a Pyrex-filtered high-pressure mercury lamp (100 W). After irradiation the solvent was evaporated and the products were separated by column chromatography on alumina. The identified products were the vinyl ethers **4**, the phenanthrenes **5**, and small amounts of the known triarylethylenes **6a**,[18] **6b**,[19] and **6c**.[20] ^{1}H NMR chemical shifts for **4** and **5** are given in Table III. Irradiation of **4a** was carried out under the same conditions as described above without a Pyrex filter for 2 h. The sole product **5a** was obtained (conversion 45%).

Photolysis of Triaryl[2-^{13}C]vinyl Bromides 1* in TFE. Irradiation of triaryl[2-^{13}C]vinyl bromides **1*** (1.5 mmol, diluted with unlabelled vinyl bromide **1** to ca. 45% ^{13}C enrichment) was similarly carried out in a mixture of TFE (80 mL) and methylene chloride (20 mL) containing 2,6-lutidine (0.2 mL) at room temperature. For ^{13}C NMR analysis, the main products, i.e., the trifluoroethyl ethers **8** and **8*** were converted to triarylethanols **7** and **7*** in the following manner: after irradiation the solvent was removed, 5 mL of concentrated HCl and 50 mL of ethanol was added to the residue, and the solution was refluxed for 1 h. Extraction with ether gave the product mixture which was treated with sodium borohydride (120 mg) in ethanol (50 mL) without further purification to give the triarylethanols **7** and **7***. Column chromatography on silica gel gave both **7** and **7*** and the phenanthrenes **9**. The analytical and spectral data of compounds **9** are given in Table III. [2-^{13}C]-labelled triphenylethanol **7a**, mp 85–88 °C (aqueous ethanol) (lit.[8a] mp 88 °C), tri-*p*-tolylethanol **7b**, mp 93–96 °C (aqueous ethanol) (lit.[8f] 93–94 °C), and tri-*p*-anisylethanol **7c**, mp 110–111 °C (EtOH) (lit.[8c] mp 113–114 °C), were identical with the authentic samples.

Photolysis of Triaryl[2-^{13}C]vinyl Bromides 1* in MeOH. Irradiation of triaryl[2-^{13}C]vinyl bromides **1*** (diluted with unlabelled vinyl bromide **1** to ca. 45% enrichment, 1.5 mmol) was carried out in a mixture of methanol (90 mL) and methylene chloride (10 mL) containing pyridine (0.15 mL) at 5 °C under conditions similar to the photolysis of unlabelled **1** in methanol. Workup similar to that described above gave the main products, the vinyl ethers **4**. They were converted to the triarylethanol **7** and analyzed by ^{13}C NMR spectroscopy.

Registry No. **1a**, 1607-57-4; **1b**, 66184-02-9; **1c**, 25354-46-5; **4a**, 62456-54-6; **4b**, 91083-68-0; **4c**, 91083-69-1; **5a**, 91083-70-4; **5b**, 91083-71-5; **5c**, 91083-72-6; **9a**, 91083-73-7; **9b**, 91083-74-8; **9c**, 91083-75-9.

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Aspects of Tautomerism. 13. Alkaline Hydrolysis of γ-, δ-, and ε-Keto Esters and Their Desoxy Analogues. Geometrical Constraints on Keto Participation[1]

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The rates of alkaline hydrolysis of methyl β-benzoylpropionate (I), methyl γ-benzoylbutyrate (II) and methyl δ-benzoylvalerate (III) decrease in the order I > II > III. Keto participation is the predominant pathway in the case of γ-keto esters. Evidence has also been obtained for keto participation in the case of δ-keto esters, whereas no such evidence is available in the case of ε-keto esters studied.

