*E*1cB Eliminations. Substituent and Solvent Effects on the *E*1cB Elimination of the Second Type from 2-Aryl-1,1,2-tricyanopropanes

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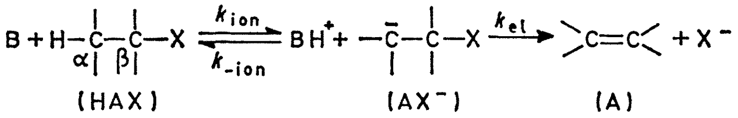
Tri-n-butylamine-promoted elimination of HCN from 2-aryl-1,1,2-tricyanopropanes shows 'catalysis' by the amine in chloroform and in acetonitrile. The reaction is of first order in the amine at low amine concentrations and zeroth order at high amine concentrations. In the latter region the reaction is faster in chloroform than in acetonitrile, the Hammett ρ^+ values being $-0{\cdot}36$ and $k_H/k_D = 1{\cdot}0 \pm 0{\cdot}08$. The reaction is discussed in terms of non-steady-state formation of the conjugate base of 2-aryl-1,1,2-tricyanopropane, which leads to complete ionisation (*E*1cB of the second type) at the high amine concentrations with rate-determining C–CN bond cleavage. In chloroform (and in some cases in acetonitrile) the kinetics fit the ion-pair variant $(E1cB)_{ip}$.

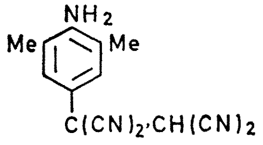
SEVERAL variants of the base (B)-catalysed carbanion elimination (*E*1cB) from saturated compounds (Scheme 1) are known.[1,2] Both the 'irreversible' case ($k_{el} > k_{-ion}$ $k_{obs} = k_{ion}$) and the 'pre-equilibrium' case ($k_{-ion} > k_{el}$; $k_{obs} = k_{ion}k_{el}/k_{-ion}$) where the intermediate anion AX^- is formed in a steady-state concentration [2,3] were recognised.

Aspects of the *E*1cB mechanism of the second type which were not investigated include the dependence of the rate on the solvent and the influence of structural variations in HAX [*e.g.*, see (*f*) above]. Moreover, a non-steady-state behaviour of a system with a moderate K value was not reported with amines, although observed with buffers in aqueous solutions.[6b,c] For such systems the ionisation of HAX is not complete at moderate base concentrations and the reaction is governed both by K and by k_{el}: the rate equation is $d[A]/dt = k_{el}$[Intermediate], where the intermediate is either the dissociated AX^- ion or the ion pair $\{AX^-\ BH^+\}$. If at sufficient high base concentrations the ionisation is complete, [Intermediate] = $[HAX]_0$, and the reaction is apparently of the first order in HAX with k_{el} as the first-order coefficient. Hence, at different base concentrations [Intermediate] = $(d[A]/dt)/k_{el}$. These [Intermediate] values can be inserted into the expressions for two equilibrium constants: K_{diss} for the formation of dissociated ions {equations (1) and (2), [Intermediate] = $[AX^-]$} and K_{ip} for the formation of ion pairs {equations (3) and (4), [Intermediate] = $[AX^-\ {}^+HB]$}. The importance of ion pairs in the elimination [*i.e.*, whether



SCHEME 1

Another *E*1cB variant was described recently [4-6] in systems where the α-hydrogen atom is highly acidic and the β-leaving group is very sluggish: AX^- is formed in a non-steady-state concentration and its decomposition is rate-determining ($k_{obs} = k_{el}$). It was designated *E*1cB of the second type [7] or 'irreversible first-order carbanion elimination'.[5] For the reaction of HAX with amines under conditions of complete ionisation ($K = k_{ion}/k_{-ion}$ is very high) and with $pK_a(HX) \gg pK_a(HAX)$ some of the predictions are: (*a*) zeroth order in the amine within a run; (*b*) first order in HAX when [Amine] > [HAX]; (*c*) lack of dependence of k_{obs} on the base strength; (*d*) fast H–D exchange; (*e*) small or no isotope effects; (*f*) negative ρ value for β-aryl substituents. Predictions (*a*)—(*e*) were realised in the Et_3N- and in the $Bu^n{}_3N$-catalysed elimination of HCN from 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I).[4]



