3-(*o*-Hydroxyphenyl)-5-phenyl-1,2,4-triazole (VIa) formed colorless crystals from benzene, m.p. 204°, yield *ca.* 82%. VIa is soluble in aqueous sodium hydroxide solution and gives violet color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.88; H, 4.64; N, 17.72. Found: C, 70.61; H, 4.42; N, 17.90.

VIa was similarly prepared by the action of hydrazine hydrate on 1 g. of Va, as described above, in an almost quantitative yield. Identification was carried out by m.p. and mixed m.p. determination.

3-(*o*-Hydroxyphenyl)-5-(*p*-methoxyphenyl)-1,2,4-triazole (VIb) formed colorless crystals from ethyl alcohol, m.p. 186°, yield *ca.* 79%. It behaves in a similar manner to VIa toward ferric chloride and sodium hydroxide solutions.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.41; H, 4.87; N, 15.73. Found: C, 67.52; H, 4.65; N, 15.80.

Action of Grignard Reagents on Ic. (a) Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide (prepared from 0.9 g. of magnesium and 9 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.5 g. of Ic in 50 ml. of dry benzene. The ether was evaporated and the reaction mixture heated for 3 hr. on a steam-bath. After the mixture had stood overnight at room temperature, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution and extracted with ether. The precipitate which separated from the ether-benzene mixture was crystallized from benzene-light petroleum as colorless crystals, m.p. 122°, yield *ca.* 0.89 g.

Anal. Calcd. for $C_{21}H_{17}NO_3$: C, 76.13; H, 5.13; N, 4.23; active H, 0.30. Found: C, 75.68; H, 4.96; N, 4.15; active H, 0.27.

2-(*p*-Methoxyphenyl)-4-phenyl-1,3-benzoxazine (VIIa) is easily soluble in benzene and hot ethyl alcohol, difficultly soluble in light petroleum and insoluble in cold aqueous sodium hydroxide solution. It gives red color with sulfuric acid. The alcoholic solution of VIIb does not become colored when treated with alcoholic ferric chloride solution.

(b) Benzylmagnesium Chloride.—To a Grignard solution of benzylmagnesium chloride (prepared from 0.8 g. of magnesium, 5.5 g. of benzyl chloride and 50 ml. of dry ether) was added a solution of 1 g. of Ic in 40 ml. of benzene. The reaction mixture was worked up in the usual manner. The oily product, obtained upon evaporation of the ethereal extract, solidified after working with light petroleum. 2-(*p*-Methoxyphenyl)-4-benzal-1,3-benzoxazine (IXb) was obtained as yellow crystals from petroleum ether, yield 0.68 g., m.p. 126°.

Anal. Calcd. for $C_{22}H_{17}NO_2$: C, 80.73; H, 5.20; N, 4.28. Found: C, 80.62; H, 4.91; N, 4.05.

IXb is easily soluble in chloroform and benzene, difficultly soluble in cold petroleum ether and insoluble in cold aqueous sodium hydroxide solution; it gives an orange red color with sulfuric acid.

Action of Grignard Reagents on X. (a) Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide was added 1 g. of X[13] in 30 ml. of dry benzene. The reaction mixture was worked up as described above. The oily residue, obtained on evaporation of the ethereal extract, solidified on scratching and cooling. N-Benzohydrylsalicylamide (XIIa) was crystallized from petroleum ether (b.p. 100–120°) as colorless crystals, m.p. 140°, yield 0.64 g.

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.21; H, 5.61; N, 4.62. Found: C, 79.20; H, 5.46; N, 4.32.

XIIa is easily soluble in benzene and hot alcohol, difficultly soluble in light petroleum and soluble in cold aqueous sodium hydroxide; it gives an orange-red color with alcoholic ferric chloride solution.

Acetylation.—A solution of 0.5 g. of XIIa in 30 ml. of acetic anhydride was refluxed for 2 hr. The reaction mixture was poured into cold water, and the solid, so obtained after cooling, was filtered off, washed thoroughly with water and crystallized from alcohol as colorless crystals (*ca.* 0.39 g.), m.p. 148°. The acetyl derivative XIIc is insoluble in cold aqueous sodium hydroxide solution and gives no color with ferric chloride. It gives an orange-red color with sulfuric acid.

Anal. Calcd. for $C_{22}H_{19}NO_3$: C, 76.52; H, 5.51; N, 4.06. Found: C, 76.50; H, 5.34; N, 3.82.

Action of Hydrochloric Acid on XIIa.—A solution of 1 g. of XIIa in 40 ml. of glacial acetic acid was treated with 5 ml. of concentrated hydrochloric acid. The reaction mixture was refluxed for 3 hr., cooled, poured into ice-cold water and neutralized with sodium carbonate. It was extracted with ether, dried and evaporated. The solid residue was crystallized from ethyl alcohol as colorless crystals (*ca.* 0.41 g.), m.p. 136°; identified as salicylamide (m.p. and mixed m.p.).

Anal. Calcd. for $C_7H_7NO_2$: C, 61.31; H, 5.10; N, 10.21. Found: C, 61.42; H, 4.96; N, 10.12.

