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The Solvolysis of Arylphenylmethyl Chlorides in 90% Acetone<sup>1</sup>BY LAWRENCE VERBIT<sup>2</sup> AND ERNST BERLINER<sup>3</sup>

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Rates of reaction and activation parameters were determined for the solvolysis of arylphenylmethyl chlorides,  $\text{Ar}(\text{C}_6\text{H}_5)\text{CHCl}$ , in 90% aqueous acetone. The rate constants correlate reasonably well with Hückel molecular orbital reactivity parameters, but compounds with a 1-naphthalene-like structure fall on a separate line of lower reactivity. Several new MO parameters, appropriate to the  $\text{ArC}^+\text{HC}_6\text{H}_5$  system, have been calculated.

In a previous communication it was shown that the  $\text{S}_{\text{N}}1$  solvolysis of  $\alpha$ -arylethyl chlorides,  $\text{ArCHClCH}_3$ , in 80% aqueous acetone correlates reasonably well with various molecular orbital reactivity parameters.<sup>4</sup> The same is also true for the solvolysis of the primary halides  $\text{ArCH}_2\text{Cl}$  in a variety of different solvents,<sup>5-7</sup> of the tertiary halides  $\text{ArCCl}(\text{CH}_3)_2$  in ethanol,<sup>5</sup> and of the tosylates  $\text{ArCH}_2\text{OTs}$  in acetic acid.<sup>8</sup> We now report the results of the solvolysis of arylphenylmethyl chlorides,  $\text{ArCHClC}_6\text{H}_5$ , in 90% aqueous acetone, where  $\text{Ar}$  comprises different polynuclear aromatic hydrocarbon residues. The purpose of the study was to obtain more quantitative data on the reactivity of polynuclear aromatic systems with which the reactivity indices of the simple molecular orbital theory (HMO) could be compared.

The carbonium ions  $\text{Ar}\dot{\text{C}}\text{HC}_6\text{H}_5$ , which for purposes of comparison with MO parameters serve as models of the transition state of the  $\text{S}_{\text{N}}1$  solvolysis, comprise larger  $\pi$ -electronic systems than the ions  $\text{Ar}\dot{\text{C}}\text{R}_1\text{R}_2$  ( $\text{R}_1, \text{R}_2 = \text{H}$  or  $\text{CH}_3$ ) involved in previous studies. They not only include the variable  $\text{Ar}$ - group, but also the phenyl group which stays constant throughout the series. They are therefore stabler ions, and presumably less sensitive to changes in hydrocarbon structure than the arylmethyl ions, and it was of added interest to see how MO parameters which take account of the constant phenyl group will compare with experimental reactivities.

## Results and Discussion

Rate constants for the solvolysis of 12 different arylphenylmethyl chlorides in 90% by volume aqueous acetone were determined at three temperatures. Because of its great reactivity and low solubility, the rate of solvolysis of 9-anthrylphenylmethyl chloride was only obtained at one temperature. Kinetic complications were encountered only with this compound. As in the case of  $\alpha$ -(9-anthryl)ethylchloride,<sup>4</sup> first-order plots had marked curvatures, and the rate constants decreased with time. For this compound, integrated first-order rate

constants were calculated for each point and plotted against percentage reaction. A least-square parabola gave the best fit to the data, and extrapolation to 0% reaction afforded the initial rate constant. This decrease in rate for the most reactive compound is very likely due to a mass-law effect, because when reaction was conducted in the presence of a large initial excess of lithium chloride first-order plots remained linear throughout a kinetic run.<sup>9</sup>

All rate constants, as well as the activation parameters, are listed in Table I. In Table II are recorded rate constants at 25° and relative rates, in the order of increasing reactivity. For the pyrene derivative, the constant for 25° was extrapolated from runs at lower temperatures, and the rate constant for the solvolysis of the 9-anthryl compound was estimated from the rate constant at 0° on the assumption that the entropies of activation are the same for all compounds in the series (see Experimental). Because of that, and the extrapolations mentioned earlier, this value is only approximate. In Table II are also listed some of the appropriate MO parameters.

In relating the experimental rate constants to the MO reactivity indices, the usual assumption is made that the carbonium ion is a suitable model for the transition state of the reaction, and the calculations are then based on the carbonium ion structure. All changes in reactivity, caused by changes in the hydrocarbon structure, are considered to be due only to changes in the  $\pi$ -electron energy, and all other factors, such as variations in entropy or solvation, are assumed to be constant for the whole series, or a constant fraction of the  $\pi$ -energy change. Probably the most appropriate reactivity index for carbonium ion reactions of the present type are the values  $\Delta M$ , which represent the  $\pi$ -electron energy difference between the original hydrocarbon  $\text{ArH}$  and the carbonium ion intermediate  $\text{ArCH}_2^+$  which results from solvolysis.<sup>7</sup> They can be considered to represent the gain in stabilizing energy when an exocyclic carbon atom conjugates with the aromatic system. Because in the present system the phenyl group may be considered to contribute a constant amount to the  $\pi$ -energy, these parameters are suitable for the solvolysis of the arylphenylmethyl chlorides, but in Table II are also listed the new values  $\Delta M'$ , which include the phenyl group and represent the  $\pi$ -energy difference between the arylphenylmethyl carbonium ion and the hydrocarbon  $\text{ArH}$  plus benzene (see Appendix). They have the same meaning as  $\Delta M$ , and larger values of  $\Delta M$  and  $\Delta M'$  correspond to greater  $\text{S}_{\text{N}}1$  reactivity than lower values. Theoretical indices comparable to the  $\Delta M$  values are Dewar's numbers  $2a_{\text{or}}$ , where the  $a_{\text{or}}$  values are the co-

(9) This is the treatment of L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 974 (1940).

