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# Reactions of Carbonyl Compounds in Basic Solutions. Part IV.<sup>1</sup> The Mechanism of the Alkaline Hydrolysis of Methyl 3-Benzoylacrylates

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Rate coefficients for the alkaline hydrolysis of a series of 3'- and 4'-substituted methyl cis- and trans-3-benzoylacrylates, 3'- and 4'-substituted methyl cis- and trans-3-benzoyl-3-methylacrylates, and 4'-substituted methyl trans-3-benzoyl-2-methylacrylates have been measured in 70% (v/v) dioxan-water at 1.0 °C. Rate coefficients for the unsubstituted parent esters were measured at several temperatures, from which the entropies and enthalpies of activation were evaluated. The effects of substitution were assessed by means of the Hammett equation. The reaction constants, p, for the two series of cis-esters are comparable to those for the hydrolysis of methyl benzoates under the same conditions. Those for the three series of trans-esters were only about one third those for the cisesters and are compatible with simple transmission of the substituent polar effect to the ester group. Three criteria for the occurrence of intramolecular catalysis in the alkaline hydrolysis of keto-esters, i.e., activation parameters, relative rates, and substituent effects, all indicate its presence in the hydrolysis of cis-3-benzoylacrylates.

IN Part III,<sup>1</sup> an attempt was made to survey the extent and importance of intramolecular catalysis in the alkaline hydrolysis of 2-keto- and 2-formyl-benzoates. A number of previous studies had indicated its occurrence in some diverse systems.<sup>2-6</sup> A number of possible criteria were applied and evaluated for the benzoate system.<sup>1,4</sup> It is our intention to use these mechanistic probes on a model system, the alkaline hydrolysis of *trans*- and *cis*-3-benzoylacrylates, (I) and (II). In these esters, the geometry on the one hand permits, i.e. (II), and on the other hand forbids, *i.e.* (I), the possibility of intramole-



cular catalysis. In particular, a study of the three criteria found most useful previously,<sup>1,4</sup> i.e., activation parameters, relative rates, and substituent effects, have been made and the results are reported here.

### EXPERIMENTAL

The substituted trans-3-benzoylacrylic, trans- and cis-3-benzoyl-3-methylacrylic, and trans-3-benzoyl-2-methyl-

- <sup>1</sup> Part III, K. Bowden and G. R. Taylor, preceding paper.
- <sup>2</sup> M. S. Newman and S. Hishida, *J. Amer. Chem. Soc.*, 1962, **84**, 3582; M. S. Newman and A. L. Leegwater, *ibid.*, 1968, **90**, 4410.
- <sup>3</sup> M. L. Bender and M. S. Silver, J. Amer. Chem. Soc., 1962, 84, 4589; M. L. Bender, J. A. Reinstein, M. S. Silver, and R. Mikulak, ibid., 1956, 87, 4545.

acrylic acids were prepared by Friedel-Crafts acylations of substituted benzenes with maleic or citraconic anhydride, except for the nitro-acids. The latter were synthesised by direct nitration of the corresponding 3-benzoylacrylic acids. After isolation and separation of the isomers, if necessary, the acids were carefully purified.7 The methyl trans-3-(3- and 4-substituted benzoyl)acrylates, trans- and cis-3-(3- and 4-substituted benzoyl)-3-methylacrylates, and trans-(4-substituted benzoyl)-2-methylacrylates were prepared either by a modified Fischer-Speier esterification (Method 1; the acid was refluxed in a methanol-benzeneconcentrated sulphuric acid mixture) 8 giving yields of 65-85% or esterification with diazomethane (Method 2; the acid reacted with 1 equiv. of diazomethane in ether) <sup>9</sup> giving almost quantitative yields, except for the nitro-acids. The latter gave yields of only 50-60% of the corresponding methyl esters. The methyl cis-3-(4-substituted benzoyl)acrylates were prepared by isomerisation of the corresponding trans-esters (Method 3; the trans-esters were dissolved in ether and were exposed to sunlight in a Pyrex vessel) <sup>10</sup> in very high yields. The latter method was found to be preferable to the use of u.v. lamps. After repeated recrystallisation to constant m.p. and drying in a vacuum desiccator  $(P_2O_5)$  or fractionally distilling at reduced pressure, the

