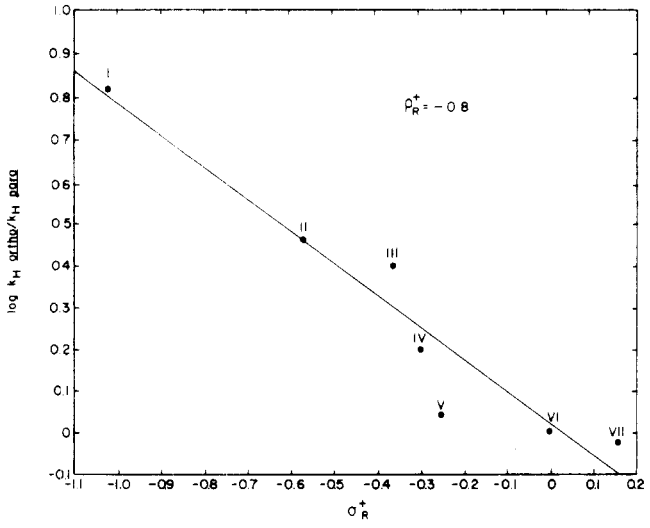

Figure 3. Logarithms of ortho/para ratios for the hydronium-catalyzed reaction of formation of carbinolamine from phenylhydrazine and several benzaldehydes, in 20% aqueous ethanol at 25.0 °C and ionic strength 0.50 plotted as function of σ_R^+ (I, methoxy; II, fluor; III, chloro; IV, bromo; V, methyl; VI, hydrogen; VII, nitro). Data have been taken from Tables V and VI.

is approximately −0.8, a value which emphasizes the importance of electron donation by resonance in decreasing the reactivity of para isomers relative to ortho ones (Figure 3).

Acknowledgment. The author is indebted to Dr. Eugene H. Cordes for helpful comments concerning this work.

Registry No.—Phenylhydrazinium ion, 55668-06-9; phenylhydrazine, 100-63-0.

Supplementary Material Available: Table I, determinations of the acidity constant data for phenylhydrazinium ion, and Table V, values of Hammett substituent constants used in this work (2 pages). Ordering information is given on any current masthead page.

References and Notes

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Aspects of Tautomerism. 7. Study of Keto Participation in Alkaline Hydrolysis of Normal Esters of γ-Keto Acids[1]

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Study of the alkaline hydrolysis of a number of variously substituted normal *o*-benzoylbenzoic esters has been reported. Although carbonyl-assisted hydrolysis is the general rule, in compounds containing strongly electron-donating groups, the ester function is directly attacked. The cause of rate enhancement in carbonyl-assisted hydrolysis and in greater detail the case of 6-substituted derivatives are discussed. It is shown that the carbonyl-assisted hydrolyses are characterized by decreased sensitivity to leaving-group structure. The implications of this result are pointed out.

In the past decade or so, a number of examples of intramolecular catalysis in basic hydrolysis of carboxylic acid derivatives have been encountered.[2-16] It has been found that γ-keto and δ-keto functions enhance the rate of alkaline hydrolysis. These rate enhancements vary over a wide range, and values up to 10^5 times have been recorded.[5] Diverse explanations have been put forward by the authors for the observed effects (see below).

The present investigation is concerned with hydrolysis of normal methyl *o*-benzoylbenzoates with various substituents in both of the rings. The kinetics of saponification have been studied with a view to understanding (a) the causes of rate enhancements and (b) the influence of leaving-group structure on the rates of carbonyl-assisted basic hydrolysis.

Results and Discussion

The rate constants for the alkaline hydrolysis of "A" ring substituted *o*-benzoylbenzoates (cf. Scheme I) in 70% aqueous acetone are given in Table I. A good linear correlation exists between log *k* and Hammett substituent parameters (Figure 1). The ρ value is 2.22 (γ = 0.998). This value is almost identical with that for the alkaline hydrolysis of meta- and para-substituted methyl benzoates (ρ = 2.2).[7] If the base was reacting directly at the methoxycarbonyl group, values should have been comparable to the alkaline hydrolysis of pseudo esters, i.e., 0.56, and lactones, 0.64,[1] and the dissociation constants of A ring substituted *o*-benzoylbenzoic acids, viz., 0.6 (in 80% w/w 2-methoxyethanol–water).[7] It is clear that there is substantial transmission of polar effects to the reaction center. This observation is rather an expected one and fully corroborates the work of Bowden and Taylor.[7] The case of 4′-*N*,*N*-dimethylamino substituent is, however, untypical, as reflected in a large positive deviation from the Hammett plot (Figure 1). Clearly, this compound reacts by a mechanism

