TABLE III

RELATIVE REACTION CONSTANTS OF POLYSUBSTITUTED BENZHYDRYL CHLORIDES

Substituents	k_{rel} Calculated	k_{rel} Observed	$\Delta E'$, cal.[e]
2,4-Cl_2	0.0059	0.0071	+110
3,4-Cl_2	.012	.018	+241
4,4′-Cl_2[a]	.22	.13	−312
[b]	.26	.17	−252
2,4,4′-Cl_3	.0028	.0023	−122
4-Me-4′-Cl	11.9	8.0	−236
4-MeO-3-Cl	118 (112–123)[c]	141 (116–160)[d]	+106
4-MeO-3,4′-Cl_2	60 (56–64)[c]	70 (60–81)[d]	+ 91

[a] For methanolysis. [b] For isopropanolysis. [c] Limits of prediction based on probable error of values used in calculation. [d] Limits derived from probable error of rates. [e] $\Delta E' = RT \ln (k \text{ calcd.}/k \text{ obsd.})$.

the reaction of the polysubstituted derivative was in isopropyl alcohol. This appears to be the only proper course although alternative values for k_{rel} would sometimes give better agreement with observation. The last column in Table III shows the variations in activation energy corresponding to the deviations between calculated and observed relative rates (always, of course, on the assumption of constancy in the PZ factor).

Acknowledgment.—We wish to express our gratitude to Miss Gertrude Elion for determination of ultraviolet absorption spectra and to Dr. Levy and Mr. Hachem of the Trubek Laboratories for the gift of a sample of *p*-nitrobenzhydrol.

BROOKLYN 2, NEW YORK
TUCKAHOE 7, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Rates of Saponification of Substituted Ethyl 2-Naphthoates[1]

BY CHARLES C. PRICE AND RUDOLPH H. MICHEL[2]

RECEIVED FEBRUARY 8, 1952

The rates of saponification of ethyl 2-naphthoates and derivatives containing 6- and 7-methoxyl, 5- and 8-amino, 8-dimethylamino and 5- and 8-nitro groups have been measured in 70% aqueous dioxane, for most of the compounds at two temperatures. The data are interpreted in terms of resonance and electrical influences. The dipole moment of ethyl 8-nitro-2-naphthoate can be adequately accounted for by assuming that the rotational conformation of the ester group is influenced by the electric field of the nitro group. Calculations of the magnitude of the interaction are in excellent agreement with the observations. The fact that ethyl 5-nitro-2-naphthoate saponifies more rapidly than the 8-nitro isomer indicates that resonance by a nitro group on the α-position of a napthalene ring is sterically inhibited. The observations may be accounted for by the direct electrical influence of the nitro groups on the negatively charged carbethoxyl–hydroxyl ion complex in the transition state. Calculations of the magnitude of the electrical interaction indicate it is adequate to account for the observations.

The influence of substituents on the rate of alkaline hydrolysis of substituted ethyl benzoates has been studied[2] extensively. The results have been found to fit the Hammett equation[3]

$$\log k - \log k^\circ = \sigma\rho$$

where ρ is a constant for the particular reaction series and σ is a constant for the substituent, indicating the magnitude and direction of its electrical effect, and k and k° are, respectively, the rate constants for the alkaline hydrolysis of the substituted and unsubstituted ethyl benzoate. This paper represents an extension of these studies to heteronuclear substituted ethyl 2-naphthoates which may be looked upon as para- and meta-disubstituted ethyl benzoates.

Experimental

A. **Preparation of Compounds. 6-Methoxy-2-naphthoic Acid.**—This compound was prepared from 6-bromo-2-methoxynaphthalene[4] by the Rosemund–von Braun reaction[5] and hydrolysis of the resulting nitrile.[6] A 44% yield of product melting at 194–197°[7] was realized. Two recrystallizations from an ethanol–water mixture raised the melting point to 200–202° (reported[8] m.p. 200–203°).

2-Naphthoic Acid.—Methyl 2-naphthyl ketone (Eastman Kodak Co. "White Label") was converted to 2-naphthoic acid by oxidation with potassium hypochlorite.[9]

7-Hydroxy-2-naphthoic Acid.—2-Naphthoic acid was sulfonated and the acid potassium salt of the 7-sulfo-2-naphthoic acid was converted to 7-hydroxy-2-naphthoic acid, m.p. 266–268° (reported[10] m.p. 269–270°) according to the methods of Butler and Royle.[10] The yield was 27% based on 2-naphthoic acid.

7-Methoxy-2-naphthoic Acid.—In a 1-l., three-necked flask, equipped with a stirrer and two dropping funnels, 21 g. (0.11 mole) of crude 7-hydroxy-2-naphthoic acid and 10 g. of sodium hydroxide were dissolved in 500 ml. of water. The solution was warmed on a water-bath and 56 g. (0.44 mole) of dimethyl sulfate was added over 15 minutes. The addition of a solution of 30 g. (0.75 mole) of sodium hydroxide in 150 ml. of water was started simultaneously with the addition of dimethyl sulfate, but was extended over one hour. The solution was allowed to stir a total of four hours and was kept on the water-bath throughout this time. It was then cooled, poured into a beaker and acidified with concentrated hydrochloric acid. One recrystallization of the crude product from an ethanol–water mixture yielded 19 g. (84%) of acid, m. p. 193–194°. When the crude product was dissolved in ethanol, decolorized with Norit, and recrystallized three times from ethanol–water mixtures, colorless, thin needles were isolated, m.p. 195.5–196.0°.