<sup>4</sup> K. Bowden and G. R. Taylor, Chem. Comm., 1967, 1112; Part II, J. Chem. Soc. (B), 1970, 145.
 <sup>5</sup> H. D. Burrows and R. M. Topping, Chem. Comm., 1969,

- 904. <sup>6</sup> K. C. Kemp and M. L. Mieth, *Chem. Comm.*, 1969, 1260.
- <sup>7</sup> K. Bowden and M. P. Henry, unpublished studies.
  <sup>8</sup> E.g., A. I. Vogel, 'Practical Organic Chemistry,' Longmans, Green, and Co., Ltd., London, 3rd edn., 1962.
- <sup>9</sup> R. E. Lutz, D. T. Merritt, and M. Couper, J. Org. Chem., 1939, 4, 95.
- <sup>10</sup> G. P. Rice, J. Amer. Chem. Soc., 1924, 46, 214.

esters had either m.p.s in good agreement with literature values 11-14 or, if previously unreported, satisfactory elemental analyses (see spectral studies below). The physical constants of the esters are listed in Table 1, together with

## TABLE 1

Physical constants of substituted methyl 3-benzoylacrvlates

	401 9 140			
Cubatituant	M = 190	Lit. m.p./	Paf	Synthetic
Substituent	M.p./ C	C	Nei.	methou ·
trans-H	3234	32	11	14
trans-4'-F	8086			14
trans-4'-Cl	8182		10	10
trans-4 -Br	7070	77	12	1 *
trans-4 -1	102			10
trans-4 -Me	4047	71 79	10	15
trans 2' NO	102 104	1112	10	20
11ans-3 -1102	102104			2.
cis-H	6566	67	11	34
cis-4'-F	61 - 62			3 d
cis-4'-Br	5556	56.5	12	3.
cis-4'-I	5758			34
cis-4'-Me	4344			30
cis-4'-OMe	6061	62	10	37
trans-H(3-Me)	B.p. 100° at			20
( )	0.5  mmHg			
trans-4'-Cl(3-Me)	53 - 55			2 •
trans-4'-Br(3-Me)	72 - 74	74-75	13	2 •
trans-4'-Me(3-Me)	B.p. 130° at			2 9
. ,	0.5  mmHg			
trans-3'-NO <sub>2</sub> (3-Me)	85-87			2 *
cis-H(3-Me)	50 - 52			24
cis-4'-Cl(3-Me)	56-58			20
cis-4'-Br(3-Me)	69-70	69	14	2.
cis-4'-Me(3-Me)	53 - 54			20
cis-4'-OMe(3-Me)	104 - 105			20
trans 1' Cl(2-Me)	71-73			
$t_{mans-4'-Br(2-Me)}$	85-86	86	12	21
$t_{M}$	Bp 130° at	30	10	2.
<i>viuns</i> + mc( <i>a</i> -mc)	0.5 mmHg			2.
trans-4'-OMe(2-Me)	62-63			21
	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~			-

\* See text for synthetic methods. Details refer to appearance and recrystallisation solvent.

" Pale yellow needles from light petroleum (b.p. 60-80°). <sup>b</sup> Pale yellow needles from benzene. <sup>c</sup> Yellow needles from acetone. <sup>d</sup> Colourless plates from light petroleum (b.p. 60-80°). • Colourless needles from light petroleum (b.p.  $60-80^\circ$ ). Colourless prisms from light petroleum (b.p.  $60-80^\circ$ ). Pale yellow oil. Pale yellow prisms from light petroleum (b.p.  $60-80^\circ$ ). Yellow needles from light petroleum (b.p.  $60-80^\circ$ ).

their method of preparation, appearance, and recrystallisation solvent, and the elemental analyses of the previously unreported esters are given in Table 2. Esters absent from these Tables normally could not be prepared pure or were not stable in our hands. Methyl acrylate was fractionally distilled as a colourless liquid, b.p. 80.5-81° at 760 mmHg, immediately before use. Solvents were purified as previously described.1,15

<sup>1</sup>H N.m.r. Spectra.—The <sup>1</sup>H n.m.r. spectra of all the esters

 G. P. Rice, J. Amer. Chem. Soc., 1923, 45, 222.
 R. E. Lutz and G. W. Scott, J. Org. Chem., 1948, 13, 284. <sup>13</sup> R. E. Lutz and R. J. Taylor, J. Amer. Chem. Soc., 1933,

55, 1168. <sup>14</sup> R. E. Lutz and A. W. Winne, J. Amer. Chem. Soc., 1934,

56, 445. <sup>15</sup> K. Bowden, M. J. Hanson, and G. R. Taylor, J. Chem. Soc.