(b) Methylmagnesium Iodide.—A solution of 1 g. of XIIa in 40 ml. of dry benzene was added to methylmagnesium iodide (prepared from 0.9 g. of magnesium, 3.6 g. of methyl iodide and 50 ml. of dry ether); the reaction mixture was refluxed on a steam-bath for 3 hr., allowed to stand overnight at 25° and worked out as usual. N-(α-Phenylethyl)-salicylamide (XIIb) was crystallized from light petroleum as colorless crystals, m.p. 103°, yield 0.51 g.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.68; H, 6.22; N, 5.81. Found: C, 74.46; H, 5.98; N, 5.85.

XIIb is easily soluble in benzene and hot alcohol, difficultly soluble in light petroleum and soluble in cold aqueous sodium hydroxide solution; it gives yellow color with sulfuric acid. The alcoholic solution of XIIb gives violet color with alcoholic ferric chloride solution.

Acetylation.—The acetyl derivative XIId was similarly prepared as previously described in the case of XIIc. It was obtained in colorless crystals from chloroform-light petroleum mixture, m.p. 98°, yield 82%. It was insoluble in aqueous sodium hydroxide solution and gives no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{17}H_{17}NO_3$: C, 72.08; H, 6.00; N, 4.94. Found: C, 71.78; H, 5.82; N, 5.00.

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

Relative Reactivities of Polynuclear Aromatic Systems. The Solvolysis of α-Arylethyl Chlorides[1]

BY ERNST BERLINER AND NAN SHIEH

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The rates of reaction, activation energies and entropies were determined for the SN1 solvolysis of 13 different α-arylethyl chlorides, $ArCHClCH_3$, in 80% or 90% aqueous acetone. The relative reactivities, referred to 25° and 80% aqueous acetone, correlate satisfactorily with various theoretical parameters, but compounds with an "α-naphthalene-like" structure react slower than predicted.

Although polynuclear aromatic hydrocarbons have played an important part in organic chemical theories, an experimental knowledge of the relative reactivities of polycyclic aromatic systems is very scanty. This is in contrast to the theoretical treatment accorded these systems, particularly in

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[1] Taken from a dissertation submitted by Miss Nan Shieh to the Graduate School of Bryn Mawr College in partial fulfillment of the requirements for the Ph.D. degree, June, 1957.

Table I

Kinetic Data for the Solvolysis of α-Arylethyl Chlorides

Ar– in ArCHClCH$_3$	Solvent, % acetone	Temperature, °C. 25.00	32.00	40.00	45.00	E, kcal.	log A	ΔS^* e.u.
		$k \times 10^6$ sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$					
2-Phenanthryl	80	3.31	0.843	2.14	3.76	22.9 ± 0.2	11.3 ± 0.2	−8.75
		3.29		2.18	3.77			
2-Naphthyl	80	4.71	1.13	2.92	5.28	22.6 ± .1	11.3 ± .1	−8.96
		4.81	1.16	2.98	5.26			
9-Phenanthryl	80	5.83	1.45	3.85	6.86	23.2 ± .1	11.8 ± .1	−6.53
		5.85	1.42	3.85	6.83			
4-Biphenylyl	80	7.45	1.76	4.59	7.91	22.2$_5$ ± .1	11.2 ± .1	−9.35
		7.46	1.85	4.56	7.89			
3-Phenanthryl	80	8.96	2.20	5.77	10.4	22.8 ± .1	11.7 ± .1	−6.99
		9.31	2.23	5.76	10.3			
		9.20						
1-Naphthyl	80	11.7	2.75[a]	6.94[b]	12.1	22.3 ± .1$_5$	11.4 ± .1	−8.30
		11.7	2.71	6.81	12.5			
			2.74		12.4			
2-Chrysenyl	80	24.8	6.05	15.6	27.1	22.8 ± .1	12.1 ± .1	−5.04
		24.0	6.05	15.8	27.9			
	90	2.30	0.564	1.40	2.41	22.0 ± .2	10.5 ± .1	−12.5
		2.31		1.37	2.39			
2-Anthryl	90	2.69	0.629	1.56	2.62	21.5 ± .1	10.2 ± .1	−13.9
		2.69	0.623	1.54	2.61			
1-Anthryl	90	5.65			5.50	21.4	10.4	−12.9
		5.77						
2-Fluorenyl	90	31.6	6.98	15.9	26.7	20.1 ± .1	10.2 ± .1	−13.7
		31.5	6.87	16.2	26.7			
		Temperature, °C. 0.00	12.00	18.00	25.00			
2-Fluorenyl	80	19.7	9.60	20.5	47.7	20.6 ± .1	11.8 ± .1	−6.51
		19.6	9.67	20.1	47.6			
				21.0				
3-Pyrenyl	90	26.0	10.8	21.6	44.0	18.5 ± .1	10.2 ± .1	−14.0
		25.5	10.7	21.4	44.3			
9-Anthryl	90	89.5	33.2			17.0	9.57	−16.7
		87.5	33.0					
		Temperature, °C. 45.00	55.00	65.00	70.00			
Phenyl	80	7.23	2.12	5.83	9.47[c]	22.2 ± .1	10.1 ± .1	−14.2
		7.29	2.09	5.68	9.39			