(I)

$$B + HAX \overset{K_{diss}}{\rightleftharpoons} BH^+ + AX^- \qquad (1)$$

$$K_{diss} = \frac{[AX^-][BH^+]}{\{[HAX]_0 - [AX^-]\}\{[B]_0 - [BH^+]\}} \qquad (2)$$

$$B + HAX \overset{K_{ip}}{\rightleftharpoons} \{BH^+AX^-\} \qquad (3)$$

$$K_{ip} = \frac{[BH^+AX^-]}{\{[HAX]_0 - [BH^+AX^-]\}\{[B]_0 - [BH^+AX^-]\}} \qquad (4)$$

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[1] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., 1969, Cornell Univ. Press, Ithaca, New York, pp. 653, 955.

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

[3] L. R. Fedor, *J. Amer. Chem. Soc.*, 1969, **91**, 908, 913; L. R. Fedor and R. C. Cacestri, *ibid.*, 1970, **92**, 4610; R. A. More O'Ferrall and S. Slae, *J. Chem. Soc.* (*B*), 1970, 260; R. A. More O'Ferrall, *ibid.*, pp. 268, 274; J. Crosby and C. J. M. Stirling, *J. Amer. Chem. Soc.*, 1968, **90**, 6869; *J. Chem. Soc.* (*B*), 1970, 672, 679; T. I. Crowell, R. T. Kemp, R. E. Lutz, and A. A. Wall, *J. Amer. Chem. Soc.*, 1968, **90**, 4638; F. G. Bordwell, M. M. Vestling, and K. C. Yee, *ibid.*, 1970, **92**, 5950.

[4] Z. Rappoport and E. Shohamy, *J. Chem. Soc.* (*B*), 1971, 2060; see also *Israel J. Chem.*, 1968, **6**, 15p.

[5] F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5945.

[6] (*a*) A. Berndt, *Angew. Chem. Internat. Edn.*, 1968, **8**, 613; (*b*) T. C. Bruice and R. F. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 5956; (*c*) L. R. Fedor and W. R. Glave, *ibid.*, 1971, **93**, 285.

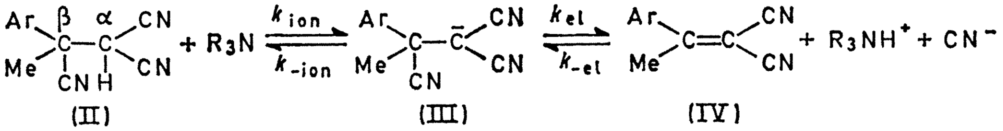
[7] Z. Rappoport, *Tetrahedron Letters*, 1968, 3601.

the reaction is $(E1cB)_{ip}$[8]] could then be assessed by observing whether K_{diss} is more constant than K_{ip} or *vice versa*.

Several polycyano-compounds eliminate HCN by the E1cB mechanism,[4,9] and we now report the E1cB elimination of HCN from 2-aryl-1,1,2-tricyanopropanes (II) (Scheme 2). These compounds are less acidic than (I) but since they contain the sluggish β-cyano-leaving group we hoped that they would enable us to study the elimination under conditions of incomplete ionisation, and the effect of the aryl substituents on the C–CN bond cleavage.

RESULTS

The elimination reactions of three 2-aryl-1,1,2-tricyanopropanes (IIa—c), were studied in acetonitrile and in chloroform in the presence of tri-n-butylamine, and occasionally in the presence of triethylamine. The reactions were followed spectrophotometrically up to 60% and in a few cases up to >95% or up to equilibrium at $\lambda_{max.}$ of the elimination products, 2-aryl-1,1-dicyanoprop-1-enes (IV) where the reactants have little or no absorbance.



