421. *The Transmission of Polar Effects through Aromatic Systems. Part I. Substituted Anthracenes.*

By R. O. C. NORMAN and P. D. RALPH.

The effects of substituents in the 10-position of the anthracene nucleus on the acid strengths of 9-anthroic acids and on the stretching frequencies of the carbonyl bonds in the corresponding methyl esters have been determined. The results show that the carbonyl group in the acids and esters is precluded from resonance interaction with the aromatic ring, as is a nitro-group at position 10. This conclusion is supported by the results of measurements of the CN stretching frequencies in certain aromatic nitriles, and evidence is also adduced from these measurements that a substituent capable of mesomeric interaction interacts more strongly when bonded to a *meso*-carbon in anthracene than when bonded to a benzenoid carbon atom.

IN anthracene, both the atom localisation energy of a *meso*-carbon atom and the *para*-localisation energy of the central ring have smaller values than in benzene.[1] These

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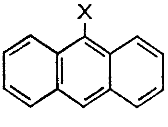
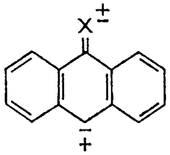
[1] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

differences arise since the resonance energy of anthracene is less than three times the resonance energy of benzene, so that, for example, less resonance energy is lost when anthracene is reduced to the 9,10-dihydro-compound than when benzene is reduced to cyclohexa-1,4-diene. For the same reason, the difference in energies between structures (I) and (II) should be smaller than that between (III) and (IV). Thus, (II) should be a relatively more important canonical form in the resonance hybrid of the 9-substituted anthracene than is (IV) in the corresponding benzenoid hybrid. If X is a substituent capable of mesomeric interaction, its *mesomeric* effect should be greater, if the above is true, when it is attached to the central ring in anthracene than when it is bonded to benzene.



(I)



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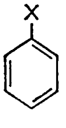

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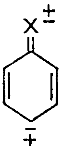

(IV)

It was therefore of interest to examine the polar effects of groups attached to a *meso*-position of anthracene on the properties of a functional centre at the other *meso*-position, and to compare these effects with those in benzenoid compounds.

The anthracene nucleus also provides a convenient system for an investigation of the effects of the steric inhibition of resonance. A substituent in a *meso*-position is subject to repulsive forces from two *peri*-hydrogen atoms, and, if it lacks spherical or cylindrical symmetry, can as a result be twisted from coplanarity with the ring. For example, it is known that the nitro-group in 9-nitroanthracene is twisted through an angle of 85° in the solid.[2] Such non-coplanarity should result in reduced π-orbital overlap between the substituent and the nucleus which in turn should alter the polar effect of the substituent on the aromatic nucleus. Conversely, by investigating the polar effect of such a substituent on the properties of a functional group at some other position in the molecule, evidence concerning the steric inhibition of resonance can be obtained.

Three techniques were chosen for these studies: measurement of the acid-dissociation constants of 10-substituted 9-anthroic acids; of the carbonyl stretching frequencies of 10-substituted-9-anthroates; and of the rates of alkaline hydrolysis of the same esters.

DISCUSSION

Preparation of Materials.—Most of the compounds were known and were prepared by methods reported in the literature. Methyl 10-nitro-9-anthroate was prepared by nitration of methyl 9-anthroate with concentrated nitric acid in boiling acetic acid, attempts to carry out the reaction at lower temperatures being unsuccessful. The position taken up by the nitro-group was confirmed by oxidation of the compound to anthraquinone. The corresponding acid was obtained by vigorous alkaline hydrolysis of the ester. Attempts to make methyl 10-cyano-9-anthroate were unsuccessful. Treatment of methyl 10-bromo-9-anthroate with cuprous cyanide in refluxing quinoline resulted not only in the displacement of bromide by cyanide but also in the removal of the methoxycarbonyl-group, presumably by attack of cyanide ion on the methyl group in an S_N2 reaction to give the corresponding carboxylate ion which should decarboxylate readily.[3] When the lower-boiling solvents, 2,4,6-collidine and dimethylformamide, were used 9-anthronitrile was again obtained, together, in the latter solvent, with some starting material. It did not appear possible to carry out the reaction so that only the bromide was displaced, and attempts to make

