The Nature of the Ortho Effect. VII. Nuclear Magnetic Resonance Spectra

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Twenty-seven sets of nmr chemical shifts and related data for ortho-substituted benzenes and naphthalenes were correlated with the equation $Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi r_V + h$ and the extended Hammett equation $Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h$. Significant correlations were obtained for 22 of 26 sets correlated with the former equation and 24 of 27 sets correlated with the latter equation. The results obtained show that ψ is not significant in most of the sets studied and that better correlation is generally obtained with the latter equation than with the former. There is no steric effect exerted by the ortho substituents in most of the sets studied. The substituent effect, thus, is purely electrical. The composition of the electrical effect depends upon structure and solvent. For the chemical shifts of aromatic ring protons, the resonance effect predominates. In the majority of the sets studied, the value for the unsubstituted compound does lie on the correlation line.

In continuation of our studies[1-6] on the nature of the ortho effect, it seemed of interest to investigate nmr spectra. A number of authors have attempted the correlation of nmr data with the simple Hammett equation

$$Q_X = \rho\sigma_X + h \tag{1}$$

Thus, Bray and Barnes[7] found a linear correlation between the Cl^{35} pure quadrupole resonance frequencies in substituted dichlorobenzenes, including ortho-substituted compounds, and Hammett substituent constants. For the ortho-substituted compounds, substituent constants were defined from the ionization constants of 2-substituted benzoic acids. A correlation between the chemical shifts of ortho protons in substituted benzenes and the σ_p constants was reported by Diehl[8] and Kondo, *et al.*,[9] report the correlation of the infinite dilution chemical shifts of 2-substituted benzoic acids with σ_p and with the Taft $\sigma_o{}^*$ constants The definition of σ_o constants from the OH chemical shifts of 2-substituted phenols has been proposed by Traynham and his coworkers.[10,11] The correlation of OH chemical shifts for 2-substituted phenols with $\sigma_o{}^*$ has been reported by Dietrich, Nash, and Keller.[12] The NH chemical shifts of 2-substituted anilines have been correlated with both σ_p and σ_o by Lynch, MacDonald, and Webb.[13] The chemical shifts of the S ring protons of 2-substituted N^4-acetyl-N^1-phenylsulfanilamides are said to be correlated by the $\sigma_o{}^*$ constants according to Cammarata and Allen.[14] The proton and ^{13}C chemical shifts in 2-substituted pyridines are correlated with σ_p by Retcofsky and McDonald.[15] Infinite dilution chemical shifts of substituted benzenes were correlated with the extended Hammett equation

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \tag{2}$$

by Hayamizu and Yamamoto.[16]

In all of this work, there has been no systematic attempt to determine whether or not steric effects are present or with the exception of the work of Hayamizu and Yamomoto to ascertain the composition of the electrical effect.

It will be useful at this point to review our method[6] for determining the presence or absence of steric effects. There are four cases of interest to us. They are the following. (1) The steric effect obeys a linear free energy relationship. Then using a suitable steric parameter, we may write an equation including both electrical and steric effects such as

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi\zeta_X + h \tag{3}$$

where σ_I is a measure of the localized electrical effect, σ_R is a measure of the delocalized electrical effect, and ζ_X is a measure of the steric effect. As a steric effect parameter, we have chosen the van der Waals radius of that atom or group of atoms which is bonded to the benzene ring. Thus, we have the expression

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi r_{V,X} + h \tag{4}$$

(2) The steric effect does not obey a linear free energy relationship. We may then write for any particular datum in the set

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + S_X + h \tag{5}$$

where S_X is the steric effect of the X substituent and is independent of any linear free energy relationship.

(3) The steric effect is constant. In this event

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h' \tag{6}$$

where

$$h' = h + S_X \tag{7}$$

(4) The steric effect is negligible or nonexistent. Then

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \tag{2}$$

Equations 2 and 6 are equivalent.

In order to detect the presence or absence of a steric effect the data are correlated with eq 2 and 4.

Successful correlations with eq 4 are not in themselves sufficient to imply the existence of case 1. Conclusive

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[2] M. Charton, *J. Amer. Chem. Soc.*, **91**, 615 (1969).
[3] M. Charton, *ibid.*, **91**, 619 (1969).
[4] M. Charton, *ibid.*, **91**, 624 (1969).
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[9] Y. Kondo, K. Kondo, T. Takemoto, and T. Ikenoue, *Chem. Pharm. Bull.*, **14**, 332 (1966).
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[11] M. T. Tribble and J. G. Traynham, *J. Amer. Chem. Soc.*, **91**, 379 (1969).
[12] M. W. Dietrich, J. S. Nash, and R. E. Keller, *Anal. Chem.*, **38**, 1474 (1966).
[13] B. M. Lynch, B. C. MacDonald, and J. G. K. Webb, *Tetrahedron*, **24**, 3595 (1968).
[14] A. Cammarata and R. C. Allen, *J. Med. Chem.*, **11**, 204 (1968).
[15] H. L. Retcofsky and F. R. McDonald, *Tetrahedron Lett.*, 2575 (1968).
[16] K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, **29**, 183 (1969).