(B), 1968, 174.
 <sup>16</sup> K. Bowden and D. C. Parkin, Canad. J. Chem., 1968, 46,

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were measured, as described previously.<sup>16</sup> The esters were found to be both normally and isomerically pure by this criterion, i.e., >98%. The spectral shifts and coupling constants (Table 3) confirm the structure given for all these esters.

I.r. Spectra.—The carbonyl-stretching vibrations of the carbonyl groups of the methyl esters in carbon tetrachloride (Merck Uvasol) were measured, as described previously,<sup>4</sup> with a Perkin-Elmer spectrophotometer, model 231.

Kinetic Procedure.- The kinetic procedure was as previously described 1 for reactions arbitrarily defined as ' fast ' The method of Daniels et al.<sup>17</sup> was used in the calculation of the rate coefficients from the conductivities. The products of hydrolysis were found to be the anions of the corresponding benzoylacrylic acids in quantitative yield, with the exception of the 3'- and 4'-substituted cis-benzoylacrylic acids. The latter acids are unstable (isomerisation to trans-acids) and could not be prepared directly.7 The corresponding carboxylate anions have been found to be stable under similar conditions to the hydrolysis studied here.7 The conductivity kinetics and studies of the reaction by u.v. spectroscopy indicated that no isomerisation could be detected in these hydrolyses.

### RESULTS AND DISCUSSION

The alkaline hydrolysis of all the esters studied is of the first order both in the ester and hydroxide anion. The esters are stereochemically stable under the conditions of hydrolysis over the reaction period. Rate coefficients for five series of substituted methyl trans- and cis-3-benzoylacrylates in 70% (v/v) dioxan-water at 1.0 °C are shown in Table 4. The four parent unsubstituted esters available were also studied at several temperatures as shown in Table 5.

Reaction Constants.-The hydrolysis of the five separate series of both trans- and cis-esters have been successfully correlated by the Hammett equation (1), by use of the substituent constants  $\sigma$  and  $\sigma^{n}$ .<sup>18,19</sup> These

$$\log\left(k/k_0\right) = \rho\sigma \tag{1}$$

correlations are shown in Table 6. The trans-esters give successful correlations with  $\sigma$  and, marginly better, with  $\sigma^n$ . The reaction constants,  $\rho$ , for these *trans*-ester series are in the range 0.75-0.78, when using  $\sigma^n$ . These can be compared with the reference reaction constant,  $\rho_0$ , for the hydrolysis of methyl benzoates in the same medium,<sup>4</sup> which is 2.44 when corrected to  $1.0 \ ^{\circ}C.^{20}$  The reaction constant ratio,  $\rho/\rho_0$ , is 0.32 and is in good agreement with that calculated  $(0.3_0 \pm 0.0_5)^{21}$  on the basis of the simple attenuation of the substituent polar effect by transmission from the phenyl to the ester group. Further, the reaction constant ratios found for the ionisation of 2-benzoylbenzoic  $(0.33)^4$  and three series of trans-3-benzoylacrylic  $(0.17-0.35)^7$  acids confirm that the

<sup>17</sup> F. Daniels, J. W. Williams, P. Bender, R. A. Alberty, and C. D. Cornwall, 'Experimental Physical Chemistry,' McGraw-Hill, New York, 1962, p. 135. <sup>18</sup> D. H. McDaniel and H. C. Brown, J. Org. Chem., 1958, 23,

420. <sup>19</sup> H. van Bekkum, P. E. Verkade, and B. M. Webster, *Rec.* Trav. chim., 1959, 78, 815. <sup>20</sup> H. H. Jaffé, Chem. Rev., 1953, 53, 191.

<sup>21</sup> K. Bowden, Canad. J. Chem., 1963, 41, 2781.

