

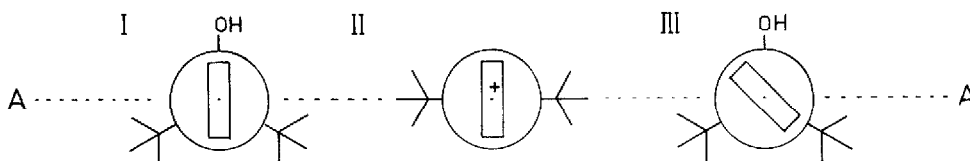
THE STRUCTURE OF ARYLDI-t-BUTYLCARBINOLS

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Studies by ir and nmr spectroscopy (1) of aryldi-t-butylcarbinols, 1 have been interpreted in terms of structure I which is held to explain the non-equivalence of the two orthohydrogens and the two hydroxyl group absorptions in the $3610-40\text{ cm}^{-1}$ range.



It is difficult, however, to reconcile this structure with the data of Tanida and Matsumura (2) for the solvolysis of aryldi-t-butylcarbinylyl p-nitrobenzoates, 2 in aqueous acetone ($\rho = -1.79$ and $r = 0.49$ in the Yukawa-Tsuno equation (3) : $\log k/k_0 = \rho (\sigma^\circ + r \Delta\sigma^\circ)$). The parameter r is defined so as to indicate the importance of resonance stabilisation of the incipient carbonium ion by electron-donating para substituents. Clearly, a value as high as 0.49 is not consistent with the orthogonal structure, II proposed for the intermediate (2).

TABLE : RATE CONSTANTS ($10^4 k$; k in sec^{-1}) FOR DEHYDRATION OF ALCOHOLS 1 (25° , HOAc, 10% v/v H_2SO_4) AND SOLVOLYSIS OF p-NB's 2 (85° , HOAc, 0.01M NaOAc)

X	<u>1</u>	<u>2</u>
p-MeO	160	6.18
p-Me	42	1.74
m-Me	22	1.26
H	12	0.805
p-Cl	1.4	0.220
m-Cl	0.41	0.100
m-CF ₃	0.15	0.0364
ρ	-3.93	-2.48
r	0.29	0.41



1 : Y = H

2 : Y = p-NO₂C₆H₄CO₂⁻

We have now reexamined the solvolysis of 2 and the dehydration of the corresponding carbinols, 1 in anhydrous acetic acid. The kinetic data (Table) were correlated by the Yukawa-Tsuno equation, with r equal to 0.41 (2) and 0.29 (1).

Assuming (4) that r can be replaced by E_{θ}/E_0 where $E_{\theta} = E_0 \cos^2 \theta$ (E_{θ} and E_0 are the resonance energies corresponding to rotations of θ° and 0° relative to the plane A - A) (5) we calculate that the rotation is of the order of 56° and 51° for 1 and 2, respectively.

Inspection of Stuart-Briegleb space-filling models reveals that the least strained conformation, wherein two t-butyl groups are attached to an sp^3 carbon (6), prohibits the introduction of the aryl ring as required by structure I. There is, however, no difficulty in positioning the ring if it is first turned through approximately 45° (structure III) : one ortho-hydrogen is then in close proximity to three hydrogen atoms ; the other is quite uncongested. Steric constraints are less severe in the carbocation, and the angle of rotation could probably vary between 75 and 90° , depending on the relative importance of non-bonding interactions and resonance stabilisation. In any case, the passage from the molecule to the intermediate will be accompanied by an increase in θ . The transition state for solvolysis of 2 is considered to be reactant-like (7) and will, therefore, be associated with a smaller degree of rotation than in the case of alcohol dehydration : this idea is confirmed by the respective r -values.

The spectroscopic data do not appear to be inconsistent with the new structure. We are currently attempting to confirm our conclusions by strain energy calculations.

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