phases of this work and to the National Institutes of Health whose generous grants (A-2398) have continued the support. We express our thanks to Mr. Charles M. Blair and Mrs. Franziska Schleppnik for their help in carrying out some of the assays.

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TRANSFER REACTIONS INVOLVING BORON. I. ALKYL TRANSFER FROM OXYGEN TO SULFUR[1]

Sir:

It has been observed that on generation of diborane in the presence of a mercaptan in an ether solvent, an alkyl transfer occurs from the solvent molecule to sulfur giving sulfides often in good yields.[2] Table I lists experiments in which 0.05 mole of mercaptan and 0.0313 mole of sodium borohydride were dissolved in 40 ml. of the ether, with in *situ* generation of diborane by the addition of 0.025 mole of boron trifluoride etherate. The reaction mixtures were allowed to stand at room temperature for 20 hours, then hydrolyzed with aqueous sodium hydroxide and extracted with diethyl ether to recover the sulfide. Although the experiments were carried out by the *in situ* generation of diborane, it was shown that the reaction was not dependent on the presence of a strong Lewis acid (boron trifluoride). Diborane generated externally and bubbled into a solution of thiophenol in diethylene glycol dimethyl ether also led to alkyl transfer.

In cases of otherwise similar ethers, entries 1 and 2, and the cyclic ether, entry 5, it is apparent that methyl reacts more rapidly than methylene which in turn reacts more rapidly than methine. The over-all structure of the ether greatly affects the rates of transfer as is illustrated in entries 8, 9 and 10 in which the transfer of ethyl competes with the transfer of methyl. The reaction rate appears to be greatly dependent on the steric bulk of the radicals attached to oxygen and on the basicity of the ether oxygen. At the present time the synthetic utility of this reaction lies mostly in preparation of various sulfides. The usefulness of the reaction as a means to carry out O-demethylations is severely hindered by competing reactions with the solvent. Further work is being carried out in this respect.

Chemical evidence in the case of thiophenol indicates that monothiophenoxyborane ($C_6H_5SBH_2$) is the reactive species which takes part in the alkyl transfer. The graph illustrates the effect on the extent of reaction over a given period of time when the ratio of diborane to trithiophenoxyborane is progressively increased. Attempted alkyl exchange in the presence of thiophenoxide ion and diborane failed, indicating that a species corresponding to $[C_6H_5SBH_3]^-$ is not operative in this reaction. Alkyl exchange did not occur in the presence of trithiophenoxyborane $[(C_6H_5S)_3B]$ generated by treating thiophenol with an equivalent of sodium borohydride.

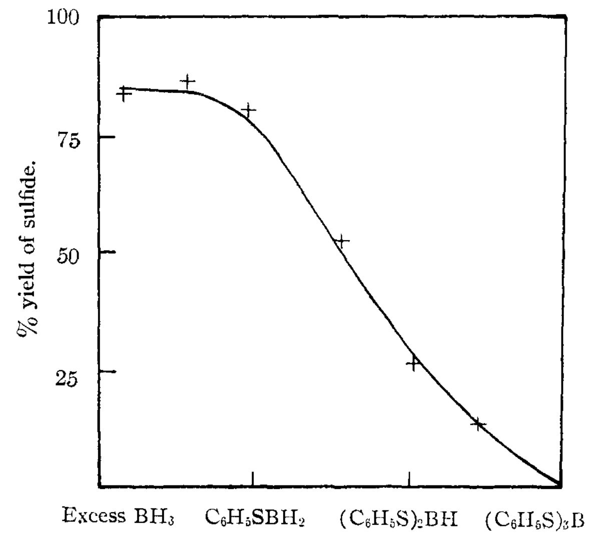
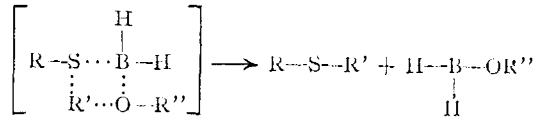


Fig. 1.—Exchange with thiophenol in diglyme after 20 hours.