Unexpected reactivity patterns are sometimes encountered when two or more functional groups are in close proximity. These effects cannot be accounted in terms of well-studied effects like steric, inductive, mesomeric, or field effects. A systematic study of the neighboring group effects as they pertain to carboxylic acids, their derivatives, and the keto group has been the subject of previous papers of this series.[1,2]

Rate enhancement of alkaline hydrolysis of esters by a suitably placed keto group has been recognized for almost 30 years.[3] However, a number of features of the keto participation have been analyzed only recently. One of the factors, sometimes the most important which has bearing on the extent of rate enhancement, is found to be the rate of initial attack of the base on the carbonyl group.[4] In this paper we attempt to define the geometrical constraints to keto participation in conformationally nonrigid systems.

The ring–chain tautomeric behavior of γ-keto acids and their derivatives is a frequently encountered phenomenon and also the one which has received detailed study. In contrast, information on the involvement of γ-keto and δ-keto function in the reactions of carboxylic acid and its derivatives is scanty. It is common knowledge that the formation of a five-membered ring tautomer or reaction product is generally preferred over a six-membered one when possibilities for the formation of either of them exists.[5] This generalization breaks down with carbohydrates. Factors like hydrogen bonding and conformational preferences tilt the stability order in favor of the six-membered rings. However, in the case of keto acid chlorides preference for five-membered ring formation is observed. While overhwelmingly a large number of γ-keto acids yields only pseudoacid chlorides, the situation regarding δ-keto acids is less clearcut.[6]

In the present investigation, we report two types of studies: (a) alkaline hydrolysis of methyl esters of β-benzoylpropionic acid (I), γ-benzoylbutyric acid (II), δ-benzoylvaleric acid (III) (Figure 1) and their desoxy analogues IV, V, and VI in 70% (v/v) acetone–water at three temperatures; (b) alkaline hydrolysis of methyl esters of meta- or para-substituted derivatives of I, II, and III and

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Table I. Second-Order Rate Constants and Thermodynamic Parameters for the Alkaline Hydrolysis of Keto Esters in 70% (v/v) Acetone–Water[a]

ester	$k_2 \times 10^2$ [b] 25.0 °C	30.0 °C	35.0 °C	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] cal mol^{-1} K^{-1}
$PhCO(CH_2)_nCOOMe$					
n = 2 (I)	10.95	13.30	15.85	7.0	−42.7
n = 3 (II)	6.80	8.57	10.59	9.7	−31.6
n = 4 (III)	2.97	4.15	5.81	10.8	−29.2
$PhCH_2(CH_2)_nCOOMe$					
n = 2 (IV)	2.84	4.26	6.02	12.7	−23.0
n = 3 (V)	2.73	3.96	5.60	12.7	−23.1
n = 4 (VI)	2.60	3.78	5.25	12.0	−25.2

[a] Rate constants were reproducible to within ±3%. Esters and base were 0.01 M each. Values of $\Delta H^{\ddagger}$ are accurate to within ±0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ to within ±2 cal mol^{-1} K^{-1}. [b] k_2 values given in the literature in mol^{-1} s^{-1}.

Table II. Comparison of the Rate of Alkaline Hydrolysis of Keto Esters and Their Corresponding Desoxy Analogues

keto ester $PhCO(CH_2)_nCOOCH_3$	$k_{>C=O}/k_{>CH_2}$[a]
n = 2	3.86
n = 3	2.49
n = 4	1.14

[a] $k_{>C=O}$ is the second-order rate constant for the keto compound and $k_{>CH_2}$ is the corresponding rate constant for the desoxy compound.

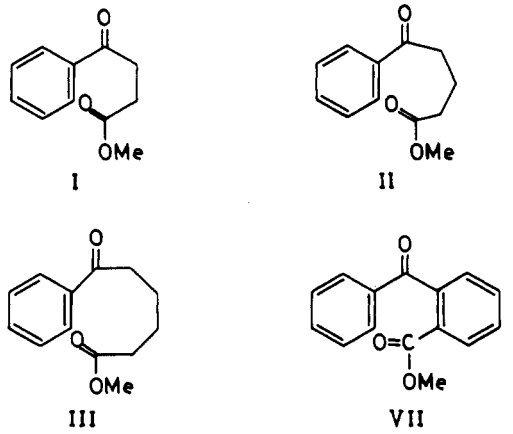


Figure 1.

the measurement of dissociation constants of meta- and para-substituted derivatives of I and II.

