Substituent Constants for Polycyclic Aromatic Hydrocarbons. I. Solvolysis of Arylmethylmercuric Perchlorates in Acetic Acid[1,2]

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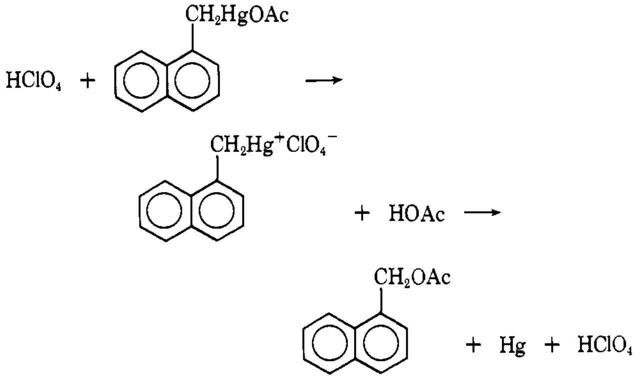
Abstract: The rates of solvolysis of ten arylmethylmercuric perchlorates in acetic acid at 24.90° have been determined. The reactivity index, ΔE_π, which represents the π-electron energy difference between the hydrocarbon, ArH, and the carbonium ion intermediate, $ArCH_2^+$, is used to correlate the rate constants. Both the HMO quantities calculated by Streitwieser and the SCF–MO quantities calculated by Dewar are used. The HMO energies generate the usual dual correlation lines which separate compounds into α-naphthyl- and β-naphthyl-type structures. A single correlation line with scatter results for the SPO values calculated for fixed β and carbon–carbon bond lengths. A comparison of the data with those of other solvolytic systems is given. An approach originated by Streitwieser is employed and "ρ" = 4.95 is obtained. The magnitude of the positive charge generated in the transition state is larger than for the reaction of arylmethyl chlorides and tosylates. Accordingly, the solvolysis system studied is better suited than others to serve as a standard for the evaluation of both MO quantities and empirical constants. Streitwieser "σ" values are reevaluated for 1-naphthyl and 2-phenanthryl and are calculated for 4-phenanthryl, 1-anthryl, and 9-fluorenyl. Brown σ^+ values are calculated by using a substituted benzyl correlation line and are compared with values obtained from solvolytic and aromatic substitution reactions. The σ_r values of Streitwieser also are examined.

The experimental knowledge of the reactivity of polycyclic aromatic compounds is relatively small when compared to the theoretical treatments which have been derived in the last two decades. Accordingly, our interest and approach has involved the pursuit of additional experimental systems which may be used to provide criteria for the testing of presently known theoretical and empirical constants.

The solvolytic behavior of organomercuric salts in a number of solvents indicates that participation of the solvent and the leaving group in stabilizing the incipient carbonium ion is less important than in the related reactions of tosylates and halides.[3] The rates of solvolysis of organomercuric salts are very dependent upon the structure of the resultant carbonium ion. Therefore, the relatively high positive charge generated in the solvolysis of arylmethylmercuric salts should provide a sensitive and accurate probe of the function of structure on both molecular orbital quantities and empirical constants.

Results

1-Naphthylmethylmercuric acetate in a solution of acetic acid containing perchloric acid solvolyzes to yield 99% of the theoretical quantity of 1-naphthylmethyl acetate and 97% of the theoretical quantity of mercury.



The rate constants for solvolysis of the arylmethylmercuric perchlorates were obtained at 24.90 ± 0.03° in anhydrous acetic acid. The arylmethylmercuric perchlorates were formed by addition of a standard solution containing a known catalytic amount of perchloric acid (0.001 *M*) to a solution containing a weighed quantity of the corresponding arylmethylmercuric acetate. The formal concentrations of the arylmethylmercuric species were maintained at 0.02 *M*. The reaction was followed by removing aliquots from the reaction mixture and quenching them in an excess quantity of a standard sodium thiocyanate solution. The quantity of excess thiocyanate was determined by titration with standard silver nitrate to a ferric ion end point. The pseudo-zero-order rate constants were converted to first-order rate constants[3] which are reproducible to ±2%. The first-order rate constants and the logarithm of the rates relative to benzylmercuric perchlorate are reported in Table I.

