and Bronvitshaya[5] in 82% crude yield. Recrystallizations from ethanol yielded very bright yellow plates, m.p. 225–226°; reported 217–219°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12; Neut. Equiv., 236. Found: C, 81.13; 81.19; H, 5.21, 5.13; Neut. Equiv., 233, 244.

9-Bromo-10-anthroic acid (IIIc). This was prepared from 9,10-dibromoanthracene by the procedure of Mikhailov and Bronvitshaya[5] in 73% yield. Recrystallization from 75% ethanol–25% benzene gave a fluffy yellow solid, m.p. 267–268°; reported 265–267°.

Anal. Calcd. for $C_{15}H_9O_2Br$: C, 59.82; H, 3.01; Br 26.54; Neut. Equiv., 301. Found: C, 60.09; 60.02; H, 3.09, 3.08; Br, 26.48, 26.63; Neut. Equiv., 286, 299.

Methyl esters. A. *Methyl 9-anthroate.* The acid (IIIa), 9.3 g. (0.042 mole) in ether, was esterified with an ethereal solution of diazomethane (0.068 mole) prepared from *N*-methyl-*N*-nitrosourea. After evaporation of the ether 7.6 g. (78%) of ester, m.p. 105–108°, was obtained. Recrystallization from ethanol gave pale yellow needles, m.p. 110–111°; reported 113°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 80.23, 81.51; H, 5.15, 5.17.

B. *Methyl 9-methyl-10-anthroate.* In the same manner as in part A there was obtained a 35% yield of methyl ester which when purified melted at 162–163°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.57; H, 5.64. Found: C, 82.00, 80.17; H, 5.78, 5.77.

C. *Methyl 9-Bromo-10-anthroate.* In the same manner as in part A *there was obtained an* 85% yield *of* methyl ester which when purified melted at 109–110°.

Anal. Calcd. for $C_{16}H_{11}C_2Br$: C, 60.97; H, 3.52; Br, 25.36. Found: C, 60.71; H, 3.37; Br 25.32.

Diels-Alder adducts with p-benzoquinone. A. *Methyl 2,5-diketo-2,5,15,16-tetrahydro-1-triptoate.* This adduct was prepared by the method of Bartlett and Greene[3] except that the reaction was carried out under a nitrogen atmosphere. The product, obtained in 58% yield, melted at 199–200°; reported, 199–201°.

B. *Methyl 6-methyl-2,5,16,16-tetrahydro-1-triptoate.* This was prepared in 65% yield in a manner similar to that of A above except that the mixture was refluxed for only 24 hr. When the reflux time was extended to 44 hr., the yield was increased to 84%. The product melted at 196.5–197°.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08: H, 5.06. Found: C, 76.81; H, 5.00.

C. *Methyl 6-bromo-2,4-diketo-2,5,15,16-tetrahydro-1-triptoate.* When the method described in part A above was applied to the bromo ester only a 4% yield was obtained. Substitution of *p*-xylene for benzene as solvent gave only intractable tars plus a trace of starting material. When the mole ratio of *p*-benzoquinone to ester was increased from 3:1 to 10:1 the yield using benzene as a solvent was 17% in one run and 10% in another run. The purified product melted at 211–211.5°.

Anal. Calcd. for $C_{22}H_{15}O_4Br$: C, 62.43; H, 3.57. Found C, 62.87, 62.99; H, 3.53, 3.61.

Conversion of the keto form to the hydroquinone. A. *Methyl 2,5-dihydroxy-1-triptoate.* The procedure of Bartlett and Greene was followed to obtain a 97% yield of fine colorless needles which sintered at 265° and melted at 272–273°; reported 265–266°.

B. *Methyl 6-methyl-2,4-dihydroxy-1-triptoate.* The procedure in part A was followed to obtain a 95% yield of fine colorless needles which melted at 274–275°.

Anal. Calcd. for $C_{23}H_{28}O_4$: C, 77.08; H, 5.06. Found: C, 77.52; H, 5.22.

C. *Methyl 6-bromo-2,5-dihydroxy-1-triptoate.* The procedure in part A was followed to obtain a 97% yield of fluffy off-white needles which melted at 286–287°.

Anal. Calcd. for $C_{22}H_{15}O_4Br$: C, 62.43; H, 3.57. Found C, 62.83; H, 3.77.

Oxidation of the triptycenehydroquinones to the triptycenequinones. A. *Methyl 2,4-diketo-2,5-dihydro-1-triptoate.* The procedure of Bartlett and Greene was followed to obtain a 72% yield of quinone which melted at 221–224°; reported 225°.

