utable to a $\Delta m = 2$ transition was found.[9] These absorptions were stable for at least 8 hr. after irradiation ceased, indicative of a ground state triplet molecule. The above data can be fitted to the spin Hamiltonian[10]

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + DS_z^2 + E(S_x^2 - S_y^2)$$

with $D = 0.518$ cm.$^{-1}$ and $E = 0.024$ cm.$^{-1}$

A similar treatment of diazofluorene gave lines at 1254, 1618 (half field), 4446, 5493 and 7600 gauss (free spin at 3242 gauss). These absorptions, which are attributed to biphenylenemethylene, may be fitted to the Hamiltonian with $D = 0.407$ cm.$^{-1}$ and $E = 0.027$ cm.$^{-1}$.

The parameters for diphenylmethylene oriented in a single crystal, which were obtained by Brandon, Closs and Hutchison,[3] are $D = 0.4050$ cm.$^{-1}$ and $E = 0.0186$ cm.$^{-1}$. In the rigid glass, our corresponding values are 0.401 cm.$^{-1}$ and 0.018 cm.$^{-1}$ (similar values are obtained for perdeuteriodiphenylmethylene).[11]

The larger D for phenylmethylene as compared with diphenylmethylene can be interpreted in terms of a greater spin–spin dipole interaction in phenylmethylene since only one p-orbital can conjugate with a phenyl ring in this species. The non-zero value of E for diphenylmethylene[3] eliminates a structure with D_{2d} symmetry (the aromatic rings perpendicular to each other and the bonds to the central carbon colinear[4]). In the case of phenylmethylene, E would not be expected to vanish even if the bonds to the divalent carbon atom were colinear. However, if we assume that the ratio of D for diphenylmethylene and phenylmethylene is the same as that for phenylmethylene and methylene we may estimate the value of D for methylene, CH_2, as 0.6–0.7 cm.$^{-1}$.[12]

For II, the value of D is similar to that of diphenylmethylene. This may be rationalized by noting that one orbital of the divalent carbon can conjugate with both rings when they are coplanar, while the other orbital is localized on the central carbon atom. In diphenylmethylene the two orbitals of the divalent carbon atom may each conjugate chiefly with one ring.

We wish also to report a luminescent reaction which occurred during the warmup of rigid glasses containing diphenylmethylene. Emission of a blue-white light was noted initially near the air interface of the sample tube, but the emission occurred throughout a sample which was saturated previously with oxygen. No emission was produced from a deoxygenated sample. Examination of the emission with a hand spectroscope gave a spectrum which was very similar to the phosphorescence spectrum of benzophenone, and distinctly different from the emission of tetraphenylethylene or benzophenone azine (possible decomposition products of the diphenyldiazomethane). Since the luminescence could appear during a warmup which was conducted several hours after irradiation had ceased, it is presumed to be associated with a reaction of oxygen and a stable high-energy species, very probably diphenylmethylene.[13] The chemistry of this ground state triplet molecule is currently being investigated.

NOTE ADDED IN PROOF.—We have recently learned that Dr. Robert Harrell also has observed this luminescent reaction (R. Harrell, unpublished results).

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[9] The authors acknowledge the assistance of W. A. Yager and R. M. R. Cramer in obtaining the e.p.r. spectra. In some experiments, a very weak line at ~8800 gauss was found.

[10] K. W. H. Stevens, *Proc. Roy. Soc.* (*London*), Ser. A, **214**, 237 (1952); C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961).

[11] From the photolysis of perdeuteriodiphenyldiazomethane. Perdeuteriobenzophenone was obtained from Merck, Sharp and Dohme of Canada, Limited.

[12] Computations by J. Higuchi have given a D value of 0.905 cm.$^{-1}$ for linear CH_2 (J. Higuchi, private communication).

[13] A study of the mechanism of the reaction of oxygen with diphenyldiazomethane has been reported recently by P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **84**, 3408 (1962).