Table I. Solvolysis Data for Arylmethylmercuric Perchlorates ($ArCH_2HgClO_4$) in Acetic Acid at 24.90°

Compd	Nucleus	k, sec^{-1}	Log k_{rel}
1	Phenyl	9.6×10^{-5}	0.0
2	1-Naphthyl	4.0×10^{-3}	2.62
3	1-(2-Methylnaphthyl)	5.0×10^{-2}	3.72
4	2-Naphthyl	3.1×10^{-4}	1.51
5	2-Phenanthryl	1.5×10^{-4}	1.19
6	3-Phenanthryl	1.9×10^{-3}	2.30
7	4-Phenanthryl	8.6×10^{-3}	2.95
8	9-Phenanthryl	4.7×10^{-3}	2.69
9	1-Anthryl	1.1×10^{-1}	4.06
10	9-Fluorenyl	2.7×10^{-4}	1.45

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[1] This research was supported in part by a Grant in Aid from The Ohio State University.

[2] Abstracted from the Ph.D. Thesis of B. G. van Leuwen, The Ohio State University, 1968.

[3] F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961); **89**, 363, 367 (1967).

Discussion

Molecular Orbital Correlations. The stabilization afforded a developing carbonium ion reflects the ability of the molecule to disperse that charge and is related to the increase in total π energy of an aromatic system as a result of the formation of an additional p orbital which can conjugate with the π system. Comparison of the π-energy differences of carbonium ions and the corresponding aromatic hydrocarbons with the relative reactivities of a series of reference compounds results in linear free energy relationships.[4]

A correlation of the logarithms of the relative rates for arylmethylmercuric perchlorates with ΔE_π (HMO)[5,6] in units of β is shown in Figure 1. It is apparent that, with the exception of 1-(2-methylnaphthyl)methyl and 4-phenanthrylmethylmercuric perchlorate which will be discussed separately, there are two linear correlations. 9-Fluorenylmercuric perchlorate will also be discussed separately. One correlation line represents the β-naphthyl-type compounds and the other the α-naphthyl-type compounds where there is a *peri*-hydrogen interaction. Similar correlations have been obtained for other solvolysis data.[4] The *peri*-hydrogen apparently sterically interferes with a methylene hydrogen of the developing carbonium ion prohibiting maximum overlap of the p orbital with the π system and retarding the rate of reaction from that to be expected in the absence of the steric effect. The slopes of the two lines are not parallel in keeping with Streitwieser's statement that there is little justification for the correlation lines being parallel.

Dewar has calculated the relative energy differences between arylmethyl cations for the parent hydrocarbons by four variations of the SCF method.[7] PPP and SPO values for both fixed β and C–C bond length and self-consistent β and C–C bond length are available for many of the common aromatic rings. While Dewar states that each of the SCF methods gives a better correlation of the experimental rate factor for aromatic ring nitration than does the Hückel method, Berliner has pointed out that the correlations for aromatic ring bromination[8] are satisfactory for all parameters including the simple HMO method. Dewar has shown that the SCF calculations do not show the distinction between the solvolysis rates of α-naphthylmethyl-type chlorides and β-naphthylmethyl-type chlorides in moist formic acid. Accordingly, one correlation line suffices to account for the reactivity of both types of compounds, and the duality of ΔE_π correlation by HMO is removed. Berliner correlated the rates of bromination of aromatic hydrocarbons with both the solvolysis rates of arylphenylmethyl chlorides and the solvolysis rates of α-arylethylchlorides and found that the compounds group themselves approximately into two classes. Therefore, Berliner questioned Dewar's suggestion that the occurrence of two lines for solvolysis systems as a function of HMO parameters is due to deficiencies in the method stem-