B. *Methyl 6-methyl-2,5-diketo-2,5-dihydro-1-triptoate.* In the same manner as in part A the methylhydroquinone was oxidized in 85% yield to the quinone which melted at 249–250°.

Anal. Calcd. for $C_{23}H_{16}O_4$: C, 77.51; H, 4.53. Found: C, 75.88; H, 4.57.

C. *Methyl 6-bromo-2,5-diketo-2,5-dihydro-1-triptoate.* The bromohydroquinone was oxidized by the method of part A in 85% yield to the quinone which melted at 265.5–266°.

Anal. Calcd. for $C_{22}H_{13}O_4Br$: C, 62.72; H, 3.13; Br, 18.97. Found C, 62.68; H, 3.21; Br, 19.52.

ITHACA, N. Y.

[CONTRIBUTION NO. 120 FROM THE INSTITUTO DE QUÍMICA DE LA UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO]

The Intensity of the Carbonyl Band in the Infrared Spectra of Methyl Benzoates

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The quantitative infrared spectra of *meta* and *para* substituted methyl benzoates were measured, and it was found that the changes of the integrated absorption intensity (*A*), were in full agreement with the theoretical values. No linear relation was found when plotting *A vs.* Hammett σ values.

In the study of absorption intensities of infrared bands it is now customary to report not only their frequency but also their intensity. Cole,[1] Jones,[2] Brown,[3] and others, have shown that the empirical application of the infrared data is useful for structural studies of simple and complex organic molecules. Some values of infrared intensities are reported in the literature, but much work has to

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[1] A. R. W. Cole, G. T. A. Muller, D. W. Thornton, and R. S. L. Willix, *J. Chem. Soc.*, 1218 (1959).

[2] R. N. Jones, D. A. Ramsay, D. S. Keir, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 80 (1952).

[3] T. L. Brown, *J. Am. Chem. Soc.*, **80**, 794 (1958).

be done before a complete picture of the factors that control the intensity and shape of the infrared bands can be completely understood.

As a contribution in this field, we wish to report the integrated absorption values for methyl benzoates with substituents in the *meta* and *para* positions. The purpose of this work was to determine if their intensity values would follow a linear relation when plotted against Hammett σ constants. No such relation could be found for the results (Tables I and II) and this is in accordance with the findings of Brown[3] when he studied substituted benzonitriles and with Jones,[4] on substituted acetophenones. On the other hand, Califano[5] claimed that such a relation existed in the case of anilines and *N*-methylanilines, and Thompson,[6] in the case of benzonitriles.

TABLE I

CARBONYL INFRARED ABSORPTION DATA OF *para* SUBSTITUTED METHYL BENZOATES

Substituent	ν_{max} cm.$^{-1}$	ϵ	$\Delta\nu^1/_2$	A^a	σ
Nitro	1736.9	573	14.0	2.88	+1.27
Fluoro	1732.4	649	12.6	2.95	+0.062
Hydrogen	1731.9	718	11.3	2.99	0.00
Chloro	1730.6	752	11.6	3.11	+0.266
Iodo	1733.0	771	11.7	3.25	+0.276
Bromo	1734.8	666	14.3	3.45	+0.232
Methoxy	1722.1	644	15.8	3.69	−0.268
Amino	1717.2	677	15.1	3.70	−0.660
Hydroxy	1722.7	580	15.1	3.87^b	−0.357
Methyl	1728.3	703	15.1	3.89	−0.170
Dimethylamino	1715.0	683	17.9	4.44	−0.600

[a] One intensity unit (A) = 1×10^4 l. mole^{-1} cm.$^{-2}$ [b] Value obtained by addition of two overlapping bands. Values of ν_{max}, ϵ, and $\Delta\nu^1/_2$ are of the stronger maximum.

TABLE II

CARBONYL INFRARED ABSORPTION DATA OF *meta* SUBSTITUTED METHYL BENZOATES

Substituent	ν_{max}, cm.$^{-1}$	ϵ	$\Delta\nu^1/_2$	A^a	σ
Chlorine	1737.3	634	12.3	2.86	+0.373
Nitro	1740.9	707	11.3	2.88	+0.710
Hydrogen	1731.9	718	11.3	2.99	0.00
Bromine	1735.9	654	12.5	2.99	+0.391
Iodine	1732.8	695	12.7	3.08	+0.352
Amino	1730.2	627	13.9	3.17	−0.161
Methyl	1731.0	705	12.9	3.22	+0.069
Dimethylamino	1730.4	611	14.8	3.27	−0.211
Hydroxy	1732.2	490	14.2	3.55^b	−0.002
Methoxy	1731.3	612	15.4	3.39	+0.115

[a] One intensity unit (A) = 1×10^4 l. mole^{-1} cm.$^{-2}$ [b] Value obtained by addition of two overlapping bands. Values of ν_{max}, ϵ, and $\Delta\nu^1/_2$ are of the stronger maximum.