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TRANSFER REACTIONS INVOLVING BORON. II. HYDROBORATION OF ENOL AND ENETHIOL ETHERS[1]

Sir:

Hydroboration recently has gained prominence as a powerful synthetic tool in organic chemistry.[2] Although the vast majority of the systems thus far studied have been olefins having no vinylic-hetero substituents, a few systems such as vinyltrimethylsilane,[3] dimethyldivinylsilane,[4] divinyl ether,[4] ethyl vinyl ether[5] and vinyl chloride[6] have been studied. No unusual results were reported except in the case of vinyl chloride in which the β-chloroörganoborane undergoes elimination of ethylene.[7] It seemed to be of interest to study the effects of various substituents on the stability of the substituted organoboranes. Our interest in the chemistry of enol and enethiol ethers prompted our entry into this area.

The results listed in Table I show that the original organoborane has undergone transfer reactions in which the thiophenyl moiety has been displaced from carbon by hydrogen from boron (alcohols III, IV, VIII and IX) and carbon from boron (dimeric alcohols, X and XI). The saturated sulfides V and XII are formed by base-catalyzed reductive dealkylation[8] during hydrolysis. Deuterium studies have shown that this occurs only *via* the organoborane having geminal sulfur and boron substituents. The thioanisole is formed by an alkyl transfer from the ether solvent to sulfur which is bonded to boron.[9]

Preliminary results from the hydroboration of β-ethoxystyrene, giving α-methylbenzyl alcohol

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[1] Part I of this series: D. J. Pasto, *J. Am. Chem. Soc.*, **84**, 3777 (1962). Taken in part from the Bachelor's Thesis of J. L. M.

[2] For an excellent review of the work in this area see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[3] D. Seyferth, *J. Inorg. and Nuclear Chem.*, **7**, 152 (1958).

[4] M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2541 (1961).

[5] B. M. Mikhailov and T. A. Shchegoleve, *Isvest. Akad. Nauk, S.S.S.R.*, 546 (1959).

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

[7] The β-chloroörganoborane derived from 3-chlorocyclohexene undergoes a similar elimination to give cyclohexene (P. Binger and R. Köster, *Tetrahedron Letters*, No. **4**, 156 (1961)).

[8] A. J. Weinheimer and W. E. Marisco, *J. Org. Chem.*, **27**, 1926 (1962), and references cited therein.

[9] See Part I of this series (ref. 1). It should be noted here that this transfer can occur with two carbon residues on boron, as well as two hydrogens (ref. 1), in addition to the thiophenyl group.

TABLE I

REACTIONS OF ENETHIOL ETHERS WITH DIBORANE[a]

Products	Yield, %
$C_6H_5CH{=}CHSC_6H_5$ (I)	
$C_6H_5CHOHCH_3$ (III)	27.8 (5.2)[b]
$C_6H_5CH_2CH_2OH$ (IV)	40.3 (20)[b]
Dimeric alcohols[c]	11.8
$C_6H_5CH_2CH_2SC_6H_5$ (V)	2.1
$C_6H_5CHOHCH_2SC_6H_5$ (VI)	1.2
$C_6H_5SCH_3$ (VII)	68
$C_6H_5C(SC_6H_5){=}CHCH_3$ (II)	
$C_6H_5CHOHCH_2CH_3$ (VIII)	26.5
$C_6H_5CH_2CHOHCH_3$ (IX)	0.3
3,4-Diphenylhexan-2-ol (X)[d]	12
3,4-Diphenylhexan-3-ol (XI)[d]	1.6
$C_6H_5CH(SC_6H_5)CH_2CH_3$ (XII)	9.4
$C_6H_5SCH_3$	50
$(C_6H_5S)_2$	22

