Kinetics of the Dehydration of *N*-(α-Cyanobenzyl)-*N*-phenylhydroxylamines

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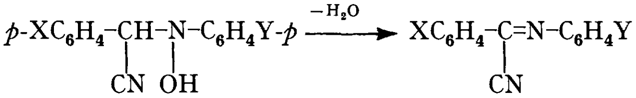
The rate of dehydration of *N*-(α-cyanobenzyl)-*N*-phenylhydroxylamines (I) catalysed by triethylamine and tri-n-butylamine were measured in 95% ethanol at 25°. The triethylamine catalysed rate of dehydration of α-cyano-*p*-chlorobenzyl derivative (Ic) was linearly correlated with the ionization ratio of *p*-cyanophenol in the same medium. Hammett ρ values of 2.90 and 1.57 were obtained for *C*- and *N*-phenyl substituents, respectively. The primary deuterium isotope effect for the reaction of (Ic) was *ca.* 6. An irreversible *E*1cB mechanism is suggested for the reaction except for the α-cyano-*p*-dimethylamino-derivative (Ie). The large positive deviation of (Ie) from the Hammett plot and its smaller deuterium isotope effect (*ca.* 3) are explained in terms of a transition to an *E2* mechanism.

PREVIOUSLY we have reported the first isolation of *N*-(α-cyanobenzyl)-*N*-phenylhydroxylamines (Ia—i) formed by reactions of α,*N*-diphenyl nitrones with liquid hydrogen cyanide.[1] These hydroxylamines are stable in acidic media and nonpolar solvents, but they are readily dehydrated to give the corresponding cyano-imines (II) in basic media and polar solvents.



$$p\text{-}XC_6H_4\text{-}\underset{CN}{CH}\text{-}\underset{OH}{N}\text{-}C_6H_4Y\text{-}p \xrightarrow{-H_2O} XC_6H_4\text{-}\underset{CN}{C}\text{=}N\text{-}C_6H_4Y$$

(I) (II)

a; X = Y = H
b; X = Me, Y = H
c; X = Cl, Y = H
d; X = MeO, Y = H
e; X = Me_2N, Y = H
f; X = CN, Y = H
g; X = H, Y = Cl
h; X = H, Y = Me
i; X = H, Y = MeO

There are many reports of β-elimination reactions in the formation of olefins and, apart from a few details, the mechanisms of the reactions have been elucidated. However, there seem to have been few studies on base catalysed elimination reactions in formation of bonds other than carbon–carbon double bonds from H–C–E–X type compounds where E denotes oxygen, nitrogen, or sulphur. It seems interesting to investigate the dehydration of (I), a β-elimination reaction leading to the formation of a carbon–nitrogen double bond, and examine the mechanism in the light of findings for olefin-forming reactions. This paper reports kinetic studies on the dehydration of (I) in 95% ethanol catalysed by triethylamine and tri-n-butylamine. Excess of water was added to the medium, because small amounts of water produced in the reaction or contaminating the ethanol might have complex effects on the kinetics.

RESULTS

The rate of dehydration of all the hydroxylamines tested was first-order with respect to the substrate at a constant catalyst concentration. The final products were the corresponding cyano-imines (II). Under the conditions used for rate measurements, no side reactions were detected spectrophotometrically, *i.e.* the absorption spectra of the reaction mixtures at infinite time coincided with those of authentic cyano-imines.

Effects of Amine Concentration.—The effects of triethylamine concentration on the dehydration of (Ic) was examined to establish the mode of base catalysis. This substrate was chosen because the rate of its dehydration could be measured over a wide range of the amine concentration. Plots of the observed pseudo-first-order rate constant k_{obs} against the amine concentration gave a curve, as shown in Figure 1. This behaviour is explained by the concurrent contributions of both lyate ion and free triethylamine catalysed terms, as suggested for the hydrogen exchange

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[1] M. Masui, M. Yamauchi, C. Yijima, K. Suda, and K. Yoshida, *Chem. Comm.*, 1971, 312.

reaction of pyrrole in aqueous acetonitrile,[2] though in the latter reaction general acid catalysis was demonstrated.

