

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.

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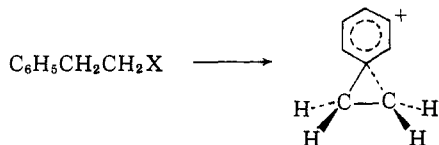
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PHENYL PARTICIPATION IN THE SOLVOLYSIS OF ORGANOMERCURIALS^{1,2}

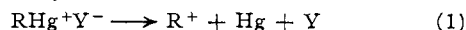
Sir:

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.

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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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