68758-36-1; **9a**, 68758-37-2; **9b**, 68758-38-3; **9c**, 68758-39-4; **9d**, 68758-40-7; **13**, 68758-41-8; **14a**, 68758-42-9; **14b**, 68758-43-0; **14c**, 68758-44-1; **14d**, 68758-45-2; **15**, 68758-46-3; **16b**, 68758-47-4; **17**, 68758-48-5; **18a**, 68758-49-6; **18b**, 68758-50-9; **18c**, 68758-51-0; *o*-cresol, 95-48-7; 2,3-epoxy-3-methylcyclohexanone, 21889-89-4; phenylbenzene thiosulfonate, 1212-08-4; benzenethiol, 108-98-5; pyrrolidine, 123-75-1; piperidine, 110-89-4; trimethylchlorosilane, 75-77-4; *tert*-butyldimethylsilyl chloride, 18162-48-6; phenylselenyl chloride, 5707-04-0.

Supplementary Material Available: Preparation and reactions of **5–9**, **14**, and **16** (14 pages). Ordering information is given on any current masthead page.

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Modified Extended Selectivity Treatment for Biphenyl, Naphthalene, and Benzothiophene

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Electrophilic substitution at position 4 in biphenyl, 1 and 2 in naphthalene, and 2 and 3 in benzothiophene is correlated by an equation, $\log f = \rho\{\sigma_1^+ + (\sigma_2^+ - \sigma_1^+)\} + E_R$, which, because of variations in the magnitudes of $\sigma_2^+ - \sigma_1^+$ and E_R, is best applied as two linear equations, $\log f = \rho\sigma_1^+$, for $0 > \rho \geq -4.5$, and $\log f = \rho\sigma_2^+ + E_R$, for $-4.5 > \rho$. The parameters σ_1^+, σ_2^+, and E_R are discussed in terms of dual activation mechanisms for the bicyclic systems, and reactivity in position 1 in naphthalene is explained without invoking steric interaction with the peri hydrogen.

The extended selectivity treatment (EST) of Stock and Brown[1] produces linear plots passing through the origin (hence defining a unique σ^+ constant) for monosubstituted benzenes,[1] furan,[2] thiophene,[3,4] and fluorene,[5] but nonlinear plots have been obtained for 4-biphenyl (I),[5] 1- and 2-naphthalene (II and III),[1,6] and 2- and 3-benzothiophene (IV and V).[6] Attempts to explain the curvature in terms of polarizability or steric effects (for I) or variable mesomeric contributions (for II–V) have not been successful,[6] and the four-parameter Yukawa–Tsuno equation[7] has been found not to improve the correlation, except for III.[6]

Two *linear* equations, eq 1 and 2, give good correlations of the reactivity of I–III in electrophilic substitution, each over a limited range of ρ values:

$$\log f = \rho\sigma_1^+ \qquad (1)$$

i.e., the normal EST equation, for $0 > \rho \geq -4.5$, over which range a single σ_1^+ value suffices for II and III, and

$$\log f = \rho\sigma_2^+ + E_R \qquad (2)$$

where E_R is constant, for $-4.5 \geq \rho \geq -12.1$. The parameters σ_1^+, σ_2^+, and E_R, evaluated by least squares, are listed in

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Table I. Parameters for Equation 1

substrate	$-\sigma_1^+$	$-\sigma^+$	f[a]	n[b]
I	0.183[f]	(0.179)	0.10	4[c]
II	0.136[f]	(0.137)	0.06	6[d]
III		(0.135)		
IV	0.350			1[e]
V				