Assuming that the lyonium ion concentration is negligible, the observed pseudo-first-order rate constant can be expressed by equation (1) where LO^- is the sum of hydroxide and ethoxide ions, a is the total concentration of triethylamine, and K_N is the apparent dissociation constant of the amine [equation (2)]. The contribution of the solvent catalysed reaction ($k_0 = 5.02 \times 10^{-4}$ min^{-1} at 25°) is negligible, even at the lowest amine concentration used. The parameters K_N, k_N, and k_L in equation (1) were estimated by the non-linear least squares method of Rubin[3] as 5.61×10^{-4} mol l^{-1}, 12.99 l mol^{-1} min^{-1}, and 83.00 l mol^{-1} min^{-1}, respectively. These values gave the theoretical line in Figure 1, which agrees well with the observed rate constants.

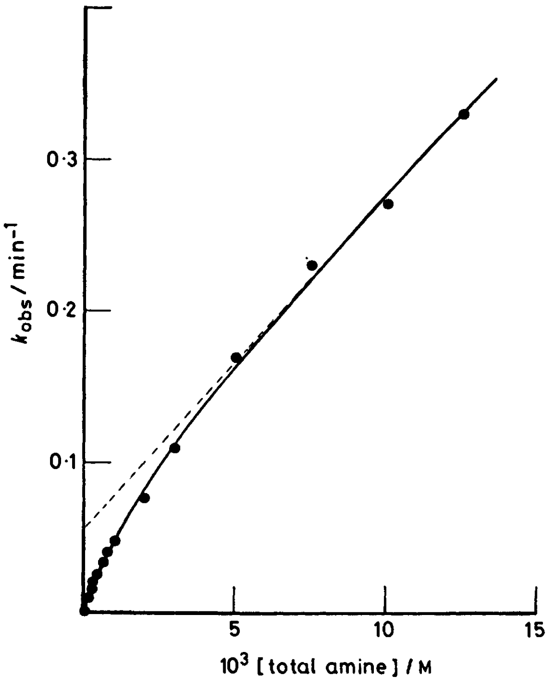

FIGURE 1 Plot of the observed pseudo-first-order rate constant for the dehydration of (Ic) against concentration of triethylamine in 95% ethanol at 25°. The solid line was calculated by a nonlinear least-squares method (see text)

$$\begin{aligned} k_{obs} &= k_0 + k_N[Et_3N] + k_L[LO^-] \\ &= k_0 + k_N\{a + 0.5K_N - (0.25K_N^2 + aK_N)^{\frac{1}{2}}\} \\ &\quad + k_L\{(0.25K_N^2 + aK_N)^{\frac{1}{2}} - 0.5K_N\} \end{aligned} \quad (1)$$

$$K_N = [Et_3NH^+][LO^-]/[Et_3N] \quad (2)$$

However, the smallest possible value of k_L, measured separately using sodium hydoxide as catalyst, was 1.29×10^3 l mol^{-1} min^{-1} * and this is not compatible with the estimated value. The value of K_N as the base dissociation constant of triethylamine in the present medium also seems improbable because the value predicts that *ca.* 1.2×10^{-4}M-triethylamine will liberate 10^{-4}M-lyate ion. This concentration of amine is almost the smallest employed in the present experiments (see Figure 1), but at the latter concentration of sodium hydroxide the rate was too fast to measure by the method employed. Thus equation (1) does not explain the behaviour in Figure 1.