[a] $T = 32.13°$. [b] $T = 39.70°$. [c] Values of 9.04 (titrimetric) and 10.0 (polarimetric) are reported by E. D. Hughes, C. K. Ingold and A. D. Scott, ref. 8.

the last decades. Various parameters arising out of modern theories, such as free valences, atom- and bond-localization energies, charge densities, molecular diagrams and others, have made it possible to predict relative reactivities at various positions within the same molecule, as well as differences among different molecules.[2]

Two lines of approach suggest themselves for a collection of data by which relative reactivities of polynuclear aromatic systems can be ascertained. One is a kinetic study of an electrophilic substitution reaction, the other a study of a suitable side-chain reaction. The latter was chosen for a preliminary survey because a definite position in the polynuclear aromatic compound can be studied without the complicating factor of isomer distribution or polysubstitution.

Most of the older quantitative data refer to various side-chain reactions and dissociation constants in the benzene and naphthalene series, but some extend to biphenyl, anthracene and phenanthrene.[3] In direct electrophilic substitution, there is abundant qualitative information, based usually on preparative ease of substitution, that the reactivity is anthracene > phenanthrene > naphthalene > benzene for the most reactive positions.[4] Systematic quantitative data were practically completely missing, until Dewar, Mole and Warford recently demonstrated an excellent correlation between theoretical parameters and relative rates of nitration for polynuclear aromatic hydrocarbons.[5]

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[2] For general discussions see, for instance, L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1944; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955; C. A. Coulson, "Valence," Oxford University Press, London, 1952; B. Pullman and A. Pullman, "Les Theories electroniques de la Chimie organic," Masson and Co., Paris, 1952; M. J. S. Dewar, This Journal, **74**, 3341 ff. (1952); M. J. S. Dewar in J. W. Cook, "Progress in Organic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1953, p. 1.

[3] Some of the older literature has been reviewed by E. A. Braude and J. S. Fawcett, *J. Chem. Soc.*, 800 (1950).

[4] For instance, see the discussion in L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd Ed., Heath and Co., Boston, 1956, Ch. 31, 32.

[5] M. J. S. Dewar, T. Mole and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956); also, M. J. S. Dewar and T. Mole, *ibid.*, 342 (1957).

Relative reactivites in free radical reactions (methyl or trichloromethyl affinities and others)[6] correlate well with free valence numbers or the atom localization energies.[6,7] Since the point of attack in these reactions is not known with certainty, the assumption is always made that the attack occurs at the position predicted to be the most reactive.

The side-chain reaction chosen for the present study is the SN1 solvolysis of α-arylethyl chlorides, $ArCHClCH_3$, in aqueous acetone, partly because the mechanism of the reaction and the nature of the transition state are fairly well understood[8] and partly because of the similarity of the transition state, as far as electronic effects are concerned, to the transition state in aromatic substitution. Since this work was initiated, two very similar studies on the solvolysis of arylmethyl chlorides, $ArCH_2Cl$, have been reported by Fierens, *et al.*,[9] and by Dewar and Sampson.[10] The aim of these papers was the same as the present one, and the results are very similar. A study has also been reported on the reaction of polynuclear amines with 2,4-dinitrochlorobenzene.[11]

Results and Discussion

The kinetic data for the solvolysis of 13 compounds, most of them studied at four different temperatures, are collected in Table I. Because of a considerable spread in reactivity and solubility it was not possible to compare all compounds in the same solvent mixture or at the same temperature. Four compounds were studied in 90% aqueous acetone and all the others in 80% acetone. Two compounds, 2-fluorenyl and 2-chrysenyl, were investigated in both solvents, and the results obtained were used to refer all compounds to 80% aqueous acetone. This was not wholly satisfactory, because, as expected, the factors thus obtained differed for the two standard compounds, but the uncertainty introduced by taking an average value was probably not too serious, and in no case was a reactivity order inverted. Where necessary, rate constants were extrapolated to 25° by means of the Arrhenius equation. The only kinetic complication was experienced with the 9-anthryl compound. The first-order rate constants fell within one run, and the data could be analyzed very well for two concurrent first-order reactions by the method of Brown and Fletcher.[12] But neither the crystalline solid starting material nor the products revealed the presence of two compounds. A more likely explanation is that this compound, the fastest of all, is subject to a mass law effect by the chloride ion [13] When analyzed on this assumption, a smooth curve was obtained on plotting the apparent k_1 against time, which was extrapolated to zero time, to give the rate constants recorded in Table I.

