should be ca. 14 pK_a units less acidic than pyrrole, but it is actually 5.3 pK_a units *more* acidic. This provides a means of estimating the aromaticity of the cyclopentadienyl anion as 26 kcal/mol, which agrees reasonably well with estimates of 24 and 27 kcal/mol based on other models. The progressive increase in acidity along the series pyrrole, indole, carbazole is explained by increases in inductive and/or resonance effects resulting from the presence of an additional benzene ring(s). The reversal of this acidity order in the corresponding carbon acid series, cyclopentadiene, indene, fluorene, is explained by a progressive decrease in the aromatic stabilization energy of the cyclopentadienyl moiety, which overshadows the inductive and/or resonance effects of the additional benzene ring(s). Aromatic stabilization energies of 20 and 14.5 kcal/mol are estimated for the indenyl and fluorenyl anions, respectively.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. 1,3-Cyclopentadiene, 542-92-7; indene, 95-13-6; fluorene, 86-73-7; pyrrole, 109-97-7; indole, 120-72-9; carbazole, 86-74-8; acetonitrile, 75-05-8; sulfonylbismethane, 67-71-0; (methylsulfonyl)benzene, 3112-85-4; methylbenzene, 108-88-3; methane, 74-82-8; cyanamide, 420-04-2; methanesulfonamide, 3144-09-0; benzenesulfonamide, 98-10-2; benzenamide, 62-53-3; ammonia, 7764-41-7.

Correlation of Gas-Phase Proton Affinities with S_N2 Nucleophilicities. A Quantitative Assessment of Steric Hindrance in S_N2 Reactions

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The factors underlying nucleophilicity of ions and molecules involved in S_N2 reactions have long held the interest of mechanistic chemists. By definition, nucleophilicity is the relative ability of an ion or molecule to donate a pair of electrons to assist displacement of a leaving group.[1] Yet correlation of this kinetic property with thermodynamic properties of the nucleophile, such as basicity and ionization potential, has generally been unsatisfactory. While poor correlation is probably a consequence of variations in solvation and steric factors,[1b,2-4] there has rarely been sufficient evidence to warrant firm assignment of a specific reason for poor correlation. Experimental sophistication and advances in experimental methods have produced new data which make a new attempt at such correlations timely.

Our interest in correlating nucleophilicity with some intrinsic property of the nucleophile was derived from our solvolysis studies of bulky secondary alkyl substrates in mixed solvents. There have been reports of inversion of the normal order of nucleophilicity in the aqueous ethanolysis of 1-octyl,[5] 2-octyl,[5] and 2-adamantyl[6,7] substrates. In each instance, a new solvolysis mechanism was proposed to account for the inversed nucleophilic order. Peterson and co-workers[8] have argued that the 1-octyl and 2-octyl results are not unexpected based on the various factors which may influence nucleophilicity in such systems. Our own results for 2-octyl substrates[9] led us to suggest that steric factors were the primary cause of the inversion of nucleophilic order with the octyl derivatives.

Table I. Rate Constants, N Values ($MeOSO_2F$ Scale), and Proton Affinities for 3- and 4-Substituted Pyridines

substituent	relative proton affinity[a]	k_2, $MeOSO_2F$,[b] 25 °C, i-$PrNO_2$	nucleophilicity, N[c]
3-Me	2.7	8.84	0.22
H	(0.0)	5.36	(0.0)
3-Cl	−5.8	0.514	−1.01
3-F	−6.6	0.582	−0.96
4-CN	−10.5	0.204	−1.42

[a] Reference 18. [b] Reference 16. [c] Calculated using the Swain-Scott equation, $\log (k/k_0) = sN$ assuming $s = 1$, an arbitrary choice; cf. ref 8.

