

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)⁸ 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.

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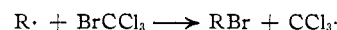
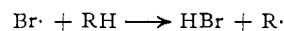
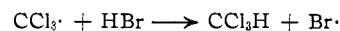
MECHANISMS OF BENZYLIC BROMINATION¹

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			$\text{CCl}_3\cdot$ (Kooyman) ^d
	$\text{Br}_2 + h\nu^a$	$\text{NBS} + h\nu^b$	$\text{BrCCl}_3 + h\nu^c$	
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).

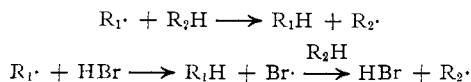
(1) Directive Effects in Aliphatic Substitutions, Part XVII. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

(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.



Products of ring bromination could not be found by gas-liquid chromatography and must be present in very low concentration if they are formed at all.

The fact that the reactivity sequence observed in photo and NBS bromination is fairly unique, particularly in regard to the reactivities of ethylbenzene and diphenylmethane, adds support to the conclusion that the bromine atom is the hydrogen-abstracting species in both reactions. Table II gives reactivity series observed with other common atoms and radicals. Only the chlorine and bromine atoms give a reactivity series in which diphenylmethane is less reactive than ethylbenzene.

TABLE II
RELATIVE REACTIVITIES OF ARAKYL HYDROCARBONS TOWARD ATOMS AND RADICALS (PER α -HYDROGEN ATOM)

Hydrocarbon	Atom or radical				
	Cl ^a	ROO ^b	Poly. styrenyl ^c	(CH ₃) ₂ CO ^d	C ₆ H ₅ ^e
Toluene	1.0 ^f	1.0 ^f	1.0 ^f	1.0 ^f	1.0 ^f
Ethylbenzene	2.5	7.8	8.2	3.2	4.4
Cumene	5.5	13.3	20	6.8	9.7
Diphenylmethane	2.0	16	28	4.7	7.5
Triphenylmethane	7.2	...	85	9.6	...

^a At 40°, extrapolated to zero hydrocarbon concentration in carbon tetrachloride solution (results of Dale G. Hendry, A. Ito and H. McBride). ^b At 90°, G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956). ^c At 60°, R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947). ^d At 40°, C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960). ^e At 60°, from competitive experiments between carbon tetrachloride and aralkyl hydrocarbons.¹⁰ ^f Assumed.

The data for reactivity toward phenyl radicals are part of a comprehensive study of the hydrogen-abstracting ability of phenyl radicals generated by the thermal decomposition of phenylazotriphenylmethane.¹⁰ At low phenyl radical concentrations we have found little substitution of phenyl radicals in the ring of nitrobenzene, chlorobenzene, diphenyl ether, diphenyl, triphenylamine or pyridine (all at about 1 M in the presence of excess carbon tetrachloride) as evidenced by the high yields of chlorobenzene from reaction with the carbon tetrachloride in the reaction mixture.¹⁰

(10) Work with Robert F. Bridger.

(11) (a) Alfred P. Sloan Foundation Fellow; (b) National Science Foundation Undergraduate Research Participant, 1960-1962.

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ON THE SPECIFIC REACTIVITY OF CHLORINS TOWARD AN ELECTROPHILIC ATTACK ON THE METHENE BRIDGES

Sir:

Recent proton magnetic resonance measurements have shown¹ that the exchangeable hydrogen atom of chlorophyll *a* is located on the δ -bridge carbon of the porphyrin ring, in accordance with previous findings of Woodward and Škarić,² showing that chlorins display a selective high reactivity toward electrophilic attack on the δ and γ positions, whereas the α and β carbons do not react under the same conditions. The latter authors have predicted that no such reactivity of any bridge atom should exist in the porphyrins, a hy-

pothesis confirmed by the non-exchangeability of the corresponding hydrogens in rhodoporphyrin dimethyl ester.²

We wish to report that calculations of the electronic structure of chlorins and porphyrins in the Hückel approximation of the method of molecular orbitals give a straightforward account of these properties.

The calculations have been performed for porphyrin, I, chlorin, II and 2-vinyl, 6-formyl, 7,8-dihydroporphyrin, III, considered as a model for the conjugated system of chlorophyll, taking into account the conjugation of two nitrogen lone-pairs and assuming the same electronegativity parameters for the four nitrogen atoms, namely, $\delta = 0.7$.³

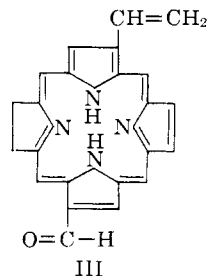
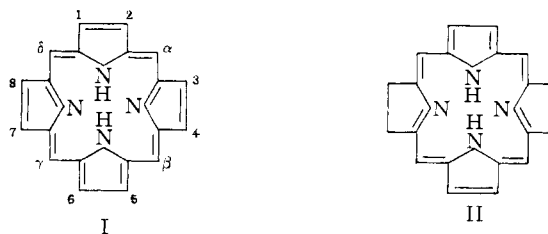
It should be pointed out that whereas identical parameters for =N- and -NH- should not be used in general, the case of porphyrins is a justifiable exception to the rule as, here, the equal sharing of the two central hydrogen atoms by the four nitrogens corresponds better to the situation in the metalloporphyrins. Moreover calculations performed in discriminating between the different possible tautomeric forms of porphyrin³ show that the outstanding features of the electronic structure and of the energy indices are not affected by the approximation adopted.

The electronic charges of the bridge carbon atoms in I, II and III are

	I	II	III
α	0.948	0.943	0.954
β	0.948	0.943	0.930
γ	0.948	1.063	1.073
δ	0.948	1.063	1.068

These data show a striking difference between the δ , γ and the α , β bridge carbons of the chlorins, and at the same time a fundamental difference between chlorin and porphyrin: in porphyrin all the bridge-atoms are electron-deficient (electronic charge less than unity), and thus carry a positive net charge, whereas, in chlorin only the α and β carbons are electron-deficient while the carbons γ and δ carry an excess of π electrons (charge greater than unity). These last two carbons will thus be the only ones to have a tendency toward an attack by electrophilic reagents. Moreover, when the γ -position is blocked to substitution as in chlorophyll *a* or in chlorintrimethyl ester, the δ carbon will remain the only position reactive to electrophilic attacks.

The calculations of Wheland's localization energies entirely confirm these results: in porphyrin (I) the



(3) For a detailed discussion of the problem of the parameters in the Hückel approximation, see: B. Pullman and A. Pullman, "Quantum Biochemistry," chapters III and IX, Wiley's Interscience Division, New York, N. Y., in press.

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

(2) R. B. Woodward and V. Škarić, *ibid.*, **83**, 4676 (1961).