Anal.[11] Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.95. Found: C, 71.48; H, 5.18.

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(1) Presented at the Buffalo Meeting of the American Chemical Society, March 26, 1952.

(2) A.E.C. Predoctoral Fellow, 1949–1951.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(4) H. E. French and K. Sears, THIS JOURNAL, **70**, 1279 (1948).

(5) C. F. Koelsch and A. G. Whitney, *J. Org. Chem.*, **6**, 795 (1941).

(6) H. E. Ungnade and F. V. Morriss, THIS JOURNAL, **72**, 2114 (1950).

(7) All melting points are uncorrected.

(8) L. E. Miller and E. F. Morello, THIS JOURNAL, **70**, 1900 (1948).

(9) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

(10) C. Butler and F. A. Royle, *J. Chem. Soc.*, **123**, 1649 (1923).

(11) All analyses were carried out by Micro-Tech Laboratory, Skokie, Ill.

Ethyl 5-Nitro-2-naphthoate and Ethyl 8-Nitro-2-naphthoate.—2-Naphthoic acid was nitrated according to the method described by Ekstrand.[12] No separation of the mixed acids was attempted.

The mixed nitro acids were esterified in 100-g. batches by dissolving them in 500 ml. of absolute ethanol, adding 25 ml. of concentrated sulfuric acid and refluxing the solution for eight hours. The solution was then poured on ice, diluted to 2 l. and neutralized with sodium bicarbonate. The solid esters were immediately filtered off, washed with water, dried at room temperature and then recrystallized from Skellysolve L (b.p. 93–130°). The esterification of 542 g. of nitro acids yielded 419 g. (65%) of esters. The mixed esters were separated by fractional crystallization from ethyl acetate. The pure 8-isomer, m.p. 120.5–121.0° (reported[12] m.p. 121°), was isolated more easily than the 5-isomer, m.p. 110.2–110.5° (reported[12] m.p. 111°), because of its comparatively low solubility in ethyl acetate. The isomers were considered to be pure when further recrystallization from ethyl acetate and Skellysolve L did not change their melting points.

Ethyl 5-Amino-2-naphthoate and Ethyl 8-Amino-2-naphthoate.—A solution of 5 g. of the pure nitro-2-naphthoate in 80 ml. of ethyl acetate and 80 ml. of absolute ethanol was reduced at room temperature, over Raney nickel and under 50 lb. of hydrogen. After the theoretical amount of hydrogen had been taken up, the catalyst was filtered off and the solvent evaporated. The product was recrystallized once from a toluene–pentane mixture. The yield was 3.2 g. (73%) of ethyl 5-amino-2-naphthoate, pale-yellow plates, m.p. 95.5–96.0°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.55; H, 6.09; N, 6.51. Found: C, 72.70; H, 6.30; N, 6.47.

Ethyl 8-amino-2-naphthoate formed bright-yellow needles, m.p. 99.8–100.0°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.55; H, 6.09; N, 6.51. Found: C, 72.25; H, 6.02; N, 6.62.

8-Amino-2-naphthoic Acid.—To a solution of 5 g. of sodium hydroxide in 150 ml. of 50% ethanol was added 25 g. of ethyl 8-amino-2-naphthoate. The solution was refluxed for one hour and then diluted to 500 ml. with water. This solution was acidified with glacial acetic acid. The precipitated amino acid was filtered off and dried. The yield was 20.5 g. (95%), m.p. 215–216° (reported[13] m.p. 219).

8-Dimethylamino-2-naphthoic Acid.—To a solution of 8.6 g. (0.21 mole) of sodium hydroxide and 20 g. (0.11 mole) of 8-amino-2-naphthoic acid in 250 ml. of water was added 7 g. (0.055 mole) of dimethyl sulfate with vigorous shaking. The mixture was allowed to stand for 18 hours at room temperature and then was acidified with acetic acid and extracted with 500 ml. of ether. The ether was evaporated and the solid residue was subjected to the same process twice more, with the exception that two equivalents (14 g.) of dimethyl sulfate were used. The dry, crude product from the last methylation weighed 19 g., m.p. 155–160°. By fractional crystallization from methanol 6 g., m.p. 168.5–170.5°, and 5 g., m.p. 167–169°, were isolated. A sample of pure 8-dimethylamino-2-naphthoic acid which was prepared by further recrystallization from methanol melted at 172–173°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.55; H, 6.09; N, 6.51; neut. equiv., 215. Found: C, 72.73; H, 6.30; N, 6.73; neut. equiv., 217.

