ethanol. The mixture was stirred at 75° for 80 minutes, and then was poured into water and extracted with ether. The residue obtained from the ether was recrystallized from ethanol to give 0.51 g. (75%) of 3,4-diphenylfuroxan, m.p. 113–115°, reported[19] m.p. 115–117°.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

Hydrolysis of Diethyl Methoxyphthalates

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The rate of saponification and acid-catalyzed hydrolysis of the diethyl methoxytere- and methoxyisophthalates have been determined and compared with the previously reported unsubstituted diethyl phthalates. The effect of the methoxyl group is similar to that noted in the methoxybenzoic acid esters.

The effects of the position of substitution of various electron donating and withdrawing groups upon the rates of saponification and acid-catalyzed hydrolysis of substituted ethyl benzoates have been reported.[2] No data of this type are available for the substituted isomeric diethyl phthalates. During a recent study of the esters and polyesters of the isomeric methoxyphthalic acids, it became of interest to determine quantitatively the effect of the position of substitution of the methoxyl group upon the over-all rate of saponification and acid-catalyzed hydrolysis of the diethyl esters of the methoxyiso- and methoxyterephthalic acids. It is the purpose of this paper to report these results and to make a comparison of the over-all rates with those of the unsubstituted diethyl phthalates as well as ethyl benzoate and ethyl anisate.

Experimental

Preparation of the Esters.—The diethyl methoxyphthalates were prepared by the method used by Fosdick[3] for the preparation of diethyl 4-methoxyisophthalate. A mixture of 10 g. of the methoxyphthalic acid, 50 g. of thionyl chloride and several drops of dry pyridine was heated at reflux for four hours after complete solution of the acid had been attained. In several cases this required 18 hours. The excess thionyl chloride was removed by a vacuum flash distillation, followed by an addition of 30 ml. of dry benzene and a second vacuum flask distillation to dryness. Absolute ethanol, 100 ml., was added and the mixture was heated at reflux for 3 hours. The diethyl ester separated as an oil when the alcohol solution was drowned in cold water. The ester was removed from the aqueous suspension by extraction with ether, and the extract was dried over anhydrous calcium chloride. Evaporation of the ether and the subsequent distillation of the dry recovered liquid esters in a Podbielniak spinning-band column gave the compounds listed in Table I.

Several of the compounds were purified either by distillation in the Podbielniak spinning-band column or by recrystallization: diethyl phthalate, n^{20}_{D} 1.5021; diethyl isophthalate, n^{20}_{D} 1.5071; diethyl terephthalate, m.p. 44°; ethyl benzoate, n^{20}_{D} 1.5049; and ethyl anisate, n^{20}_{D} 1.5241.

Saponification Procedure.—Reaction mixtures (100 ml.) containing 0.05 equivalent per liter of ethyl ester and of sodium hydroxide in 85% by weight ethanol were prepared. In each case 0.005 equivalent of ester and 40.6 ± 0.2 g. of aqueous ethanol (85% by weight ethanol) were weighed in 250-ml. glass-stoppered flasks and placed in a water-bath maintained at 25 ± 0.1°. At the start of a reaction 50 ml. of 0.1 *N* alcoholic sodium hydroxide (85% by weight ethanol), also adjusted to 25°, was added by pipet to the ester solution. To effect solution the flask was swirled in the bath for about two minutes. Zero time was taken at half the delivery time of the 50-ml. pipet. During a run at least five 10-ml. aliquots of reaction mixture were taken out at intervals and added to 15 ml. of 0.1 *N* aqueous hydrochloric acid which had been cooled in ice to stop the reaction. Sampling time was taken when half the aliquot had been delivered into the acid. The resulting acid solution was promptly titrated with 0.1 *N* aqueous sodium hydroxide to a greenish-blue end-point with brom thymol blue. It was established by direct titration of each of the seven dibasic acids under consideration that in all cases both carboxyl groups are determined quantitatively under the analytical conditions employed. Duplicate saponification runs gave satisfactory checks.

Acid-catalyzed Hydrolysis Procedure.—*p*-Toluenesulfonic acid was chosen as a catalyst for the hydrolysis because of the resistance of this acid to esterification with ethanol and to decomposition under the conditions used. Other strong acids[2e] can react with the solvent. A control run indicated that *p*-toluenesulfonic acid did not change strength within the duration of the present experiments (about 100 hours at 100°).