TABLE I

DATA USED IN CORRELATIONS

1. δ_0. Disubstituted benzenes (Pr_2):[a] NH_2, 68; OH 56; OMe, 42; F, 25; Me, 17; Cl, −5; Br, −22; CN, −35; I, −41; CO_2Me, −74; NO_2, −98.
2. δ_0. Disubstituted benzenes (CCl_4, 35°):[b] MeNH, 0.80; NH_2, 0.75; OH, 0.52; OMe, 0.47; Me, 0.21; Et, 0.18; *i*-Pr, 0.16; *tert*-Bu, −0.02; Cl, −0.03; CH_2Cl, −0.05; CH_2Br, −0.18; Br, −0.18; I, −0.35; CN, −0.35; Ac, −0.60; CO_2Me, −0.67; NO_2, −0.93.
3. $\Delta\delta_0$. Substituted benzenes ($c\text{-}C_6H_{12}$):[c] F, 18.5; Cl, −1.2; Br, −13.4; I, −24.0; OMe, 26.0; NH_2, 45.3; NMe_2, 36.0; CHO, −34.8; NO_2, −56.9.
4. δ_0. Substituted benzenes (CCl_4):[d] NO_2, −95.2; COCl, −84.0; COBr, −80.1; SO_2Cl,[e] −76.5; CO_2Me, −71.3; CO_2-*i*-Pr, −70.2; CO_2-*i*-Bu, −71.5; Ac, −61.9; COEt, −62.5; CHO, −56.1; SO_2Me, −60.4; CCl_3, −63.8; CN, −36.1; I, −38.8; Br, −18.3; Cl, −2.6; OAc, 25.2; OMe, 48.4; OH, 55.8; NH_2, 74.6; NHMe, 79.5; NMe_2, 65.9; Me, 20.1; *tert*-Bu, −1.9.
5. δ_{H^2}. 1-Substituted 3,4-dimethoxybenzenes ($c\text{-}C_6H_{12}$):[f] NH_2, 1.09; OMe, 0.80; Me, 0.62; H, 0.47; Br, 0.35; CHO, −0.11; CO_2Me, −0.28; NO_2, −0.37.
6. δ_{H^6}. 1-Substituted 3,4-dimethoxybenzenes ($c\text{-}C_6H_{12}$):[f] NH_2, 1.17; OMe, 0.96; Me, 0.62; H, 0.47; Br, 0.31; CHO, −0.05; CO_2Me, −0.35; NO_2, −0.52.
7. δ_{H^1}. 2-Substituted naphthalenes ($c\text{-}C_6H_{12}$):[g] NH_2, 0.43; OMe, 0.25; Me, −0.13; H, −0.50; Cl, −0.53; Br, −0.66; CN, −0.83; Ac, −1.12; CHO, −0.96; CO_2Me, −1.23.
8. δ_{H^3}. 2-Substituted naphthalenes ($c\text{-}C_6H_{12}$):[g] NH_2, 0.50; OMe, 0.16; Me, −0.09; H, −0.16; Cl, −0.18, Br, −0.26; CN, −0.32; Ac, −0.78; CHO, −0.66; CO_2Me, −0.70.
9. δ_{H^1}. 2-Substituted 6-methoxynaphthalenes (CCl_4):[g] NH_2, 0.44; OMe, 0.32; Et, −0.17; H, −0.44; Br, −0.56; Ac, −0.98; CO_2Me, −1.17.
10. δ_{H^3}. 2-Substituted 6-methoxynaphthalenes (CCl_4):[g] NH_2, 0.45; OMe, 0.36; Et, 0.08; H, −0.03; Br, −0.11; Ac, −0.64; CO_2Me, −0.68.
11. δ_{H^4}. 5-Substituted benzo[*b*]thiophenes ($CDCl_3$):[h] NH_2, 0.75; OH, 0.61; OMe, 0.54; Me, 0.35; OAc, 0.34; D, 0; OSO_2Me,[e] 0.07; Cl, 0.07; CH_2OH, 0.09; CH_2Cl, 0.01; Br, −0.10; CN, −0.28; NHAc, −0.29; I, −0.34; CHO, −0.46; CO_2Me, −0.72; CO_2H, −0.80; NO_2, −0.89.
12. δ_{H^6}. 5-Substituted benzo[*b*]thiophenes ($CDCl_3$):[h] NH_2, 0.60; OH, 0.43; OMe, 0.35; Me, 0.31; OAc, 0.31; D, 0; OSO_2Me,[e] 0.08; Cl, 0.07; CH_2OH, 0.08; CH_2Cl, −0.01; Br, −0.06; CN, −0.18; NHAc, 0.02; I, −0.25; CHO, −0.51; CO_2Me, −0.66; CO_2H, −0.73; NO_2, −0.84.
13. δ sulfanilyl ring protons. 2′-Substituted *N*⁴-acetyl-*N*¹-phenylsulfanilamides (THF):[i] MeO, 6.0; Cl, 4.0; Br, 3.7; I, 3.5; NO_2, −1.0.
14. $\tau_{o\text{-Me}}$. Substituted mesitylenes (Pr_2):[j] F, 7.85; Cl, 7.74; Br, 7.68; I, 7.62; OH, 7.90; NH_2, 7.98; NO_2, 7.81; H, 7.81.
15. $\tau_{o\text{-Me}}$. Substituted durenes (Pr_2):[j] F, 7.91; Cl, 7.76; Br, 7.71; I, 7.62; OH, 7.92; NH_2, 8.07; NO_2, 7.95; H, 7.88.
16. δ_{Me}. 2-Substituted toluenes (neat, 11–12°):[k] NO_2, 1.09; CN, 0.99; Cl, 0.78; Me, 0.61; OH, 0.76; NH_2, 0.37; H, 0.75.
17. δ_{Me}. 2-Substituted toluenes (Ph, 11–12°):[k] NO_2, 0.80; CN, 0.73; Cl, 0.71; Me, 0.61; OH, 0.69; NH_2, 0.39; H, 0.71.
18. δ_{Me}. 2-Substituted toluenes (pyridine, 11–12°):[k] NO_2, 1.14; CN, 1.02; Cl, 0.85; Me, 0.74; OH, 1.11; NH_2, 0.88; H, 0.81.
19. δ_{Me}. 2-Substituted toluenes (dioxane, 11–12°):[k] NO_2, 1.18; CN, 1.12; Cl, 0.91; Me, 0.77; OH, 0.74; NH_2, 0.61; H, 0.89.
20. δ_{Me}. 2-Substituted toluenes (CCl_4, 11–12°):[k] NO_2, 1.16; CN, 1.11; Cl, 0.93; Me, 0.81; OH, 0.77; NH_2, 0.58; H, 0.90.
21. δ_{OH}. 2-Substituted phenols (Me_2SO, 28°):[l] Me, −9.14; Ph, −9.38; Cl, −9.96; Br, −10.14.
22. δ_{OH}. 2-Substituted phenols (Me_2SO, 40°):[m] F, 9.70; Cl, 10.00; Br, 10.07; I, 10.20; NO_2, 10.8; Cn, 10.97; CF_3, 10.44; Me, 9.10; Et, 9.07; Pr, 9.06; *i*-Pr, 9.07; *sec*-Bu, 9.03; *tert*-Bu, 9.17; $ViCH_2$, 9.19; $PhCH_2$, 9.29; CH_2OH, 9.18; Ph, 9.46; CHO, 10.75; Ac, 11.97; Bz, 10.61; CO_2Me, 10.55; OH, 8.70; OMe, 8.76; OEt, 8.66; NHAc, 9.29; NMe_2, 8.78; MeS, 9.59; MeSO, 10.50.
23. δ_{OH}. 2-Substituted phenols (hexamethylphosphoramide, 40°):[n] H, 10.30; Me, 10.22; Et, 10.20; Pr, 10.18; *i*-Pr, 10.22; *sec*-Bu, 10.17; *tert*-Bu, 10.33; $c\text{-}C_6H_{11}$, 10.15; Ac, 11.88; Br, 11.27; CHO, 11.67; I, 11.35; MeO, 9.92; NO_2, 12.1; Ph, 10.57.
24. δ_{NH}. 2-Substituted anilines (Me_2SO, 37°):[o] Me, 278.0; OMe, 276.0; OEt, 274.0; Cl, 312.0; Br, 312.0; NO_2, 440.0.
25. τ_{OMe}. 2-Substituted anisoles (CCl_4, 30°):[p] Me, 6.35; NH_2, 6.34; NO_2, 6.16; Br, 6.18; I, 6.22; CO_2H, 6.22; AcNH, 6.24; Ph, 6.37; H, 6.34.
26. $J^{13}{}_{C\text{-}F}$. 2-Substituted fluorobenzenes (neat or CCl_4, 25°):[q] NH_2, 236.7; OH, 241.6; OMe, 246.2; F, 254.5; CHO, 256.4.
27. $f_{^{35}Cl}$. 2-Substituted chlorobenzenes (77°K):[r] NO_2, 37.260; Cl, 35.755; CO_2H, 36.305; NHAc, 35.150; CN, 35.500.