Table II. Rate Constants, N Values (EtI Scale), and Proton Affinities for 3- and 4-Substituted Pyridines

substituent	relative proton affinity[a]	$k_2 \times 10^4$, EtI,[b] 60 °C, $PhNO_2$	N[c]
4-MeO	6.7	8.20	0.42
4-Me	4.0	6.65	0.33
3-Me	2.7	6.35	0.30
H	(0.0)	3.15	(0.0)
4-Ac	−3.5	0.740	−0.63
3-Cl	−5.8	0.287	−1.04
4-CN	−10.5	0.107	−1.47
3-CN	−11.3	0.0531	−1.77

[a] Reference 18. [b] Reference 17. [c] Calculated using the Swain-Scott equation, $\log (k/k_0) = sN$, assuming $s = 1$.

Since steric factors are absent from gas-phase proton-exchange equilibria,[10] it was hoped that a plot of nucleophilicity vs. gas-phase basicity would unequivocally reveal steric factors operative on nucleophilic order. The major question was whether or not solvation effects would interfere in such a correlation.

Peterson[8] and Schleyer[11] and their co-workers have recently treated solvolytic reactivity of simple primary and secondary substrates in terms of major factors which affect solvolytic rate. Following the approaches advocated by Swain[12] and Winstein,[13] each group refined and evaluated equations designed to quantify, and thus separate, solvent ionizing power, substrate sensitivity, and nucleophilicity (N). None of the treatments quantified a nucleophile's sensitivity to steric factors. Despite this and the use of

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[1] (a) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969. (b) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill Publishing Co.: New York, 1962.

[2] Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.

[3] Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

[4] (a) Taagepera, M.; Defrees, D.; Hehre, W. J.; Taft, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 424. (b) Taft, R. W.; Taagepera, M.; Abboud, J. L. M.; Wolf, J. F.; DeFrees, D. J.; Hehre, W. J.; Bartmess, J. E.; McIver, R. T., Jr. *Ibid.* **1978**, *100*, 7765.

[5] Pross, A.; Aronovitch, H.; Koren, R. *J. Chem. Soc., Perkin Trans. 2* **1978**, 197.

[6] Harris, J. M.; Becker, A.; Fagan, J. F.; Walden, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 4484.

[7] Karton, Y.; Pross, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 595.

[8] Peterson, P. E.; Vidrine, D. W.; Waller, F. J.; Hendrichs, P. M.; Magaha, S.; Stevens, B. *J. Am. Chem. Soc.* **1977**, *99*, 7968.

[9] McManus, S. P.; Roberts, F. E.; Lam, D. H., to be submitted for publication.

[10] Taft, R. W. In "Proton-Transfer Reactions"; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975; Chapter 2.

[11] Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

[12] Swain, C. G.; Moseley, R. B.; Bown, D. E. *J. Am. Chem. Soc.* **1955**, *77*, 846. Swain, C. G.; Scott, C. B. *Ibid.* **1953**, *75*, 141.

[13] Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846. Winstein, S.; Grunwald, E.; Jones, H. W. *Ibid.* **1951**, *73*, 2700. Winstein, S.; Fainberg, A. H.; Grunwald, E. *Ibid.* **1957**, *79*, 4146.

0022-3263/81/1946-0635$01.00/0

Table III. Experimental Rate Constants and Proton Affinities for 2-Alkylpyridines. Calculated Steric Retardation Factors

substituent	relative proton affinity[a]	$k_2 \times 10^5$, EtI,[b] 60 °C, $PhNO_2$	obsd N[c]	calcd steric-free N	steric retardation factor, SRF ($N_{calcd} - N_{obsd}$)	calcd steric-free k, $k_2 \times 10^5$
H	(0.0)	31.5[d]	(0.0)	-	-	-
2-Me	3.2	7.85[e]	−0.60	0.21	0.81	51.0
2-Et	4.5	3.77	−0.92	0.38	1.30	76.0
2-*i*-Pr	5.0[f]	1.15[e]	−1.44	0.44	1.88	87.0

[a] Reference 20. [b] Reference 19. [c] Using the Swain–Scott equation, $\log (k/k_0) = sN$, assuming $s = 1$. [d] Reference 17. [e] Calculated from data at other temperatures. [f] Estimated.

