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

The Alkaline Hydrolysis of Polynuclear Methyl Arylacetates¹

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Rates of the alkaline hydrolysis of 13 methyl arylacetates, $\text{ArCH}_2\text{COOCH}_3$, were determined in 85% aqueous methanol and/or in 75% aqueous acetone at four temperatures. Esters in which the side chain is attached to a 1-naphthalene-like position react at considerably reduced rates; this is ascribed to steric hindrance to the approach of the reagent. The rates of the unhindered compounds do not correlate well with various Hückel molecular orbital reactivity parameters but can be correlated with much better precision with a reactivity index suggested by Streitwieser and Lawler. These indices can be considered to express the electronegativity of an aromatic hydrocarbon residue.

Almost all of the recent studies of polynuclear reactivities involved carbonium ion reactions in compounds where the reaction site is attached directly to the aromatic ring.^{4,5} In most of these reactions the reactivity is lower than predicted by various theoretical parameters for those compounds in which the reaction site is situated at a 1-naphthalene-like position. Frequently, two classes of reactivity have been observed, the unhindered or benzene-like series, and the hindered or 1-naphthalene-like series. Within each series the compounds often fall within the predicted order. This difference has commonly been ascribed to steric hindrance by the *peri* hydrogen.

In order to assess the importance of this factor, we wish to report data on the alkaline hydrolysis of methyl arylacetates, $\text{ArCH}_2\text{COOCH}_3$. This system was chosen because the reaction site is removed by one methylene group from the aromatic ring. By analogy to the early investigations on the esterification of mesitoic and mesitylacetic acids⁶ it was anticipated that there would be less, or no, hindrance in the hydrolysis of the methyl arylacetates. There are other aspects of the reaction which are of interest. In these esters direct conjugation between the ester group and the aromatic ring is precluded by the intervening methylene group, and the significance of other factors pertaining to aromatic reactivities, such as relative electronegativities of aromatic hydrocarbon residues, may be assessed.

Results and Discussion

Rates of saponification of methyl arylacetates in 85% by volume aqueous methanol were measured at four temperatures. Average rate constants are listed in Table I, in which are also included the activation parameters. Two esters, methyl 2-anthrylacetate and methyl 6-chrysylacetate, were insufficiently soluble in the above solvent, and were saponified in 75% by volume aqueous acetone. In order to extrapolate the reactivities of these two compounds from one solvent

to the other, nine of the esters studied in aqueous methanol were also hydrolyzed in aqueous acetone, and the average rate constants for hydrolysis in the latter solvent at 25° are collected in Table II. It was of interest to observe that the relationship between hydrolysis rates in the two solvents is not linear, but tapers off at either end of the reactivity scale. The change from 85% methanol to 75% acetone results in a large increase in rate. This is only partly the result of the lower water content in the former solvent. It is partly the result of the alkoxide-hydroxide ion equilibrium, which decreases the concentration of the hydroxide ion in the alcoholic solvent.⁷

In order to interpret the effect of polynuclear substituents on the rate of hydrolysis, it will be helpful to consider first what effects might be expected. The saponification of ethyl phenylacetates in 87.83 wt. % ethanol has a ρ -value of +0.824.⁸ Electron-attracting substituents favor the reaction, but, because of the intervening methylene group, the effect of substituents is compressed compared to the hydrolysis of ethyl benzoates, for which ρ in the same solvent is +2.498. Since aromatic rings are intrinsically electron attracting, the rates of hydrolysis of the arylacetates should increase with the number of rings and the size of the aromatic system. This is a less ambiguous prediction than can be made for the hydrolysis of aryl acetates, where the inductive effect of the aryl group and the conjugation of the ester group with the ring act in opposite directions.⁹

Examination of the data in Table I reveals that this expectation is fulfilled for the compounds listed above methyl phenylacetate, for which the reactivity decreases in the order 2-phenanthryl \sim 3-phenanthryl $>$ 2-anthryl $>$ 4-biphenyl \sim 2-naphthyl $>$ phenyl $>$ 2-fluorenyl $>$ *p*-tolyl. On that basis, the first five compounds should be the most reactive, whereas they are the least so. All of them belong to the class of 1-naphthalene-like compounds. This is in contrast to the original expectation that extension of the side chain by a methylene group might eliminate steric interference from the *peri* hydrogen.¹⁰ In fact,

(1) Relative Reactivities of Polynuclear Aromatic Systems. 111.

(2) Taken from the Ph.D. thesis of N. Acton, Bryn Mawr College, June, 1963.

(3) To whom inquiries should be addressed.

(4) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957); L. Verbit and E. Berliner, *ibid.*, **86**, 3307 (1964).

(5) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 12. This chapter contains an up-to-date bibliography of these reactions.

(6) V. Meyer and J. J. Sudborough, *Ber.*, **27**, 1580 (1894).

(7) M. L. Bender and W. A. Glasson, *J. Am. Chem. Soc.*, **81**, 1590 (1959).

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter 7.

(9) See, for instance, M. Adams-Briers, P. J. C. Fierens, and R. H. Martin, *Helv. Chim. Acta*, **38**, 2021 (1955).