- (1) Relative Reactivities of Polynuclear Aromatic Systems. II.
- (2) Taken from the Ph.D. Thesis of L. Verbit, Bryn Mawr College, June, 1963. National Science Foundation Cooperative Graduate Fellow, 1961-1962; U. S. Public Health Service Predoctoral Fellow, 1962-1963.
- (3) To whom inquiries should be addressed.
- (4) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).
- (5) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2946, 2952 (1957).
- (6) P. J. C. Fierens, H. Hannaert, J. Van Rysselberge, and R. H. Martin, *Helv. Chim. Acta*, **38**, 2009 (1955); G. Geuskens, G. Klopman, J. Nasielski, and R. H. Martin, *ibid.*, **43**, 1927, 1934 (1960), and earlier references quoted there.
- (7) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 12. This chapter contains a complete bibliography of these reactions.
- (8) Unpublished results by A. Streitwieser, Jr., R. H. Jagow, and R. M. Williams, quoted in ref. 7, p. 370.

TABLE I  
 RATE CONSTANTS FOR THE SOLVOLYSIS OF ARYLPHENYLMETHYL CHLORIDES IN 90% ACETONE

Ar- in ArCHClC <sub>6</sub> H <sub>5</sub>	Temperature, °C.										<i>E<sub>a</sub></i> , kcal./mole	log <i>A</i>	Δ <i>S</i> <sub>25</sub> , e. u.
	0.0	10.0	15.0	25.0	40.0	45.0	50.0	55.1	60.0	65.0			
	<i>k</i> <sub>1</sub> × 10 <sup>5</sup> sec. <sup>-1</sup>												
Phenyl				0.554			7.36			28.3	19.7 ± 0.1	9.19 ± 0.04	-18.5
1-Naphthyl				3.54	17.4			68.5			19.2 ± .2	9.59 ± .16	-16.7
2-Naphthyl				2.61	12.6				75.6		19.0 ± .2	9.33 ± .13	-17.8
4-Biphenyl				3.86	18.0 <sup>a</sup>		46.7				19.2 ± .1	9.62 ± .03	-16.5
2-Triphenyl				2.58		20.5			78.9		19.3 ± .1	9.58 ± .08	-16.7
1-Phenanthryl				2.06		17.3			66.3		19.6 ± .2	9.70 ± .16	-16.1
9-Phenanthryl				2.60		21.6			83.9		19.6 ± .2	9.80 ± .11	-15.7
<i>p</i> -Tolyl	0.621			11.5		81.3					18.7 ± .1	9.77 ± .05	-15.8
2-(9,10-Dihydro)- phenanthryl	1.11			19.3	84.0						18.4 ± .1	9.78 ± .03	-15.8
2-Fluorenyl	5.92		27.7	76.3							16.5 ± .2	8.97 ± .16	-19.5
6-Chrysyl				7.09	35.2		87.6				19.3 ± .3	10.0 ± .2	-14.7
1-Pyrenyl	16.4	40.6	69.9								14.9 ± .6	8.16 ± .45	-23.2
9-Anthryl	44.7												
<sup>a</sup> <i>T</i> , 39.9°.													

<sup>a</sup> *T*, 39.9°.

efficients of the nonbonding molecular orbitals for the exocyclic carbon atom in ArCH<sub>2</sub><sup>+</sup>.<sup>5,7</sup> The values of 2*a*<sub>or</sub> in Table II were calculated by the method of

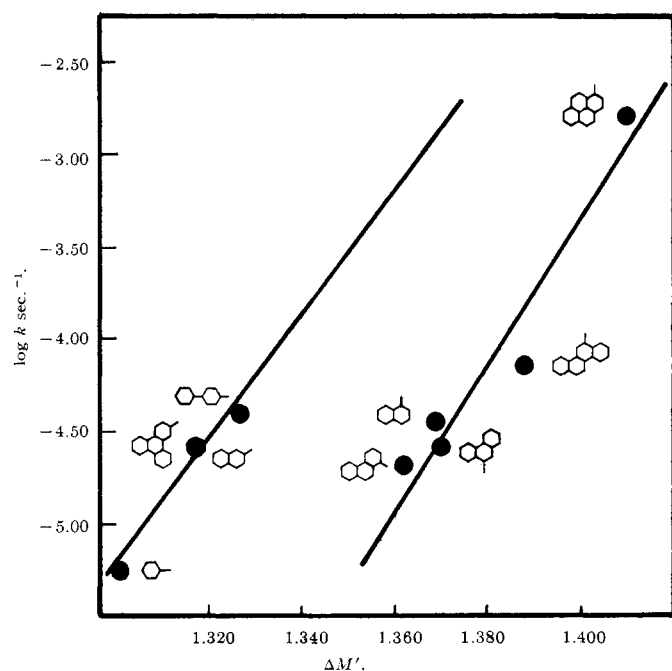


Fig. 1.—Correlation of rates of solvolysis of arylphenylmethyl chlorides with Δ*M'* values.