Reaction mixtures (10 ml.) containing 0.05 equivalent per liter of ethyl ester and of 0.05 equivalent per liter of *p*-toluenesulfonic acid in ethanol (85% by weight ethanol) were prepared. In the case of each ester to be hydrolyzed, 0.005 equivalent of ester was weighed in a 50-ml. volumetric flask and was then made up to 50 ml. with aqueous ethanol (85% by weight ethanol). In each of five heavy-walled Pyrex tubes, capacity about 20 ml., was placed by pipet 5 ml. of stock ester solution and 5 ml. of 0.1 *N* *p*-toluenesulfonic acid in aqueous ethanol (also 85% by weight ethanol). The tubes were cooled in an ice-bath and sealed. The group of five tubes for each ester was placed in a wire basket and submerged at zero time in an oil-bath maintained at 100 ± 0.3°. The reaction mixtures remained homogeneous during the heating period. One tube for each ester was removed from the bath at intervals, cooled in ice, opened, and the contents promptly titrated, at about 0°, with 0.1 *N* aqueous sodium hydroxide to a brom thymol blue end-point. When precipitation occurred during titrations, 15 ml. of 95% ethanol was added to restore homogeneity.

Results and Discussion

Saponification of Ethyl Esters.—In preliminary runs the second-order rate constants were determined for ethyl benzoate and ethyl anisate and were found to agree closely with those previously reported[2b,c]; Table II.

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(1) Locomotive and Car Equipment Department, General Electric Co., Erie, Penna.

(2) (a) E. Berliner, M. C. Beckett, E. A. Blommers and B. Newman, THIS JOURNAL, **74**, 4940 (1952); (b) D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, 1430 (1937); (c) C. K. Ingold and W. S. Nathan, *ibid.*, 222 (1936); (d) W. B. S. Newling and C. N. Hinshelwood, *ibid.*, 1357 (1936); (e) E. W. Timm and C. N. Hinshelwood, *ibid.*, 862 (1938); (f) E. Tommila, *Ann. Acad. Sci. Fennicae Ser. A*, **57**, No. 13, 3 (1941); (g) E. Tommila, L. Brehmer and H. Elo, *ibid.*, **59**, No. 9, 3 (1942); (h) E. Tommila, L. Brehmer and H. Elo, *ibid.*, II, **16**, 14 (1945); (i) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938); (j) E. Tommila and L. Ketonen, *Suomen Kemistilehti*, **18B**, 24 (1945); (k) S. Tommila and E. Tommila, *Ann. Acad. Sci. Fennicae, Ser. A*, **57**, No. 5, 3 (1941).

(3) L. S. Fosdick and O. E. Fancher, THIS JOURNAL, **63**, 1277 (1941).

TABLE I

DIETHYL METHOXYPHTHALATES

					Analyses, %					
					Calcd.			Found		
Phthalate diethyl ester	B.p., °C.	Mm.	M.p., °C.	$n^{20}D$	C	H	Sapn. equiv.	C	H	Sapn. equiv.
2-Methoxyiso-	114	0.95		1.5048	61.89	6.39	126	61.6	6.4	127
4-Methoxyiso-[a]			56–57							
5-Methoxyiso-	124	.7	*Ca.* 5	1.5142	61.89	6.39	126	61.9	6.5	132
Methoxytere-	123	.25		1.5194	61.89	6.39	126	61.7	6.8	130

[a] This compound was reported previously, see ref. 3.

TABLE II

SAPONIFICATION RATES

Ester	$k_{25} \times 10^4$, l. mole^{-1} sec.$^{-1}$ This work	Previous work	Ref.
Ethyl benzoate	6.31	5.50	2c
		6.21	2b
Ethyl anisate	1.40	1.15	2c

The diethyl esters of all the dibasic acids were saponified under precisely the same conditions used for the anisate and benzoate. The experimentally determined extents of saponification were plotted against time and from these curves the values given in Table III have been selected at convenient points for the purpose of kinetic analysis. These show that there is a considerable difference in the rates of saponification of the isomeric esters and clearly demonstrate the effect of the methoxyl group and its position on the aromatic nucleus.

