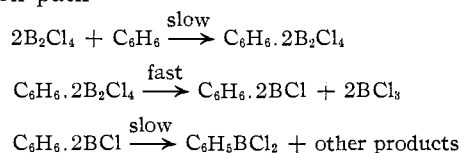


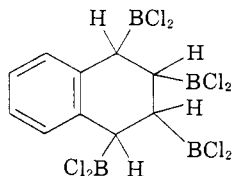
but no description of its behavior with aromatic substances has appeared. We wish to describe the behavior of diboron tetrachloride with benzene and with naphthalene.

At room temperature diboron tetrachloride reacts with an excess of benzene over a period of many days to produce ultimately phenyldichloroborane. Despite the finding that maximum yields of phenyldichloroborane were not achieved except on long standing (84.5% yield, based on benzene consumed, was obtained after 85 days but only 57.8% after 36 days), it was observed that all of the diboron tetrachloride and all of the benzene consumed disappeared within eight days. Further, about one mole of trichloroborane was released for every mole of diboron tetrachloride used. Though further confirmation is desirable, the above observation and the reaction stoichiometries suggest the reaction path



The phenyldichloroborane was identified by chloride analysis (44.5% found, 44.7% calculated), by the melting point of the phenyldihydroxyborane produced on hydrolysis (215° found, 216° reported³), and by comparing the infrared spectrum of this phenyldihydroxyborane with that of a known sample. The remaining reaction products, non-volatile dark red solids, have not yet been identified. It may be mentioned that benzene was found to be inert to the action of trichloroborane at room temperature under the conditions utilized.

Though with benzene diboron tetrachloride ultimately yields a substitution product, with naphthalene addition takes place. When approximately equimolar quantities of naphthalene and diboron tetrachloride were placed in contact with each other in a sealed tube at room temperature, a bright yellow color was immediately observed despite the fact that both reagents are colorless. Nevertheless, it was found possible to separate the unchanged reagents quantitatively by fractional condensation after a one-hour period,⁴ from which behavior we infer the reversible formation of a loose complex. After about two weeks, however, all of the diboron tetrachloride had disappeared. Removal of residual naphthalene by pumping left a pale yellow non-volatile liquid with a composition corresponding to $\text{C}_{10}\text{H}_8 \cdot 2\text{B}_2\text{Cl}_4$. We believe this material has the structure



Support for this structure is based on various types of evidence.

(3) A. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).

(4) Since liquid diboron tetrachloride would have shown extensive decomposition after one hour at room temperature, naphthalene is clearly behaving as a stabilizer.

1. All of the chlorine content is lost readily through hydrolysis at room temperature, which suggests that the chlorine is bound to boron rather than to carbon.

2. Treatment with strong aqueous base at 160° released no hydrogen, which suggested the absence of boron-to-boron bonding.

3. The treatment described in (2) produced 1,2,3,4-tetrahydronaphthalene (identified by comparison of its infrared spectrum with that of a standard), which behavior would be predicted for a product of the postulated structure.

4. Although treatment with aqueous base at 100° produced little or no boron-to-carbon bond cleavage, the substance was extremely sensitive to an oxidation. These observations suggest that the boron atoms are bonded to aliphatic rather than aromatic carbon atoms. (Aromatic boron compounds are normally less sensitive to air oxidation and more sensitive to hydrolytic cleavage.⁵)

5. The proton magnetic resonance spectra of $\text{C}_{10}\text{H}_8(\text{BCl}_2)_4$ showed a sharp peak characteristic of protons in the benzene ring and a diffuse doublet characteristic of protons in the saturated ring.

6. $\text{C}_{10}\text{H}_8(\text{BCl}_2)_4$ absorbed three, rather than four, moles of trimethylamine. Construction of appropriate molecular models showed that, with four BCl_2 groups in one ring, steric limitations prevent the introduction of more than three trimethylamine molecules.

Though reactions between diboron tetrachloride and naphthalene were allowed to proceed for periods of up to one year, the addition of more than four BCl_2 groups to naphthalene was not observed, nor in shorter experiments was a product containing fewer than four BCl_2 groups per molecule ever observed.

The new substance $\text{C}_{10}\text{H}_8(\text{BCl}_2)_4$ is a pale yellow, viscous liquid which, even at 65° in a high vacuum, could not be distilled. At this temperature it began to discolor slightly; at 145° it was converted rapidly to gaseous trichloroborane and an amorphous yellow-brown solid.

