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An Examination of the Applicability of the Selectivity Relationship to the Electrophilic Substitution Reactions of Biphenyl and Fluorene[1-3]

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The partial rate factors for the substitution reactions of biphenyl and fluorene have been examined for adherence to the Selectivity Relationship. The data for *meta*-substitution in biphenyl provide reasonable agreement with the linear free energy treatment. The deviations for the *m*-phenyl group, although not small, are entirely random. The value of $\sigma^+_{m\text{-Ph}}$ is estimated to be 0.05 ± 0.01. On the other hand, the results for electrophilic substitution *para* to the phenyl group exhibit two important anomalies. First, analysis of the *para* observations for adherence to the Selectivity treatment reveals the inapplicability of the relationship. Second, the degree of activation induced in the benzene ring by this phenyl substituent is far less than anticipated on the basis of its stabilization of other electron-deficient systems. These facts are interpreted in terms of the variable and depressed resonance stabilization of the activated complex. The inhibition of resonance is attributed to the steric energy barrier to the achievement of coplanarity of the phenyl nuclei. The view was subjected to test through an examination of the substitution reactions of fluorene. The anomalies apparent in the substitution data for biphenyl appear to be absent for substitution in the 2-position of fluorene. First, the available data appear to be correlated by the Selectivity Relationship with satisfactory precision. Second, the 2-position in fluorene, corresponding to the *para* position in biphenyl, is greatly activated toward electrophilic substitution. Thus, the two enigmas observed for biphenyl are absent in planar fluorene supporting the contention of a true steric inhibitory factor as an important influence on the reactivity of biphenyl.

Introduction

Several years ago, it was suggested that the electrophilic substitution reactions of toluene[6-8] and other monosubstituted benzenes adhered to a linear free energy relationship. At the time the available data did not permit a rigorous test of the proposal. Accordingly a research program was initiated to obtain the necessary information.

These observations with additional data from the literature recently provided the basis for a critical examination of the applicability of the treatment to the substitution reactions of toluene,[9] *t*-butylbenzene[10] and anisole.[11]

For toluene, an examination of the available data for 47 electrophilic substitution reactions rigorously established the applicability of the Selectivity treatment to this compound.[9] Moreover, the quantitative data for the *p*-*t*-butyl substituent were correlated satisfactorily. The deviations observed were no greater than had been found for the methyl group. The experimental observations relating to the *m*-*t*-butyl substituent were more limited and the deviations appeared to be somewhat larger. However, these discrepancies were small in view of the experimental errors involved in the determination of the minor quantities of the *meta* isomer formed in these reactions.[10] Quantitative data for the substitution reactions of anisole are even more limited. The available information, however, is correlated by the Selectivity Relationship with excellent precision.

In 1954, de la Mare pointed out the existence of a major discrepancy in the observations for the chlorination of biphenyl in an attempted correlation based on the Hammett equation.[12] More recently Eaborn has examined the available data for the substitution reactions of biphenyl.[13] His analysis revealed the ratio log p_f^{Ph}/log p_f^{Me} to be quite variable.[13] Moreover, the observation that the phenyl substituent failed to enhance the substitution reaction to the extent anticipated from its behavior in other systems indicated the area to be a fruitful one for further investigation. Accordingly, we decided to include biphenyl in our survey of the applicability of the Selectivity Relationship.

Data for the nitration,[14] hypobromous acid bromination,[15] brominolysis of the arylboronic acids[16] and detrimethylsilylations[13,17] had already appeared in the literature. To provide a broad spectrum on the selectivity scale, the mercuration,[18] ethylation,[19] acylation[20] and non-catalytic bromination[21] of biphenyl were investigated. In the interval several studies have been reported concerning the results for other reactions.[22]

In the course of the experimental work, it became clear the observations for the substitution reactions of biphenyl constituted a real deviation from the Selectivity Relationship. The non-coplanar configuration of biphenyl offered an attractive explanation for the deviations. Accordingly, the study was extended to include selected substitution

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(9) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

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(12) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

(13) (a) F. B. Deans, C. Eaborn and D. E. Webster, *ibid.*, 3031 (1959); (b) C. Eaborn and R. Taylor, *ibid.*, 1012 (1961).

(14) M. J. S. Dewar, T. Mole and W. T. Warford, *ibid.*, 3576 (1956).

(15) P. B. D. de la Mare and M. Hassan, *ibid.*, 3004 (1957).

(16) H. G. Kuivila and L. E. Benjamin, *J. Am. Chem. Soc.*, **77**, 4834 (1955).

(17) C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

(18) H. C. Brown, M. Dubeck and G. Goldman, *J. Am. Chem. Soc.*, **84**, 1229 (1962).

(19) H. C. Brown and A. Neyens, *ibid.*, **84**, 1233 (1962).

(20) H. C. Brown and G. Marino, *ibid.*, **84**, 1236 (1962).

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(22) We are indebted to C. Eaborn, P. B. D. de la Mare, O. Simamura and R. A. Benkeser for informing us of their observations prior to publication.