Preparation of Ethyl Esters from Acids.—The ethyl esters of 2-naphthoic acid, 6-methoxy-2-naphthoic acid, 7-methoxy-2-naphthoic acid, 8-N,N-dimethylamino-2-naphthoic acid, *p*-chlorobenzoic acid (Eastman Kodak Co. "White Label") and *p*-toluic acid (Eastman "White Label") were prepared by dissolving the acid in approximately eight times its weight of absolute ethanol and saturating the solution with hydrogen chloride, except in the case of 6-methoxy-2-naphthoic acid for which concentrated sulfuric acid (about 3% by weight of the reaction mixture) was used as catalyst. While the solutions of 2-naphthoic acid and 7-methoxy-2-naphthoic acid were allowed to stand at room temperature for 48 hours, the solutions of all other acids were refluxed for 12 hours. The reaction mixtures were then reduced to one-third volume and poured on ice. The esters were taken up in ether. The ether solutions were washed with aqueous sodium bicarbonate and dried over anhydrous sodium sulfate.

In the case of ethyl 2-naphthoate, ethyl 8-N,N-dimethyl-2-naphthoate, ethyl *p*-chlorobenzoate and ethyl *p*-toluate the ether was removed from the dry solution and the residual ester was distilled discarding large foreruns and residues. The physical constants for these esters as well as the analysis for the ethyl 8-N,N-dimethylamino-2-naphthoate, are given below. Ethyl 2-naphthoate: b.p. 146–147° (1–2 mm.), m.p. 35.5–36.2° (reported[14] m.p. 32°). Ethyl *p*-chlorobenzoate: b.p. 131–132° (32 mm.) (reported[15] b.p. 121–122° (16 mm.)). Ethyl *p*-toluate: b.p. 66.5° (0.1 mm.), $n^{25}D$ 1.5056. Ethyl 8-N,N-dimethylamino-2-naphthoate: b.p. 175–177° (1 mm.), $n^{25}D$ 1.6046.

Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.07; H, 7.04; N, 5.76. Found: C, 73.75; H, 6.93; N, 5.82.

The pure ethyl 6-methoxy-2-naphthoate was isolated by recrystallization of the crude ester from ether cooled in a 2-propanol–Dry Ice-bath. A 50% yield of colorless plates melting at 92.5–93.5° was realized. *Anal.* Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.10. Found: C, 73.05; H, 6.22.

The crude ethyl 7-methoxy-2-naphthoate was purified by dissolving it in Skellysolve L and passing it through a 10-cm. column packed with alumina. After removal of the solvent the residual oil was most easily crystallized by redissolving it in Skellysolve F (b.p. 35–50°) and allowing most of the solvent to evaporate while the solution was kept near 0°. Further purification was achieved by recrystallization from ethanol, cooled in a 2-propanol–Dry Ice-bath. The product (yield 35%) was a colorless crystalline substance melting at 36.0–36.5°. *Anal.* Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.10. Found: C, 73.12; H, 6.26.

Ethyl Benzoate.—Commercial ethyl benzoate was redistilled. A large forerun and a large residue were discarded; b.p. 208.5–209.0° (745 mm.), $n^{25}D$ 1.5025.

B. Chemical Degradations of the Ethyl Nitro-2-naphthoates.—The ethyl nitro-2-naphthoates were hydrolyzed by refluxing them with a small excess of alkali in a 50% ethanol–water solution for 1.5 hours. The acidified reaction mixture was filtered and the crude nitro acid dried. The ester, m.p. 120.5–121.0°, gave an acid, m.p. 290–291°, while the ester, m.p. 110.2–110.5°, gave an acid, m.p. 294–295°.

Decarboxylation of Nitro-2-naphthoic Acids.—To a solution of 0.17 g. of nitro-2-naphthoic acid in 6 ml. of redistilled quinoline, in a 50-ml. flask equipped with a nitrogen bubbler, an air condenser and a thermometer was added 0.10 g. of copper powder. A slow stream of nitrogen was bubbled through the mixture. The temperature was raised to 230° and held there for 20 minutes. After allowing the reaction mixture to cool, 30 ml. of water and an excess of concentrated hydrochloric acid were added. The flask was shaken vigorously and the copper was filtered off the resulting solution. The aqueous solution was extracted with 70 ml. of ether in three portions. The combined ether extract was washed with 30 ml. of 10% sodium carbonate, with water and was then dried with anhydrous sodium sulfate. The removal of the ether from the dried extract left a brown, oily residue. The oil was dissolved in approximately 20 ml. of ether and passed through a 4-cm. tube packed with alumina. Evaporation of the ether left a brown solid. After 5 recrystallizations from Skellysolve L, the solid was sublimed under reduced pressure. Both nitro-2-naphthoic acids yielded a light-yellow solid, m.p. 57–58° (reported[16] melting point for 1-nitronaphthalene, 57.8°).

