Solvents Effects on Aromatic Nucleophilic Substitutions. Part 5.[1] Kinetics of the Reactions of 1-Fluoro-2,4-dinitrobenzene with Piperidine in Aprotic Solvents[1]

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The kinetics of the reaction between 1-fluoro-2,4-dinitrobenzene and piperidine were studied in toluene, benzene, dioxane, trichloroethane, tetrahydrofuran, chlorobenzene, ethyl acetate, chloroform, dichloromethane, acetone, acetonitrile, and nitromethane. The second-order rate coefficient is almost insensitive to the amine concentration in chloroform, acetonitrile, and nitromethane; for the other solvents this value of k_3/k_2 is greater than 10^2, indicating neat base catalysis. The trend in k_3/k_2 does not follow the solvent basicity order; the solvents insensitive to base catalysis are those which exhibit hydrogen-bond donor (HBD) properties. These results are interpreted as an indication that in this reaction the detachment of the nucleofuge is the rate-limiting step in most of the aprotic solvents studied; those solvents which are HBD assist the departure of fluoride, and the formation of the intermediate is the rate-determining step. This conclusion was confirmed by k_F/k_{Cl} determinations. A simple linear energy solvation correlation was found between the parameter $E_T(30)$ and k_A obtained at [B] < 10^{-2}M. For higher amine contents increasing deviations were found.

Some of the most important evidence for the mechanism of aromatic nucleophilic substitution (ANS) (Scheme 1) comes from studies of base catalysis of reactions involving amine nucleophiles.[2] Although since its discovery in 1958[3] the reaction has been extensively studied,[2,4–6] the mechanism by which it operates in aprotic solvents is still unclear.[7] If the zwitterionic σ intermediate ZH does not accumulate to an appreciable extent during the course of reaction, the overall-order rate constant, k_A, derived by standard steady-state approximation, has the form of equation (1). According to

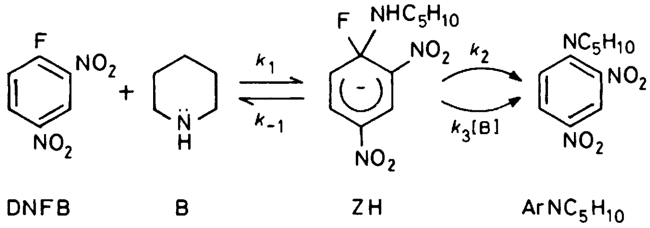
$$k_A = (k_1k_2 + k_1k_3[B])/(k_{-1} + k_2 + k_3[B]) \quad (1)$$

equation (1) if $k_{-1} \gg (k_2 + k_3[B])$ the reaction is base-catalysed and k_A depends linearly on base concentration. If k_2 is relatively small and $k_{-1} \approx k_3[B]$, k_A depends on base concentration in curvilinear fashion (downward curvature): the linear dependence at low [B] changes to a plateau at high [B].

We have recently reported studies of solvent effects in aprotic[8] and protic[1] solvents for a model aromatic nucleophilic substitution free of complications, namely the reaction of 1-chloro-2,4-dinitrobenzene with piperidine. It was therefore of interest to study the influence of the media in other ANS reactions where complications are known to occur. Base catalysis is probably the most important complication found in this type of reaction and the title reaction was found to be subject to base catalysis in some aprotic solvents.[3,9,10] The relationship between k_A and [B] depends on environmental factors[2,10,11] but although several solvent effect studies have been performed,[6,12] especially by Russian workers,[13–16] no systematic study of solvent influence on the catalysed and uncatalysed steps has been performed.

Results

The reaction of 1-fluoro-2,4-dinitrobenzene (DNFB) with piperidine (B) in all the solvents studied proceeds straightforwardly to give the expected *N*-(2,4-dinitrophenyl)piperidine.



Scheme 1.

A usual complication in ANS of DNFB in aprotic solvents is the solvolysis of the substrate by traces of water, producing 2,4-dinitrophenol; in the present work formation of the expected product was quantitative for all the solvents studied. The kinetics of the reactions were studied in the presence of varying excess of amounts of nucleophile under pseudo-first-order conditions. The reactions proved to be first order in substrate, and on division of the pseudo-first-order rate coefficients, k_ψ, by the appropriate concentration of piperidine, the second-order rate coefficients, k_A, were calculated. Table 1 gathers the data for the title reactions in toluene, benzene, dioxane, trichloroethane (TCE), tetrahydrofuran (THF), chlorobenzene, ethyl acetate, chloroform, dichloromethane (DCM), acetone, acetonitrile, and nitromethane, at 15 °C.