Another possibility of correlating the rate with the amine concentration, or with the basicity of the medium, was examined. The degree of ionization of *p*-cyanophenol in 95% ethanol, measured at a triethylamine concentration of 2×10^{-4}—1×10^{-1}M, was linearly correlated with the amine concentration by equation (3) (r 0.999, n 11) where a is the total concentration of the amine.† When the rate of dehydration of (Ic) was replotted against the degree of ionization of the phenol calculated from equation (3), a straight line was obtained (Figure 2). This indicates that log k_{obs} is linearly correlated with the particular acidity function defined by the ionization of *p*-cyanophenol with a unit slope.

$$\log([PhO^-]/[PhOH]) = 0.772\log a + 1.673 \quad (3)$$

Substituents and Deuterium Isotope Effects.—The effects of substituents on the rate of dehydration catalysed by triethylamine and tri-n-butylamine were parallel. The observed pseudo-first-order rate constants for (I) with substituents on the *C*-phenyl ring [except (Ie)] and with those on the *N*-phenyl ring were correlated giving ρ values of 2.90 and 1.57, respectively (Figures 3 and 4).

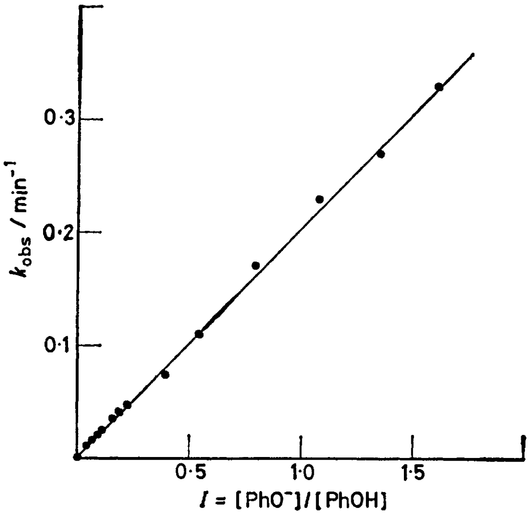

FIGURE 2 Plot of the observed pseudo-first-order rate constant for the dehydration of (Ic) against the ionization ratio of *p*-cyanophenol in 95% ethanol at 25°

Deuterium kinetic isotope effects for the dehydration of (Ic and e) were measured and the results are shown in Table 1. The value of k_H/k_D for (Ie) was about one-half that for (Ic).

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* The dehydration rate measured in 1—5 × 10^{-5}M-sodium hydroxide did not show first-order dependence on the lyate ion concentration: it was less than first-order in 1—3 × 10^{-5}M- and more than second-order in 3—5 × 10^{-5}M-sodium hydroxide. The value of k_L cited in the text was evaluated from the rate observed in 2 × 10^{-5}M-sodium hydroxide.

† The linear relation may be fortuitous because there seems to be no theoretical grounds for it. [PhO$^-$] does not necessarily mean the concentration of free phenoxide ion. It can be the sum of free and ion-paired phenoxide ion. If all the phenoxide ion is present as an ion-pair the slope of equation (3) should be unity (*cf.* M. M. Davis, *J. Amer. Chem. Soc.*, 1962, **84**, 3623).

[2] D. M. Muir and M. C. Whiting, *J.C.S. Perkin II*, 1976, 388.

[3] D. I. Rubin, *Chem. Eng. Progr. Symp.*, 1963, **59**, 90.

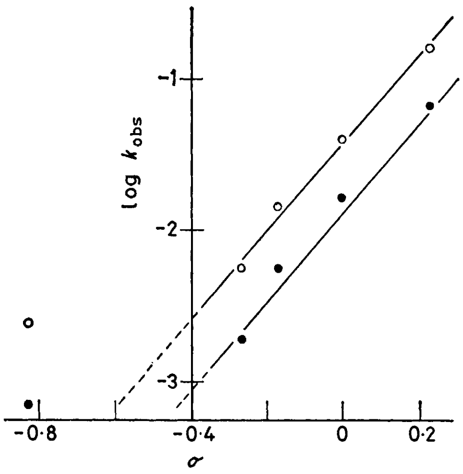

FIGURE 3 Logarithm of the observed pseudo-first-order rate constants for the dehydration of (I) substituted on the *C*-phenyl ring against σ constants in 95% ethanol at 25° catalysed by ○, triethylamine (5.0mM) and ●, tri-n-butylamine (5.0mM)

TABLE 1

Deuterium isotope effects in dehydrations of (Ic and e) at 25°

Compound	Catalyst	10^3[Catalyst]/M	k_H/k_D [a]
(Ic)	Et_3N	1.0	5.5 ± 0.4
		2.0	5.8 ± 0.3
		3.0	6.1 ± 0.2
	$Bu^n{}_3N$	5.0	5.5 ± 0.2
(Ie)	Et_3N	5.0	2.9 ± 0.3

[a] Average of at least three measurements.