[2] Trotter, *Canad. J. Chem.*, 1959, **37**, 351.
[3] Schenkel, *Helv. Chim. Acta*, 1946, **29**, 436.

the cyano-ester were discontinued. On the other hand, 9,10-dicyanoanthracene (required for infrared measurements) was prepared from 10-bromo-9-anthronitrile by displacement with cuprous cyanide in boiling quinoline. 10-Bromo-9-anthronitrile was itself prepared by uncatalysed bromination of the 9-nitrile in boiling nitromethane, and its structure was confirmed by its oxidation to anthraquinone.

pK_A *Values of* 9-*Anthroic Acids*.—The strengths of the 10-substituted-9-anthroic acids in 80% " Methylcellosolve " at 25° (Table) were measured by Dr. W. Simon at Eidgenössische Technische Hochschule, Zurich. The pK_A values were plotted against both the Hammett σ values derived by Jaffé[4] and the σ_n values derived by van Bekkum, Verkade, and Wepster,[5] both sets of chosen values being those applicable to *para*-substituents. In each case the point corresponding to the nitro-group lay on the best straight line only when the σ-value assumed for it was Taft's (inductive) σ_I value,[6] and, with this value included, the best straight lines were drawn by the method of least squares. The better linear graph was obtained when σ_n values were employed. More specifically, when new σ values for the substituents were derived from the graphs, the mean deviation of the new values from those used to obtain the graphs was 0·08 σ-unit when Hammett σ values were employed, but only 0·045 σ-unit relative to σ_n values. The derived σ values from this graph are also shown in the Table, and the mean deviation (0·045) falls within Taft's limits[7] in respect of the criterion which he has suggested should be applied to any new set of σ values. σ_n Values being used, the ρ value for the ionization reaction was found to be 1·82.

Acid	pK_A value	σ_n value	Derived σ value
9-Anthroic acid	5·59	0	0
10-Bromo-9-anthroic acid	5·00	0·265	0·324
10-Chloro-9-anthroic acid	5·03	0·238	0·307
10-Nitro-9-anthroic acid	4·40	(σ_I) 0·630	0·653
10-Methyl-9-anthroic acid	5·71	−0·129	−0·066

The σ_n value of a group is the Hammett constant appropriate when resonance interaction between the group and the functional centre is precluded,[5] and we therefore conclude that such interaction is prevented in the present case because the carbonyl group of the acid is sterically inhibited from the coplanarity required for such interaction. This conclusion is also consistent with the fact that the σ_I value for the nitro-group is appropriate in this case; evidently the nitro-group is unable to exert its mesomeric effect because it is not coplanar with the ring. Our derived σ value, 0·65, for the nitro-group is only slightly greater than Taft's σ_I value of 0·63, suggesting that resonance interaction is close to zero. This substantiates Trotter's conclusion that there is a considerable angle of twist between the plane of the nitro-group and that of the anthracene nucleus.[2] It is also notable that the σ value of 0·72 obtained for a nitro-group in the 4-position of naphthalene,[8] where only one *peri*-hydrogen atom is present to hinder coplanarity, is about half way between our value and the σ_n value, 0·78,[5] for the nitro-group. Finally, our conclusion that the carbonyl group is not coplanar with the aromatic nucleus is in accord with the fact that anthroic acid, like 2,6-dimethylbenzoic acid, is stronger than benzoic acid itself,[9] Taft having computed that conjugation of the carbonyl group with the benzene nucleus in benzoic acid stabilises the acid relative to its anion by about 1 kcal. mole.$^{-1}$, thereby producing an acid-weakening effect.[10]

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[4] Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[5] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.
[6] Taft, *J. Phys. Chem.*, 1960, **64**, 1805.
[7] Taft and Lewis, *Tetrahedron*, 1959, **5**, 210.
[8] Fischer, Fountain, and Vaughan, *J.*, 1959, 1310.
[9] Lauer, *Ber.*, 1937, **70**, 1288.
[10] Taft, in Newman, " Steric Effects in Organic Chemistry," Wiley, New York, 1956, pp. 580, 581.