The measurement of A has many applications such as the determination of the number of carbonyl groups in a steroid[2]; in the determination of C—H present in aliphatic hydrocarbons,[7] or the determination of different types of carbonyl groups.[8,9] It was also found that this method could be used in the determination of the spacial conformation of halogens α to a carbonyl in cycloalkanones.[10] In Table III the values of A for substituted benzene compounds are collected. These data could be used to characterize the number and type of substituents in aromatic rings.

EXPERIMENTAL

The infrared spectra were measured with a double beam single pass Perkin-Elmer Model 21 spectrophotometer, equipped with sodium chloride prism and cells. In order to plot 1 μ in 40 cm. of the chart two number 45 gears were installed in the *A* and *C* positions.[11] The solutions (in 10 ml. of carbon tetrachloride), were approximately 0.015*M* depending on the band intensity, and in each case at least five independent measurements were made. The average results are reported on Table I and II. A pair of matched cells 1 mm. thick was used and all the measurements were made under the same experimental conditions in order to minimize errors. The slit width used was 49 μ and the spectral slit width 7 cm.$^{-1}$ The error in the infrared measurements is ±0.1 for the A value and ±2 cm.$^{-1}$ in the wave number.

Methyl esters of substituted benzoic acids. The methyl esters were prepared from the acids by esterification with methanol and hydrogen chloride by the usual technique. The acids were prepared by standard methods reported in the literature. The physical constants of the esters were in good agreement with literature values.

The values ν_{max}, molecular extinction coefficient, half band width and integrated absorption areas of the 19 methyl esters studies, are given in Tables I and II.

DISCUSSION

The values of ν_{max} of the *para* substituted methyl benzoates (Table I) are between 1715 and 1737 cm.$^{-1}$ Since the value of ν_{max} indicates the energy needed to produce a dipolar excited state, one can assume that a variation of ν_{max} is directly related to the increase or decrease in energy produced by the introduction of the substituent in the molecule. For example, ν_{max} of methyl benzoate was 1732 cm.$^{-1}$ while the value for *p*-dimethylaminobenzoic acid methyl ester was 1715 cm.$^{-1}$, 17 cm.$^{-1}$ lower. The sequence in which the substituents increase ν_{max} was $p - N(CH_3)_2$, $p - NH_2$, $p - CH_3O$, $p - OH$, $p - CH_3$, $p - Cl$, $p - H$, $p - F$, $p - I$, $p - Br$, $p - NO_2$.

In some cases it is possible to ascribe the change in energy to a specific effect: For example, in the

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(4) R. N. Jones, W. F. Forbes, and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957).

(5) S. Califano and R. Moccia, *Gazz. chim. ital.*, **87**, 58 (1959).

(6) H. W. Thompson and G. Steel, *Trans. Faraday Soc.*, **52**, 1451 (1956).

(7) S. A. Francis, *J. Chem. Phys.*, **18**, 861 (1950); **19**, 942 (1951).

(8) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

(9) J. Wenograd and R. Spurr, *J. Am. Chem. Soc.*, **79**, 5844 (1957).

(10) R. Cetina and J. L. Mateos, *J. Org. Chem.*, **25**, 704 (1960).

(11) For a more complete description consult the Perkin-Elmer Manual.

TABLE III

INTEGRATED ABSORPTION AREAS OF SUBSTITUTED AROMATIC COMPOUNDS[a]