SCHEME 2

a; Ar = p-MeO·C_6H_4 (An) b; Ar = p-MeC_6H_4 (Tol) c; Ar = Ph

Reactions in Acetonitrile.—In the Bu^n_3N-catalysed eliminations in acetonitrile, equilibria are achieved after 60—90% reaction, and the absorbance of the reaction mixtures remained constant for four days. The positions of the equilibria are base- and HAX-dependent. At *ca*. 0·0015M-tolyl-compound (IIb) the percentages of (IVb) at equilibrium at 25 °C are 62, 66, 75, and 89% at 0·017, 0·009, 0·005, and 0·0016M-Bu^n_3N respectively. At 0·009M-Bu^n_3N equilibria were achieved after 73, 66, and 63% reaction at $2{\cdot}5 \times 10^{-4}$, $1{\cdot}43 \times 10^{-3}$, and $2{\cdot}87 \times 10^{-3}$M-(IIb) respectively. The elimination products were isolated from the p-methoxyphenyl compound (Ia) and the phenyl derivative (Ic), and t.l.c. and u.v. spectra showed that they are the only products formed.

The [HAX] : [Base] ratios used were between 30 and 0·015, but even for the high ratios the reaction is ' catalytic ' in the base, *i.e.*, equilibrium is obtained when the base concentrations are lower than those of the HCN formed. At the high [HAX] : [Base] ratio the reaction is of zeroth order within a run. For example, with $1{\cdot}96 \times 10^{-3}$M-(IIb) and $6{\cdot}88 \times 10^{-5}$M-$Bu^n_3N$ $\Delta[(IVb)]/\Delta t$ $(= k_0)$ at 25 °C are $2{\cdot}8 \times 10^{-9}$, $2{\cdot}8 \times 10^{-9}$, $3{\cdot}1 \times 10^{-9}$, and $3{\cdot}0 \times 10^{-9}$ l mol^{-1} s^{-1} at 6, 33, 43, and 65% reaction respectively. At such high ratios the first-order coefficients k_1 were calculated by dividing k_0 by the $[HAX]_0$ concentration, but usually they were calculated by dividing the initial rates (measured up to 4% reaction) by the $[HAX]_0$ concentration (Table 1). Values of k_2 were obtained from k_1/[Amine]. In several runs with high [Amine] : $[HAX]_0$ ratios the reaction was followed up to equilibrium. Straight lines were obtained by plotting $\ln\{(A_0^2 - A_eA)/[(A - A_e)/A_0]\}$ against time (A_0, A_e, and A are the optical densities at the beginning, at equilibrium, and at time t) as expected from the rate equation of opposing first- and second-order reactions. The rate coefficients were identical with those obtained from the initial rates of the same runs.

A plot of k_1 (at constant [HAX]) against the stoicheiometric amine concentrations is curved (Figure 1). At 25 °C a plateau is reached at Bu^n_3N concentrations of *ca*. 0·03M for the three compounds and the k_1 values at the plateau (k_1^{pl}) are given in Table 3. A plot of log [Initial rates] against log [Base] is also curved. The plot for 0·0015M-(IIc) shows a first-order dependency on the base up to 0·003M, but at higher base concentrations (0·011—0·093M) the slope is *ca*. 0. This behaviour is demonstrated by the decrease in k_1 values with the increase in [Amine] (Table 1). The activation parameters based on k_1^{pl} values are in Table 3. A plot of log k_1^{pl} against σ^+ values[10] for the three compounds is nearly linear with $\rho^+ = -0{\cdot}36$, while a plot with σ values is more curved. On the assumption that k_1^{pl} refers to complete ionisation, the concentrations of the intermediate at different base concentrations were calculated by dividing the initial rates by k_1^{pl}. These concentrations were used to calculate K_{diss} [equation (2)] and K_{ip} [equation (4)] for points at the intermediate part of Figure 1, *i.e.*, when the ionisation is incomplete. The large error associated with the term $\{[HAX]_0 - [AX^-]\}$ made meaningless the equilibrium constants calculated in the vicinity of the plateau, while the sensitivity to the term $\{[B]_0 - [BH^+]\}$ introduced high errors in K_{diss} and K_{ip} at low base concentrations. The relevant data are in Table 1.

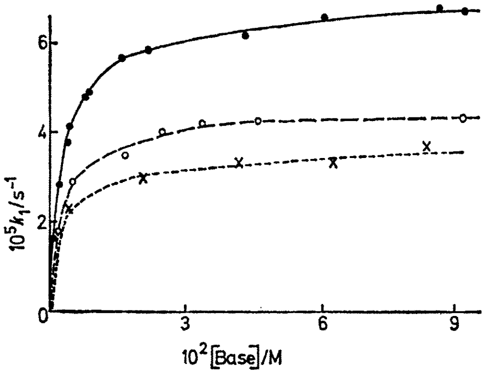


FIGURE 1 Plot of k_1 against [Base] for the reaction of (II) with tri-n-butylamine in acetonitrile at 25 °C, ●, Ar = An (IIa); ○, Ar = Tol (IIb); ×, Ar = Ph (IIc)

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[8] W. K. Kwok, W. G. Lee, and S. I. Miller, *J. Amer. Chem. Soc.*, 1969, **91**, 468.