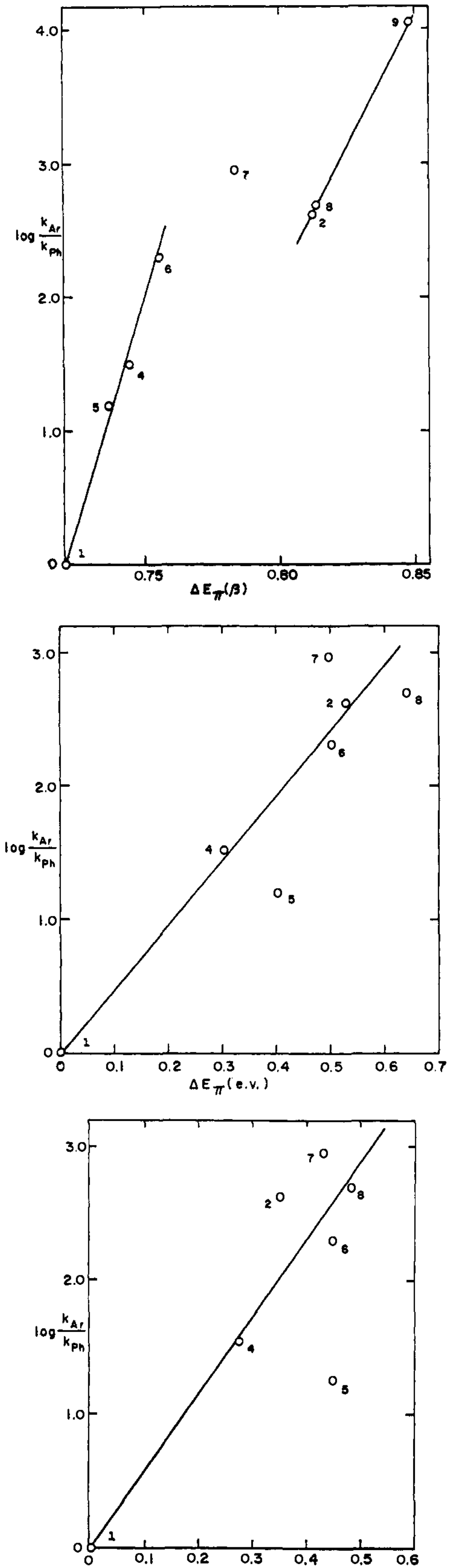

Figure 1. π-Energy differences between arylmethyl cations and parent hydrocarbons *vs.* logarithms of relative rates of solvolysis in acetic acid: top, HMO; middle, SPO with fixed β; bottom, SPO with self-consistent β.

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(4) A. Strietweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 12.

(5) A. Streitwieser, Jr., and C. Coulson, "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965.

(6) A. Streitwieser, Jr., and J. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. 1 and 2, Pergamon Press, London, 1965.

(7) M. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, 87, 4414 (1965).

(8) L. Altschuler and E. Berliner, *ibid.*, 88, 5837 (1966).

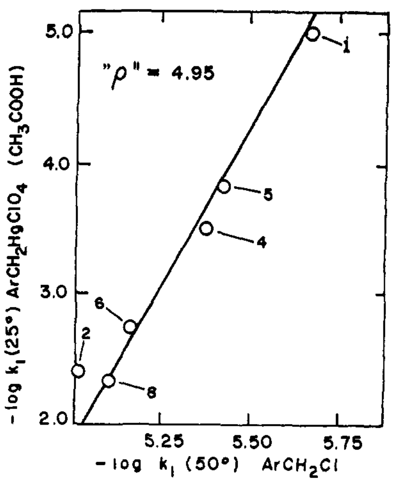

Figure 2. Correlation of rates of solvolysis of $ArCH_2HgClO_4$ with rates of solvolysis of $ArCH_2Cl$.

ming from the neglect of electron repulsion terms in the first-order treatment. Berliner suggests that the lower reactivity of α-naphthyl-like compounds is real and inherent in these systems.

Correlations of the solvolysis rates for arylmethylmercuric perchlorates with both SPO parameters calculated by Dewar are shown in Figure 1. As in the case for electrophilic substitution, ΔE_π calculated with self-consistent β values shows considerably more scatter than for fixed β values. One line suffices to correlate the data for three β-naphthyl-type compounds (*i.e.*, phenyl, 2-naphthyl, and 3-phenanthryl) and two α-naphthyl-type compounds (*i.e.*, 1-naphthyl and 9-phenanthryl). The significant deviations from the lines include both 1-naphthyl-type (9-phenanthryl) and 2-naphthyl-type (2-phenanthryl) compounds. The small number of compounds studied may not constitute a fair test of the SPO method, but the deviation of the two points from the line appear to make the correlation line of less utility than the HMO lines. Steric features should be important in compounds such as phenylarylmethyl chlorides and α-arylethyl chlorides. However, the solvolysis of the arylmethyl chlorides and arylmethylmercuric perchlorates should proceed *via* a transition state in which steric effects are less severe at the reaction center. Unfortunately these latter compounds do not allow a ready distinction between the relative advantages of the HMO and SPO correlation methods.