(10) It has only recently been shown that in the alkaline hydrolysis of

TABLE I
 RATES OF HYDROLYSIS OF METHYL ARYLACETATES IN 85% AQUEOUS METHANOL^a

Ar- in ArCH ₂ COOCH ₃	Temperature, °C.					<i>E</i> , kcal./mole	log <i>A</i>	Δ <i>S</i> *, e.u., 25°
	24.9 <i>k</i> ₂ × 10 ³	32.5 <i>k</i> ₂ × 10 ³	40.0 <i>k</i> ₂ × 10 ²	50.0 <i>k</i> ₂ × 10 ²	60.2 <i>k</i> ₂ × 10 ²			
9-Anthryl	0.568	1.22		0.543	1.13	16.7 ± 0.2	9.04 ± 0.15	-19.2
6-Chrysyl	1.17 ^b							
9-Phenanthryl	1.18	2.44		1.08	2.45	16.9 ± 0.1	9.49 ± 0.03	-17.1
1-Naphthyl	1.19	2.49		1.09	2.20	16.4 ± .2	9.09 ± .16	-18.9
1-Pyrenyl	2.01	4.14		1.71	3.70	16.2 ± .1	9.21 ± .11	-18.4
<i>p</i> -Tolyl	2.45	4.91		2.04	4.26	16.0 ± .1	9.12 ± .06	-18.8
2-Fluorenyl	2.76	6.08		2.47	5.14	16.2 ± .3	9.37 ± .19	-17.6
Phenyl	2.97	5.83	1.07	2.42		16.0 ± .1	9.21 ± .01	-18.4
2-Naphthyl	3.64	7.16	1.30	2.99		16.1 ± .1	9.33 ± .09	-17.8
4-Biphenyl	3.66	7.11	1.27	2.91		15.8 ± .2	9.14 ± .12	-18.7
2-Anthryl	4.05 ^b							
3-Phenanthryl	4.21	8.82		3.47	7.34	15.9 ± 0.2	9.28 ± 0.12	-18.1
2-Phenanthryl	4.28	8.42	1.53	3.45		15.9 ± 0.1	9.30 ± 0.07	-18.0

^a Rate constants are in l. mole⁻¹ sec.⁻¹. ^b Extrapolated from runs in 75% aqueous acetone.

 TABLE II
 RATES OF HYDROLYSIS OF METHYL ARYLACETATES IN 75%
 AQUEOUS ACETONE AT 24.9°

Ar- in ArCH ₂ COOCH ₃	<i>k</i> ₂ × 10 ^b	Ar- in ArCH ₂ COOCH ₃	<i>k</i> ₂ × 10 ^b
9-Anthryl	0.144	Phenyl	1.36
9-Phenanthryl	.405	2-Naphthyl	1.43
6-Chrysyl	.413	4-Biphenyl	1.56
1-Naphthyl	.463	2-Anthryl	1.66
1-Pyrenyl	.774	3-Phenanthryl	1.68 ^a
<i>p</i> -Tolyl	1.10	2-Phenanthryl	1.69

^a Extrapolated from runs in 85% aqueous methanol. ^b *k*₂ in l. mole⁻¹ sec.⁻¹.

steric hindrance is more severe than in the previously investigated carbonium ion reactions. In Fig. 1 is shown a logarithmic plot of the rate constants, obtained in aqueous acetone, against Streitwieser's σ -values.⁵ These were derived from the rates of solvolysis of arylmethyl chlorides in 80% aqueous ethanol. If steric hindrance were comparable in magnitude in both systems, a single line should have been obtained, while in reality the hindered compounds define a line of lower reactivity.

Because the only structural feature that the "hindered" compounds have in common is the presence of the *peri* hydrogen, it is not unreasonable to ascribe the low reactivity to steric hindrance. However, the steric hindrance encountered in the ester hydrolysis is of a different kind from that commonly found in carbonium ion reactions. A molecular model indicates that the least hindered conformation of methyl 1-naphthylacetate is one in which the plane defined by the trigonal carbon of the ester and the attached atoms is perpendicular to the aromatic plane. For maximum overlap, the attacking hydroxide ion must approach the carbonyl carbon along a line perpendicular to the plane of the carbonyl carbon, but this pathway is blocked on one side by the *peri* hydrogen. In the ester series, there is therefore steric hindrance to the attack of the hydroxide ion, while in the carbonium ion reactions it is considered to be steric hindrance to planarity, or to solvation, of the ion.

In order to compare the degree of steric hindrance in the arylacetate system with that in the arylcarboxylate system, rates of saponification of methyl benzoate ethyl phenylacetates all *ortho* substituents, including *o*-nitro groups, hinder the reaction: J. G. Watkinson, W. Watson, and B. L. Yates, *J. Chem. Soc.*, 5437 (1963).

and of methyl 1- and 2-naphthoate were determined in 85% methanol (Table III). Methyl 1-naphthoate is hydrolyzed slower than both methyl 2-naphthoate and methyl benzoate. The ratio of rate constants methyl 1-naphthoate/methyl 2-naphthoate is 0.406 in aqueous methanol, similar to the ratios obtained for the methyl and ethyl esters in many other solvents,¹¹ while that

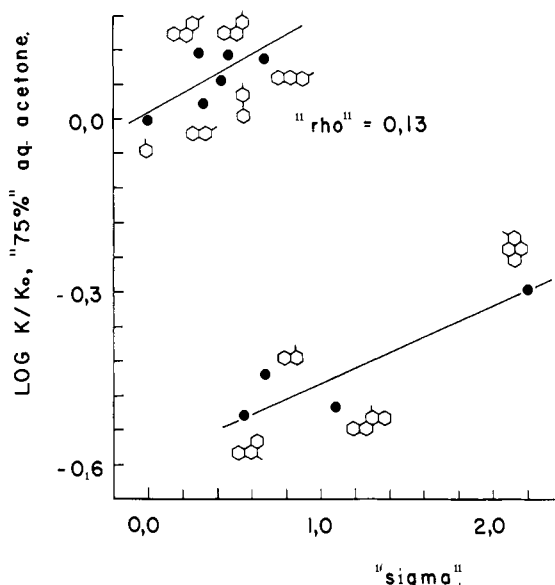


Fig. 1.—Correlation of hydrolysis rates of methyl arylacetates with Streitwieser's σ -values.⁵

for the two methyl naphthylacetates is even lower, 0.327.¹² However, it is impossible from the data to make a quantitative comparison of steric hindrance in the two systems, because in the arylcarboxylate system an uncertain extent of conjugation of the ester with the ring lowers the rate of hydrolysis, while lack of coplanarity of the ester with the ring, because of *peri*-hydrogen interference, may actually raise it. On purely electronic grounds, methyl 1-naphthyl-

(11) S. Oae and C. C. Price, *J. Am. Chem. Soc.*, **79**, 2347 (1957); P. Fitzgerald, J. Packer, J. Vaughan, and A. F. Wilson, *J. Chem. Soc.*, 170 (1956); P. H. Gore, E. C. Vignes, and A. Feinstein, *Chem. Ind. (London)*, 1514 (1958); ref. 9.