[9] E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc. (B)*, 1970, 1401; 1971, 220.

[10] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913; Y. Okamoto and H. C. Brown, *J. Org. Chem.*, 1957, **22**, 485.

The reactions in the presence of triethylamine were slightly faster than those with similar concentrations of tri-n-butylamine (Table 1).

Addition of trichloroacetic acid to a reaction mixture which contained sufficient base to keep the reaction in the region of k_1^{pl} did not change k_1.

Reactions in Chloroform.—The eliminations in chloroform were studied only with Bu^n_3N and were found to reach near completion (85—100%). T.l.c. and the spectra of the reaction mixtures showed only the formation of (IV) and the infinity readings remained stable for 10 h.

The same k_1 values were calculated for (IIa) either by

TABLE 1

Bu_3N-Catalysed elimination of HCN from $ArC(CN)Me{\cdot}CH(CN)_2$ in MeCN

Ar = *p*-Methoxyphenyl (IIa)

10^3[HAX]/M	10^3[Bu^n_3N]/M	10^4[AX^-] [a]/M	$10^5 k_1$/s^{-1}	$\dfrac{10^2 k_2}{\text{l mol}^{-1}\text{ s}^{-1}}$	$10K_{\text{diss}}$	K_{ip}/l mol^{-1}
			At 25 °C			
6·94	0·052		0·045	0·86		
6·94	0·174		0·14	0·82		
1·47	0·87	3·8	1·67	1·92	2·6	685
1·59	2·18		2·85	1·31		
1·47	2·18	6·0	2·84	1·30	2·6	420
1·58	4·99	10·0	4·14	0·89	4·3	430
1·47	4·36	8·6	3·79	0·87	3·5	410
1·58	8·32	12·0	4·80	0·58	5·0	420
1·46 [b]	8·77	11·0	4·89	0·56	4·4	400
1·58	16·6	14·0	5·69	0·35	4·6	330
1·46	21·8	13·0	5·81	0·26	5·2	400
1·46	43·6	13·9	6·20	0·14	6·5	470
1·53	61·0		6·53	0·11		
1·53	87·0		6·80	0·078		
0·3	92·8		5·53	0·059		
0·9	92·8		6·38	0·069		
1·5	92·8		6·65	0·070		
			At 40 °C			
1·5	0·35	2·2	0·50	21·2	2·84	1282
1·5	1·18	4·6	1·02	14·9	2·82	614
1·5	2·35	6·4	1·43	10·4	2·78	435
1·5	3·10	7·6	1·7	8·29	3·33	439
1·5	10·4	12·4	2·8	4·07	6·45	520
1·5	20·8	13·2	3·0	2·16	4·96	376
1·5	31		3·22	1·55		
1·5	104		3·27	0·472		
1·5	208		3·4	0·249		
1·5	182		3·53	0·29		
1·5 [c]	182 [c]		3·33	0·18		
1·5 [d]	182 [d]		3·46	0·19		
Ar = *p*-Tolyl (IIb)						
			At 25 °C			
1·44	1·61	6·0	1·82	1·13	0·446	730
1·50	5·03	9·9	2·91	0·58	0·518	513
1·52 [b]	16·7	12·1	3·5	0·21	0·355	286
1·50 [b]	25·0	13·8	3·99	0·16	0·830	553
1·41 [b]	33·4	13·4	4·17	0·125	1·34	918
1·52	46·0		3·74	0·08		
1·52	92·0		4·32	0·047		
1·52	184·0		4·49	0·024		
6·72	0·052		0·039	0·75		
6·72	0·174	0·15	0·01	0·063	0·304	189
1·96	0·069	0·58	0·13	1·88	0·161	277
1·96	0·29	1·7	0·39	1·34	0·155	876
1·47 [e]	1·82 [e]	8·4	2·53	1·39	1·29	1500
1·47 [e]	5·47 [e]	11·7	3·5	0·64	1·25	1040
1·47 [e]	18·2 [e]	12·7	3·8	0·21	0·588	452
			At 40 °C			
1·48	0·32	2·0	3·3	10·32	2·69	1347
1·48	0·63	3·3	5·3	8·34	3·14	950
1·48	1·26	5·1	8·2	6·50	3·57	701
1·49	3·17	7·6	12·0	3·82	3·38	445
1·49	6·34	9·8	15·5	2·44	3·51	358
1·49	12·7	12·4	19·7	1·55	5·35	431
1·51	52·9		23·5	0·45		
1·51	106·0		24·0	0·23		
1·51	211·0		23·3	0·11		