Longuet-Higgins and of Dewar,<sup>10,11</sup> and are also different from those commonly listed, because the phenyl group is included, and they refer to the ArCHC<sub>6</sub>H<sub>5</sub> system. The third parameter is the charge density, *q<sub>r</sub>*, which was also calculated to take account of the phenyl group. Because in larger carbonium ions more of the charge is dispersed into the aromatic system, a stabler carbonium ion corresponds to a smaller value of *q<sub>r</sub>*.

In Fig. 1 is shown a plot of log *k* against Δ*M'*. This correlation is typical of plots with all the parameters, including that with Δ*M*. Since such indices as localization energies, or Dewar reactivity numbers, which refer to direct aromatic substitution rather than to

(10) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950).

(11) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952); M. J. S. Dewar, n J. W. Cook, Ed., "Progress in Organic Chemistry," Vol. 2, Butterworths, London, 1953, Chapter 1.

TABLE II  
 RATES OF SOLVOLYSIS OF ARYLPHENYLMETHYL CHLORIDES IN 90% AQUEOUS ACETONE AT 25°

Ar- in ArCHClC <sub>6</sub> H <sub>5</sub>	<i>k</i> <sub>1</sub> × 10 <sup>5</sup> , sec. <sup>-1</sup>	Rel. rate, <sup>a</sup> <i>k</i> / <i>k</i> <sub>0</sub>	Δ <i>M</i> <sup>b,c</sup>	Δ <i>M'</i> <sup>c,d</sup>	2 <i>a</i> <sub>or</sub> <sup>c,d</sup>	<i>q<sub>r</sub></i> <sup>c,d</sup>
Phenyl	0.554	1.00	0.721	1.301 <sup>e</sup>	1.265	0.400
2-Triphenyl	2.58	4.66	.745	1.317	1.231	.379
2-Naphthyl <sup>f</sup>	2.61	4.71	.744	1.317	1.231	.379
4-Biphenyl	3.86	6.97	.756 <sup>g</sup>	1.327	1.220	.372
<i>p</i> -Tolyl	11.5	20.8 <sup>h</sup>	...	...	...	...
2-(9,10-Dihydro)- phenanthryl	19.3	34.8	...	...	...	...
2-Fluorenyl	76.3	138	...	...	...	...
1-Phenanthryl	2.06	3.72	0.803	1.362	1.172	0.344
9-Phenanthryl	2.60	4.69	.813	1.370	1.156	.334
1-Naphthyl <sup>f</sup>	3.54	6.39	.812	1.369	1.160	.336
6-Chrysyl	7.09	12.8	.838	1.388	1.120	.314
1-Pyrenyl	162 <sup>i</sup>	292	.868	1.410	1.069	.286
9-Anthryl	458 <sup>j</sup>	827	.947 <sup>g</sup>	1.477	0.970	.235

<sup>a</sup> Rates relative to the phenyl compound. <sup>b</sup> Values from ref. 7, except where otherwise noted. <sup>c</sup> The slopes of the correlation lines for the rate constants of the unhindered compounds at 25° with the reactivity parameters are 25.0 for Δ*M* (*β*<sub>eff</sub> = -34.1 kcal./mole), 34.6 for Δ*M'* (*β*<sub>eff</sub> = -47.2 kcal./mole), -19.1 for 2*a*<sub>or</sub> (*β*<sub>eff</sub> = -26.0 kcal./mole), and -30.7 for *q<sub>r</sub>* (*β*<sub>eff</sub> = -41.9 kcal./mole). <sup>d</sup> Present calculations. These values refer to the arylphenylmethyl system. <sup>e</sup> The same value is reported in ref. 7, p. 414. <sup>f</sup> The ratio of reactivities of the 1-naphthyl to the 2-naphthyl compound is 1.4; a ratio of 0.9 has been reported for reaction in 100% isopropyl alcohol (S. Altscher, R. Baltzly, and S. W. Blackman, *J. Am. Chem. Soc.*, **74**, 3649 (1952)), and of 1.2 in 100% ethanol (J. Packer, J. Vaughan, and A. F. Wilson, *J. Org. Chem.*, **23**, 1215 (1958)). <sup>g</sup> J. J. Elliott and S. F. Mason, *J. Chem. Soc.*, 2352 (1959). <sup>h</sup> A ratio of 20.6 was reported by L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *ibid.*, 979 (1940). <sup>i</sup> Extrapolated from runs at lower temperatures. <sup>j</sup> Estimated from runs at 0°; see Experimental.

side-chain reactions, are related to the carbonium ion parameters,<sup>5,7</sup> similar plots are also obtained with these.