(12) A ratio of 0.347 has been reported for the hydrolysis of the ethyl esters in aqueous ethanol by Y. Otsuji, Y. Koda, M. Kubo, M. Furukawa, and E. Imoto, *Nippon Kagaku Zasshi*, **80**, 1300 (1959) [*Chem. Abstr.*, **55**, 6476 (1961)]. According to these authors, ethyl 9-phenanthrylacetate is hydrolyzed almost as fast as ethyl 2-naphthylacetate, and considerably faster than the 1-naphthyl ester.

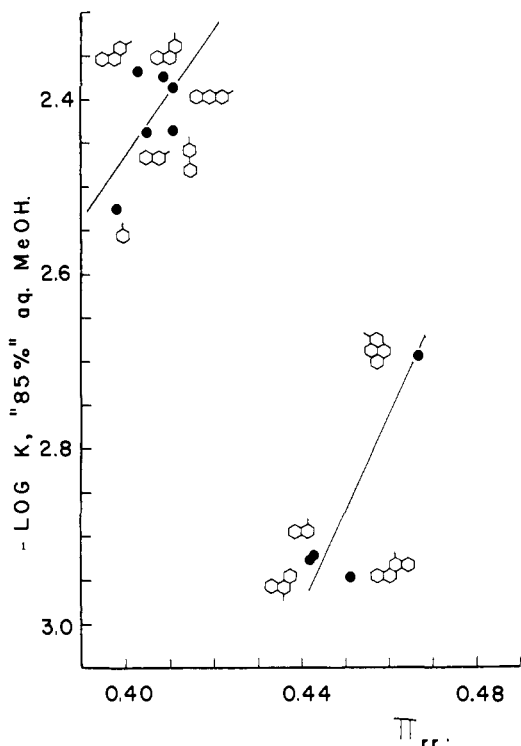


Fig. 2.—Correlation of hydrolysis rates of methyl arylacetates with self-polarizabilities.

acetate would be expected to be hydrolyzed faster than the 2- isomer, because 1-naphthylacetic acid is a slightly stronger acid than the 2- acid,^{13,14} and the above low ratio is therefore best identified with steric hindrance. Steric hindrance in the arylacetate system is sufficiently severe that *all* hindered esters are hydrolyzed slower than methyl phenylacetate (Table I), and the reaction of the doubly hindered methyl 9-anthrylacetate falls in a class by itself. Differences in rate among the hindered compounds, which might have been anticipated on electronic grounds, and which are observed in carbonium ion reactions,^{4,5} have been completely leveled out, and the 1-naphthyl, 9-phenanthryl, and 6-chrysil derivatives, representing, respectively, compounds with two, three, and four aromatic rings, react at about equal rates. Only the 1-pyrenyl compound reacts faster, but still slower than the phenyl derivative.

TABLE III
RATES OF HYDROLYSIS OF METHYL ARYLCARBOXYLATES IN
85% AQUEOUS METHANOL

Ar-in ArCOOCH ₃	Temperature, °C.			
	2.49 $k_2 \times 10^4$ ^b	32.5 $k_2 \times 10^4$	50.0 $k_2 \times 10^3$	60.2 $k_2 \times 10^3$
Phenyl ^a	2.49	5.39	2.83	7.02
1-Naphthyl	1.39 ^c	2.99	1.52	3.64
2-Naphthyl	3.42			

^a E is 18.7 kcal./mole and $\log A$ 10.09. ^b k_2 in 1. mole⁻¹ sec.⁻¹.
^c Extrapolated from runs at higher temperatures.

Methyl *p*-tolyl- and methyl 2-fluorenylacetates both react slower than methyl phenylacetate, as would be expected from the electron-releasing effect of a methyl or methylene group. The order 2-fluorenyl > *p*-methyl follows from the smaller electron-releasing

(13) J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *J. Chem. Soc.*, 4102 (1954); A. Bryson, *J. Am. Chem. Soc.*, **82**, 4862 (1960).

(14) The reverse order has been reported in ref. 12.

TABLE IV
RATES OF HYDROLYSIS IN 85% AQUEOUS METHANOL AT 25°
AND REACTIVITY PARAMETERS

Ar-in ArCH ₂ COOCH ₃	$k_2 \times 10^3$, 1. mole ⁻¹ sec. ⁻¹	π_{rr} ^a	ΔM ^{-b}	E_{π} ^{-c}	$\Sigma 1/r_j$ ^d
Unhindered esters					
<i>p</i> -Tolyl	2.45		0.654 ^e	8.203 ^{f,g}	
Phenyl	2.97	0.398	.721	8.721	3.655
2-Naphthyl	3.64	.405	.744	14.627	4.932
4-Biphenyl ^g	3.66	.411	.756 ^h	17.139	5.179
2-Anthryl ⁱ	4.05 ⁱ	.411	.769	20.083	5.761
3-Phenanthryl	4.21	.409	.754	20.203	5.963
2-Phenanthryl	4.28	.403	.736	20.185	5.846
Hindered esters					
9-Anthryl	0.568	0.526	0.947 ^c	20.261	6.988
6-Chrysil ⁱ	1.17 ⁱ	.451	.838	26.028	7.630
9-Phenanthryl	1.18	.442	.813	20.262	6.599
1-Naphthyl	1.19	.443	.812	14.495	5.321
1-Pyrenyl	2.01	.466	.868	23.374	6.918

^a From ref. 5. ^b From ref. 5, except where noted. ^c Most values are from G. Geuskens, G. Klopman, J. Nasielski, and R. H. Martin, *Helv. Chim. Acta*, **43**, 1934 (1960); additional ones were calculated from the total π -energy of the hydrocarbon plus ΔM . ^d From ref. 20 and present calculations. ^e Present calculations; see Appendix. ^f Not included in the correlation. ^g The relative reactivity order 4-biphenyl > 2-naphthyl > 1-naphthyl has recently also been noted in the alkaline hydrolysis of the ethyl esters in aqueous acetone; R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.*, 5431 (1963). ^h J. J. Elliott and S. F. Mason, *ibid.*, 2352 (1959). ⁱ Extrapolated from 75% aqueous acetone.

effect of the methylene than the methyl group, and from the electron-attracting effect of the phenyl group in the biphenyl system of fluorene.