In Table II are listed all rate constants referred to 80% by volume aqueous acetone at 25°. A number of relevant theoretical parameters are also listed. In Fig. 1 the logarithms of the rate constants (log k/k_0) are plotted against the atom-localization energies ($E_0 - E$), where k_0 and E_0 refer to benzene. The atom-localization energies (in units of β) are those obtained by Dewar by a simplified molecular orbital treatment.[14] These values were used rather than those obtained by the more rigorous method[15] because they easily can be extended to a wide variety of alternant hydrocarbons;[16] the results of the plots are identical. Although atom-localization energies refer strictly to the π-electron energy difference between the initial and the transition state in aromatic substitution, *i.e.*, for a direct attack on the nucleus, rather than the side-chain, they were chosen as the most general ones for a possible future comparison. Also, the various parameters are interrelated, and from a general knowledge of carbonium ion stability, one would expect a relation between the power of conjugation of Ar– with a carbonium ion, and hence the stabilizing effect of Ar–, and some of the

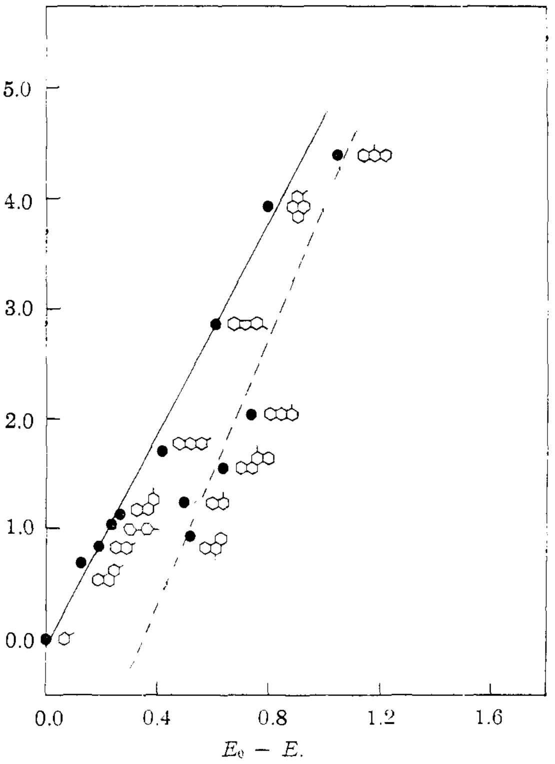

Fig. 1.—A plot of log k against localization energies. The point corresponding to the 2-fluorenyl compound was obtained from the line.

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[6] M. Levy and M. Szwarc, This Journal, **77**, 1949 (1955); J. Smid and M. Szwarc, *ibid.*, **78**, 3322 (1956); M. Szwarc and F. Leavitt, *ibid.*, **78**, 3590 (1956); E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953); J. R. Dunn, W. A. Waters and I. M. Roitt, *J. Chem. Soc.*, 580 (1954).

[7] C. A. Coulson, *ibid.*, 1435 (1955); P. M. G. Bavin and M. J. S. Dewar, *ibid.*, 164 (1956).

[8] C. K. Ingold, "Structure and Mechanism in Organic Chemistry." Cornell University Press, Ithaca, N. Y., 1953, Ch. 7; S. Winstein, E. Grunwald and H. W. Jones, This Journal, **73**, 2700 (1951); E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

[9] P. J. C. Fierens, H. Hannaert, J. Van Rysselberge and R. H. Martin, *Helv. Chim. Acta*, **38**, 2009 (1955).

[10] M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956).

[11] F. L. J. Sixma, *Rec. trav. chim.*, **74**, 168 (1955).

[12] H. C. Brown and R. S. Fletcher, This Journal, **71**, 1845 (1949).

[13] C. K. Ingold, ref. 8.

[14] M. J. S. Dewar, ref. 2.

[15] F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

[16] See, for instance, P. H. Gore, *J. Chem. Soc.*, 3166 (1954).

parameters referring to ArH.[17] In their more strict treatment, Dewar and Sampson[10] have plotted rate constants against the parameters $2a_{or}$, which are related to the energy difference between $ArCH_2X$ and $ArCH_2^+$. When our data were plotted against these quantities, a plot similar to Fig. 1 is obtained. Another readily available quantity is the charge density on the exocyclic carbon atom in the carbonium ion, which can be calculated by the method of Longuet-Higgins.[18] When these values are plotted against log *k*, a straight line similar to that shown is obtained.

TABLE II

RATE CONSTANTS FOR THE SOLVOLYSIS OF α-ARYLETHYL CHLORIDES IN 80% AQUEOUS ACETONE AT 25°

Ar– in $ArCHClCH_3$	$k \times 10^5$, sec.$^{-1}$	Localization energy E_A (β) *A*[a]	Localization energy E_A (β) *B*[b]	Free valence number, *N*[c]	$2a_{or}$[d] (β)	Charge density on $ArCH_2^+$, *q*[e]
Phenyl	0.0679	2.31	2.54	0.081	1.51	0.571
2-Phenanthryl	.330	2.18	2.50	.086	1.47	.543[f]
2-Naphthyl	.476	2.12	2.48	.086	1.46	.529
9-Phenanthryl	.584	1.79	2.30	.133	1.34	.446
4-Biphenylyl	.746	2.07	2.44	.094	1.44[f]	.516
3-Phenanthryl	.916	2.04	2.41	.089	1.43	.511[f]
1-Naphthyl	1.17	1.81	2.30	.134	1.34	.450
2-Chrysenyl	2.44	1.67	2.24[g]	.139[h]	1.28[f]	.410[f]
2-Anthryl	3.45[i]	1.89	2.40	.090	1.37[f]	.471
1-Anthryl	7.33[i]	1.57	2.25	.141	1.23[f]	.381
2-Fluorenyl	47.7					
3-Pyrenyl	567[i]	1.51	2.19[g]	.151[h]	1.21	.364[f]
9-Anthryl	1640[i]	1.26	2.01	.202	1.07	.286