In all correlations the compounds group themselves into two classes, of which one defines a line of lower reactivity. This has been observed in almost all of such correlations.<sup>4-7</sup> On the faster line fall compounds with the phenyl, 2-naphthyl, 2-triphenyl, and 4-biphenyl groups, and on the lower line compounds with the side chain attached to the 1-naphthyl-, 1- and 9-phenanthryl, 6-chrysyl, and 1-pyrenyl positions. All these latter compounds have a 1-naphthalene-like structure and a *peri* hydrogen with regard to the side chain, and their lower reactivity has been

customarily ascribed to steric hindrance in the transition state, either to coplanarity or to solvation, or both.<sup>4-7</sup> In the present systems, coplanarity of the aryl group with the phenyl group will certainly be difficult to achieve in the hindered compounds. The explanation is therefore not unreasonable and is borne out by many similar examples on record. In fact, there are indications that even unhindered diaryl-carbonium ions may not be completely coplanar.<sup>12</sup> To what extent lack of coplanarity affects even the unhindered compounds cannot be estimated from our data, but if it is a constant factor, a linear relationship will still be observed. By the method used by Streitwieser, Langworthy, and Brauman,<sup>13</sup> the angle of twist of the exocyclic group out of the plane of the aromatic ring can be calculated from the horizontal distance between the two correlation lines.<sup>13</sup> The average twist is about 15°, and this would represent the difference in angle of twist between the compounds on the hindered and unhindered lines. The 9-anthryl compound, in which the side chain is attached to a doubly hindered position, falls even below the hindered line and outside of Fig. 1.

If the division into two groups is accepted, then within each group the reactivities follow closely the theoretical predictions. Only one pair is out of order: the 9-phenanthryl compound is predicted to be as reactive as the 1-naphthyl compound but reacts somewhat slower. This has also been observed in the  $\alpha$ -arylethyl series.<sup>4</sup> There is some arbitrariness about the way in which the hindered line has been drawn. In all correlations, lines of somewhat smaller probable error can be drawn which would place the 9-anthryl compound on the slow line, and which would leave the 1-pyrenyl derivative in a place between the two lines. This compound would then be faster than predicted, and this has also been noted in some other reactions.<sup>4,7</sup> However, the value for the 9-anthryl compound was obtained through two extrapolations and is probably the least accurate. It is certainly chemically more significant, and seems more reasonable to draw the line as shown, even if the numerical fit is less good.

The theoretical parameters ought to be compared with the experimental activation energies. There is a trend in the expected direction, with the  $\Delta E$ 's decreasing with increasing reactivity, particularly when the two reactivity groups are considered separately. But as usual, rate constants provide a superior means of comparison, and reasons have been given why free energies of activation are to be preferred over activation energies in linear relationships of the present type.<sup>14</sup>

In Table II are listed the slopes of the correlation lines of  $\log k$  and the theoretical parameters. All parameters fit about equally well; the probable errors for the unhindered lines range from 1.5 ( $\Delta M$ ) to 11.3% ( $\Delta M'$ ), but there are not enough points to draw any conclusions from the differences in deviations. The errors in the hindered lines are about 10%. The hindered and unhindered lines are almost parallel, as has been observed before,<sup>4-7</sup> and this indicates that the rate reduction due to steric hindrance is often approximately a constant fraction of the total rate.

From the various slopes, the values of  $\beta_{\text{eff}}$  can be calculated (slope =  $\beta_{\text{eff}}/2.303RT$ ), where  $\beta_{\text{eff}}$  is an empirical measure of how far the transition state of the reaction resembles the model that was chosen for the theoretical calculations.<sup>5</sup> These values (Table II) have a meaning only when different reactions are compared with the same reactivity index. In this connection, a comparison of the solvolysis rates of the  $\alpha$ -arylethyl chlorides,  $\text{ArCHClCH}_3$ , in 80% acetone<sup>4</sup> with those of the arylphenylmethyl chlorides,  $\text{ArCHClC}_6\text{H}_5$ , in 90% acetone is instructive. The absolute rates in the latter system are much greater than in the former. Under identical conditions, the solvolysis of diphenylmethyl chloride proceeds about 400 times faster than the solvolysis of  $\alpha$ -phenylethyl chloride.<sup>15</sup> This is reflected in the greater  $\Delta M'$  than  $\Delta M$  values. However, rate differences in the arylphenylmethyl system are greatly compressed, as are also the  $\Delta M'$  values.<sup>16</sup> For instance, the ratio of rates of the 2-fluorenyl to the phenyl compound is 700 in the  $\alpha$ -arylethyl series, and 138 in the arylphenylmethyl series. This agrees with the expectation that the greater reactivity of the diarylcarbonium system is accompanied by a lower selectivity. This becomes also evident when the two reaction series are plotted against the same MO parameter. In the correlation with  $\Delta M$  values, the compounds of the  $\alpha$ -arylethyl series fall on a correlation line of slope 32.8,<sup>17</sup> and those of the arylphenylmethyl system on a line of slope 25.0. However, when the two reaction series are compared to the parameters which are appropriate to them ( $\Delta M$  and  $\Delta M'$ ), then the slopes become indistinguishable ( $32.8 \pm 2.1$  and  $34.6 \pm 3.9$ ) within their probable errors, in spite of the small difference in solvent composition of the two reactions. In the interpretation of Dewar and Sampson,<sup>5</sup> this means that the transition states of both reactions have reached the same extent of carbonium ion character, and both are equally limiting ( $\beta_{\text{eff}}$  -44.7 and -47.2 kcal./mole, respectively).