For a comparison of the relative reactivities with the available Hückel molecular orbital reactivity parameters, it is first necessary to decide which of the several reactivity indices are appropriate to the hydrolysis of methyl arylacetates. Most of the parameters depend in one way or another on conjugation or localization effects, which are not important for the system under consideration. The self-atom polarizabilities, π_{rr} , would seem to be the most suitable for the hydrolysis of the present esters, because they reflect the perturbation of the aromatic system with the approach of the charged reagent, and are not based explicitly on conjugation phenomena.⁵ In Table IV are listed the saponification rates of the esters at 25°, now classed into the benzene-like compounds listed first, followed by the 1-naphthalene-like compounds, along with numerical values of the self-polarizabilities and other reactivity indices. The rates tend to increase with an increase in π_{rr} , but the quantitative relationship, shown in Fig. 2, is far from satisfactory. In fact, it requires the chemical foreknowledge about the "hindered" line to draw two separate lines as shown, although any other correlation would be without chemical or theoretical significance. The benzene-like line shows considerably more scatter than is customary, and the least-square correlation line has a probable error of 39%.

The correlation shown in Fig. 2 is typical of the correlations obtained with a variety of theoretical reactivity parameters.¹⁵ For instance, correlation lines

(15) All the reported correlations refer to data obtained in aqueous methanol, but the results are very similar when the data obtained in aqueous acetone are used.

with L^- , the localization energies, ΔM values, which represent the π -energy difference between the aromatic hydrocarbon ArH and the anion ArCH_2^- , and which correlate carbonium ion reactions well, or Dewar's similar values $2a_{\text{or}}$,¹⁶ have probable errors of 44, 43.7, and 42%, respectively. With this relatively large scatter, one can speak of no more than a qualitative trend of the rate constants in the direction of the theoretical indices. It is of interest that a value for ΔM^- for the *p*-methylbenzyl anion, calculated from the inductive model with the recommended value of $h_{\text{C}} = -0.5$,¹⁷ fits exactly on the correlation line, which then has a probable error of only 16%. From the slopes of the correlation lines with ΔM and with $2a_{\text{or}}$, values of -2.9 and -1.1 kcal. mole⁻¹, respectively, are calculated for β_{eff} .¹⁸ These are very small values, as is the value for ρ (Fig. 1), which mostly reflect the dampening effect of the intervening methylene group.

It would be theoretically more satisfactory to compare the molecular orbital energy terms with experimental activation energies. A trend in the expected direction exists, but variation in activation energies are small and somewhat irregular, and logarithms of rate constants, and hence free energies of activation, are used for all correlations, a procedure for which a theoretical justification has been given.¹⁹

Although there thus exist qualitative correlations between saponification rates and the various MO parameters, the theoretical validity of most of the correlations, with the exception of that with self-polarizabilities, is open to question. They reflect more the mathematical interrelation of the various MO parameters than any chemical relation between the transition states which the parameters imply, and the actual transition state of ester hydrolysis. What is needed for the present case is a parameter that will express the electronegativity or the inductive effect of an aryl group. Such an effect, for which at present no numerical MO parameters are available, would presumably depend on the size of the aromatic system. We found that a logarithmic plot of the rate constants of the unhindered compounds against the number of aromatic rings in each compound gives an excellent correlation with a probable error in the slope of only 4.6%. For what must be similar reasons, a correlation with E_{π^-} , the total π -energy of an arylcarbiny anion, ArCH_2^- , also gives a superior correlation with a probable error in the slope of 7.0%. This correlation is probably the indirect result of the relationship between E_{π^-} and the size of the aromatic system. Streitwieser and Lawler recently studied rates of exchange of aryl hydrogens of deuterated or tritiated arenes.²⁰ Their data did not correlate well with self-polarizabilities, but they could be accounted for by a simple electrostatic model which involved the summations $\sum 1/r_{ij}$ as an index of reactivity. In this expression, the terms r_{ij} are the distances from the reacting carbon to every other carbon atom in the aromatic system, and the total parameter clearly de-

(16) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); ref. 5, p. 373.

(17) Reference 5, p. 135.

(18) For the meaning of β_{eff} see ref. 16 and M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2946 (1957).

(19) Reference 5, p. 311.

(20) A. Streitwieser, Jr., and R. G. Lawler, *J. Am. Chem. Soc.*, **85**, 2854 (1963).

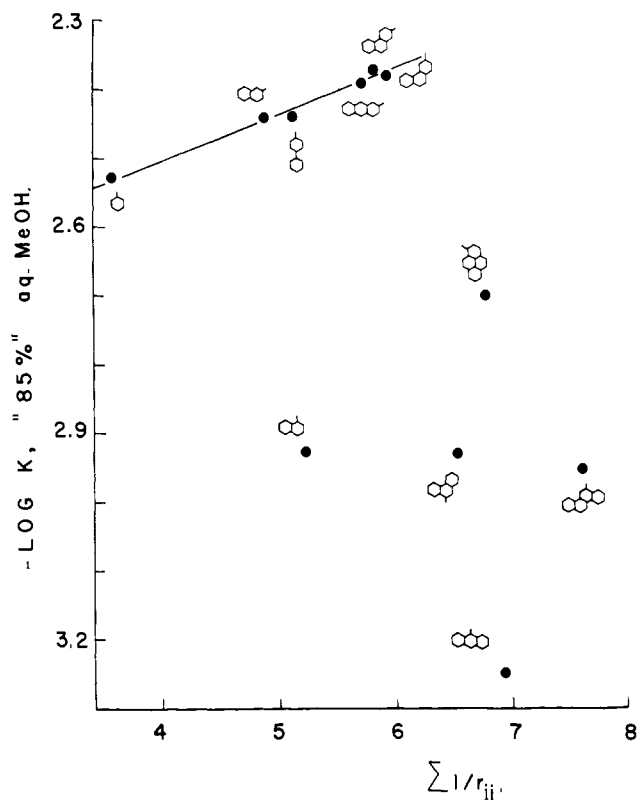


Fig. 3.—Correlation of hydrolysis rates of methyl arylacetates with the parameter $\sum 1/r_{ij}$.