TABLE 2

Activation parameters for dehydration of (I) catalysed by triethylamine (5.0mM) in 95% ethanol

		Compound				
	T/°C	(Ia)	(Ic)	(Ie)	(If)	(Ig)
	0				10.1 [c]	
	5				15.2 [c]	
	10	1.31	6.90		19.4 [c]	3.58
	18	2.49	11.5			6.70
10^2k_{obs}/min^{-1} [a]	25	3.99	16.5	0.243		10.6
	30			0.306		
	35		27.9	0.442		21.0
	40			0.636		
	42	10.7	40.6			30.0
E_a/kcal mol^{-1}		11.6 ± 1.1	0.74 ± 0.43	12.0 ± 2.0	10.0 ± 3.2	11.8 ± 0.6
$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}		−26 ± 4	−29 ± 2	−30 ± 7	−26 ± 12	−23 ± 2

[a] Average of at least three measurements. [b] Based on the second-order rate constants in l mol^{-1} s^{-1} calculated from k_{obs} and the catalyst concentration, at 25°. [c] Obtained at a triethylamine concentration of 0.50mM.

Activation Parameters.—The activation parameters for the reactions of (Ia, c, and e—g) catalysed by triethylamine (5×10^{-3}M) are summarized in Table 2 with the rate constants obtained at several temperatures. The dehydration of (If) was too fast to measure by the method used with the amine concentration at 25°. However, the value of the activation parameters obtained at lower amine concentrations and lower temperatures suggest that the reaction was similar to those of other compounds.

DISCUSSION

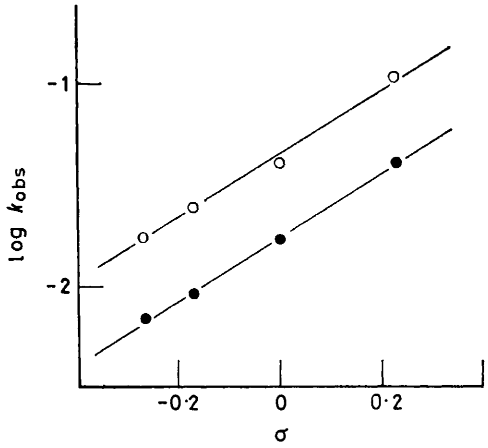

FIGURE 4 Logarithm of the observed pseudo-first-order rate constants for the dehydration of (I) substituted on the *N*-phenyl ring against σ constants in 95% ethanol at 25° catalysed by ○, triethylamine (5.0mM) and ●, tri-n-butylamine (5.0mM)

The linear correlation of the observed pseudo-first-order rate constant for (Ic) with the particular acidity function (Figure 2) does not necessarily preclude some of the normal modes of base catalysis, in contrast with similar relations in concentrated solutions of strong bases, because in the present study the amine concentration was low and the activity of the solvent can be regarded as constant. However, the results at least suggest that the interaction of the substrate with the amine is similar to that of *p*-cyanophenol, probably one to one, and that a proton transfer from the substrate either preceding or during the rate-determining step is involved in the reaction.

Rappoport and Shohamy extended the spectrum of the β-elimination mechanism suggested by Bunnett [5] from a second type of *E*1 mechanism at one extreme to a second type of *E*1cB mechanism on the other.[6] Judging from the structure of (I), the dehydration should proceed

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[4] C. H. Rochester, 'Acidity Functions,' Academic Press, London and New York, 1970, ch. 7.

[5] J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225.