The above experimental results would suggest that the alkyl transfer occurs *via* a four-centered transition state involving the ether and monothiophenoxyborane. A nucleophilic attack by sulfur on the alkyl carbon adjacent to a complexed oxygen does not seem reasonable in that the nucleophilicity of the sulfur will be reduced by interaction of its electron pairs with the vacant orbital of boron. Likewise, partial carbon–oxygen bond cleavage leading to the partial formation of a carbonium ion, which then is attacked by sulfur, is not a reasonable mechanism if one considers entry 5 of Table I. Had the mechanism proceeded by partial carbonium ion formation, the expected product would have been 4-thiophenoxypentanol-1 instead of the observed 5-thiophenoxypentanol-2.

The reaction mechanism may thus be illustrated as

$RSBH_2 + R'—O—R'' \longrightarrow$



The greater reactivity of $C_6H_5SBH_2$ over that of $(C_6H_5S)_2BH$ and $(C_6H_5S)_3B$ may be explained in part by the steric restrictions in forming the four-centered transition state and in part by the reduced Lewis acid character of the boron atom, due to interaction with a greater number of thiophenoxy groups, leading to a weaker complex with the ether oxygen.

Four-centered transition states and reactions are quite common in boron chemistry: *i.e.*, the addition of B–H to unsaturated linkages[4], base-catalyzed reductive cleavage of carbon-boron bonds to produce hydrocarbons,[5] disproportiona-

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(1) Presented at the 1962 Fall American Chemical Society Meeting at Atlantic City, New Jersey.

(2) All product sulfides were converted to known derivatives for identification or were satisfactorily analyzed if not previously reported. In cases of mixtures, analyses were carried by vapor phase chromatography or nuclear magnetic resonance spectroscopy.

(4) H. C. Brown, "Organo Metallic Chemistry," H. Zeiss, ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 163.

(5) A. J. Weinheimer and W. E. Marsico, *J. Org. Chem.*, **27**, 1926 (1962), and references cited therein.

TABLE I

	Mercaptan	Ether	Product(s)	Yield,[a] %
1	Thiophenol	Diethylene glycol dimethyl ether	Thioanisole	89
2	Thiophenol	Diethylene glycol diethyl ether	Thiophenetole	26
3	Thiophenol	Ethylene glycol dimethyl ether	Thioanisole	59
4	Thiophenol	Tetrahydrofuran	4-Thiophenoxybutanol	36
5	Thiophenol	2-Methyltetrahydrofuran	5-Thiophenoxypentanol-2	82
			4-Thiophenoxypentanol-1	2
6	*n*-Amyl	Diethylene glycol dimethyl ether	*n*-Amyl methyl sulfide	76[b]
7	Benzyl[c]	Diethylene glycol dimethyl ether	Benzyl methyl sulfide	56
8	Thiophenol	Diethylene glycol diethyl ether and diethylene glycol dimethyl ether (1:1 mole ratio)	Thioanisole	95
			Thiophenetole	0
9	Thiophenol	Anisole and diethylene glycol diethyl ether (1:5 mole ratio)	Thioanisole	6
			Thiophenetole	15
10	Thiophenol	4-*tert*-Butyl cyclohexyl methyl ether and diethylene glycol diethyl ether	Thioanisole	11
			Thiophenetole	7

[a] The reaction of the mercaptan, for example thiophenol, with sodium borohydride gives trithiophenoxyborane and sodium thiophenoxide, the latter being inert in the transfer reaction. The additional diborane generated *in situ* converts the trithiophenoxyborane into the active monothiophenoxyborane. The yields of product are calculated on the basis of the available thiophenoxy groups for transfer. [b] This yield is based on *n*-amyl methyl sulfone isolated after permanganate oxidation of the crude sulfide. [c] Reaction time of 18 hours, the rest being 21 hours.

tion of substituted boranes[6] and certain other intramolecular transfer reactions currently under study.[7]

The mechanism proposed for the above ether cleavage is distinctly different from that proposed for the cleavage of ethers as their boron trichloride complex which proceeds by a carbonium ion mechanism.[8]

Experiments designed to investigate intramolecular alkyl exchange *via* four-centered transition states resembling bicyclo[2.1.1], [3.1.1] and [4.1.1] systems are being carried out.

[6] R. Köster and B. Günther, *Ann.*, **629**, 89 (1960).

[7] D. J. Pasto and J. L. Miesel, manuscript in preparation.

[8] W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1486 (1952).