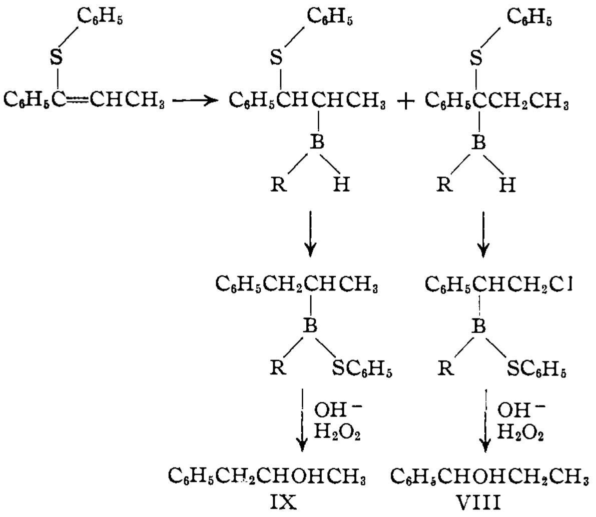
[a] The enethiol ether in diglyme was treated with 1.5 equivalents of diborane per mole of olefin (results from several experiments indicated that triorganoboranes could not be formed in several systems such as these) and the resulting mixture stirred at room temperature for 18 hr. The mixture was hydrolyzed with 30% sodium hydroxide, oxidized with 30% hydrogen peroxide, and the products were extracted with ether. The volatile components were analyzed by g.l.c. techniques using a Silicone GE-SF-96 and a QF-1 column in a Wilkens Aerograph instrument. The amounts of material present were determined by the addition of a known amount of one component and then by using known weight:area ratios the amount of each component was determined. The non-volatile components were separated by column chromatography on Florisil after the volatiles had been removed by distillation. All compounds were identified by spectral comparison or conversion to known derivatives. Previously unreported compounds gave correct analyses. [b] These figures are for a reaction time of 10 min. (other products were not analyzed for). [c] No attempt was made to separate this complex mixture. [d] Two additional alcohol fractions (apparently dimeric) were isolated in 1.4 and 0.7% but could not be identified unambiguously.

(34%) and β-phenethyl alcohol (30%), indicates that similar rearrangement reactions occur with organoboranes derived from enol ethers. The rearrangement reactions in this case are much faster than those observed in the sulfur containing systems and are complete in ten minutes at 0°. In addition to the rearrangement reactions, elimination has been observed giving rise to small amounts of styrene.

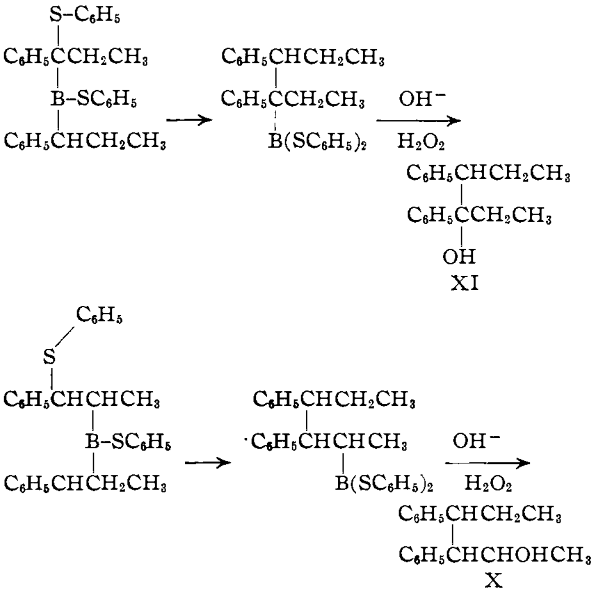
The reactions of these enol and enethiol ethers with diborane are visualized as proceeding by normal addition to the carbon-carbon double bond in both possible directions. The organoboranes thus formed undergo rearrangements in which hydrogen (H) and carbon (C) replace the hetero group. The rate of H transfer is much faster than C transfer (H transfer is favored thermodynamically over C transfer by about 5 kcal.) as evidenced by the fact that only H transfer products are isolated after short reaction times (where both H and C transfer can compete) and that the dimeric products isolated do not contain the hetero group.

Since H-B addition can occur in either direction, the diorganoborane may contain organic residues which are bonded to boron by the same or different atoms. As the rate of α-H transfer appears to be only slightly faster than β-H transfer, there will be no selective reduction of the organic residues. If the ratio of rates of C transfer are similar one would then expect to derive a mixture of four dimeric alcohols (if the H-B addition occurs predominantly at one position, as in the case of II then only one or two dimeric products will predominate). The following reactions, using II as starting material, illustrate the H and C transfer reactions. Analogous paths may be used to derive the products in the other systems.

Reaction scheme:



C transfer:



The foregoing work indicates that the use of hydroboration in vinyl heterosubstituted systems for preparative methods in many cases will not be feasible. Several other sulfur containing systems have been studied giving similar results.

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