TABLE 2 Elemental analyses of previously unreported substituted methyl 3-benzoylacrylates

	Molecular		Ca	lc. (%)			For	und (%)	
Substituent	formula	C	Н	0	Other	C	Н	0	Other
trans-4'-F	C <sub>11</sub> H <sub>9</sub> FO <sub>3</sub>	63.6	4.3	$23 \cdot 1$		$63 \cdot 4$	4.4	$23 \cdot 3$	
trans-4'-Cl	C <sub>11</sub> H <sub>9</sub> ClO <sub>3</sub>	58.8	<b>4</b> ·0	21.4	15·8 (Cl)	58.7	3.9		15·6 (Cl)
trans-4'-I	$C_{11}H_9IO_3$	<b>41</b> ·3	$2 \cdot 8$	15.0		41.7	$2 \cdot 9$	15.1	
trans-4'-Me	$C_{12}H_{12}O_{3}$	70.6	$5 \cdot 9$	23.5		70.7	6.0	23.7	
$trans-3'-NO_2$	$C_{11}H_9NO_5$	$56 \cdot 1$	$3 \cdot 9$	34.0	6·0 (N)	56.2	3.9		6·0 (N)
cis-4'-F	C <sub>11</sub> H <sub>9</sub> FO <sub>3</sub>	63.6	4.3	$23 \cdot 1$		$63 \cdot 4$	4.4	$23 \cdot 2$	
cis-4'-I	$C_{11}H_9IO_3$	41.3	$2 \cdot 8$	15.0		41.5	$2 \cdot 9$	15.0	
cis-4'-Me	$C_{12}H_{11}O_{3}$	70.6	$5 \cdot 9$	$23 \cdot 5$		70.4	5.7	$23 \cdot 6$	
trans-H(3-Me)	$C_{12}H_{12}O_{3}$	70.6	5.9	23.5		70.5	6.0	23.6	
trans-4'-Cl(3-Me)	$C_{12}H_{11}ClO_3$	60-4	<b>4</b> ·6	20.1	14·9 (Cl)	60·4	4.6		14·7 (Cl)
trans-4'-Me(3-Me)	$C_{13}H_{14}O_{3}$	71.5	6.5	22.0	· · ·	71.6	6.5	$22 \cdot 1$	. ,
trans-3'-NO <sub>2</sub> (3-Me)	$C_{12}H_{11}NO_5$	57.8	<b>4</b> · <b>4</b>	$32 \cdot 1$	5·7 (N)	57.7	4.5		5·8 (N)
cis-H(3-Me)	$C_{12}H_{12}O_{3}$	70.6	5.9	23.5		70.7	6.0	23.5	
cis-4'-Cl(3-Me)	C <sub>12</sub> H <sub>11</sub> ClO <sub>3</sub>	60.4	4.6	20.1	14·9 (Cl)	60.3	4.6		14·7 (Cl)
cis-4'-Me(3-Me)	$C_{13}H_{14}O_{3}$	71.5	6.5	22.0	. ,	71.7	6.5	22.0	• • •
<i>cis</i> -4'-OMe(3-Me)	$C_{13}H_{14}O_4$	66.7	6.0	27.3		66.5	6.1	27.5	
trans-4'-Cl(2-Me)	C <sub>12</sub> H <sub>11</sub> ClO <sub>3</sub>	<b>60·4</b>	<b>4</b> ·6	20.1	14·9 (Cl)	<b>60·4</b>	4.7		14·8 (Cl)
trans-4'-Me(2-Me)	$C_{13}H_{14}O_{3}$	71.5	6.5	22.0	( )	71.6	$6 \cdot 3$	21.9	- (- )
trans-4'-OMe(2-Me)	$C_{13}H_{14}O_{4}$	66·7	6.0	27.3		<b>66</b> ·7	$5 \cdot 9$	27.4	

hydrolysis of the trans-3-benzoylacrylates is governed by simple transmissive factors with normal, direct ester hydrolysis occurring. The two series of *cis*-3-benzoylacrylic acids have a reaction constant ratio for their

#### TABLE 3

<sup>1</sup>H N.m.r. spectral shifts and coupling constants for the substituted methyl 3-benzoylacrylates

		τ		
Series	<b>2</b> -н	3-H	2- or 3-Me	J/Hz
trans-2,3-H <sub>2</sub> *	3.11 - 3.22	1.89 - 2.08		$12.0(\pm 0.2)$
cis-2,3-H <sub>2</sub> *	3.48 - 3.67	2.60 - 2.84		$5.7(\pm 0.2)$
trans-2-H,3-Me†	3.62 - 3.79		7.45 - 7.60	$2.0(\pm 0.5)$
cis-2-H,3-Me †	3.70 - 3.78		7.86 - 7.90	$2.0(\pm 0.5)$
trans-2-Me,3-H †		$2 \cdot 10 - 2 \cdot 21$	7.82 - 7.90	$2.0(\pm 0.5)$
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In  $[{}^{2}H_{6}]$ dimethyl sulphoxide. † In  $[{}^{2}H_{6}]$ acetone.