[a] Reference 8. [b] N. Van Meurs, *Recl. Trav. Chim. Pays-Bas.*, **87**, 145 (1968). [c] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961). [d] Reference 16 and K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, **28**, 89 (1968). [e] This value was not included in the correlation as constants for it are unknown. [f] M. Suzuki, *Chem. Pharm. Bull.*, **16**, 1193 (1968). [g] Y. Sasaki, M. Suzuki, T. Hibino, K. Karai, M. Hatanaka, and I. Shiraishi, *ibid.*, **16**, 1367 (1968). [h] B. Caddy, M. Martin-Smith, R. K. Norris, S. T. Reid, and S. Sternhell, *Aust. J. Chem.*, **21**, 1853 (1968). [i] Reference 14. [j] P. Diehl and G. Svegliado, *Helv. Chim. Acta*, **46**, 461 (1963). [k] N. Nakagawa and S. Fujiwara, *Bull. Chem. Soc. Jap.*, **34**, 143 (1961). [l] Reference 10. [m] Reference 11. [n] Reference 12. [o] Reference 13. [p] C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962). [q] S. Mohanty and P. Venkateswarlu, *Mol. Phys.*, **12**, 277 (1967). [r] Reference 7.

evidence may be obtained from the confidence level of ψ, the coefficient of the van der Waals radius term in eq 4. This confidence level is obtained by means of a "Student's t test" for the significance of ψ. When the confidence level of ψ is ≥ 90.0, the steric effect term is considered significant. A lack of correlation with eq 4 coupled with a lack of correlation by eq 2 does not imply case 2. It may also be the result of case 1 due to faulty choice of the steric parameter. Correlation by eq 2 implies the existence of either case 3 or case 4, as, if steric effects are present and unaccounted for, no correlation with eq 2 is to be expected. Case 3 may be distinguished from case 4 by a comparison of h_{obsd} (the value for the unsubstituted compound) with h_{calcd} from the correlation. When

$$h_{obsd} \neq h_{calcd} \qquad (8)$$

case 3 occurs, whereas when

$$h_{obsd} = h_{calcd}$$

case 4 results. The data have been correlated with eq 2 and 4 by means of multiple linear regression analysis.[17] The data used in the correlation are set forth in Table I.

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(17) K. A. Brownlee, "Statistical Theory and Methodology in Science and Engineering," 2nd ed, Wiley, New York, N. Y., 1965; E. L. Crow, F. A. Davis, and M. W. Maxfield, "Statistics Manual," Dover Publications, New York, N. Y., 1960.

TABLE II

SUBSTITUENT CONSTANTS

Subst	σ_I	Ref	σ_R	Ref	Subst	σ_I	Ref	σ_R	Ref
COCl	0.44	*a*	0.19	*b*	COBr	0.45	*c*	0.19	*b*
CO_2-*i*-Pr	0.34	*d*	0.11	*e*	CO_2-*i*-Bu	0.34	*d*	0.11	*e*
COEt	0.29	*f*	0.09	*b*	NH_2	0.10	*a*		
NHMe	0.10	*a*			NMe_2	0.10	*a*		
$ViCH_2$			−0.13	*g*	$PhCH_2$			−0.14	*h*
MeS			−0.35	*i*	*c*-C_6H_{11}			−0.12	*j*
OAc	0.42	*a*	−0.12	*k*					

[a] M. Charton and B. I. Charton, *J. Chem. Soc. B*, 43 (1967). [b] σ_p was calculated from $\sigma_{p,\mathrm{COX}} = 0.546\,\sigma_{m,\mathrm{X}} + 0.422$; σ_R was then calculated from eq 4. [c] This value is an average of values of 0.25 and 0.21 calculated from the equation $\sigma_{I,\mathrm{COX}} = 0.308\,\sigma_{m,\mathrm{X}} + 0.31$ (determined from pK_a values) and $\sigma_{I,\mathrm{COX}} = 0.648\,\sigma_{m,\mathrm{X}} + 0.21$ (determined from ^{19}F shielding in nmr spectra, respectively: M. Charton, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964, p 56V. [d] Assumed equal to σ_I for CO_2Me. [e] Assumed equal to σ_R for CO_2Me. [f] Calculated from $\sigma_{I,\mathrm{X,COX}} = 0.308\sigma_{m,\mathrm{X}} + 0.31$. [g] σ_p was calculated from $\sigma_{p,\mathrm{XCH_2}} = 0.522\sigma_{I,\mathrm{X}} - 0.131$. σ_R was then calculated from eq 4. [h] Calculated from eq 4 using the σ_p value given by O. Exner and J. Jonas, *Collect. Czech. Chem. Commun.*, **27**, 2296 (1962). [i] M. Charton, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967, p 137S. [j] Assumed equal to $\sigma_{R,i\text{-Pr}}$. [k] Calculated from eq 4 using value of σ_p given by C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

The σ_I constants are from our compilation[18] when available. The σ_R constants were obtained from the equation

$$\sigma_R = \sigma_p - \sigma_I \tag{9}$$

using where possible the σ_p constants of McDaniel and Brown.[19] Substituent constants from other sources are given in Table II. Values of r_V used were from the collection of Bondi[20] or are group values calculated by us ($r_{V,\min}$).[2]

It would be well at this point to consider our choice of electrical effect parameters in the light of the recent work of Swain and Lupton[21] who have proposed a new separation of electrical effects into localized and delocalized contributions. These authors agree with most other workers that the σ_I constants are a true measure of the localized effect. They have proposed a new definition of resonance effect constants however, and believe that the σ_R values are not pure resonance effect parameters. We believe that the Swain–Lupton treatment is invalid for the following reasons. (1) The results are based on σ_m and σ_p values for Me_3N^+ which are reported by McDaniel and Brown. These authors report probable errors of ±0.2 for these substituent constants. A scale based on values subject to so much error seems to us of dubious value.