[a] "Goodness of fit" parameter (see text). [b] Number of data points for correlation. [c] Reactions 12, 13, 16, and 18 (see footnote *g*). [d] Reactions 11, 12, 14, 15, 17, and 18. [e] Reaction 11. [f] σ_1^+ from the least-squares line of zero intercept. [g] Reactions included in the correlations [(no.) reaction, $-\rho$, data from references]: (1) bromination, 12.1, 1 and 6; (2) chlorination, 10.0, 1 and 6; (3) benzoylation, 9.5, 1; (4) acetylation, 9.1, 1; (5) protodetritiation, 8.8, 1 and 6; (6) nitration, 6.5, 1; (7) bromination with HOBr, 6.2, 1 and 6; (8) bromodesilylation, 6.2, 1 and 6; (9) solvolysis of 1-arylethyl chlorides, 6.1, 19; (10) solvolysis of 1-arylethyl acetates, 5.7, 6; (11) protodesilylation, 4.6, 1 and 6; (12) solvolysis of 2-aryl-2-propyl chlorides, 4.54, 1 and 6; (13) mercuration, 4.0, 1; (14) protodegermylation 3.9, 1 and 6; (15) iododestannylation, 2.5, 14; (16) ethylation, 2.4, 1; (17) protodestannylation, 2.2, 13; and (18) pyrolysis of 1-arylethyl acetates, 0.66, 12 and 6.

Table II. Parameters for Equation 2

substrate	$-\sigma_2^+$	$-E_R$	f[a]	r[b]	n[c]
I	0.365	0.967	0.05	0.991	9[d]
II	0.590	1.77	0.13	0.972	6[e]
III	0.380	1.18	0.11	0.976	6[e]
IV	0.775	1.97	0.08	0.982	8[f]
V	0.956	2.47	0.10	0.973	8[f]

[a] "Goodness of fit" parameter (see text). [b] Correlation coefficient. [c] Number of data points for correlation. [d] Reactions 1–8 and 12 (see footnote *g*, Table I). [e] Reactions 1, 5, 6, 8, 11 (mean log f for II and III was used), and 12. [f] Reactions 1, 2, 4, 5, 7, 9, 10, and 11.

Tables I and II, together with n, the number of data points employed in the correlation, r, the correlation coefficient, and f, the "goodness of fit" parameter of Ehrenson et al.[8] A value of $f \leq 0.1$ is considered satisfactory for correlations by a four-parameter equation;[8] the two- and three-parameter equations 1 and 2 meet this criterion with only two exceptions, for which the discrepancy is not great. In fact, less than is often observed for a correlation of a series of substrates in one reaction by the four-parameter equation,[8] although the EST is "a more sensitive probe of the applicability of a free-energy relationship."[9]