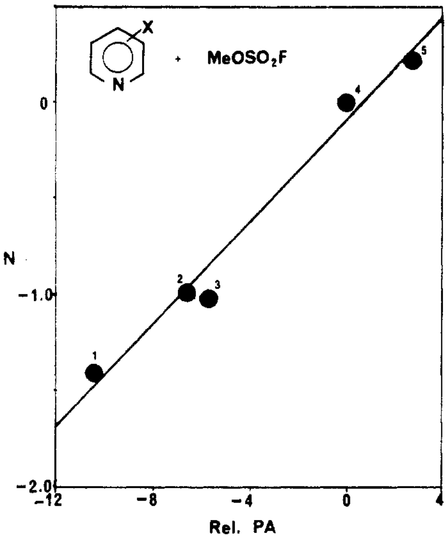

Figure 1. Correlation of proton affinities (gas phase) with nucleophilicities (solution) for 3- and 4-substituted pyridine derivatives reacting with methyl fluorosulfonate at 25 °C in 2-nitropropane. Pyridine substituents are **1**, 4-CN, **2**, 3-F, **3**, 3-Cl, **4**, hydrogen, **5**, 3-Me (correlation coefficient = 0.990).

quite different reference systems and different solvents the experimental nucleophilicities determined in the Peterson and Schleyer studies are in remarkable agreement with each other and with those earlier reported by Swain.[12] The agreement indicates the derived N values are relatively independent of solvent and substrate factors.[14,15] Also available for correlation attempts are proton affinities and rates for 2-, 3-, and 4-substituted pyridine derivatives in a single solvent.[16-20]

Results and Discussion

Pyridine Derivatives. To minimize solvation and steric effects in order to see if a good correlation exists between nucleophilicity and gas-phase basicity, studies of 3- and 4-substituted pyridine derivatives in a single solvent were selected. The available rate data for 3- and 4-substituted pyridine derivatives reacting with a primary (methyl fluorosulfonate)[16] and a secondary (ethyl iodide)[17] substrate are shown in Tables I and II along with gas-phase proton affinities (PA)[18] of the pyridine derivatives. By use of the Swain–Scott equation,[12] the rate data were converted to nucleophilicity values and are shown in Tables I and II. Plots of N vs. PA for the 3- and 4-substituted pyridine derivatives show excellent correlations with each substrate (Figures 1 and 2). However, when the N values of 2-substituted derivatives (Table III)[18,19] are placed on the plot for the ethyl iodide reactions,[21] steric factors[19] cause the points to fall well below the correlation line for 3- and 4-substituted pyridines.

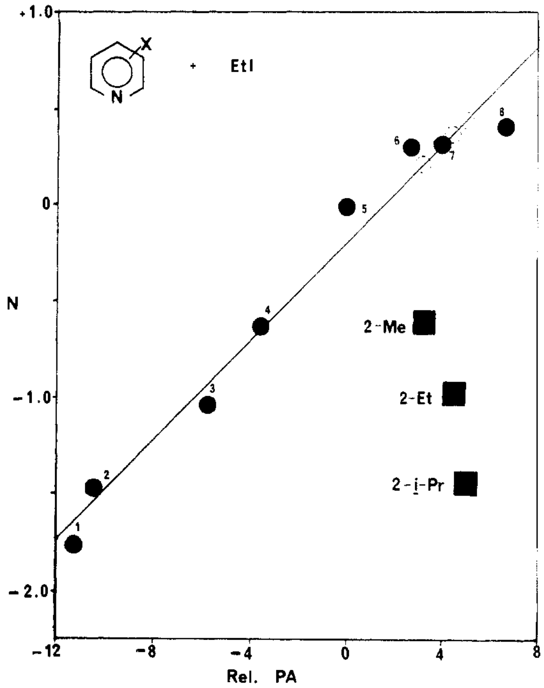

Figure 2. Correlation of proton affinities (gas phase) with nucleophilicities (solution) for the reaction at 60 °C in nitrobenzene of ethyl iodide with 3- and 4-substituted pyridines (●), correlation coefficient = 0.985, and 2-substituted pyridines (■). Pyridine substituents used in obtaining the least-squares correlation are **1**, 3-CN, **2**, 4-CN, **3**, 3-Cl, **4**, 4-Ac, **5**, hydrogen, **6**, 3-Me, **7**, 4-Me, **8**, 4-MeO. Theoretical values for the 2-substituted pyridine derivatives are shown as broken-line open circles.