The second-order rate coefficient in chloroform, acetonitrile, and nitromethane, are almost completely insensitive to the nucleophile concentration; the rate of the reactions in the rest of the solvents increases steadily with base content. This kinetic behaviour indicates that $k_{-1} \gg (k_2 + k_3[B])$, and then equation (1) can be simplified to equation (2), according to which k_1k_2/k_{-1}, k_1k_3/k_{-1}, and k_3/k_2 can be obtained from the plot of k_A *vs.* [B]. The results are reported in Table 2, which also shows the statistical parameters revealing satisfactory linear dependence for all the solvents studied.

$$k_A = (k_1k_2 + k_1k_3[B])/k_{-1} \quad (2)$$

Table 1. Reaction of 1-fluoro-2,4-dinitrobenzene (DNFB) with piperidine in aprotic solvents at 15 °C; second-order overall rate coefficients[a]

			10^3 [Piperidine]/M							
No.	Solvent	$E_T(30)$[b]	0.625	1.25	2.50	5.00	7.50	10.0	12.5	15.0
1	Toluene	33.9			1.38	2.55	3.58	4.48	5.41	6.19
2	Benzene	34.5			2.34	3.70	5.09	6.45		
3	Dioxane	36.0		2.06	2.57	3.42	4.11	5.05	5.83	6.67
4	Trichloroethane	36.2	2.48	3.28	5.35	8.48	11.7	15.0	17.5	20.7
5	Tetrahydrofuran	37.4	2.94	4.59	7.83	13.3	18.0	22.3	26.5	30.6
6	Chlorobenzene	37.5	4.23	5.22	8.42	13.7	18.4	22.4	24.7	28.0
7	Ethyl acetate	38.1	3.48	6.34	9.55	15.6	20.3	25.0	28.7	32.3
8	Chloroform	39.1		18.9	19.5	20.0	20.2	20.4	20.6	
9	Dichloromethane	41.1			39.7	42.4	45.3	47.4		
10	Acetone	42.2	24.8	31.6	44.3	64.9	79.5			
11	Acetonitrile	46.0		87.9	99.4	110	114	116		
12	Nitromethane	46.3		163	172	192				

[a] [DNFB] = 5×10^{-5}M; k_A in l mmol^{-1} s^{-1}. [b] Ref. 13.

Table 2. Reaction of 1-fluoro-2,4-dinitrobenzene (DNFB) with piperidine in aprotic solvents at 15 °C; partial rate coefficients,[a] and solvent parameters[23]

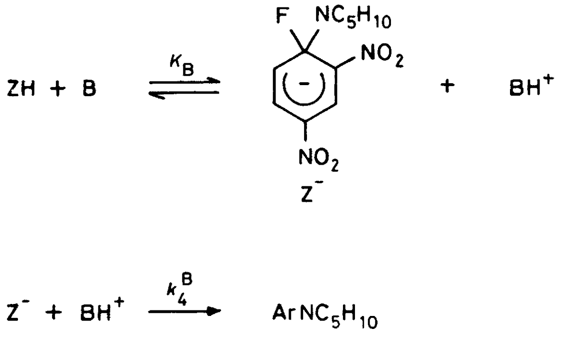
Solvent	β	k_1k_2/k_{-1}	k_1k_3/k_{-1}	k_3/k_2	r[b]	s[c]
Toluene	0.112	0.579	383	662	0.998	0.131
Benzene	0.100	0.965	549	569	0.999	0.0095
Dioxane	0.369	1.70	331	195	0.999	0.0562
1,1,1-Trichloroethane	0.000	1.97	1 264	641	0.999	0.310
THF	0.550	2.74	1 915	698	0.997	0.827
Chlorobenzene	0.071	4.16	1 687	405	0.991	1.300
Ethyl acetate	0.450	4.57	1 945	426	0.995	1.172
Acetone	0.480	22.1	7 981	361	0.994	2.891

[a] Calculated values from equation (2). [b] Regression coefficient. [c] Standard deviation; in all cases but acetone the confidence level is 99.999% (acetone 99.94%).

Table 3. Reaction of 1-fluoro-2,4-dinitrobenzene (DNFB) and 1-chloro-2,4-dinitrobenzene (DNCB) with piperidine in acetonitrile[a]

Substrate	T/°C	$10^3[NHC_5H_{10}]$/M	k_A/l mol s^{-1}
DNFB	30	0.625	290
		1.25	312
		2.50	320
DNCB	15	2.50	0.287
		3.75	0.288
		5.00	0.291

[a] [Substrate] = 5×10^{-5}M.



