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ELECTRONIC EFFECTS IN SOLVOLYSIS REACTIONS. I. A STUDY OF p-CYCLOPROPYLPHENYLDIMETHYLCARBINYL CHLORIDE

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During the past fifteen years theoretical and experimental studies[1] have indicated that the cyclopropane ring is particularly effective in stabilizing electron deficient centers. The rate enhancements as well as carbon skeletal rearrangements which have been observed in cyclopropylcarbinyl systems have been interpreted as evidence for increased electron delocalization in the transition state[1a,2] leading ultimately to the "bicyclobutonium ion". On the other hand, Brown[3] has interpreted these same observations as due to a "decrease in strain" in going from reactant to transition state. We felt, therefore, that it would be informative to investigate the solvolysis reaction of a system in which the cyclopropyl group was not in the immediate vicinity of the reaction site, but nevertheless located in a position where it might be expected to significantly interact with the reaction site by inductive and/or "resonance" interaction mechanisms. We report here our results on the solvolysis of p-cyclopropylphenyldimethylcarbinyl chloride in aqueous acetone at a series of temperatures.

Cyclopropylbenzene was prepared by the method of Corbin, Hahn and Shechter.[4] Bromination of this compound by the procedure of Levina, *et. al.*,[5] yielded *p*-bromophenylcyclopropane as the only product as shown by gas chromatography and n.m.r. spectrum. Preparation of the Grignard reagent and subsequent reaction with acetone gave in good yield *p*-cyclopropylphenyldimethylcarbinyl carbinol. The compound was characterized by analytical data, infrared spectrum and the n.m.r. spectrum,[a] which shows absorption at δ 7.55 and 7.18 (two 2H doublets, $J = 8.5$ c.p.s. further split into multiplets $J \leq 1$ c.p.s.) typical of a *p*-disubstituted benzene, and peaks at δ 2.12 (1H singlet, $-OH$), 2.00-1.67 (1H multiplet, tertiary cyclopropyl hydrogen), 1.52 (6H singlet, $-CH_3$) and 1.0-0.5 (4H multiplet, cyclopropyl methylene hydrogens). The chloride was prepared from the carbinol by the procedure of Brown, *et.al.*[6] and used directly for rate measurements without further treatment. The chloride shows n.m.r. peaks[b] at δ 7.52 and 7.00 (two 2H doublets, $J = 9$ c.p.s., further split into multiplets, $J \leq 1$ c.p.s.), 2.35 (6H singlet, $-CH_3$), 1.90-1.25 (1H multiplet, tertiary cyclopropyl hydrogen) and 0.80-0.20 (4H multiplet, cyclopropyl methylene hydrogens).

The solvolysis rates were determined in 94.8 weight percent aqueous acetone at relatively low temperatures (-20.0° to $+3.0^{\circ}$) by the procedures described by Brown, *et.al.*[6,7] The hydrogen chloride formed during the reaction was determined by titration with a standard solution of sodium ethoxide (0.0320N.) in absolute ethanol at -20° to -10° using bromcresol green as indicator.

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[a] Taken in carbon tetrachloride solution.

[b] Taken as a pure liquid.

Rate data were obtained at three temperatures. These experimental rate constants were then extrapolated to 25.0° and further extrapolated to 90 volume percent aqueous acetone as described by Okamoto and Brown.[8] These data are presented in Table I along with the corresponding activation parameters and substituent constants $\sigma^{\oplus}$.[9] Included for comparison are the data for the unsubstituted,[6,9] *p*-methyl,[6,9] *p*-isopropyl,[6,9] *p*-*t*-butyl[6,9] and *p*-methoxyphenyldimethylcarbinyl chloride.[8,9]

From the rate ratios listed in the table it is apparent that the *p*-cyclopropyl group[d] is considerably more effective in enhancing the solvolytic rates than the other alkyl groups. The relative magnitudes of the substituent constants $\sigma^{\oplus}$ reflect these results.