On the basis of the correlation for 3- and 4-substituted pyridines, an N value and a theoretical rate for 2-substituted derivatives can be calculated for the reactions if steric retardation were absent. The difference between the observed and calculated N values (Table III) represents a quantitative assessment of the magnitude of the steric retardation (called steric retardation factor, SRF) for these reactions. Since 2-*tert*-butylpyridine shows no readily

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(14) There are obvious exceptions, e.g., acetic and formic acid; see ref 1.

(15) Kevill, D. N.; Lin, G. M. L. *J. Am. Chem. Soc.* **1979**, *101*, 3916.

(16) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892.

(17) Fischer, A.; Galloway, W. J.; Vaughan, J. *J. Chem. Soc.* **1964**, 3591.

(18) Arnett, E. M.; Chawla, B.; Bell, L.; Taagepera, M.; Hehre, W. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5729. Beauchamp, J. L.; Taft, R. W., and co-workers, to be published.

(19) Brown, H. C.; Cahn, A. *J. Am. Chem. Soc.* **1955**, *77*, 1715. Professor Brown's elegant work on steric effects in pyridine derivatives have been summarized in his book: "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.

(20) Aue, D. H.; Webb, H. M.; Bowers, M. T.; Liotta, C. L.; Alexander, C. J.; Hopkins, H. P., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 854.

(21) A similar effect is observed when 2-substituted pyridines are placed on plots for methyl iodide, but fewer rates for deactivated derivatives were available, hence the ethyl iodide example was used here.

Table IV. Table of PA, IP, and N Values. Comparison of Observed and Calculated Nucleophilicities of Alcohols

			MeOTs scale^c			pentamethyleneiodonium scale^d		
ROH R =	proton affinity, kcal/mol	IP,^{b} eV	N_{SBS}, obsd	N_{SBS}, calcd^e	SRF ($N_{calcd} - N_{obsd}$)	N_{PW}, obsd	N_{PW}, calcd^f	SRF ($N_{calcd} - N_{obsd}$)
H	168.9	12.59	−0.26	−0.26	0.00	0.00	0.00	-
Me	182.1	10.85	0.01	0.02	0.01	0.57	0.57	-
Et	186.8	10.46	0.09	0.08	−0.01	0.50	0.74	0.24
i-Pr	190	10.29	0.09	0.14	0.05	0.33	0.84	0.51
t-Bu	192	9.97	<−.12^g	0.20	>0.32	−0.41	0.91	1.32

[a] Reference 22. [b] Reference 28. [c] Reference 11. [d] Reference 8. [e] Calculated from the least-squares line drawn through the first three points (Figure 3); correlation coefficient = 0.993. [f] Calculated from the line drawn through the first two points (Figure 4). [g] This work; see ref 23.

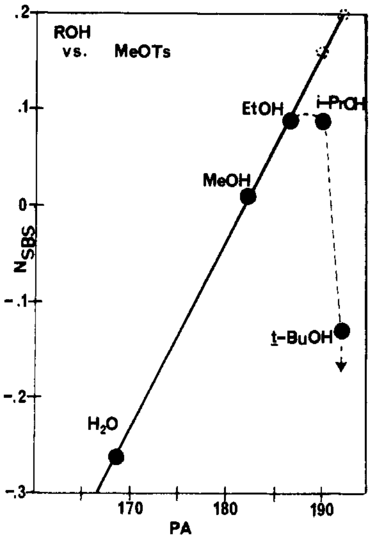

Figure 3. Correlation of proton affinities (gas phase) with nucleophilicities (solution) for the reaction of water and some alcohols with methyl tosylate at 50 °C in excess nucleophile as solvent. The least-squares line ($r = 0.993$) is based on the first three points. Theoretical values for i-PrOH and t-BuOH are shown as broken-line open circles.

measureable reaction with ethyl iodide, no steric retardation factor can be calculated for it.