There is no evidence from the acid strengths that there is an enhancement of the mesomeric effect of a group attached to a *meso*-position in anthracene. Of the compounds studied, only the chloro- and bromo-compounds might have provided such evidence, for the nitro-group is apparently unable to exert its mesomeric effect in this system, while the polar effect of a methyl group is in any case small. Positive evidence would have required that the chloro- and bromo-acids were either weaker than the unsubstituted acid (if the enhanced mesomeric effect were to outweigh the inductive effect), or at least were weaker than the values predicted from a consideration of their σ_n values and the strengths of the other acids. Neither of these requirements was fulfilled. It is therefore reasonable to assume that the chloro- and bromo-substituents are here exerting their normal electron-attracting effects.

Carbonyl and Nitrile Stretching Frequencies.—The carbonyl stretching frequencies (in cm.^{-1}) of the substituted methyl anthroates were measured both in carbon tetrachloride and in chloroform on a Unicam S.P. 100 instrument, and are as follows (values in carbon tetrachloride reported first): methyl anthroate, 1734, 1722·5; methyl 10-bromo-9-anthroate, 1734, 1726; methyl 10-chloro-9-anthroate, 1734, 1724; methyl 10-nitro-9-anthroate, 1735, 1728; methyl 10-methyl-9-anthroate, 1730, 1719·5. The lower frequencies observed on changing from carbon tetrachloride to chloroform agree with similar observations by Thompson, Needham, and Jameson.[11]

The variation of the carbonyl frequency in carbon tetrachloride is small and irregular, but in chloroform a regular variation of the group frequency with the polar character of the substituent is apparent. The frequency values are accurate and reproducible to ± 1 cm.^{-1} but the range of frequencies is only 8·5 cm.^{-1}. Within the limitations of precision implied by this, the results obtained correlate satisfactorily with the $\text{p}K_\text{A}$ values. Similarly, a graph of the frequencies against σ_n values is linear, though again only when the nitro-group is given Taft's σ_I value. The mean deviation of the points from the best straight line is 0·76 cm.^{-1}, and the line has a gradient of 8·9 cm.^{-1} per unit of σ.

The satisfactory correlation obtained by using the σ_I value for the nitro-group further points to the fact that this group is sterically inhibited from resonance interaction with the aromatic ring, but to obtain further evidence that the carbonyl group is so inhibited another approach was employed. Measurements were made of the stretching frequencies of the carbonyl bond in methyl benzoate and methyl mesitoate, and of the cyano-bond in a series of nitriles, again in carbon tetrachloride and chloroform. The results are: methyl benzoate, 1729, 1718; methyl mesitoate, 1732, 1723; benzonitrile, 2229, 2228·5; *p*-bromobenzonitrile, 2231, 2231; mesitonitrile, 2217·5, 2217; 9-anthronitrile, 2217, 2216; 10-bromo-9-anthronitrile, 2217, 2217; 9,10-dicyanoanthracene, insoluble, 2222·5. The cyano-group, having cylindrical symmetry, cannot be inhibited from resonance interaction with the aromatic nucleus. The CN stretching frequencies of mesitonitrile and 9-anthronitrile are, to within 1 cm.^{-1}, the same, and about 12 cm.^{-1} lower than that of benzonitrile. The CN bonds in the first two compounds therefore have less triple-bond character than that in benzonitrile, which is diagnostic of the release of electrons to the cyano-group. That is, the 2,3:5,6-dibenzo-substituent (in 9-anthronitrile) behaves as an electron-releasing substituent to the same extent as the 2,4,6-trimethyl grouping in mesitonitrile. Hence, the anthracene nucleus is electron-releasing relative to benzene; structure (V) is relatively more important in 9-anthronitrile than is (VI) in benzonitrile. On the other hand, methyl mesitoate and methyl 9-anthroate both absorb at higher frequencies than methyl benzoate. Yet, from consideration of polar factors, the shift in carbonyl frequencies should be in the same direction (to lower frequency) as in the corresponding nitriles. The conclusion is that inhibition of resonance is sufficient in each case to cause a shift in the opposite direction from that predicted by the electron-releasing natures of the 2,3:5,6-dibenzo- and 2,4,6-trimethyl groupings, this restriction of conjugation

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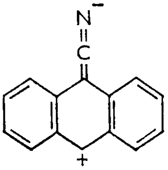
[11] Thompson, Needham, and Jameson, *Spectrochim. Acta*, 1957, **9**, 208.

giving the carbonyl bonds higher double-bond character than that in their unsubstituted analogue.

