

Transmission of Polar Effects. Part XIV.¹ Ionisation of Substituted *trans*-3-Benzoylacrylic Acids

By K. Bowden * and M. P. Henry, Department of Chemistry, University of Essex, Colchester, Essex

The pK_a values of a series of substituted *trans*-3-benzoylacrylic acids have been determined in 80% (w/w) 2-methoxyethanol-water. The effect of substitution in the phenyl group has been assessed by means of the Hammett equation. The transmission of polar effects in the systems under study is discussed.

RECENTLY we have made studies of the alkaline hydrolysis of substituted methyl *trans*- and *cis*-3-benzoylacrylates² and both the ring-chain tautomerism in and the ionisation of substituted *cis*-3-benzoylacrylic acids.³ The elucidation of the mechanistic path in the former study² and the comparison with the corresponding *cis*-systems³ made necessary a knowledge of the transmission of polar effects in *trans*-3-benzoylacrylic acids. The present study reports an investigation of the ionisation of substituted *trans*-3-benzoylacrylic, *trans*-3-benzoyl-3-methylacrylic, and *trans*-3-benzoyl-2-methylacrylic acids.

EXPERIMENTAL AND RESULTS

The substituted *trans*-3-benzoylacrylic acids were prepared by Friedel-Crafts acylation of substituted benzenes with maleic anhydride,^{4,5} except for the nitro-acid. Use of citraconic anhydride, instead of maleic anhydride, gave the corresponding substituted *trans*-3-benzoyl-2-methylacrylic acids as the minor product.⁶⁻⁸ The substituted *trans*-3-benzoyl-3-methylacrylic acids were prepared from the corresponding *cis*-isomers, obtained from the latter as the major product of the above Friedel-Crafts reaction,^{6,7} by addition of morpholine and, then, by acid-catalysed elimination of morpholine from the adduct.⁹ The nitro-acids were synthesised by direct nitration of the corresponding *trans*-3-benzoylacrylic acids.¹⁰ After repeated recrystallisation to constant m.p. and drying in a vacuum desiccator (P_2O_5), the acids had either m.p.s in good agreement with literature values^{4-6,7,11,12} or, if previously unreported, satisfactory elemental analyses (see also spectral

studies below). The physical constants of the acids are listed in Table 1, together with their appearance and recrystallisation solvent. The elemental analyses of the

TABLE I
Physical constants of substituted *trans*-3-benzoylacrylic acids

Substituent	M.p./°C	Lit. m.p./°C	Ref.
H	95—96 ^a	98—99	4
4'-F	131—132 ^a	132—138	5
4'-Cl	157—158 ^a	154—155	4
4'-Br	158—159 ^a	159—160	4
4'-I	188—189 ^b	186—187	4
4'-Me	137—139 ^a	137.5—138.5	4
4'-OMe	135—136 ^a	138—139	4
3'-NO ₂	192—194 ^a	189—190	4
H(3-Me)	99—100 ^c	102—103	6
4'-Cl(3-Me)	124—125 ^c		
4'-Br(3-Me)	143—144 ^d	144.5—145	7
4'-Me(3-Me)	126—128 ^c		
4'-OMe(3-Me)	133—134 ^d		
3'-NO ₂ (3-Me)	122—125 ^e		
H(2-Me)	107—108 ^f	109—110	6
4'-Cl(2-Me)	167—169 ^g		
4'-Br(2-Me)	182—184 ^g	188	7
4'-Me(2-Me)	139—140 ^g	138—139	11
4'-OMe(2-Me)	123—124 ^h	119—120	12
3'-NO ₂ (2-Me)	161—163 ^a		

^a Yellow needles from benzene. ^b Pale yellow plates from ethanol. ^c Colourless needles from benzene-light petroleum (b.p. 60—80 °C). ^d Colourless plates from benzene. ^e Colourless prisms from benzene. ^f Yellow needles from water. ^g Yellow needles from chloroform. ^h Pale yellow needles from light petroleum (b.p. 60—80 °C).

previously unreported acids given in Table 2. Neutralisation equivalents of the acids were determined by titration

⁷ R. E. Lutz and R. J. Taylor, *J. Amer. Chem. Soc.*, 1933, **55**, 1168.

⁸ R. E. Lutz and A. W. Winne, *J. Amer. Chem. Soc.*, 1934, **56**, 445.

⁹ P. S. Bailey and C-K. Dien, *J. Org. Chem.*, 1956, **21**, 624.

¹⁰ M. T. Bogert and J. J. Ritter, *J. Amer. Chem. Soc.*, 1925, **47**, 526.

¹¹ F. Mayer and G. Stamm, *Ber.*, 1923, **56**, 1424.

¹² A. Fleifel, *J. Org. Chem.*, 1959, **24**, 1343.