"σ" Parameters. Streitwieser has correlated a number of rate constants for the solvolysis of side-chain-substituted aromatic hydrocarbons with a modified Hammett equation[4] where "σ" is characteristic of the arylmethyl moiety and "ρ" is characteristic of there action. The solvolysis of arylmethyl halides in 80% aqueous ethanol is the reference system with a "ρ" of 1.00. The "σ" values are defined from the rates of the reference system and may be used to correlate rates at a side-chain center for other substrates in a variety of solvents.

A correlation of $-\log k_1(ArCH_2HgClO_4)$ in acetic acid with $-\log k_1(ArCH_2Cl)$ in 80% aqueous ethanol is shown in Figure 2. With the exception of 1-naphthyl, a good linear correlation is obtained with "ρ" = 4.95. The reported solvolysis rate for 1-naphthylmethyl chloride in 80% aqueous ethanol is faster than 9-phenanthrylmethyl chloride. This order of reactivity does not agree with the prediction on the basis of ΔE_π values obtained by either the HMO or SCF calculations. In our system, as predicted, 9-phenanthryl is faster than 1-naphthyl. It appears that the anomalous value is probably 1-naphthylmethyl chloride in 80% aqueous ethanol. Therefore, the correlation line excludes this value.

Using the relative rates obtained for arylmethylmercuric perchlorates and "ρ" = 4.95, the "σ" values were calculated and are reported in Table II. The values calculated by Streitwieser are listed for comparison. With exception of 1-naphthyl and 2-phenanthryl the agreement between the "σ" constants is very good. The "σ" values for 4-phenanthryl, 1-anthryl, and 9-fluorenyl substituents have not been previously assigned. If "σ" is plotted *vs.* ΔE_π (HMO), a linear correlation results, and the slope multiplied by the "ρ" gives the effective β (83 kcal/mol) for the reaction. The value of effective β and the magnitude of "ρ" are larger than those observed in the other system.[4]

Table II. "σ" Values

Aryl	"σ"	This work
Phenyl	0.0	0.0
1-Naphthyl	0.68	0.53
2-Naphthyl	0.31	0.31
2-Phenanthryl	0.30	0.24
3-Phenanthryl	0.46	0.47
4-Phenanthryl		0.60
9-Phenanthryl	0.56	0.54
1-Anthryl		0.82
9-Fluorenyl		0.29

σ^+ Parameters. Stock and Brown[9] have presented the development of the quantitative treatment of directive effects of substituents in aromatic hydrocarbons in concise historical perspective. The models for the evaluation and testing of the constancy of σ^+ constants of ring substituents are very adequately described. The σ^+ parameters derived from studies of the phenyldimethylcarbinyl chlorides are in agreement with the σ^+ values derived from data on electrophilic substitution. While the σ^+ constants accurately describe the influence of substituents on aromatic substitution, the rates of reaction for attached side-chain sites are not as adequately correlated by these constants.

Stock and Brown state, "The conclusion that the substituent constants for electrophilic substitution reactions are far more constant than the values for the side-chain reactions is inescapable."

Extension of Brown's procedures to multi-ring aromatic hydrocarbons to yield σ^+ constants is hindered by the paucity of data. There are a limited number of reliable quantitative data for the electrophilic substitution reactions of multi-ring aromatic hydrocarbons. The extended selectivity treatment cannot be used under such limited conditions. The extended selectivity treatment of reactions at the 2 position of naphthalene yields a correlation line with somewhat larger deviations than those observed in phenyl-substituted com-

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(9) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

pounds. The σ^+ constants for 2-naphthyl based on the available data are -0.24 and -0.27 for the selectivity relationship and the extended selectivity relationship, respectively. On the basis of the solvolysis of β-naphthyldimethylcarbinyl chloride the σ^+ constant is -0.135.