Results and Discussion

In Table I are compared the rates of keto esters I to III in 70% (v/v) acetone–water. The rates of alkaline hydrolysis of the desoxy analogues IV, V, and VI are also presented. It can be seen that the rates of hydrolysis and enthalpy and entropy of activation values are fairly steady for the three desoxy esters IV–VI. In contrast marked differences are found in the case of keto esters I–III. The highest rate among these compounds is shown by I, clearly indicating operation of some feature which enhances the rate (Table II). Slightly less, but nevertheless definite, rate enhancement (over the desoxy analogues) is found in the case of II also. In the case of III, the rate of hydrolysis is higher than its desoxy analogue by about 14% and could have been caused by the inductive effect of the keto group.

The significant differences in the enthalpies and entropies of activation of I and II (Table III), and those of the corresponding desoxy analogues IV and V ($\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$) canot be accounted for on the basis of inductive effect alone. Also, a high negative entropy of activation for the reaction of I, much higher than that of II and III, strongly argues in favor of a highly ordered transition state, which could only mean keto participation. The case of II

Table III. Differences in the Enthalpy and Entropy of Activation between the Keto Esters and the Corresponding Desoxy Analogues

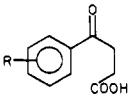
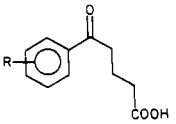
keto ester $PhCO(CH_2)_nCOOMe$	$\Delta\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
n = 2	−5.7	−19.7
n = 3	−3.0	−8.5
n = 4	−1.2	−4.0

Table IV. Second-Order Rate Constants for the Hydrolysis of γ-, δ-, and ε-Keto Esters[a,b]

structure	R	$k_2 \times 10^2$, L mol^{-1} s^{-1}
$RC_6H_4CO(CH_2)_2COOMe$	H	13.3
VIIIa,b,c	m-NO_2	56.1
	p-Br	19.7
	p-CN	44.6
$RC_6H_4CO(CH_2)_3COOMe$	H	8.6
IXa,b	m-NO_2	11.9
	p-Br	9.8
$RC_6H_4CO(CH_2)_4COOMe$	H	4.15
Xa,b	m-NO_2	4.26
	p-Br	4.14

[a] The rates were reproducible to ±3%. The temperature was maintained to ±0.1 °C. [b] [ester] = 0.01 M; [alkali] = 0.01 M; temperature = 30 °C.

Table V. The Dissociation Constants of γ-Keto and δ-Keto Acids[a]

keto acid	R	dissociation constant $(K_a) \times 10^7$	pK_a
 XVIIa,b,c,d	H	4.266	6.37
	m-NO_2	5.012	6.30
	p-Br	4.571	6.34
	p-CN	4.898	6.31
 XVIIIa,b,c	H	3.715	6.43
	m-NO_2	3.981	6.40
	p-Br	3.802	6.42

[a] The pK_a values were reproducible to ±0.01 unit.

is intermediate between I and III. It indicates that both pathways, viz., direct attack on the methoxycarbonyl function and indirect attack through the keto group, could be taking place. When the substituent effects on the alkaline hydrolysis of β-benzoylpropionic esters VIIIa,b,c (Table IV) were determined, the results fit a good Hammett plot with ρ = 0.88. That the substituent effect did not arise from the transmission of the effect of substituents to the carboxyl group became clear on examination of the dissociation constants of the corresponding acids which showed zero ρ value (Table V). Similar comparison (Figures 2 and 3) of the rates of hydrolysis of γ-benzoyl-