Schmidt Reaction on 8-Nitro-2-naphthoic Acid (m.p. 290–291°).—A solution of 0.12 g. of 8-nitro-2-naphthoic acid (m.p. 290–291°) in 10 ml. of 98% sulfuric acid and 1 ml. of 15% fuming sulfuric acid was covered with 15 ml. of chloroform. The mixture was warmed to 45° and 0.5 g. of sodium azide was added with vigorous stirring over about 15 minutes. The mixture was then allowed to stir for 24 hours and was kept warm by keeping it clamped above a gently boiling water-bath. At the end of the 24 hours the chloroform had all evaporated. The solution was poured on 20 g. of ice, made just basic with ammonium hydroxide and extracted with 100 ml. of ether in three portions. The ether

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[12] A. G. Ekstrand, *J. prakt. Chem.*, [2] **42**, 275, 292 (1890).

[13] A. G. Ekstrand, *ibid.*, [2] **42**, 295 (1890).

[14] W. H. Perkin, *J. Chem. Soc.*, **69**, 1179 (1896).

[15] K. Kindler, *Ann.*, **450**, 1 (1926).

[16] H. E. Fierz-David and R. Sponagel, *Helv. Chim. Acta*, **26**, 98 (1943).

was evaporated and the solid residue recrystallized from aqueous ethanol. The product consisted of 0.07 g. of bright-red needles, m.p. 103–104° (reported[17] melting point for 8-nitro-2-naphthylamine, 103–104°).

C. **Electric Moments of the Ethyl Nitro-2-naphthoates.**—The dielectric constant measurements for benzene solutions of the ethyl nitro-2-naphthoates at 25° were carried out by means of the heterodyne beat method.[18] A variable oscillator was used which was tuned against a quartz crystal of one megacycle frequency. The dielectric cell was similar to that described by Svirbely and co-workers.[19]

The densities of the solutions at 25° were determined with a 4-ml. pycnometer.

For the data pertaining to these measurements see Table I.

TABLE I

EXPERIMENTAL RESULTS OF ELECTRICAL MOMENT MEASUREMENTS

N_2 is the weight fraction of ester in grams, ϵ is the dielectric constant of the solution, d is the density of the benzene solution in g./ml., and P_∞ is the polarization of the solute at infinite dilution.

Ethyl nitro-2-naphthoate	M.p. 120.5–121.0°	M.p. 110.2–110.5°
N_2	0.01821	0.01865
ϵ	2.415	2.423
d	0.8823	0.8828
P_∞	396.7	406.6
MR_D	67.66	67.66
μ	3.99	4.05

D. **Saponification Rate Measurements.**—The method is essentially that described by Tommila and Hinshelwood.[20] The solvent used was aqueous dioxane and was prepared by diluting 30 ml. of water to 100 ml. with dioxane. These proportions were determined by the solubility limits of the esters and alkali. The rate measurements were carried out by mixing equal volumes of catalyst and ester solutions of the same concentration at the desired temperature and then withdrawing samples at intervals by means of volumetric pipets. The sample was quenched in an excess of standard hydrochloric acid and back-titrated with standard sodium hydroxide solution using phenolphthalein as indicator.

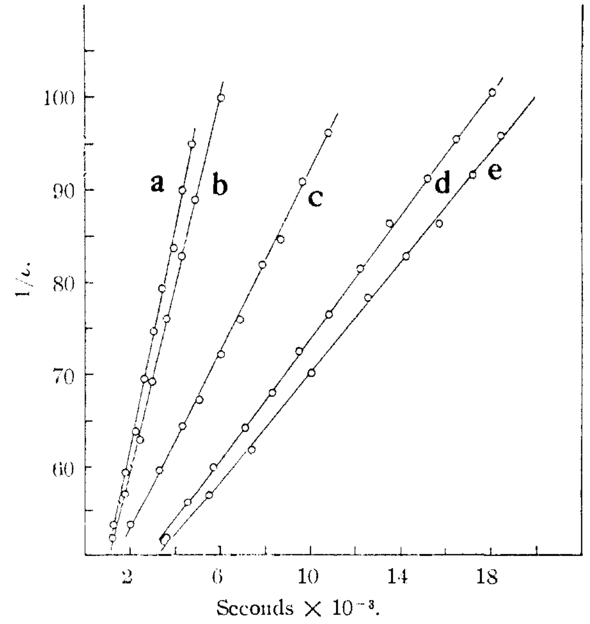

Fig. 1.—Alkaline hydrolysis of: (a) ethyl *p*-chlorobenzoate at 25°; (b) ethyl benzoate at 40°; (c) ethyl 6-methoxy-2-naphthoate at 40°; (d) ethyl benzoate at 25°; (e) ethyl 7-methoxy-2-naphthoate at 25°, all in 70% dioxane.