[a] From M. J. S. Dewar, ref. 2. [b] From F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, ref. 15. [c] Ref. b and 15. Values obtained by the molecular orbital method. A completely analogous but numerically different set of figures obtained by the same method is listed in B. Pullman and A. Pullman, ref. 2, pp. 587–589. [d] From M. J. S. Dewar and R. J. Sampson, ref. 10. [e] Calculated by the method of H. C. Longuet-Higgins, ref. 18. These values were also used by F. L. J. Sixma (ref. 11) and our values agree with those that are duplicated. [f] Present calculations. [g] From E. C. Kooyman and E. Farenhorst, ref. 6. [h] G. Berthier, C. A. Coulson, H. H. Greenwood and A. Pullman, *Compt. rend.*, **226**, 1906 (1948). [i] Value extrapolated from kinetic data in 90% aqueous acetone.

In general, high reactivity corresponds to low values for the localization energies, the $2a_{or}$ parameters and the charge densities, and high values for the maximum free valence numbers.[9] On a more quantitative comparison, a very satisfactory agreement and a good linear relation is obtained when the compounds are classed in two groups. The lower curve in Fig. 1, which defines a line of lower reactivity than predicted and which is practically parallel to the first line, contains without exception compounds which have the substituent in an α-naphthalene-like structure, next to a *peri*-hydrogen. The same was observed by the other two groups of workers ("α-naphthalene effect") and has been ascribed by them to a steric effect.[9,10] This is the most reasonable explanation that can be offered, and it shows that the SN1 solvolysis of α-arylethyl chlorides is subject to steric hindrance toward either coplanarity or solvation, even by the somewhat remote *peri* grouping. That the lower reactivity might be due to a theoretical value which is uniformly too high for just these compounds is unlikely and can be ruled out by the observation that it is not observed in cases where no hindrance might be expected, such as in direct nitration[5] or free radical attack.[6,7]

The slope of the straight line in Fig. 1, which is measured in terms of the resonance integral β, has a least square value of 4.82 ± 0.16. It has a meaning similar to Hammett's ρ-value,[19] and the magnitude of the slope should make it possible to draw conclusions about the susceptibility of various reactions to changes in hydrocarbon structure. Particularly, in direct aromatic substitution it should be related to the activity of the substituting agent.[20] A more detailed discussion of the significance of the slopes in both side-chain and substitution reactions has been given by Dewar, *et al.*,[5,7,10] who has pointed out that β, obtained from the slope,[21] should not be considered the usual universal constant, but a variable parameter dependent on the particular reaction. In a plot of our rate constants (log k_1) against $2a_{or}$ the slope has the value 12.6 ± 0.31, and β is 17.1 kcal. as compared to 30 kcal. obtained for β in the SN1 solvolysis of arylmethyl chlorides, $ArCH_2Cl$, in moist formic acid.[10] In the interpretation of Dewar and Sampson, this means that the transition state of α-arylethyl chloride solvolysis in 80% aqueous acetone has not progressed as far in free carbonium ion character as that of arylmethyl chloride solvolysis in moist formic acid. Viewed differently, the carbonium ion formed from $ArCHClCH_3$ is more stable than that formed from $ArCH_2Cl$ and therefore the reaction less "selective,"[20] giving rise to a smaller slope.

If it is accepted that the results group themselves into two classes of compounds and if each class is considered separately, only one pair of compounds shows an inverted order: 9-phenanthryl should be faster than 1-naphthyl but is slower. Both are less reactive than predicted, and an additional steric effect may possibly be operative in the 9-position of phenanthrene. Such an additional effect should then also be operative in 9-anthryl, where it is not observed, but the value for 9-anthryl is probably the least accurate because it was obtained by several extrapolations. Also, the 3-pyrenyl compound should by analogy fall on the low reactivity line but does not. It is gratifying that certain observed orders of reactivity, which could not easily have been predicted on the basis of preparative reactivities, agree with the theory. For instance, the 4-biphenylyl and 2-naphthyl compounds fall within the 2- and 3-phenanthryl derivatives. Other orders, found and predicted by the various theoretical parameters are, for instance, 9-anthryl > 3-pyrenyl > 1-anthryl > 2-anthryl, or 2-chrysenyl > 1-naphthyl > 2-naphthyl, etc. To the extent to which the deviations from the least square lines can be taken as a measure of agreement between theoretical and ex-

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[17] For instance, see C. A. Coulson and H. C. Longuet-Higgins, *Proc. Royal Soc. (London)*, **195**, 188 (1948); R. Daudel, C. Sandorfy, C. Vroelant, P. Yvan and O. Chalvet, *Bull. soc. chim.*, 66 (1950); also ref. 9.

[18] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 ff. (1950).

[19] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. 7.

[20] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

[21] The slope is equal to $\beta/2.303RT$.