(2) The results depend on the assumption that the trimethylammonio substituent is free of resonance interaction; that is, it has no resonance effect. As this substituent is isoelectronic with the *tert*-butyl group which is well known to be an electron donor by resonance, we find this hard to believe. We have continued to use σ_R values, therefore, because we do not believe that a better resonance parameter is as yet available.

Results

Results of the correlations are presented in Table III. Sets labeled A were correlated with eq 4; sets labeled B were correlated with eq 2.

Aromatic Ring Proton Sets.—Of the 13 sets of data involving chemical shifts of aromatic ring protons (sets 1–13) which were correlated with eq 4, ten gave excellent correlations, two gave fair results, and one gave poor results. Correlations of these sets with eq 2 gave excellent results for 11 sets, very good results for one set, and poor results for one set.

Methylbenzene Proton Sets.—The substituted mesitylene and substituted durene sets gave fair and not significant correlations, respectively, with eq 4 (sets $14A_1$, $15A_1$), and no significant correlation with eq 2 (sets $14B_1$ and $15B_1$). Exclusion of the value for the nitro group from these sets gave excellent and good correlations, respectively, with eq 4 (sets $14A_2$, $15A_2$) but fair correlations, respectively, with eq 2 (sets $14B_2$ and $15B_2$).

The substituted toluene sets in various solvents gave two excellent correlations (sets 19A, 20A), one poor correlation (set 16A), and two correlations which were not significant (sets $17A_1$, $18A_1$) with eq 4. Exclusion of the value for the hydroxy group gave improved correlations with eq 4 for the substituted toluenes in the liquid state (set $16A_2$), and was without effect on the significance of the correlation of the substituted toluenes in benzene (set $17A_2$) and in pyridine (set $18A_2$). Correlation of the substituted toluenes with eq 2 gave excellent results for two sets (sets 19B, 20B), good results for one set (set $16B_1$), and results which were not significant for two sets (set $17B_1$, $18B_1$). Exclusion of the value for the hydroxy group gave improved results for two sets ($16B_2$ and $17B_2$) and was without effect in one set ($18B_2$).

OH and NH Chemical Shift Sets.—Of the three sets correlated with eq 4 (sets $22A_1$, 23A, 24A), two gave excellent and one gave very good results. Exclusion of the value for the acetyl group gave improved results for the 2-substituted phenols in DMSO (set $22A_2$). Of the four sets correlated with eq 2 (sets 21B, $22B_1$, 23B, 24B), two gave excellent results, one gave fair results, and one did not give significant correlation. Again, exclusion of the value for the acetyl group gave improved results for the 2-substituted phenols in DMSO (set $22B_2$).

Miscellaneous Sets.—The chemical shifts of the methoxy protons in 2-substituted anisoles gave very good correlation with eq 4 and excellent correlation with eq 2 (sets $25A_1$, $25B_1$). Exclusion of the value for the phenyl group improved the correlation with both eq 4 and eq 2 (sets $25A_2$, $25B_2$). The coupling constants of 2-substituted fluorobenzenes did not give significant

(18) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

(19) D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

(20) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(21) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