TABLE 1 (*Continued*)

Ar = Ph(IIc)

10^3[HAX]/M	$10^3[\mathrm{Bu^n}_3]$/M	$10^4[\mathrm{AX^-}]$ [a]/M	$10^5k_1/\mathrm{s^{-1}}$	$\frac{10^2k_2}{\mathrm{l\ mol^{-1}\ s^{-1}}}$	$10K_{\mathrm{diss}}$	K_{ip}/l mol^{-1}
			At 25 °C			
1·46	0·071	0·63	0·17	2·39	3·29	5260
1·46	0·237	1·76	0·43	1·8	3·97	2260
1·51	4·2	9·61	2·29	0·54	5·19	540
1·51	21·0	12·5	2·97	0·14	3·07	243
1·51 [b]	42·0	13·8	3·30	0·08	3·74	271
1·51	63·0	13·8	3·29	0·05	2·37	172
1·51	84·0		3·71	0·045		
0·30	42·0		2·94	0·07		
3·00	42·0		3·8	0·09		
1·11	0·67 [e]	3·97	1·29	1·91	0·8	202
1·11	1·35 [e]	5·72	1·86	1·38	7·8	1360
1·11	4·5 [e]	7·08	2·31	0·51	3·3	465
1·11	11·2 [e]	7·56	2·45	0·29	1·55	205
1·11	22·5 [e]	7·72	2·50	0·11	0·83	107
			At 40 °C			
1·47	0·53	3·3	4·35	8·24	4·82	1461
1·47	1·06	5·3	6·94	6·55	5·64	1063
1·47	2·11	7·6	10·0	4·74	6·02	792
1·53	5·28	10·4	13·1	2·48	5·21	500
1·53	10·6	12·4	15·7	1·48	5·67	457
1·53	21		19·4	0·92		
1·51	51		17·8	0·34		
1·51	103		17·4	0·17		
1·51	210		18·2	0·087		
1·5	172		21·3	0·124		
1·5 [f]	172		21·3	0·124		
1·5 [g]	172		19·8	0·115		

[a] Values of k_1^{pl} from Table 3 were used for the calculation of [AX$^-$]. [b] Average of two experiments. [c] 1·4 × 10^{-3}M-$\mathrm{CCl_3{\cdot}CO_2H}$ was added. [d] 5·8 × 10^{-4}M-$\mathrm{CCl_3{\cdot}CO_2H}$ was added. [e] In the presence of $\mathrm{Et_3N}$. [f] 6·5 × 10^{-4}M-$\mathrm{CCl_3{\cdot}CO_2H}$ was added. [g] 1·62 × 10^{-3}M-$\mathrm{CCl_3{\cdot}CO_2H}$ was added.

dividing the initial rates by $[\mathrm{HAX}]_0$ or by using a computer programme for the first-order reaction (KINDAT) [11] which searches for and uses the best infinity value. In the runs with relatively high base concentrations a much faster increase in the optical density than that expected from the first-order plot was observed with both compounds (IIb) and (IIc). This gave high error in the initial rates and only the KINDAT k_1 values are given (Table 2). No such effect was observed at low base concentrations for which k_1 based on initial rates are given.

A plot of k_1 against [Amine] was similar to that in acetonitrile (Figure 2). The reaction is of the first order in the amine up to amine concentrations of *ca.* 0·003M with (IIc). At higher amine concentrations (up to 0·4M) the reaction order approaches zero, whereupon a plateau is nearly achieved at 30 °C but not at 40 °C. This prevented accurate determination of the activation parameters. The K_{diss} and K_{ip} values (Table 2) were calculated as in acetonitrile and the Hammett ρ^+ value based on k_1^{pl} is $-0{\cdot}35$.