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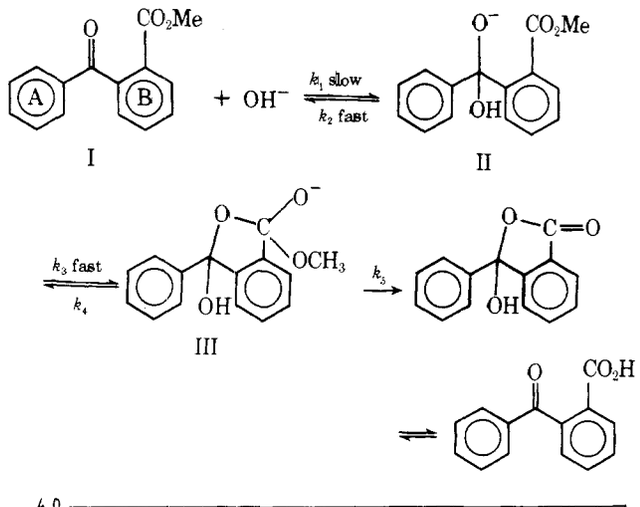
Scheme I



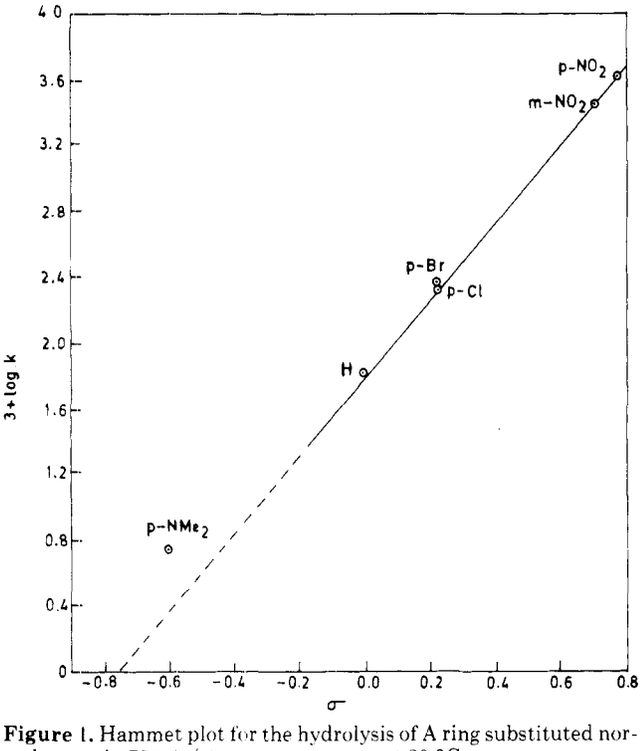
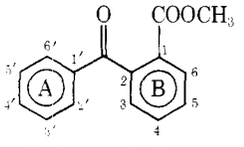


Figure 1. Hammet plot for the hydrolysis of A ring substituted normal esters in 70% (v/v) aqueous acetone at 30 °C.

Table I. Rate Coefficients for the Alkaline Hydrolysis of Methyl *o*-(3′- and 4′-Substituted Benzoyl)benzoates in 70% Aqueous Acetone[a]



substituent	registry no.	10^2k_2, L mol^{-1} s^{-1} 30 °C	35 °C	40 °C
H	606-28-0	6.31	9.2	12.7
4′-chloro	32017-70-2	20.60	30.4	40.8
4′-bromo	32017-71-3	22.20	31.4	42.8
4′-nitro	21646-09-3	419.0		
3′-nitro	32017-74-6	214.0		
4′-methyl	6424-25-5	3.02	4.56	7.21
4′-NMe$_2$	68854-19-3	0.546	0.927	1.145

[a] Rate coefficients were reproducible to within ±3%. The rate coefficient for the hydrolysis of methyl *o*-benzoylbenzoate in 70% (v/v) aqueous dioxane is 7.8×10^{-2} L mol^{-1} s^{-1} at 30 °C.