¹ Part XIII, K. Bowden and M. J. Shaw, *J. Chem. Soc. (B)*, 1971, 161.

² K. Bowden and M. P. Henry, *J. Chem. Soc. (B)*, 1971, 156.

³ K. Bowden and M. P. Henry, *J.C.S. Perkin II*, 1972, 201.

⁴ D. Papa, E. Schwenk, F. Villani, and E. Klingsberg, *J. Amer. Chem. Soc.*, 1948, **70**, 3356.

⁵ F. K. Kirchner and E. J. Alexander, *J. Amer. Chem. Soc.*, 1959, **81**, 1721.

⁶ R. E. Lutz, P. S. Bailey, C-K. Dien, and J. W. Rinker, *J. Amer. Chem. Soc.*, 1953, **75**, 5039.

to be within $\pm 1\%$ of the calculated values. Solvents were purified as previously described.¹³

pK_a Measurements.—The pK_a values of the acids were measured in 80% (w/w) 2-methoxyethanol–water at 25 (± 0.1) °C, as described previously,¹³ and are shown in

studied were measured using a Varian A60-A spectrometer operating at 60 MHz. A 10% or saturated solution of the compound, depending on the solubility and containing 2% tetramethylsilane (TMS) as the internal standard, was used for each spectrum. The chemical shifts were measured on

TABLE 2
Elemental analyses of previously unreported substituted *trans*-3-benzoylacrylic acids

Substituent	Molecular formula	Calc. (%)				Found (%)			
		C	H	O	Other	C	H	O	Other
4'-Cl(3-Me)	C ₁₁ H ₉ ClO ₃	58.8	4.0	21.4	15.8 (Cl)	58.7	4.1		15.7 (Cl)
4'-Me(3-Me)	C ₁₂ H ₁₂ O ₃	70.6	5.9	23.5		70.3	6.1		
4'-OMe(3-Me)	C ₁₂ H ₁₂ O ₄	65.4	5.5	29.1		65.9	5.6	28.5	
3'-NO ₂ (3-Me)	C ₁₁ H ₉ NO ₅	56.1	3.9	34.0	6.0 (N)	56.3	4.0	33.8	5.9 (N)
4'-Cl(2-Me)	C ₁₁ H ₉ ClO ₃	58.8	4.0	21.4	15.8 (Cl)	58.9	4.2		15.7 (Cl)
3'-NO ₂ (2-Me)	C ₁₁ H ₉ NO ₅	56.1	3.9	34.0	6.0 (N)	56.1	3.8		5.9 (N)

Table 3. All the values were the result of at least two separate determinations.

¹H N.m.r. Measurements.—The spectra of the compounds

TABLE 3

Ionisation of substituted *trans*-3-benzoylacrylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C

Substituent		pK_a *	
		3-Me	2-Me
H	5.33	5.65	5.74
4'-F	5.28		
4'-Cl	5.26	5.49	5.54
4'-Br	5.20	5.46	5.57
4'-I	5.24		
4'-Me	5.37	5.77	5.83
4'-OMe	5.39	5.76	5.86
3'-NO ₂	5.11	5.20	5.35

* The observed pK_a values were reproducible to ± 0.02 unit.

TABLE 4

¹H N.m.r. spectral results for the *trans*-3-benzoylacrylic acids *

Substituent	τ	
	2-H	3-H
H	3.09	1.91
4'-F	3.23	2.03
4'-Cl	3.23	2.03
4'-Br	3.23	2.03
4'-I	3.24	2.03
4'-Me	3.18	2.00
4'-OMe	3.04	1.99
3'-NO ₂	3.13	1.99
	2-H	3-CH ₃
H(3-Me)	3.73	7.56
4'-Cl(3-Me)	3.68	7.54
4'-Br(3-Me)	3.70	7.65
4'-Me(3-Me)	3.77	7.58
4'-OMe(3-Me)	3.96	7.80
3'-NO ₂ (3-Me)	3.62	7.54
	2-CH ₃	3-H
H(2-Me)	7.83	2.08
4'-Cl(2-Me)	7.80	2.07
4'-Br(2-Me)	7.81	2.13
4'-Me(2-Me)	7.82	2.10
4'-OMe(2-Me)	7.84	2.13
3'-NO ₂ (2-Me)	7.74	2.03

* Solvents were [²H₆]dimethyl sulphoxide for 2,3-H₂ (coupling constants, J , equal to 15.5 ± 0.5 Hz) and [²H₆]acetone for 2-Me, 3-H and 2-H, 3-Me systems (coupling constants, J , equal to 1.7 ± 0.3 Hz). τ Values are considered to be accurate to ± 0.02 unit.

the δ peak relative to TMS in p.p.m., before conversion into τ values. The spectral results are shown in Table 4. The aromatic protons were also observed and the *para*-substituted systems had a coupling constant, J , of 9.0 ± 0.5 Hz. The structures of the acids were confirmed and the acids were shown to be $>98\%$ pure by this spectral method.