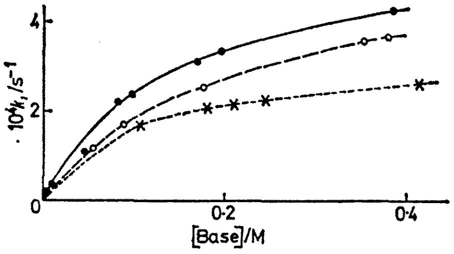

FIGURE 2 Plot of k_1 against [Base] for the reaction of (II) with tri-n-butylamine in chloroform at 30 °C, ●, Ar = An (IIa); ○, Ar = Tol (IIb); ×, Ar = Ph (IIc)

Addition of trichloroacetic acid to a reaction mixture with relatively high amine concentration had no effect on the rate coefficient.

Deuterium Exchange and Isotope Effects.—When 0·0004M-(IIa) was shaken for 1 h with 0·45M-$\mathrm{D_2O}$ in anhydrous chloroform, benzene, or acetonitrile (10 ml), the n.m.r. of the recovered *p*-methoxyphenyl compound (IIa) showed *ca.* 75% $\mathrm{C_\alpha}$–D. The incomplete deuteriation is probably due to traces of adventitious water (or HCl) in the n.m.r. solvent (commercial $\mathrm{CDCl_3}$) since the n.m.r. spectrum of deuteriated (IIa) in our 'kinetic' anhydrous acetonitrile showed complete α-deuteriation.

The isotope effect in the elimination from completely α-deuteriated *p*-methoxyphenyl compound (IIa) as compared with the undeuteriated compound is $k_{\mathrm{H}}/k_{\mathrm{D}} = 0{\cdot}93$. Since partial H–D exchange may take place in our chloroform, a run for the deuteriated (IIa) in chloroform saturated with $\mathrm{D_2O}$ was compared with a run for the unlabelled (IIa) in chloroform saturated with $\mathrm{H_2O}$. The rate coefficients of these runs were similar to those in the unmoistened solvents, and $k_{\mathrm{H}}/k_{\mathrm{D}} = 1{\cdot}08$ (Table 2). Within the accuracy of determining k_1^{pl} values (±5%) there seems to be no appreciable isotope effect.

Preliminary experiments on the $\mathrm{Et_3N}$-promoted elimination from 1,1,2-tricyano-2-phenylethane in acetonitrile showed a similar behaviour to that of compounds (II). The elimination product is benzylidenemalononitrile according to the u.v. spectra at early reaction times. The reaction is 'catalytic', a plot of k_1 against $[\mathrm{Et_3N}]$ being similar to Figure 1, with $k_1^{\mathrm{pl}} = 1{\cdot}9 \times 10^{-6}\ \mathrm{s^{-1}}$ at 25 °C, and at 0·0065—0·0003M-$\mathrm{Et_3N}$ the reaction is of the second order with

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[11] R. C. Williams and J. W. Taylor, *J. Chem. Educ.*, 1970, **47**, 129.

TABLE 2

Bu_3N-Catalysed elimination of HCN from ArC(CN)Me·CH$(CN)_2$ in chloroform

Ar = *p*-Methoxyphenyl (IIa)