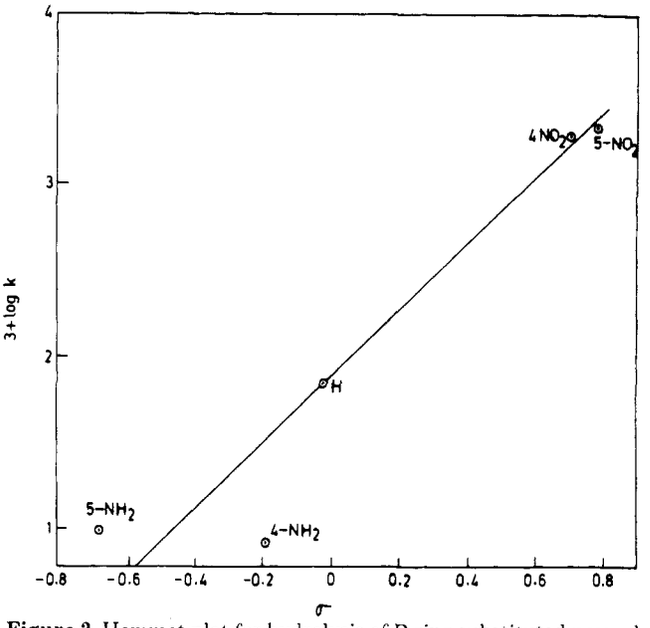


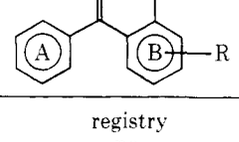
Figure 2. Hammet plot for hydrolysis of B ring substituted normal esters in 70% (v/v) aqueous dioxane at 30 °C.

different from the other similarly substituted compounds. The strong electron-donating ability of the dimethylamino group suppresses the reactivity of the carbonyl group to such an extent that the carbonyl-assisted pathway becomes slower than that involving direct attack of hydroxide ion at the methoxycarbonyl group.

This example provides additional confirmation for keto participation in other members of the series. The question of whether a "dual attack", i.e., both at the carbonyl and methoxycarbonyl groups, or a totally "direct attack" pathway is followed can now be examined. The rate calculated for "indirect attack", i.e., through keto participation, is 0.2154×10^{-2} L mol^{-1} s^{-1} (in 70% aqueous acetone at 30 °C), whereas the actual rate is 0.546×10^{-2} L mol^{-1} s^{-1}. Because the observed rate is not even twice that of the "indirect attack", the individual rates by the two alternative pathways are not sufficiently different as to lead to exclusive reaction by the "direct attack" pathway.

The rates of hydrolysis of B ring substituted methyl *o*-benzoylbenzoates in 70% aqueous dioxane are presented in Table II. Linear correlation between rates of hydrolysis and

Table II. Rate Coefficients for the Alkaline Hydrolysis of B Ring Substituted Methyl *o*-Benzoylbenzoates[a] in 70% (v/v) Aqueous Dioxane at 30 °C



substituent R	registry no.	10^2k_2, L mol^{-1} s^{-1}
H[b]		7.8
6-nitro	7531-35-6	663.0
5-nitro	42156-50-3	256.0
4-nitro	42156-49-0	235.0
3-nitro	7340-54-7	41.4
6-amino	68854-20-6	0.943
5-amino	68854-21-7	1.01
4-amino	68854-22-8	0.864

[a] Rate coefficients are reproducible to within ±3%. [b] Bowden et al.[7] reported the rate of hydrolysis of methyl *o*-benzoylbenzoates as 11.2 ± 10^2 L mol^{-1} s^{-1}. However, our value coincides with that of Newman and Leegwater.[4]

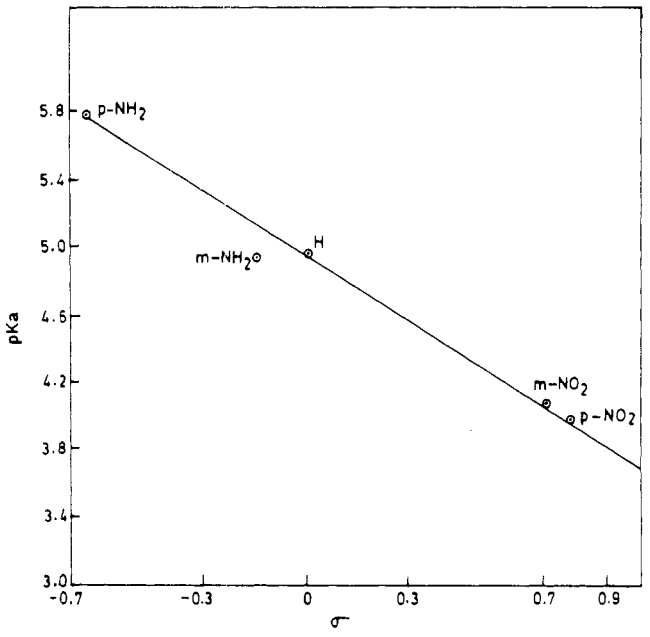


Figure 3. Hammett plot for ionization of B ring substituted *o*-benzoylbenzoic acids.