TABLE III

TIME REQUIRED TO ATTAIN A DEFINITE PER CENT. OF SAPONIFICATION OF THE ETHYL ESTER, 25°

Percentage saponification	10	20	30	40	50	60
Acid			Time, seconds			
Terephthalic	300	775	1450	2500	5600	15400
Methoxyterephthalic	320	850	1600	2700	5900	16200
Isophthalic	540	1360	2680	4750	9200	19400
2-Methoxyisophthalic	1000	2450	4370	7050	11500	19500
4-Methoxyisophthalic	1230	3100	6100	10700	20200	47500
5-Methoxyisophthalic	490	1240	2400	4150	7700	16500
Phthalic	3250	8400	15100	25600	42000	69000
Benzoic	3250	7800	13800	22000	33000	49400
Anisic	15400	40500	69000	90000	107000	120000

The rates of saponification of the separate ester groups in the symmetrical diethyl methoxyisophthalates, *i.e.*, diethyl 2- and 5-methoxyisophthalate, were calculated by the method of Frost and Schwemer.[4] These rates are given in Table IV. The unsymmetrical esters have four rate constants and as such cannot be calculated by this method.

The results agree with the earlier conclusion of Kivinen and Tommila,[5] namely, that the intact ester group serves as a strong accelerating and electron-attracting group and consequently produces a faster rate of saponification for the first ester grouping when compared to the second. The observed difference in k_1 and k_2 can also be attributed to the repulsive effect of the carboxylate ion upon the hydroxyl ion in its approach to the second ester group.

TABLE IV

RATES OF SAPONIFICATION OF DIETHYL METHOXYISOPHTHALATES

Diethyl ester	$k_1 \times 10^4$ l. mole^{-1} sec.$^{-1}$	$k_2 \times 10^4$	k_1/k_2
2-Methoxyisophthalate	22	4.5	4.9
5-Methoxyisophthalate	45	3.8	11.9

Diethyl 2-methoxyisophthalate saponified at a substantially slower rate than did diethyl isophthalate. In this compound the methoxyl is *ortho* to both carbethoxyl groups. The rate of saponification of diethyl 4-methoxyisophthalate was found to be even less than that of the diethyl 2-methoxyisophthalate. In the 4-methoxyisophthalate the methoxyl is *ortho* to one carbethoxyl group and *para* to the other. The placement of the methoxyl group in a position *meta* to both carbethoxyl groups, as in diethyl 5-methoxyisophthalate, resulted in an increased rate of saponification over that observed for diethyl isophthalate. These observations indicate that the relative effect of the methoxyl group upon the rate of saponification of the diethyl methoxyisophthalates follows the same pattern found for the ethyl alkoxybenzoates.[2f,g] In the ethyl alkoxybenzoates it was found that the *m*-alkoxyl group increases, while the *o*- and to an even greater extent the *p*-alkoxyl group decrease the rate of saponification.

The work of Ingold[6] suggests that the methoxyl group in the 2-methoxyisophthalate ester shields the carbethoxyl group from the carboxylate ion to a greater extent than in the 5-methoxyisophthalate ester since the ratio of k_1/k_2 for the former ester is nearer to the statistically derived value of 2, which is the ratio for an ideal ester having no interaction between the two ester groups undergoing saponification.

Diethyl methoxyterephthalate was found to saponify at only a slightly slower rate than that of diethyl terephthalate. In this case the methoxyl group is *ortho* to one carbethoxyl group and *meta* to the other.

From these results it is seen that the relative effects of position of the methoxyl group in the methoxyiso- and methoxyterephthalic acids are similar in magnitude to that shown by the alkoxyl group in the alkoxybenzoates. The extent of influence of the monocarboxylate ion does not appear to override the effect of the methoxyl group in these compounds. In fact from the results in Table IV the carboxylate ion exhibits less influence on the saponification rate than does the carbethoxyl group.

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(4) A. A. Frost and W. C. Schwemer, THIS JOURNAL, **74**, 1268 (1952).

(5) E. Kivinen and E. Tommila, *Suomen Kemistilehti*, **14B**, 7 (1941).

(6) C. K. Ingold, *J. Chem. Soc.*, 1375 (1930); J. Greenspan, *Chem. Revs.*, **12**, 356 (1933).