#### TABLE 4

Rate coefficients for the alkaline hydrolysis of substituted methyl 3-benzoylacrylates in 70% (v/v) dioxan-water at 1.0 °C \*

	$10^{3}k_{2}/l \text{ mol}^{-1} \text{ s}^{-1}$		
Substituent	trans	cis	
H	460	1150	
4′-F	628	1430	
4′-Cl	740		
4'-Br	735	5170	
4'-I	572	3440	
4'-Me	<b>340</b>	<b>495</b>	
4'-OMe	371	144	
$3'-NO_2$	1590		
H(3-Me)	12.6	18.0	
4'-Cl(3-Me)	$22 \cdot 3$	46.2	
4'-Br(3-Me)	20.4	54.4	
4'-Me(3-Me)	9.74	7.09	
4'-OMe(3-Me)		4.45	
$3'-NO_2(3-Me)$	44.1		
4'-Cl(2-Me)	281		
4'-Br(2-Me)	260		
4'-Me(2-Me)	135		
4'-OMe(2-Me)	142		
Methyl acrylate	14.0		

\* Rate coefficients were reproducible to within  $\pm 3\%$ . Ester and base were at 0.01M concentration.

ionization (0.25-0.29), after correction of the observed  $pK_a$  values for the presence of a cyclic tautomer,<sup>7</sup> within the range of the related systems described above.

## TABLE 5

Rate coefficients for the alkaline hydrolysis of substituted methyl 3-benzoylacrylates in 70% (v/v) dioxan-water \*

		$10^{3}k_{2}/1 \text{ m}$	ol <sup>-1</sup> s <sup>-1</sup> at	
Substituent	1.0 °C	10.0 °C	20.0 °C	30.0 °C
trans-2,3-H <sub>2</sub>	460	934	2050	
cis-2,3-H,	1150	1800	3390	
trans-2-H,3-Me	12.6	$28 \cdot 8$	71.8	164
cis-2-H,3-Me	18.0	$29 \cdot 2$	53.6	89·3
	* Se	e Table 4.		

#### TABLE 6

Hammett reaction constants for the alkaline hydrolysis of the methyl esters in 70% (v/v) dioxan-water at 1.0 °C

Series		ρ	log ka	r	s	n
$trans-2, 3-H_2$	(a) (b)	$0.685 \\ 0.756$	$-0.222 \\ -0.256$	$0.981 \\ 0.981$	0·044 0·044	8 8
<i>cis</i> -2,3-H <sub>2</sub>	$\substack{(a)\\(b)}$	$2.561 \\ 2.808$	-0.178 - 0.199	$0.972 \\ 0.906$	$0.148 \\ 0.289$	6 6
trans-2-H,3-Me	$\substack{(a)\(b)}$	$0.759 \\ 0.783$	$-1.873 \\ -1.891$	0·993 0·993	$0.035 \\ 0.035$	$5 \\ 5$
cis-2-H,3-Me	$\substack{(a)\\(b)}$	$2.098 \\ 2.478$	$-1.782 \\ -1.900$	$0.997 \\ 0.965$	0·043 0·143	$5 \\ 5$
trans-2-Me,3-H	$\begin{pmatrix} a \\ b \end{pmatrix}$	0·628 0·779	-0.717 -0.765	0.975 0.991	0·046 0·028	4 4

\* r is the correlation coefficient, s is the standard deviation, and n is the number of substituents used. Correlations (a) are those using  $\sigma$  and (b) those using  $\sigma^n$ .