In this work the standard reaction for the definition of σ^+ constants is the correlation line ($\rho^+ = -7.0$) for the solvolysis rates of substituted benzylmercuric perchlorates.[10] For the solvolysis of 2-naphthylmercuric perchlorate the $\sigma^+ = -0.20$ is obtained. This value is closer to those obtained from electrophilic substitution than is the value derived from the solvolysis of the tertiary chloride.

The σ^+ constants for other β-type-substituted compounds examined in this work are compared in Table III with those for the solvolysis of the aryldimethylcarbinyl chloride and α-arylethyl chlorides. In addition, the available data on nitration and chlorination of hydrocarbons are listed. For all compounds where comparison can be made the σ^+ values derived in this work are more negative than the values derived from the solvolysis of aryldimethylcarbinyl chlorides and are less negative than the values derived from electrophilic aromatic substitution. Unfortunately the data for aromatic substitution are subject to more experimental uncertainty than for the solvolysis reactions. However, it does appear that the σ^+ constants vary and may reflect the operation of variables that differ from reaction to reaction.

Table III. σ^+ Constants of Polycyclic Aromatic Hydrocarbons

Aryl group	*a*	*b*	*c*	*d*	*e*
1-Naphthyl	−0.35		−0.45	−0.50	−0.44
2-Naphthyl	−0.20	−0.135	−0.28		−0.27
2-Phenanthryl	−0.20	−0.119	−0.33		
3-Phenanthryl	−0.31	−0.196	−0.41		
9-Phenanthryl	−0.36		−0.45	−0.62	−0.53
9-Fluorenyl	−0.18				

[a] This work. [b] Solvolysis of aryldimethylcarbinyl chlorides: H. C. Brown and T. Inukai, *J. Am. Chem. Soc.*, **83**, 4825 (1961); E. Berliner and N. Shieh, *ibid.*, **79**, 3849 (1957). [c] Nitration.[9] [d] Chlorination.[9] [e] Bromination calculated from ref 8 using $\rho = -12.1$.[9]

The relative differences between the σ^+ values for solvolysis of arylmethylmercuric perchlorates and aromatic nitration as a function of ring position are comparable. The difference between the values for the two reaction systems in the case of 1-naphthyl and 2-naphthyl are proportionately the same. Therefore there is little indication of a significant difference in the steric effects for the two reactions. The solvolysis of the mercury compounds might serve as a model for σ^+ constants for polycyclic aromatic hydrocarbons when aromatic electrophilic reactions are lacking or of questionable experimental validity. The solvolysis reaction has the advantage of yielding a specific value for a ring position without a dependence on isolation of small quantities of products. The question of the constancy of σ^+ constants for polycyclic aromatic compounds must remain open until additional reaction systems are examined.

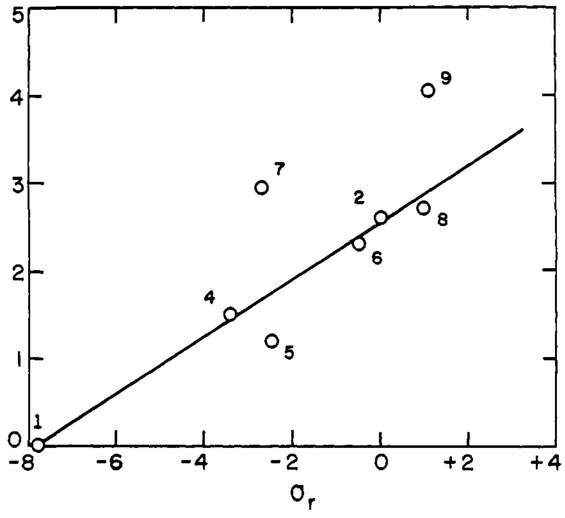

Figure 3. Correlation of rates of solvolysis with σ_r values.

σ_r Values. Streitwieser[4] has defined a $\sigma_r\rho^*$ relationship for electrophilic aromatic substitutions in which the standard reaction is the protonation equilibrium. Unfortunately the σ_r values are known only for the most reactive positions, and therefore, the method is as limited as the σ^+ approach using partial rate factors for reactions such as chlorination or nitration. The σ_r values for unreactive positions are calculated from ρ^* value for other electrophilic reactions whose log k_{rel} are linearly related to log K_{basicity}. Therefore, the σ_r values for unreactive position have the same experimental limitations built into them as do partial rate factors, *i.e.*, isolation of small quantities of kinetically controlled reaction products.