Hammett σ values is shown by nitro derivatives only (Figure 2). When amino substituents are considered, a scatter is observed. This is again rather expected on the basis of the "dual attack" pathway in the case of amino-substituted compounds only. The dissociation constants of both the B ring nitro- and amino-substituted acids give a satisfactory correlation with Hammett σ constants (Figure 3, $\rho = -1.15$).

For the compounds with nitro groups in the B ring, the ρ value for hydrolysis is 2.38 ($\gamma = 0.991$). This value is close to that observed for A ring substituted methyl *o*-benzoylbenzoates, i.e., 2.22, and for methyl benzoates, 2.2.[7] As both functionalities are affected by the nitro group, it would not be unreasonable to expect higher values. The fact that this is not observed argues against intramolecular cyclization being the rate-controlling step.

The mechanism of alkaline hydrolysis involving keto participation may be described as shown in Scheme I.

Applying the steady-state approximation to the intermediates, $k_{obsd} = k_1k_3k_5/(k_5k_3 + k_5k_2 + k_4k_2)$. Making the reasonable assumption that $k_3 \gg k_2$, it follows that $1 + k_2/k_3 \simeq 1$.

$$k_{obsd} = \frac{k_1k_5}{k_5(1 + k_2/k_3) + k_4k_2/k_3} = \frac{k_1k_5}{k_5 + k_4k_2/k_3}$$

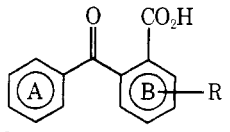
$$= \frac{k_1}{1 + (k_4k_2/k_5k_3)} = \frac{k_1}{1 + \alpha}$$

where $\alpha = k_4k_2/k_5k_3$. It can be seen from the above expression that the maximum k_{obsd} would be k_1 whatever the values of α (ordinarily, values of α are generally less than unity). If one compares the carbonyl-assisted rate enhancements in the literature, the close parallel between the carbonyl reactivity and rate enhancements due to carbonyl participation can be noticed. The examples shown in Chart I are illustrative. The figures indicate rate enhancements, computed after compensating for structural differences.

One of the consequences that follows from the above discussion is that the intramolecular steps (like k_3) do not have much bearing on the overall rate.

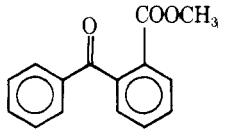
Influence of 6-Substituents. Newman and Hishida[3] made the observation that the rate of basic hydrolysis of the methyl ester of 6-methyl-*o*-benzoylbenzoic acid (IV) was 9-fold higher than that of the parent compound (I). They attributed this rate enhancement to keto participation in the case of the 6-methyl compound (IV), but not in the case of I.

Table III. pK_a Values for the B Ring Substituted *o*-Benzoylbenzoic Acids in 50% (v/v) Aqueous Ethanol at 30 °C [a]

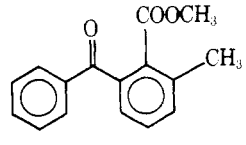


substituent R	registry no.	pK_a
H	85-52-9	4.95
6-nitro	7335-77-5	3.88
5-nitro	2159-46-8	4.10
4-nitro	2158-91-0	4.00
3-nitro	7335-60-6	4.18
6-amino	68854-23-9	5.80
5-amino	2162-57-4	4.93
4-amino	68854-24-0	5.78

[a] pK_a values are reproducible to within ±0.02%. The concentration of the acid was 0.001 M and that of sodium hydroxide used was 0.05 M. The pK_a value for benzoic acid was 5.91.



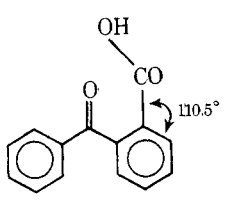
I

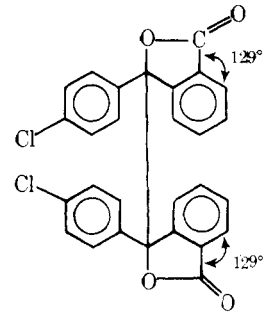


IV

Later, Newman and Leegwater[4] attributed the higher rate of IV and similar 6-substituted derivatives to the favorable orientation of the ester function for intramolecular attack, caused by the steric overcrowding effect of the 6-substituent. The implication of this view is that the cyclization step (represented by k_3) is rate limiting. From our discussion above, this seems unlikely.

