i.e.*, olefins, have been observed in homogeneous media under mild conditions.² The base-catalyzed proton migration of simple olefins is particularly well suited to serve as a model for carbanions of very weak acids. Indeed, the ready availability of a wide variety of olefin structures and the lack of complicating functional groups greatly facilitate mechanistic studies. It is also anticipated that knowledge obtained with such simple models could be widely applied to a broad study of anionic intermediates.

Several recent publications in this area have discussed the kinetics and the effect of solvent and olefin structure upon the rate of isomerization.^{2,3} It has been shown with alkylidene cycloalkanes that activation of the allylic hydrogen is rate controlling. A linear relationship between the log of the rate of isomerization and the log of the rate of bromination has also been found with cyclic and acyclic olefins and structurally similar ketones.^{2b,c} There are several questions that remain unanswered; namely, does the reaction involve ionic or partially ionic species; what is the degree of freedom of the species; is the reaction intramolecular?^{2,1,2}

An examination of the rates of isomerization and deuterium exchange between a protium substituted olefin and a deuterium substituted olefin could provide meaningful answers to these questions. The extent of carbon–hydrogen bond cleavage in the transition state, as determined by the ratio k_H/k_D , bears directly on the question of ionic character. The isomerization of the labeled olefin in the presence of an unlabeled olefin is expected to provide information concerning the question posed in preceding papers concerning the intra- or intermolecular nature of the prototropic shift. Preliminary results of this work have been disclosed¹ and a similar study of exchange *vs.* isomerization has been investigated independently by Cram.⁴

(1) Presented by A. Schriesheim in a preliminary communication of the 1962 Gordon Research Conference on Catalysis, Colby Junior College, New London, N. H.

(2) A. Schriesheim, J. E. Hofmann and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961).

(3) (a) A. Schriesheim and C. A. Rowe, Jr., *ibid.*, **84**, 3160 (1962); (b) A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962); (c) A. Schriesheim, C. A. Rowe, Jr., and L. Naslund, *ibid.*, **85**, 2111 (1963).

(4) D. J. Cram and R. T. Uyeda, *ibid.*, **84**, 4358 (1962).

Results

The rates of isomerization of 1-pentene (Ia) and perdeuterio-1-pentene (Ib) were studied as a function of temperature. These rate measurements were carried out in dimethyl sulfoxide–potassium *tert*-butoxide solutions. Premixed solutions of each pentene olefin and equimolar quantities of 2-methyl-1-pentene were injected at time zero. Since it has been shown that the rate of isomerization of any olefin is independent of added olefin, the inclusion of 2-methyl-1-pentene serves as a convenient internal standard. The reaction is first order in olefin and, at these base concentrations, ($>0.2 M$) is zero order in base.² The disappearance of α -olefin was followed to greater than 75% reaction and no deviations from linearity were found in the first-order rate plots. The composition of a thermodynamic mixture of the pentene olefins at this temperature was determined to be 60.2% *trans*-2-pentene, 36.9% *cis*-2-pentene and 3.1% 1-pentene. The pertinent rate constants as well as the values for the enthalpies are summarized in Tables I and II.

TABLE I
RATES OF ISOMERIZATION OF 1-PENTENE AND PERDEUTERIO-1-PENTENE AT 55.0°

Olefin ^a	Rate constant ^b $\times 10^4, \text{ sec.}^{-1}$	k_H/k_D
1-Pentene	9.54 ± 0.10	
2-Methyl-1-pentene	$1.22 \pm .08$	4.4
Perdeuterio-1-pentene	$2.19 \pm .09$	
2-Methyl-1-pentene	$1.28 \pm .06$	

^a Olefin concentration 0.36 M. ^b Using potassium *tert*-butoxide (0.4 M) in dimethyl sulfoxide.