The relatively larger contribution of structure (V) than of structure (VI) to the respective hybrids is the first evidence from these results in accord with the theory that substituents capable of mesomeric interaction should interact more strongly when bonded at the *meso*-position of anthracene than when substituted in benzene. Confirmation of this was obtained from measurements of the stretching frequencies of the CN bonds in *p*-bromobenzonitrile and 10-bromo-9-anthronitrile. The shift to lower frequencies (2 and 2·5 cm.$^{-1}$ in carbon tetrachloride and chloroform, respectively) brought about by the *p*-bromo-substituent in *p*-bromobenzonitrile is consistent with electron-withdrawal by the bromine atom. The shift to lower frequencies on introduction of the 10-bromo-substituent into 9-anthronitrile is markedly less (0 and 1 cm.$^{-1}$ in carbon tetrachloride and chloroform, respectively). The 10-bromo-group appears to have a very small, perhaps negligible, electron-withdrawing effect, consistent with an enhanced mesomeric effect counterbalancing its inductive effect. Evidently structure (VII) is a relatively more important canonical structure than the corresponding structure in *p*-bromobenzonitrile.



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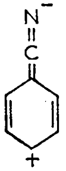

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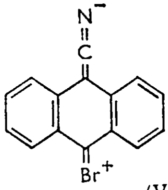

(VII)

It has to be explained why the bromo-substituent shows an enhanced mesomeric effect in 10-bromo-9-anthronitrile but not in the corresponding ester. In the nitrile this effect appears to be due to conjugation between the bromine and the cyano-group, nitrogen being a stable sink for negative charge [see structure (VII)]. In the ester the corresponding structure is sterically precluded. There should be no conjugation between the two cyano-groups in 9,10-dicyanoanthracene, so that the shift to higher frequencies on introduction of the 10-cyano-substituent into 9-anthronitrile should be about the same as that on introduction of a *p*-cyano-substituent into benzonitrile. We measured the CN stretching frequency of 9,10-dicyanoanthracene in chloroform solution (the dicyanide was insoluble in carbon tetrachloride) and found it to be 5·5 cm.$^{-1}$ higher than that of 9-anthronitrile (see p. 2224); the corresponding difference between the benzene analogues in chloroform solution is reported[12] to be 7 cm.$^{-1}$ (9,10-Dicyanoanthracene has a second, weak, CN band because of vibrational coupling.)

Hydrolysis of Anthroic Esters.—The bimolecular rate constant for the alkaline hydrolysis of ethyl 9-anthroate has been reported.[13] We found that the corresponding methyl ester and methyl 10-bromo-9-anthroate could not be hydrolysed under the same conditions, even though methyl esters are hydrolysed faster than their ethyl analogues.[14] A slow decrease in base concentration was observed, but a blank experiment showed that this was due to uptake of base by the glass vessel. In any case the rate of loss of base was slower by at least a factor of 4 than that expected for a reaction having a rate constant equal to or greater than the value reported for ethyl 9-anthroate. We concluded that alkaline hydrolysis of anthroic esters, like that of mesitoic esters,[15] is subject to a powerful steric retardation.

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[12] Krueger and Thompson, *Proc. Roy. Soc.*, 1959, *A*, **250**, 22.

[13] Adam-Briers, Fierers, and Martin, *Helv. Chim. Acta*, 1955, **38**, 2021.

[14] Gore, Vignes, and Feinstein, *Chem. and Ind.*, 1958, 1514.

[15] Goering, Rubin, and Newman, *J. Amer. Chem. Soc.*, 1954, **76**, 787.

We discovered that anthroic esters are also similar to other hindered esters[16] in that they can be hydrolysed to the corresponding acids by dissolution in concentrated sulphuric acid followed by pouring into water. This procedure was successful for all the methyl esters we prepared save the 10-nitro-compound; and it was possible to hydrolyse this ester under alkaline conditions of extreme vigour.

EXPERIMENTAL

M. p.s were taken on a micro-Kofler block and are corrected. Alumina was P. Spence and Sons, Ltd., Type " H." Light petroleum had b. p. 60—80°.