pends on the size and shape of the hydrocarbon residue. The justification presumably is that each carbon atom in the aromatic ring, treated as a substituent, lies in the nodal plane of the aromatic π -electrons, and is therefore electron attracting. The treatment is reminiscent of Dewar and Grisdale's recent treatment of the field effect, which also utilizes the inverse distance to the substituents.²¹

In Fig. 3 the summations $\sum 1/r_{ij}$ are plotted against $\log k$. The unhindered esters correlate with a probable error of only 4.7%. All hindered esters fall below the line, although in the exchange reaction of arenes only a single correlation line is obtained.²⁰ The smaller probable error in the three last-mentioned correlations is perhaps not very significant, but it would seem that Streitwieser's new parameter expresses the electronegativity of an aryl group very well, and that it is a meaningful index of reactivity.

Since the field effect is appreciable in the methyl arylacetate system, it should be even more so in systems where the reaction site is directly attached to the aromatic nucleus. Interpretations of relative reactivities of polynuclear aromatic systems should include a consideration of this effect, in addition to conjugation or steric effects, even if the latter usually outweighs the former.

Experimental

Preparation of Methyl Arylacetates.—All esters were prepared by esterification of the acid with methanol and sulfuric acid, except methyl 6-chrysylacetate, which was prepared with diazomethane. The acids were mostly obtained through a Willgerodt reaction, using morpholine, of the methyl ketones, which in turn were made by Friedel-Crafts acylation of the hydrocarbons. These had been purified by recommended procedures. In a few cases, the acids were prepared from the nitriles. In

(21) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3548 (1962).

TABLE V
 PHYSICAL PROPERTIES OF ESTERS^a

Ar- in ArCH ₂ COOCH ₃	M.p. or b.p. (mm.), °C.	<i>n</i> ^{25-D} _D	Formula	Carbon, % ²⁶		Hydrogen, % ²⁶	
				Calcd.	Found	Calcd.	Found
Phenyl ^b	83-85 (6)	1.5051 (<i>n</i> ¹⁶ 1.5091) ^c					
1-Naphthyl ^b	160-170 (15-20)	1.5939 (<i>n</i> ¹⁹ 1.5989) ^d					
2-Naphthyl	158-168 (15-20)						
<i>p</i> -Tolyl ^b	73-74 (0.2)	1.5028					
4-Biphenyl ^l	131-132 (0.15) (140-143 (0.5)) ^e 27.5-28.4 ^f	1.5880 (<i>n</i> ²⁶ 1.5890) ^e					
2-Fluorenyl	81.0-82.1 (83-84) ^g						
2-Phenanthryl	79.5-80.5 (78.5-79.0) ^h						
3-Phenanthryl	43.6-44.6 ⁱ		C ₁₇ H ₁₄ O ₂	81.58	81.75	5.64	5.45
9-Phenanthryl	76.2-76.8 (75.0-75.5) ^j						
2-Anthryl	144.7-146.2 ^k		C ₁₇ H ₁₄ O ₂	81.58	82.08	5.64	5.47
9-Anthryl	87.2-88.0 ^k		C ₁₇ H ₁₄ O ₂	81.58	81.78	5.64	5.38
1-Pyrenyl	93.3-94.9 (90-91.5) ^l						
6-Chrysyl	184.4-186.1 ^k		C ₂₁ H ₁₆ O ₂	83.97	83.98	5.37	5.49
Ar- in ArCOOCH ₃							
Phenyl	40-41 (1)	1.5153 (<i>n</i> ¹⁶ 1.5205) ^c					
2-Naphthyl ^l	76.5-77.3 (77.8) ^m						
1-Naphthyl ^l	98-99.5 (1)	1.6093 (<i>n</i> ²⁰ 1.6068) ⁿ					

^a Values in parentheses are literature values. All melting points are corrected. ^b Prepared from a commercial sample of the acid. ^c From I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953. ^d J. L. Siemons and M. Vigeau, *Bull. soc. chim. France*, 90 (1951). ^e L. F. Fieser, M. T. Leffler, and co-workers, *J. Am. Chem. Soc.*, **70**, 3186 (1948). ^f After standing for about 2 months, the ester solidified and had the above m.p. ^g Y. Ogata, M. Inoue, and Y. Kitamura, *J. Org. Chem.*, **18**, 1329 (1953). ^h A. L. Wilds, *J. Am. Chem. Soc.*, **64**, 1421 (1942). ⁱ From petroleum ether; various authors have reported this ester as a liquid or viscous oil; R. G. Jones, Q. F. Soper, O. K. Behrens, and J. W. Corse, *ibid.*, **70**, 2843 (1948); A. L. Wilds and W. J. Close, *ibid.*, **68**, 83 (1946); E. Mosettig and J. van de Kamp, *ibid.*, **55**, 2995 (1933). ^j E. Mosettig and J. van de Kamp, footnote *i*. ^k From methanol. ^l R. J. Shozda, E. A. Depp, C. M. Stevens, and M. B. Neuwirth, *J. Am. Chem. Soc.*, **78**, 1716 (1956). ^m K. Lauer, *Ber.*, **70**, 1288 (1937). ⁿ C. C. Price and C. F. Huber, *J. Am. Chem. Soc.*, **64**, 2136 (1942).

our hands, the Arndt-Eistert reaction was less successful for the preparation of the polynuclear acids when silver oxide was used in the Wolff rearrangement, but the benzyl alcohol procedure was more reliable.²² The physical properties of all esters, as well as analytical data for the new esters, are listed in Table V. The preparation of the other new compounds is described below. All melting points are corrected.

