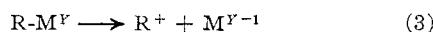


may be small, appreciable stabilization of the system is achieved by small variations in the amount of participation.

If the ideas presented here are correct, participation by neighboring groups in demercuration should result in substantial rate enhancements. In accord with these postulates, kinetic evidence for phenyl participation is given in the next paper of this series,⁷ and for the norbornylmercuric perchlorates, $k_{exo}/k_{endo} = 1500$.⁸

A reasonable generalization of the ideas presented above is that bond scissions which are accompanied by changes in hybridization can often be expected to exhibit unusual behavior.

An important example of this type of reaction is the amine-nitrous acid reaction; however, the unusual results obtained in this reaction frequently have been ascribed to other factors. The most numerous examples of this type of reaction can be expected to be found in the heterolytic cleavage of carbon-metal bonds in general. It should be noted that this type of reaction probably is encountered frequently in oxidations by many metals having variable valences. Studies are



underway to compare the carbonium ions from alkyllead⁹ and related compounds with those from other sources.

(7) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **85**, 367 (1963).

(8) Unpublished results.

(9) R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

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CHLOROBIMUM CHLOROPHYLLS. NUCLEAR MAGNETIC RESONANCE STUDIES ON A CHLOROBIMUM PHEOPHORBIIDE-660 AND -650¹

Sir:

On the basis of elegant degradative work, the various pheophorbides of both chlorobium chlorophylls-650 and -660 have been assigned structures that are homologs of 2-desvinyl-2- α -hydroxyethyl pyropheophorbide a (I), with a variation among the fractions obtained by partition chromatography apparently resulting from side chains of different lengths on ring B.² A detailed investigation of a fraction from chlorobium pheophorbide-660 also led to the assignment of an alkyl substituent (methyl or ethyl) at the δ -methine bridge.^{2b}

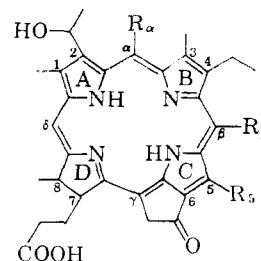
We have isolated a pure pheophorbide-660, the main fraction from a mixture of chlorobium chlorophylls-660 obtained from a culture of *Chlorobium thiosulfatophilum* (strain PM).³ Nuclear magnetic resonance studies of this pheophorbide have led to structural evidence which is in most, but not all, aspects complementary to that presented by Holt, *et al.*, for their fraction 5.^{2b} Also, from n.m.r. studies, we have made a structural correlation between this pheophorbide-660 and a pheophorbide-650.

The pigments were extracted from dried cells with aqueous acetone, washed into methylene chloride, and precipitated from the concentrated solution with petroleum ether. The mixture of chlorophylls was washed with petroleum ether and dissolved in ether to

(1) This work was sponsored in part by Grant AI-0488 from the National Institutes of Health, United States Public Health Service.

(2) (a) A. S. Holt and H. V. Morley, *J. Am. Chem. Soc.*, **82**, 500 (1960); (b) A. S. Holt, D. W. Hughes, H. J. Kende and J. W. Purdie, *ibid.*, **84**, 2835 (1962); (c) D. W. Hughes and A. S. Holt, *Can. J. Chem.*, **40**, 171 (1962); (d) A. S. Holt and D. W. Hughes, *J. Am. Chem. Soc.*, **83**, 499 (1961); (e) H. V. Morley and A. S. Holt, *Can. J. Chem.*, **39**, 755 (1961).

(3) R. Y. Stanier and J. H. C. Smith, *Biochem. Biophys. Acta*, **41**, 478 (1960); H. Rapoport and H. P. Hamlow, *Biochem. Biophys. Res. Commun.*, **6**, 134 (1961).



I, $R_5 = CH_3$, $R_\alpha = R_\beta = H$

Ia, $R_5 = CH_3$ (or C_2H_5)

$R_\beta = C_2H_5$ (or CH_3), $R_\alpha = H$, or

$R_\beta = H$, $R_\alpha = C_2H_5$ (or CH_3)

which concd. hydrochloric acid then was added. After being stirred at room temperature under argon for one hour, the solution was evaporated *in vacuo* to remove the ether and was passed through a column of powdered polyethylene.⁴ The effluent pheophorbides were extracted into methylene chloride and precipitated from the concentrated solution by adding petroleum ether; yield, *ca.* 5% from dried cells.⁵