R—C_6H_4-	—CHO[b]	—CN[c]	—$COCH_3$[d]	—OH[e]	—CN[f]	—CO_2CH_3[g]	—NH_2[h]	—OH[i]
	(CCl_4)	(CCl_4)	(CCl_4)	(CCl_4)	($CHCl_3$)	(CCl_4)	(CCl_4)	(CCl_4)
R = H	2.25	0.20	2.20	0.99	0.37	2.99		1.15
m-F			1.66					
m-Cl			1.90	1.31		2.86	0.45	1.5
m-Br				1.29		2.99	0.50	
m-I						3.08		
m-NO_2	1.91 2.41[j]		2.02		0.17	2.88	0.58	2.42
m-NH_2			2.15		0.47	3.17		
m-$N(CH_3)_2$						3.27		
m-CH_3		0.20				3.22	0.30	1.37
m-OCH_3	2.50					3.39		
m-OH	2.90[j]				0.47	3.35		
p-F		0.20	2.17			2.95	0.32	
p-Cl	2.55	0.20	2.25	1.19		3.11	0.42	1.46
p-Br			2.24	1.23		3.45	0.46	1.45
p-I			2.39			3.25		
p-NO_2	1.85		1.93		0.13	2.88	1.13	2.36
p-NH_2		0.82	2.38		1.48	3.70		
p-$N(CH_3)_2$	2.25					4.44		
p-CH_3	2.37	0.28	2.44			3.89	0.29	1.16
p-OCH_3	2.88	0.44	1.06			3.69		1.27
p-OH	3.22[j]				0.91	3.77		

[a] One intensity unit (A) = 1 × 10^4 l. mole^{-1} cm.$^{-2}$ [b] Unpublished results of this laboratory. [c] Ref. 3. [d] Ref. 4. [e] T. L. Brown, *J. Chem. Phys.*, **65**, 821 (1957). [f] P. Sensi and G. G. Gallo, *Gazz. chim. ital.*, **85**, 235 (1955). [g] This paper. [h] S. Califano and R. Moccia, *Gazz. chim. ital.*, **87**, 58 (1957). [i] R. Moccia and S. Califano, *Gazz. chim. ital.*, **88**, 342 (1958). [j] Measured in chloroform.

case of the *p*-dimethylamino and similar groups containing $p\pi$ electrons, the delocalization of the $p\pi$ electrons of the substituent stabilize the molecule in the basal state and probably it stabilizes too the dipolar excited state. The *p*-methyl group facilitates the dipolar structure by hyperconjugation. On the other hand, the *p*-nitro reduces the carbonyl dipole formation due to its inductive and resonance effect, increasing the force constant of the carbonyl, and therefore $\nu_{\max}$. However, in the case of the halogens, the effect produced is not related to their electronegativity or to their polarizability.

In Table I, the half band width is also given. It increased with the substituents bromo, methyl, amino, methoxy, and dimethylamino. All these groups are electron donors. It seems that this is one factor which contributes to the increase of the band width. The *p*-dimethylamino benzoic ester has the largest set of values. It is probable that in this case the substituent effect may decrease the energy of the molecule in the excited state, increasing, therefore the probability of transitions among different energy levels. If more rotational transitions are allowed, the band width will increase. The substituents in the *meta* position, affect the carbonyl by their inductive effect, which can be positive or negative, while the same substituent in the *para* position affects the carbonyl by the inductive and resonance effects.

Since the value of A was greater when *para* substituents are present, one can assume that the inductive effect is very small, and therefore, that it is the electron delocalization which is the factor responsible for the change in the value of A. For example, the value of A for methyl benzoate was 2.99 units; the *m*-dimethylamino group had a value for A of 3.27 units giving a ΔA of 0.28. The same substituent in the *para-* position had a value for A of 4.44 units, ΔA was 1.45 and one can assume that the resonance effect is five times greater than the inductive effect.

When a substituent was a halogen in the *para*-position, the ΔA values were greater than when it was *meta*, but there was only a small difference in the two values. This indicates that the resonance effect of the halogen is of less importance than for the other substituents.[12]

The A values when the substituent is a methyl, are, respectively 3.22 for *meta* and 3.89 for *para*. In the latter, one can assume it is due to inductive and hyperconjugative effects acting in the same direction. Finally, the *meta-* and *para*-nitro have similar A values which were 0.11 units smaller than the values of the original compound, indicating that the inductive effect in the *meta-* position is as the inductive and resonance effects operating in *para*.

In the *m-* and *p*-hydroxybenzoates, two bands were present in the carbonyl region, which overlap in the falling branch of lower frequency. They can be resolved as follows: if the branch of the band

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(12) This is in agreement with NMR data since halobenzenes have δ values of nearly zero. P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1957).

where no overlapping is present is projected on the other side, a symmetric band is obtained. The log I_0/I differences of the overlapped band and the symmetric band can be taken at each point, and the second band can be built with these values.

The addition of the two bands will give the true integrated absorption area. The origin of the second band at lower frequencies in the hydroxy compounds is due to the association between the hydroxy and the carbonyl groups. This association was shown to be intermolecular, since the intensity ratio of the two bands changed with concentration and the percentage of association increased regularly with increasing molarity of the solution (Table IV).