Methyl 9-Anthrylacacetate.—9-Anthraldehyde was reduced to 9-hydroxymethylanthracene with sodium borohydride in ethanol, and the latter was converted to 9-chloromethylanthracene with thionyl chloride in dioxane.²³ A solution of 14.5 g. of the above in 300 ml. of dioxane was warmed for 15 min. on the steam bath with a solution of 6 g. of potassium cyanide in 150 ml. of water. The product was precipitated with water and crystallized from 90-100° ligroin; a 45.9% yield of product melting at 156.8-160.3° was obtained. A sample was sublimed at 140-150° (0.2 mm.) and again recrystallized. The pure 9-anthrylacetonitrile melts at 163.0-163.8° (lit.²⁴ 163.5-164.5°).

*Anal.*²⁵ Calcd. for C₁₆H₁₁N: C, 88.45; N, 5.10. Found: C, 88.30; H, 5.14.

Three grams of the above nitrile was refluxed for 22 hr. with 200 ml. of 15% alcoholic KOH solution. The solution was poured into 500 ml. of water, filtered, and the filtrate was acidified. Reprecipitation of the yellow product from sodium carbonate solution afforded 3 g. of crude acid. After two recrystallizations from glacial acetic acid, 9-anthrylacetic acid had m.p. 229-231.4° dec. (lit.²⁴ 226-228°), which varied with the rate of heating.

Anal. Calcd. for C₁₆H₁₂O₂: C, 81.33; H, 5.12. Found: C, 81.23; H, 5.30.

Stewart²⁴ reported the syntheses of the above two compounds after our syntheses had been completed.

9-Anthrylacetic acid (4.6 g.) was esterified by refluxing with 100 ml. of methanol and 5 ml. of concentrated H₂SO₄. After one recrystallization from methanol, the ester was obtained in 61.5% yield, m.p. 87.0-88.0°. The analytical sample (Table V) was sublimed and again recrystallized from methanol.

2-Anthrylacetic Acid.—2-Acetylthianthracene (4 g.), 1.45 g. of sulfur, and 10 ml. of morpholine were refluxed for 12 hr. The

cooled mixture was diluted with 20 ml. of methanol, and 5.5 g. of crude thiomorpholide was collected. A sample crystallized from benzene as tan crystals, m.p. 200-205° dec. The crude thiomorpholide (2.8 g.) was hydrolyzed by refluxing for 24 hr. with 30 ml. of Butyl Cellosolve containing 3 g. of KOH in a little water. Dilution of the solution with water caused the precipitation of the sparingly soluble potassium salt of 2-anthrylacetic acid. Acidification, followed by recrystallization from benzene, afforded a 65.5% yield of acid, m.p. 239-242.5° dec. Sublimation at 185-195° (0.2 mm.), followed by two more recrystallizations from benzene, afforded 2-anthrylacetic acid as slightly green fluorescent plates, m.p. 238.2-240.8° dec.

Anal. Calcd. for C₁₆H₁₂O₂: C, 81.33; H, 5.12. Found: C, 81.09; H, 5.18.

Methyl 2-anthrylacacetate was prepared as described for the 9-isomer.

1-Anthrylacetic Acid.—Benzanthrone was oxidized to 1-anthraquinonecarboxylic acid, which was reduced to 1-anthroic acid with zinc and ammonia in 94% yield of crude product.²⁶ Methyl 1-anthroate (12 g.) was reduced with lithium aluminum hydride in 500 ml. of refluxing ether; a 94.7% yield of once-crystallized (benzene) 1-hydroxymethylanthracene was obtained. A sample was sublimed and recrystallized from methanol and afforded the product as white, silky needles, m.p. 126.8-127.4°.

Anal. Calcd. for C₁₅H₁₂O: C, 86.51; H, 5.81. Found: C, 86.25; H, 5.97.

The above carbinol (9.9 g.) was refluxed for 5 hr. in 400 ml. of benzene and 5 ml. of thionyl chloride. An 87.9% yield of crude 1-chloromethylanthracene was obtained. A sample, recrystallized from ligroin-benzene, formed yellow brown crystals, m.p. 93.3-96.2° dec.

Anal. Calcd. for C₁₅H₁₁Cl: C, 79.46; H, 4.90. Found: C, 79.28; H, 5.03.

Eighteen grams of 1-chloromethylanthracene was refluxed for 20 hr. in 1 l. of acetone with 15.0 g. of KCN dissolved in 30 ml. of water. The KCl was removed by filtration, the acetone removed *in vacuo*, and the residual oil was distilled, with much decomposition, at 225° (4 mm.). Recrystallization of the distillate from methanol afforded a 35.6% yield of yellow crystals, m.p. 96-98°. A sample was further purified by sublimation and two crystallizations from 90-100° ligroin-benzene. 1-

(22) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

(23) W. T. Hunter, J. S. Buck, F. W. Gubitz, and C. H. Bolen, *ibid.*, **21**, 1512 (1956).

(24) F. H. C. Stewart, *Australian J. Chem.*, **13**, 478 (1960).

(25) All analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

(26) E. de B. Barnett, J. W. Cook, and H. H. Grainger, *Ber.*, **57**, 1775 (1924); C. Graebe and S. Blumenfeld, *ibid.*, **30**, 1115 (1897).

Anthrylacetonitrile forms white plates, m.p. 111.0–111.8°.

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.45; H, 5.10. Found: C, 88.60; H, 4.93.

Seven grams of the above nitrile was hydrolyzed by refluxing for 20 hr. with 15% alcoholic KOH solution. The potassium salt of the acid, which slowly precipitated, was collected and acidified (46%). Sublimation and two recrystallizations from 90–100° ligroin–benzene afforded 1-anthrylacetic acid as bright yellow crystals, m.p. 169.1–171.2° (lit.²⁷ 170–171.2°).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.14; H, 5.18.

1-Anthrylacetic acid was also prepared by the Arndt-Eistert reaction with the collidine–benzyl alcohol procedure in the final step.²² The yield was 19% from anthroic acid.