Scheme 2.

The kinetic behaviour observed in the present work for the reaction in acetonitrile differs slightly from others previously reported for reaction at 29.8 °C;[17] however, the present results were carefully checked and confirmed and the reaction was also run at 30 °C. These data are reported in Table 3, which also shows the values for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in the same solvent at 15 °C.

Discussion

The low nucleofugacity of the fluoride ion, and the facts that the nucleophile is a secondary amine and the solvents are aprotic are accepted contributing factors for the observation of base catalysis, but the mechanism(s) by which this process occurs is the subject of controversy at present.[5–7,18,19] Two interpretations are currently advocated. One is that the base abstracts the ammonium proton from the intermediate (Scheme 2) in a rate-limiting step, to form the deprotonated intermediate Z^- from which the nucleofuge is rapidly detached.[4,7] The other is that ZH and Z^- are in reversible acid–base equilibrium and that the rate-limiting step is general acid-catalysed detachment of the nucleofuge from Z^-.[5,20,21] The latter process has been called the SB–GA (specific base–general acid) mechanism, but it has been recently advocated[5a] that the mechanism is better characterized as a rate-limiting nucleofuge detachment.

The mechanism of rate-limiting proton transfer seems to be firmly established for the reactions run in protic solvents, mainly as a result of the work of Bernasconi *et al.*[4,7] but some doubt has been recently cast on its application to some ANS reactions with amines run in aqueous dioxane.[5] On the other hand, the SB–GA mechanism seems to be correctly applicable in aprotic solvents,[4] and these authors have suggested that the mechanism of the uncatalysed path could be similar to that of the catalysed one with a solvent molecule acting as base as shown in Scheme 3. Notwithstanding, it has been recently argued that this approach is untenable in dipolar aprotic solvents when a secondary[6a] or a primary[18a] amine is the nucleophile.

The question of whether proton transfer or nucleofuge detachment is rate-limiting is directly related to the relative rates of the acid–base equilibrium, measured by K_B, and the nucleofuge departure, k_4^B. In a non-polar, aprotic solvent it is reasonable to assume that the Scheme 2 does not apply to an appreciable extent and that the rate of the proton transfer would be linearly related to the relative base strengths of intermediate ZH and the nucleophile in the solvent (K_B). It is well known that pK_B values vary greatly as the solvent is changed,[22] and one would expect that large changes in solvent basicity give rise to corresponding changes in the rates of the paths involved in the decomposition

$$\mathrm{ZH} + \mathrm{S} \underset{}{\overset{K_S}{\rightleftharpoons}} \mathrm{Z}^- + \mathrm{SH}^+$$

$$\mathrm{Z}^- + \mathrm{SH}^+ \xrightarrow{k_4^S} \mathrm{ArNC_5H_{10}}$$

Scheme 3.

of ZH. Only a few attempts have been made previously to compare the relative rates of the catalysed and uncatalysed pathways in different aprotic solvents; in one case they were all dipolar solvents[6b] and in the other mainly dipolar solvents,[18a] and in both cases the number of solvents studied was relatively small.

Table 2 gathers results for the solvents studied in the present work for which base catalysis is clearly detected. If proton transfer were the rate-limiting step in the catalysed pathway one would expect that k_3/k_2 would be directly related to the basicity of the solvent. Taft *et al.*[23] have developed a useful scale of solvent dipolarity [measured by their solvatochromic parameter (π^*) and acidity (α) and basicity (β) terms]. The β parameter shown in Table 2 can be considered a good measure of solvent basicity and it is easily concluded that the k_3/k_2 is not correlated with the solvent basicity strength measured by β. Furthermore, if one assumes that the solvent plays the role of the base in the uncatalysed pathway (Scheme 3) it is again clear that k_1k_2/k_{-1} is not related to the β parameter. These results seem to indicate that proton transfer is not the rate-limiting step in these reactions.