TABLE I

SUMMARY OF PARTIAL RATE FACTORS AND ASSOCIATED QUANTITIES FOR TOLUENE, BIPHENYL AND FLUORENE

	Toluene[b]				Biphenyl					
Reaction, conditions[a]	o_f^{Me}	m_f^{Me}	p_f^{Me}	S_f	o_f^{Ph}	m_f^{Ph}	p_f^{Ph}	$\log p_f^{Ph}/\log p_f^{Me}$	Fluorene 2-Fl_f	Ref.[c]
Bromn., Br_2, 85% HOAc, 25°	600	5.5	2420	2.644	37.5	0.3[d]	2920	1.03	6.3×10^6	21
Chlorn., Cl_2, HOAc, 25°	617	4.95	820	2.219	338	.74[d]	600	0.95	3.4×10^5	23
Acetyln., CH_3COCl, $AlCl_3$, $C_2H_4Cl_2$, 25°	4.5	4.8	749	2.192		.3[d]	248	.82	3.8×10^4	20
Benzoyln., C_6H_5COCl, $AlCl_3$, $C_2H_4Cl_2$, 25°	32.6	4.9	626	2.107		.3[d]	245	.85		20
Tritium exch., ArT, H_2SO_4,H_2O-CF_3CO_2H, 25°		9.2	702	1.883	133		143	.76		13b, 24
Tritium exch., ArT, $HClO_4$, H_2O–CF_3CO_2H, 25°	330	7.2	313	1.638	52	.68	52	.69		13b, 24
Tritium exch., ArT, CF_3CO_2H, 70°			450				163	.83	1.68×10^4	57
Nitrtn., $AcONO_2$, Ac_2O, 25°	47	3.0	62	1.314	18.5		11	.58	2.10×10^3[e]	14, 25
Nitrtn., $AcONO_2$, Ac_2O, 25°	47	3.0	62	1.314	41		38	.88		26
Bromn., HOBr, $HClO_4$, 50% dioxane, 25°	76	2.5	59	1.373	10.7	.28	15.6	.67		15
Brominol., $ArB(OH)_2$, Br_2, 20% HOAc, 25°		3.33	78.5	1.373			21.7	.70		16
Bromodesilyln., $ArSiMe_3$, Br_2, 98.5% HOAc	82	2.9	49	1.227	1.18	.41	12.5	.65		27
Protodesilyln., $ArSiMe_3$, $HClO_4$, H_2O–MeOH, 51.2°	17.8	2.3	21.1	0.964			3.55	.41	45.6	17, 57
Protodesilyln., $ArSiMe_3$, H_2SO_4, H_2O–HOAc, 50.2°			18.0		5.85	.33	2.83	.36		28
Protodesilyln., $ArSiMe_3$, HCl, HOAc–H_2O, 25°		2.14	20.1	.971			3.22	.39		29
Protodegermyln., $ArGeEt_3$, $HClO_4$, MeOH–H_2O, 50°	12.4	2.10	14.0	.842	3.22		2.69	.37		30
Protodestannyln., $ArSnMe_3$, $HClO_4$, EtOH–H_2O, 50°		1.84	5.5	.476	1.99		1.77	.34		31
Mercuridesilyln., $ArSiMe_3$, 0.2 *M* $Hg(OAc)_2$, HOAc, 25°		2.53	10.8	.630		.68	2.73	.42		29
Mercuridesilyln., $ArSiMe_3$, $Hg(OAc)_2$, 80% HOAc, 25°	11.0	2.5	17.5	.845	2.5	.58	3.3	.42		13a
Mercurn., $Hg(OAc)_2$, HOAc, 25°	5.71	2.23	23.0	1.014	0.089	.787	6.32	.58	1.22×10^2	18
Mercurn., $Hg(OAc)_2$, HOAc, 50°	4.60	1.98	16.8	0.928	.132	.735	5.23	.58		18
Mercurn., $Hg(OAc)_2$, HOAc, 70°	4.03	1.83	13.5	.868	.156	.705	4.52	.58		18
Mercurn., $Hg(OAc)_2$, HOAc, 90°	3.51	1.70	11.2	.819	.216	.664	3.92	.56		18
Ethyln., EtBr, $GaBr_3$, $C_2H_4Cl_2$, 25°	2.69	1.48	5.70	.586	.905	.695	2.23	.45		19
Solvol., $ArCMe_2Cl$, 90% acetone, 25°	3.63	2.00	26.0	1.113		.32	6.52	.57	1.68×10^2	32, 33
Solvol., $ArCMe_2Cl$, EtOH, 25°		2.28	(24.5)[f]	(1.082)		.55	10.5			33

[a] Reaction is presented first followed by electrophilic reagent, catalyst, solvent and temperature. [b] Partial rate factors for toluene and references are presented in ref. 9. [c] References refer to data for biphenyl and fluorene. [d] Based on indirect estimate from relative rate data; see text. [e] Partial rate factors, 3-Fl_f 60 and 4-Fl_f 944 have also been established. [f] Calculated from $\log p_f^{Me} = 4.026 \log m_f^{Me}$.

reactions of planar fluorene. This paper summarizes these results and examines the applicability of a linear free energy relationship to the electrophilic substitution reactions of both biphenyl and fluorene.

Discussion

Summary of Data for Electrophilic Substitution of Biphenyl.—The partial rate factors and associated quantities for the substitution of biphenyl and fluorene are presented in Table I. For convenient comparison, the results for the corresponding reactions of toluene are also included.

The partial rate factors, Table I, are based on isomer distributions, obtained by the application of modern analytical methods, and on relative rates, obtained from kinetic or competitive procedures. With the exception of the few observations discussed in the following paragraph, the results are on a firm experimental basis.

