transfer agent in the vital transition state, probably in a general acid catalyzed detachment of the alkoxy "group" from the carbonyl-hydrate ($>C(OH)_2$) of the lactone. For methyl phosphate hydrolysis ($w = +6$)[7] an analogous mechanism, involving an intermediate with 5-coördinate phosphorus, is implied.

As an empirical criterion of mechanism the above rules promise to succeed the Zucker–Hammett hypothesis,[5,8] which recently has been sharply criticized. Much of the difficulty stems from the fact that reactions with w values of about -3 to $+3$ all give reasonably straight plots of log k_ψ against $-H_0$, with slope > 1.00 when w is negative and <1.00 when w is positive. Thus reactions both of the sort in which transformation of SH^+ to transition state requires no water and of the sort in which water is a nucleophile in the slow step (*e.g.*, epichlorohydrin hydrolysis[8,9]) were classified, by the Zucker–Hammett hypothesis, as being of the former sort. A linear plot of log k_ψ against log [HA] implies w of about $+6$ and indicates not just water in the transition state, but water acting as a proton transfer agent.

These empirical principles are tempered by theoretical considerations. The theory regards w as closely related to u of equation 1, and broadly indicative of the difference in hydration of transition state *versus* initial state, on a scale set by the "water balance" in determination of H_0 values.[10] This interpretation is supported by the rough parallelism of w with ΔS^* (large positive w is associated with large negative ΔS^*, and *vice versa*), an independent measure of solvent constriction in forming the transition state. Certain deviations from expected w values are intelligible in terms of this theory.

(7) C. A. Vernon, Chem. Soc. London Special Publication No. 8, 1957, p. 17.

(8) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

(9) J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 815 (1959).

(10) K. N. Bascombe and R. P. Bell, *Faraday Soc. Discussions*, **24**, 158 (1957).

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THE ALKOXYLATION OF DECABORANE

Sir:

We wish to report the discovery of a novel and useful reaction which first occurred during the attempted iodination of the decaborane anion. The addition of solid iodine to a diethyl ether solution of sodium decaborane resulted in rapid decolorization of the iodine and the precipitation of sodium iodide. Approximately one mole of iodine was employed per mole of sodium decaborane. Work-up of the product under anhydrous conditions afforded an intractable resin, decaborane and a distillable liquid, ethoxydecaborane.

This reaction now has been extended to a series of symmetrical and unsymmetrical ethers, and the reaction· conditions optimized. One gram-atom of iodine was employed per mole of sodium decaborane. Yields varied from 13 to 26%. All products were high boiling, colorless liquids which hydrolyzed rapidly to boric acid. The table summarizes the preparative data obtained from 0.10 mole runs. All products showed proper analyses for C, H and B.

$B_{10}H_{13}$ OR PRODUCTS

Reactant ROR′	R in $B_{10}H_{13}OR$	Yield, %[a]
$(CH_3)_2O$	CH_3-	20
$(C_2H_5)_2O$	C_2H_5-	26
$(n\text{-}C_3H_7)_2O$	$n\text{-}C_3H_7$-	13
$(n\text{-}C_4H_9)_2O$	$n\text{-}C_4H_9$	25
$C_6H_5OCH_3$	C_6H_5	15

[a] Based on $B_{10}H_{14}$ consumed.

That phenoxydecaborane was the product of the anisole reaction was shown by the isolation of 2,4,6-tribromophenol from the hydrolysis of the product in bromine water.

The B^{11} n.m.r. spectra of all the products are similar. It is clear that the 2 and 4 positions have not been attacked; however, the spectra are complicated either by chemical shifts or by substitution in random positions so that it is not possible as yet to state definitely the position of attack. The H^1 n.m.r. spectrum of the ethoxyl derivative is in agreement with the proposed structure.

In diethyl ether solution the alkoxyl derivatives displayed absorption maxima at 295 mμ (ϵ 3000) while decaborane absorbs most strongly at 268 mμ under the same conditions.

The infrared spectra of these new derivatives contained B–H bands at 3.90 and 5.25 μ. A strong band near 8μ was present in all cases and may be associated with the C–O–B system.

The fate of the alkyl group cleaved from the ether reactants has not been determined. No ethane or ethylene could be detected during the preparation of the ethoxyl derivative.

A possible mechanism for these reactions might involve a two electron oxidation of an ether coordinated $B_{10}H_{13}$ anion.

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RECEIVED DECEMBER 9, 1959

CHLOROBIUM CHLOROPHYLL[1]

Sir:

All chlorophylls of known structure possess a cyclopentanone ring between $C\gamma$ and C_6, with a hydrogen atom and carbomethoxy group at C_{10}, *i.e.*, Ring V. Such pigments and those derivatives which contain an unchanged ring give a positive Molisch phase test, and undergo methanolysis with ring opening.[2,3] This communication describes a chlorophyll which gives neither of these tests. Furthermore, it is unique in not containing a methoxyl group.

The pigment was obtained from *Chlorobium thiosulfatophilum* (Strain VN)[4] and was designated

(1) N.R.C. Paper No. 5437.

(2) H. Fischer and A. Stern, "Die Chemie des Pyrrols," Vol. 2 (2), Akademische Verlagsgesellschaft m.b.H., Leipzig, 1940, pp. 48, 242, 330, 313.

(3) H. Fischer and J. Riedmair, *Ann.*, **506**, 107 (1933).

(4) The culture was supplied by Dr. H. Larsen, Norwegian Technical Univ., Trondheim, Norway.