[6] Z. Rappoport and E. Shohamy, *J. Chem. Soc.* (*B*), 1971, 2060.

through the second type of or pre-equilibrium *E*1cB mechanism,[6,7] which involves rapid formation of a carbanion followed by rate-determining departure of the hydroxy-group, because the hydroxy-group should be a poor leaving group [*] and α-H [†] in (I) should be fairly acidic owing to the electron-withdrawing effects of the cyano and phenyl groups. However, these mechanisms were ruled out by the kinetic isotope effects observed (Table 2). These two types of *E*1cB mechanism should have deuterium isotope effects of near unity.[10,11] The large positive ρ values observed (Figures 3 and 4) exclude the possibilities of reversible and irreversible *E*1 mechanisms, and even of an *E*1-like *E*2 process, since in these mechanisms a carbonium ion intermediate or a highly carbonium ion-like transition state is involved and the ρ value would be negative. A second type of *E*1 mechanism, in which a stable carbonium ion is formed, is highly improbable because no species other than the reactant and the product was detected·spectrophotometrically during the reaction, and no induction period was observed in kinetic runs. Thus the present system may have an irreversible *E*1cB mechanism, in which proton transfer from the α-carbon to form a carbanion is rate-determining, or an *E*1cB-like *E*2 mechanism, which involves a carbanion-like transition state with large degree of α-C–H bond breaking and small degree of N–OH bond breaking. Both mechanisms are consistent with the results in Figure 2.

Although it is difficult to distinguish an irreversible *E*1cB mechanism from a concerted *E*2 mechanism,[11,12] the following findings support the former mechanism. In the *E*2 eliminations of β-phenylethyl compounds in sodium ethoxide–ethanol at 30°, the Hammett ρ values for substituents on the β-phenyl ring increased from 2.07 to 3.77 with decrease in reactivity of the system.[5,13,14] The ρ value for compounds (I) substituted on the *C*-phenyl ring (2.90) can be located near the largest value for the β-phenylethyl compounds,but (I) is more reactive than any of the phenylethyl compound.[‡] An elimination reaction with an irreversible *E*1cB mechanism is characterized in part by a larger ρ value and a faster rate of reaction compared to a similar elimination with an *E*1cB-like *E*2 mechanism.[15,16]

In studies on the effects of substituents on the α-phenyl ring in *E*2 eliminations a rather poor correlation with σ and small ρ values (<1) have usually been found.[17,18] The poor correlation has been ascribed to two opposing effects of the α-phenyl substituents on the reaction rate: an effect on the partial negative charge on β-carbon $(\rho > 0)$ and an effect on breaking of the α-C–X bond $(\rho < 0)$.[17] On the other hand, an irreversible *E*1cB mechanism will require the former effect alone and a fairly large positive ρ value will be expected for substituents on the α-phenyl ring, as reported in the reaction of stereoisomeric 1-acetoxy-1-aryl-2-nitrocyclohexanes with piperidine (ρ 1.45).[19] The ρ value of 1.57 for substituents on the *N*-phenyl ring of (I) together with the large positive ρ value for substituents on the *C*-phenyl ring and the high reactivity of the system suggest an irreversible *E*1cB mechanism.

The observed kinetic deuterium isotope effects for (Ic) are consistent with the *E*1cB mechanism, though sometimes a small value may be expected for highly carbanion-like transition state.[11] Fairly large primary deuterium isotope effects have been observed in many reactions with an irreversible *E*1cB mechansim.[8,15,19-22]

If the present system proceeds by this mechanism, the removal of the hydroxy-group from the intermediate carbanion must be a fast step. This seems strange because a hydroxy-group is usually regarded as a very poor leaving group. However, covalent bonds of the type N–X, O–X, or S–X are less stable than C–X bonds, and in the formation of C=E bonds from compounds of the type H–C–E–X more energy will be obtained than in formation of C=C bonds from H–C–C–X type compound.[23] Thus elimination to form C=E bonds may be faster than elimination to form C=C bonds and more basic atoms or groups can be easily removed.[12,13] Moreover an irreversilbe *E*1cB mechanism has been suggested for the dehydration of fluoroen-9-ylmethanol in t-butyl alcohol.[22]

As shown in Figures 3 and 4 the substituent effects in triethylamine and tri-n-butylamine catalysed dehydr-

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[*] In *E*lcB eliminations forming olefins, the departure of the alkoxy,[8] or phenoxy-groups [9] was suggested to be the slow step.