The mixture of pheophorbides was partitioned on powdered polyethylene with 75% aqueous methanol.⁶ Paper chromatography of the acids isolated from chromic acid oxidations indicated the presence of methyl (acetic acid) and ethyl (propionic acid) substituents in the main fraction. Later fractions gave butyric acid and valeric acid(s). The main fraction Ia, after rechromatography on polyethylene, was homogeneous by thin layer chromatography and had the following properties: *Anal.* Calcd. for $C_{38}H_{40}N_4O_4$: H_2O : C, 70.2; H, 7.1; N, 9.4; C- CH_3 , 7/599. Found: C, 70.4; H, 6.6; N, 9.4; C- CH_3 , 5.6/599. Visible and ultraviolet absorption: $\lambda_{max}^{CH_3OH}$ 667 $m\mu$ (ϵ 43,000), 610 (7,400), 553 (12,500), 517 (8,300), 485 (2,700), 410 (102,000), 330 (26,200); infrared absorption: $\nu_{max}^{CHCl_3}$ 3090, 1715, 1675 cm^{-1} . With diazomethane, the methyl pheophorbide-660, was formed; infrared absorption: $\nu_{max}^{CHCl_3}$ 3060, 1737, 1690 cm^{-1} ; *Anal.* Calcd. for $C_{36}H_{42}N_4O_4$: C, 72.7; H, 7.1; N, 9.4; OCH_3 , 5.2; Found. C, 72.9; H, 7.8; N, 9.3; OCH_3 , 4.8.

The n.m.r. spectrum⁸ of Ia showed absorption at these δ values (p.p.m., TMS = 0): one proton singlet at 9.67 (10.01) and 9.34 (9.49) assigned to bridge methine hydrogens,⁹⁻¹¹ a one proton multiplet at 6.10 (6.58) assigned to the alpha hydrogen of a hydroxyethyl group,¹⁰ a two proton singlet at 4.92 (5.33) assigned to a cyclopentenone methylene,^{10,11} and three singlets at 3.33 (3.28), 3.40 (3.50), 3.75 (3.84) assigned to methyls attached to the macrocyclic aromatic ring.^{10,11} After acetylation of Ia, the multiplet at 6.10 now appeared at 7.25. Reduction of Ia with borohydride caused a hypsochromic shift of the 410 and 667 $m\mu$ peaks to 396 and 647 $m\mu$, respectively, removed the 1675 cm^{-1} infrared absorption, and replaced the two-proton singlet at 4.92 in the n.m.r. spectrum with a new multiplet under the existing absorption at 6.10. Treatment of Ia with ethoxide in C_2H_5OD removed the signal at 4.92; similar treatment in ethanol restored this signal. Treatment of Ia with warm CH_3COOD for three hours⁹ removed the lower field, 9.67, methine

(4) We wish to thank the Dow Chemical Co. for a gift of powdered polyethylene.

(5) The technical assistance of Mr. F. Cahn in this isolation we gratefully acknowledge.

(6) M. Calvin and A. F. H. Anderson, *Nature*, **194**, 285 (1962).

(7) Dehydration at 80° (0.1 mm.) results in partial alteration.

(8) N.m.r. spectra were taken in $CDCl_3$ and $CDCl_3-CD_2OD$; those taken in the latter solvent are given in parentheses.

(9) R. B. Woodward and V. Skarić, *J. Am. Chem. Soc.*, **83**, 4676 (1961).

(10) E. D. Becker, R. B. Bradley and C. J. Watson, *ibid.*, **83**, 3743 (1961).

(11) W. S. Caughey and W. S. Koski, *Biochem.*, **1**, 923 (1962).

hydrogen peak (and reduced the amplitude of the methylene absorption). A similar treatment with acetic acid then restored this peak.

A pheophorbide-650, prepared from chlorobium chlorophylls-650, obtained from *C. thiosulfatophilum* (strain L)³ and purified as described above, exhibited a n.m.r. spectrum very similar to that of the pheophorbide-660: three methyl singlets at δ 3.34, 3.50, and 3.64; a methylene singlet at 5.30; a hydroxyethyl proton multiplet at 6.16; and three methine proton singlets at 9.20, 9.41, and 9.78. The higher field signal at δ 9.20 disappeared after treatment with warm CH_3COOD .

This exchange behavior in CH_3COOD parallels that observed for three 2-vinyl-6-acylchlorins derived from chlorophyll a,⁹ and establishes the presence of a methine hydrogen at the δ (or γ) position in both our pheophorbide-660 and -650. Therefore, pheophorbide-660 differs from pheophorbide 650 in having an additional alkyl substituent at the α or β methine bridge. On the basis of these observations and the close similarity of our pheophorbides to those described by Holt, *et al.*,^{2,12} we have assigned structures Ia and I to our 660 and 650 pheophorbides, respectively. The sequence of groups and rings has been assumed by analogy with chlorophyll a and from biosynthetic considerations.¹³ Although highly likely, these features await definite proof.

The interesting observation of the lability of the δ -hydrogen in chlorophyll a¹⁴ also pertains to our chlorobium chlorophyll-660, in which only the δ -hydrogen had been exchanged after eight hours at 70° in $\text{C}_2\text{H}_5\text{OD}-\text{CHCl}_3$. The possibility¹⁴ that this labile δ -hydrogen may be pertinent to the chemical behavior of chlorophylls in photosynthesis is consistent with its presence in our chlorobium chlorophylls.

(12) On the basis of comparison of the methine peaks of a 660 derivative with the α and β proton peaks of mesopyropheophorbide a and its δ -chloro derivative, Holt, *et al.*,^{2b} have assigned a δ -substituted structure to a 660 pheophorbide. In view of the unusual position found above for this δ -hydrogen, such an assignment in the absence of exchange data may be questionable.