Attempted Synthesis of Methyl 1-Anthrylacetate.—Conventional esterification of the acid with methanol and concentrated H_2SO_4 afforded a mixture of red and yellow crystals. The red crystals were high melting and were probably unchanged acid. The yellow crystals were sublimed, and the sublimate melted at 72.5–74.3° and was probably the ester, but only trace amounts were obtained, and extension of the reaction time did not seem to improve the yield or purity of the product. Treatment of the acid with diazomethane in methanol resulted in recovery of the acid. 1-Anthrylacetic acid has been obtained from the methyl ester, prepared by a different route, but no physical data for the ester are reported.²⁷

6-Chrysylic Acid.—6-Chrysylicacetonitrile was prepared from 6-chloromethylchrysene²⁸ by the method described for the preparation of 2-anthrylacetonitrile. The yield of once crystallized (benzene) product was 64%. A sample was sublimed and recrystallized from ligroin–benzene and afforded white needles of 6-chrysylicacetonitrile, m.p. 215.7–216.7°.

Anal. Calcd. for $C_{20}H_{13}N$: C, 89.86; H, 4.90. Found: C, 89.94; H, 5.00.

The above nitrile (120 mg.) was hydrolyzed with alcoholic KOH as described above. A 62.2% yield of acid, m.p. 265–269° dec., was obtained. Two recrystallizations from glacial acetic acid afforded white crystals of 6-chrysylic acid, m.p. 268.6–271.6° dec.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.70; H, 4.88.

The low solubility of all chrysene derivatives made it difficult to carry out the syntheses on a more than 1-g. scale. Attempts to do so resulted in lower yields and less pure products.

Kinetic Determinations.—Purified methanol²⁹ (8.5 l. of $n_{24.9}^{24.9D}$ 1.3270) which had been thermostated at 24.9° was mixed with 1.5 l. of freshly boiled distilled water. This constitutes the 85% by volume methanol. It had $n_{24.9}^{24.9D}$ 1.3354 and sp.gr.^{24.9} 0.83857. From plots of literature data of the density and refractive index of aqueous methanol solutions,³⁰ the 85% methanol is extrapolated as 82 and 81 w./w. % methanol, respectively. The physical constants, as well as the kinetic data, were reproduced in a second preparation of the same solvent mixture. Purified acetone³¹ had b.p. 56.2° (766.2 mm.) and $n_{24.9}^{24.9D}$ 1.3566. The mixed solvent was prepared by mixing 3 l. of thermostated acetone with 1 l. of distilled water at 24.9°.

All runs conducted at 24.9 and 32.5° were run in a 100-ml. volumetric flask; above that temperature sealed tubes were used. The following is typical of the first method. A hydrolyzing solution was prepared daily by mixing 85 ml. of absolute methanol with 15 ml. of 0.28 *N* aqueous sodium hydroxide at 24.9°. This solution was standardized, and an amount of ester, exactly equivalent to the amount of base in the hydrolyzing solution in the final mixture, was transferred to a 100-ml. volumetric flask and dissolved in 85% methanol. At bath temperature, 50 ml. of the hydrolyzing solution was added, and the solution was quickly made up to the mark, shaken, and replaced in the bath. The time of delivery of half of the hydrolyzing solution was taken as zero time. Ten-ml. samples were periodically withdrawn, quenched with 5 ml. of 0.0471 *N* HCl, and back-titrated with 0.0551 *N* NaOH. The initial and final titers were calculated from the normalities of the solutions. When sealed

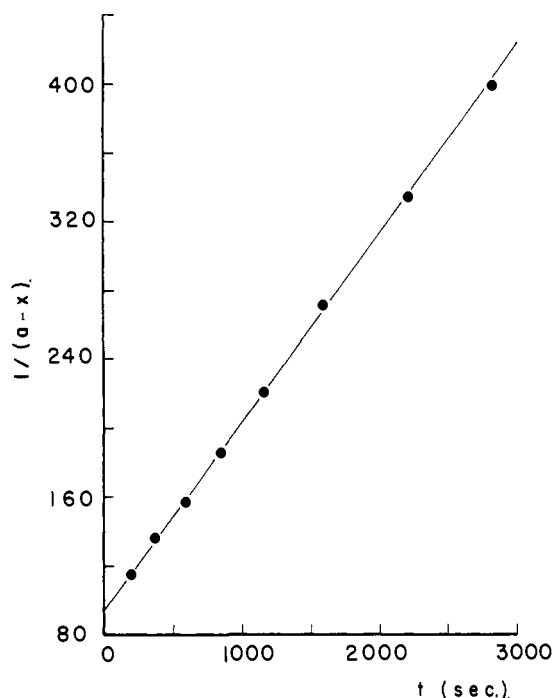


Fig. 4.—A first-order plot for the hydrolysis of methyl *p*-tolylacetate in 75% aqueous acetone at 25°: [ester] = [OH⁻] = 0.0108 *M*. $k_2 = (1.09 \pm 0.006) \times 10^{-1}$ l. mole⁻¹ sec.⁻¹.

tubes were used, the hydrolyzing solution was standardized at ice-bath temperature, and solutions were made up at 0°. Eight samples of about 11 ml. were transferred into drawn-out test tubes, which were sealed and replaced in the thermostat at zero time. One 10-ml. sample, still at ice-bath temperature, was analyzed for the experimental initial titer. Tubes were put in an ice bath at the end time and allowed to stand for 8 min. before a sample was withdrawn for titration. An expansion factor was determined in a Cassia flask by measuring the solvent expansion between ice-bath temperature and the reaction temperature. Two esters were hydrolyzed by both methods, and the results agreed within 3%. The concentration of esters was usually between 0.01 and 0.02 *M*, depending on their solubility; in a few cases it was 0.005 *M*. The indicator was cresol red, and separate experiments showed that no indicator blank was necessary. Thermometers were calibrated against an NBS thermometer.

Rate constants were obtained graphically from the integrated form of the second-order rate equation for equal concentrations. Calculated rate constants showed a slight downward drift, probably because of some uncertainty in the calculated initial titer, but the graphical method afforded straight lines throughout the kinetic runs, and usually to 60–80% reaction. The plot for a typical run is shown in Fig. 4. The slopes were calculated by the method of least squares, and all errors listed are probable errors obtained from the least-square calculations. Within a single run, the probable errors were rarely larger than 2%, and the average probable error in all runs was 0.6%. Duplicate runs usually agreed within 2%, and runs which deviated from the average rate constant by more than four times the average deviation were discarded.

