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STUDIES IN TAUTOMERISM
NEW GENERALIZATIONS ON o-BENZOYLBENZOIC ACIDS

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A recent publication (1) prompts us to disclose some of the generalizations that have resulted from our studies on the structural and environmental influences on the tautomerism of o-benzoylbenzoic acids and their derivatives (2,3).

All the acids studied except VI exist in the open form in the solid state. In solution, an equilibrium exists between the predominant open form and the cyclic form I $\rightleftharpoons$ II. There is a linear free energy relationship with Hammett's substituent constants (FIG. 1). The equilibrium can be interpreted on the basis of decrease in relative stability of the ketocarbonyl group by electron withdrawing substituents in the non-carboxyl bearing ring (ring A). In accordance with this view, the ρ values are positive when the equilibrium constant bears direct relation to the proportion of the lactol and the ρ values decrease with increase in the dielectric constant of the medium (TABLE I) [Dioxane is a special case. The inadequacy of dielectric constant as a measure of solvent polarity is well

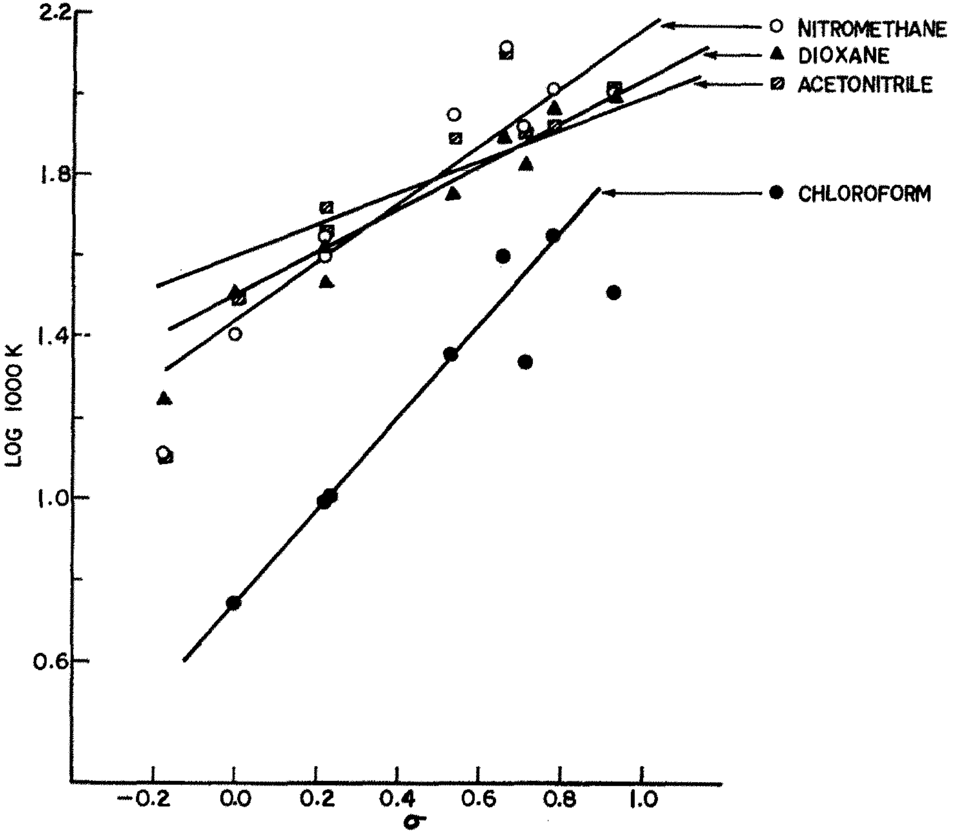


FIG.1: RELATION BETWEEN HAMMET σ- CONSTANTS AND LOG $K \times 10^3$ ($K = \frac{\text{LACTOL}}{\text{OPEN ACID}}$) OF SUBSTITUTED O-BENZOYLBENZOIC ACIDS IN DIFFERENT SOLVENTS.

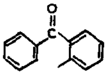
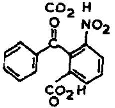
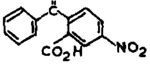
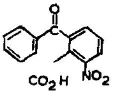
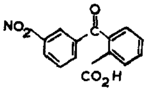
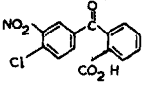
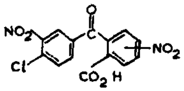
TABLE. 1.

EFFECT OF SOLVENTS

SOLVENT	DIELECTRIC CONSTANT	ρ
1,4-DIOXANE	2.21	0.52
CHLOROFORM	4.70	1.15
ACETONITRILE	37.5	0.40
NITRO METHANE	38.6	0.73

TABLE. 2.