The chlorination of biphenyl in acetic acid has been examined by several investigators.[23] Although the reported relative rates differ significantly,[23] the uncertainty can be tolerated for the purposes of the present treatment. Eaborn and Taylor have recently presented their observation for the tritium exchange reaction.[13b,24] The partial rate factors for *m*- and *p*-phenyl exhibit a reasonable magnitude in view of the behavior of these substituents in other reactions. However, the reported value for m_f^{Me} is too large by a factor of two. This value is essential for the calculation of the Selectivity Factor, S_f. The deviation of this result from the relationship established for toluene is not dissimilar to the observations for a number of other exchange processes.[9] The simple exchange reaction in which the introduction of a proton and the expulsion of a deuterium (or tritium) are both involved in the rate-determining process may possibly constitute a real deviation from the Selectivity Relationship. However, the difficulty may also be primarily experimental in nature—independent workers have failed to agree on the partial rate factors for exchange under sensibly identical conditions.

The nitration of biphenyl with acetyl nitrate in

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(23) P. B. D. de la Mare, D. M. Hall, M. M. Harris and M. Hassan, *Chemistry & Industry*, 1086 (1958). These authors determined k_{BP}/k_B as 422. The ratio is also reported to be 720, (S. F. Mason, *J. Chem. Soc.*, 1233 (1959)) and 1150 (M. J. S. Dewar and T. Mole, *ibid.*, 342 (1957)).

(24) C. Eaborn and R. Taylor, *Chemistry & Industry*, 949 (1959).

(25) M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 3079 (1958).

(26) O. Simamura and Y. Mizuno, *Bull. Chem. Soc., Japan*, **30**, 196 (1957).

(27) C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 4449 (1957).

(28) F. B. Deans and C. Eaborn, *ibid.*, 2299 (1959).

(29) R. A. Benkeser, W. Schroeder and O. H. Thomas, *J. Am. Chem. Soc.*, **80**, 2283 (1958), and unpublished results with T. V. Liston.

(30) C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 297 (1961).

(31) C. Eaborn and J. A. Waters, *ibid.*, 542 (1961).

(32) Y. Okamoto, T. Inukai and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 4972 (1958).

(33) H. C. Brown and T. Inukai, *ibid.*, **83**, 4825 (1961).

acetic anhydride has been studied in independent laboratories, unfortunately with discordant results.[14,25,26] The principal difficulty is the disagreement in the relative rates of nitration. The relative rate, biphenyl to benzene, was determined by a direct competition experiment to be 40.[26] A series of competitive experiments with benzene, phenanthrene and biphenyl indicated the relative reactivity to be 16.[14] Eaborn and his associates studied the acid cleavage of the silanes employing a spectrophotometric method.[17,28,34] Benkeser and his coworkers have investigated the same reaction employing dilatometry.[29] In view of the different experimental conditions employed in each investigation, the small variations in partial rate factors are understandable. The mercuridesilylation reaction has also been studied by these workers. Employing slightly different conditions and methods, the values obtained for m_f^{Me}, m_f^{Ph} and p_f^{Ph} are in essential agreement. There is, however, a major discrepancy in the values obtained for p_f^{Me}.

For comparison with the observations obtained for electrophilic substitution reactions, the relative rates of solvolysis of the *t*-cumyl chlorides in 90% acetone and anhydrous ethanol are also presented in Table I. The data for the reaction in ethanol are included since the relative rate of solvolysis of *m*-phenyl-*t*-cumyl chloride exhibited a significant variation in the two solvents.[32,33]

Biphenyl in the Selectivity Treatment.—Prior to an examination of the substitution reactions of biphenyl, it is of interest to examine the approach adopted for the evaluation of linear treatments for substitution reactions. After the original suggestion of the possible application of a linear free energy relationship to these reactions,[6] de la Mare pointed out that the Hammett σ-constants, based on side-chain reactions of benzene derivatives, did not provide any sensible agreement with experimental facts for either nitration or chlorination.[12]

It was proposed that a new set of electrophilic substitution constants might be successful in achieving the desired correlation.[6] However, the problem was to devise a method for testing the utility of a linear free energy relationship for these reactions without prior knowledge of either the electrophilic substituent constant, σ^+, or the reaction constant, ρ.

This difficulty was overcome by algebraic manipulation of the Hammett eq. 1.

$$\log k/k_0 = \rho\sigma \qquad (1)$$

This provided the expression[7] 2

$$\log p_f^{\mathrm{Me}} = \frac{\sigma^+_{p\text{-}\mathrm{Me}}}{\sigma^+_{p\text{-}\mathrm{Me}} - \sigma^+_{m\text{-}\mathrm{Me}}} \log (p_f^{\mathrm{Me}}/m_f^{\mathrm{Me}}) \qquad (2)$$

$$= \frac{\sigma^+_{p\text{-}\mathrm{Me}}}{\sigma^+_{p\text{-}\mathrm{Me}} - \sigma^+_{m\text{-}\mathrm{Me}}} S_f$$

The derived expression, the Selectivity Relationship,[8] is general and can be written in the form

$$\log (k_{\mathrm{R}}/k_{\mathrm{H}}) = \frac{\sigma^+_{\mathrm{R}}}{\sigma^+_{p\text{-}\mathrm{Me}} - \sigma^+_{m\text{-}\mathrm{Me}}} S_f \qquad (3)$$

Alternatively, one can write

$$\log (k_{\mathrm{R}}/k_{\mathrm{H}}) = (\sigma^+_{\mathrm{R}}/\sigma^+_{p\text{-}\mathrm{Me}}) \log p_f^{\mathrm{Me}} \qquad (4)$$

Thus, a diagram of log $(k_{\mathrm{R}}/k_{\mathrm{H}})$ against S_f provides the means for a test of the adherence of experimental data to a linear relationship without the prior assignment of either substituent or reaction constants.