The values in parentheses in Table I are σ^+ values obtained from the standard solvolysis reaction ($\rho = -4.54$).[1] This has not been measured for IV and V, and only one reaction, pyrolysis of the 1-arylethyl acetates ($\rho = -0.66$),[10] at ρ less negative than -4.6 has been measured for these two substrates, so the σ_1^+ value for IV and V was obtained by applying eq 1 to the data for protodesilylation ($\rho = -4.6$).[11] More results are urgently needed for IV and V at $0 > \rho \geq -4.6$, but examination of Table I suggests that no significant difference in reactivity will be observed between IV and V over this range of ρ values. Supporting this suggestion are the following: (i) the low f values for the correlations for I–III, indicating that behavior at $\rho \sim -4.5$ is typical of that for $0 > \rho \geq -4.6$; (ii) the virtually identical rates for IV and V at $\rho = -4.6$; (iii) the virtually identical rates for II and III, not only at $\rho = -4.54$ but for most reactions measured over the range $0 > \rho \geq -4.54$ [Thus, for each of the reactions, pyrolysis of the 1-arylethyl acetates ($\rho = -0.66$),[12] protodestannylation ($\rho = -2.2$),[13] iododestannylation ($\rho = -2.5$),[14] and solvolysis ($\rho = -4.54$),[1] the individual log f values for II and III differ from their mean by less than 0.02. Only protodegermylation ($\rho = -3.9$)[15] and protodesilylation ($\rho = -4.6$)[16] show $\log f_{\mathrm{II}} > \log f_{\mathrm{III}}$.]; (iv) the excellent agreement shown between σ^+ (-0.137 and -0.135, respectively, for II and III) and σ_1^+ in Table I (-0.136) obtained from the mean log f values for the six reactions referred to in iii (omission of the protodegermylation and protodesilylation results changes σ_1^+ to -0.139 and f to 0.07); and (v) the good agreement shown for I between σ^+ (-0.179)[1] and σ_1^+ (-0.183). Evaluation of the latter involves some degree of selection of data since inspection of the data in Stock and Brown's Table VII[1] suggests that many of the results should be remeasured. For bromodeboronation ($\rho = -4.3$) the quoted log f (which shows the greatest divergence from an average line through the others) has already been criticized as being too high,[17] and the log f values of 0.42, 0.81, 0.43, 0.81, and 0.48 at $-\rho$ values of 3.9, 4.0, 4.4, 4.54, and 4.6, respectively, if not reflecting errors in some of the measurements, indicate a widely fluctuating reactivity for I at $0 > \rho > -4.6$, quite at variance with the good linearity observed for $-4.6 > \rho$ and the f value of 0.05 for the nine reactions in Table II. The σ_1^+ value of -0.183 for I was obtained from the four reactions, pyrolysis of 1-arylethyl acetates ($\rho = -0.66$),[12] ethylation ($\rho = -2.4$),[1] mercuration ($\rho = -4.0$),[1] and solvolysis ($\rho = -4.54$),[1] as the slope of the least-squares line with a zero intercept. If log f for mercuration is replaced by its average with that for protodegermylation ($\rho = -3.9$),[1] σ_1^+ changes to -0.166 and f to 0.08. Inclusion of the log f values at $\rho = -4.4$ and -4.6 leads to $\sigma_1^+ = -0.138$ and $f = 0.28$; the deviation between this latter σ_1^+ value and σ^+ (-0.179) supports the reservations expressed above about the accuracy of some of the results, as does the large f value.

Correlation of the reactivities of II and III by a single σ_1^+ value for $0 > \rho \geq -4.6$ implies the absence of steric interactions from the peri hydrogen in II. Steric hindrance in II was proposed to explain the similar rates observed for II and III in the standard solvolysis reaction[1,18] and appeared to be confirmed by the increased relative rate $k_{\mathrm{II}}/k_{\mathrm{III}} = 2.5$ for solvolysis in 80% acetone of the 1-arylethyl chlorides.[18] However, the latter reaction almost certainly has a more negative ρ value than -4.54 since hydrolysis of these secondary halides in 80% ethanol has a ρ value of -6.1,[19] and the increased rate ratio can be explained from the change in ρ without the necessity of invoking steric effects; thus, at $\rho = -6.1$, eq 2 gives $k_{\mathrm{II}}/k_{\mathrm{III}} = 4.9$.

From the data at present available, the changeover from eq 1 to 2 occurs for I–V at about $\rho = -4.5$–-4.6, but more results are required for more precise evaluation. A simple interpretation of the need for two correlation equations for the bicyclic systems requires two postulates only: (a) dual activation mechanisms exist for bicyclic systems, involving, for $0 > \rho \geq -4.6$, only the ring containing the reacting site (the "reacting" ring), and, at $-4.6 > \rho$, both rings, in the supply of electrons to satisfy the demand of the attacking electrophilic reagent and in the delocalization of the positive charge on the transition state; (b) an approximately constant change in resonance energy in forming the transition state for electrophilic substitution when only one ring is involved, whether it is the sole ring in a monocyclic system or the "reacting" ring of a bicyclic (polycyclic) system.