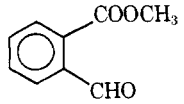
A lot of data in the literature point to the fact that lactol ring formation leads to the relieving of steric compression by the 6-substituent. The crystal structure of dilactones[22] derived from *o*-benzoylbenzoic acids, by the X-ray diffraction method, has shown that the exocyclic bond angle increases from 110.5 to 129° as a result of lactol ring formation.





Also, the ring chain tautomeric equilibrium in the case of acids shifts toward the lactol form in the case of 6-substituted derivatives.[28] *o*-Benzoylbenzoic acid is reported to be completely open in methanol solution, whereas the 6-methyl de-

Chart I



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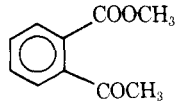

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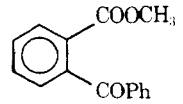
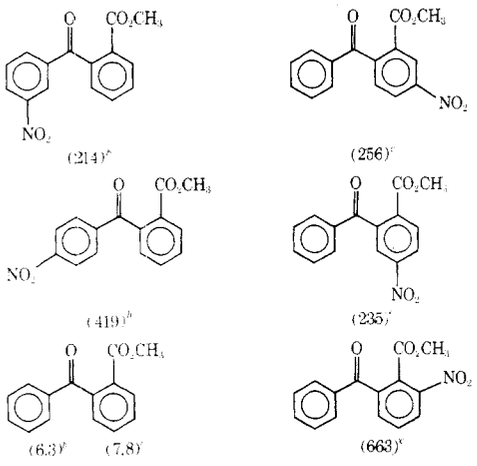


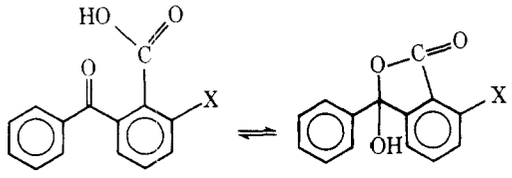
5.6

Table IV. Rate Coefficients [a] for the Alkaline Hydrolysis of Nitro-Substituted Methyl *o*-Benzoylbenzoates at 30 °C



[a] 10^2k_2 values (L mol^{-1} s^{-1}) are given in parentheses. [b] In 70% (v/v) aqueous acetone. [c] In 70% (v/v) aqueous dioxane.

rivative exists to the extent of 65% in the lactol form at room temperature.



X = H, CH_3

Although the increased preference for the lactol form in the 6-substituted derivative is an interesting property, this feature may not have a bearing on the overall rate as the cyclization step is not rate limiting.

The proximity of the three groups in the vicinal positions presumably would force all of them to go out of the plane of the benzene ring to increase their separation. This should result in turn in (a) a decrease in the steric hindrance at the carbonyl group by its neighbor and (b) a decrease in the con-

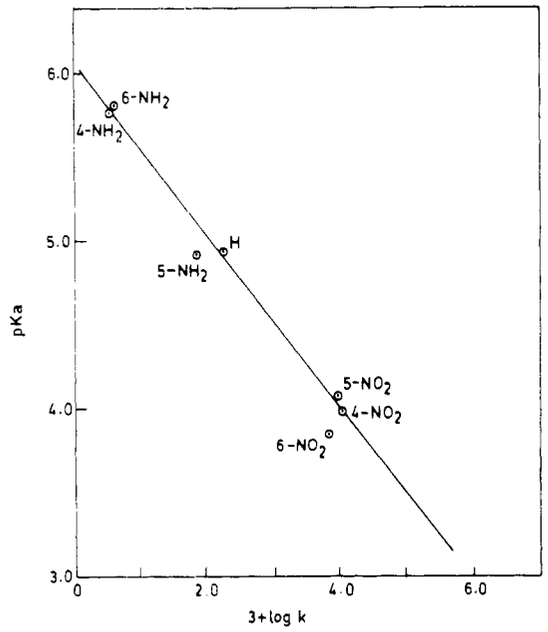


Figure 4. Plot of log k (hydrolysis) of pseudo esters vs. pK_a values of B ring substituted *o*-benzoylbenzoic acids.