[†] The α-carbon of the present substrates corresponds to the β-carbon of compounds undergoing β-elimination reactions to form olefins.

[‡] The most reactive β-phenylethyl compounds in the series are β-phenylethyl iodides (ρ 2.07) and the ethoxide ion catalysed second-order rate constant for the unsubstituted derivative is $2.66 \times 10^{-3}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ at 30°.[13] Assuming first-order dependence on triethylamine, the second-order rate constant for (Ia) is calculated to be $1.33 \times 10^{-1}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ at 25° (k_{obs} $6.65 \times 10^{-4}\ \mathrm{s^{-1}}$ at 5.0×10^{-3}M-triethylamine).

[7] M. Albeck, S. Hoz, and Z. Rappoport, *J.C.S. Perkin II*, 1975, 628.

[8] F. G. Bordwell, M. M. Vertling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5950; F. G. Bordwell, K. C. Yee, and A. C. Knipe, *ibid.*, p. 5945.

[9] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671, 679.

[10] Z. Rappoport, *Tetrahedron Letters*, 1968, 3601.

[11] D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490.

[12] F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374.

[13] C. H. DePuy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, 1957, **79**, 3710; C. H. DePuy and C. A. Bishop, *ibid.*, 1960, **82**, 2532, 2535.

[14] W. H. Saunders and R. A. Williams, *J. Amer. Chem. Soc.*, 1957, **79**, 3712; W. H. Saunders and A. F. Cockerill, *ibid.*, 1968, **90**, 1775.

[15] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 1373; A. B. N. Gray and D. J. McLennan, *ibid.*, p. 1377.

[16] H. F. Kock, D. B. Dahlberg, A. G. Toczko, and R. L. Solsky, *J. Amer. Chem. Soc.*, 1973, **95**, 2029.

[17] E. Baciocchi, P. Perucci, and C. Rol, *J.C.S. Perkin II*, 1975, 329.

[18] Y. Yoshida, Y. Yano, and S. Oae, *Tetrahedron*, 1971, **27**, 5343; P. J. Smith and S. K. Tsui, *Tetrahedron Letters*, 1972, 917.

[19] F. G. Bordwell, R. L. Arnold, and J. B. Biranowski, *J. Org. Chem.*, 1963, **28**, 2496.

[20] (*a*) D. J. McLennan, *J.C.S. Perkin II*, 1976, 932; (*b*) D. J. McLennan and R. J. Wong, *ibid.*, 1974, 526.

[21] A. Thibblin and P. Ahlberg, *Acta Chem. Scand.*, 1976, **B30**, 555.

[22] R. A. More O'Ferrall and S. Slae, *J. Chem. Soc.* (*B*), 1970, 260; R. A. More O'Ferrall, *ibid.*, p. 268.

[23] J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, 2nd edn., ch. 8.

ation of (I) are parallel. The slower rate of the latter reaction is mainly due to steric hindrance, because the basicities of the two amines will be similar in the present medium. However, the similar ρ values and deuterium isotope effects for (Ic) suggest that the transition state structure of the two amine-catalysed reactions are essentially the same. Similar steric effects have been observed in linear free energy relationships (l.f.e.r.s.) in the reactions between amines and ethyl methanesulphonate.[24]