This approach differs substantially from the familiar Hammett treatment in which the invariance of the substituent constants is assumed. To test a given reaction for conformity to the Hammett treatment, it is customary to plot log $(k_{\mathrm{R}}/k_{\mathrm{H}})$ *versus* the substituent constants. In other words, log $(k_{\mathrm{R}}/k_{\mathrm{H}})$ is plotted against σ, maintaining ρ constant. A reasonable linear correlation is generally considered to indicate adherence of the reaction to the Hammett equation.

On the other hand, the basic assumption, the constancy of the σ values, is not necessarily valid for electrophilic substitution reactions. This research program was designed to test this point for selected substituents. The most direct approach would be to assume the inductive influences operative at the *meta* position are identical in Hammett side-chain and in electrophilic substitution reactions. Thus, the reaction constants could be established from the *meta* reactivity of the substituents under study. A plot of log $(k_{\mathrm{R}}/k_{\mathrm{H}})$ *versus* ρ for the various reactions, maintaining the substituent constant, would test whether the electronic contributions of that particular substituent could be represented satisfactorily by a constant, σ^+_{R}. Again this attack is not feasible because of the experimental difficulties and uncertainties involved in the evaluation of the partial rate factors for *meta* substitution.

In the absence of adequate data to establish the reaction constant ρ with the requisite precision, another method was devised. The Selectivity Factor, S_f, is a quantity proportional to the reaction constant ρ. Likewise the quantity log p_f^{Me} is proportional to ρ. Accordingly, the Selectivity Relationship provides an alternative method for the evaluation of the adherence of experimental data for a given substituent to a linear free energy relationship. Important is the fact that prior assignment of either substituent or reaction constants is unnecessary.

Figures 1 and 2 reveal that plots of log p_f^{Ph} *versus* either the Selectivity Factor, S_f, or log p_f^{Me} exhibit a marked curvature. In contrast to the results for toluene, *t*-butylbenzene and anisole previously examined, the reactivity of the *para* position in biphenyl increases significantly with the increasing electronic demand of the substitution reaction. We must conclude with Eaborn[13] that the substitution reactions of biphenyl do not adhere to the Selectivity Relationship.

It is much more difficult to assess the results for the deactivated *meta* position of biphenyl. The relative reactivity of the *meta* position has been examined in 17 electrophilic reactions. Understandably direct evaluation of the partial rate factor has not been possible in all cases and indirect kinetic relationships were employed to estimate m_f^{Ph} for halogenation and acylation.

Equation 5 is obtained directly from expression 4.

$$\log m_f^{\mathrm{Ph}}/\log p_f^{\mathrm{Me}} = \sigma^+_{m\text{-}\mathrm{Ph}}/\sigma^+_{p\text{-}\mathrm{Me}} \qquad (5)$$

Analysis of the information for *meta* substitution in terms of this expression yields −0.17 ± 0.06 for the

(34) C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 179 (1960).

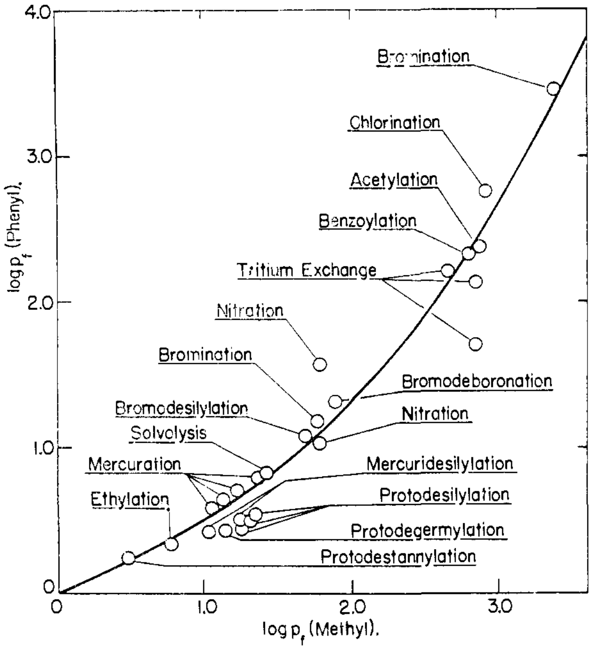

Fig. 1.—Relationship between log p_f^{Ph} and log p_f^{Me} for electrophilic substitution reactions.

ratio of the σ-constants. Excluding the results based on kinetic estimates provides -0.19 ± 0.07 for the ratio. In view of the approximations and experimental difficulties, the constancy of the logarithmic ratio is most encouraging. Graphical presentation of the partial rate factors, Fig. 3, indicates m_f^{Ph} is independent of reagent selectivity. Deviations from the relationship, although not minor, are random. Adoption of $\sigma^+_{p\text{-Me}}$ as -0.270 and the average value of the logarithmic ratio indicates $\sigma^+_{m\text{-Ph}}$ to be 0.05 ± 0.01.

It was previously suggested that the solvolysis of substituted *t*-cumyl chloride might serve as a convenient means of obtaining the values of the σ^+ constants.[35,36] The solvolysis results, Table I, provide $\sigma^+_{m\text{-Ph}}$ constants of 0.109 and 0.054, respectively.[32] The $\sigma^+_{m\text{-Ph}}$ value derived from the solvolysis in ethanol, 0.054, is in good agreement with the value derived from the substitution data.