The relative rates of 4-biphenyl-, 2-fluorenyl- and 2-(9,10-dihydro)phenanthrylphenylmethyl chlorides, compared to that of the phenyl compound, are 7.0, 138, and 35. The greater reactivity of the fluorenyl than the biphenyl derivative in the  $\alpha$ -arylethyl series was ascribed to coplanarity in the fluorenyl compound, in addition to the rate-enhancing effect of the methylene group.<sup>4</sup> A similar situation was found in the solvolysis of *t*-cumyl derivatives,<sup>18</sup> as well as in direct substitution reactions.<sup>19-21</sup> If forced coplanarity is the main reason for the enhanced rate of the fluorene derivatives, 2-(9,10-dihydro)phenanthrylphenylmethyl chloride should be in an intermediate position, because the two-carbon bridge allows some twisting of the phenyl groups, although the rings are more constrained than in biphenyl itself. The experimental data bear

(15) H. C. Brown, Y. Okamoto, and T. Inukai, *ibid.*, **80**, 4964 (1958).

(16) The values  $2a_{\text{or}}$  and  $q_r$  for the arylphenylmethyl system are also more compressed than those for the arylmethyl system.

(17) Data from ref. 4; the 1-pyrenyl derivative was not included in the correlation.

(18) H. C. Brown and T. Inukai, *J. Am. Chem. Soc.*, **83**, 4825 (1961).

(19) H. C. Brown and L. M. Stock, *ibid.*, **84**, 1238 (1962).

(20) P. B. D. de la Mare, D. M. Hall, M. M. Harris, and M. Hassan, *Chem. Ind. (London)*, 1086 (1958); P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 5973 (1963).

(21) U. P. Zimmerman and E. Berliner, *J. Am. Chem. Soc.*, **84**, 3953 (1962).

(12) M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, **73**, 3644 (1951).

(13) A. Streitwieser, Jr., W. C. Langworthy, and J. I. Brauman, *ibid.*, **85**, 1761 (1963).

(14) Reference 7, p. 311.

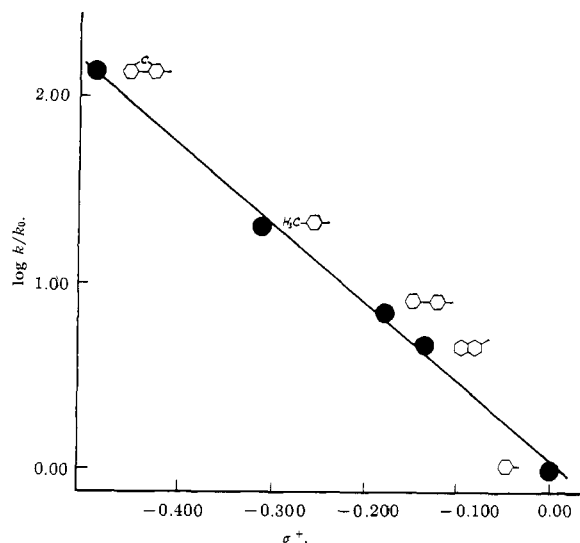


Fig. 2.—Correlation of rates of solvolysis of arylphenylmethyl chlorides with  $\sigma^+$ .

this out. The 9,10-dihydrophenanthrene derivative reacts five times faster than the biphenyl compound, but one-fourth as fast as the fluorene derivative, in spite of the presence of an additional methylene group.<sup>22</sup> The rates of chlorination of the three parent hydrocarbons fall in the same relative order.<sup>20,23</sup> It is also noted that the *p*-methyl group has a much larger rate-enhancing effect than the *p*-phenyl group (relative rates 21 and 7, respectively). This is not an obvious result, but one which nevertheless recurs in other solvolytic and most electrophilic substitution reactions.<sup>24</sup>

Several of the compounds investigated have saturated alkyl groups, for which at present no generally useful theoretical parameters are available. Their solvolysis rates, however, correlate well with a set of  $\sigma^+$  values recently put forth by Brown and Inukai for polynuclear aromatic compounds,<sup>25</sup> and which were derived from the solvolysis of *t*-cumyl and  $\alpha$ -arylethyl chlorides. The very good agreement which is obtained on plotting  $\log k$  against  $\sigma^+$  is shown in Fig. 2 ( $r = 0.998$ ), and it indicates that the three solvolytic reactions are very similarly affected by changes in hydrocarbon structure. The  $\rho$ -value for the present correlation is  $-4.26$ , which, as expected, is lower than that for the  $\alpha$ -arylethyl system ( $-5.78$ ). From the correlation line, an electrophilic substituent constant,  $\sigma^+$ , of  $-0.147$  is obtained for the 2-triphenyl group, and of  $-0.352$  for the 2-(9,10-dihydro)phenanthryl group.