Appendix

The molecular orbital parameters for the *p*-methylbenzyl system were calculated by standard methods,³ using the inductive parameter $h_C = -0.5$ for carbon atom no. 1, and C_2 symmetry. The total π -energy for toluene is then $E_\pi = 6\alpha + 7.549\beta$. The total π -energy for the *p*-tolylcarbiny cation is $6\alpha + 8.3440\beta$, for *p*-tolylcarbiny radical $7\alpha + 8.2736\beta$, and for *p*-tolylcarbiny anion $8\alpha + 8.2032\beta$. From these figures the following ΔM values result: cation, $\Delta M^+ 0.795$; radical, $\Delta M^\cdot 0.725$; anion, $\Delta M^- 0.654$. Varying the value of α for C-1 eliminates the nonbonding molec-

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(30) V. S. Griffiths, *J. Chem. Soc.*, 860 (1954); J. Griswold and C. B. Buford, *Ind. Eng. Chem.*, **41**, 2347 (1949).

(31) J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924).

ular orbital which is otherwise found in odd alternant hydrocarbons. This results in different π -energies for the cation, radical, and anion, and hence in different ΔM values. In the approximation used here, ΔM for the *p*-methylbenzyl cation is greater, and ΔM for the *p*-methylbenzyl anion is smaller than ΔM for the benzyl system (0.721). These results are in qualitative agreement with the fact that *p*-methyl groups favor carbonium ion reactions but hinder reactions involving

transition states which have carbanion character, such as ester hydrolysis.

The distances r_{ij} (Table IV) were calculated on the assumption that all carbon-carbon distances are equal to that in benzene,²⁰ including the pivot bond in biphenyl.

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[CONTRIBUTION FROM THE IBM WATSON RESEARCH CENTER, YORKTOWN HEIGHTS, N. Y.]

Photochemical Transformations of 1,5-Cyclooctadiene

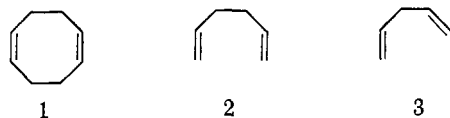
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RECEIVED MARCH 2, 1964

Photolyses are reported of 1,5-cyclooctadiene: (i) by sensitization with mercury (³P₁) atoms in the vapor phase, (ii) by direct irradiation in solution in the presence of cuprous chloride, and (iii) by irradiation in solution in a complexed state with rhodium chloride. The products from i are a polymer, bicyclo[5.1.0]octene-3 and tricyclo[3.3.0.0^{2,6}]octane. The polymer is believed to arise from a primary process which gives rise to free radicals. The other two products which are isomeric to 1,5-cyclooctadiene seem to be formed by intramolecular processes, analogs of which may be found in the photochemistry of 1,5-hexadiene. Process ii gives tricyclo-octane in 30% yield while process iii gives 1,3-cyclooctadiene, bicyclo[4.2.0]octene-7, and 1,4-cyclooctadiene. It has been deduced that in ii the cuprous chloride acts merely as a catalyst for the isomerization reaction.

Introduction

Of all the aliphatic and alicyclic olefins which have hitherto been used as donor molecules in the formation of π -complexes with transition metal salts, 1,5-cyclooctadiene (1) is one of the best from the point of

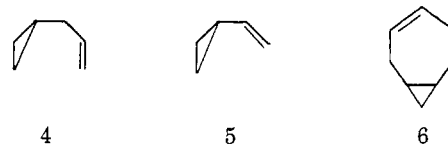


view of the stability of the complexes.¹ It was of interest to examine the photochemical behavior of these compounds, as the possibility of causing the photoisomerization of molecules in "frozen" conformations was visualized. The results of some of these studies are reported here. Photolysis of 1,5-cyclooctadiene by sensitization with mercury (³P₁) atoms was also carried out to help compare the results that were obtained with the π -complexes with those obtained by a more conventional procedure.

Results

Mercury-Photosensitized Reaction.²—Mercury-sensitized photolysis of 1,5-cyclooctadiene in the vapor phase at 2537 Å.² gave rise to a polymeric liquid as the major product along with two compounds which together accounted for about 2 to 3% of the yield. Both compounds gave analytical figures and a molecular weight corresponding to the molecular formula C₈H₁₂. The first of these products had absorptions at 3.3 and 9.85 μ in its infrared spectrum, which suggested the presence of protons and carbons located in a cyclopropane ring.³ The nuclear magnetic resonance spectrum of the compound showed a complex absorption

centered at 9.7 τ which confirmed the existence of cyclopropane protons in the molecule.⁴ It is known that both 1,5-hexadiene (2)⁵ and 1,4-pentadiene (3)⁶ undergo two types of isomerizations on sensitization by mercury (³P₁) atoms. One of these leads to cyclopropane derivatives, the products in the two cases being allylcyclopropane (4) and vinylcyclopropane (5), respectively. Cvetanovic and Doyle⁷ have observed



the isomerization of 1-butene to methylcyclopropane under similar conditions, but did not detect a corresponding isomerization in 2-butene. Although the double bonds in 1,5-cyclooctadiene are both symmetrically disubstituted, it is possible that the molecule undergoes an isomerization reaction that is analogous to those observed in linear terminal olefins. Thus, the structure of the first isomer that is formed is probably bicyclo[5.1.0]octene-3(6). This structure was compatible with the n.m.r. spectrum which showed four sets of absorptions of relative areas 2:4:2:4 which were centered at 4.35, 7.80, 8.25, and 9.70 τ , respectively. The first of these would correspond to the two olefinic protons, the second to the four allylic protons, the third to the two protons on the third methylene group, and the fourth to the four protons on the cyclopropane ring.

At about the time this work was completed, an independent synthesis of 6 by an alternative route was reported by Cope, Moon, and Park.⁸ A comparison of

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(4) J. B. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 236.

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