TABLE III

PREPARATION OF α-ARYLETHYL CHLORIDES AND INTERMEDIATES[a]

Ar–	°C. (mm.) M.p. or b.p. Ketone	Carbinol	Chloride	Formula	Analyses,[b] % Carbon Calcd.	Found	Hydrogen Calcd.	Found
Phenyl		69.0–70.0 (1.3–1.7)[c]	41.0–42.0 (0.9–1.0) 39–40 (0.5)[d]					
1-Naphthyl	[e]	62.4–63.5 (66[e])	133–134 (7)[f] 128–129 (4)					
2-Naphthyl	[c]	71.3–72.1 (72)[g]	66.4–67.3 (62–63)[h]					
4-Biphenylyl	[c,i] 120.5 (121)[k]	96.4–97.6 (97)[k]	52.6–53.7	$C_{14}H_{13}Cl$	77.59	77.38	6.05	5.97
2-Phenanthryl	145 (143)[l]	131.5–132.2 (131–131.5; 134–135)[m,n]	80.5–81.5[o]	$C_{16}H_{13}Cl$	79.83	79.70	5.44	5.49
3-Phenanthryl	71.0–72.0 (72)[l]	77.8–80.0 (79–81; 76–78; 83–83.5)[p,o,n]	85.5–86.5	$C_{16}H_{13}Cl$	79.83	79.81	5.44	5.57
9-Phenanthryl	74.0–74.5 (73–74)[q]	134.5–135.5 (134–135)[r]	93.5–94.5	$C_{16}H_{13}Cl$	79.83	79.89	5.44	5.53
1-Anthryl	109.4–109.8[s] (103–105)[t]	107.2–108.0[u]	60.0–61.1	$C_{16}H_{13}Cl$	79.83	79.97	5.44	5.47
2-Anthryl	186–187[s] (183–185;[t] 188)[v]	162.8–163.3[w]	177.3–178.8 d.	$C_{16}H_{13}Cl$	79.83	79.98	5.44	5.47
9-Anthryl	73.0–74.5 (75–76)[x]	124.0–125.0 (124–125)[y]	75.5–77.0	$C_{16}H_{13}Cl$	79.83	79.94	5.44	5.33
2-Fluorenyl	129.0–130.0 (128–129)[z]	134.0–135.6 (139–140)[aa]	90.5–92.0	$C_{15}H_{13}Cl$	78.77	79.06	5.73	5.80
3-Pyrenyl	89.0–90.0 (89–90)[bb]	112.0–113.2 (112–112.5)[bb]	98.5–99.5 d.	$C_{18}H_{13}Cl$	81.66	81.66	4.95	5.04
2-Chrysenyl	141.5–142.7 (142–143)[dd]	159.0–160.5[cc]	149.0–150.0 d.	$C_{20}H_{15}Cl$	82.61	82.89	5.20	5.04

[a] Values in parentheses are literature values. The melting points of the chlorides and the new carbinols are corrected.
[b] Carbon and hydrogen analyses of all new chlorides by Galbraith Laboratories, Knoxville, Tenn.
[c] Commercial.
[d] G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 2405 (1954).
[e] R. H. Pickard and J. Kenyon, *ibid.*, **105,** 1126 (1914).
[f] Reported in the patent literature without physical constants; French Patent 724,105 (*Chem. Zentr.*, **104,** I, 505 (1933)).
[g] H. Lund, *Ber.*, **70,** 1520 (1937).
[h] W. Gerrard and B. D. Shepherd, *J. Chem. Soc.*, 2069 (1953).
[i] We are indebted to Dr. D. T. Mowry of the Monsanto Chemical Co., Dayton, Ohio, for a generous sample of this compound.
[k] W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, THIS JOURNAL, **68,** 1109 (1946).
[l] E. Mosettig and J. van de Kamp, *ibid.*, **52,** 3704 (1930).
[m] W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **5,** 416 (1940).
[n] E. Mosettig and J. van de Kamp, THIS JOURNAL, **55,** 3442 (1933).
[o] A different compound is obtained when the carbinol is treated with pyridine and thionyl chloride; C. C. Price and B. D. Halpern, *ibid.*, **73,** 818 (1951).
[p] W. E. Bachmann and J. M. Chemerda, *J. Org. Chem.*, **6,** 36 (1941).
[q] J. E. Callen, C. A. Dornfeld and G. H. Coleman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 26.
[r] W. E. Bachmann, THIS JOURNAL, **56,** 1363 (1934).
[s] The 1- and 2-acetylanthracenes were separated by chromatography over alumina in benzene–ligroin mixtures.
[t] German Patent 492,247 (*C. A.*, **24,** 2472 (1930)).
[u] *Anal.* Calcd. for $C_{16}H_{14}O$: C, 86.46; H, 6.35. Found: C, 86.42; H, 6.27. Recrystallized from ligroin; all other new carbinols were crystallized from benzene. Analysis, footnote *b*. The analytical sample was obtained by hydrolysis of the pure chloride.
[v] Ng. Ph. Buu-Hoi and P. Cagniant, *Rec. trav. chim.*, **62,** 713 (1943).
[w] *Anal.* Calcd. for $C_{16}H_{14}O$: C, 86.46; H, 6.35. Found: C, 86.26; H, 6.59. Analysis by Geller Laboratories, Hackensack, N. J.
[x] C. Merritt, Jr., and C. E. Braun, footnote *q*, Vol. 30, 1950, p. 1.
[y] E. L. May and E. Mosettig, THIS JOURNAL, **73,** 1301 (1951).
[z] F. E. Ray and G. Rieveschl, Jr., footnote *q*, p. 23.
[aa] D. T. Mowry, M. Renoll and W. F. Huber, THIS JOURNAL, **68,** 1105 (1946).
[bb] W. E. Bachmann and M. Carmack, *ibid.*, **63,** 2494 (1941).
[cc] *Anal.* Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.46; H, 6.21. Analysis by N. S.
[dd] W. Carruthers, *J. Chem. Soc.*, 3486 (1953).