Whereas all the above reactions are best correlated by  $\sigma^n$ , the hydrolyses of the *cis*-esters have been correlated more successfully with  $\sigma$ . Further, the reaction constants for the hydrolysis of these cis-esters are 2.6 and  $2 \cdot 1$ . The former behaviour indicates the importance of more direct resonance interactions, while the latter corresponds to the alkaline hydrolysis of methyl 2-(3- and 4-substituted benzoyl)benzoates 4 and contrasts markedly with the reaction constants for the trans-esters. Bowden <sup>21, 22</sup> and Hogeveen <sup>23</sup> have both found that reaction constants for *cis*- and *trans*-3-substituted acrylic acids, whether the substituent is directly bonded to the 3-position or is attached to a phenyl group itself linked directly or indirectly to this position, are about the same. However, this is not found for the alkaline hydrolysis of the cis- and trans-benzovlacrylates in this study. The reaction constants for the cis-esters are about three times those for the trans-esters and are in close agreement with those previously obtained for the hydrolysis of methyl 2-(3- and 4-substituted benzoyl)benzoates in the same medium <sup>4</sup> ( $\rho$ , using  $\sigma$ , is 2.3 when corrected <sup>20</sup> to 1.0 °C). For the reasons stated previously,<sup>4</sup> the reaction constants for the alkaline hydrolysis of the *cis*-esters indicate that hydrolysis occurs with intramolecular catalysis and the primary process is attack at the keto-carbonyl carbon by the hydroxide anion.

Carbonyl Stretching Frequencies.-The carbonyl stretching frequencies of the methyl cis- and trans-benzoylacrylates have been measured in carbon tetrachloride. Two carbonyl absorptions were observed for each ester; absorptions corresponding to the keto- and estercarbonyl groups, as shown in Table 7. Within any

#### TABLE 7

Carbonyl-stretching frequencies of methyl 3-(3- and 4-substituted benzoyl)acrylates in carbon tetrachloride \*

Keto $\nu_{\rm m}$		arbonyl /cm <sup>-1</sup>	Ester-carbonyl <sub>vmax.</sub> /cm <sup>-1</sup>		
Substituent	trans	cis	trans	cis	
Н	1676	1680	1731	1735	
4′-F	1677	1680	1731	1735	
4'-Cl	1677		1733		
4′-I	1677	1680	1733	1734	
4'-Me	1675	1676	1733	1735	
4'-OMe	1672	1673	1732	1735	
3'-NO <sub>2</sub>	1684		1734		
H(3-Me)	1667	1680	1729	1731	
4'-Cl(3-Me)	1669	1681	1730	1730	
4'-Br(3-Me)	1669	1681	1730	1730	
4'-Me(3-Me)	1664	1678	1729	1731	
4'-OMe(3-Me)		1675		1731	
3'-NO <sub>2</sub> (3-Me)	1674		1732		
4'-Cl(2-Me)	1671		1728		
4'-Br(2-Me)	1671		1728		
4'-Me(2-Me)	1666		1727		
4'-OMe(2-Me)	1665		1726		
		-			

\* The  $\nu_{\text{max}}$  are considered accurate to  $\pm 1 \text{ cm}^{-1}$ .

series the variation of the ester carbonyl frequencies was never greater than  $\pm 1.5$  cm<sup>-1</sup>. However the frequencies of the keto-carbonyl group varied with the substituent and can be correlated by the Hammett relation (2). These correlations are shown in Table 8 and compare

$$\nu = \rho \sigma + \nu_0 \tag{2}$$

closely with those found previously for related sys-

 <sup>22</sup> K. Bowden, Canad. J. Chem., 1965, 43, 3354.
 <sup>23</sup> H. Hogeveen, Rec. Trav. chim., 1964, 83, 813, 836.
 <sup>24</sup> H. W. Thompson, R. W. Needham, and D. Jameson, Spectrochim. Acta, 1957 9, 208; R. N. Jones, W. F. Forbes, and W. A. Musller, Canad. J. Chem. 1957, 25, 504 W. A. Mueller, Canad. J. Chem., 1957, 35, 504.

tems.<sup>4,24</sup> Two general trends can be noted; the correlations using  $\sigma$  and those involving trans-systems are the more satisfactory. These results indicate efficient transmission of the substituent polar effects to the keto-carbonyl group; but without any significant

## TABLE 8

Hammett reaction constants for the carbonyl-stretching frequencies of methyl 3-(3- and 4-substituted benzoyl)acrylates in carbon tetrachloride \*