TABLE II
RATE CONSTANTS AND DERIVED DATA FOR THE ISOMERIZATION OF 1-PENTENE AND PERDEUTERIO-1-PENTENE

Compound	Temp., °C.	Rate constant $k_1 \times 10^4,$ sec.^{-1}	$\Delta H^\ddagger,$ kcal./mole	$\Delta S^\ddagger,$ e.u.
1-Pentene	55.0	9.54	16.3 ± 0.3	-22.9 ± 1.0
	44.0	2.66		
	25.0	0.70		
Perdeuterio-1-pentene	70.0	7.15	17.5 ± 0.4	-22.2 ± 1.2
	55.0	2.19		
	40.0	0.56		

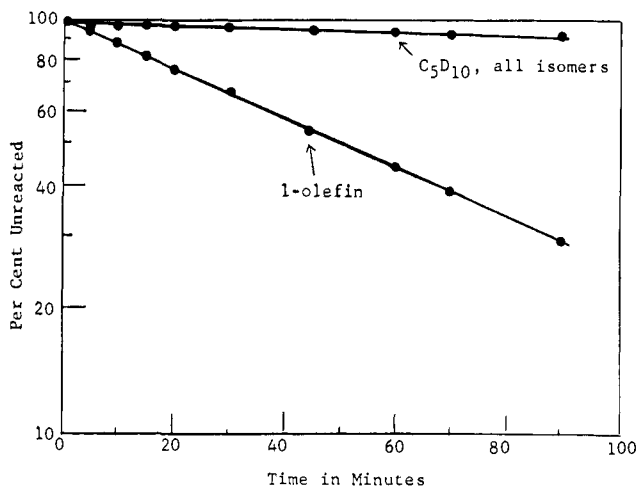


Fig. 1.—Rates of deuterium exchange and isomerization of perdeuterio-1-pentene at 55°.

The value for the rate constant for the isomerization of 2-methyl-1-pentene at 55.0° in the absence of added olefin was found to be 1.2×10^{-4} sec.⁻¹.² There is excellent agreement between this value and those obtained for this olefin in the presence of the two pentene olefins. These data enable the kinetic isotope effect to be experimentally determined with confidence.

The observed ratio k_{1a}/k_{1b} at 55.0° is 4.4. The difference in the enthalpies of reaction (1.2 kcal./mole) and the similar entropies of reaction for the pentene compounds substantiates that the rate differences are largely the result of differences in the zero point energy. Such an analysis is necessary for meaningful inferences about the degree of carbon to hydrogen bonding in the transition state.

Exchange Studies (Cross-over Experiments).—The amounts of exchange and isomerization of perdeuterio-1-pentene at 55.0° as a function of time are plotted in Fig. 1. It is noted that when 75% of the α -olefin has isomerized, less than 6% of the deuterium has exchanged from the total pentenes. From duplicate runs, the rate constant for the exchange reaction is calculated to be 1.37×10^{-5} sec.⁻¹. Thus, isomerization is 16 times faster than exchange.

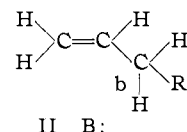
In separate experiments premixed solutions of perdeuterio-1-pentene and 2-methyl-1-pentene were isomerized in this base-solvent system at 55.0°. The olefins were isolated from the samples taken at various intervals, using preparative scale gas chromatography. In a sample taken at 3 half-lives of the pentene isomerization, it was found that when 18% of the deuterium had been lost from the pentene olefins, less than 0.4% deuterium had been incorporated in the 2-methyl-1-pentene or 2-methyl-2-pentene. Moreover, the rate of the exchange reaction for the perdeuteriopentenes was unaffected by the inclusion of 2-methyl-1-pentene.

The isomerization and exchange of a premixed solution of perdeuterio-1-pentene and 2-methyl-1-pentene was studied in the presence of added *tert*-butyl alcohol. The concentrations of olefins, base and alcohol were 0.36, 0.40 and 0.43, respectively. At the end of 31.5 hr. at 55°, the reaction mixture was quenched and the olefins were separated by preparative scale gas chromatography. This reaction time corresponds to more than 7 half-lives of the pentene-1 isomerization (> 99.5% complete) for this base-solvent system. The separated fractions of total pentenes, 2-methyl-1-pentene and 2-methyl-2-pentene were analyzed for exchange by mass spectrometry. It was found that 35% of the deuterium had been exchanged from the total pentene fraction (1-pentene, *trans*-2-pentene and

cis-2-pentene). The ratio of isomerization to exchange is therefore the same as was obtained in the absence of added alcohol. Moreover, less than 0.4% deuterium had been incorporated in the 2-methyl-1-pentene or 2-methyl-2-pentene. These data constitute conclusive proof that the isomerization reaction does not involve two molecules of olefin and that the exchange reaction does involve solvent. This is in accord with the observed increase of radioactivity of solvent in the base-catalyzed reaction of tritiated pentene.¹