perimental values, the experimental values agree almost equally well with any of the theoretical parameters. The localization energies (*A* and *B*), the $2a_{or}$ constants and the charge densities (Table II) give straight lines with probable errors of 3.3, 4.5, 2.5 and 2.4%, respectively, but the error is larger (12.4%) when the maximum free valence numbers are plotted.[22]

No theoretical value is available for 2-fluorenyl, but it is very reactive, and the effect of the 5-membered ring and the methylene group raises the reactivity greatly over that of 4-biphenylyl. Forced coplanarity and hyperconjugation may be a contributing factor.

The most desirable situation would obtain if the localization energies could be compared directly with the experimental activation energies. Although the errors obtained for the activation energies are small, and logarithms of rate constants at four different temperatures fall virtually on a straight line when plotted against $1/T$, the differences among the activation energies for the various compounds are not sufficiently large or regular to be usable in place of the rate constants.[23] In a very approximate way, rate differences appear to be determined by differences in activation energies. The log *A* factors are of the same order of magnitude for reaction in the same solvent, and the activation entropies are, as expected, negative. Some of the deviations from the straight line may be due to variations in activation entropy, because one of the assumptions made in calculating the theoretical parameters is that the entropies remain constant. It is also noted that the differences in rate on going from the more to the less aqueous solvent is due almost exclusively to a lowering of the activation entropies in the less aqueous solvent. This is expected for reactions where ions are formed from neutral molecules.[24]

Experimental

Materials.—All chlorides were prepared by passing a stream of HCl gas, in the presence of calcium chloride, into the cold ethereal solutions of the carbinols[25]; yields of crude product were 80–90%. For the phenyl and the two naphthyl compounds, thionyl chloride was used.[26] After evaporation of the solvent, the chlorides were repeatedly recrystallized from 60–70° ligroin (petroleum ether in the case of 9-anthryl), until the melting point remained constant. The phenyl and the two naphthyl compounds were distilled *in vacuo*. The carbinols were made by aluminum isopro-

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(22) Not only is the error small when the parameters $2a_{or}$ are plotted, but the "low reactivity" line is almost exactly parallel; the slopes of the two lines are 12.61 and 12.21, respectively, and 4.82 and 6.05 when the localization energies are used. In either case, however, the low reactivity line contains rate constants that were obtained by several extrapolations and are probably not as accurate as those of the other line.

(23) See also ref. 9, and the relevant discussion in ref. 10.

(24) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Ch. 7.

(25) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940). The treatment with anhydrous sodium carbonate was omitted.

(26) G. Baddeley, J. Chadwick and H. T. Taylor, *ibid.*, 2405 (1954).

poxide reduction of the corresponding ketones (yields of crude product usually 80–90%); lithium aluminum hydride was used for the reduction of 2- and of 9-anthryl methyl ketone (87 and 85%), as well as of 2-chrysenyl methyl ketone (85%). The 1-anthryl methyl ketone was reduced by both reagents, but aluminum isopropoxide proved superior (70%). All the ketones were made by methods described in the literature, usually involving a Friedel and Crafts acylation of hydrocarbons, which had been purified by recommended procedures. The physical properties of all compounds and the carbon, hydrogen analyses of the new compounds are listed in Table III.[27]

Kinetic Runs.—Purified acetone[28] and boiled-out distilled water were thermostated at 25° and the necessary volumes, measured in 2-l. volumetric flasks (for instance 8 l. of acetone and 2 l. of water), were mixed in a 5 gal. Pyrex bottle. Enough of the 80 and the 90% aqueous acetone was prepared to last throughout the entire investigation. Kinetic runs below 25°, and some at 25°, were conducted in a 100-ml. volumetric flask, and 10-ml. samples were withdrawn at appropriate time intervals. Most runs at 25°, and all runs above 25°, were run in sealed tubes, prepared from 15-mm. Pyrex tubing. For these runs, an exactly weighed amount of chloride was made up to volume in a 100-ml. volumetric flask at room temperature, the mixture was cooled and eight approximately 12-ml. samples were pipetted into the ampules, sealed at ice-bath temperature and placed in the thermostat. When the tubes had reached the temperature of the thermostat, one ampule was opened and a 10-ml. sample was withdrawn and titrated for the zero titer. The contents of one sealed tube were allowed to react for at least 10 half-life times, in order to get the infinity reading. All samples, including the one for the infinity reading, were withdrawn at the reaction temperatures, which were maintained at ±0.02°. The 10-ml. samples were allowed to run into 60–80 ml. of ice-cold acetone and were titrated with a NaOH solution contained in a 5-ml. microburet graduated in hundredths; a 0.5% alcoholic lacmoid solution was used as an indicator. Initial concentrations of chloride were usually around 0.01 *M*, except for the less soluble 2-anthryl (0.006–0.007 *M*) and 2-chrysenyl (0.005 *M* in 80% acetone) compounds. A check with the 2-fluorenyl compound at a 0.01 and 0.005 *M* concentration showed that the rates were not affected by the initial concentrations. Reactions were conducted to at least 60% completion, and usually more. Isolation runs were conducted with all compounds, except the phenyl, 1-naphthyl and 4-biphenylyl compounds, and the only products that were isolated were the corresponding carbinols, whose identity was checked by mixed melting points. The purity of the chlorides was obtained from infinity readings at 25°; all titrated for 99–100% purity except for the 1-naphthyl compound which was only 84% pure. This was undoubtedly due to some decomposition which was noticeable during vacuum distillation, but runs conducted with samples of various chloride content (60–84%) gave identical results.