A plot of the logarithms of the relative rate constants for the solvolysis of arylmethylmercuric perchlorates *vs.* σ_r values is given in Figure 3. Excluding the 4-phenanthryl compound, there are two significant deviations from the apparent best line. The σ_r value for 2-phenanthryl is too large and the σ_r value for 1-anthryl is too small. Both of these values are derived from data in which the indicated ring positions are relatively unreactive. The 2 position of phenanthrene is the least reactive, excluding the 4 position from consideration. The 1-anthryl position is 8 powers of 10 less basic than the 9-anthryl position according to the chosen σ_r values. Streitwieser states that the σ_r values are "clearly first approximations because of neglect of possible varying steric effects in different reactions and because of the experimental errors in the original determinations." The solvolysis data suggest the σ_r for the 2 position of phenanthrene and the 1 position of anthracene ought to be closer to -4 and $+5$, respectively.

The $\rho^* = 0.31$ for the solvolysis line shown in Figure 3 indicates that the reaction presented in this paper is quite similar in electronic features to the nitration reaction ($\rho^* = 0.26$). This fact reinforces the previously stated similarity noted for the σ^+ values for the two reactions.

Structural Contribution. An additional steric factor has been introduced into 1-(2-methylnaphthyl)methylmercuric perchlorate. A methyl group at a position adjacent to the reaction center in a molecule which already has a *peri*-hydrogen interaction should increase

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(10) R. J. Ouellette, Ph.D. Thesis, The University of California, 1962.

the steric hindrance exerted upon the developing carbonium ion and should result in a rate retardation. However, the rate is 13 times faster than 1-methylnaphthyl indicating that the electronic contribution of the methyl group also must be considered. Neglecting steric factors the electronic effect of a methyl group in the 2 position should be comparable to a methyl group in the 4 position. The difference in $-\log k_1$ for 4-methylbenzylmercuric perchlorate and benzylmercuric perchlorate at 25° in acetic acid is 2.33.[10] If an extrapolation to the naphthyl system is valid and 1-naphthylmethylmercuric perchorate is used as a reference, the value of $-\log k_1$ for 1-(2-methylnaphthyl)methylmercuric perchlorate should be -0.17 in the absence of steric effects. The observed rate is approximately 20 times slower. This assessment of the magnitude of the steric effect is approximate. A similar effect has been observed in 9-(chloromethyl)anthracene which has two *peri*-hydrogen interactions.[11,12]

The steric crowding at the reaction center in 4-phenanthrylmethylmercuric perchlorate is the most severe of the molecules studied. One might conclude *a priori* that the reactivity of the molecule should be significantly retarded compared with β-type and α-type compounds. The observed rate is indeed 15 times slower than compounds on the α-correlation line but is 28 times faster than compounds on the β-correlation line. On the basis of the SCF correlation line, the compound solvolyzes 5 times faster than predicted on the basis of the planar model. The only relative rate data available which include 4-phenanthrylmethyl intermediates were reported by Fierens.[13] He studied not only the solvolysis of the chloride in a ternary mixture of dioxane, water, and formic acid but also the S_N2 displacement by iodide ion in acetone. 4-Methylphenanthrene is known to be nonplanar,[14] and the relatively rapid rate of solvolysis might be due to stabilization of the developing carbonium ion by the proximate terminal ring. In a planar model this would not be possible, but in a warped structure the developing p orbital may approach the approximate π system in an orientation suitable for overlap. The warped ring system should effectively lower the actual value of ΔE_π from that predicted on the basis of a planar molecule, so that the observed rate is even more indicative of an unusual stabilizing influence.[15,16]