Table V. Rate Coefficients for the Alkaline Hydrolysis of *tert*-Butyl *o*-Benzoylbenzoate in 70% (v/v) Aqueous Dioxane[a]

temp, °C	10^3k_2, L mol^{-1} s^{-1} *tert*-butyl *o*-benzoylbenzoate[c]	methyl *o*-benzoylbenzoate	*tert*-butyl benzoate[b,d]	methyl benzoate[b,e]
30	1.97 (1)	78 (39.5)	0.013 (1)	9.02 (680)
35	2.49			
40	3.19			
45	3.85			

[a] Rate coefficients are reproducible to within ±3%. [b] At 25 °C in 56% (w/w) aqueous acetone (relative rates are given in parentheses.[21] [c] Registry no. 54354-02-8. [d] Registry no. 774-65-2. [e] Registry no. 93-58-3.

Table VI. Activation Parameters for the Alkaline Hydrolysis of *tert*-Butyl *o*-Benzoylbenzoate in 70% (v/v) Aqueous Dioxane at 30 °C

ΔH = 7700 cal mol^{-1}
ΔS = 31.15 cal mol^{-1} K^{-1}

Table VII. Normal Esters of *o*-Benzoylbenzoic Acids (A Ring)

substitution	yield, %	mp, °C	infrared frequency max, cm^{-1} ester carbonyl	infrared frequency max, cm^{-1} diaryl carbonyl
unsubstituted	92	51–52	1715	1663
m-nitro	95	99–100	1720	1680
p-nitro	94	155–155.5	1720	1685
p-bromo	94	105	1780	1680
p-methyl	97	62–63	1710	1660
p-chloro	98	111	1720	1665
p-dimethylamino	90	114–115	1740	1680

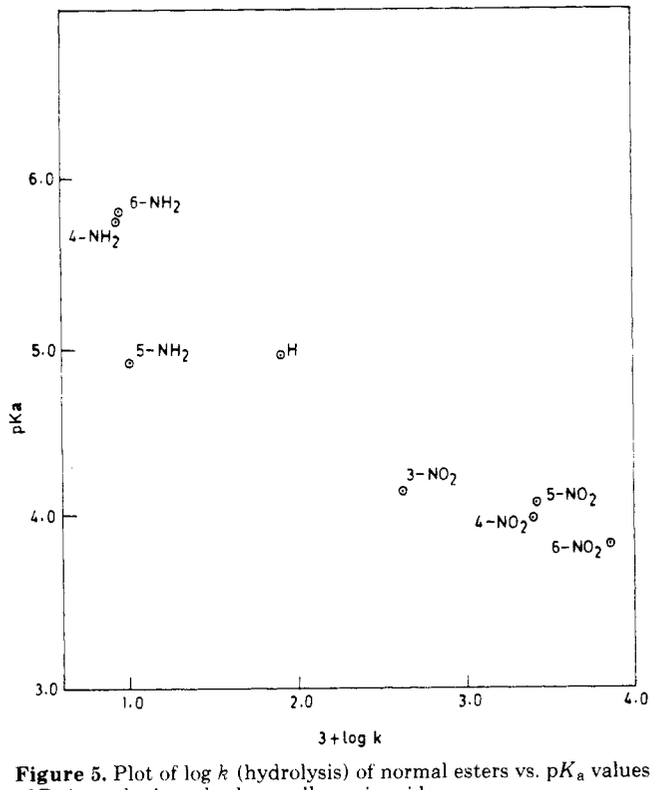


Figure 5. Plot of log k (hydrolysis) of normal esters vs. pK_a values of B ring substituted *o*-benzoylbenzoic acids.

Table VIII. Normal Esters of *o*-Benzoylbenzoic Acids (B Ring)

substitution	mp, °C	yield, %	ν_{max} (Nujol), cm^{-1} ester nitro	ν_{max} (Nujol), cm^{-1} aromatic	analysis[a] (found) C	H	N
6-nitro	93[b]	92	1728 1540	1675 1350	63	3.7	5.0
5-nitro	124[c]	94	1728 1540	1675 1350	63.1	3.9	4.9
4-nitro	109	93	1730 1540	1675	63.2	3.9	4.92
3-nitro	122.3	95	1728 1540	1675	63.1	3.8	5.0

[a] All nitro esters have the same molecular formula, $C_{15}H_{11}O_5N$. [b] Lit.[23] mp 94–95 °C. [c] Lit.[23] mp 123–124 °C.

jugation of the carbonyl group with the aromatic ring. The carbonyl reactivity should increase on both counts (and overall rate, consequently) by two distinct but not mutually exclusive ways. The former explanation as the cause of rate enhancement by a 6-substituent has been advanced in the literature.[7] We wish to suggest that the data in the literature and our own data do not enable us to exclude either of the above two possibilities.