### Experimental

**Materials.**—The chlorides were prepared by saturating a cold benzene solution of the arylphenylmethanols, containing calcium chloride, with hydrogen chloride gas. Yields ranged

from 66 to 91%. 9-Anthrylphenylmethyl chloride was obtained in purer form when prepared with thionyl chloride. Most of the carbinols were prepared by reduction, with either aluminum isopropoxide or lithium aluminum hydride, of the corresponding phenyl ketones. 9-Phenanthrylphenylcarbinol was obtained by a Grignard reaction of 9-phenanthraldehyde and phenylmagnesium bromide, and 9-anthrylphenylcarbinol was made by both methods. The phenyl aryl ketones were prepared by Friedel-Crafts benzoylation through the Perrier complex, as described by Fieser,<sup>26</sup> except for 2-fluorenyl, 2-pyrenyl, and 1-phenanthryl phenyl ketones, which were made by conventional methods described in the literature. 2-Naphthyl phenyl ketone was obtained by a Friedel-Crafts reaction between 2-naphthoyl chloride and benzene, but this method was not suitable for the preparation of 1-anthryl phenyl ketone. All hydrocarbons were purified by recommended procedures, and the m.p.'s of all known intermediates agreed with literature values. In Table III are recorded the m.p.'s of all chlorides, and the analyses of those that are new.<sup>27</sup> All m.p.'s are corrected. The preparation of the new intermediates is described below.

**Phenyl 2-Triphenyl Ketone.**—Benzoyl chloride (6.0 g.) and anhydrous  $\text{AlCl}_3$  (6.2 g.) were swirled together and heated gently over a free flame for 5 min. On cooling to room temperature, 50 ml. of carbon disulfide was added and the mixture refluxed for 30 min. Triphenylene (6.2 g.) was added slowly. After refluxing for 30 min., the reaction was worked up as usual. Recrystallization from ethanol-benzene afforded yellow crystals of phenyl 2-triphenyl ketone (89%), m.p. 165.8–166.8°.

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{16}\text{O}$ : C, 90.33; H, 4.85. Found: C, 90.55; H, 4.69.

For proof of structure of the above ketone, its oxime was subjected to a Beckmann rearrangement. The oxime, prepared by the method of Bachmann and Boatner,<sup>28</sup> forms pale yellow needles (from ethanol), m.p. 214.7–215.2°.

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{17}\text{ON}$ : C, 86.43; H, 4.93. Found: C, 86.28; N, 4.80.

Beckmann rearrangement of the above oxime, using  $\text{PCl}_5$  in a mixture of ether and benzene,<sup>28</sup> afforded a quantitative yield of white needles of 2-triphenylene acid anilide (from acetone), m.p. 294.2–295.8°.

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{17}\text{ON}$ : C, 86.43; H, 4.93. Found: C, 86.57; H, 4.99.

Hydrolysis of the anilide with polyphosphoric acid and sublimation of the resulting acid at 1 mm. and 220° afforded white needles of triphenylene-2-carboxylic acid, m.p. 335–338° (lit.<sup>29</sup> 336–338°).

**Phenyl-2-triphenylmethanol** was obtained from the ketone in 85% yield by aluminum isopropoxide reduction and was crystallized from benzene-ligroin. It forms white needles, m.p. 198.4–200.4°.

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{18}\text{O}$ : C, 89.79; H, 5.42. Found: C, 89.63; H, 5.40.

**Phenyl-2-triphenylmethylbenzoate**, prepared from the above alcohol with benzoyl chloride in pyridine, forms white crystals (ethanol-benzene), m.p. 181.1–183.1°.

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{22}\text{O}_2$ : C, 87.64; H, 5.06. Found: C, 87.41; H, 5.07.

**2-(9,10-Dihydro)phenanthrylphenylmethanol** was obtained from the ketone (m.p. 73.2–74.6°, lit.<sup>30</sup> 72–73°) by reduction with either lithium aluminum hydride or aluminum isopropoxide. It forms an oil, which was sublimed at 1 mm. and 160° and formed a clear, glass-like sublimate.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{18}\text{O}$ : C, 88.08; H, 6.34. Found: C, 88.04; H, 6.40.

**6-Chrysilphenylmethanol** was obtained by reduction with either aluminum isopropoxide (25%) or lithium aluminum hydride (79%) of the corresponding ketone (m.p. 187–188°, lit.<sup>31</sup> 192°). It was crystallized from ethanol-benzene and formed white granules, m.p. 159.4–160.6°.

*Anal.* Calcd. for  $\text{C}_{26}\text{H}_{18}\text{O}$ : C, 89.79; H, 5.42. Found: C, 89.93; H, 5.31.

(26) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 192.

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

(28) W. Bachmann and C. Boatner, *J. Am. Chem. Soc.*, **58**, 2097 (1936).