9-Fluorenyl derivatives have been studied, but no correlation has been attempted with ΔE_π values. Streitwieser calculates the resonance stabilization energy of 9-fluorenyl anion by subtracting the total π energy of biphenyl from the calculated total π energy of the 9-fluorenyl anion. If this same procedure is applied to the 9-fluorenyl cation using the calculated values, a ΔE_π value of 1.160 is obtained. If it is assumed that the steric requirements of the transition state of the 9-fluorenyl derivative are the same as β-type compounds, a predicted ΔE_π value of 0.74 is obtained using our rate data. The 9-fluorenyl anion is a $4n + 2$ π-electron system while the 9-fluorenyl cation is analogous to the cyclopentadienyl carbonium ion. It is apparent that biphenyl cannot be used as a model ArH system for the calculation of ΔE_π for the 9-fluorenyl cation, and therefore, no reference compound is available for a theoretical calculation. The experimental value of ΔE_π obtained from the solvolysis of 9-fluorenylmercuric perchlorate is probably a reasonable approximation of the true value. A "σ" constant of 0.29 has been assigned to the 9-fluorenyl cation. The stabilization of 9-fluorenyl cation is only slightly better than the benzyl cation.

Experimental Section

The arylmethyl halides necessary for this study have been prepared previously.[17-20] The physical constants were in agreement with literature values.

Each halide was converted to the Grignard reagent by the use of a modified version of the Grignard machine described by Rowlands.[21] All glassware was clean, dry, and maintained under an atmosphere of nitrogen throughout the course of the reaction. Amalgamation of the magnesium was essential for the efficient use of the cyclic reactor. The magnesium was washed by refluxing with ether prior to the reaction, and ethylene dibromide was added to further activate the metal. Mercuric halides were placed in the reservoir flask to react with the Grignard after its formation.

The organomercuric halides were converted into the organomercuric acetates without purification. The halides are difficult to crystallize due to their low solubility in many common solvents. The organomercuric acetates can be purified easily when slightly impure mercuric halides are used. The mercuric acetates were prepared from the halides by stirring for 24 hr with an equimolar amount of silver acetate in anhydrous methanol. The solution was filtered, and the methanol was evaporated. The crystalline product was crystallized from hexane or heptane. The analysis and melting points are listed in Table IV.

Table IV. Elemental Analysis of Arylmethylmercuric Acetates

	Calcd, %			Found, %			
Compd	C	H	Hg	C	H	Hg	Mp, °C
2	38.93	3.02	50.06	38.90	2.96	50.22	85.0–87.0
3	40.53	3.40	48.35	40.38	3.53	48.23	134.0–135.0
4	38.93	3.02	50.06	38.89	3.13	50.09	139.5–140.5
5	45.25	3.13	44.51	45.20	3.24	44.72	124.0–125.0
6	45.25	3.13	44.51	45.51	3.22	44.44	153.5–154.5
7	45.25	3.13	44.51	45.10	3.01	44.37	148.0–149.0
8	45.25	3.13	44.51	45.19	3.00	44.43	158.0–159.0
9	45.25	3.13	44.51	45.55	3.16	44.32	190.0–191.0
10	42.38	2.84	47.21	42.31	2.78	47.08	178.0–179.0

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(11) M. Fierens and J. Berkowitch, *Tetrahedron Letters*, No. 1, 129 (1957).

(12) M. Planchen, P. Fierens, and R. Martin, *Helv. Chim. Acta*, 42, 517 (1959).

(13) P. J. C. Fierens, H. Hannaert, J. Van Rysselberge, and R. H. Martin, *ibid.*, **38**, 2009 (1955).

(14) C. Reid, *J. Mol. Spectry.*, **1**, 18 (1957).

(15) Rate acceleration in substitution in the 4 position of phenanthrene has been examined and discussed by de la Mare.[16]

(16) P. B. D. de la Mare and H. D. Ridd, "Aromatic Substitution," Academic Press, New York, N. Y., 1959.

(17) J. Shoesmith and H. Rubli, *J. Am. Chem. Soc.*, **49**, 3098 (1927).

(18) G. Darzens and A. Levy, *Compt. Rend.*, **202**, 73 (1936).

(19) A. Kliegl, A. Wunch, and R. Weigele, *Ber.*, **59**, 631 (1926).

(20) P. Fierens, R. Martin, and J. van Rysselberge, *Helv. Chim. Acta*, **38**, 2005 (1955).

(21) D. Rowlands, M.S. Thesis, The Ohio State University, 1948.