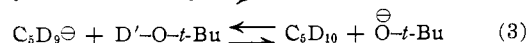
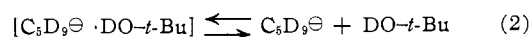
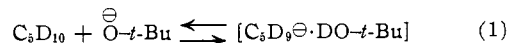
Discussion

The stretching frequencies of the allylic C-H and C-D bonds in Ia and Ib were determined as 2920 and 2180 cm.⁻¹, respectively. Using the usual expressions⁵ for the calculation of the isotope effect and these frequencies, the ratio k_H/k_D was found to be 5.2 at 55.0°. The observed ratio, 4.4, is in fact that arising from a combination of primary and secondary isotope effects. It is expected that contributions from the secondary isotope effect will be small in comparison with the primary isotope effect.⁶ Moreover, the direction of the secondary isotope effect for this type of process would be such as to diminish the value of k_{1a}/k_{1b} . These considerations lead to the conclusion that the observed rate ratio may be taken as lower limit primary isotope effect. This means that in II bond b is largely broken in the transition state



It has been postulated that the base-catalyzed isomerization of olefins in these systems involves carbanion formation.¹ The linear free energy relationship between the base-catalyzed ketone bromination and the base-catalyzed olefin isomerization strongly suggests similar transition states for these two reactions. The occurrence of a primary isotope effect found in this work shows quite clearly that carbon to hydrogen cleavage is rate determining. This is not an unexpected result since a primary isotope effect is found for ketone bromination.⁷ However, in view of the results of the ratio of isomerization to exchange, these results become very important toward characterizing the energy profile of this reaction.

Certainly the most striking phenomenon found in this work is the rapid prototropic shift compared to the loss of deuterium. Most of the isomerization reaction does not involve exchange. This may be interpreted as either an intramolecular proton transfer or a process in which the anion and the deuterated *tert*-butyl alcohol separate and later react (eq. 1-3)



where *t*-BuOD' represents a molecule of alcohol not produced from the C₅D₁₀ shown in eq. 1 and 2. The latter scheme is inconsistent with the results obtained in the presence of unlabeled 2-methyl-1-pentene and added unlabeled *tert*-butyl alcohol for the following reasons.

The reaction sequence 1-3 for unlabeled 2-methyl-1-pentene would produce hexenyl anion and unlabeled

(5) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, Chap. 2.

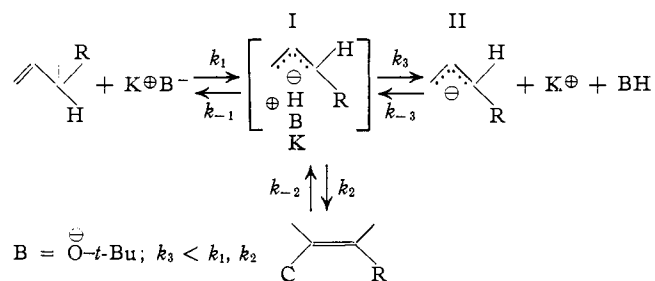
(6) L. Melander, *ibid.*, Chap. 5.

(7) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 201.

t-butyl alcohol (*t*-BuOH). Therefore in the competition experiments the solution contains deuterated pentenyl and unlabeled hexenyl anions as well as *t*-BuOH and *t*-BuOD. A free anion will proton abstract from both *t*-BuOH and *t*-BuOD in solution. It is reasonable that the amounts of *t*-BuOH and *t*-BuOD in solution are comparable since the rates of isomerization of the two olefins are similar. On this basis, deuterated pentenyl anions would abstract from *t*-BuOH giving rise to an increased rate of exchange. Similarly, the unlabeled hexenyl anion would abstract from *t*-BuOD leading to incorporation of deuterium in the methylpentenes. Even if the concentrations of *t*-BuOH and *t*-BuOD are not strictly comparable and either the labeled or unlabeled olefin predominate, then either or both rates of exchange should still be affected during the cross-over experiment according to the reaction sequence 1-3. The presence of unlabeled olefin has no effect on the rate of exchange of perdeuteriopentene, and the unlabeled olefins have not incorporated deuterium. These results can only mean that the sequence 1-3 is not operative.

