

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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RECEIVED OCTOBER 16, 1962

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

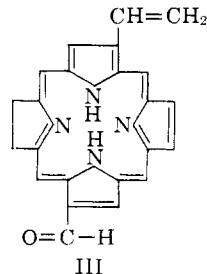
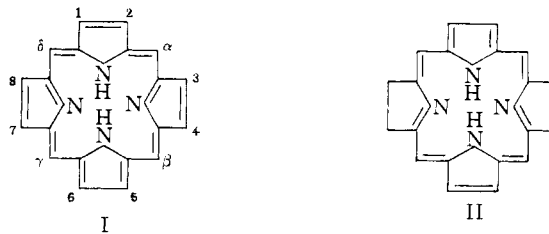
It should be pointed out that whereas identical parameters for =N- and -NH- should not be used in general, the case of porphyrins is a justifiable exception to the rule as, here, the equal sharing of the two central hydrogen atoms by the four nitrogens corresponds better to the situation in the metalloporphyrins. Moreover calculations performed in discriminating between the different possible tautomeric forms of porphin³ 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 porphin (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).

smallest localization energy on the δ -carbon is the nucleophilic localization energy (1.76 β), whereas in chlorin (II), the smallest localization energy on the same atom is the electrophilic one (1.93 β).

It may be useful to add that the examination of results of calculations on porphin⁴ and chlorin⁵ in the homocyclic approximation ($\delta_N = 0$) shows very clearly that the phenomenon emphasized here will be reflected in the Hückel approximation of the molecular orbital method whatever be the choice of the value of δ_N provided this choice is reasonable, namely, $\delta > 0$. Indeed, with $\delta = 0$ the charge on the δ -carbon goes from 0.965 in I to 1.100 in II, whereas the charge on the α -carbon is increased only to 1.005 by hydrogenation.

It is clear that any sensible choice of $\delta_N \neq 0$ will maintain this last charge below unity while a very high and thus improbable value of the parameter would be necessary to lower the charge of the δ -carbon below one.

(4) H. C. Longuet-Higgins, C. W. Rector and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(5) J. R. Barnard and L. M. Jackman, *J. Chem. Soc.*, 1172 (1956).

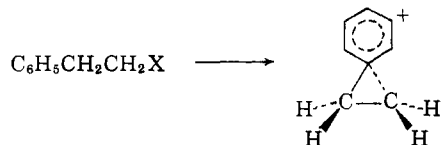
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RECEIVED OCTOBER 26, 1962

PHENYL PARTICIPATION IN THE SOLVOLYSIS OF ORGANOMERCURIALS^{1,2}

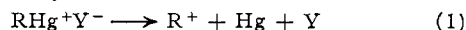
Sir:

Phenyl participation in solvolytic reactions has been widely studied.³ However, the concept of phenyl participation has received more substantiation from prod-



uct than kinetic studies. Thus, although *p*-anisyl gives a large rate enhancement, the largest factor previously observed for phenyl was for tosylates in formic acid,⁴ $k_{\text{phenethyl}}/k_{\text{ethyl}} = 2$ (uncorrected for electronic effects). Substantial evidence for substituted aryl participation has been given by the isolation of the intermediate in the solvolysis of 2-*p*-hydroxyphenethyl bromide.⁵

Since the solvolysis of mercurials⁶ is known to be very



sensitive to changes in structure⁶ and nucleophilicity of solvent,⁷ a large effect by phenyl participation should be noted.

(1) Organomercurials. XI.

(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(3) For early references, see A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(4) S. Winstein, C. R. Lindgren, H. Marshall and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

(5) R. Baird and S. Winstein, *ibid.*, **79**, 4238 (1957).

(6) F. R. Jensen and R. J. Ouellette, *ibid.*, **83**, 4777, 4778 (1961).

(7) F. R. Jensen and R. J. Ouellette, *ibid.*, **85**, 363 (1963).

The rates of solvolysis of β -phenethylmercuric perchlorate and methyl substituted compounds in acetic and formic acids (containing a small amount of water) are listed in Table I. As expected, the rate differences are larger in formic acid. It can be seen readily that β -phenyl does enhance the rate of reaction. Furthermore, substitution of methyl on the ring results in additional enhancement. There would seem to be little doubt that this rate increase is due to participation by phenyl even in the unsubstituted compound in acetic acid.

TABLE I

RATES AND ENERGY PARAMETERS FOR THE SOLVOLYSIS OF SUBSTITUTED ETHYLMERCURIC PERCHLORATES IN ACETIC AND FORMIC ACIDS

Substituent	Acetic Acid			Formic acid		
	ΔH^\ddagger , kcal./ mole	ΔS^\ddagger , e. u.	$k_1 \times 10^6$, sec. ⁻¹ (75°)	ΔH^\ddagger , kcal./ mole	ΔS^\ddagger , e. u.	$k_1 \times 10^7$, sec. ⁻¹ (50°)
H	27.24	-6.1	2.40	32.47	11.7	2.62
Phenyl	29.76	+5.1	19.9	31.75	16.4	79.5
<i>m</i> -Methyl- phenyl	29.38	4.0	43.2	30.74	15.3	254
<i>p</i> -Methyl- phenyl	27.84	3.7	142	29.3	14.2	1310
2,2-Di- methyl-2- phenyl (nophyl)	26.4	4.1	1810	28.34	16.8	1986

Further indication of phenyl participation is obtained by the solvolysis data for neophylmercuric perchlorate. Whereas the effect of β -methyl substitution on the rate of solvolysis of propylmercuric perchlorate is relatively small,⁸ the rate enhancement for β -methyl substitution on phenethyl is a factor of 91 in acetic acid (75°) and 248 in formic acid (50°). If no phenyl participation occurred, the rate enhancement of the two methyl groups would be approximately equivalent to the change in going from propyl to 2,2-dimethylpropyl.

The relative substituent effects of *m*- and *p*-methyl indicate that the source of participation is the localized π -orbital, but the data in no way provide information as to whether the intermediate ion is symmetrical.

These limited data do not give close agreement with σ^9 or σ^+ ,¹⁰ however, the ρ for the reaction is as great as those obtained for conventional solvolyses of benzylic compounds. The lack of close correlation with the substitution constants may be due to interaction of the mercuronium group with the π -cloud. It should be noted, however, that this interaction could only be expected to lead to decreased reactivity for these compounds.

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RECEIVED AUGUST 28, 1962

(8) R. J. Ouellette, Ph.D. Thesis, University of California, Berkeley 4, California.

(9) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(10) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **84**, 1668 (1962).