Transmission of Electronic Effects by the Oxiran Ring. Ionization Constants of *meta*- and *para*-substituted 2,3-Epoxy-3-phenylpropionic Acids in 50% Ethanol

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The ionization constants of *meta*- and *para*-substituted 2,3-epoxy-3-phenyl propionic acids have been measured in 50% ethanol. The results show that the oxiran ring transmits conjugation slightly better than the cyclopropane ring.

THE electronic properties of three-membered rings have received considerable attention in recent years. We report the transmission of resonance effects by the oxiran ring in a series of *trans-meta*- and *para*-substituted 2,3-epoxy-3-phenylpropionic acids.

The electronic interaction of the oxiran ring with an adjacent carbonyl group has been reported by Cromwell and his co-workers.[1] Their results showed that oxiran group in *trans*-arylaroylethylene oxide can transmit the electrical effects of a β-phenyl group to the α-carbonyl function as measured by the u.v. absorption spectra. More recently Ketcham,[2] from u.v. spectra, has concluded that the oxiran ring is able to transmit electronic effects by charge-transfer perturbation. A further investigation has been reported by Pews.[3] The ^{19}F n.m.r. shielding parameters for a series of *trans-p*-fluoro-*m'*- and -*p'*-substituted stilbene epoxides have been determined and the results show that the oxiran ring transmits conjugation to the same extent as the cyclopropane ring. This investigation was criticized by Dewar [4] who showed that the effects of substituents on the n.m.r. chemical shifts of fluorine are qualitatively different from their effects on chemical properties.

In view of these considerations, it was decided to study the problem from a different approach, *i.e.*, by comparing the relative abilities of some *meta*- and *para*-substituents to affect the acidity of the carboxy-group in 2,3-epoxy-3-phenylpropionic acid, *trans*-2-phenylcyclopropanecarboxylic acid, and 2-phenylpropionic acid. Table 1 lists the $\mathrm{p}K_a$ values of the acids studied together with the σ values used in the Hammett comparisons.[5]

TABLE 1

Ionization constants of *meta*- and *para*-substituted 2,3-epoxy-3-phenylpropionic acids in 50% ethanol at 25°

Substituent	$\mathrm{p}K_a$	σ	*n* [a]	Mean deviation
4-NO_2	5·12	0·78	3	0·02
3-NO_2	5·16	0·71	3	0·02
4-Cl	5·41	0·23	3	0·02
3-Cl	5·30	0·37	3	0·03
H	5·52	0·00	4	0·02

[a] *n* = Number of determinations.

ρ Values have already been derived from the $\mathrm{p}K_a$ values of a series of substituted compounds in the case of 2-phenylpropionic acid,[6] *cis*- and *trans*-2-phenylcyclopropanecarboxylic acid,[6] and *trans*-cinnamic acid [7] in 50% ethanol and the values of ρ for the three cases calculated. We have extended this investigation to derivatives of 2,3-epoxy-3-phenylpropionic acid. Comparison of the ρ values (Table 2) allows an evaluation of the relative conjugative abilities. The data in Table 2 show clearly that the ρ value of the oxiran ring is slightly higher than that of the cyclopropane ring and lower than that of the cinnamyl group. From the results we can conclude that the oxiran and cyclopropane rings transmit electronic effects to roughly the same extent, in fair agreement with the spectral evidence of Pews.[3] The small difference (*ca.* 10%) between the oxiran and cyclopropane rings may be due to the enhanced electronegativity of the oxygen-containing ring.

TABLE 2

ρ Values obtained from $\mathrm{p}K_a$ measurements of some series of acids

Series	ρ (50% Ethanol at 25°)
2-Phenylpropionic acid	0·344 [a]
trans-2-Phenylcyclopropanecarboxylic acid	0·473 [a]
trans-2,3-Epoxy-3-phenylpropionic acid	0·510 [b,c]
trans-Cinnamic acid	0·680 [d]

[a] Ref. 6. [b] This work. [c] ±0·016; *r* 0·9961. [d] Ref. 7.

TABLE 3

Physical properties and analyses of 2,3-epoxy-3-phenylpropionic acid derivatives

Acid substituent	M.p. (°C) [lit., m.p. (°C)]	Calc. (%)		Found (%)	
		C	H	C	H
4-NO_2	187—188 [188] [a]				
3-NO_2	124—125	51·65	3·35	51·5	3·3
4-Cl	150—152	54·55	3·55	54·55	3·5
3-Cl	141—143 [144] [a]				
H	83—84 [83] [b]				

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EXPERIMENTAL

Preparation of Acids.—The acids were prepared from the corresponding esters [8] by alkaline hydrolysis in ethanol.[9] The physical properties and analyses are listed in Table 3.

Measurement of p*K*.—Samples of each acid (*ca.* 10^{-2} mol) were dissolved in ethanol–water (1 : 1 v/v) (75 ml), the titration flask at 25° in a water-bath was purged with nitrogen, and the acid solution was titrated with 0·2N-sodium hydroxide. A Radiometer model 26 pH meter with standard glass and calomel electrodes was employed. The pH meter was standardized against a hydrogen phthalate buffer solution prepared by dissolving potassium hydrogen phthalate (10·211 g) in ethanol–water (1 l) (pH 4·00 ± 0·02) and against a phosphate buffer solution prepared by Radiometer (pH 6·50 ± 0·02). The pK_a values were calculated from the Henderson equation [10] and are the average of three determinations at *ca.* 20, 40, and 60% neutralization.

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