Alcohols. Peterson et al.[8] have previously reported that steric retardation accounts for a mixed order of nucleophilicity for alcohols. Furthermore, it is well documented[1] that steric factors in the alkyl substrate affect the magnitude of the rate constant in S_N2 reactions. Therefore, a methyl derivative should be the least susceptible organic substrate to steric factors originating in the nucleophile. A plot of the N values of water, methanol, and ethanol on the methyl tosylate scale (N_{SBS})[11] shows a near perfect correlation with the respective gas-phase proton affinities[22] (Figure 3). Steric factors, however, cause the points for isopropyl and $tert$-butyl alcohols[23-25] to fall below the line as was observed with the 2-substituted pyridines. The steric retardation factors (SRF) calculated from these data

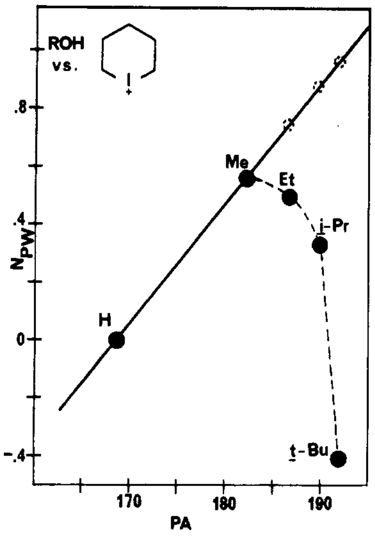

Figure 4. Correlation of proton affinities (gas phase) with nucleophilicities (solution) for the reaction of water and some alcohols with pentamethyleneiodonium hexafluoroantimonate in water. Theoretical values for EtOH, i-PrOH, and t-BuOH are shown as broken-line open circles.

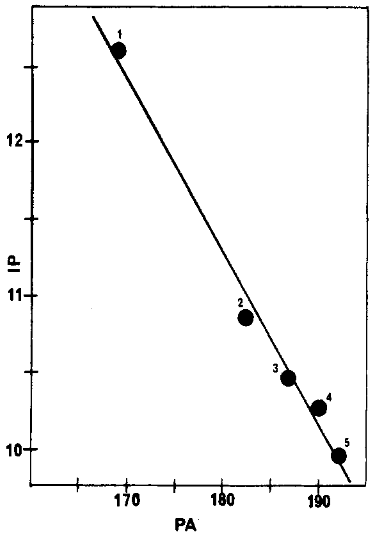

Figure 5. Correlation of proton affinities with ionization potentials for water and some alcohols: 1, H_2O; 2, MeOH; 3, EtOH; 4, i-PrOH; 5, t-BuOH.

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(22) The PA for water, MeOH, and EtOH are from: Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 1320. The PA for i-PrOH and t-BuOH are from: Kiraoka K.; Kebarle, P. *Ibid.* **1977**, *99*, 360.

(23) Attempts to measure the necessary rates of t-BuOH for determination of N and Y were largely unsuccessful owing to the dehydration of t-BuOH as HOTs is produced. Some dehydration occurred even in the presence of 0.03 M 2,6-lutidine. A maximum rate of 1.2×10^{-6} is estimated for MeOTs at 50 °C based on estimates of k during the first 5% of reaction at 100, 125, and 135 °C. Rates were measured conductimetrically in dried and distilled t-BuOH according to previously reported procedures.[24] Attempts to determine Y by measurements of the rate of 1-adamantyl bromide in t-BuOH were unsuccessful owing to the very slow rates (no observable rate after 4 h at 100 °C) and the observed decomposition of t-BuOH in reactions with MeOTs. Y was estimated to be −3.7 ± 0.17 based on correlations of ϵ, π^*, E_T, Z, and σ_I values of MeOH, EtOH, i-PrOH, and t-BuOH with Y values of the first three alcohols.[25]

(24) McManus, S. P.; Lam, D. H. *J. Org. Chem.* **1978**, *43*, 650.