The marked deviation of (Ie) in the Hammett plot (Figure 3) can be explained in terms of a change in mechanism, that is, from irreversible *E*1cB for (Ia—d) to *E*2 for (Ie), as usually suggested for such a break in a l.f.e.r.[25] The strongly electron-supplying dimethylamino-group will raise the energy of the irreversible *E*1cB transition state by reducing the stability of the intermediate carbanion, and will also lower the energy of the *E*2 transition state in which the α-C–H bond breaking is assisted by the N–OH bond breaking. The reduced stability of the carbanion will make the *E*1cB transition state more carbanion-like, whereas it will render the *E*2 transition state less carbanion-like.[26] The smaller isotope effect for (Ie), therefore, corresponds to a smaller degree of proton transfer in the transition state. The fact that the isotope effect in the ireversible *E*1cB elimination of 1,1-diaryl-2,2,2-trichloroethane is independent of the nature of the *para*-substituent [20b] may be support for the change in mechanism for (Ie). A similar transition of an *E*2 to an *E*1cB mechanism caused by changing substituents has been reported for the dehydrochlorination of 1,1-diaryl-1,2-dichloroethane.[27]

TABLE 3

Physical and spectroscopic data for (I) [a]

Compound		Elemental analysis (%)			I.r. (KBr)		N.m.r. (DMSO)			
		C	H	N	ν_{OH}/cm^{-1}	ν_{CN}/cm^{-1}	τ_{CHCN} [b]	τ_{OH} [c]	ν_{max}(EtOH)/nm [d]	
(Ia)	Found	75.3	5.1	12.5	3 270	2 240	6.23	9.23 [e]	280	362
	Required	75.0	5.4	12.5						
(Ib)	Found	75.8	5.8	11.4	3 490	2 235	6.14	9.17	293	361
	Required	75.6	5.9	11.8						
(Ic)	Found	64.45	4.0	10.9	3 260	2 245	6.26	9.24 [e]	288	365
	Required	65.0	4.3	10.8						
(Id)	Found	70.7	5.4	10.8	3 360	2 230	6.12	9.16	320	355 [f]
	Required	70.9	5.55	11.0						
(Ie)	Found	71.8	6.35	15.5	3 275	2 235	6.00	9.11	250	405
	Required	71.9	6.4	15.7						
(If)	Found	72.5	4.4	16.6	3 340	2 235	*g*	*g*	280	375
	Required	72.3	4.45	16.9						
(Ig)	Found	75.75	6.15	11.7	3 275	2 245	6.12	9.12	280	372
	Required	75.6	5.9	11.8						
(Ih)	Found	64.9	4.1	10.8	3 275	2 240	6.25	9.38	282	364
	Required	65.0	4.3	10.8						
(Ii)	Found	71.1	5.45	10.8	3 275	2 245	5.99	9.11	284	389
	Required	70.85	5.55	11.0						

[a] M.p.s of (I) could not be determined since the compounds were converted into cyano-imines on heating. [b] (1 H, s). [c] (1 H, s). [d] For the corresponding cyano-imine (II). [e] In [$^2H_6$]DMSO. [f] Shoulder. [g] Rapidly converted into the corresponding cyano-imine in DMSO.

The activation parameters (Table 2) do not allow definite conclusions to be drawn, but the fairly large negative entropies of activation are consistent with a transition state in which charge separation occurs from neutral substrates.[28] A large negative entropy of activation has been observed for an irreversible *E*1cB elimination under similar conditions.[19]

EXPERIMENTAL

Materials.—*N*-(α-Cyanobenzyl)-*N*-phenylhydroxylamines were prepared as described previously.[1] Analytical results are summarized in Table 3, together with the absorption maxima of the corresponding cyano-imines in ethanol. *p*-Cyanophenol was recrystallized from benzene–hexane and gave expected analytical values. Triethylamine and tri-n-butylamine were purified by distillation. Ethanol was distilled first from calcium oxide after refluxing for two days and then from sodium.