(29) C. C. Barker, R. G. Emmerson, and J. D. Periam, *J. Chem. Soc.*, 4482 (1955).

(30) J. W. Cook and R. W. G. Preston, *ibid.*, 553 (1944).

(31) P. Mabile and N. P. Buu-Hoi, *J. Org. Chem.*, **25**, 1092 (1960).

(22) Very similar results have been obtained by Professor W. R. Moore of MIT for the solvolysis of the same three halides in aqueous acetone, and by Dr. R. Bolton of Bedford College of the University of London for the alcoholysis in ethanol-acetone. We are very grateful to Dr. Moore and Bolton for this information prior to publication.

(23) Distortion of the fluorene molecule has recently been suggested as an additional factor for the greater reactivity of the fluorene system; forthcoming publication by P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas. We are very grateful to Professor de la Mare for this information prior to publication.

(24) See, for instance, F. B. Deans, C. Eaborn, and D. E. Webster, *J. Chem. Soc.*, 3031 (1959).

(25) H. C. Brown and T. Inukai, ref. 18; H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

TABLE III  
 PROPERTIES OF ARYLPHENYLMETHYL CHLORIDES<sup>a</sup>

Ar- in ArCHClC <sub>6</sub> H <sub>5</sub>	M.p. or b.p. (mm.), °C.	Formula	Carbon, % <sup>27</sup>		Hydrogen, % <sup>27</sup>	
			Calcd.	Found	Calcd.	Found
Phenyl <sup>b</sup>	121.5–122 (1)					
p-Tolyl	129–130 (0.4)					
1-Naphthyl	58.4–59.4 (59) <sup>c</sup>					
2-Naphthyl	73.6–74.7 (74.8) <sup>d</sup>					
4-Biphenyl	72.3–73.1 (72–73) <sup>e</sup>					
2-Triphenyl	107.4–108.9 <sup>f</sup>	C <sub>25</sub> H <sub>17</sub> Cl	85.10	85.11	4.86	4.96
1-Phenanthryl	131.8–132.9 <sup>f</sup>	C <sub>21</sub> H <sub>15</sub> Cl	83.30	83.19	4.99	5.00
9-Phenanthryl	111.4–112.4 (114–116) <sup>g</sup>					
2-(9,10-Dihydro)phenanthryl	<sup>h</sup>	C <sub>21</sub> H <sub>17</sub> Cl	82.75	83.01	5.62	5.86
2-Fluorenyl	123.4–125.3 (122.5–123.5) <sup>g</sup>					
6-Chrysyl	150.2–151.4 <sup>f</sup>	C <sub>25</sub> H <sub>17</sub> Cl	85.10	85.25	4.86	4.86
1-Pyrenyl	106.5–107.9 <sup>f</sup>	C <sub>28</sub> H <sub>15</sub> Cl	84.53	84.63	4.63	4.51
9-Anthryl	136.6–138.4 <sup>i</sup>	C <sub>21</sub> H <sub>15</sub> Cl	83.30	83.43	4.99	5.06

<sup>a</sup> Values in parentheses are from the literature. All melting points are corrected. <sup>b</sup> Commercial sample. <sup>c</sup> R. E. Dabby, A. G. Davies, J. Kenyon, and B. J. Lyons, *J. Chem. Soc.*, 3619 (1953). <sup>d</sup> J. Packer, J. Vaughan, and A. F. Wilson, *J. Org. Chem.*, **23**, 1215 (1958). <sup>e</sup> M. P. Balfe, J. Kenyon, and C. E. Searle, *J. Chem. Soc.*, 3311 (1950). <sup>f</sup> From benzene and 60–70° ligroin. <sup>g</sup> W. E. Bachmann and G. Osborn, *J. Org. Chem.*, **5**, 29 (1940). <sup>h</sup> The product was a clear, colorless oil, which was purified by molecular distillation. <sup>i</sup> Pale yellow prisms from ether–petroleum ether.

1-Pyrenylphenylmethanol was prepared by lithium aluminum hydride reduction of the ketone, which had m.p. 126.5–128° (lit.<sup>32</sup> 126°). Crystallization from ethanol afforded pale yellow crystals (73%), m.p. 129.5–130.9°.

Anal. Calcd. for C<sub>28</sub>H<sub>16</sub>O: C, 89.58; H, 5.23. Found: C, 89.82; H, 5.49.

**Kinetic Runs.**—Acetone was purified by the method of Conant and Kirner,<sup>33</sup> followed by a second distillation from Drierite.<sup>34</sup> The fraction boiling at 57.0° was collected. A stock solution of 90% by volume of acetone was prepared by mixing 9 l. of acetone with 1 l. of boiled-out distilled water in a 12-l. Pyrex bottle. This constitutes the 90% aqueous acetone. The solvents had been previously thermostated at 25°. The stock solution, which had *n*<sub>D</sub><sup>20</sup> 1.3609, lasted through all kinetic determinations.