DISCUSSION

The pK_a values of the three separate series of *trans*-acids have been successfully correlated by the Hammett equation (1), by use of the substituent constants σ ¹⁴

$$\log(k/k_0) = \rho\sigma \quad (1)$$

and σ° .¹⁵ These correlations are shown in Table 5 and are successful, overall marginally better using σ° .

TABLE 5

Hammett reaction constants for the ionisation of the substituted *trans*-3-benzoylacrylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C *

Series	ρ	$\log K_0$	r	s	n
2,3-H ₂	(a) 0.296	-5.31	0.976	0.022	8
	(b) 0.317	-5.33	0.994	0.012	8
2-Me, 3-H	(a) 0.551	-5.72	0.988	0.034	6
	(b) 0.599	-5.75	0.987	0.036	6
2-H, 3-Me	(a) 0.612	-5.63	0.992	0.030	6
	(b) 0.669	-5.66	0.997	0.020	6

* r is the correlation coefficient, s the standard deviation, and n the number of substituents studied. Correlations (a) are those using σ and (b) those using σ° .

These reaction constants, ρ , can be compared with that for the reference system, ρ_0 , for the ionisation of benzoic acids under the same conditions, which is 1.69.¹³ The reaction constant ratios, ρ/ρ_0 , are 0.19 (2,3-H₂), 0.35 (2-Me, 3-H), and 0.40 (2-H, 3-Me) for the three *trans*-3-benzoylacrylic acid systems. The ratio obtained by Bowden and Taylor¹³ for the ionisation of 2-benzoylbenzoic acids (0.33), although a *cis*-type system, agrees well with values obtained for the 2- and 3-methyl systems. These values closely compare with those for all three methyl *trans*-3-benzoylacrylate systems in their

¹³ K. Bowden and G. R. Taylor, *J. Chem. Soc. (B)*, 1971, 145.

¹⁴ D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420; R. A. Robinson and K. P. Ang, *J. Chem. Soc.*, 1959, 2314.

¹⁵ R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

alkaline hydrolysis reaction, with ρ/ρ_0 equal to 0.32.² Further, a value of 0.30 ± 0.05 can be calculated from the transmission coefficients tabulated by Bowden.¹⁶ The smaller value for the 2,3-H₂ system seems somewhat surprising as the latter system will be almost planar and highly conjugated. Thus, it would seem reasonable that it should be able to transmit polar effects effectively. Hogeveen¹⁷ has studied the effect of substitution on the pK_a values of both *cis*- and *trans*-3-arythio-, 3-arylsulphinyl-, and 3-arylsulphonyl-acrylic acids in 50% ethanol-water. Reaction constant ratios, ρ/ρ_0 , can be calculated for the *trans*-systems as 0.44 (thio link), 0.19 (sulphinyl link), and 0.23 (sulphonyl link), using ρ_0 equal to 1.47.¹⁸ The more efficient transmission of the thio-link was attributed to the greater polarisibility of this particular link. A related explanation has been made previously in a comparison of the acetylenic and ethylenic links.¹⁹ It is conceivable that the methyl groups in the systems under present study could increase the polarisibility of the transmitting link; but, in view

¹⁶ K. Rowden, *Canad. J. Chem.*, 1963, **41**, 2781.

¹⁷ H. Hogeveen, *Rec. Trav. chim.*, 1964, **83**, 813.

of the results from the hydrolysis of the esters, it seems unlikely. However, both the steric 'bulk' effect of the 2-methyl and 3-methyl, which is *cis* to the reaction site, could inhibit solvation of the carboxylate anion group. Previously, evidence¹⁶ has been given that such an effect could increase ρ by polar facilitation of steric inhibited solvation.

The pK_a values of the three parent unsubstituted acids show the expected trends. All three systems are much more acidic than acrylic acid (pK_a equal to 6.50 in this medium),²⁰ which is caused by the strongly electron-withdrawing ability of the benzoyl group.¹ The electron-releasing methyl group reduces this result. The 2-methyl is more effective than the 3-methyl substituent because of its proximity to the carboxylic acid group.

We thank Geigy (U.K.) Ltd. for financial support (to M. P. H.).

[1/1535 Received, August 23rd, 1971]

¹⁸ K. Bowden and G. E. Manser, *Canad. J. Chem.*, 1968, **46**, 2941.

¹⁹ M. Charton, *J. Org. Chem.*, 1961, **26**, 735.

²⁰ K. Bowden and M. P. Henry, preceding paper.