The Influence of the Phenyl Substituent on Reactivity.—The failure of the data for biphenyl to conform to the Selectivity Relationship creates a serious problem. Will this behavior prove to be relatively general among other benzene derivatives, or is it an exception arising from some unique characteristic of the biphenyl system? It is therefore important to explore in some detail the behavior of the phenyl substituent in influencing reactivity.

The *m*-phenyl substituent reduces the rate of electrophilic substitution in the benzene nucleus, Table I. Qualitatively, this effect is in agreement with the expectation of deactivation as indicated by the increased acidity of *m*-phenylbenzoic acid[37] and the decreased rate of solvolysis of *m*-phenyldimethylcarbinyl chloride.[36] These observations are clearly reflections of the significant $-$I inductive effect of the phenyl group.

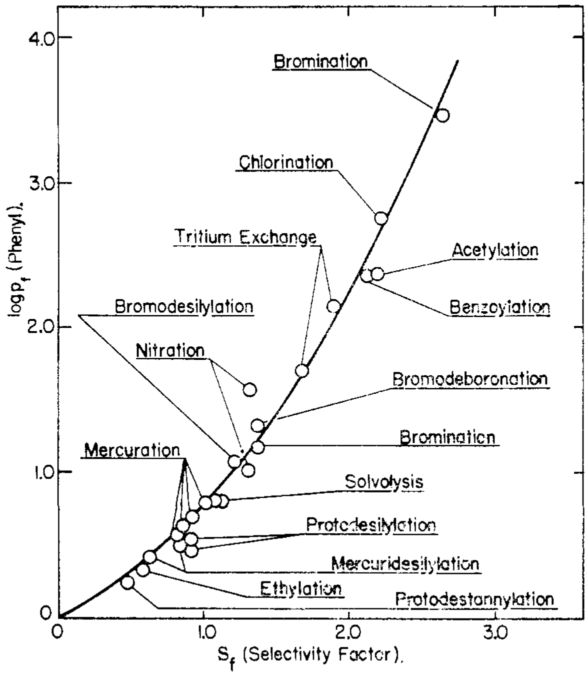

Fig. 2.—Relationship between log p_f^{Ph} and the Selectivity Factor, S_f, for electrophilic substitution reactions.

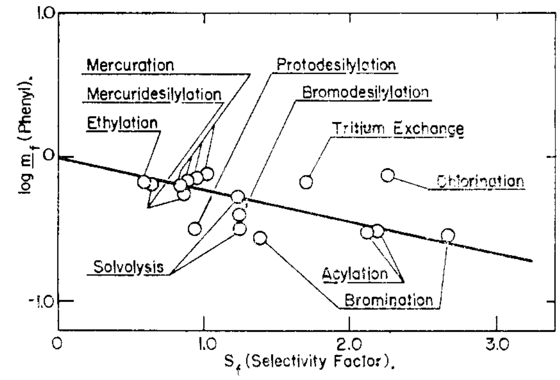

Fig. 3.—Relationship between log m_f^{Ph} and the Selectivity Factor, S_f, for electrophilic substitution reactions.

In constrast, the *p*-phenyl substituent should be capable of resonance contributions to an electron-deficient center. The available evidence for simple aliphatic systems indicates such contributions are large and far outweigh the inductive effect. For example, the ethanolysis of benzyl, α-phenylethyl and benzhydryl chloride are in the order 1.0, 13 and 3500.[38] Similarly, triphenylmethyl chloride solvolyzes 39-fold more rapidly than diphenylmethylcarbinyl chloride.[39]

In a situation where the degree of substitution of the incipient carbonium ion is unchanged, the phenyl group is a more effective electron donor

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[35] Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **79**, 1909 (1957).

[36] H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

[37] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[38] A summary of the data for this series is available in Table 23 of the review, A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

[39] Y. Okamoto, Ph.D. Thesis, Purdue University Libraries, 1957. See also H. C. Brown, "Steric Effects in Conjugated Systems," Butterworths Scientific Publication, London.

than the methyl group by a factor of from 39 to 390.[38]

To restate the problem, two major anomalies are exhibited by the *p*-phenyl substituent in aromatic substituent reactions. First, the activating influence of the phenyl group in the *para* position is not far larger than that of a methyl group. Indeed, the effects are comparable. Second, in contrast to the behavior of *p*-alkyl and *p*-methoxy substituents, the contributions of the phenyl group are variable. The variation is not random but depends on the electron demand exhibited by the reaction. Thus, in the non-selective mercuration, p_f^{Ph} (6.32) < p_f^{Me} (23.0), whereas in the very selective bromination, p_f^{Ph} (2970) > p_f^{Me} (2420). The variation in response to electron demand is illustrated convincingly in Figs. 1 and 2. Consequently, the electrophilic substitution reactions of biphenyl do not conform to a linear free energy relationship.

It is our proposal that both biphenyl anomalies have a common origin in the energy barrier to the achievement of coplanarity between the phenyl nuclei. The suppression of resonance stabilization in the activated complex because of the steric effect provides a rationale for the reduced contribution to reactivity. Further, the variation in resonance interaction as a function of the electron demand of the reaction is readily accommodated by variations in the angle between the phenyl rings.