The ester solution was prepared by adding 30 ml. of water and sufficient dioxane to make 100 ml. to a weighed amount of ester (approximately 0.005 mole) in a standard-taper volumetric flask. The saponification reagent was prepared by diluting an equivalent amount of carbonate-free sodium hydroxide from a standard stock solution (approximately 0.310 *N*) with sufficient water to make 30 ml. on the assumption that the volumes are additive. This was then diluted to 100 ml. with dioxane. The solutions which had been made up to volume at 25° were then placed into an electrically-controlled thermostat at 15, 25 or 40°. At 15° a constant stream of ice-water was passed through the cooling coil by means of a pump. The thermostats were held constant to ±0.05°. After the solutions had come to the bath temperature, they were mixed through a "Y" adapter with standard-taper joints into a long-necked Pyrex flask, which was stoppered tightly and replaced in the thermostat.

The distilled water used had been freed of carbon dioxide by passing through it for approximately 30 minutes a stream of air scrubbed by a concentrated sodium hydroxide solution.

The dioxane (Carbide and Carbon, commercial solvent grade) was purified according to the method described by Fieser,[21] b.p. 100.5° (758 mm.), n^{25}_D 1.4157.

The stock saponification reagent solution and the sodium hydroxide solution used for titrations were prepared by diluting the proper quantity of freshly-prepared 50% sodium hydroxide solution from which the sodium carbonate had been removed by filtration. These solutions were standardized against weighed quantities of primary standard potassium acid phthalate.

Results and Calculations

Electric Moments of Ethyl Nitro-2-naphthoates.—The electric moment in debye unit was calculated from the relation, $\mu = 0.221\sqrt{P_\infty - 1.05\,(Mr_D)}$.

The molar refractions of the ethyl nitro-2-naphthoates for the sodium D line were not determined experimentally but were calculated with the aid of the following values: ethyl benzoate, 42.58; nitrobenzene, 32.74; naphthalene, 44.7; benzene, 26.18; and the equation

$$Mr_D\ (\text{nitro-2-naphthoate}) = Mr_D\ (\text{ethyl benzoate}) + Mr_D\ (\text{nitrobenzene}) + Mr_D\ (\text{naphthalene}) - 2\ Mr_D\ (\text{benzene})$$

Saponification Rates.—The hydrolysis of esters in basic media is a bimolecular reaction and has been shown to be first order in both ester and hydroxyl ion concentrations. The rate constants were determined graphically by plotting $1/c$, where c is the concentration in moles/liter of either reagent, against the time in seconds. Some of these plots are shown in Fig. 1.

In measuring the rates of the comparatively high melting esters of 6-methoxy, 8-nitro and 5-nitro-2-naphthoic acid the end-point of the back-titration was obscured by flocculent precipitates. Furthermore the solid esters occluded much of the organic acid which was to be titrated. To avoid these difficulties 15 ml. of chloroform was added to the quenched samples before titration and the end-point was considered to have been reached when 30 seconds of vigorous swirling did not discharge the pink color. The absorption of carbon dioxide during this extraction process was nearly constant and was compensated for by a blank. The constancy of the blank was tested by running two saponification

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(17) P. Friedlander and S. Szymanski, *Ber.*, **25**, 2076 (1892).

(18) C. P. Smyth, "Dielectric Constants and Molecular Structure," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1931, p. 54.

(19) R. Davis, H. S. Bridge and W. J. Svirbely, THIS JOURNAL, **65**, 857 (1943).

(20) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

(21) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York, N. Y., 1941, p. 368.

rates of ethyl benzoate at 40° using chloroform as well as the same technique as described above. The results were in good agreement with each other and with three runs in which no chloroform had been added to the quenched samples.

The results in Table II are the mean values of the rate constants for duplicate runs.

The σ-constants in Table II were calculated from the rate constants at 25°.

The value of ρ for the alkaline hydrolysis of ethyl benzoates and ethyl 2-naphthoates in 70% dioxane at 25°, was found to be 2.313 by plotting the logarithms of the rate constants of ethyl benzoate (3.425×10^{-3}), ethyl *p*-toluate (1.498×10^{-3}, and ethyl *p*-chlorobenzoate (1.232×10^{-2}) against their respective σ-values of 0, -0.170 and 0.227. The σ-values are those listed by Hammett.[22]

The energy of activation and log PZ were calculated by the Arrhenius equation. On the basis of a probable error of 2% in the rate constants, the probable error in E should lie between 0.36 and 0.48 kcal. and the probable error in log PZ between 0.26 and 0.35.

TABLE II

RESULTS OF ALKALINE HYDROLYSIS OF SUBSTITUTED ETHYL BENZOATES AND ETHYL 2-NAPHTHOATES IN 70% DIOXANE

Substituent	$k_{15} \times 10^3$	$k_{25} \times 10^3$	$k_{40} \times 10^3$	E, kcal.	log PZ	σ
		Ethyl benzoates				
H		3.43	10.7	14.0	7.82	0
p-Cl		12.3				
p-CH_3		1.50				
		Ethyl 2-naphthoates				
H		3.46	11.3	14.7	8.38	.019
6-OCH_3		1.50	4.79	14.3	7.69	−.155
7-OCH_3		2.85	9.33	14.7	8.20	−.035
8-NH_2		1.20				−.196
5-NH_2		2.50				−.059
8-$N(CH_3)_2$		2.46	9.14	14.8	8.23	−.062
8-NO_2	9.12	20		13.5	8.19	.322
5-NO_2	14.1	31.4		13.7	8.53	.416

Discussion

Structure of the Ethyl Nitro-2-naphthoates.—Although the structures of the ethyl 5-nitro- and 8-nitro-2-naphthoates, first prepared by Ekstrand,[12] seemed to be well established by the work of Friedlander, Heilpern and Spielfogel[23] and the reactions described in a patent of Cassella and Co.,[24] the reversal of structure assignment in the more recent work of Harrison and Royle[25] necessitated reinvestigation of these isomers.