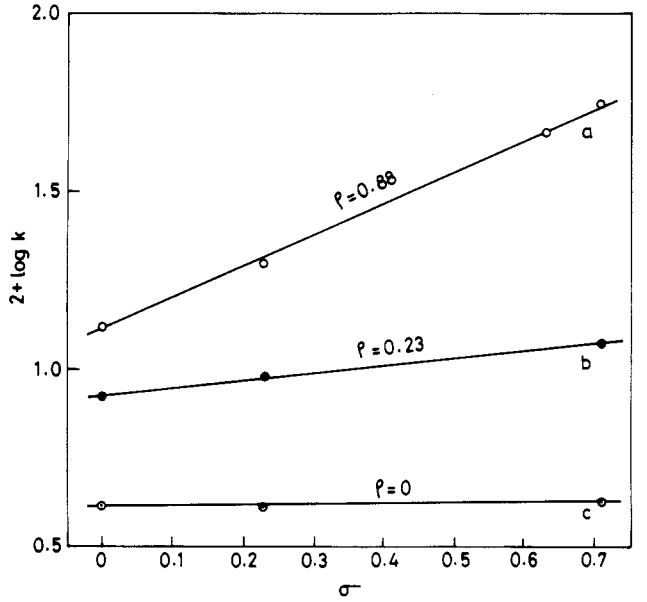


Figure 2. The plots of log k vs. Hammett σ for the three series of esters.

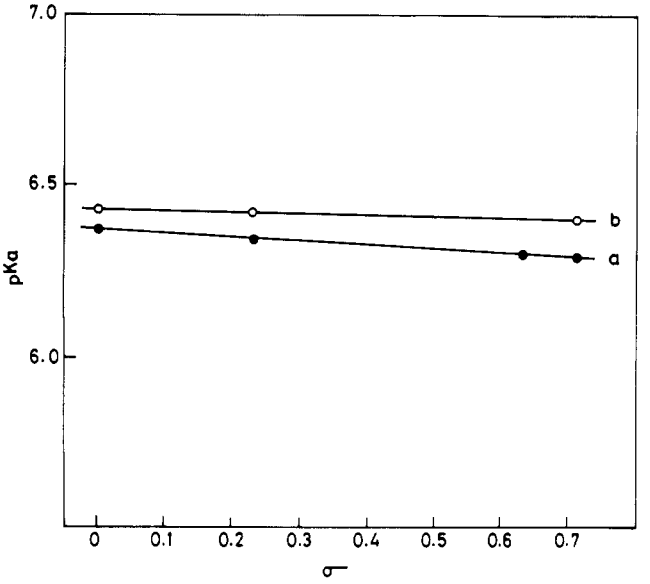


Figure 3. Plots of the dissociation constants (pK_a) vs. Hammett σ for benzoylpropionic acids and benzoylbutyric acids.

butyric esters (IXa,b) clearly establish that there is keto participation to some extent in these esters. But none whatsoever in the higher homologues, viz., δ-benzoylvaleryl esters (Xa,b).

Further evidence in favor of keto participation, i.e., direct preferential attack on the carbonyl group, was obtained in an unexpected way.[7] In an attempt to prepare XIII, β-benzoylpropionic ester I was alkylated with tetramethylene dibromide to give XII and not the expected XIII (Scheme I). The identity of XII was established by conversion to XVI, which was prepared independently from XV (Scheme I).

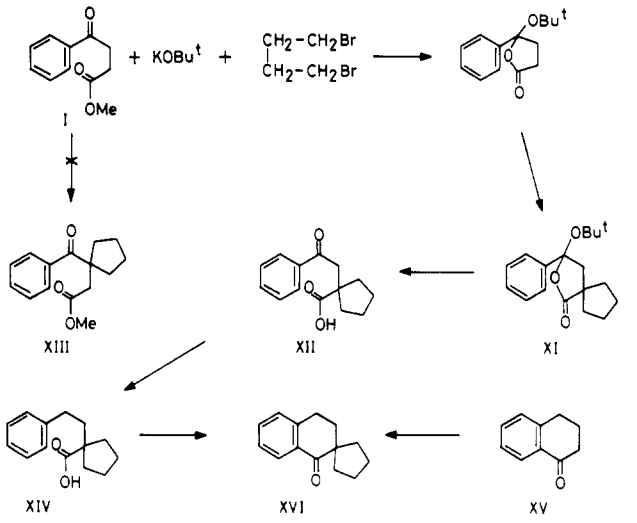
It has been suggested that the rate k_{obsd} of keto participation is given by[4]