TABLE III
RESULTS OF CORRELATIONS

Set	α	β	ψ	h	R^a	F^b	r_{12}^c	r_{13}^c	r_{23}^c
1A	−71.0	−132.0	−27.0	30.5	0.951	21.97^g	0.469	0.024	0.411
1B	−65.4	−139.0		−18.2	0.948	35.54^g	0.469		
2A	−0.937	−1.10	−0.193	0.325	0.963	54.59^g	0.283	0.391	0.293
2B	−0.826	−1.17		−0.0524	0.959	80.14^g	0.283		
3A	−34.3	−72.6	−20.2	21.2	0.950	18.40^h	0.468	0.462	0.128
3B	−44.8	−71.1		−7.48	0.942	27.68^g	0.468		
4A	−64.0	−123.0	−17.8	12.8	0.941	51.52^g	0.484^l	0.124	0.241
4B	−64.2	−127.0		−18.6	0.936	74.66^g	0.484^j		
5A	−0.954	−1.21	−0.0840	0.506	0.977	27.77^h	0.345	0.359	0.047
5B	−0.980	−1.20		0.379	0.976	51.09^g	0.345		
6A	−1.08	−1.38	−0.0911	0.526	0.977	28.42^h	0.345	0.359	0.047
6B	−1.11	−1.38		0.388	0.977	52.37^g	0.345		
7A	−0.669	−1.54	−0.292	−0.0814	0.958	22.18^h	0.256	0.509	0.107
7B	−0.799	−1.53		−0.519	0.954	35.75^g	0.256		
8A	−0.142	−1.15	−0.461	0.381	0.954	20.27^h	0.256	0.509	0.107
8B	−0.348	−1.14		−0.312	0.937	25.23^g	0.256		
9A	−1.05	−1.52	−0.0400	−0.374	0.969	14.58^l	0.128	0.585	0.116
9B	−1.08	−1.52		−0.434	0.967	29.11^h	0.128		
10A	−0.760	−1.08	−0.103	0.0348	0.954	10.14^l	0.128	0.585	0.116
10B	−0.828	−1.08		−0.117	0.953	19.91^i	0.128		
11A	−0.775	−1.32	−0.189	0.370	0.872	13.70^g	0.289	0.243	0.160
11B	−0.809	−1.33		−0.0315	0.869	21.66^g	0.289		
12A	−0.677	−1.12	−0.132	−0.182	0.861	12.36^g	0.289	0.243	0.160
12B	−0.701	−1.12		−0.0283	0.859	19.70^g	0.289		
13A	−0.669	−11.0	4.16	−5.87	0.997	64.96^m	0.913	0.115	0.171
13B	−9.24	−4.96		6.39	0.970	16.12^m	0.913^m		
14A$_1$	0.0970	−0.267	−0.349	8.25	0.934	9.089^l	0.355	0.464	0.051
14A$_2$	−0.0837	−0.331	−0.243	8.10	0.994	86.72^h	0.075	0.640	0.120
14B$_1$	−0.0956	−0.230		7.77	0.679	2.144^n	0.355		
14B$_2$	−0.286	−0.348		7.77	0.916	10.40^l	0.075		
15A$_1$	0.189	−0.256	−0.491	8.50	0.867	4.044^n	0.355	0.464	0.051
15A$_2$	−0.116	−0.364	−0.311	8.25	0.981	26.25^k	0.075	0.040	0.120
15B$_1$	−0.0811	−0.204		7.82	0.480	0.749^n	0.355		
15B$_2$	−0.375	−0.386		7.82	0.890	7.653^l	0.075		
16A$_1$	0.539	0.335	−0.235	1.05	0.945	8.425^m	0.384	0.304	0.100
16A$_2$	0.459	0.507	−0.118	0.892	0.999	299.8^h	0.412	0.300	0.169
16B$_1$	0.480	0.367		0.707	0.931	13.01^k	0.384		
16B$_2$	0.426	0.532		0.722	0.996	172.0^g	0.412		
17A$_1$	0.192	0.222	−0.122	0.846	0.833	2.264^n	0.384	0.304	0.100
17A$_2$	0.125	0.366	−0.0237	0.715	0.961	8.137^n	0.412	0.300	0.169
17B$_1$	0.162	0.238		0.669	0.819	4.069^n	0.384		
17B$_2$	0.119	0.371		0.681	0.961	18.09^k	0.412		
18A$_1$	0.532	−0.183	−0.334	1.26	0.856	2.737^n	0.384	0.304	0.100
18A$_2$	0.469	−0.0489	−0.242	1.14	0.918	3.554^n	0.412	0.300	0.169
18B$_1$	0.449	−0.138		0.775	0.777	3.051^n	0.384		
18B$_2$	0.402	0.00310		0.788	0.871	4.693^n	0.412		
19A	0.419	0.369	−0.137	1.06	0.998	330.9^g	0.384	0.304	0.100
19B	0.385	0.388		0.863	0.992	128.4^g	0.384		
20A	0.358	0.394	−0.0736	0.993	0.993	70.93^h	0.384	0.304	0.100
20B	0.340	0.403		0.886	0.991	111.3^g	0.384		
21B	−1.96	−0.680		−9.30	0.982	13.90^h	0.951		
22A$_1$	2.14	2.04	−0.112	9.73	0.897	33.02^g	0.145	0.369	0.330
22A$_2$	2.25	1.63	0.140	9.14	0.943	61.08^g	0.137	0.367	0.357
22B$_1$	2.19	2.00		9.52	0.897	51.36^g	0.145		
22B$_2$	2.18	1.68		9.41	0.942	94.19^g	0.137		
23A	2.46	2.23	0.230	10.11	0.984	109.3^g	0.193	0.337	0.114
23B	2.36	2.20		10.55	0.979	137.2^g	0.193		
24A	130.0	186.0	−0.143	554.0	0.997	118.1^i	0.392	0.032	0.300
24B	145.0	154.0		304.0	0.952	14.40^l	0.392		
25A$_1$	−0.314	−0.0156	−0.00530	6.36	0.943	13.49^i	0.314	0.312	0.005
25A$_2$	−0.272	−0.0338	−0.408	6.39	0.978	29.29^h	0.341	0.379	0.018
25B$_1$	−0.316	−0.0150		6.35	0.943	24.23^h	0.314		
25B$_2$	−0.289	−0.0281		6.33	0.971	41.59^g	0.341		
26A	26.5	25.8	9.23	239.0	0.994	25.41^n	0.522	0.306	0.955
26B	32.3	14.2		244.0	0.991	52.41^k	0.522		
27A	1.93	1.87	0.551	34.3	0.718	0.356^n	0.530	0.273	0.128
27B	1.86	1.86		35.2	0.716	10.52^n	0.530		

TABLE III (*Continued*)