The degradation of the ethyl nitro-2-naphthoate, m.p. 120.5–121.0°, to the well established 8-nitro-2-naphthylamine, m.p. 103–104°, showed the original assignment of structure to be correct.

An independent check by means of electric moments proved to be impossible. The electric moments of the ethyl nitro-2-naphthoates listed in Table III were calculated by assuming that the vector moment of the ester group makes a 74° angle[26] with the line joining the ring carbon to the carbethoxy group, while the vector moment of the nitro group passes through the C–N axis. The moment of the carbethoxy group was taken as 1.91 D[27] and the moment of the nitro group as 3.88 D.[28] The fact that the moment vector of the ester group does not pass through the ring carbon–carbonyl carbon bond implies that there are two possible electric moments for any ethyl 2-naphthoate corresponding to essentially two coplanar rotational positions of the carbethoxy group. The values in Table III were calculated on the assumption that the two conformations are energetically equivalent and that the electric moment of the esters may be calculated with the equation

$$\mu_c^2 = a\mu_1^2 + (1 - a)\mu_2^2$$

where μ_c equals the calculated moment, μ_1 and μ_2 are the resultant moments for each conformation, and a equals the fraction of molecules having one conformation.

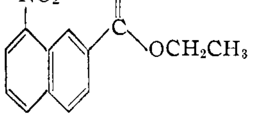
The data in Table III show that the 4-, 6- and 7-isomers are not excluded by the electric moment data. They are, however, excluded by the fact that both isomers give 1-nitronaphthalene on decarboxylation of their acids and by the decisive evidence for heteronuclear substitution in all of the work cited previously. It then remains to explain the unexpected low electric moment of ethyl 8-nitro-2-naphthoate.

TABLE III

ELECTRIC MOMENTS FOR THE ETHYL NITRO-2-NAPHTHOATES

	Calculated moment, D	Experimental moment, D
4-Nitro	4.07	..
5-Nitro	4.07	4.05
6-Nitro	3.80	..
7-Nitro	4.07	..
8-Nitro	4.55	3.99

It has already been pointed out that the calculated moments are based on the assumption that the two possible conformations of ethyl 8-nitro-2-naphthoate are energetically equivalent. If, however, it is assumed that the experimental moment (3.99 D) is the correct electric moment for this compound and this value is substituted, together with the moments of the individual conformations (5.75 D, 2.93 D) in the above equation, it is found that ethyl 8-nitro-2-naphthoate in benzene at 25° exists 30% in conformation I and 70% in conformation II.



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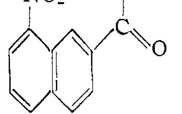

II

The free energy difference for an equilibrium mixture of this composition is 0.5 kcal./mole.

In order to determine whether the greater stability of conformation II is justified, an estimate of

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[22] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

[23] P. Friedlander, H. Heilpern and M. Spielfogel, *Mitt. Technol. Gewerbemus. Wien.* [2] **8**, 319 (1899).

[24] Cassella and Co., German Patent 92,995, *Frdl.*, **4**, 612 (1897).

[25] H. A. Harrison and F. A. Royle, *J. Chem. Soc.*, 84 (1926).

[26] M. E. Hobbs and A. J. Weith, THIS JOURNAL, **65**, 967 (1943).

[27] E. Bergmann and A. Weizmann, *ibid.*, **57**, 1755 (1935).

[28] N. Nakata, *Ber.*, **64**, 2059 (1931).

the energy difference of the two forms was made by comparing their potential energies due to the interaction of charges on the nitro group with those of the carbethoxy group. Scale models[29] were drawn and the charges under consideration, as well as the distances between them, were substituted into the equation

$$E = \Sigma \frac{e_1e_2}{Dr_{12}} \times 1.5 \times 10^{13}$$

where e_1 and e_2 are the charges on two atoms in e.s.u., r_{12} is the distance between the two atoms in cm., D is the effective dielectric constant which was taken as one for benzene and 1.5×10^{13} is the conversion factor from erg/molecule to kcal./mole.

In this way it was estimated that conformation II is actually more stable than conformation I by 0.6 kcal./mole. A comparison of this value to that of the free energy difference can, of course, be only qualitative.

Rates of Saponification.—The formation of a negatively charged transition state in the alkaline hydrolysis of aromatic esters should be favored by any substituent in the aromatic nucleus capable of withdrawing electrons and retarded by any group which releases electrons. This effect has been amply verified by investigations on the rate of alkaline hydrolysis of variously substituted ethyl benzoates and is further corroborated by the present paper.