$$k_{obsd} = \frac{k_1k_3k_5}{k_3k_5 + k_2k_5 + k_2k_4}$$

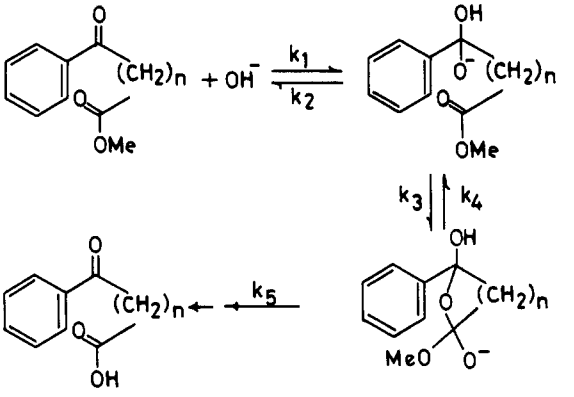
In a rather rigid system like methyl *o*-benzoylbenzoate

(7) Bhatt, M. V.; Rengaraju, S.; Rama Rao, manuscript in preparation.

Scheme I



Scheme II



(VII) k_1 becomes rate determining when $k_3 \gg k_2$.[4] In a series of related compounds changes of overall rate is controlled by changes in k_1. In contrast, where the side chain is not rigid as in the case of I and II, k_3 is probably a slow step. For these esters, although k_1 may really be the same, the differences in the overall rate arises because of differences in k_3. It decreases to zero in the case of III, resulting in direct attack on the carbomethoxy group by the base and nonoperation of the keto participation pathway.

Experimental Section

β-Benzoylpropionic acid and γ-benzoylbutyric acid were prepared by Friedel–Crafts acylation of benzene with succinic anhydride and glutaric anhydride.[8] For the preparation of δ-benzoylvaleric acid, the following sequence was followed: The reaction of cyclohexanone with phenylmagnesium bromide in ether gave 1-phenylcyclohexanol mp 62 °C (lit.[9] mp 63–65.5 °C) which was dehydrated with iodine in benzene solution. 1-Phenylcyclohexene obtained was oxidized with potassium permanganate by using the procedure of Price and Karabinos.[10] Thus from 10 g of 1-phenylcyclohexene and 20 g of potassium permanganate was obtained δ-benzoylvaleric acid (5.8 g, 46.5%), mp 75–76 °C (lit.[11] mp 75–76 °C). The Fischer–Speier esterification of the acids in methanol gave the methyl esters. The esters were purified by distillation under vacuum. Methyl δ-benzoylpropionate (I) distilled at 119–121 °C (0.5 mm) [lit.[11] 119–120 °C (0.4 mm)] and γ-benzoylbutyrate (II) at bp 177–178 °C (13 mm) [lit.[12] 177–180

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°C (13 mm)]. Methyl δ-benzoylvalerate (III) bp 132–133 °C (2 mm). Anal. $C_{13}H_{16}O_3$ Calcd: C, 70.9; H, 7.27, Found: C, 70.8; H, 7.25.

Methyl δ-benzoylvalerate was also prepared by an alternate route. See below.

β-(*m*-Nitrobenzoyl)propionic acid and γ-(*m*-nitrobenzoyl)-butyric acid were prepared according to literature procedure.[13,14] Corresponding methyl esters were prepared by Fischer–Speier esterification of the acids.

Methyl γ-(*m*-nitrobenzoyl)butyrate: mp 48 °C; IR 1710 and 1735 cm^{-1}; NMR ($CDCl_3$) δ 2.32 (m, 2 H), 2.72 (t, 2 H), 3.24 (t, 2 H), 3.66 (s, 3 H) and 7.8 (m, 4 H). Anal. $C_{12}H_{13}NO_5$ Calcd: C, 57.3; H, 5.1; N, 5.7. Found: C, 57.4; H, 5.1; N, 5.6.

