converted into a complex like III may be more reactive because of inductive electron release through the boron atom to the ring carbon. The efficiency

of sodium fluoride is undoubtedly related to the great stability of the fluoborate anion.

DURHAM, NEW HAMPSHIRE

The Rate of Saponification of Some Alkyl m- and p-Dialkylaminobenzoates

BY CHARLES C. PRICE AND WILLIAM J. BELANGER[1]

RECEIVED JANUARY 14, 1954

The influence of m- and p-dimethylamino, diethylamino and di-n-propylamino groups on the rates of saponification of methyl, ethyl and propyl benzoates have been measured. The rates of saponification decrease as the size of the alkyl groups in the amino group increases.

It has been reported by Price and Lincoln[2] that p-, and especially m-, t-butylbenzoates saponify in 60% acetone at rates considerably slower than the toluates. It was suggested that one of the factors responsible was a decrease in the solvation stabilization of the ionic intermediate in saponification due to the bulk of the t-butyl group, as compared to the methyl group.
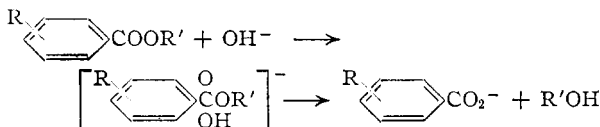
It was the purpose of the work reported herein to study this effect by changing the size of R, making it dimethylamino, diethylamino and dipropylamino with R' = methyl, ethyl or propyl.

Experimental[3]

The properties of the acids used and references to the methods of their preparation are given in Table I.

The esters of the aminoacids were prepared by refluxing the acid with alcoholic hydrogen chloride. The esters were fractionally distilled through a 90 × 1.2-cm. glass-spiral column. The properties of other esters used are summarized in Table III.

Saponification rate measurements in 60% acetone[2] were unsatisfactory because some of the aminoesters saponified so slowly that the acetone turned deep yellow, obscuring the end-point. Solvents that proved satisfactory were 80% methanol for the methyl esters, 80% ethanol for the ethyl esters and 80% 1-propanol for the n-propyl esters. The procedure was essentially the same as that described previously[2] and the results are summarized in Tables IV, V and VI.

Some rates of saponification in 60% acetone are summarized in Table VII.

The reaction constants, ρ, used for calculating the substituent constants, σ, in Tables IV, V and VI are given in each table and were estimated from the rates of saponification of the benzoate and toluate esters by the equation

$$\log (k_R/k_H) = \sigma\rho$$

The values assigned to σ are indicated in the table.

Discussion

From the data in Tables IV, V and VI it can be seen that the rates of saponification of analogous esters with dimethylamino, diethylamino and dipropylamino substituents decrease in the order indi-

(1) Socony–Vacuum Fellow, 1949–1951. Abstracted from the Ph.D. dissertation submitted by W. J. B., August, 1951.

(2) C. C. Price and D. C. Lincoln, THIS JOURNAL, 73, 5836 (1951).

(3) All melting points are corrected. Microanalyses by Micro-Tech Laboratories, Skokie, Illinois.

TABLE I
PROPERTIES OF N,N-DIALKYLAMINOBENZOIC ACIDS

Isomer	R	Prepn.	M.p., °C.	Lit. m.p., °C.
Meta	CH₃	a	150–151	151[b]
Para	CH₃	c	235–236	234–240[d]
Meta	C₂H₅	e	89–90	90[e]
Para	C₂H₅	f	191–193	188–193[g]
Meta	Allyl	e	91	90[e]
Para	Allyl	e	126–126.5	127[f]
Meta	n-C₃H₇	h	89–89.3 (or 80–80.5)	
Para	n-C₃H₇	i	142–142.2	142[i]

ᵃ A. C. Cumming, Proc. Roy. Soc. (London), A78, 103 (1906). ᵇ P. Griess, Ber., 6, 587 (1873). ᶜ J. Johnston, Proc. Roy. Soc. (London), A78, 87 (1906). ᵈ E. Bischoff, Ber., 22, 341 (1889); W. Michler, ibid., 9, 400 (1876); J. Houben and A. Schottmuller, ibid., 42, 3736 (1909). ᵉ P. Griess, ibid., 5, 1041 (1872). ᶠ A. Michael and J. F. Wing, Am. Chem. J., 7, 197 (1885). ᵍ F. Reverdin and A. de Luc, Ber., 42, 1727 (1909); J. Houben and R. Freund, ibid., 42, 4822 (1909); W. Michler and A. Gradmann, ibid., 9, 1913 (1876). ʰ The sodium salt of the diallyl acid was hydrogenated in water with Raney nickel at 1700 p.s.i. to give a 96% yield of acid, fine white needles from aqueous ethanol, m.p. 89–89.3°, but on remelting, 80–80.5°. Anal. Calcd. for C₁₃H₁₉NO₂: C, 70.59; H, 8.59; N, 6.33. Found: C, 70.75; H, 8.82; N, 6.24. ⁱ As for h. ʲ J. D. Reid and D. F. J. Lynch, THIS JOURNAL, 58, 1430 (1936).