Series		ρ	$\nu_0$	r	s	n
$trans-2, 3-H_2$	$\substack{(a)\\(b)}$	$11.5 \\ 11.4$	$\frac{1675}{1675}$	0∙939 0∙935	1∙5 1∙4	7 7
cis-2,3-H <sub>2</sub>	$\substack{(a)\\(b)}$	$13.0 \\ 13.9$	$1678 \\ 1677$	$0.898 \\ 0.831$	$1.5 \\ 2.0$	5 5
trans-2-H,3-Me	$\substack{(a)\\(b)}$	$10.8 \\ 10.8$	$1666 \\ 1666$	$0.985 \\ 0.975$	$0.7 \\ 0.9$	5 5
cis-2-H,3-Me	(a) (b)	$14.5 \\ 13.5$	$1678 \\ 1677$	$0.867 \\ 0.721$	$2 \cdot 2 \\ 3 \cdot 0$	5 5
trans-2-Me,3-H	(a) (b)	$12 \cdot 2 \\ 13 \cdot 6$	$1668 \\ 1667$	$1.000 \\ 0.984$	$0.1 \\ 0.7$	4 4
	* Se	ee footno	tes to Ta	ble 6.		

effect at the more distant ester-carbonyl group. This supports our previous interpretation of the relative extents of transmission of polar effects to these two reaction sites. A general survey of these results indicates an increase in  $v_{max}$  for both the *cis*-ester-carbonyl and keto-carbonyl compared with the trans. The former effect has previously been noted in a series of methyl cis- and trans-3-substituted acrylates.25

Relative Rates .-- Excellent evidence for intramolecular catalysis is the occurrence of a significantly enhanced rate, relative to that expected for an unassisted reaction. Estimates of the ' expected ' rate ratios, relative to that of methyl acrylate, are given in Table 9, together with the observed rate ratios. These 'expected' values are estimated from known steric and polar effects of cis- and trans-3-substituents on the alkaline hydrolysis of methyl acrylate,<sup>25</sup> together with those of ortho-substituents on the alkaline hydrolysis of methyl and ethyl benzoates.26

TABLE 9

Relative rate ratios for the alkaline hydrolysis of the parent methyl cis-3-benzoylacrylates in 70% (v/v) dioxan-water at 1.0 °C

	k/k <b>o</b> *					
Substituent	Observed	'Expected ' †	Enhancement			
cis-2,3-H,	$82 \cdot 1$	1.0	82			
cis-2-H,3-Me	1.29	0.1	13			
		<b>.</b>				

\* Rate relative to that of methyl acrylate. † Ratios are the maximum that could be reasonably be ' expected.'

Significant enhancements for both *cis*-esters, *i.e.*,  $k/k_0 =$ 82 and 13, clearly indicate hydrolysis by intramolecular catalysis. Substitution of the 3-methyl group in the cis-3-benzoyl system reduces the rate by a factor of

 <sup>&</sup>lt;sup>25</sup> K. Bowden, Canad. J. Chem., 1966, 44, 661.
 <sup>26</sup> N. B. Chapman, J. Shorter, and J. H. P. Utley, J. Chem. Soc., 1963, 1291; D. P. Evans, J. J. Gordon, and H. B. Watson, *ibid.*, 1937, 1430; Y. Iskander, R. Tewfik, and S. Wasif, J. Chem. Soc., 1968, 1066. Soc. (B), 1966, 424.

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about 64. Substitution of this group should cause a significant increase in crowding which should become even more severe on formation of the transition state for intramolecular catalysis. This confirms the importance of steric requirements at the keto-carbonyl group in hydrolysis by the latter mechanism, as found previously.<sup>1</sup>

The rate coefficients for the parent methyl trans-3-benzoyl acrylates demonstrate the effects of the 2-methyl (reducing rate by a factor of about 2·6) and the cis-3-methyl (reducing rate by a factor of about 37) groups. (The rate coefficient for the hydrolysis of the parent methyl trans-3-benzoyl-2-methylacrylate can be estimated as 0·18 1 mol<sup>-1</sup> s<sup>-1</sup> at 1·0 °C from correlations shown in Table 6.) The strongly activating polar effect of the trans-3-benzoyl (increasing rate by a factor of about 33) and the de-activating (mainly steric) effect of the cis-3-methyl groups are those expected from previous studies <sup>25</sup> of the normal alkaline hydrolysis of methyl acrylates and the known polar and steric effects <sup>26,27</sup> of these two substituents.