Rate constants were calculated from the integrated form of the first-order rate equation. All runs were conducted at least in duplicate, all runs being listed in Table I. The average deviations within one run were 1–2%; some runs had a slight upward drift. The errors quoted for the activation energies and log *A* factors are probable errors obtained from least square calculations, rounded off to the values shown in Table I. The results of two typical runs are recorded in Table IV.

TABLE IV

THE HYDROLYSIS OF α-(2-FLUORENYL)-ETHYL CHLORIDE IN 80% AQUEOUS ACETONE AT 12.00°
Concn., 0.01002 *M*

Time, sec.	NaOH[a], ml.	$k \times 10^5$, sec.$^{-1}$
0	0.501	..
1290	.855	9.58
2600	1.168	9.51
4010	1.470	9.55
5870	1.820	9.67
7985	2.140	9.68
10870	2.481	9.67
14490	2.784	9.56
∞	3.546	..

THE HYDROLYSIS OF α-(4-BIPHENYLYL) ETHYL CHLORIDE IN 80% AQUEOUS ACETONE AT 40.00°
Concn., 0.01017 *M*

Time, sec.	NaOH[a], ml.	$k \times 10^5$, sec.$^{-1}$
0	0.306	.
2370	.639	4.51
5970	1.100	4.63
9570	1.460	4.52
13170	1.790	4.56
16290	2.030	4.56
23970	2.494	4.57
∞	3.594	..

[a] 0.02803 *N*.

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BRYN MAWR, PENNA.

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(27) We are indebted to Miss N. Pearson, who prepared most of the ketones and the known carbinols during her tenure of a fellowship at Bryn Mawr College.

(28) J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

[CONTRIBUTION NO. 2173 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

On Some *cis*-Forms of Phenylundecapentaenal

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All-*trans*-11-phenyl-2,4,6,8,10-undecapentaenal (I) can be rearranged to give four *cis* isomers, termed I–IV. The pertinent experimental conditions, relative thermo- and photostabilities and certain interconversions are described. Some connected spectroscopic phenomena are discussed and tentative configurational assignments are made.

While the stereoisomerization of some α,ω-diphenylpolyenes,[1] $C_6H_5(CH{=}CH)_nC_6H_5$, and symmetrical azines,[2] $C_6H_5(CH{=}CH)_nCH{=}N{-}N{=}CH(CH{=}CH)_nC_6H_5$, was studied earlier, *cis* forms of phenylpolyene aldehydes, $C_6H_5(CH{=}CH)_nCHO$, containing a rather high number of conjugated double bonds in an unbranched chain, do not seem to be known.

All-*trans*-11-phenylundecapentaenal ($n = 5$) was first obtained by Kuhn and Wallenfels,[3] then by Schmitt[4] who used a modified procedure. Theoretically, the molecules of this unsymmetrically built compound may assume 32 spatial configurations, the all-*trans* form included.[1e] We find

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(1) (a) Diphenylbutadienes: F. Straus, *Ann.*, **342**, 190 (1905); C. Kelber and A. Schwarz, *Ber.*, **45**, 1946 (1912); E. Ott and R. Schröter, *ibid.*, **60**, 624 (1927); A. Sandoval and L. Zechmeister, THIS JOURNAL, **69**, 553 (1947); J. H. Pinckard, B. Wille and L. Zechmeister, *ibid.*, **70**, 1938 (1948). (b) Diphenylhexatrienes: K. Lunde and L. Zechmeister, *ibid.*, **76**, 2308 (1954). (c) Diphenyloctatetraenes: L. Zechmeister and A. L. LeRosen, *ibid.*, **64**, 2755 (1942); L. Zechmeister and J. H. Pinckard, *ibid.*, **76**, 4144 (1954). (d) Biphenylene derivatives: E. F. Magoon and L. Zechmeister, *ibid.*, **77**, 5642 (1955). (e) Survey articles: L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944); *Experientia*, **10**, 1 (1954).

(2) J. Dale and L. Zechmeister, THIS JOURNAL, **75**, 2379 (1953).

(3) R. Kuhn and K. Wallenfels, *Ber.*, **70**, 1331 (1937).

(4) J. Schmitt, *Ann.*, **547**, 270 (1941).