On the other hand, the solvents in which no base catalysis was detected (chloroform, acetonitrile, and nitromethane) are the only ones that exhibit hydrogen-bond-donor abilities, as shown by non-zero α values (0.44, 0.29, and 0.23,[23] respectively, in the order given). This observation, added to the findings already noted, could be interpreted as an indication that nucleofuge departure is rate-determining in these reactions. It is well known that fluoride ion is a extremely poor leaving group in non-polar solvents owing to its high demand for solvation,[24] which cannot be provided by the solvent. Only those aprotic solvents with HBD ability can effectively assist fluoride detachment and in these cases decomposition of the intermediate ZH is not rate-limiting and its formation is the slow step. This conclusion agrees with previous findings in protic solvents: in fact, no base catalysis was observed when the title reaction was run in methanol.[25]

To prove the last point, the rates of reactions of the present system were compared with the rates of the reactions of 1-chloro-2,4-dinitrobenzene in aprotic solvents previously determined.[8] The latter system had not been studied in acetonitrile; therefore reaction rates were determined in this solvent at several amine concentrations.†

A useful alternative criterion for base catalysis can be applied when the nucleofuges are halogens. If the rate-constant sequence $F \gg$ other halogens is observed, then breaking of the carbon–fluorine bond is not involved in the rate-determining step.[26] Table 4 shows the values of $k_A{}^F/k_A{}^{Cl}$ collected into two sets: the first includes solvents where base catalysis was detected; the second includes the other solvents for which k_3/k_2 is close to unity. It is easy to conclude that for the second set $k_A{}^F/k_A{}^{Cl}$ ratio is high, consistent with the foregoing interpretation that in these solvents formation of the intermediate is rate-determining; the huge decrease in the ratio observed for the first solvent set indicates a change in the rate-determining step from formation of the intermediate to its decomposition to products. To strengthen the argument the order of increasing $k_A{}^F/k_A{}^{Cl}$ is nearly the inverse order of k_3/k_2 shown in Table 2.

Table 4. Values of $k_A{}^F/k_A{}^{Cl}$ for the reactions of DNFB and DNCB with piperidine at 15 °C

Solvent	$k_A{}^F/k_A{}^{Cl}$
Dioxane	23.5
Trichloroethane	15.4
Ethyl acetate	25.0
Chlorobenzene	31.1
THF	14.5
Acetone	30.2
Chloroform	282
Nitromethane	288
Acetonitrile	375

Table 5. Reaction of 1-fluoro-2,4-dinitrobenzene with piperidine in aprotic solvents; log k_A *vs.* $E_T(30)$[a]

[Piperidine]/ M	Solvents[b]	*a*	*m*	*r*	*s*
0.0025	1—12	−5.07	0.158	0.981	0.136
	1—10,12	−5.51	0.170	0.985	0.116
	1,2,4—10,12	−5.33	0.166	0.990	0.0953
0.0050	1—12	−4.33	0.143	0.976	0.138
	1—10,12	−4.74	0.154	0.980	0.120
	1,2,4—10,12	−4.51	0.149	0.992	0.0742
0.0075	1—11	−3.82	0.132	0.951	0.162
	1,2,4—10	−4.40	0.149	0.988	0.0836
0.0100	1—11	−3.38	0.122	0.938	0.169
	1,2,4—7,9,10	−4.03	0.142	0.980	0.0900

[a] *a,m,r,s*, are the intercept, the slope, the correlation coefficient, and the standard deviation, respectively. [b] Numbers from Table 1, in all cases but [B] = 0.01M; confidence level 99.999% (for 0.01M 99.998%).

The lack of evidence for general acid catalysis has been a strong argument against the SB–GA mechanism as well as some 'suitable estimations' of pK_{ZH} Although no estimates of K_B in the different solvents have been made in the present work, it can be qualitatively concluded that acidity (not basicity) of the solvent helps the decomposition of ZH. This is an argument based on analogy, but it can be reasonably considered as indirect evidence of 'acid-catalysis'.

Linear Solvation Energy Correlations.—It was of interest to find out if some of the linear solvation energy correlations tried for the reactions of 1-chloro-2,4-dinitrobenzene (model reaction, free of complications)[1,8] could be applied to the present system. According to the data in Table 2 and by application of equation (2) it is easy to estimate that for piperidine concentration of *ca.* 10^{-2}M, k_3 is of the same order of magnitude as k_2, being smaller at lower [B]. It would then be expected that at low piperidine concentration the response of the specific rate coefficients of the present system to the solvation parameters might be similar to that in the model reaction. Table 5 shows some correlations between Reichardt's parameters $E_T(30)$[27] and the rates of reactions performed at 0.0025, 0.005, 0.0075, and 0.01M-piperidine. The correlation is remarkably good for the reactions at the lowest [B], even when