In the solid state, the aromatic rings of biphenyl[40-42] and *p*-terphenyl[43] are fully coplanar. On the other hand, 1,3,5-triphenylbenzene and 2,6-diphenylnaphthalene are distorted from a planar conformation in the solid.[44] An early electron diffraction investigation of gaseous biphenyl was inconclusive.[45] More recently, Bastiansen and his associates have studied the structure of biphenyl and 4-halobiphenyls in the gas phase by electron diffraction.[46] These workers found a 45° angle between the aromatic rings. Deviations from coplanarity are greater for 2-substituted derivatives. In the extreme case of hexaphenylbenzene, the center ring and its substituted phenyl rings were reported to be orthogonal.[47]

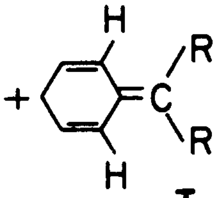
The conformation of biphenyl in solution is not established. It has been argued to be coplanar on the basis of Kerr constants.[48] The problems associated with the interpretation of the ultraviolet spectra have been presented in detail.[49] A more recent investigation of the electronic spectrum of biphenyl and certain derivatives in the solid, solution and vapor states has been interpreted to indicate a 20° deviation from coplanarity in solution.[49a]

In spite of the uncertainty in the conformation of biphenyl in solution, it is not unreasonable to anticipate the existence of an energy barrier to free rotation and coplanarity. Adoption of the highly successful Westheimer-Mayer model[50] for the racemization of optically active biphenyls leads to a calculated value of 3.9 kcal. mole^{-1} for the barrier to free rotation.[51] The calculation was made on the basis of the large stabilization energy of 7 kcal. mole^{-1} for the coplanar molecule.[52]

One of the formal rules for resonance is the requirement for coplanarity among contributory structures. The existence of an energy barrier provides the basis for an interpretation of the variable and reduced influence of the phenyl group. Non-coplanar structures make significant contributions to the hybrid, but their importance is dependent upon the deviation from coplanarity.[53] Adrian has examined the problem for biphenyl; he argues the energy minimum, balancing the steric repulsive forces and the resonance contributions, to be a shallow well of −0.4 kcal. mole^{-1} with the rings 20 to 30° from the coplanar conformation.[54]

The evidence discussed relates primarily to the situation existent in the ground state of the aromatic. The estimated energy barrier and predicted deviation from coplanarity are not large. The variations are, however, more than sufficient to cause major changes in reactivity. Moreover, in the electron-deficient, incipient ions, the degree of resonance stabilization is possibly magnified through a further resonance shortening[55] of the interannular bond.

This evidence provides a rationale explanation for the variable and diminished reactivity of biphenyl. The phenyl substituted alkyl carbonium ions I achieve a high degree of resonance stabilization from the aryl substituent.



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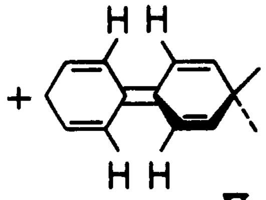

II

The *ortho* hydrogens are easily accommodated in a planar conformation. The incipient biphenyl carbonium ion II does not achieve the full resonance of the substituent ring because of the steric effect. Thus, the steric inhibition of resonance provides the basis for reduced reactivity. As the selectivity of the electrophilic reaction increases, the steric forces

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(40) J. Dhar, *Indian J. Phys.*, **7**, 43 (1932).

(41) A. Kitaigorodsky, *Acta Physicochem. URSS*, **21**, 575 (1946).

(42) Several recent unpublished reports have been called to our attention confirming the coplanarity of biphenyl; see also A. Hargreaves, S. H. Rizvi and J. Trotter, *Proc. Chem. Soc.*, 122 (1961).

(43) L. W. Pickett, *Proc. Roy. Soc.* (*London*), **A142**, 333 (1933).

(44) M. S. Farag, *Acta Cryst.*, **7**, 117 (1954).

(45) I. L. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 1974 (1944).

(46) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949); **4**, 926 (1950); **6**, 205 (1952). O. Bastiansen and L. Smedvik, *ibid.*, **9**, 1593 (1954).

(47) A. Almenningen, O. Bastiansen and P. M. Skancke, *ibid.*, **12**, 1215 (1958).

(48) J. Y. Chau, C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.* 2666 (1959).

(49) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 157, 263, 317. The views of a number of workers, with references, are reviewed.

(49a) H. Suzuki, *Bull. Chem. Soc.* (*Japan*), **32**, 1340 (1959), and subsequent papers in this series.

(50) The model and calculations are reviewed, F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 12.

(51) K. E. Howlett, *J. Chem. Soc.*, 1055 (1960).

(52) J. Guy, *J. chim. phys.*, **46**, 469 (1949).

(53) For a discussion of this question with particular reference to biphenyl, see L. I. Ingraham, in ref. 50, pp. 481–484.

(54) F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

(55) For a discussion of bond shortening through resonance, see ref. 49, pp. 163–183.

