

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.<sup>3</sup> HI in acetic acid<sup>4</sup> converted (I) into a porphyrin (III) with a spectrum almost indistinguishable from that of phylloerythrin.<sup>5</sup> The oxime of (III) has a "rhodo" spectrum indicating that the carbonyl group is contained in a ring between  $C_7$  and  $C_8$ .<sup>6</sup> Oxidation of (III) with  $SeO_2$  effected a spectral change identical with that obtained by the same treatment of phylloerythrin.<sup>7</sup> 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*.<sup>8</sup> Oxidation of this product with permanganate<sup>9,10</sup> or catalytic reduction with hydrogen<sup>11</sup> 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*.<sup>12</sup> This product was converted into a porphyrin with a "rhodo" spectrum identical with that of 2-oxophylloerythrin.<sup>13</sup> Reduction with sodium borohydride regenerated (II).

Oxidative degradation of (II) and subsequent separation and identification of the imides by gas-liquid partition chromatography<sup>14</sup> 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- $\alpha$ -hydroxyethylpyropheophorbide *a* was prepared<sup>2</sup> 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

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- (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.*, **615**, 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),<sup>15</sup> chlorophyll *a* retained its capacity to give a positive Molisch phase test,<sup>16</sup> while (I) gave a negative test. The failure of (I) to give a positive test agrees with earlier results.<sup>17</sup> (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  $\alpha$ -hydroxyalkyl substituent. (2) Each yields methyl-*n*-propylmaleimide upon oxidative degradation.<sup>18</sup> (3) Each yields an alcohol upon hydrolysis. By paper chromatography<sup>19</sup> these appear to be identical with each other but to differ from phytol. (4) Each gives a negative Molisch phase test.<sup>17,18</sup>

(15) Cultures were kindly supplied by Drs. J. Lascales, 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 INTERMEDIATES<sup>1</sup>

Sir:

Cyclopropanes are formed when neoalkyl chlorides react with sodium or sodium alkyls.<sup>2</sup> 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%).<sup>2a</sup> Similar results were obtained when propyl sodium was employed.<sup>2b</sup> An explanation<sup>2b</sup> of this unusual dehydrohalogenation assumed abstraction of a  $\gamma$ -hydrogen atom by carbanion followed by intramolecular substitution, *i.e.*,  $\gamma$ -elimination.<sup>3</sup>

(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)  $\gamma$ -Eliminations are observed when the  $\gamma$ -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  $\gamma$ -arylpropyl halides and their corresponding quaternary trimethylammonium salts see: C. L. Bumgardner, *Chem. and Ind.*,

This investigation of the dehydrohalogenation of neoalkyl halides by strong base was made to elucidate the reaction mechanism. From the experimental data it can be concluded that carbanions and/or strong bases attack and remove an  $\alpha$ -hydrogen atom with displacement of halide ( $\alpha$ -elimination) to form the carbene intermediate which gives cyclopropanes by intramolecular-insertion<sup>4a,c</sup> and olefins by rearrangement.<sup>4</sup>

Thus, neopentyl halides and sodium, sodamide in diethyl Carbitol, or phenyl sodium in decane give 1,1-dimethylcyclopropane, small amounts of 2-methyl-2-butene, neopentane<sup>5</sup> and corresponding substitution products (Table I).

TABLE I  
REACTION OF NEOPENTYL HALIDES WITH STRONG BASES  
—Dehydrohalogenation products<sup>a, b</sup>—

X	Base	Neopentane	1,1-Dimethylcyclopropane	2-Methyl-2-butene	Yield <sup>c</sup>
Cl-1-d <sub>2</sub>	PhNa <sup>d</sup>	14 <sup>e</sup>	82	4.3	71
Cl	PhNa	9.2	87	3.5	70
Cl	NaNH <sub>2</sub>	6.9	90	2.9	60
Cl	Na <sup>f</sup>	5 <sup>f</sup>	82	7	60
Br	PhNa	5.5	86	7.3	25
DMPT	NaOMe	...	89	9	85 <sup>g</sup>

<sup>a</sup> % composition. Products analyzed, separated and identified by v.p.c. <sup>b</sup> Traces (<0.1%) of 2-methyl-1-butene also present, presumably from base-catalyzed isomerization of 2-methyl-2-butene. <sup>c</sup> Conversion of neopentyl halides 100%. <sup>d</sup> SN<sub>2</sub> products account for the balance. <sup>e</sup> Reaction conditions: 10% excess base; PhNa suspension in decane (100°), NaNH<sub>2</sub> in diethyl Carbitol (reflux, ca. 180°), Na, no solvent (Wurtz reaction). <sup>f</sup> Increased amount apparently due to primary isotope effect. <sup>g</sup> Product composition corrected for large amount (110% of theory) of neopentane formed as a result of neopentyl sodium functioning as the base. <sup>h</sup> 2,2-Dimethylpropanal (pivaldehyde) tosylhydrazone treated with NaOMe in diethyl Carbitol at 180°. 2-Methyl-1-butene (2%) also formed.