We wish to acknowledge the assistance of Professor Richard Glick in the interpretation of n.m.r. spectra. We are grateful to the Koppers Company, Inc., for their generous support of this work.

(5) M. Lappert, *Chem. Rev.*, **56**, 959 (1956).

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STUDIES OF CHLOROBIUM CHLOROPHYLLS. III. CHLOROBIUM CHLOROPHYLL (650)¹

Sir:

The evidence presented below is consistent with the conclusion that Chlorobium chlorophyll (650) (I) is derived from a homolog of 2-desvinyl-2- α -hydroxyethylpyropheophorbide *a*.²

Hydrolysis of (I) in concentrated HCl or dilute, hot methanolic KOH, and subsequent chromatography on sucrose gave two zones of pigment having identical visible absorption spectra. Only results obtained with pigment in the lower, major zone will be discussed. Chlorobium pheophorbide (650) (II)

(1) N. R. C. Paper No. 6165.

(2) H. Fischer and J. Hasenkamp, *Ann.*, **519**, 42 (1935).

crystallized from ether. *Anal.* Calcd. for $C_{24}H_{38}O_4N_4$: C, 72.06; H, 6.76; N, 9.89. Found: C, 72.10; H, 7.13; N, 9.55. Methyl ester. *Anal.* Calcd. for $C_{34}H_{37}O_3N_4(OCH_3)$: OCH_3 , 5.34. Found: OCH_3 , 5.3.

The change in the visible spectrum upon reduction with sodium borohydride showed the presence of a conjugated carbonyl group.³ HI in acetic acid⁴ converted (I) into a porphyrin (III) with a spectrum almost indistinguishable from that of phylloerythrin.⁵ The oxime of (III) has a "rhodo" spectrum indicating that the carbonyl group is contained in a ring between C_7 and C_8 .⁶ Oxidation of (III) with SeO_2 effected a spectral change identical with that obtained by the same treatment of phylloerythrin.⁷ Acetylation of (II) indicated the presence of hydroxyl group and dehydration at 220° gave a product with a spectrum almost identical with that of pyropheophorbide *a*.⁸ Oxidation of this product with permanganate^{9,10} or catalytic reduction with hydrogen¹¹ resulted in spectral changes indicating the presence of a C_2 -alkenyl group. Oxidation of (II) by chromic acid in benzene yielded a product with a spectrum almost identical with that of 2-desvinyl-2-acetyl-pheophorbide *a*.¹² This product was converted into a porphyrin with a "rhodo" spectrum identical with that of 2-oxophylloerythrin.¹³ Reduction with sodium borohydride regenerated (II).

Oxidative degradation of (II) and subsequent separation and identification of the imides by gas-liquid partition chromatography¹⁴ gave methyl-*n*-propylmaleimide and dihydroematinic acid imide. Degradation of (III), however, yielded methyl-*n*-propylmaleimide and methylethylmaleimide in the neutral fraction. This may be explained by assuming reduction of a C_2 -hydroxyethyl group to ethyl by HI. Absence of the hydroxyl group in (III) is supported by analysis of the methyl ester. *Anal.* Calcd. for $C_{35}H_{38}O_3N_4$: C, 74.70; H, 6.81; N, 9.96. Calcd. for $C_{35}H_{38}O_4N_4$: C, 72.63; H, 6.62; N, 9.68. Found: C, 74.90; H, 7.21; N, 10.34. This is further confirmed by (1) its failure to form an *O*-acetyl derivative, and (2) its failure to be oxidized to the 2-oxo-phylloerythrin-type compound by chromic acid in benzene.

2-Desvinyl-2- α -hydroxyethylpyropheophorbide *a* was prepared² and its visible absorption maxima shown to be at the same wave lengths as those of (II). Minor differences in the relative intensities of these maxima are assumed to result from the *n*-propyl group.