cated. This is in agreement with the predicted bulk effect but could also be explained by increased resonance donation of electrons to the ring, facilitated by increasing inductive electron release in the series methyl, ethyl, propyl.[4]

Some evidence as to the relative importance of the two possible explanations can be obtained from a study of the effects these dialkylamino groups show on reactions of opposite electrical type, i.e., those with negative, as well as positive, values for the reaction constant ρ. A striking example of this is the work of Hertel and Dressel[5] on the rate of reaction of the dimethylamino group with methyl picrate in acetone to form the quaternary picrate (ρ −2.382).[6] In this reaction, a p-methyl group or p-methoxy group promoted the rate but the latter no more than a p-dimethylamino group. It was in fact on the basis of this reaction that Hammett as-

(4) Increasing rates observed for nitration of p-alkoxyanisoles in the series methoxy, ethoxy, n-propoxy has been ascribed to increased inductive electron release (see L. J. Goldsworthy, J. Chem. Soc., 1148 (1936)).

(5) E. Hertel and J. Dressel, Z. physik. Chem., B29, 178 (1935).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

Table II

Properties of Alkyl N,N-Dialkylaminobenzoates, $R_2NC_6H_4CO_2R'$

Isomer	R	R'	B.p. °C.	B.p. Mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Meta	CH_3	CH_3	76	0.03	1.5582	66.96	66.92	7.25	7.26	7.81	8.00
Para	CH_3	CH_3	102	.05	a	...	...	..	..	..	..
Meta	CH_3	C_2H_5	77	.04	1.5443	...	...	..	..	..	..
Para	CH_3	C_2H_5	112	.02	b	...	...	..	..	..	..
Meta	CH_3	C_3H_7	105.5	.05	1.5365	69.46	69.87	8.20	8.43	6.76	6.82
Para	CH_3	C_3H_7	127	.2	c	69.46	69.50	8.20	8.29	6.76	6.82
Meta	C_2H_5	CH_3	134	1.0	1.5447	69.46	69.40	8.20	8.15	6.76	6.73
Para	C_2H_5	CH_3	117	0.05	d	69.46	69.78	8.20	8.60	6.76	6.75
Meta	C_2H_5	C_2H_5	160	5.0	1.5333	70.49	70.71	8.58	8.51	6.33	6.42
Para	C_2H_5	C_2H_5	134	1.5	e	...	...	..	..	..	..
Meta	C_2H_5	C_3H_7	100	0.15	1.5272	71.40	71.16	8.92	8.92	5.95	6.13
Para	C_2H_5	C_3H_7	130	0.2	1.5573	71.40	71.26	8.92	8.94	5.95	6.03
Meta	C_3H_7	CH_3	117	1.0	1.5317	71.40	71.32	8.92	8.94	5.95	5.94
Para	C_3H_7	CH_3	110.5	0.03	f	71.40	71.70	8.92	8.96	5.95	6.54
Meta	C_3H_7	C_2H_5	110	.2	1.5232	72.20	72.30	9.22	9.56	5.61	5.60
Para	C_3H_7	C_2H_5	93	.05	g	72.20	72.48	9.22	9.39	5.61	5.70
Meta	C_3H_7	C_3H_7	114	.2	1.5193	72.89	72.52	9.49	9.60	5.31	5.44
Para	C_3H_7	C_3H_7	140	.05	1.5466	72.89	72.73	9.49	9.55	5.31	5.50

a M.p. 102°; E. Bischoff, Ber., 22, 341 (1889), m.p. 102°. b M.p. 62–64°; F. H. Westheimer and R. P. Metcalf, This Journal, 63, 1339 (1941), m.p. 63–63.5°. c M.p. 37–38°. d M.p. 46–47°. e M.p. 43°; F. Reverdin and A. de Luc, Ber., 42, 1727 (1909), m.p. 43°. f M.p. 36.5–37.2°. g M.p. 34.0–34.8°.