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† The reaction of 1-fluoro-2,4-dinitrobenzene with piperidine in acetonitrile has been previously studied by Hirst *et al.*[17] at 29.8 °C; they found that the second-order rate coefficients are completely insensitive to the piperidine concentration. Our results at 15 °C show that there is slight steady increase in rate with amine content. The reaction was also run under the conditions of Hirst *et al.*;[17] the results are also shown in Table 3. Even at 30 °C a slight increase in rate is observed. Nevertheless, this can be considered a case of 'small acceleration' but not of base catalysis.

all the solvents are included; it becomes better when acetonitrile is excluded or when this and dioxane are excluded. The correlations can still be considered satisfactory for [B] < 10^{-2}M, but it is easy to see that for [B] $\geqslant$ 0.01M the increasing importance of k_3 perturbs the correlation. The shift in the rate-determining step is evident; if the solvents in which the first-step is rate-determining (solvents 8, 11, and 12) and dioxane are excluded the correlation becomes satisfactory.

The behaviour of dioxane is surprising. Although it is a solvent of relatively low polarity it exhibits lower values of k_3/k_2. It has been suggested[28] that when the dioxane molecules solvate a solute they might partially adopt a boat conformation, which has an appreciable dipolar moment, and this might be the cause of the relative low k_3/k_2 value.

It is likely that in complex ANS reactions where changes in the relative rates of formation and decomposition(s) of the intermediate complex ZH are taken within a given set of solvents the application of multiparameter equations may prove preferable to the single-parameter correlations reported here. Examination of the Reichardt's equation for the present case was important for comparison with previous work;[1,6] determination of other parameters is in progress to test their applications in multi-parameters equations at [B] $\geqslant$ 10^{-2}M.

Experimental

Reagents and Solvents.—1-Fluoro-2,4-dinitrobenzene was crystallized from ethanol to constant m.p. 25—26 °C. *N*-(2,4-Dinitrophenyl)piperidine (m.p. 92—93 °C) was prepared[29] and piperidine (b.p. 106.4 °C) was purified[8] as previously described. Dichloromethane (b.p. 39.7 °C) was purified by washing with concentrated sulphuric acid, then with dilute sodium hydroxide solution, and finally with distilled water.[30] It was kept over sodium hydroxide pellets overnight, then treated with calcium chloride and distilled. Acetonitrile (b.p. 81—82 °C) was kept over calcium chloride for several days and then distilled and kept over phosphorus pentaoxide for several days. It was distilled over phosphorus pentaoxide, refluxed (1 h) over calcium hydride, and slowly distilled.

The rest of the solvents were purified as previously described.[8] All solvents were kept over 4 Å molecular sieves and stored in special vessels which allow delivery without air contamination.

Kinetic Procedures.—The kinetics of the reactions were studied spectrophotometrically.[31] A Perkin-Elmer 124 spectrophotometer was used, with a data-aquisition system based on a microprocessor. This set-up has a 12-bit analogue–digital converter which allows absorbance measurements with an error <0.1% at a maximum rate of 12 readings per s. The microprocessor controls data aquisition; it also measures time through a quartz-crystal-controlled oscillator. Once data aquisition is over, data can be read in the system display and/or transferred to a computer through an RS 232-C interface. To ensure satisfactory mixing of the reactants an electric micromixer was fitted over the spectrophotometer cell compartment. The reactions were run by mixing known amounts of standard solutions of 1-fluoro-2,4-dinitrobenzene and piperidine in the desired solvent (the substrate solution was added by automatic micropipette) in the thermostatically controlled cells of the spectrophotometer; optical densities were recorded at 390 nm. The pseudo-first-order (k_ψ) and second-order (k_A) rate coefficients were obtained as previously described.[31] In all cases the 'infinity' value, A_∞, was determined experimentally for each run at the working temperature. This value agreed, within experimental error, with the 'theoretical' value calculated from application of Beer's law to a solution of *N*-(2,4-dinitrophenyl)-piperidine in the working solvent. All the kinetic runs were carried out at least by triplicate; the error in k_A was $\leqslant$2%.

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References

1 Part 4, P. M. E. Mancini, R. D. Martinez, L. R. Vottero, and N. S. Nudelman, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1427.

2 For recent reviews see (*a*) C. F. Bernasconi, MTP Int. Series in Org. Chem., Series One, vol. 1, ed. H. Zollinger, Butterworths, London, 1973; (*b*) N. S. Nudelman, *An. Acad. Nac. Cienc. Exactas. Fis. y Nat.*, (*Buenos Aires*), 1980, **32**, 109.