Ethyl Benzoate and Ethyl 2-Naphthoate.—The rate of hydrolysis of ethyl 2-naphthoate was found to be slightly faster than that of ethyl benzoate. Its σ value calculated from the rate at 25° was 0.019. Hammett[19] lists a value of 0.117 which was derived from data on the acidity constants of anilinium ions in water, at 25°. Since Hammett indicates a probable error of 0.10 for his value the disagreement is not surprising.

Effect of the 6-Methoxy and 7-Methoxy Groups.—The rate of saponification of ethyl 6-methoxy-2-naphthoate ($\sigma = -0.155$) was found to be considerably slower than that of the 7-methoxy ester ($\sigma = -0.035$). This order of reactivity is to be expected when the transition states of the two esters are taken into account. Resonance between the methoxy group in the 6-position and the rings increases the electron density on the carbon adjacent to the carbethoxyl carbon, hence destabilizing the transition state and increasing the energy of activation. The 7-methoxy group is not in a position where resonance between the substituent and the ring increases the electron density on the carbon adjacent to the carboxyl carbon. That the rate of ethyl 7-methoxy-2-naphthoate is slower than that of ethyl-2-naphthoate is somewhat surprising, considering the electron-withdrawing character of the *m*-methoxy group in reactions of the benzene series. It seems reasonable to assume that the inductive effect of the *m*-methoxy group, which is the decisive factor in the benzene series, has become sufficiently damped in the second ring of naphthalene that another effect becomes more important. Resonance between the 7-methoxy group and the rings will raise the electron densities on carbon 1 and carbon 3. A smearing of these charges onto carbon 2 by a secondary inductive effect would explain the weak electron-releasing properties of the 7-methoxy group.

Effect of the 8-Amino and 5-Amino Groups.—The rates of alkaline hydrolysis of the 8-amino ester ($\sigma = -0.196$) and the 5-amino ester ($\sigma = -0.059$) were found to be slower than the rate of ethyl 2-naphthoate. The rate of the 8-amino ester was slower than that of the 5-isomer. The 8-amino group is in a position where resonance with the ring destabilizes the transition state, while the 5-amino group is not. The case of these two groups is then quite similar to the case of the 6-methoxy and 7-methoxy esters.

Effect of the 8-N,N-Dimethylamino Group.—The rate of hydrolysis of the 8-N,N-dimethylamino ester ($\sigma = -0.062$) was found to be about twice the rate of the 8-amino ester ($\sigma = -0.196$) and about the same as that of the 5-amino ester ($\sigma = -0.059$). Since the 8-N,N-dimethylamino group is in a position where resonance between the substituent and the rings would bring about a less stable transition state, the unexpected high rate must be interpreted as damping of resonance by the peri hydrogen. If this were not so, the rate of the 8-N,N-dimethylamino compound would have to be at least as slow as that of the 8-amino compound. On the other hand, resonance cannot be entirely inhibited or the 8-N,N-dimethylamino group would act as an electron-withdrawing group (by the inductive effect) and the rate of alkaline hydrolysis of this compound would exceed that of both ethyl 5-amino-2-naphthoate and ethyl 2-naphthoate.

Effect of the 8-Nitro and 5-Nitro Groups.—The 5-nitro ester ($\sigma = +0.416$) saponified at a higher rate than the 8-nitro ester ($\sigma = +0.332$). Since the 8-nitro group is in the position where resonance with the naphthalene nucleus lowers the electron density on the carbon adjacent to the carbethoxy group, its transition state should be more highly stabilized and its reaction rate should be faster. Strong damping of resonance due to the proximity of the peri hydrogen is indicated.[30] This alone, however, would not explain the higher reaction rate of the 5-nitro ester.

In order to be able to compare the effect of the nitro group in the two different positions on the energy of activation of the saponification, it was assumed that the resonance contribution of the nitro group to the energy of activation of the 8-isomer is small. It should then be possible to estimate the stabilization of the negative charge on the carbon atom of the carbethoxy group by the electrostatic charges on the nitro group in either position. Scale models of the transition states were drawn with the same data cited in the discussion of the electric moments. The nitro group was assumed to lie in a plane perpendicular to the nucleus. The interaction energy for each transition state was calculated with the aid of the coulombic relation by substituting in it the respective charges and the distance between them as indicated in the scale models. The

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(29) Bond distance and bond moment data were taken from C. C. Price, "Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 14.

(30) Similar cases of steric inhibition of resonance have been reported by Berliner, *et al.*, THIS JOURNAL, **72**, 5305 (1950).

effective dielectric constant, *D*, was taken as 2.5 for 70% dioxane.

The transition state of the 5-isomer was thus found to be stabilized by a coulombic energy of 1.32 kcal./mole and that of the 8-isomer by an energy of 1.13 kcal./mole. If these stabilization energies were subtracted from an accurate value of the energy of activation for ethyl 2-naphthoate, the resulting values should represent the energy of activation for the respective ethyl nitro-2-naphthoates.