Methyl 9-anthroate,[17] 10-bromo-9-anthroate,[18] 10-chloro-9-anthroate,[18] and 10-methyl-9-anthroate[18] were prepared from the acids by using diazomethane and were purified by chromatography on alumina followed by recrystallisation from light petroleum. Methyl 9-anthroate had m. p. 115° (lit.,[19] 112·1—113·2°) (Found: C, 81·6; H, 5·1. Calc. for $C_{16}H_{12}O_2$: C, 81·3; H, 5·0%). Methyl 10-bromo-9-anthroate had m. p. 114° (lit.,[20] 114—115°), methyl 10-chloro-9-anthroate had m. p. 123° (lit.,[21] 123°), and *methyl* 10-*methyl*-9-*anthroate* had m. p. 164° (Found: C, 81·3; H, 6·1. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

Methyl 10-*Nitro*-9-*anthroate*.—A solution of methyl 9-anthroate (5·6 g.) and concentrated nitric acid (1·4 ml.) in glacial acetic acid (260 ml.) was boiled for 20 min. and poured into water. The ethereal extract was washed, dried (Na_2SO_4), and distilled. The residue was taken up in light petroleum and filtered through alumina; further purification by repeated recrystallisation from light petroleum and ethanol gave yellow needles (0·29 g., 4%), m. p. 171—171·5°, which were shown to be *methyl* 10-*nitro*-9-*anthroate* (Found: C, 68·7; H, 4·0; N, 5·0. $C_{16}H_{11}NO_4$ requires C, 68·2; H, 3·9; N, 5·0%) as follows: The infrared spectrum showed bands characterstic of the ester (1720 cm.$^{-1}$) and nitro (1530 and 1360 cm.$^{-1}$) groupings, while the ultraviolet spectrum showed the bands characteristic of anthracenes ($\lambda_{\text{max.}}$ = 2520 and 3610 Å). The ester (23 mg.) was oxidised to anthraquinone by potassium dichromate (0·5 g.) and concentrated sulphuric acid (2 ml.) in 95% acetic acid (8 ml.) at 100° for 30 min. The solution was poured into water and extracted with chloroform followed by washing, drying ($CaCl_2$), and evaporation of the solvent; material was obtained identified as anthraquinone (m. p. 274—278°; infrared spectrum identical with that of an authentic sample).

Attempts to prepare Methyl 10-*Cyano*-9-*anthroate*.—A typical experiment was as follows. Methyl 10-bromo-9-anthroate (0·5 g.) was dissolved in dimethylformamide (20 ml.), cuprous cyanide (1 g.) was added, and the solution, after being boiled for 20 min., was poured whilst hot into excess of dilute aqueous ammonia. A benzene extract was washed and evaporated; recrystallisation of the residue from light petroleum gave 9-anthronitrile (0·15 g.), m. p. 177—178° (no depression with an authentic sample) (Found: C, 88·8; H, 4·7; N, 6·4. Calc. for $C_{15}H_9N$: C, 88·7; H, 4·5; N, 6·9%). Evaporation of the mother liquor and recrystallisation from light petroleum gave starting material (0·20 g.), m. p. 112—113°. Similar experiments were performed with quinoline and 2,4,6-collidine as solvents. In each case a small yield (about 15%) of 9-anthronitrile was the only isolable product.

10-*Substituted* 9-*Anthroic Acids*.—Newman's hydrolytic method[16] was successful with all the methyl esters except methyl 10-nitro-9-anthroate. The acids were recrystallised from ethanol.

Compound	Crystal form	Yield (%)	M. p.	Lit. m. p.
9-Anthroic acid	Needles	63	219°	218—219°[19]
10-Bromo-9-anthroic acid	Needles	66	285	265—267;[18] 273[20]
10-Chloro-9-anthroic acid	Needles	55	275—276	268·5—269·5[18]
10-Methyl-9-anthroic acid	Plates	66	220	219—220[18]

10-*Nitro*-9-*anthroic acid*.—Methyl 10-nitro-9-anthroate (0·24 g.) and sodium hydroxide (3·5 g.) in 85% ethanol (300 ml.) were boiled for 24 hr. (by which time reaction was not completed), and the solution was poured into water, the mixture filtered, and the filtrate acidified,

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[16] Newman, *J. Amer. Chem. Soc.*, 1941, **63**, 2431.

[17] Mikhailov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1948, 420.