Two equations of the form of eq 1 and 2 follow from the combination of these two postulates with Taft's subdivision of the free energy of activation into polar (P), steric (S), and resonance (R) components[20] (eq 3). Equation 3 reduces to eq 1 when $\Delta\Delta G^{\ddagger}_{\mathrm{R}} = 0$ (provided $\Delta\Delta G^{\ddagger}_{\mathrm{S}} = 0$), i.e., for monocyclic systems at all ρ and for bicyclic systems for $0 > \rho \geq -4.6$, where $\rho\sigma_1^+ = -\Delta\Delta G^{\ddagger}_{\mathrm{P}}/2.3RT$. When $\Delta\Delta G^{\ddagger}_{\mathrm{S}} = 0$, $\Delta\Delta G^{\ddagger}_{\mathrm{R}} \neq 0$; i.e., for bicyclic systems for $-4.6 > \rho$, eq 3 reduces to eq 2, and identifying $\rho\sigma_2^+$ with $-\Delta\Delta G^{\ddagger}_{\mathrm{P}}/2.3RT$ gives $E_{\mathrm{R}} = -\Delta\Delta G^{\ddagger}_{\mathrm{R}}/2.3RT$. E_{R} is thus a "resonance energy substituent parameter", analogous to Taft's steric substituent parameter E_S.[20] Previous application of eq 2 appears to have been limited to hyperconjugation,[21] although the remaining possible variation of eq 3, namely, $\Delta\Delta G^{\ddagger}_{R} = 0$, $\Delta\Delta G^{\ddagger}_{S} \neq 0$, has been extensively documented.[20]

$$-2.3RT \log f = \Delta\Delta G^{\ddagger} = \Delta\Delta G^{\ddagger}_{P} + \Delta\Delta G^{\ddagger}_{S} + \Delta\Delta G^{\ddagger}_{R} \quad (3)$$

For monocyclic systems, electrophilic reactivities are successfully correlated by eq 1 over the whole range of ρ; thus, for anisole, $\sigma^{+}_{p\text{-OMe}}$ from the standard solvolysis reaction is -0.778[1] compared with $\sigma_1^{+} = -0.774$ as the least-squares slope of eq 1 (data: reactions 1–3, 9, 37, 41, 42, 44, 50, and 51 from Stock and Brown's Table **VC**[1]). That this applies for a range of substituents and for monocyclic heterocycles[2–4] attests to the small effect of substituent or ring-type change on $\Delta\Delta G^{\ddagger}_{R}$. This is not unexpected when only one ring is involved since $\Delta\Delta G^{\ddagger}_{R}$ arises from a comparison with benzene or a monosubstituted benzene for displacement[1] reactions. Comparison, at $0 > \rho \geq -4.6$, of the bicyclic systems with benzene as a reference substrate (for evaluation of $\log f$) leads to $\Delta\Delta G^{\ddagger}_{R} \approx 0$ and to equation 1 because of the approximate constancy of $\Delta G^{\ddagger}_{R}$ *for involvement of a single ring.* At more negative ρ values, the greater electron demand of the reagent is met by an additional contribution from the "nonreacting" ring, leading to an increased polar effect (more negative σ^{+}). Involvement of the second ring leads to greater delocalization of the positive charge on the transition state and a further loss of resonance energy, so that now $\Delta\Delta G^{\ddagger}_{R}$ is no longer 0. Hence, $\rho(\sigma_2^{+} - \sigma_1^{+})$ measures the increased polar effect and E_r the increased resonance energy change when both rings are involved in the activation process at more negative ρ values, i.e., when eq 1 is replaced by eq 2. It should be emphasized that equations 1 and 2 do not represent two independent equations, but rather two aspects of one general equation, as can be seen by rewriting eq 2 in the alternative form shown in eq 4. When the electron demand of the electrophile is low (low $|\rho|$), the minimum free energy of activation results from supplying the charge from the reacting ring only (polar effect measured by σ_1^{+} and $(\sigma_2^{+} - \sigma_1^{+}) \approx 0$), and by not disrupting the aromatic resonance of the nonreacting ring ($E_R \approx 0$); under these conditions, eq 4 reduces to eq 1. When the electron demand of the attacking reagent becomes greater (larger $|\rho|$), the increased demand can be met only by involving the second ring. Minimum free energy of activation now results from the balance between the greater reactivity resulting from increased electron supply from the second ring (the additional polar effect being measured by $\sigma_2^{+} - \sigma_1^{+}$) and the decreased reactivity resulting from loss of resonance energy in the second ring (measured by E_R); under these conditions eq 4 reduces to eq 2.