(25) The values for π^* were taken from a preprint of a table in a review: Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Progr. Phys. Org. Chem.*, in press, kindly provided by Professor Taft. The other solvent parameters either came from the same compilation or from: Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972.

are shown in Table IV.

A plot of proton affinities against the N values of alcohols based on the pentamethyleneiodonium (N_{PW}) ion,[8] a primary substrate, reveals an earlier onset of steric retardation in the series, as expected (Figure 4). These steric retardation factors (SRF) are also shown in Table IV.[26] These values support the contention[8,9] that inversion of the nucleophilicity order in 2-octyl solvolyses[5,9] is an expected consequence of steric factors.

Correlation of N vs. Ionization Potential (IP). Dougherty[27] has previously suggested that there should be a correlation between IP and N. Bentley and Schleyer[3] showed that the correlation between experimental solvent nucleophilicities and the IP's of a wide range of hydroxylic solvents was not good. However, for limited series, IP's plot linearly vs. proton affinities (Figure 5),[28-30] and, therefore, IP's should correlate with N values for such compounds. Nevertheless, large differences in solvent electrophilicity[15] and differences in solvent bulk properties (e.g., dimerization of neat acetic acid[8]) are expected to cause correlations between gas-phase properties and solutions properties to be poor.[4] Steric factors,[31] as shown here, may also make such correlations poor.

Solvent Effects on Correlations of Basicity and Nucleophilicity. As stated earlier, correlations of nucleophilicity with solution-phase basicity have generally been poor. There have been some successes, however, when solvation differences were minimized.[32] Other than the Schadt–Bentley–Schleyer (SBS) study,[11] the data treated here were for a single functional class of nucleophiles in a single solvent. While the SBS study has moved toward the separation of solvation factors in assessing nucleophilicity, there is reason[3,4] to believe that the present treatment may be inapplicable to widely different types of nucleophiles and solvents.[33] Nevertheless, the present method is useful for quantifying steric hindrance to nucleophilicity at least over a modest range of structural differences.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Helpful comments and suggestions from E. M. Arnett, T. W. Bentley, J. M. Harris, and R. W. Taft are kindly acknowledged. Professors Arnett and J. L. Beauchamp kindly provided data prior to publication.

Registry No. 4-Cyanopyridine, 100-48-1; 3-fluoropyridine, 372-47-4; 3-chloropyridine, 626-60-8; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 3-cyanopyridine, 100-54-9; 4-acetylpyridine, 1122-54-9; 4-methylpyridine, 108-89-4; 4-methoxypyridine, 620-08-6; 2-methylpyridine, 109-06-8; 2-ethylpyridine, 100-71-0; 2-isopropylpyridine, 644-98-4; $MeOSO_2F$, 421-20-5; EtI, 75-03-6; H_2O, 7732-18-5; MeOH, 67-56-1; EtOH, 64-17-5; i-PrOH, 67-63-0; t-BuOH, 75-65-0; MeOTs, 80-48-8; pentamethyleneiodonium, 41688-68-0.

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[26] Similar plots have been constructed with the N values from ref 12 and 15 with similar results; data are not available in those cases for i-PrOH and t-BuOH; therefore, they add nothing to this discussion.

[27] Dougherty, R. C. *Tetrahedron Lett.* **1975**, 385.

[28] IP's were measured by PE spectroscopy: Danby, C. J.; Cocksey, B. J.; Eland, J. H. D. *J. Chem. Soc. B* **1971**, 790.