N-(*α-Cyano-α-deuterio*-p-*chlorobenzyl*)-N-*phenylhydroxylamine*.—*p*-Chloro[*formyl*-^{2}H]benzaldehyde (290 mg),[29] obtained by $LiAlD_4$ reduction and then Collins oxidation [30] of ethyl *p*-chlorobenzoate, and phenylhydroxylamine (290 mg) were dissolved in a small amount of ethanol. The white crystals that precipitated immediately were recrystallized from benzene–hexane to give the deuteriated nitrone (400 mg) as needles, m.p. 155°. The nitrone was dissolved in ethanol (30 ml), and liquid hydrogen cyanide (1.5 ml) was added to the solution. The reaction mixture was kept in an ice-box until no starting nitrone was detected by t.l.c. (*ca*. 3 h). The crystals precipitated by addition of cold water to the solution were recrystallized from n-hexane (300 mg): $\nu_{max.}$ (KBr) 3 270 (OH), 2 275 (C–D), and 2 245 cm^{-1} (CN); *m*/*e* 259 (M^+).

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[24] R. F. Hudson and R. J. Withey, *J. Chem. Soc.*, 1964, 3513.

[25] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York and London, 1963, pp. 189—190.

[26] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334; E. R. Thornton, *ibid*., 1967, **89**, 2915; R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274.

[27] A. Grout, D. J. McLennan, and I. H. Spackman, *J.C.S. Chem. Comm*., 1976, 775.

[28] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York and London, 1961, 2nd edn., ch. 7.

[29] K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.*, 1955, **77**, 1786.

[30] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Letters*, 1968, 3363.

N-(α-*Cyano*-α-*deuterio*-p-*dimethylaminobenzyl*)-N-*phenylhydroxylamine*.—By applying the above treatment to ethyl *p*-dimethylaminobenzoate the hydroxylamine was obtained in poor yield, *m/e* 268 (M^+).

Apparatus.—Spectroscopic measurements were carried out with a Hitachi 124 recording spectrophotometer. Nonlinear least-squares calculations were made on an NEAC 2 200 mode 700 computer at Osaka University using Fortran programmed by Hashimoto and Miyamoto.[31]

Kinetic Measurements.—Kinetic measurements were made spectrophotometrically by following the appearance of the corresponding cyano-imines at the appropriate absorption maximum (Table 3) in aqueous 95% ethanol. All measurements were made at 25 ± 0.1° except those runs to obtain activation parameters. Except for slow reactions, dehydration was initiated by injecting a small amount (*ca.* 5—10 μl) of an ethanolic solution of the substrate prepared before each set of experiments into 3 ml of reaction medium containing a known amount of triethylamine or tri-n-butylamine equilibrated at 25° in a cuvette. The initial concentrations of the substrates were 1—5 × 10^{-5}M. The stock solutions of the amines were standardized before each set of kinetic runs with standard hydrochloric acid solution. When the reaction was slow, the reaction was carried out in a volumetric flask so that the final products could be examined. The absorption spectrum of the reaction mixture at infinite time (*ca.* 19 half-lives) coincided with that of the corresponding cyano-imine prepared as described previously.[32] Observed pseudo-first-order rate constants were estimated from the slope of $\log(A_\infty - A_t)$ against time, where A_t and A_∞ represent the absorbances at time t and infinite time. A good first-order plot was obtained for >70% completion of the reaction in every run. When the rate constants were obtained by both methods described above they were in good agreement.

Measurement of the Ionization Ratio.—The degree of ionization of *p*-cyanophenol was measured at the absorption maximum of the ionized molecule (280 nm). The concentration of the phenol was 4.03 × 10^{-4}M. The degree of ionization I was calculated from equation (4) where A_{H} is the

$$I = [\mathrm{PhO^-}]/[\mathrm{PhOH}] = (A - A_{\mathrm{H}})/(A_{\mathrm{O}} - A) \quad (4)$$

absorbance in 95% ethanol without triethylamine, A_{O} is that with 5 × 10^{-3}M-sodium hydroxide, and A is that with a given concentration of triethylamine.

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[31] K. Hashimoto and K. Miyamoto, personal communication.

[32] M. Masui, H. Ohmori, C. Ueda, and M. Yamauchi, *J.C.S. Perkin II*, 1974, 1448.