It is important to indicate a danger in too great a reliance on small rate enhancements as a mechanistic criterion. The observed rate ratio at different temperatures can vary markedly (see Tables 4 and 5; and our earlier study  $^{1}$ ).

Activation Parameters.—The activation parameters for the alkaline hydrolysis of the parent methyl *cis*- and *trans*-3-benzoylacrylates in 70% (v/v) dioxan-water are shown in Table 10. The enthalpies of activation for the

#### TABLE 10

Activation parameters for alkaline hydrolysis of substituted methyl 3-benzoylacrylates in 70% (v/v) dioxan-water at 1.0 °C \*

	$\Delta H^{\ddagger}/$	$\Delta S^{\ddagger}/$
Substituent	cal mol <sup>-1</sup>	cal mol <sup>-1</sup> K <sup>-1</sup>
$trans-2, 3-H_2$	12,000	-16
cis-2,3-H <sub>2</sub>	8500	-27
trans-2-H,3-Me	14,300	-15
<i>cis</i> -2-H,3-Me	9000	-34

\* Values of  $\Delta H^{\ddagger}$  are accurate to within  $\pm 300$  cal mol<sup>-1</sup>, and of  $\Delta S^{\ddagger}$  to within  $\pm 1$  cal mol<sup>-1</sup> K<sup>-1</sup>; with the exception of methyl *cis*-3-benzoylacrylate whose accuracy limits are thrice that of the other esters.

two *cis*-esters are very much smaller than those for the corresponding *trans*-esters, *i.e.*,  $\Delta\Delta H^{\ddagger} = 5300$  and 3500 cal mol<sup>-1</sup>, while the entropies of activation of the *cis*-esters have much larger negative entropies of activation than the corresponding *trans*-esters, *i.e.*,  $\Delta\Delta S^{\ddagger} = 19$  and 11 cal mol<sup>-1</sup> K<sup>-1</sup>. It seems quite impossible to consider that these effects can be caused by the proximity and steric effects to be expected <sup>26</sup> on transfering a 3-substituent from the *trans*- to the *cis*-position. The effects noted here for *cis*-esters are very closely analogous to

those previously noted by Bowden and Taylor.<sup>1</sup> Similar effects have been noted for the enthalpies of activation of certain  $\gamma$ -keto-aliphatic esters.<sup>6</sup> It is clear that, while the *trans*-esters hydrolyse by rate-determining attack at the ester-carbonyl carbon, the *cis*-esters hydrolyse with an energetically favourable intramolecular catalysis. The *cis*-esters probably have a rate-determining step involving intramolecular nucleophilic attack with the transition state requiring a high degree of orientation, such as (III) or (IV) (see Discussion section in Part III <sup>1</sup>).



It appears that the behaviour of the *cis*-esters is very similar to that of the fluoren-1-one.<sup>1</sup> In both cases the keto-carbonyl groups are conjugated through both links and yet the systems are not as excessively crowded as in the 2-benzoylbenzoate. The latter ester, although having evidence for intramolecular catalysis from the reaction constant<sup>4</sup> and relative rate ratio<sup>1</sup> criteria, has activation parameters unlike the *cis*-esters but very close to those of the *trans*-esters. It seems likely that the 2-benzoylbenzoate, as stated previously,1 has a ratedetermining attack at the keto-carbonyl carbon whose transition state is analogous to that for normal ester hydrolysis. It is conceivable that an ester hydrolysis could occur with a normal hydrolysis mechanism prevailing at high and an intramolecular catalytic route at low temperatures. A curved Arrhenius relation would then be observed caused by this mechanistic switch.

The effect of substitution of the 3-methyl group on the activation parameters is small. It seems very likely that the small variations are caused by the steric requirements of the methyl groups inhibiting the formation of both the transition states for normal, for the *trans*ester, and assisted, for the *cis*-ester, hydrolyses.

In conclusion, the alkaline hydrolysis of methyl *cis*benzoylacrylates, in direct contrast to the *trans*-esters, occurs by an intramolecular catalytic path, which has been detected by a study of three criteria; reaction constants, relative rates, and activation parameters.

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<sup>27</sup> W. N. White, R. Schlitt, and D. Gwynn, J. Org. Chem., 1961, 26, 3613.