The kinetic method was essentially as described before.<sup>4</sup> Kinetic runs at 25° or below were conducted in a 100-ml. volumetric flask, while for runs above 25° sealed ampules were used. These were sealed at ice-bath temperature and were cooled in an ice bath before opening; 10-ml. samples were periodically withdrawn, run into 100 ml. of ice-cold acetone, and the liberated HCl was titrated with standard NaOH contained in a 5-ml. microburet. A lacmoid solution was used as an indicator. The final titer was determined after 10 half-times. The concentration of chlorides was usually approximately 0.01 *M*. Thermometers were calibrated against an NBS thermometer, and temperatures were constant to 0.02°, and above 50° to 0.1°. First-order rate constants were determined graphically; the results of a typical run are illustrated in Fig. 3. Reaction was usually conducted to between 60 to 80% completion, but first-order plots remained linear to beyond 90% reaction. Varying the initial chloride concentration by a factor of two had no effect on the rate constants. The best straight lines were fitted by the method of least squares, which was carried out on an IBM computer at the Bryn Mawr–Haverford Computer Center, using a Fortran program. The few points which on visual inspection deviated obviously from the straight line were omitted from the calculations. The probable errors in the slope were calculated for 10 representative runs, and were less than 0.5%. All runs were conducted in duplicate, and duplicate runs agreed within 2% or better. All errors listed in the tables are probable errors of the slopes or intercepts obtained from the least-square calculations.

The rate constant for the solvolysis of 9-anthrylphenylmethyl chloride at 25° was estimated as follows: the log *k* for all compounds at 25° were plotted against log *k* at 0° (some of the latter values were obtained by extrapolation through  $\Delta E$ ). This resulted in an excellent straight line, and the value for the 9-anthryl compound was obtained from this line. The linear

relationship is expected to apply if the activation entropies are constant for the whole reaction series.<sup>36</sup> The experimental slope of the line was 0.886 and the calculated one 0.916.

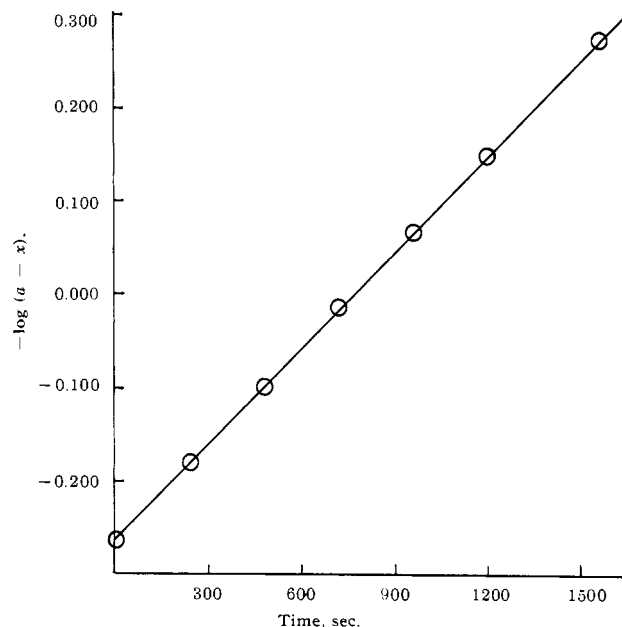


Fig. 3.—A first-order plot for the solvolysis of 2-triphenylphenylmethyl chloride in 90% aqueous acetone at 60°; [chloride] = 0.01055 *M*; *k*<sub>1</sub> = 78.8 × 10<sup>-5</sup> sec.<sup>-1</sup>.

The purity of the final chlorides was between 96 and 100% as determined by the final titer. In four representative examples, isolation runs of the completed reaction mixtures afforded the carbinols in 75 to 91% yields.

**Appendix.**—The  $\Delta M'$  values listed in Table II were calculated as the difference between the total  $\pi$ -energy of the arylphenylmethyl system and the isolated arenes (ArH plus benzene). The values of the  $\pi$ -energies of the hydrocarbons were taken from the literature.<sup>36</sup> The calculations of the  $\pi$ -energies of the arylphenylmethyl systems were carried out by L. V. on an IBM 7090 computer at the Computer Center of the University of California using a program written by Dr. J. I. Brauman and made available by Professor Andrew Streitwieser, Jr.

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(35) For instance, A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 1006 (1928).

(36) B. Pullman and A. Pullman, "Les Théories Électroniques de la Chimie Organique," Masson and Co., Paris, 1952, p. 226.

(32) R. O. C. Norman, G. A. Thompson, and W. A. Waters, *J. Chem. Soc.*, 175 (1958).

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

(34) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., in "Technique of Organic Chemistry," Vol. 7, "Organic Solvents," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1955, p. 383.

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## The Alkaline Hydrolysis of Polynuclear Methyl Arylacetates<sup>1</sup>

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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.<sup>4,5</sup> 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 acids<sup>6</sup> 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-chrysylicetate, 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.<sup>7</sup>

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  $\rho$ -value of +0.824.<sup>8</sup> 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  $\rho$  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 esters, where the inductive effect of the aryl group and the conjugation of the ester group with the ring act in opposite directions.<sup>9</sup>

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 > 3-phenanthryl > 2-anthryl > 4-biphenyl > 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.<sup>10</sup> In fact,

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

(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