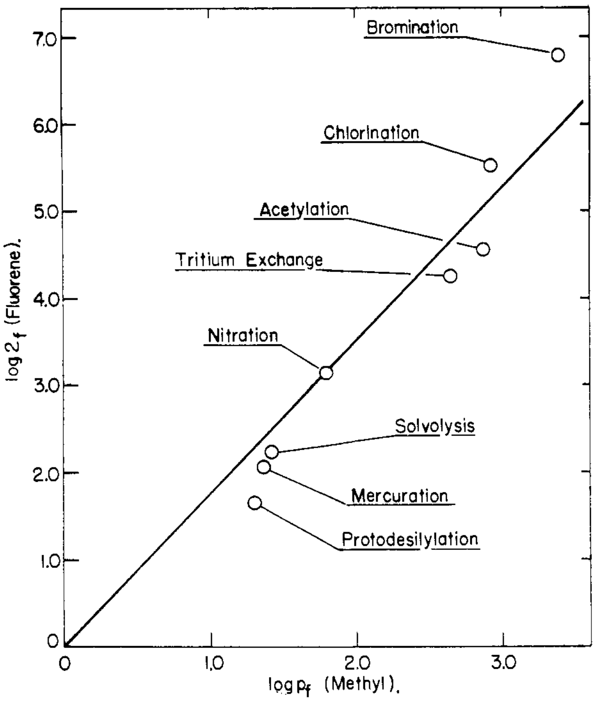


Fig. 4.—Relationship between log 2-Fl$_f$ and log p_f^{Me} for electrophilic substitution reactions.

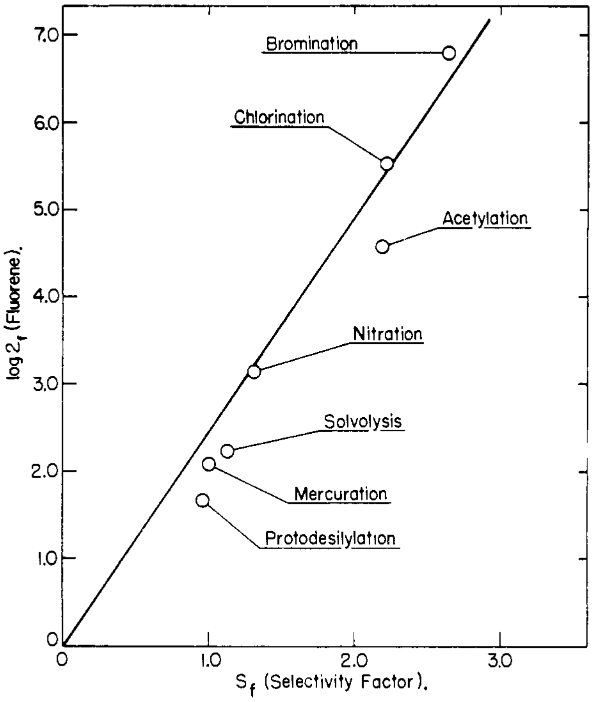
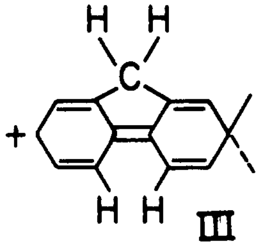


Fig. 5.—Relationship between log 2-Fl$_f$ and the Selectivity Factor, S_f, for electrophilic substitution reactions.

are, in part, overcome by the increased energy requirements of the transition state. The result is the observed variation in the degree of stabilization by the phenyl group.

In this discussion, the anomalous behavior of biphenyl has been identified with the steric effect inhibiting the coplanarity of the phenyl nuclei. Another interpretation for the deviation of biphenyl from a linear treatment has been suggested.[56] This explanation is based on the variability of resonance stabilization merely as a function of electron demand.

It appeared that the behavior of fluorene might provide a test of these proposals. Fluorene contains the elements of the biphenyl system, forced into coplanarity by the methylene bridge (III).



III

Accordingly, we turned our attention to an assessment of the reactivity of fluorene in substitution reactions and an examination of the applicability of the Selectivity Relationship to this hydrocarbon.

Summary of Available Data on Electrophilic Substitution of Fluorene.—Unfortunately, the electrophilic substitution reactions of fluorene subjected to quantitative examinations are more limited. The investigations of the bromination,[21] acylation[20] and mercuration[18] reactions are reported in this present group of papers. A preliminary account of the reactivity of fluorene in the non-catalytic chlorination,[23] tritiation[57] and desilylation[27,57] has been made available. The nitration reaction has also been examined.[58]

Fluorene in the Selectivity Treatment.—An examination of the available data for substitution in the 2-position of fluorene, Table I, is readily made in terms of eq. 6

$$\log 2\text{-Fl}_f/\log p_f^{\text{Me}} = \sigma^+_{2\text{-Fl}}/\sigma^+_{p\text{-Me}} \qquad (6)$$

The average value of this ratio is 1.70 ± 0.20 for the 7 substitution reactions. Graphical presentation of the results, Figs. 4 and 5, reveals a resonable correlation. The data exhibit some scatter, but not more so than is generally encountered in any application of the Hammett treatment to reaction data covering a wide range of reactivity.[59] Certainly,

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(56) J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960). Other important references discussing the problem of resonance and electron demand are reviewed.

(57) C. Eaborn, private communication.

(58) The nitration partial rate factor, Table I, is a corrected value. In ref. 25, the relative rate should be 6084 relative to benzene as 6.00. The partial rate factor, 2-Fl$_f$, is 2098. The other values reported in ref. 25 are correct; private communication from Professor M. J. S. Dewar.

(59) There appears to be some misconception regarding the precision with which many typical side-chain reactions of aromatic systems are correlated by the Hammett expression. For example, in a recent proposal of a three parameter treatment of the data for electrophilic substitution, ref. 56, the following statement appears: "If the Hammett equation is obeyed rigorously, for side-chain reactions (as it appears to be) . . . ." We have already pointed out that the precision of the correlations achieved for electrophilic substitution in toluene is obviously superior to the correlations obtained for Hammett side-chain reactivity of *m*- and *p*-tolyl groups and for *m*- and *p*-methyl substituents in electrophilic side-chain reactions, ref. 9. The variation in σ has also been discussed in detail by others, H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959). We believe some of the criticism of the possible correlation for aromatic substitution reactions to be premature. It is clear that the transition state for the aromatic substitution processes are far more alike then are

there is no evidence for a pronounced curvature of the kind observed in the related treatment of the data for biphenyl, Figs. 1 and 2.