The C_{10} -carbomethoxy group of chlorophylls of

- (3) A. S. Holt, *Plant Physiol.*, **34**, 310 (1959).
- (4) H. Fischer and A. Hendschel, *Z. physiol. Chem.*, **206**, 255 (1932).
- (5) H. Fischer, L. Filser, W. Hagert and O. Moldenhauer, *Ann.*, **490**, 33 (1931).
- (6) A. Stern and H. Wenderlein, *Z. physik. Chem.*, **176**, 81 (1936).
- (7) H. Fischer and J. Ebersberger, *Ann.*, **609**, 19 (1934).
- (8) H. Fischer, J. Riedmair and J. Hasenkamp, *ibid.*, **508**, 237 (1934).
- (9) H. Fischer and H. Walter, *ibid.*, **549**, 44 (1941).
- (10) A. S. Holt and H. V. Morley, *Can. J. Chem.*, **37**, 507 (1959).
- (11) H. Fischer and G. Spielberger, *Ann.*, **515**, 130 (1935).
- (12) H. Fischer, R. Lambrecht and H. Mittenzwei, *Z. physiol. Chem.*, **253**, 32 (1938).
- (13) A. Stern and H. Wenderlein, *Z. physik. Chem.*, **175**, 405 (1936).
- (14) H. V. Morley, F. P. Cooper and A. S. Holt, *Chemistry and Industry*, 1018 (1959).

known structure is absent from (II). That this group was absent from (I) seems probable since when either boiling 2-propanol or methanol solutions of chlorophyll *a* were used to extract (I) from freshly isolated cells of *Chlorobium thiosulfatophilum* (Strain L),¹⁵ chlorophyll *a* retained its capacity to give a positive Molisch phase test,¹⁶ while (I) gave a negative test. The failure of (I) to give a positive test agrees with earlier results.¹⁷ (I) prepared in this manner, and purified, contained no methoxyl group.

The nature of the C_3 substituent of Ring III must await the preparation of sufficient "pyroporphyrin" to permit oxidative degradation. Of further interest is the fact that both *Chlorobium* chlorophylls (650) and (660) can now be stated to be closely related by the following: (1) each possesses an α -hydroxyalkyl substituent. (2) Each yields methyl-*n*-propylmaleimide upon oxidative degradation.¹⁸ (3) Each yields an alcohol upon hydrolysis. By paper chromatography¹⁹ these appear to be identical with each other but to differ from phytol. (4) Each gives a negative Molisch phase test.^{17,18}

(15) Cultures were kindly supplied by Drs. J. Lascalles, Department of Biochemistry, University of Oxford, and H. Larsen, Norwegian Technical University, Trondheim, Norway.

(16) H. Fischer and A. Stern, "Die Chemie des Pyrrols," Vol. 2 (2), Akademische Verlagsgesellschaft m.b.H., Leipzig, 1940, pp. 26, 331.

(17) R. Y. Stanier and J. H. C. Smith, *Biochim. Biophys. Acta*, **41**, 478 (1960).

(18) A. S. Holt and H. V. Morley, *J. Am. Chem. Soc.*, **82**, 500 (1960).

(19) F. G. Fischer and H. Bohn, *Ann.*, **611**, 224 (1958).

(20) N. R. C. Postdoctoral Fellow, 1959-1960.

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DEHYDROHALOGENATION OF NEOALKYL HALIDES BY STRONG BASE: EVIDENCE OF CARBENE INTERMEDIATES¹

Sir:

Cyclopropanes are formed when neoalkyl chlorides react with sodium or sodium alkyls.² Thus, neopentyl chloride (1-chloro-2,2-dimethylpropane) and sodium gave 1,1-dimethylcyclopropane (51%), neopentane (41%) and 2,2,5,5-tetramethylhexane (1.4%).^{2a} Similar results were obtained when propyl sodium was employed.^{2b} An explanation^{2b} of this unusual dehydrohalogenation assumed abstraction of a γ -hydrogen atom by carbanion followed by intramolecular substitution, *i.e.*, γ -elimination.³

(1) (a) Presented in part at the Meeting-in-Miniature, New York Section, A.C.S., March 11, 1960, paper H-9. (b) J. G. Berger, M.S. Thesis, New York University, June, 1960.

(2) (a) F. C. Whitmore, A. H. Popkin and J. R. Pfister, *J. Am. Chem. Soc.*, **61**, 1616 (1939); F. C. Whitmore, A. H. Popkin, H. I. Bernstein and J. P. Wilkins, *ibid.*, **63**, 124 (1941). This was originally explained by a free radical mechanism. (b) F. C. Whitmore and H. D. Zook, *ibid.*, **64**, 1783 (1942). (c) F. C. Whitmore and T. P. Carney, *ibid.*, **63**, 2633 (1941).

(3) γ -Eliminations are observed when the γ -hydrogens are activated by electronegative groups. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1956, p. 168; R. A. Raphael in E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Co., Amsterdam, 1953, Vol. II, p. 24. For related examples with γ -arylpropyl halides and their corresponding quaternary trimethylammonium salts see: C. L. Bumgardner, *Chem. and Ind.*,