Set	s_{est}^{d}	s_{α}^{d}	s_{β}^{d}	s_{ψ}^{d}	s_{h}^{d}	t_{α}^{e}	t_{β}^{e}	t_{ψ}^{e}	t_{h}^{e}	n^{f}
1A	19.5	33.9	26.5	44.1	81.2	20.93^{m}	4.966^{i}	0.612^{q}	0.375^{q}	11
1B	18.8	31.4	22.3		15.9	2.085^{m}	6.237^{g}		1.144^{p}	11
2A	0.145	0.195	0.133	0.176	0.351	4.805^{g}	8.269^{g}	1.095^{p}	0.928^{p}	17
2B	0.147	0.168	0.119		0.0633	4.918^{g}	9.795^{g}		8.29^{p}	17
3A	12.5	24.6	13.5	21.7	32.5	1.391^{p}	5.371^{i}	0.933^{p}	0.651^{q}	10
3B	12.4	21.7	13.3		10.6	2.068^{m}	5.349^{i}		0.708^{q}	10
4A	20.2	24.1	14.0	14.5	27.2	2.650^{j}	8.823^{g}	1.234^{p}	0.470^{q}	24
4B	20.5	24.4	13.8		9.72	2.627^{j}	9.170^{g}		1.914^{m}	24
5A	0.150	0.265	0.190	0.311	0.479	3.598^{l}	6.339^{i}	0.270^{r}	1.057^{p}	8
5B	0.135	0.223	0.171		0.0884	4.400^{i}	7.024^{g}		4.291^{i}	8
6A	0.169	0.298	0.214	0.350	0.539	3.609^{l}	6.443^{i}	0.260^{r}	0.976^{p}	8
6B	0.152	0.251	0.192		0.0994	4.411^{i}	7.146^{g}		3.906^{j}	8
7A	0.197	0.379	0.223	0.426	0.651	1.764^{o}	6.892^{g}	0.685^{q}	0.125^{r}	10
7B	0.190	0.316	0.214		0.117	2.532^{l}	7.152^{g}		4.454^{i}	10
8A	0.146	0.281	0.165	0.315	0.482	0.504^{q}	6.948^{g}	1.463^{o}	0.719^{p}	10
8B	0.158	0.262	0.178		0.0969	1.325^{p}	6.408^{g}		3.216^{j}	10
9A	0.218	0.596	0.259	0.523	0.786	1.771^{o}	5.881^{i}	0.077^{r}	0.476^{q}	7
9B	0.189	0.421	0.224		0.121	2.568^{m}	6.798^{i}		3.590^{l}	7
10A	0.188	0.512	0.223	0.450	0.676	1.484^{p}	4.829^{j}	0.228^{r}	0.051^{r}	7
10B	0.164	0.365	0.194		0.105	2.269^{m}	5.550^{i}		1.118^{p}	7
11A	0.267	0.355	0.267	0.406	0.661	2.186^{l}	4.956^{g}	0.466^{q}	0.409^{q}	17
11B	0.259	0.337	0.258		0.134	2.402^{l}	5.171^{g}		0.235^{r}	17
12A	0.238	0.316	0.238	0.362	0.589	2.141^{m}	4.687^{g}	0.365^{q}	0.309^{q}	17
12B	0.230	0.299	0.229		0.119	2.340^{l}	4.899^{g}		0.237^{r}	17
13A	0.367	3.93	2.75	1.29	4.15	0.170^{r}	4.005^{o}	3.231^{o}	1.414^{p}	5
13B	0.879	6.94	4.82		4.03	1.332^{p}	1.030^{p}		1.586^{p}	5
14A$_1$	0.0553	0.112	0.0751	0.0976	0.144	0.863^{p}	3.555^{l}	3.582^{l}	57.22^{g}	8
14A$_2$	0.0190	0.0506	0.0284	0.0387	0.0563	1.653^{o}	11.69^{i}	6.279^{i}	143.9^{g}	7
14B$_1$	0.101	0.181	0.136		0.0941	0.528^{q}	1.685^{o}		82.49^{g}	8
14B$_2$	0.0620	0.127	0.0919		0.0576	2.252^{m}	3.787^{j}		134.9^{g}	7
15A$_1$	0.0959	0.195	0.130	0.169	0.250	0.971^{p}	1.964^{o}	2.901^{l}	33.98^{g}	8
15A$_2$	0.0410	0.109	0.0611	0.0834	0.121	1.060^{p}	5.968^{i}	3.734^{l}	68.02^{g}	7
15B$_1$	0.151	0.270	0.203		0.140	0.300^{q}	1.003^{p}		55.76^{g}	8
15B$_2$	0.0844	0.173	0.125		0.0784	2.168^{m}	3.085^{l}		99.83^{g}	7
16A$_1$	0.109	0.179	0.145	0.268	0.397	3.009^{m}	2.305^{o}	0.877^{p}	2.638^{m}	7
16A$_2$	0.0193	0.0328	0.0313	0.0490	0.0722	13.99^{i}	16.21^{i}	2.406^{o}	12.36^{i}	6
16B$_1$	0.106	0.161	0.137		0.0763	2.978^{l}	2.679^{m}		9.266^{g}	7
16B$_2$	0.0311	0.0481	0.0474		0.0225	8.852^{i}	11.21^{i}		32.02^{g}	6
17A$_1$	0.104	0.170	0.139	0.255	0.378	1.127^{p}	1.605^{p}	0.476^{q}	2.235^{o}	7
17A$_2$	0.0630	0.107	0.102	0.160	0.235	1.170^{p}	3.586^{m}	0.148^{r}	3.040^{m}	6
17B$_1$	0.0933	0.142	0.121		0.0672	1.139^{p}	1.977^{o}		9.957^{g}	7
17B$_2$	0.0517	0.0799	0.0788		0.0374	1.482^{p}	4.703^{j}		18.19^{g}	6
18A$_1$	0.113	0.186	0.151	0.278	0.412	2.861^{m}	1.211^{p}	1.199^{p}	3.055^{m}	7
18A$_2$	0.0925	0.157	0.150	0.234	0.345	2.990^{m}	0.327^{q}	1.033^{p}	3.294^{m}	6
18B$_1$	0.119	0.182	0.154		0.0859	2.470^{m}	0.897^{p}		9.021^{g}	7
18B$_2$	0.0935	0.145	0.412		0.0677	2.783^{m}	0.022^{r}		11.64^{i}	6
19A	0.0159	0.0261	0.0212	0.0391	0.580	16.02^{g}	17.40^{g}	3.503^{l}	18.32^{g}	7
19B	0.0311	0.0474	0.0402		0.0223	8.115^{i}	9.642^{g}		38.53^{g}	7
20A	0.0333	0.0547	0.0444	0.0818	0.121	6.548^{i}	8.857^{i}	0.899^{p}	8.178^{i}	7
20B	0.0325	0.0495	0.420		0.0234	6.861^{i}	9.600^{g}		37.82^{g}	7
21B	0.152	1.11	4.26		0.494	1.774^{p}	0.159^{r}		18.83^{l}	4
22A$_1$	0.396	0.392	0.326	0.380	0.744	5.464^{g}	6.263^{g}	0.294^{q}	13.09^{g}	28
22A$_2$	0.261	0.259	0.227	0.254	0.501	8.688^{g}	7.177^{g}	0.552^{q}	18.25^{g}	27
22B$_1$	0.389	0.344	0.291		0.124	6.368^{g}	6.881^{g}		76.62^{g}	28
22B$_2$	0.257	0.227	0.200		0.0840	9.593^{g}	8.409^{g}		112.0^{g}	27
23A	0.149	0.182	0.251	0.129	0.250	13.57^{g}	8.873^{g}	1.790^{o}	40.51^{g}	15
23B	0.162	0.187	0.273		0.0585	12.62^{g}	8.081^{g}		180.4^{g}	15
24A	7.53	14.9	16.4	25.5	45.1	8.733^{j}	11.30^{i}	5.623^{l}	12.27^{g}	6
24B	25.2	49.2	51.7		27.1	2.737^{m}	2.983^{m}		11.21^{i}	6
25A$_1$	0.0339	0.0564	0.0485	0.0566	0.0903	5.568^{i}	0.321^{r}	0.094^{r}	70.36^{g}	9
25A$_2$	0.0211	0.0377	0.0307	0.0371	0.0575	7.203^{i}	1.100^{p}	1.100^{p}	111.3^{g}	8
25B$_1$	0.0310	0.0486	0.0440		0.0190	6.493^{g}	0.342^{q}		334.6^{g}	9
25B$_2$	0.0215	0.0351	0.0309		0.0144	8.221^{g}	0.908^{p}		439.0^{g}	8
26A	1.91	11.2	17.8	13.8	8.80	2.364^{p}	1.449^{p}	0.668^{q}	27.12^{l}	5
26B	1.62	6.10	3.00		2.88	5.292^{l}	4.711^{l}		84.81^{g}	5
27A	1.15	4.17	3.44	6.49	11.2	0.463^{q}	0.542^{q}	0.085^{r}	3.074^{p}	5
27B	0.813	2.90	2.44		1.47	0.642^{q}	0.763^{q}		23.92^{i}	5

[a] Multiple correlation coefficient. [b] *F* test for significance of regression. [c] Partial correlation coefficients of σ_I on σ_R, σ_I on r_V, and σ_R on r_V, respectively. All values of r_{12}, r_{13}, and r_{23} have confidence level < 90.0% unless otherwise noted. [d] Standard errors of the estimate, α, β, ψ, and h. [e] "Student t tests" for significance of α, β, ψ, and h. [f] Number of points in set. [g] 99.9% confidence level (cl). [h] 99.5% cl. [i] 99.0% cl. [j] 98% cl. [k] 97.5% cl. [l] 95% cl. [m] 90.0% cl. [n] <90.0% cl. [o] 80.0% cl. [p] 50% cl. [q] 20.0% cl. [r] <20% cl.

correlation with eq 4, but gave good results with eq 2 (sets 26A, 26B). The nuclear quadrupole frequencies of 2-substituted chlorobenzenes did not give significant correlation with either eq 4 or eq 2 (sets 27A, 27B).