Typically, a 6-nitro substituent enhances the rate more than is attributable to its electronic effects alone.[19,20] Steric effects are also operative (Table IV). 6-Amino substituent presents an interesting but not unexpected example of electronic effects dominating over the steric effect.

The ionization constants of "B" ring substituted *o*-benzoylbenzoic acids were measured in 50% aqueous ethanol. The pK_a values are collected in Table III. A good linear correlation is obtained between pK_a values and Hammett substituent parameters (Figure 3). The ρ value is -1.15 ($\gamma = 0.998$). Plots of the log k values for the hydrolysis of pseudo esters and normal esters against pK_a values of the corresponding acids are given in Figures 4 and 5. A good linear correlation exists for pseudo esters, whereas a wide scatter is observed in the case of normal esters. This further confirms the point made earlier that pathways followed in the case of strongly electron-donating substituents are different from those of others.

Influence of the Leaving Group. An interesting question that needed exploration was the influence of the leaving group on the overall rate of assisted reactions. Our foregoing analysis would lead us to expect that the effect of the leaving group on the rate should be marginal. If this is indeed so, keto participation may have implication in the biological field in the selective hydrolysis of proteins and polypeptides.

Ordinarily, *tert*-butyl benzoate hydrolyzes 700 times slower than methyl benzoate at 30 °C in 56% (w/w) aqueous acetone.[21] It may be expected that in carbonyl-assisted hydrolysis this difference should be considerably narrowed down. Similar effects may be expected in the case of amides too, which are ordinarily hydrolyzed very much slower than the esters in basic media.

To test this view, alkaline hydrolysis of *tert*-butyl *o*-benzoylbenzoate was studied in 70% (v/v) aqueous dioxane. Considerable difficulties were encountered in the preparation of this compound. Fischer–Speier esterification of the acid or reaction of sodium and silver salts with *tert*-butyl chloride gave back the acid. However, reaction of pseudo phenyl *o*-benzoylbenzoate in dry butanol with potassium *tert*-butoxide gave the required compound in 83% yield. The rate coefficients for the alkaline hydrolysis of *tert*-butyl *o*-benzoylbenzoate are given in Table V along with the rates for hydrolysis of methyl and *tert*-butyl benzoates. The observed ratio of the rates is only 40 as contrasted with 680 observed for the corresponding benzoic esters. Even this value could arise partly from the steric hindrance of the *tert*-butoxycarbonyl group for reaction at the keto function. Data in the literature also follow the same trend. Bowden and Taylor[7] observed that the ratios of basic hydrolysis of isopropyl benzoate and diphenylmethyl benzoates to methyl benzoate were 16–20-fold, whereas in the case of the corresponding *o*-benzoylbenzoates they were reduced to 5-fold.

Table IX. B Ring Amino-Substituted *o*-Benzoylbenzoic Acids

position of substituent	mp, °C	yield, %	ν_{max} (Nujol), cm^{-1}
6-amino	159–160	98	1700, 1680 3325, 3440
5-amino	197–198	97	1700, 1675 3400, 3500
4-amino	194–195	97	1695, 1675 3370, 3470

Experimental Section

All of the melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 700 instrument. Petroleum ether refers to the petrol fraction boiling between 40 and 60 °C.

The preparation of all ortho-(para-)substituted benzoylbenzoic acids has been described elsewhere.[22]

3-, 4-, 5-, and 6-Nitro-*o*-benzoylbenzoic acids were prepared by the method of Chase and Hey.[23] Fischer–Speier esterification in methanol yielded the corresponding normal esters.[24] Tables VII and VIII summarize the normal esters prepared.

Methyl 6-Amino-, 5-Amino-, and 4-Amino-*o*-benzoylbenzoates. These esters were prepared by catalytic reduction of the corresponding nitro esters. A solution of the nitro compound in ethyl acetate was hydrogenated in the presence of platinum oxide. The esters were purified by crystallization from benzene–petroleum ether mixtures (Table X).