Acid-catalyzed Hydrolysis.—Unlike the saponification of the esters, the acid-catalyzed hydrolysis of these compounds proceeded as a first-order reaction. This indicates that the liberation of one carboxyl group in the phthalate ester has little influence on the hydrolysis of the remaining carbethoxyl group. Under the conditions of the experiment it was possible to attain equilibrium.

The rate constants for the hydrolysis reaction were calculated by the usual equation. Table V is a presentation of the first-order rate constants and also the percentage hydrolysis at equilibrium. The reaction medium was 85% ethanol by weight.

TABLE V

ACID-CATALYZED HYDROLYSIS OF ETHYL ESTERS

Constituent acid	$k_{100°} \times 10^6$, sec.$^{-1}$	Hydrolysis at equilibrium, %
Benzoic	3.93	18.4
Anisic	2.27	17.8
Phthalic	1.09	13.8
Isophthalic	4.13	19.9
2-Methoxyisophthalic	3.09	18.3
4-Methoxyisophthalic	3.33	20.3
5-Methoxyisophthalic	4.81	19.5
Terephthalic	4.44	19.3
Methoxyterephthalic	5.48	20.5

Ethyl anisate hydrolyzes under these conditions at a rate about one-half that of ethyl benzoate, indicating that the 4-methoxyl group causes a pronounced retardation of hydrolysis. Similarly, it was observed that the diethyl 2- and 4-methoxyisophthalates hydrolyzed at a rate considerably less than that of diethyl isophthalate. In contrast both diethyl 5-methoxyiso- and methoxyterephthalate hydrolyzed at a rate greater than that of the corresponding unsubstituted diethyl phthalates. It again appears that the methoxyl group in the m-position exerts an accelerating effect upon the hydrolysis, and in the o- or p-position the effect is opposite.

Within the series of the unsubstituted phthalate esters, it is of particular interest to note that diethyl phthalate hydrolyzes at a rate only about one-quarter of that of the diethyl iso- and terephthalates.

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SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Rates of Solvolysis of m-Alkylbenzhydryl Chlorides[1,2]

BY ERNST BERLINER AND MABEL M. CHEN

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Rate constants for the solvolysis of four m-alkylbenzhydryl chlorides have been determined at three temperatures in 80% by volume aqueous acetone. The order in which the alkyl groups enhance the rate is m-Me > m-Et > m-i-Pr < m-t-Bu. This order, which is essentially the same as that for p-alkyl groups but more closely spaced, is attributed to carbon–hydrogen hyperconjugation from the m-position. Alternate explanations are discussed.

The iodination of p-alkylphenols and p-alkylanilines in the position *meta* to the alkyl groups proceeds in the order m-t-Bu > m-i-Pr > m-Et > m-Me, *i.e.*, the alkyl groups affect the rates in accordance with the order of their inductive effects.[3] Two explanations have been advanced. One is that resonance effects are not effectively transmitted through the m-position, and that therefore only the inductive effect can be operative. The other, and preferred, explanation is that the obtainment of the inductive order is not so much a consequence of the position of the alkyl groups on the benzene ring as of the nature of the substituting agent. The substituting agent in aqueous iodination is thought to be a cationic species, H_2OI^+ or I^+,[4] of great electrophilic activity and therefore of low selectivity,[5] and not sufficiently electron demanding to bring about the operation of the hyperconjugation effect. The situation would be analogous to p-nitration of alkylbenzenes,[6] but unlike p-bromination[7,8] or chlorination.[7] In order to support this latter view, it seemed of importance to study the effect of m-alkyl groups in a reaction which is known to proceed through a highly electron-demanding transition state. In such a reaction a hyperconjugation effect might be expected to be transmitted even through the m-positions.

One of the best documented cases of an electron-demanding reaction which follows a hyperconjugation order of alkyl groups is the solvolysis of p-alkylbenzhydryl chlorides in 80% by volume aqueous acetone.[9] As a test case for the m-alkyl groups, we have chosen therefore the similar S$_N$1 solvolysis of the m-alkylbenzhydryl chlorides in the same solvent. The mechanism of the reaction can

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(1) Electronic Effects of Alkyl Groups. IX. This title is now given to a number of previous papers, *i.e.*, Hyperconjugation, I–V: ref. 3, 8, 13, 29.

(2) Taken from a dissertation submitted by Miss M. M. Chen to the Graduate School of Bryn Mawr College in partial fulfillment of the requirements for the Ph.D. degree, June, 1956.

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