Methyl β-(*p*-bromobenzoyl)propionate, methyl γ-(*p*-bromobenzoyl)butyrate and methyl δ-(*p*-bromobenzyl)valerate were prepared according to literature[14-16] procedure.

Methyl δ-Benzoylvalerate (III). A Friedel–Crafts reaction of 5-(carbomethoxy)valeroyl chloride (adipic acid half ester chloride, 52 g) with benzene (350 mL) and aluminum chloride (80 g) and the usual workup gave, on fractionation, methyl 5-benzoylvalerate: bp 140–141 °C (4 mm) yield, 48 g (77%): IR 1705 (keto) and 1740 cm^{-1} (ester); NMR ($CDCl_3$), δ 1.78 (m, 4 H), 2.36 (t, 2 H), 3.02 (t, 2 H), 3.64 (s, 3 H), 7.8 (m, 5 H). Anal. $C_{13}H_{16}O_3$ Calcd: C, 70.9; H, 7.3. Found: C, 70.8; H, 7.25.

δ-(*m*-Nitrobenzoyl)valeric Acid (Xa). δ-Benzoylvaleric acid (25 g) was nitrated with a fuming nitric acid (50 mL) and concentrated sulfuric acid (20 mL) mixture at −5 °C. On working up the mixture, δ-(*m*-nitrobenzoyl)valeric acid was obtained, 17.5 g (56%). The methyl ester: bp 212 °C, (6 mm); IR 1710 and 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.76 (m, 4 H), 2.34 (t, 2 H), 3.02 (t, 2 H), 3.72 (s, 3 H), 7.78 (m, 4 H). Anal. $C_{13}H_{15}NO_5$ Calcd: C, 58.9; H, 5.6; N, 5.3. Found: C, 58.8; H, 5.7; N, 5.3.

Methyl β-(*p*-Cyanobenzoyl)propionate (VIIIc). The general method of preparing aryl nitriles from aryl halides described by Friedman and Schechter[17] was employed to prepare the cyano ester. Methyl β-(*p*-bromobenzoyl)propionate (6 g) was dissolved in dimethylformamide (10 mL) and cuprous cyanide (2.2 g) was added to it. The mixture was refluxed for 4 h and the resulting brown reaction product was poured into a solution of ferric chloride (6 g) in concentrated hydrochloric acid (3 mL) and water (10 mL). This was kept at 60–70 °C for $^1/_2$ h to decompose the complex and extracted with benzene (3 × 20 mL). The combined benzene extracts were washed with dilute (1:1) hydrochloric acid (2 × 20 mL), water, 10% sodium hydroxide solution, and brine. The organic layer was then filtered through glass wool and dried with sodium sulfate, and the benzene was evaporated. The crude cyano ester was carefully hydrolyzed with methanolic potassium hydroxide to give the acid, mp 153 °C. The acid was reesterified to give pure ester: mp 61 °C; IR 1710, 1735, 2240 cm^{-1}; NMR ($CDCl_3$) δ 2.74 (t, 2 H), 3.22 (t, 2 H), 3.70 (s, 3 H), 7.8 (m, 4 H). Anal. $C_{12}H_{11}NO_3$ Calcd: C, 66.4; H, 5.1; N, 6.5. Found: C, 66.5; H, 5.2; N, 6.4.