TABLE IV

INTENSITY VALUES OF METHYL *p*-HYDROXYBENZOATE[a]

Concn. Mole L.$^{-1}$ × 10^3	A_1	A_2	$A_1 + A_2$	% Association $\frac{A_2}{A_1 + A_2}$
2.925	3.45	0.37	3.82	9.69
8.280	3.17	0.62	3.79	16.36
9.460	3.19	0.74	3.93	18.83
13.730	2.78	1.16	3.95	29.37

[a] A_1 = Area at higher frequency; A_2 = Area at lower frequency.

This second band disappeared when the hydroxy compounds were measured in carbon tetrachloride with 10% pyridine, as would normally be expected, since pyridine is a stronger base than the carbonyl and the association takes place with the solvent.

TABLE V

INTENSITY VALUES OF METHYL *m*-HYDROXY BENZOATE[a]

Concn. Mole L.$^{-1}$ × 10^3	A_1	A_2	$A_1 + A_2$	% Association, $\frac{A_2}{A_1 + A_2}$
9.885	2.23	1.04	3.27	31.8
12.100	2.16	1.11	3.27	34.0
19.251	1.76	1.32	3.08	42.8
22.950	1.69	1.46	3.15	46.4

[a] Area at higher frequency (nonassociated carbonyl); A_2 = Area at lower frequency (associated carbonyl).

If the values of concentration are plotted against the values of A_1 from Table IV, a straight line is obtained, and by extrapolation to zero concentration, the theoretical value for A_t mon can be obtained. This value was found to be 3.665.

Mills and Thompson[13] found that the concentration is directly related to the integrated absorption area. Therefore, it is possible to calculate the amount of monomer present at each concentration by means of the formula.

$$\frac{A_t}{A\text{ mon}} C_t = C_t\text{ mon}$$

where A_t is the integrated absorption value of the monomer at a concentration C_t.

The equilibrium constant of the reaction

$$n(\text{ester}) \rightleftharpoons (\text{ester})n$$

can be calculated with the formula:

$$K = \frac{(\text{ester})n}{(\text{ester})^n} = \frac{\dfrac{C_t - C_t\text{ mon}}{n}}{(C_t\text{ mon})^n}$$

If this formula is written in a logarithmic form: Log $(C_t - C_t\text{ mon}) = n \log C_t\text{ mon} + \log nK$ it is possible to plot log $(C_t - C_t\text{ mon})$ against log C_t mon, whereby a straight line is obtained, in which the slope is the number of associated molecules n and the intercept, log nK.

Doing these calculations by the minimum square method, the values for n and K were 2.09 and 17.2, respectively. The value of 2.09 for n suggest that there is a cyclic dimer, in which each carbonyl is associated with the hydroxy groups of the other molecule, while the benzene rings are parallel to each other (Fig. 1).

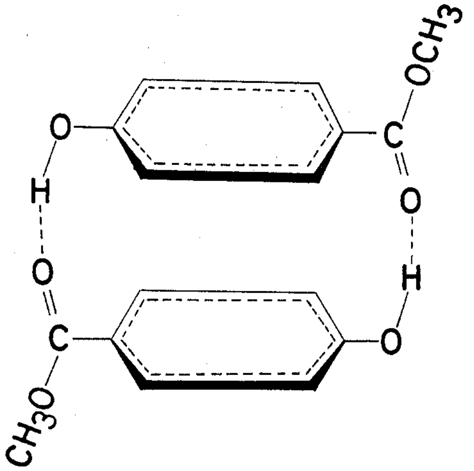

Figure 1

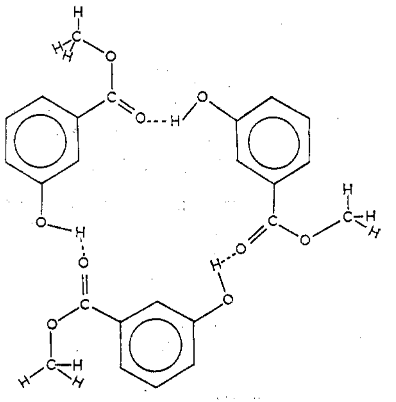

Figure 2

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(13) I. M. Mills and H. W. Thompson, *Proc. Roy. Soc.*, 228A, 287 (1955).

It would be very improbable to have a linear structure, because in that case the number of associated molecules should be greater than two.