$$\log f = \rho\{\sigma_1^{+} + (\sigma_2^{+} - \sigma_1^{+})\} + E_R \quad (4)$$

All E_R values in Table II are negative, indicating decrease in reactivity from the greater loss in resonance energy, but this is more than offset, at sufficiently negative ρ values, by the more negative σ_2^{+} resulting from greater electron availability. The value of $\Delta\Delta G^{\ddagger}_{R}$ amounts to some 14 kJ mol^{-1} for IV and less for the other substrates; II and III, and also IV and V, give different $\Delta\Delta G^{\ddagger}_{R}$ values, as they do different localization energies and Dewar reactivity numbers.[22] The results for II in Table II, like those in Table I, require no additional steric effect for their interpretation. Covering, as they do, a range of substituting reagents of differing bulk, as well as displacement reactions, any steric effect could hardly be constant, and the good linearity of the correlation for II would be quite unexpected if steric effects in II differed significantly from those in III.

Previous attempts to separate polar and resonance effects[8,23] cannot at present be extended to include electrophilic substitution in bicyclic systems. Thus, the treatment of Ehrenson, Brownlee, and Taft[8] lacks the necessary ρ_I and ρ_R parameters since, as pointed out by these authors,[8] for only one electrophilic substitution reaction, namely, protodesilylation, have enough suitable substituents been studied to constitute a minimal basis set for application of their treatment. Swain and Lupton's treatment incorporated only one electrophilic substitution reaction[23] (solvolysis of the 2-aryl-2-propyl chloride, $\rho = -4.54$) and is not notable for its success with bicyclic systems. Thus, for I they quote $\sigma^{+}_{\text{calcd}} = -0.085$ (their Table I),[23] whereas the σ_m and σ_p values of 0.060 and -0.010 (their Table I[23] also[1]) and the a and b values of -0.84 and 1.81, respectively (their Table III),[23] lead to $\sigma^{+}_{\text{calcd}} = -0.069$, while the $\mathscr{f}$ and $\mathscr{r}$ values of 0.51 and 1.58 (their Table IV)[23] with the $\mathcal{F}$ and $\mathcal{R}$ values of 0.139 and -0.088, respectively (their Table I),[23] lead to $\sigma^{+}_{\text{calcd}} = -0.068$. None of these three calculated σ^{+} values would give a satisfactory correlation for the solvolysis reaction since $\rho^{-1} \log f$ is -0.179[1] (cf. our calculated value of -0.183 in Table I). Swain and Lupton also tabulated an intercept i of -0.07 ± 0.06 for both the a,b and $\mathscr{f},\mathscr{r}$ correlations of σ^{+}; incorporation of -0.07 for i in either treatment more than doubles the absolute value of $\sigma^{+}_{\text{calcd}}$, but still gives a poor correlation for the solvolysis reaction.

Nonlinear EST curves passing through the origin, corresponding to eq 5, where a and b are constants, after the treatment of Knowles, Norman, and Radda[24] (but retaining the normal ρ values instead of introducing a new parameter ϕ), gave considerably smaller correlation coefficients and considerably larger $\mathscr{f}$ values than those listed in Tables I and II. Until more ρ_I and ρ_R values are available for application of the treatment of Ehrenson, Brownlee, and Taft,[8] we consider that equations 1 and 2 give the most satisfactory correlation of reactivity in electrophilic substitution of bicyclic aromatic/heterocyclic systems, and we hope that the challenge to confirm or disprove their applicability will stimulate kineticists to measure more rates, especially, e.g., those for benzothiophene in the range $0 > \rho > -4.6$.

$$\log f = \rho\sigma^{+}_{\text{effective}} = \rho(a + b\rho) \quad (5)$$

Registry No.—Biphenyl, 92-52-4; naphthalene, 91-20-3; benzothiophene, 95-15-8.

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