Table III

Properties of Some Alkyl Benzoates and Toluates, (RC_6H_4COOR')

Isomer	R	R'	B.p. °C.	B.p. Mm.	$n^{25}D$
..	H	CH_3	86	15	1.5140
..	H	C_2H_5	103	21	1.5025
..	H	C_3H_7	113	14	1.4981
Meta	CH_3	CH_3	64.5	0.04	1.5133
Meta	CH_3	C_2H_5	71.5	.2	1.5030
Meta	CH_3	C_3H_7	79.5	.1	1.4978
Para	CH_3	CH_3	69.5	.4	a
Para	CH_3	C_2H_5	66.5	.1	1.5056
Para	CH_3	C_3H_7	91.5	.07	1.4996

a M.p. 35.5–36°; H. Fischli, Ber., 12, 616 (1879), m.p. 34–35°.

dimethylamino group, as expected less negative than the amino group (σ −0.66), just as the p-methoxyl group (σ −0.268) is less negative than the p-hydroxyl group (σ −0.356).[7]

The fact that all three m-di-n-propylamino esters saponify at rates appreciably slower than the corresponding m-diethylamino esters, whereas there is much less difference in the rates for the corresponding $para$ series, can be explained by the increased importance of the "bulk effect" in the $meta$ position. Obviously more detailed and extensive data are necessary before it will be possible to make a satisfactory evaluation of the relative contributions of the electrical effect and of the "bulk effect" on solvation to the influence of dialkylamino groups on reactivity. We are undertaking experimental work

Table IV

Saponification Rates of Methyl Benzoates in 80% Methanol, $\rho_{25} = +2.014$, $\rho_{40} = +1.796$

Substituent	$k_{25} \times 10^4$	$k_{40} \times 10^3$	E, kcal.	log PZ	σ_{25}	σ_{40}
H	4.21 ± 0.04	1.87 ± 0.02	18.4	10.1	0	0
m-CH_3	3.07 ± .02	1.42 ± .001	19.0	10.4	(−0.069)	(−0.069)
p-CH_3	1.91 ± .02	0.894 ± .006	19.1	10.3	(− .170)	(− .170)
m-$N(CH_3)_2$	2.20 ± .02	1.032 ± .006	19.1	10.3	− .140	− .143
p-$N(CH_3)_2$	0.116 ± .007	0.0634 ± .0001	21.0	10.4	− .774	− .818
m-$N(C_2H_5)_2$	1.45 ± .01	.706 ± .025	19.6	10.5	− .231	− .235
p-$N(C_2H_5)_2$	0.064 ± .0004	.0363 ± .0003	21.4	10.5	− .902	− .953
m-$N(n$-$C_3H_7)_2$	1.25 ± .005	.605 ± .005	19.5	10.4	− .261	− .272
p-$N(n$-$C_3H_7)_2$	0.0572 ± .0001	.0353 ± .0003	22.5	11.2	− .927	− .959

signed an abnormally small value to the reaction constant (σ −0.205)[6] for the p-dimethylamino compared to the value (σ −0.72)[2] based on saponification (ρ 2.37). Both reactions may actually be slower than expected on the basis of the electrical influence of the dimethylamino group. The proper value for the σ-value, uninfluenced by solvation effects, is perhaps somewhere between the extremes of −0.2 and −0.7. Data reviewed and summarized by Jaffe[7] lead to σ −0.60 for the p-

(7) H. H. Jaffe, Chem. Revs., 53, 191 (1953).

for this purpose and hope additional data will merit a more quantitative interpretation.

One interesting influence revealed by the data in Tables IV, V and VI is the marked decrease in the σ-value for all three of the p-dialkylamino groups depending on whether it was determined by saponification of the methyl, ethyl or propyl esters. Since this change is not observed in the m-isomers, we would like to suggest that it arises from progressively less and less resonance stabilization in the original molecule, due to increased steric hin-