[29] Other LFER have previously been developed by several groups: cf. ref 28; Kurylo, M. J.; Jurinski, N. B. *Tetrahedron Lett.* **1967**, 1983; Henderson, W. G.; Beauchamp, J. L.; Holtz, D.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 4728; Dekock, R. L.; Barbachyn, M. R. *Ibid.* **1979**, *101*, 6415; Olmstead, W. N.; Brauman, J. I. *Ibid.* **1977**, *99*, 4219; Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *Ibid.* **1978**, *100*, 1240; Levitt, L. S.; Widing, H. F. *Prog. Phys. Org. Chem.* **1976**, *12*, 119.

[30] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1972**, *94*, 4726.

[31] Steric retardation has been recently suggested as one reason for the poor nucleophilicity of some fluorinated alcohols; cf.: Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.* **1979**, *101*, 2486.

[32] Two recent articles, published after submission of this manuscript, provide dramatic evidence of steric factors on nucleophilicity and correlate nucleophilicity and solution basicity; cf.: Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314, 3320.

[33] Plots of $\Delta G°$ or $\Delta H°$ for solution protonation vs. PA are linear for 3- and 4-substituted pyridines but 2-substituted pyridines with polar groups in the 2-position fail to give a high correlation coefficient (ref 20). It was suggested that these deviations could be explained with field-effect theories. Such effects should not be operative with the 2-alkyl groups treated here, but one should be aware of the possibility of this competing factor with polar 2-substituents. Rate data are available for several polar 2-substituted pyridines in Me_2SO relative to the rate of pyridine (Deady, L. W.; Zoltwiez, J. A. *J. Org. Chem.* **1972**, *37*, 603). However, rates of the 3-substituted pyridine derivatives in Me_2SO have been reported relative to pyrazine (Deady, L. W.; Zoltewiez, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 5475). Converting the latter rates to values relative to pyridine, and then to N values, resulted in a relatively poor correlation of N vs. PA for the 3-substituents (R = 0.93). Therefore, we have not further treated this data. Since Deady and Zoltewiez discuss steric effects on their rates, the reader is referred to the first mentioned article.

Reaction of 2′-Hydroxychalcone Dibromides with Pyridine

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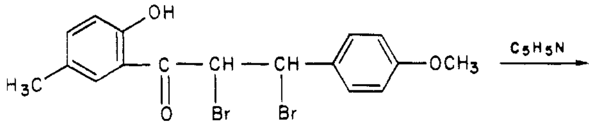
2′-Hydroxychalcone dibromides react with pyridine to give a variety of products. Thus Ghiya and Marathey[1] observed that heating 2′-hydroxy-4-methoxy-5′-methylchalcone dibromide (1) with pyridine gave the nuclear halogenated chalcone (2).



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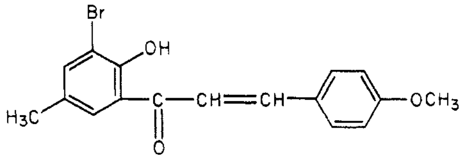

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Jadhav et al.[2] studied the reactions of a large number of chalcone dibromides and found that these are converted to either α-bromochalcones, flavones, or aurones, depending upon the nature and position of the substituents in the aromatic nuclei. The formation of bromoflavones has also been reported.[3,4]

Keeping in view the products formed in this reaction, we have treated a series of variously substituted chalcone dibromides with pyridine at the boiling point. In order

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[1] B. J. Ghiya and M. G. Marathey, *J. Sci. Ind. Res., Sect. B*, **20**, 41 (1961).

[2] F. A. Atchabba, P. L. Trivedi, and G. V. Jadhav, *J. Univ. Bombay*, **25**, 1, (1957); **27**, 8 (1958); *J. Indian Chem. Soc.*, **32**, 206 (1955).

[3] P. N. Wadodkar, *Indian J. Chem.*, **1**, 163 (1963).

[4] K. R. Kutumbe and M. G. Marathey, *Chem. Ber.*, **96**, 913 (1963), and references therein.