Overall, of 26 sets correlated with eq 4, 17 gave excellent, one very good, one good, and two fair, and one gave poor results while four did not give significant correlation. Of 27 sets correlated with eq 2, 17 gave excellent, one very good, two good, and three fair, and one gave poor results while three did not give significant correlation. The results obtained with eq 4 are not quite so good as those obtained with eq 2.

Discussion

Steric Effect.—Of the 13 aromatic ring proton sets (1A–13A) correlated with eq 4, none gave a significant value of ψ as is shown by the "t" tests and confidence levels reported in Table III. Three of the seven sets of methylbenzenes (14A–20A) gave significant values of ψ on correlation with eq 4. Thus, there may be some steric effect in ortho-substituted methylbenzenes. Of the remaining sets studied only the NH chemical shifts of 2-substituted anilines showed a significant value of ψ. Overall, of 26 sets correlated with eq 4, four show significant values of ψ (sets 14A$_2$, 15A$_2$, 19A, and 24A). Furthermore, it has already been noted that correlation with eq 2 is generally better than correlation with eq 4. These results force us to the inescapable conclusion that *in general* steric effects are not important. In support of this conclusion we may further cite the wide range of substituent types in sets 2, 4, 11, and 12. It would seem therefore that the effect of ortho substituents on the nmr spectrum is solely an electrical effect. This is in agreement with what has been previously found with regard to the nature of the ortho electrical effect.[1–6] In all of the systems studied so far, electrical effects are *generally* predominant.

Composition of the Ortho Electrical Effect.—It will be convenient to describe the composition of the electrical effect of a substituent by means of ϵ where[22]

$$\epsilon = \beta/\alpha \tag{10}$$

Values of ϵ were calculated using α and β values obtained from correlation with eq 2 as in most cases results of correlation with eq 2 are better than those obtained with eq 4. Values of ϵ are reported in Table IV. The aromatic ring proton sets (sets 1–13) all show $\epsilon > 1$ indicating the predominance of resonance effects. This is in sharp contrast to the ionization of 2-substituted pyridines and quinolines in which the localized effect is predominant.[20] Thus the substituent effects which govern the ionization of ring protons are radically different from those which determine the chemical shifts of ring protons. The chemical shifts of the methyl protons in 2-substituted methylbenzenes (sets 14–20) show ϵ values ranging from 1.0 to 1.2. There may be some solvent dependence of ϵ in the case of the 2-substituted toluenes which gave ϵ values of 1.0 and 1.2 in dioxane and CCl$_4$, respectively. The OH chemical shifts of 2-substituted phenols (sets 22, 23) also seem to show a solvent dependence. The values are 0.77 for dimethyl sulfoxide and 0.93 for hexamethylphosphoramide. The values of ϵ for the 2-substituted phenols show a much smaller dependence on σ_R than do the values of ϵ for aromatic ring protons. The value of ϵ for the NH chemical shift of 2-substituted anilines is comparable to the values previously observed for 2-substituted phenols. The chemical shifts of the methoxy protons in 2-substituted anisoles have $\epsilon \cong 0$, corresponding to a dependence solely on the localized effect. The coupling constants of 2-substituted fluorobenzenes show an ϵ value of 0.44 indicating slight predominance of the localized effect.

TABLE IV

VALUES OF ϵ

Set	ϵ	Set	ϵ	Set	ϵ
1	2.1	10	1.3	19	1.0
2	1.4	11	1.6	20	1.2
3	1.6	12	1.6	21	. . .^{d}
4	. . .^{a}	13	. . .^{c}	22	0.77
5	1.2	14	1.2	23	0.93
6	1.2	15	1.0	24	1.1
7	1.9	16	1.2	25	. . .^{e}
8	. . .^{b}	17	. . .^{b}	26	0.44
9	1.3	18	. . .^{d}	27	. . .^{d}

[a] r_{12} was significant; therefore σ_I is a function of σ_R. [b] α was not significant. [c] α and β were not significant. [d] Correlation with eq 2 was not significant. [e] β was not significant.

Overall, the values of ϵ vary from 0.0 to 2.1. These results clearly preclude the definition of a single set of ortho-substituent constants to be applied to the nmr spectra of ortho-substituted compounds.

The Deviation of the Unsubstituted Compound.—The unsubstituted compound has often been found to deviate from the correlation line obtained for an ortho-substituted set. We have previously shown that it is indeed the case for the ionization constants of 2-substituted benzoic acids. We have also observed, however, that in the case of polarographic half-wave potentials all of the 22 sets which gave significant results with eq 2 included the value for the unsubstituted compound.[6] In the sets of nmr data studied in this paper, the value for the unsubstituted compound was included in all the sets for which it was available. Of these 19 sets, 18

TABLE V

"t" TESTS OF h_{obsd}

Set	h_{obsd}	h^{a}	Δ^{b}	$s_h{}^{a}$	t	n^{c}
3	0	−7.48	7.48	10.6	0.706^{d}	10
4	0	−18.6	18.6	9.72	1.914^{e}	24
5	0.47	0.379	0.091	0.0884	1.029^{f}	8
6	0.47	0.388	0.082	0.0994	0.825^{f}	8
7	−0.50	−0.519	0.019	0.117	0.162^{g}	10
8	−0.16	−0.312	0.152	0.0969	1.569^{h}	10
9	−0.44	−0.434	0.006	0.121	0.005^{g}	7
10	−0.03	−0.117	0.087	0.105	0.829^{f}	7
11	0	−0.0315	0.0315	0.134	0.235^{g}	17
12	0	−0.0283	0.0283	0.119	0.238^{g}	17
14	7.81	7.77	0.04	0.0576	0.694^{d}	7
15	7.88	7.82	0.06	0.0784	0.765^{f}	7
16	0.75	0.722	0.028	0.0225	1.244^{f}	6
17	0.71	0.681	0.029	0.0374	0.775^{f}	6
19	0.89	0.863	0.027	0.0224	1.205^{f}	7
20	0.90	0.886	0.014	0.0234	0.598^{d}	7
23	10.30	10.55	0.25	0.0585	4.273^{i}	15
25	6.34	6.33	0.01	0.0144	0.694^{d}	8

[a] From Table III. [b] $\Delta = |h_{\text{obsd}} - h|$. [c] Number of points in set. [d] 20% cl. [e] 90% cl. [f] 50% cl. [g] < 20% cl. [h] 80.0% cl. [i] 99.0% cl.