The desoxy acids were prepared from the keto acids by the modified (Huang–Minlon) Wolff–Kishner reduction. γ-Phenylbutyric acid, mp 52 °C (lit.[18] mp 52 °C); δ-phenylvaleric acid, mp 60 °C (lit.[19] mp 61 °C); δ-phenylcaproic acid, bp 184–186 °C (11 mm) (lit.[19] bp 186–188 °C (11 mm)). Methyl esters of desoxy acids were prepared by the Fischer–Speier esterification of the acids with methanol. The esters were distilled under reduced pressure. Methyl γ-phenylbutyrate, bp 126–128 °C (10 mm). Anal. $C_{11}H_{14}O_2$ Calcd: C, 74.15; H, 7.9. Found: C, 74.0; H, 7.8. Methyl δ-phenylvalerate, bp 122–124 °C (3 mm) (lit.[20] 110 °C (2 mm)); methyl ε-phenylcaproate, bp 135–136 °C (3 mm). Anal. $C_{13}H_{18}O_2$ Calcd: C, 75.7; H, 8.75. Found: C, 75.4; H, 8.6. All esters were tested by VPC for their purity. Acetone (Analar Reagent) was refluxed over potassium permanganate and distilled. Carbonate-free sodium hydroxide was used for titrations. Conductivity water was used for the preparation of all solutions. All the inorganic compounds used were reagent grade and were converted to the anhydrous form before preparing the solution.

Kinetic Procedure. Alkaline hydrolysis of esters was followed by titrimetric method. Rate constant k_1 was obtained by applying eq 1, the initial concentrations of the ester and base were the same.

$$t = \frac{x}{ka(a - x)} \quad (1)$$

Equation 1 can be written as

$$t = \frac{1}{k(a - x)} - \frac{1}{ka} \quad (2)$$

Since $1/ka$ is a constant, a plot of $1/(a - x)$ vs. t should be linear, the slope being $1/k$.

All the glass apparatus used were washed with chromic acid prior to use. The bath temperature was maintained to ±0.1 °C. Solutions of ester and alkali in a 70% acetone–water mixture were thermostated 2 h before the kinetic run. A solution of ester (50 mL) was pipetted out into a third flask also kept in the thermostat. Alkali solution (50 mL) was then pipetted out into this flask. A stop watch was started when half the alkali solution had run into the ester solution. Solutions were mixed well by shaking vigorously. A 5-mL aliquot was withdrawn at known intervals of time. The reaction was quenched with excess of hydrochloric acid of known strength and excess acid was determined by titrating against standard alkali by using a screened indicator consisting of methylene blue and neutral red.

The rate constant was also independently measured by following the rate of disappearance of substrate in the case of methyl β-benzoylpropionate (I). For this purpose 10-mL aliquots were withdrawn at known intervals of time and run into excess of hydrochloric acid. Excess of acid was neutralized with sodium bicarbonate, the resulting solution was saturated with sodium chloride, and the acetone layer was taken up in ether (10 mL). The aqueous layer was extracted with ether (10 mL). Combined ether extracts were dried with anhydrous magnesium sulfate and the ether was removed in vacuo. The amount of ester present was determined by gas chromatography, using lauryl alcohol as the internal standard.

The rate constant for the hydrolysis of methyl β-benzoylpropionate (I) obtained by the method above was 13.5×10^{-2} L mol^{-1} s^{-1} and that obtained by titrimetric procedure was 13.3×10^{-2} L mol^{-1} s^{-1}. Since both values agree within experimental error, all the rate constants were obtained by the titrimetric procedure, i.e., by following the decrease in the concentration of alkali during ester hydrolysis.

pK_a Measurements.[21] The pK_a of the acids were determined by a pH titration method. Measurements were made in 50% aqueous acetone.

The pH meter (NIG 333) was standardized by immersing the glass electrode of the pH meter in a freshly prepared solution of 0.05 M potassium hydrogen phthalate (pH = 4.01).

Registry No. I, 25333-24-8; II, 1501-04-8; III, 21876-11-9; IV, 2046-17-5; V, 20620-59-1; VI, 5581-76-0; VIII (acid) (R = H), 2051-95-8; VIIIa (acid), 6328-00-3; VIIIa (Me ester), 90991-20-1; VIIIb (acid), 6340-79-0; VIIIb (Me ester), 30913-86-1; VIIIc (acid), 52240-17-2; VIIIc (Me ester), 90991-21-2; IX (acid) (R = H), 1501-05-9; IXa (acid), 90991-26-7; IXa (Me ester), 90991-22-3; IXb (acid), 35333-26-7; IXb (Me ester), 90991-23-4; Xa, 90991-24-5; Xb, 90991-25-6.

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