The substituent constant $\sigma^{\oplus}$ [9] is a direct indication of the ability of a given group to supply or withdraw electron density by inductive and resonance interaction mechanisms. Available data indicate only small difference in the effects of alkyl groups on the rates of solvolysis reactions. The maximum variation of $\sigma^{\oplus}$ values for the more common alkyl substituents ($\sigma^{\oplus}_{p\text{-}t\text{-}Bu} - \sigma^{\oplus}_{-Me}$) is only 0.055. The data for the *p*-cyclopropyl substituent indicate a marked enhancement of the electron supplying ability of this group compared with other alkyl groups. Such an effect is much too large to be explained by normal hyperconjugation arguments. An unusually large effect is noted also if one compares the Hammett substituent constants for these same *para*-substituents ($\sigma_{\text{cyclopropyl}} = -0.22 \pm 0.02$[10], $\sigma_{\text{isopropyl}} = -0.15$,[11] $\sigma_{\text{isopropylene}} \cong +0.16$[10]).

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[d] It has been pointed out by a referee that unpublished studies of the same system in 90 volume percent aqueous acetone by Hahn, Corbin and Shechter have yielded similar results.

Table I

Comparative Rate Data, Activation Parameters and Substituent Constants ($\sigma^{\oplus}$) for Substituted Phenyldimethylcarbinyl Chlorides at 25°.

Substituent	Solvent (Vol. % aq. acetone)	Rate Constant $k_1 \times 10^5 (\text{sec}^{-1})$ 90 vol. % acetone	k_1/k_H	$\Delta H^{\ddagger}$ (kcal./mole)	$\Delta S^{\ddagger}$ (e.s.u.)	$\sigma^{\oplus}$
Hydrogen	90	12.4	1.00	18.8	-12.4	(0.000)
p-Methyl	90	322	26.0	17.3	-12.0	-0.311
p-Isopropyl	90	233	18.8	17.4	-12.2	-0.280
p-*t*-Butyl	90	178	14.3	17.3	-13.3	-0.256
p-Cyclopropyl	94.8[c]	907[d]	73.5	14.8	-23.1	-0.410
p-Methoxy	94.8[c]	41700	3360	12.9	-21.1	-0.778

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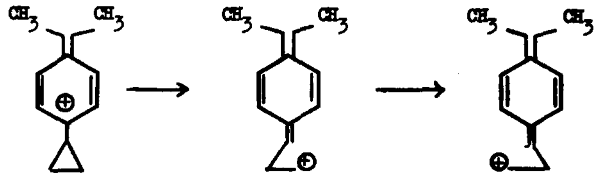
[c] Weight percent.

The activation parameters are also of interest. While these measurements and those of the p-methoxy compound[8] were carried out in 94.8 weight percent aqueous acetone, the remainder of the alkyl substituted derivatives were studied in 90 volume percent aqueous acetone. It is, therefore, not possible to make a quantitative comparison because of the extreme difficulty in assessing the relative solvation changes, extent of charge development in the various reactions, etc. However, a trend may be developing. The activation parameters are essentially constant among the commonly used alkyl groups (Table I). A group capable of strong resonance interaction such as p-methoxy shows a significantly decreased enthalpy of activation, $\Delta H,^{\ddagger}$ which is consistent with the observed rate enhancement for this substituent. A similar decrease in $\Delta H^{\ddagger}$ is observed for the p-cyclopropyl group. The enthalpy of activation for systems containing strong electron withdrawing groups such as p-nitro is large as expected even though it was measured in a somewhat more aqueous medium.[8] The entropy of activation, $\Delta S^{\ddagger}$, is constant for the alkyl substituents but shows an apparent decrease for a group capable of strong resonance interaction such as p-methoxy (94.8 weight % aqueous acetone). A similar trend is noted for the p-cyclopropyl group. This may well be an indication of a restriction of internal rotational freedom on going from reactant to transition state (if the major change is not an increased charge development in the transition state). Such a view would be consistent with the suggestion that "nonclassical" participation of the cyclopropyl group is involved in the rate determining step. This possibility is being explored



further by studying the effect of solvent on the various activation parameters.

Work is continuing on such systems as the allyl substituted cumyl chlorides as well as other systems designed to test the importance of "non-classical resonance" interactions relative to internal strain. We will report on these studies at a later date.

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