Additional proof of this conclusion is derived from the reaction in the presence of added *t*-BuOH. Under these conditions, the amount of added *t*-BuOH far exceeds the amount of *t*-BuOD produced by eq. 1 and 2. The intermolecular process would demand a large increase in the amount of exchange. The results of the experiment show that the ratio of isomerization to exchange is unaffected. Clearly the isomerization reaction involves an intramolecular proton transfer.

The intramolecular carbanion rearrangement suggests that although bond cleavage of the carbon to hydrogen bond is nearly complete in the transition state, the protonated base is not free to exchange. A reasonable mechanism that will account for these results can be developed on the basis of an intimate ion pair. According to this scheme, the tightly bound ion pair I is formed in the rate-determining step. In this picture, proton exchange occurs by way of species II. Such a mechanism will account for: the observed



primary isotope effect, the slow rate of exchange and the large negative value of ΔS^\ddagger . The extension of these conclusions, found in these straight-forward systems, should be widely applicable to other base-catalyzed reactions.

The findings of a fast intramolecular tautomeric reaction for olefins can be projected to other systems in which a competition between anion formation and prototropic rearrangement are possible. Thus, it may be possible to find systems and solvents that favor one or the other. This concept has been classically expressed by Hammett⁸ with respect to the keto-enol equilibria. The generality of the findings of this work is being explored.

Experimental

Kinetic Procedures.—A dimethyl sulfoxide solution 0.40 *M* in potassium *tert*-butoxide was prepared in a nitrogen blanketed

dry-box equipped with a moisture conductivity cell. Part of the solution (7.0 cc.) was injected into a small vial with a hypodermic syringe. The vial was capped with a self-sealing neoprene stopper and preheated in a Fisher constant temperature bath ($\pm 0.2^\circ$). A thermally equilibrated equimolar mixture (0.36 *M*) of the olefins was injected into the base solution. The vial was agitated by hand for a few seconds and returned to the constant temperature bath. Samples (0.50 cc.) were obtained at various intervals by inserting a hypodermic syringe through the self-sealing neoprene stopper. These samples were quenched in 5 cc. of ice-water containing 0.3 cc. of cyclohexane. The aqueous dimethyl sulfoxide layer was frozen and a sample of the supernatant cyclohexane extract was analyzed by gas chromatography. The mixture was analyzed on a model 500 F and M gas chromatograph equipped with a 21-ft. column containing 20% DC 200 on Chromosorb (P) 60/80 mesh. Typical operating conditions suitable for complete separations were obtained at 50° with 10 p.s.i.g. of helium pressure.

Isomerization and Exchange of Perdeuterio-1-pentene in Potassium *tert*-Butoxide-Dimethyl Sulfoxide.—The procedure for these rate studies was the same as those described in the previous section. The separated organic layers were analyzed for olefin constitution by gas chromatography. The samples containing the isomeric pentene mixtures were analyzed for hydrogen-deuterium isotopic composition on a CEC model 21-103 mass spectrometer.

The parent peak height for d_{10} -olefins at *m/e* 80 and the parent peak height for d_9 -olefins at *m/e* 79 (corrected for 5.2% impurity in starting material) were determined for each sample. It was established that within the time of experiment no d_8 (parent peak 78) material was formed, corresponding to exchange of d_9 -olefin. The peak height at *m/e* 79 is therefore proportional to the concentration of exchanged material. The per cent exchange was obtained from the ratio of the peak height at *m/e* 70 to the total peak heights at *m/e* 79 and *m/e* 80. This procedure measures the total amount of exchange for the isomerized and unreacted pentene isomers.

Isomerization and Exchange of Perdeuterio-1-pentene and 2-Methyl-1-pentene in Potassium *tert*-Butoxide-Dimethyl Sulfoxide.—The procedure used for these studies was the same as that described in the section on the isomerization kinetic studies. The olefins were separated from the organic layer by preparative scale gas chromatography into three fractions: total pentenes, 2-methyl-1-pentene and 2-methyl-2-pentene. The fractions were analyzed for hydrogen-deuterium isotopic composition by mass spectrometry. The amount of exchange of the pentene mixture was determined using the parent peak heights at *m/e* 79 and *m/e* 80 as described in the previous section.