(13) S. Granick and D. Mauzerall in "Metabolic Pathways," D. M. Greenberg, editor, Vol. II, Academic Press, New York, N. Y., 1961.

(14) J. J. Katz, M. R. Thomas and H. H. Strain, *J. Am. Chem. Soc.*, **84**, 3587 (1962).

(15) U. S. Public Health Service Postdoctoral Fellow, 1961-1963.

(16) National Science Foundation Predoctoral Fellow, 1961-1963.

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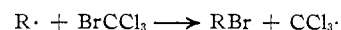
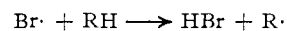
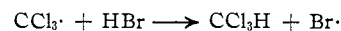
MECHANISMS OF BENZYLIC BROMINATION¹

Sir:

Despite popular opinion, considerable evidence exists that bromination by N-bromosuccinimide (NBS) can involve the bromine atom as the hydrogen-abstracting species rather than the N-succinimidyl radical as originally proposed by Bloomfield.² Among the evidence which can be cited in support of a bromine atom mechanism are (a) the near identity of the primary deuterium-isotope effects in photo and NBS brominations,³ identical values of ρ in $\rho\sigma^+$ correlations involving the competitive bromination of substituted toluenes photochemically and by NBS,^{4,5} (c) evidence that at low molecular bromine concentration allylic substitu-

tion predominates over addition to a double bond⁴ with extensive *cis-trans* isomerization of the unreacted olefin,⁶ and (d) analogy with the accepted chlorine atom mechanism for chlorination with N-chlorosuccinimide.⁷

We have studied the competitive bromination of a series of aralkyl hydrocarbons using molecular bromine in carbon tetrachloride, NBS in methylene dichloride and bromotrichloromethane⁸ in carbon tetrachloride as the brominating agents. The similarity and uniqueness of the relative reactivity series obtained for photo and NBS brominations indicates that under our conditions the same hydrogen-abstracting species, the bromine atom, is involved in both reactions. On the other hand, a completely different relative rate sequence is observed in brominations using bromotrichloromethane, indicating that here the trichloromethyl radical is the hydrogen-abstracting species and thereby eliminating the following possible reaction pathway.



The relative reactivity sequence observed in bromotrichloromethane bromination is so different from that proposed formerly by E. C. Kooyman from a study of the retarding effect of aralkyl hydrocarbons on the telomerization of carbon tetrachloride or bromotrichloromethane with olefins,⁹ that Kooyman's reactivity series as ascribed to the trichloromethyl radical must be considered erroneous.

The experiments summarized in Table I were performed by competitively brominating solutions 0.05 to 1 M in total hydrocarbon with about 50 mole % of the brominating agent. The disappearance of hydrocarbons was determined by gas-liquid chromatography and relative reactivities were calculated by an integrated equation. The data of Table I are averages of 3-13 experiments for each pair of hydrocarbons with ethylbenzene always taken as one of the reactants. Cross-checks involving other pairs of hydrocarbons gave results consistent with those reported. The results are independent of hydrocarbon concentrations or ratios, and of the concentration of the brominating agent. The reactivities reported for photobromination with molecular bromine are not influenced by an in-

TABLE I

RELATIVE REACTIVITIES (MOLECULAR) OF ARALKYL HYDROCARBONS IN FREE RADICAL BROMINATIONS AT 40°

Hydrocarbon	Brominating agent			
	$\text{Br}_2 + h\nu^a$	$\text{NBS} + h\nu^b$	$\text{BrCCl}_3 + h\nu^c$	$\text{CCl}_3 \cdot$ (Kooyman) ^d
Toluene	1.00 ^e	1.00 ^e	1.00 ^e	1.00 ^e
Ethylbenzene	11 ± 1	14 ± 2 ^f	29 ± 4	3.1
Cumene	12 ± 1	14 ± 2	72 ± 7	4.2
Diphenylmethane	7 ± 1	7 ± 1	29 ± 4	8.0
Triphenylmethane	5.5 ± 0.5	...	72 ± 7	16.7

^a In dilute carbon tetrachloride solution and at high bromine and low hydrogen bromide concentrations. ^b In dilute refluxing methylene chloride solution. ^c In dilute carbon tetrachloride solution. ^d At 91.5°, ref. 9. ^e Assumed. ^f The same value was observed under homogeneous or heterogeneous conditions and in the presence of a trace of molecular bromine.

crease in the rate of bromine addition or hydrogen bromide removal. Thus, the results are not complicated by the occurrence of reactions such as

(6) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).

(7) J. Adam, P. A. Gosselain and P. Goldfinger, *Nature*, **171**, 704 (1953); *Bull. soc. chim. Belges*, **65**, 523 (1956).

(8) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391, 394 (1960).

(9) E. C. Kooyman, *Disc. Faraday Soc.*, **10**, 163 (1951); E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

(1) Directive Effects in Aliphatic Substitutions, Part XVII. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

(2) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(3) K. B. Wiberg and L. H. Slauch, *J. Am. Chem. Soc.*, **80**, 3033 (1958).

(4) F. L. J. Sixma and R. H. Reim, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **61B**, 183 (1958).

(5) Private communication from Professor J. C. Martin, University of Illinois.