The logarithmic ratio, eq. 6, provides the $\sigma^+_{2\text{-Fl}}$ constant −0.47, based on the value −0.280 for $\sigma^+_{p\text{-Me}}$.[9] This result is in reasonable agreement with the constant derived from the solvolysis of 2-fluorenyldimethylcarbinyl chloride, −0.49.[32,33] In contrast to substitution in the *para* position of biphenyl, substitution in the structurally equivalent 2-position of fluorene conforms to the Selectivity Relationship over a wide range of reagent activity.

The Reactivity of the Fluorene System.—Berliner and Shieh observed that 2-fluorenylmethylcarbinyl chloride solvolyzed approximately 60-fold more rapidly than 4-biphenylmethylcarbinyl chloride.[60] They suggested the increased reactivity to be the consequence of coplanarity.[61] The observations summarized in Table I also indicate fluorene is considerably more reactive than biphenyl in electrophilic reactions. However, mere activation in these reactions is not sufficient to test the interpretation advanced for the anomalous behavior of biphenyl. It is essential to establish that the coplanar arrangement is responsible for an enhanced reactivity, and that the latter does not arise from other structural features.

The methylene substituent, *meta* to the 2-position, in fluorene will obviously increase the reactivity of the aromatic. For bromination, 2-Fl_f relative to p_f^{Ph} is approximately 2×10^3. A *m*-methyl substituent increases the rate of bromination by a factor of only 5.5. The contribution is important but clearly not responsible for the increased reactivity.

The methylene group may also be considered as the equivalent of a methyl group in the 2′-position of biphenyl. It is far more difficult to assess the contribution of this fragment in a coplanar system. However, it is established that the activating effect of a methyl group in the second ring of biphenyl is not large. Thus, 4-methylbiphenyl chlorinates at a rate 5-fold greater than biphenyl itself.[62] Assuming the substitution to occur exclusively at the position *para* to the *p*-tolyl substituent, a significant overestimate and statistical correction leads to an activating effect of only 10. There is no reason to anticipate that a 2′-methyl substituent will be more effective than the 4′-methyl group. Consequently, an upper estimate of the combined inductive and hyperconjugative contributions of the methylene bridge is the product of these two factors, 50.

That the factor of 50 represents an upper limit for the inductive and hyperconjugative contributions of the methylene bridge is indicated by the results of Benkeser and his associates[29] in the detrimethylsilylation reaction. The rate of protodesilylation of phenyltrimethylsilane is increased by a factor of 2.2 by a *m*-methyl substituent. In 4-biphenylyltrimethylsilane a 4′-methyl substituent increases the rate by a factor of 1.7 and a 2′-methyl group by a factor of 2.3. These observations suggest the influence of the methylene bridge in fluorene is approximated satisfactorily as m_f^2. In the bromination reaction, the factor would be 30 (5.5^2).

The experimental rate enhancement is approximately 2×10^3 for bromination. It appears definite that the methylene bridge as a substituent cannot account for this change in reactivity. The achievement of coplanarity presumably is responsible for the major increase in rate.

Conclusion

The observations for electrophilic substitution in biphenyl exhibit two anomalous characteristics. The *p*-phenyl substituent is far less activating than would have been anticipated in view of the stabilization of electron-deficient ions in aliphatic systems. Further, the data for this substituent fails to conform to the Selectivity Relationship previously utilized to correlate the electrophilic substitution data for toluene, *t*-butylbenzene and anisole.

These anomalies have been attributed to a non-coplanar structure of the biphenyl system resulting from the steric repulsion of the *ortho* hydrogen atoms. According to this interpretation, the lower reactivity results from the lower resonance contributions of the phenyl substituent in the non-coplanar configuration. Under the strong electron demand of an attacking reagent, the system strives toward coplanarity. Therefore the electronic contributions of the substituent are balanced against steric repulsive forces resulting in variable electronic influences for the *p*-phenyl group.

The related fluorene system, where the methylene bridge enforces coplanarity, does not exhibit these anomalies. The reactivity of the 2 position is markedly enhanced over the reactivity of the related *para* position of biphenyl. Moreover, the available data are correlated with satisfactory precision by the Selectivity Relationship.

The interpretation offered for the behavior of biphenyl differs from other published viewpoints in regard to the identification of the variability in reactivity with a steric effect. The experimental observations for the reactivity of fluorene appear to confirm the importance of the steric effect.

On the basis of these results, the behavior of biphenyl in the Selectivity Treatment is exceptional and cannot be considered normal for other substituents. However, a full test of this question will require data for additional substituents. We are currently exploring electrophilic substitution data for the halobenzenes in the hope of resolving this question.

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the equilibrium states and transition states for side-chain reactions. Accordingly, it is not very surprising that the substitution reactions provide remarkable correlations even in situations involving high electron demand. It is our hope to evaluate fully certain of these problems in the near future.

[60] E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

[61] Fluorene is a planar molecule with non-colinear phenyl nuclei; D. M. Burns and J. Iball, *Nature*, **173**, 635 (1954).

[62] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, p. 159.