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ACIDITY DEPENDENCE OF THE CARBON-PROTONATION OF PHLOROGLUCINOL AND ITS METHYL ETHERS

Sir:

In a recent paper, Kresge and Chiang[1] reported that equilibrium carbon-protonation of 1,3,5-trimethoxybenzene in aqueous perchloric acid is more closely dependent on the H_R' acidity function[2] than on H_0. Earlier, Deno, Groves and Saines had concluded that the protonation of diarylolefins was dependent on H_R' rather than H_0.[4]

Results bearing on the question of whether protonation on carbon is in general dependent on a different acidity function than protonation on nitrogen or oxygen have been obtained in an ultraviolet spectrophotometric examination of the protonation of phloroglucinol and its methyl ethers in aqueous perchloric acid solutions.[5,6] Values of $[BH^+]/[B]$ were obtained by direct solution of equation 1 at five or six wave lengths in each of several acid percentages. Arbitrary shifting of spectral curves before application of equation 1 (the Hammett "isosbestic method")[7] was unnecessary because medium effects on the spectral bands are relatively small.

$$[BH^+]/[B] = (\epsilon - \epsilon_B)/(\epsilon_{BH^+} - \epsilon) \quad (1)$$

$$pK_{BH^+} = H_0 + \log([BH^+]/[B]) \quad (2)$$

$$pK'_{BH^+} = H_R' + \log([BH^+]/[B]), \text{ where } H_R' = H_R - \log a_{H_2O} \quad (3)$$

$$[BH^+]/[B] = (A - A_B)/(A_{BH^+} - A) \quad (4)$$

$$K + \epsilon_{BH^+}(h/(\epsilon - \epsilon_B)) - h\epsilon/(\epsilon - \epsilon_B) = 0 \quad (5)$$

The relative constancies with changing perchloric acid of values of pK_{BH^+} (equation 2) and pK'_{BH^+} (equation 3) obtained by the direct method can be compared in Table I. The protonation of phloroglucinol shows somewhat less than an H_0 acidity dependence, $-d \log([BH^+]/[B])/dH_0$ being 0.85, and correlates poorly with H_R'. The protonation of 1-methoxy-3,5-dihydroxybenzene correlates very well with H_0, $-d \log([BH^+]/[B])/dH_0 = 0.98$, and poorly with H_R'. An acidity dependence between H_0 and H_R' is shown for the protonation of 1,3,5-trimethoxybenzene, with $-d \log([BH^+]/[B])/dH_0 = 1.26$ and $-d \log([BH^+]/[B])/dH_R' = 0.78$. Our results on the protonation of 1,3,5-trimethoxybenzene differ in detail from those reported by Kresge and Chiang.[1] However, if one excludes from consideration their calculated $[BH^+]/[B]$ values corresponding to greater than 97% and less that 2% protonation,[8] the disagreement is relatively minor.

[1] A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 81 (1961).

[2] $H_R' = H_R - \log a_{H_2O}$, where H_R is the acidity function for the complex ionization $ROH + H^+ \rightleftarrows R^+ + H_2O$.[3] The function $H_R - \log a_{H_2O}$ was first defined by Deno, Groves and Saines[4] and conveniently labeled H_R' by Kresge.[1]

[3] N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

[4] N. C. Deno, P. T. Groves and G. Saines, *ibid.*, **82**, 5790 (1959).

[5] This work was begun in 1958 as a necessary adjunct to a study of the kinetics of the hydrolysis of the ethers.

[6] Ultraviolet spectral evidence that protonation of 1,3,5-trimethoxybenzene occurs on carbon rather than on oxygen is given in reference 1. The closely similar spectral changes undergone in strong perchloric acid by phloroglucinol and its mono- and dimethyl ethers leave no doubt that they protonate in the same manner as 1,3,5-trimethoxybenzene. The n.m.r. spectrum of 1,3,5-trimethoxybenzene in 66% perchloric acid (unpublished work, these laboratories) is unequivocally interpretable as being that of the carbon conjugate acid.

[7] L. P. Hammett, C. A. Flexser and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

[8] We feel that measurements of such extremes of protonation have little reliability, even when medium effects on spectral bands are small; see, *e.g.*, footnote *g*, Table I.