Product composition and yields compare closely with those obtained from thermal decomposition of 2,2-dimethylpropanol tosylhydrazone anion in aprotic media (Table I), a reaction which proceeds via the alkyl carbene.<sup>4a</sup> In addition, the same carbene generated by an independent method gives these products in similar yield.<sup>4c</sup> This suggests that the dehydrohalogenation proceeds through the same intermediate.

To test this hypothesis, 1,1-dideutero-neopentyl chloride was treated with phenyl sodium to give dehydrohalogenation products and benzene which were analyzed for deuterium content.<sup>6</sup> 1,1-Dimethylcyclopropane and 2-methyl-2-butene formed contained *only one* deuterium/molecule. Deutero-

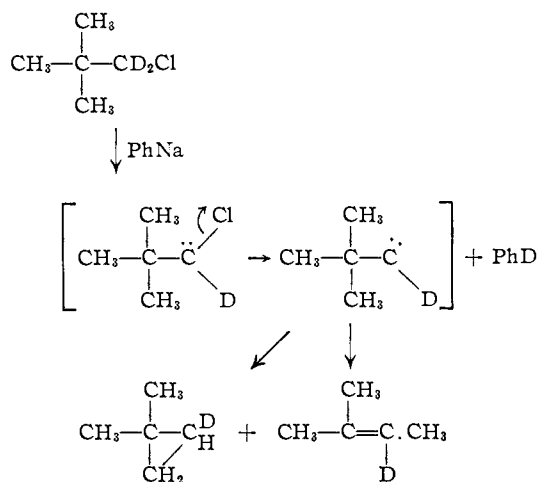
1555 (1958); Abstracts of Papers, 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 10-O.

(4) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959). (b) *Ibid.*, **82**, 1002 (1960). (c) G. L. Closs, Abstracts of Papers, 138th Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 9-P. (d) Neophyl chloride (1-chloro-2-methyl-2-phenylpropane) reacts with strong bases to give products consistent with the carbene mechanism. Cf. F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, *J. Am. Chem. Soc.*, **65**, 1469 (1943).

(5) Formed by halogen-metal interchange and subsequent hydrogen abstraction.

(6) By mass spectrographic analysis. We wish to acknowledge the assistance of Messrs. S. Zolty and R. O. Henselman, Instrumentation Laboratory, Research Division, College of Engineering, New York University.

benzene also was obtained.<sup>7</sup> These results support the proposed mechanism of the reaction.



Neohexyl chloride (1-chloro-2,2-dimethylbutane) reacts with sodium or sodamide in diethyl Carbitol to give dehydrohalogenation products consistent with the proposed mechanism, *i.e.*, 1-ethyl-1-methylcyclopropane (61, 67)<sup>8</sup> and 1,1,2-trimethylcyclopropane (32, 34) via *carbene insertion* and olefins: 2-methyl-2-pentene (0.7, 1.3), *cis*-3-methyl-2-pentene (1.4, 3.1) and *trans*-3-methyl-2-pentene (3.0, 4.2), via *carbene rearrangement*. In addition, thermal decomposition of 2,2-dimethylbutanal tosylhydrazone anion in aprotic media yields the same products in similar amounts.

These results are not in agreement with those reported previously.<sup>2c,9</sup> Part of the discrepancy can be attributed to the purity of the neohexyl chloride employed.<sup>2c</sup>

(7) Isolated yield of C<sub>6</sub> hydrocarbons 71%, deuterobenzene 76%.

(8) Product composition (%) from reaction with sodium and sodamide, respectively; adjusted for the neohexane formed.

(9) 1,1,2-Trimethylcyclopropane, neohexane and *tert*-butylethylene were obtained to the complete exclusion of 1-ethyl-1-methylcyclopropane.

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#### CHEMICAL STRUCTURE OF A PHOSPHOMUCOLIPID AND ITS OCCURRENCE IN SOME STRAINS OF SALMONELLA<sup>1</sup>

Sir:

Extraction of some gram negative bacteria with phenol<sup>2,3,4</sup> produces a water-soluble lipopolysaccharide complex containing bound amino acids. This can be split into water-insoluble lipid and degraded polysaccharide by dilute acetic acid,<sup>5</sup> hydrochloric acid,<sup>4</sup> or by treatment with cationic ion exchangers (unpublished observations).

(1) The Salmonella strains were kindly supplied to us by Drs. R. List and E. Ribi of the Public Health Service's Rocky Mountain Laboratory, Hamilton, Montana.

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(3) W. T. J. Morgan and S. M. Partridge, *Biochem. J.*, **35**, 1140 (1941).

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(5) G. G. Freeman, *Biochem. J.*, **36**, 340 (1942).