The amounts of exchange of 2-methyl-1-pentene and 2-methyl-2-pentene were determined using the heights of the peaks at *m/e* 84 and *m/e* 85. The peak at *m/e* 84 corresponds to the parent peak of C_8H_{12} , *i.e.*, no exchange. The peak at 85 (corrected for the natural abundance of carbon 13 in C_8H_{12}) corresponds to the parent peak of $\text{C}_8\text{H}_{11}\text{D}$.

Isomerization and Exchange of Perdeuterio-1-pentene and 2-Methyl-1-pentene in Potassium *tert*-Butoxide-Dimethyl Sulfoxide with Added *tert*-Butyl Alcohol.—A dimethyl sulfoxide solution 0.40 *M* in potassium *tert*-butoxide and 0.40 *M* in *tert*-butyl alcohol was prepared in a vial as described previously. An equimolar mixture of perdeuterio-1-pentene and 2-methyl-1-pentene was added and the resulting solution (0.36 *M* in olefin) was maintained at $55.0 \pm 2^\circ$. After 31.5 hr. the solution was poured into ice water and cyclohexane.

The aqueous dimethyl sulfoxide layer was frozen and the supernatant organic layer was separated. The olefins were separated by preparative scale gas chromatography into three fractions and analyzed for isotopic composition using the procedure described in the preceding section.

Materials.—Potassium *tert*-butoxide was obtained from the Mine Safety Appliance Co. This material was received as the sublimed, white powder. Analysis showed it to be above 98.5% pure with K_2CO_3 as the major impurity. Dimethyl sulfoxide was dried and distilled from 13X Molecular Sieves (Linde). 1-Pentene and 2-methyl-1-pentene were API samples. Gas chromatographic analysis indicated a purity greater than 99.6%.

Perdeuterio-1-pentene was obtained greater than 99% chemically pure from Merck, Sharp and Dohme of Canada, Ltd. The mass analysis indicated 94.8% d_{10} and 5.2% d_9 . The following considerations show that the effect of 5.2% $\text{C}_5\text{D}_9\text{H}_1$ impurity on the rate constant may be neglected. Since the distribution of the hydrogen is statistical, then 1/5, or 1.04%, is present as an allylic hydrogen. The rate for one hydrogen in the allylic position is $\sim 4.3 \times 10^{-4} \text{ sec}^{-1}$. Sample calculations show that the effect of a 1% impurity with a relative rate of $\sim 2-3$ upon the rate constant for perdeuterio-1-pentene is within the experimental error.

Acknowledgment.—The authors are grateful to Mr. Lars Naslund for working out the experimental de-

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 231.

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

Engineering Company for permission to publish this research.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

Transfer Reactions Involving Boron. III. Hydroboration Studies with Enethiol Ethers¹

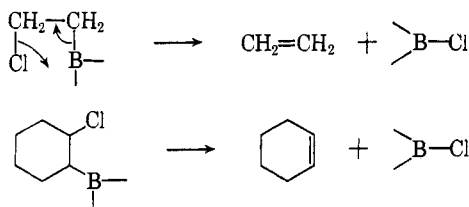
BY D. J. PASTO AND J. L. MIESEL²

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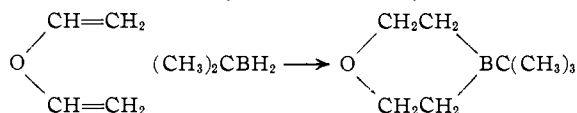
A new rearrangement reaction of unstable substituted organoboranes is reported. Hydroboration of enethiol ethers gives both possible substituted organoboranes in which hydrogen and carbon undergo an intramolecular transfer from boron to carbon with the sulfur residue migrating from carbon to boron. The 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 chlorides⁹ 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. Hawthorne⁸ 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 ether⁶ led to the formation of 1-*t*-butyl-1-bora-4-oxacyclohexane. Ac-



cordingly, Brown³ 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

(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. Shehegoleva, *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).

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% ($\text{C}_{13}\text{H}_{16}\text{S}$) 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 system¹¹ 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 desoxybenzoin¹² followed by treatment with ethylmagnesium iodide.¹³

(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).