TABLE V

SAPONIFICATION RATES OF SUBSTITUTED ETHYL BENZOATES IN 80% ETHANOL, ρ_{25} = +2.258, ρ_{40} = +1.892

Substituent	$k_{25} \times 10^4$	$k_{40} \times 10^3$	E, kcal.	log PZ	σ_{25}	σ_{40}
H	8.76 ± 0.03	3.42 ± 0.01	16.9	9.3	0	0
m-CH₃	5.94 ± .01	2.51 ± .01	17.8	9.9	(− .069)	(−0.069)
p-CH₃	3.91 ± .06	1.66 ± .002	17.9	9.7	(− .170)	(− .170)
m-N(CH₃)₂	4.31 ± .06	1.70 ± .001	17.0	9.1	− .136	− .160
p-N(CH₃)₂	0.226 ± .004	0.109 ± .0001	19.5	9.6	− .703	− .791
m-N(C₂H₅)₂	2.79 ± .002	1.13 ± .01	17.3	9.1	− .220	− .254
p-N(C₂H₅)₂	0.131 ± .003	0.0685 ± .0005	20.4	10.1	− .808	− .898
m-N(n-C₃H₇)₂	2.20 ± .04	.956 ± .012	18.2	9.7	− .262	− .292
p-N(n-C₃H₇)₂	0.127 ± .02	.0647 ± .0015	20.2	9.9	− .815	− .911

TABLE VI

SAPONIFICATION RATES OF SUBSTITUTED n-PROPYL BENZOATES IN 80% n-PROPYL ALCOHOL, ρ_{25} = +2.361, ρ_{40} = +2.02

Substituent	$k_{25} \times 10^4$	$k_{40} \times 10^3$	E, kcal.	log PZ	σ_{25}	σ_{40}
H	8.94 ± 0.03	3.17 ± 0.02	15.6	8.4	0	0
m-CH₃	5.86 ± .04	2.23 ± .04	16.5	8.9	(−0.069)	(−0.069)
p-CH₃	3.98 ± .006	1.55 ± .002	16.8	8.9	(− .170)	(− .170)
m-N(CH₃)₂	4.36 ± .03	1.66 ± .01	16.5	8.7	− .132	− .140
p-N(CH₃)₂		0.117 ± .002				− .709
m-N(C₂H₅)₂	2.78 ± .04	1.051 ± .005	16.4	8.5	− .215	− .237
p-N(C₂H₅)₂						
m-N(n-C₃H₇)₂	2.19 ± .018	0.847 ± .012	16.7	8.6	− .259	− .284
p-N(n-C₃H₇)₂	0.127 ± .002	0.162 ± .008	19.5	9.4	− .783	− .847

TABLE VII

SAPONIFICATION RATES OF SUBSTITUTED ALKYL BENZOATES IN 60% ACETONE

Compound	$k_{25} \times 10^3$	σ
Methyl benzoate	9.20	−0.02
Ethyl benzoate	3.04 ± .01	
n-Propyl benzoate	2.03 ± .003	
Methyl m-N,N-dimethylaminobenzoate	4.25 ± .03	−0.146
Ethyl m-N,N-dimethylaminobenzoate	1.29 ± .003	− .157
Methyl p-N,N-dimethylaminobenzoate	0.210 ± .0003	− .714
Ethyl p-N,N-dimethylaminobenzoate	0.0633 ± .0004	− .709
Methyl m-N,N-diethylaminobenzoate	2.13 ± .03	− .276
Ethyl m-N,N-diethylaminobenzoate	0.651 ± .003	− .282
n-Propyl m-N,N-diethylaminobenzoate	0.416 ± .003	− .290

drance in structure Ia as the bulk of R' is increased.
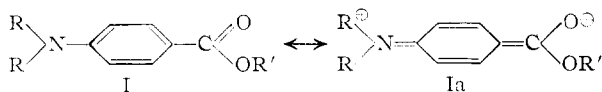
Similarly, greater bulk in R should decrease resonance contribution of electrons to the ring. Since σ actually became more negative with increasing size of R, one could argue that this further supports the "bulk effect" on solvation, rather than

the resonance explanation for the more negative σ-values in the series R = Me, Et and n-Pr.

The view that saponification is influenced by solvation energy factors is indicated by the relative rates of saponification in the various media. In 60% acetone, the rate of saponification decreased in the order methyl, ethyl, propyl as expected. In the corresponding alcohol, the saponification rates were in the reverse order. It would seem that decreasing solvation stabilization of the hydroxyl ion and of the ionic intermediate as the solvent change from 80% methanol to 80% ethanol to 80% 1-propanol could account for this reversal.

The greater importance of solvation in 60% acetone may also account for the reversal in relative rates of saponification of p-toluate and p-t-butylbenzoate in 85% ethanol[8] as compared to 60% acetone.[2,8a]

NOTRE DAME, INDIANA

(8) (a) E. Berliner, M. C. Beckett, E. H. Blommers and B. Newman, THIS JOURNAL, 74, 4940 (1952); (b) C. W. L. Bevan and E. D. Hughes in C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 327; but contrast (c) R. L. Herbst, Jr., and M. E. Jacox, THIS JOURNAL, 74, 3004 (1952).