EFFECT OF NITRO GROUP IN THE RING BEARING CARBOXYL GROUP

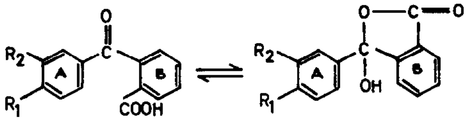
ACID	% LACTOL IN	
	ACETO NITRILE	NITRO-METHANE
	2.9	2.5
	<1	<1
	$\sim$1	$\sim$1
	0	0
	7.2	7.5
	10.5	11.1
	5.3	6.0

documented (4)]. Substituents in ring A effect only the carbonyl group, whereas increased solvation would stabilize both the ketone and the lactone carbonyl groups. That the lactone carbonyl solvation is more significant than the solvation of the carbonyl group is borne out by the larger proportion of lactol in the more polar solvent. This novel result could be rationalized by a consideration of the frequencies of the two vibrations and energy changes involved. In the present system, the lactone carbonyl requires $\sim$ 286 cals/mole more energy for its vibration compared to the ketone carbonyl (1780 vs 1680 cm^{-1}). It is not surprising that the lactone carbonyl should stand in greater need of stabilization by solvation to attain its vibrationally excited state. These considerations are confirmed by the influence of nitrogroup in ring B. Its destabilizing influence on the lactone group is far more pronounced than its destabilizing influence on the ketone (TABLE II).

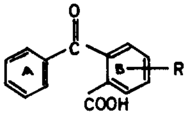
All the acid chlorides prepared exist exclusively in the cyclic form in solution (VII → VIII). The preference for the cyclic form can be accounted for on the basis of two considerations:

1. The operation of repulsive interaction between carbonyl dipoles when the like ends of the dipoles become contiguous as in IX.

2. The great facility with which a chloride group of the normal acid chloride is displaced, particularly by an intramolecular backside attack, when the unlike ends of the carbonyl dipoles are contiguous as in X.



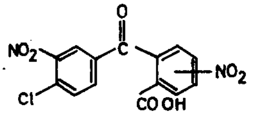
I II



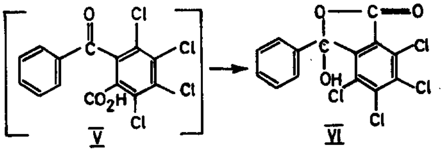
III

(a) $R_1 = R_2 = H$
(b) $R_1 = Cl, R_2 = H$
(c) $R_1 = Br, R_2 = H$
(d) $R_1 = CN, R_2 = H$
(e) $R_1 = CO_2H, R_2 = H$
(f) $R_1 = CONH_2, R_2 = H$
(g) $R_1 = NO_2, R_2 = H$
(h) $R_1 = CH_3, R_2 = H$
(i) $R_1 = H, R_2 = NO_2$
(j) $R_1 = CH_3, R_2 = NO_2$
(k) $R_1 = Cl, R_2 = NO_2$
(l) $R_1 = NH_2, R_2 = H$
(m) $R_1 = N(CH_3)_2, R_2 = H$
(n) $R_1 = OH, R_2 = H$
(o) $R_1 = OCH_3, R_2 = H$

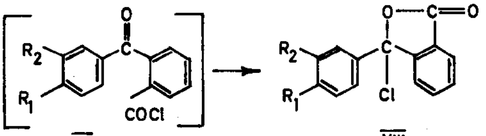
(a) $R = 3\text{-}NO_2$
(b) $R = 5\text{-}NO_2$
(c) $R = 6\text{-}NO_2$



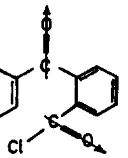
IV



V VI

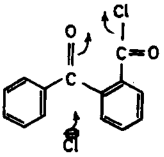


VII VIII



IX

(a) $R_1 = R_2 = H$
(b) $R_1 = Cl, R_2 = H$
(c) $R_1 = Br, R_2 = H$
(d) $R_1 = CN, R_2 = H$
(e) $R_1 = NO_2, R_2 = H$
(f) $R_1 = H, R_2 = NO_2$
(g) $R_1 = Me, R_2 = H$
(h) $R_1 = Me, R_2 = NO_2$
(i) $R_1 = Cl, R_2 = NO_2$
(j) $R_1 = OCH_3, R_2 = H$
(k) $R_1 = N(CH_3)_2, R_2 = H$



X

The proportions of the two forms were measured with the help of infrared spectroscopy using the integrated carbonyl band intensities as a measure of concentration. Standard curves were prepared by plotting the integrated band intensities of the pseudo esters (1780 ± 10 cm^{-1}) and normal esters (1730 ± 10 cm^{-1} and 1680 ± 10 cm^{-1} together) against their concentrations. Assuming that the lactol form and open form have the same intensities as the corresponding esters, the concentrations of these forms of the acids in solution were read from the graphs separately. The total of the two forms varied between 97-103%.

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