The same kind of calculations was carried out with the data of the m-hydroxybenzoic ester, and a value for A_t mon was found to be 2.68. $n = 3.08$ and $K = 1.62 \times 10^5$.

The value of n suggests, therefore, that three molecules form a cyclic compound. By building the model it agrees with this suggestion (Fig. 2).

The free energy of association for the p-hydroxy ester is -1.56 kcal. and -6.58 kcal. for the m-ester.

The ΔF difference between the m- and p-esters may be explained as follows: when the p-hydroxy ester is arranged in a cyclic dimer, the carbonyl group is not in the same plane as the benzene ring, and some resonance energy is lost. In the m-hydroxy ester, three molecules can be arranged in such a way that the three benzene rings and the three carbonyls are in the same plane and, therefore, the resonance energy of the system does not decrease.

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MEXICO 20, D. F.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Kinetics of Alkaline Hydrolysis and *n*-Butylaminolysis of Ethyl *p*-Nitrobenzoate and Ethyl *p*-Nitrothiolbenzoate[1a]

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The kinetics of alkaline hydrolysis of ethyl p-nitrobenzoate and ethyl p-nitrothiolbenzoate were studied by spectrophotometric analysis at 300 mμ. The rate of alkaline hydrolysis is first order in hydroxide ion concentration in the pH range 8 to 12 for the ester and from pH 9 to 12 for the thiol ester. The concurrent alkaline hydrolysis and n-butylaminolysis of these esters was interpreted in terms of the rate equation $v = k_1[E][OH^-] + k_2[E][RNH_2] + k_3[E][RNH_2]^2 + k_4[E][RNH_2][OH^-] + k_5[E][RNH_2][RNH_3^+] + k_6[E][RNH_3^+]$, where [E] represents the ester or thiol ester concentration. At 25.6° and ionic strength 0.50, in aqueous solution containing 1.7% v/v acetonitrile, ethyl p-nitrobenzoate did not undergo any detectable aminolysis; for this ester $k_1 = 0.63$ l./mole sec. Under the same conditions the thiol ester reacted differently, forming principally N-n-butyl-p-nitrobenzamide. The values of the rate constants of its reaction are $k_1 = 0.52$ l./mole sec., $k_2 = 0.015$ l./mole sec., $k_3 = 0.27$ l.^{2}/mole^2 sec., $k_4 = 13.6$ l.^{2}/mole^2 sec., $k_5 = k_6 = 0$. General base catalysis of thiol ester aminolysis, indicated by the k_3 and k_4 terms, probably proceeds *via* proton abstraction by a base from the tetrahedral addition intermediate.

The effects of variations in thiol ester structure upon rates of hydrolysis have been reported for many thiol acetates. Schaefgen[2a] studied the acid and alkaline hydrolysis of ethyl thiolacetate in acetone-water mixtures, and the same solvent was subsequently used by several other authors. Rylander and Tarbell[2b] compared the rates of acid and alkaline hydrolysis, and the respective energies of activation, of methyl, ethyl, isopropyl, isobutyl, and t-butyl thiolacetates with those of the corresponding acetates. Allyl, benzyl, and triphenylmethyl thiolacetates and acetates were similarly compared by Morse and Tarbell.[3] The kinetics of hydrolysis of many thiolacetates were investigated in fully aqueous solution by Noda, Kuby, and Lardy.[4] From these and other studies[5] a few generalizations can be made concerning the hydrolytic reactions of thiolesters: (1) The rates of alkaline hydrolysis of the compounds CH_3COSR are fairly sensitive to the nature of the R group. The ratios of the rate constants to the corresponding acid hydrolysis constants can be correlated with the Taft substituent constants.[6] The energies of activation in such a series are variable and tend to increase with increase in electron-donating ability of the R group. The rates of alkaline hydrolysis of the corresponding oxygen esters can be either less or greater than those of the thiol esters, though the difference is seldom large (usually within a factor of two). For the oxygen compounds neither the rate constants nor the activation energies are very sensitive to the structure of the R group. (2) The rates of acid hydrolysis of thiol esters appear to be less sensitive to structure than do the rates of al-

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[1] (a) This research was supported by Grant H-2416 of the National Institutes of Health; (b) National Institutes of Health Postdoctoral Research Fellow; (c) Present address, Department of Chemistry, Northwestern University.

[2] (a) J. R. Schaefgen, *J. Am. Chem. Soc.*, **70**, 1308 (1948); (b) P. N. Rylander and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 3021 (1950).

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