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[22] M. Charton, *J. Amer. Chem. Soc.*, **86**, 2033 (1964).

gave significant correlations with eq 2. There is generally good agreement observed between the experimentally observed values of the unsubstituted compound, h_{obsd}, and the calculated value, h of eq 2. To determine quantitatively whether h_{obsd} is significantly different from h, "Student t tests"[17] were carried out for all of the h_{obsd} values available for sets which gave significant correlations with eq 2. The results are set forth in Table V. In 16 of the 18 sets studied, h_{obsd} does not differ significantly from h. We conclude therefore that the value for the unsubstituted compound generally lies on the correlation line for ortho-substituted nmr data. We further conclude from the previous discussion of our method of detecting steric effects that no constant steric effect is generally extant in these sets.

Mobile Keto Allyl Systems. IX.[1] Kinetics and Mechanism of Amine Exchange Reactions with β-Ketoallylamines

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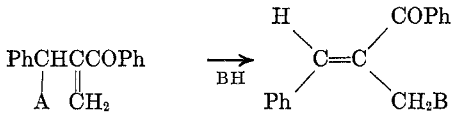
Rate data for the reaction of 2-[(α-substituted amino)benzyl]acrylophenones (**1**) with morpholine and with *tert*-butylamine in acetonitrile and in isooctane were obtained. Overall second-order kinetics were observed. From rate and thermodynamic constants, the mechanism of the proposed "SN2′-type" reaction is discussed.

In a preceding paper of this series,[3] kinetic data concerning the aminotropic allylic rearrangements of 2-[(α-substituted amino)benzyl]-1-indenones to 3-substituted amino-2-benzal-1-indanones were interpreted by a variant of an SN2′ mechanism.

The reactions of 2-[(α-substituted amino)benzyl]acrylophenones (**1**) with amines to give the corresponding α-(aminomethyl)chalcones (**2**) have been reported previously.[4] The need for quantitative information concerning the amine exchange reactions of **1** prompted this investigation.



1a, A = *tert*-BuNH **2a**, B = morpholino
b, A = (Et)$_3$CNH **b**, B = *tert*-BuNH

In a preliminary experiment, it was shown that the rates of rearrangement of 2-[(α-substituted amino)benzyl]acrylophenones (**1**) to the corresponding α-(aminomethyl)chalcones (**2**) without added amine (BH) were at least 100 times as slow as the rates of the amine exchange reactions we have studied.

Similarly, the rates of reaction of compounds **2a** and of **2b** with *tert*-butylamine and with morpholine were negligible compared with rates of the amine exchange reactions of compounds **1a** and **1b**.

The kinetic results reported below in Tables I, II, IV, and V show that the reaction of **1a** with the *tert*-butylamine produced in the reaction of morpholine with **1a** may be discounted, since in acetonitrile the ratio k(morpholine)/k(*tert*-butylamine) is *ca.* 80 and in isooctane the same ratio is *ca.* 17.

Hence the rate data for the rearrangements of compounds **1** with amines would not contain any appreciable contribution from other multistep routes.

The reaction of **1a** with morpholine in acetonitrile exhibited second-order kinetics and was first order in **1a** and in the amine; the rate coefficients are given in Table I.

TABLE I
VALUES OF SECOND-ORDER RATE COEFFICIENTS k_2 FOR THE REACTION OF 2-[α-(*tert*-BUTYLAMINO)BENZYL]ACRYLOPHENONE (**1a**) WITH MORPHOLINE IN ACETONITRILE

Temp, °C	[Aminoacrylophenone], mol/l.	[Morpholine], mol/l.	$10k_2$,[a] l. mol^{-1} min^{-1}
10.0	0.00738	0.00649	4.9
10.0	0.00742	0.0148	4.8
10.0	0.00614	0.0221	5.1
20.0	0.00904	0.0127	9.5
20.0	0.00817	0.0221	9.4
20.0	0.00395	0.0150	9.4
30.0	0.00501	0.00252	19
30.0	0.00527	0.00988	17
30.0	0.00324	0.0137	18

[a] $E = 12$ kcal/mol [$k_2 = Ae(-E/RT)$], $\Delta S^{\ddagger}_{20} = -27$ eu [$k_2 = (ekT/h)\exp(-E/RT)\exp(\Delta S^{\ddagger}/R)$].

The reaction of **1a** with *tert*-butylamine in acetonitrile was pseudo first order in **1a**, as required by the kinetic equation[3] (Table II).

TABLE II
VALUES FOR THE SECOND-ORDER RATE COEFFICIENTS k_2 IN THE REACTION OF 2-[α-(*tert*-BUTYLAMINO)BENZYL]ACRYLOPHENONE (**1a**) WITH *tert*-BUTYLAMINE, IN ACETONITRILE

Temp, °C	[Aminoacrylophenone], mol/l.	[*tert*-Butylamine], mol/l.	10^2k_2[a] l. mol^{-1} min^{-1}
20.0	0.00727	0.0942	1.2
20.0	0.00648	0.145	1.2
20.0	0.00628	0.221	1.1
30.0	0.00655	0.137	2.2
30.0	0.00797	0.177	2.2
30.0	0.0115	0.139	2.2
40.0	0.00828	0.062	4.5
40.0	0.00821	0.093	4.3
40.0	0.00882	0.124	4.3

[a] $E = 12$ kcal/mol, $\Delta S^{\ddagger}_{20} = -36$ eu.

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[1] For paper VIII in this series, see G. Maury and N. H. Cromwell, *J. Org. Chem.*, **34**, 596 (1969).

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[3] G. Maury, E.-M. Wu, and N. H. Cromwell, *J. Org. Chem.*, **33**, 1907 (1968).

[4] (a) R. P. Rebman and N. H. Cromwell, *Tetrahedron Lett.*, No. 52, 4833 (1965); (b) N. H. Cromwell and R. P. Rebman, *J. Org. Chem.*, **32**, 3830 (1967).