The actual experimental energies of activation are too sensitive to errors in the rates to be used for this purpose. Consequently the mean value of log *PZ* (8.13) and the rates of hydrolysis at 25° were used to calculate comparable activation energies for ethyl 2-naphthoate, ethyl 5-nitro-2-naphthoate and ethyl 8-nitro-2-naphthoate. These values are given below under the title, "Experimental" E_a. When the above stabilization energies were subtracted from the energy of activation for ethyl 2-naphthoate obtained in this manner, the resulting values (calculated E_a) compared favorably with the "Experimental" E_a for ethyl 5-nitro-2-naphthoate and ethyl 8-nitro-2-naphthoate.

	"Experimental"[a] E_a (kcal./mole)	Stabilization energy	Calcd. E_a[b]
Ethyl 2-naphthoate	14.45	..	(14.45)
Ethyl 5-nitronaphthoate	13.15	1.32	13.13
Ethyl 8-nitronaphthoate	13.40	1.13	13.32

[a] $E_a = 2.3\ RT(8.13 - \log k_{25})$. [b] 14.45 minus column 3.

The σ-Values.—The σ^1-values listed in Table II may be looked upon as those of a substituted, unsaturated side chain attached to ethyl benzoate in the meta and para positions. It would be expected then, that the electrical effects of the substituents on this side chain, although weaker, would be qualitatively the same as those of the analogous substituents on the benzene ring. A comparison of such σ-values shows this to be so only in cases where the special properties of the naphthalene nucleus do not enter.

TABLE IV

COMPARISON OF σ-VALUES FOR ANALOGOUS SUBSTITUENTS IN NAPHTHALENE AND BENZENE

6-Methoxy-*p*-methoxy	−0.155	−0.268
7-Methoxy-*m*-methoxy	− .035	.115
8-Amino-*p*-amino	− .196	− .653
5-Amino-*m*-amino	− .059	− .112
8-N,N-Dimethylamino-*p*-N,N-dimethylamino	− .062	− .671[a]
8-Nitro-*p*-nitro	.332	.803
5-Nitro-*m*-nitro	.416	.696

[a] D. C. Lincoln (THIS JOURNAL, **73**, 5838 (1951)) has found that $\sigma = -0.360$ for ethyl 3-methyl-4-dimethylaminobenzoate. Since $\sigma = -0.110$ for the *m*-methyl group, σ for the hindered *p*-dimethylamino group must be approximately −0.250.

Acknowledgment.—We would like to express our appreciation for the aid given to us by Brother Columba Curran, C.S.C., in connection with the measurements of the electric moment of the ethyl nitro-2-naphthoates.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. XVII. Addition of Organic Acids to *p*-Quinonedibenzimide and Related Compounds

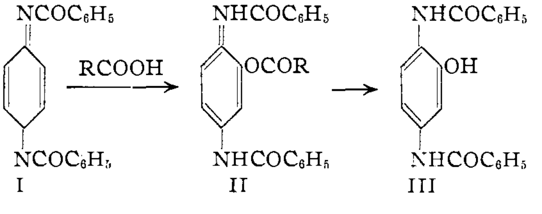
BY ROGER ADAMS AND D. S. ACKER[1]

RECEIVED FEBRUARY 26, 1952

p-Quinonedibenzimide adds various organic acids to yield 2-acyloxy-*p*-phenylenedibenzamides. These are readily hydrolyzed to the 2-hydroxy-*p*-phenylenedibenzamide. Acetic acid has also been added in a similar way to *p*-quinonedicarbethoxyimide, *p*-quinonedicarbobenzoxyimide, 2-methyl- and 2-chloro-*p*-quinonedibenzimides. 2-Acetoxy-*p*-phenylenedibenzamide is oxidized to the corresponding diimide, which is difficult to isolate but readily converted with hydrogen chloride to *x*-chloro-2-acetoxy-*p*-phenylenedibenzamide. *p*-Quinonedibenzenesulfonimide does not react with acetic acid unless a catalyst such as boron fluoride is present; it then forms 2-acetoxy-*p*-phenylenedibenzenesulfonamide.

p-Quinonedibenzenesulfonimides were frequently prepared and crystallized from glacial acetic acid. They were unreactive to this solvent. On the other hand, in the investigation of the *p*-quinonedibenzimide, it was observed that the product reacted with glacial acetic acid to form a stable substance. There are no examples recorded in the literature showing the addition of organic acids to benzoquinones.

Various organic acids were added to *p*-quinonedibenzimide (I) merely by allowing a solution of this substance in the acid to stand at room temperature. Solid acids may be added by melting the reactants. Some acids will add in a neutral solvent. The reaction is quite general and the results are shown in Table I. The 2-acyloxy-*p*-phenylenedibenzamides (II) are obtained in good yields. Infrared spectra confirm the presence of the ester carbonyl. These addition products are easily hydrolyzed by aqueous alkali to the free phenol, 2-hydroxy-*p*-phenylenedibenzamide (III).



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[1] An abstract of a thesis submitted by D. S. Acker to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.