[18] Mikhailov and Bronovitskaya, *Zhur. obshchei Khim.*, 1952, **22**, 157.

[19] Bartlett and Greene, *J. Amer. Chem. Soc.*, 1954, **76**, 1088.

[20] Beyer and Fritsch, *Ber.*, 1941, **74**, 494.

[21] Behla, *Ber.*, 1887, **20**, 701.

to give 10-*nitro*-9-*anthroic acid* (0·1 g.; 43%), m. p. 275° (from ethanol) (Found: C, 67·3; H, 3·4; N, 4·6. $C_{15}H_9NO_4$ requires C, 67·5; H, 3·4; N, 5·2%).

Methyl benzoate had b. p. 197°/749 mm.; benzonitrile had b. p. 191°/762 mm.; *p*-bromobenzonitrile [22] had m. p. 112° (lit.,[22] 113°); mesitonitrile [23] had m. p. 55°; and methyl mesitoate [16,24] had b. p. 98°/3 mm. 9-Anthronitrile [25] had m. p. 177·5—178·5° (lit.,[25] 177·5—179°).

10-*Bromo*-9-*anthronitrile*.—A solution of 9-anthronitrile (0·88 g.) and bromine (0·68 g.) in nitromethane (30 ml.) was boiled for 20 min. The material deposited on cooling was recrystallised from toluene, giving 10-*bromo*-9-*anthronitrile* (0·63 g.; 53%) which has m. p. 193°, resolidifies on further heating, and melts again at 265° (Found: C, 63·5; H, 2·8; N, 4·8; Br, 27·7. $C_{15}H_8BrN$ requires C, 63·8; H, 2·9; N, 4·9; Br, 28·4%). Oxidation to anthraquinone was brought about under the same conditions as those used for methyl 10-nitro-9-anthroate. The product had m. p. 281° and an infrared spectrum identical with that of an authentic sample of anthraquinone.

9,10-*Dicyanoanthracene* (cf. ref. 20).—10-Bromo-9-anthronitrile (0·24 g.) and cuprous cyanide (0·5 g.) were dissolved in quinoline (30 ml.) and the solution was boiled for 1 hr. The product was isolated in the usual way and purified by filtration through alumina in benzene solution, to give 9,10-dicyanoanthracene (0·12 g.; 62%), m. p. 334° (from benzene) (lit.,[20] 328—330°).

pK_A-*Measurements*.—Measurements were made in a microtitration apparatus at 25°, solutions of the acids being used in 80% " Methylcellosolve."

Spectrophotometric Measurements.—A Unicam S.P. 100 spectrophotometer, fitted with a prism grating monochromator, was employed. Under the conditions used, the spectral slit-width was probably about 5 cm.$^{-1}$. Materials were examined in dilute solution in carbon tetrachloride (" AnalaR "; B.D.H.) and chloroform (May and Baker, Ltd.). The container was a sodium chloride cell of 1 mm. path-length.

Hydrolysis Measurements.—The procedures for standardisation of solutions and attempted kinetic measurements were essentially those of Evans, Gordon, and Watson.[26] The solvent used, 85% ethanol, was made up by appropriate dilution, with boiled-out distilled water, of ethanol, purified by the method of Lund and Bjerrum.[27] Kinetic measurements were carried out at 70°, with use of a reaction vessel with a ground-glass stopper which was fitted with springs to minimise solvent evaporation. Samples were withdrawn at intervals during 24 hr. and titrated. The initial sodium hydroxide concentration (M/20) had decreased to M/40 in between 20 and 24 hr., but this decrease was independent of the presence of ester. It most nearly obeyed zero-order kinetics.

We thank Dr. W. Simon for measuring the dissociation constants of the anthroic acids.

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[22] Zappi, and Deferrari, *Anales Asoc. quim. argentina*, 1946, **34**, 146.
[23] Fuson and Denton, *J. Amer. Chem. Soc.*, 1941, **63**, 654.
[24] *Org. Synth.*, Coll. Vol. III, 1955, 553.
[25] Fieser and Hartwell, *J. Amer. Chem. Soc.*, 1938, **60**, 2555.
[26] Evans, Gordon, and Watson, *J.*, 1937, 1430.
[27] Vogel, " Textbook of Practical Organic Chemistry," Longmans, 1951, p. 167.