3 J. F. Bunnett and R. Randall, *J. Am. Chem. Soc.*, 1958, **80**, 6020.

4 C. F. Bernasconi, *Acc. Chem. Res.*, 1978, **11**, 147.

5 (*a*) J. F. Bunnett and A. V. Castaño, *J. Am. Chem. Soc.*, 1981, **103**, 4861; (*b*) J. F. Bunnett, S. Sekiguchi, and L. A. Smith *ibid.*, p. 4865.

6 (*a*) D. Ayediran, T. O. Bamkole, J. Hirst, and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1580; (*b*) T. O. Bamkole, J. Hirst, and I. Onyido, *ibid.*, 1979, 1317.

7 C. F. Bernasconi, R. H. de Rossi, and P. Schmid, *J. Am. Chem. Soc.*, 1977, **99**, 4090.

8 P. M. E. Mancini, R. D. Martinez, L. R. Vottero, and N. S. Nudelman, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1133.

9 F. Pietra and A. Fava, *Tetrahedron Lett.*, 1963, 1535.

10 C. F. Bernasconi and H. Zollinger, *Helv. Chem. Acta*, 1966, **49**, 103.

11 (*a*) N. S. Nudelman and D. R. Palleros, *J. Org. Chem.*, 1983, **48**, 1607; (*b*) D. R. Palleros and N. S. Nudelman, *J. Chem. Soc., Perkin Trans. 2*, 1985, 479 and refs. therein.

12 Hai Whang Lee and Ikchoon Lett, *J. Korean Chem. Soc.*, 1978, **22**, 221.

13 (*a*) S. M. Shein and K. V. Solodova, *J. Org. Chem. USSR* (*Engl. Transl.*), 1970, **6**, 1479; (*b*) K. V. Solodova and S. M. Shein, *ibid.*, p. 1475.

14 (*a*) S. M. Shein and N. K. Danilova, *J. Org. Chem. USSR* (*Engl. Transl.*), 1968, **4**, 1975, 1882; (*b*) S. M. Shein and A. V. Evstifeev, *ibid.*, 1969, **5**, 906.

15 (*a*) S. M. Shein, M. K. Danilova, and N. I. Kuznetsova, *Reakts. Sposobn. Org. Soedin.*, 1970, **7**, 458, 476; (*b*) N. K. Danilova and S. M. Shein, *ibid.*, 1967, **4**, 649.

16 (*a*) R. V. Vizgart and I. M. Ozdrovskaya, *Reakts. Sposobn. Org. Soedin.*, 1966, **3**, 16, 35; (*b*) I. M. Ozdrovskaya and R. W. Wisghert, *ibid.*, p. 146.

17 D. Ayediran, T. O. Bamkole, and J. Hirst, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1396.

18 (*a*) O. Banjoko and P. Otiono, *J. Chem. Soc., Perkin Trans. 2*, 1981, 399; (*b*) O. Banjoko and K. Ur-Rahmon, *ibid.*, p. 1105.

19 T. O. Bamkole, J. Hirst, and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1982, 889.

20 J. A. Orvick and J. F. Bunnett, *J. Am. Chem. Soc.*, 1970, **92**, 2417.

21 J. B. Bunnett and R. H. Garst, *J. Am. Chem. Soc.*, 1965, **87**, 3875.

22 (*a*) J. Hine, 'Structural Effects on Equilibria in Organic Chemistry,' Wiley, New York, 1975; (*b*) C. Reichardt, 'Solvent Effects on Organic Chemistry,' Verlag Chemie, Weinheim, 1979.

23 M. J. Kamlet, J.-L. M. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1981, **13**, 485.

24 A. J. Parker, *Quart. Rev. Chem. Soc.*, 1962, **16**, 163.

25 J. F. Bunnett, T. Kato, and N. S. Nudelman, *J. Org. Chem.*, 1969, **34**, 785.

26 J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.

27 C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 98.

28 M. J. Kamlet, R. W. Taft, P. W. Carr, and M. H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1689.

29 L. R. Vottero, P. M. E. Manchini, R. D. Martinez, and N. S. Nudelman, *Acta Sudam. Quim.* (*Chile*), 1982, **2**, 19.

30 J. A. Riddick and W. B Bunger, 'Organic Solvents. Physical Properties and Methods of Purification,' Wiley-Interscience, New York, 1970, 3rd edn.

31 J. F. Bunnett, T. Kato, and N. S. Nudelman, in 'Fundamental Organic Chemistry Laboratory Manual,' eds. K. T. Finley and J. Silson, Prentice-Hall, New Jersey, p. 122.

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