6-Amino-, 5-Amino-, and 4-Amino-*o*-benzoylbenzoic Acids. Catalytic reduction of the nitro acid in absolute ethyl alcohol afforded

Table X. Amino B Ring Substituted Methyl *o*-Benzoylbenzoates

substituent	mp, °C	yield, %	ν_{max} (Nujol) ester aromatic C=O amino groups, cm^{-1}	analysis[a] C	H	N
6-amino	95–96	94	1710, 1690 3500, 3380	70.55	5.13	5.49
5-amino	100.0	95	1705, 1690 3450, 3370	70.6	5.13	5.41
4-amino	175.6	96	1705, 1688 3450, 3380	70.58	5.15	5.52

[a] All amino esters have the same molecular formula. $C_{15}H_{11}O_5N$ requires C, 70.58; H, 5.13; N, 5.49.

the corresponding amino acids in quantitative yield (98%) (Table IX).

***tert*-Butyl *o*-Benzoylbenzoate.** To a solution of potassium *tert*-butoxide in *tert*-butyl alcohol (obtained by dissolving 1.17 g of potassium in 250 mL of *tert*-butyl alcohol) was added dropwise phenyl pseudo *o*-benzoylbenzoate (9.06 g) in 200 mL of dry ether. The reaction mixture was refluxed on a water bath for 3 h, and the solvents were removed under reduced pressure (water pump). Water was added to the solid residue, and then it was extracted with ether. The ether layer was washed with ice-cold 0.5 M sodium hydroxide solution in order to remove the phenol and then with distilled water. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was distilled. The residue, which was homogeneous on TLC, was crystallized from petroleum ether, which afforded a sample melting at 72–74 °C (7.96 g, 83%): IR max (Nujol) 1708 (ester C=O), 1670 (aromatic C=O) cm^{-1}.

Anal. Found: C, 76.57; H, 6.73. $C_{21}H_{18}O_3$ requires: C, 76.25; H, 6.75.

pK_a Measurements. Ethyl alcohol was purified by standard methods[25] and subsequently further distilled over zinc and sodium hydroxide twice. Double-distilled water was used to make 50% aqueous ethanol (v/v), and the solvents were stored under nitrogen. Sodium hydroxide (0.05 M) solution was prepared 1 h before use and was kept under nitrogen. The acid whose pK_a was to be determined was accurately weighed and dissolved in 50% aqueous ethanol (0.001 M).

The pH meter was standardized by measuring the pH value of 0.05 M potassium hydrogen phthalate (pH 4.01).[26] The acid solution (25 mL) was pipetted out into a double-walled beaker provided with outlets for water circulation from a thermostat in order to keep the contents of the beaker at constant temperature (30.0 ± 0.1 °C). Nitrogen was gently bubbled through the acid solution in the beaker. After 1 h, the calomel electrode of the Photovolt Digicord pH meter was immersed in the acid solution and the pH was noted. The pH reading was recorded after every 0.1 mL of 0.05 M sodium hydroxide solution was added. The process was continued until the neutralization point was reached. The pK_a value was read from the plot of the titer value against pH by measuring the half-neutralization point.[27]

Kinetic Procedure. The kinetic procedure was the same as that described for the alkaline hydrolysis of pseudo esters.[1]

Registry No.—Phenyl pseudo *o*-benzoylbenzoate, 5471-75-0; *tert*-butyl alcohol, 75-65-0.

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Effect of Strain on Singlet Oxygen ($^1O_2$) Reactions. 2.[1] Photooxidation of Methylenecyclopropanes

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In contradistinction to methylenecyclopropanes **2–4** which are inert to $^1O_2$, 2,2-diphenylmethylenecyclopropane (**1**) reacts sluggishly, producing benzophenone as the only isolable product. On the other hand 1,1-dimethyl- and 1,1-dicyclopropylmethylenecyclopropanes **5** and **6** yield a variety of products (depending on the reaction conditions) whose formation is explicable in terms of secondary rearrangements of an initially formed allylic hydroperoxide.

While the reactions of singlet oxygen have been well studied,[2] the effect of strain on the rate, mode, and direction of reaction has been almost totally neglected. Until recently there was only a handful of reports[3] in which three- and four-membered alicyclic olefins were photooxidized. In each instance, however, the double bond was flanked by at least one phenyl group. The expected formation of endoperoxides[4] explains the high yield of polymeric material, and the well-documented secondary rearrangements[2d,4,5] of endoperoxides to dioxetanes and allylic hydroperoxides may well explain the formation of what might otherwise be mistaken as "ene" or 2 + 2 cycloaddition products.[6] Hence, an unambiguous study of small ring systems was clearly warranted. The recent publication of two related reports[10,11] prompts us to communicate the results of our study on the photooxidation of methylenecyclopropanes.

For the purpose of this study we synthesized olefins **1–6**. Methylenecyclopropane **1** is the photochemical rearrangement

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