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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RECEIVED NOVEMBER 23, 1959

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.

as CbCh (660)[5] to distinguish it from another uncharacterized chlorophyll recently isolated from a different strain of presumably the same organism.[6,7]

In common with other chlorophylls CbCh contains magnesium,[8] an alcohol group which is removed by strong acids,[2] and a conjugated carbonyl group. Removal of magnesium by dilute acid yields Cb"Ph." Absorption data[9,10] from ether solutions of samples purified by column chromatography are (a) CbCh: λ_{max} 660 mμ (ϵ 95,400), 625 (15,900), 431 (143,000), 411 (72,100), 389 (45,400); (b) Cb"Ph": λ_{max} 666 mμ (ϵ 61,700), 608 (5,540), 546 (14,500), 516 (7,250), 483 (2,440), 426 (shoulder, *ca.* 55,200), 409 (114,000), 350–390 (shoulder, *ca.* 71,000). The product from strong acid hydrolysis is extractable from ether by alkali; its ether solution possesses a visible spectrum identical to that of Cb"Ph." The conjugated carbonyl group is indicated by the shift of the "red" maximum from 666 to 650 mμ on borohydride reduction of Cb"Ph." The reduced product is oxidized by chromic acid in benzene–acetic acid to one with the visible spectrum of Cb"Ph." A small amount of the alcohol obtained by alkaline hydrolysis of Cb"Ph" was isolated. Comparison of the infrared spectrum with that of phytol obtained from pheophytin a indicates that the two alcohols may be different.

It could be argued that Ring V is oxidized, *i.e.*, "allomerized," during extraction of the bacterial cells with methanol.[2,11] This is unlikely because extraction under acid conditions, which are known to prevent "allomerization," also yields Cb"Ph."

Chromic acid oxidation followed by purification of the products by gas–liquid partition chromatography[12] yields three imides, two of which, namely, methylethylmaleimide and dihydrohematinic acid imide also can be obtained from pheophorbide *a*.[13,14] The third has been identified by analysis, m.p. and nuclear magnetic resonance spectrum as methyl-*n*-propylmaleimide.[15] The isolation of the latter imide alone differentiates CbCh from other chlorophylls; moreover, this is the first recorded instance of its isolation from a naturally occurring porphyrin.

The above results, together with the fact that 2-acetylchlorophyll *a* absorbs maximally at 676 mμ,[16] appear to dispose of the possibility that "Bacterioviridin," the pigment of green sulfur bacteria, obtained by Metzner,[17] is 2-acetylchlorophyll *a*.[18]

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(5) Abbreviations used are: CbCh (660) for Chlorobium chlorophyll (660) and Cb"Ph" for Chlorobium "pheophytin." (660) is the wave length in mμ of the "red" absorption maximum of an ether solution. Cb"Ph" is used because it is not known whether phytol is present in the molecule or not.

(6) I. R. Kaplan and H. Silberman, *Arch. Biochem. Biophys.*, **80**, 114 (1959).

(7) That there exist at least two different "Chlorobium chlorophylls" was pointed out to the authors by Drs. J. H. C. Smith and R. Stanier.

(8) J. H. C. Smith and A. Benitez, "Modern Methods of Plant Analysis," Vol. 4, Springer-Verlag, Berlin, 1955, p. 161.

(9) Extinction coefficients were calculated on the assumption of a 1:1 ratio between magnesium and CbCh.

(10) Visible absorption curves obtained with partially purified samples have been published: (2) E. Katz and E. C. Wassink, *Enzymologia*, **7**, 97 (1939); (b) see reference 4; (c) T. W. Goodwin, *Biochim. Biophys. Acta*, **18**, 309 (1955).

(11) A. S. Holt, *Can. J. Biochem. Physiol.*, **36**, 439 (1958).

(12) H. V. Morley, F. P. Cooper and A. S. Holt, *Chemistry and Industry*, 1018 (1959).

(13) H. Fischer and S. Brietner, *Ann.*, **522**, 151 (1936).

(14) G. E. Ficken, R. B. Johns and R. P. Linstead, *J. Chem. Soc.*, 2272 (1956).

(15) H. Fischer and H. Orth, "Chemie des Pyrrols," Vol. 1, Akademische Verlagsgesellschaft m.b.H., Leipzig, 1934, p. 299.

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(17) P. Metzner, *Ber.*, **40**, 125 (1922).

(18) H. Fischer, R. Lambrecht and H. Mittenzwei, *Z. physiol. Chem.*, **253**, 1 (1938).

(19) N.R.C. Postdoctoral Fellow, 1957–1959.

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RECEIVED NOVEMBER 14, 1959

THE CHEMISTRY OF BORAZINE. III. B-SILYL BORAZINES

Sir:

We are able to report the first preparation of compounds containing a boron–silicon bond. These compounds were prepared by the reaction of B-trichloro-N-trimethylborazine and B-trichloro-N-triphenylborazine with triphenylsilylpotassium.

A 10% excess (over the amount required for trisubstitution of the haloborazine) of a triphenylsilylpotassium suspension was used. This suspension was prepared[1] by cleaving hexaphenyldisilane with a 1:5 sodium–potassium alloy in anhydrous ether, excess alloy being removed by amalgamation. The ethereal triphenylsilylpotassium, prepared under an atmosphere of dry nitrogen, was added to an ethereal suspension of the B-trichloro-N-trimethyl- or B-trichloro-N-triphenylborazine in the dry box, and the reaction proceeded quite rapidly and smoothly as judged by the disappearance of the green color of the triphenylsilylpotassium suspension. The B-tris-(triphenylsilyl)-N-trimethyl- and B-tris-(triphenylsilyl)-N-triphenylborazines were the only ether-soluble products, and were isolated from the filtrate obtained from the reaction by evaporation of the ether; the former was obtained as a yellowish highly viscous oil, and the latter as an off-white waxy solid melting at 55–58°. The yields were 78 and 90%, respectively.

Both compounds are decomposed readily by heating with 20% aqueous sulfuric acid and the resulting solution was analyzed for B, N and Cl using standard methods. The silicon analysis was obtained by heating the compounds with concentrated sulfuric acid and gravimetrically estimating the silica produced. Carbon analysis was carried out by decomposing the compound with fuming nitric acid at 250° and measuring the amount of carbon dioxide produced in an apparatus designed by Schlesinger.[2]

Both compounds are soluble in carbon tetrachloride, diethyl ether and benzene; the N-phenyl compound was crystallized from benzene.

Anal. Calcd. for $B_3[Si(C_6H_5)_3]_3N_3(CH_3)_3$: B, 3.62; C, 76.25; Cl, 0.00; N, 4.62; Si, 9.39;

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(1) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

(2) H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 622 (1935).