10^3[HAX]/M	10^3[Bu^n_3N]/M	10^3[AX^-]/M	$10^5k_1/s^{-1}$	$\frac{10^2k_2}{l\ mol^{-1}\ s^{-1}}$	10^3K_{diss}	K_{ip}/l mol^{-1}
			At 30 °C			
1·5 [a]	0·48	7·9 × 10^{-3}	0·23	0·477	0·088	11·2
1·5	0·95	1·5 × 10^{-2}	0·36	0·463	0·156	10·6
1·5 [a]	4·8	7·3 × 10^{-2}	2·7	0·461	0·8	10·8
1·5	9·6	0·147	4·1	0·426	1·68	11·4
1·6	44·4	0·444	12·5	0·281	3·89	8·8
1·5	85·0	0·729	22·5	0·255	8·08	11·1
1·5	97·0	0·86	24·0	0·258	12·0	13·9
1·5	170·0	1·00	31·0	0·176	11·6	11·6
1·5	194·0	1·07	32·8	0·165	13·4	12·5
1·5 [a]	402·0	1·26	45·3	0·09	15·3	12·1
0·6	216·0	0·433	33·7	0·15	5·2	12·0
1·5	216·0	1·04	31·7	0·15	10·7	10·3
3·0	216·0	2·19	33·8	0·15	27·7	12·6
1·5 [b]	402·0		48·9	0·09		
1·5 [c]	402·0	1·29	48·9	0·10	19·8	15·3
1·3 [d]	402·0		45·3	0·11		
			At 40 °C			
1·5	156·0		78·6	0·50		
1·5	312		113·0	0·36		
1·5	625		146·0	0·23		
1·3	99		57·0	0·57		
1·3	296		91·7	0·31		
1·3	394		98·7	0·25		
Ar = *p*-Tolyl (IIb)						
			At 30 °C			
1·52	0·239	4·2 × 10^{-3}	0·09	0·366	0·048	11·6
1·52	0·955	0·0166	0·36	0·38	0·196	11·6
1·52	2·39	0·0391	0·85	0·36	0·44	11·3
1·52	54·0	0·545	11·9	4·68	5·69	10·4
1·52	88·0	0·80	17·4	3·79	10·2	12·7
1·52	108	0·81	17·6	3·92	8·63	10·6
1·52	176	1·18	25·6	2·41	23·4	19·8
1·52	352	1·41	30·6	1·14	51·8	36·7
1·52	380	1·45	31·4	1·41	79·2	54·6
			At 40 °C			
2·48	490		108	0·22		
1·49	300		82	0·27		
1·49	590		106	0·18		
Ar = Ph (IIb)			At 30 °C			
1·16	25	0·39	9·46	0·38	0·081	20·7
1·16	50	0·51	12·3	0·25	0·081	15·8
1·16	100	0·7	16·9	0·17	0·106	15·2
1·6	105	1·02	17·8	0·17	0·18	17·6
1·6	182	1·18	20·7	0·11	0·167	14·1
1·6	209	1·22	21·3	0·10	0·20	16·7
1·6	418	1·5	26·2	0·06	0·77	51·3
0·6	245	0·48	22·5	0·092	0·08	16·6
1·5	245	0·12	22·6	0·092	0·21	17·0
3·0	245	0·234	21·9	0·089	0·24	10·1
			At 40 °C			
1·52	144		61·7	0·43		
1·52	288		82·9	0·29		
1·52	575		144	0·20		
1·50	487		100	0·20		
1·50 [e]	487 [e]		106	0·22		
1·50 [f]	487 [f]		104	0·21		

[a] Average of two runs. [b] Reaction of α-deuteriated (IIa). [c] Reaction of (IIa) in chloroform saturated with H_2O. [d] Reaction of α-deuteriated (IIa) in chloroform with D_2O. [e] In the presence of 0·0021M-$Cl_3C·CO_2H$. [f] In the presence of 0·0052M-$Cl_3C·CO_2H$.

$k_2^{25} = 4 \times 10^{-4}$ l mol^{-1} s^{-1}. These values are accurate only to ±50% since benzylidenemalononitrile decomposes rapidly in acetonitrile in the presence of Et_3N, probably by a cleavage of the double bond by traces of water.[12]

DISCUSSION

The first-order dependence on the base at low base concentrations and the evidence for carbanion formation are compatible with either the *E*2,[13] the pre-equilibrium, or the irreversible *E*1cB mechanisms.[2] However, the absence of deuterium isotope effects and the curved plot of the graph of k_1 against [Base] eliminate all these routes. The kinetics and the evidence for carbanion formation suggest the following variant of the *E*1cB elimination: In chloroform an $\{AX^-BH^+\}$ ion pair is formed in a non-steady-state concentration, and abstraction of CN^- within the ion pair is rate-determining [$(E1cB)_{ip}$ [8] of the second type; [7] Scheme 3]. In acetonitrile, the free ions may be also involved in the elimination.

$$HAX + B \underset{}{\overset{K_{ip}}{\rightleftharpoons}} (AX^- \ ^+HB)$$

$$(AX^- \ ^+HB) \xrightarrow{k_{el}} [A\cdots X\cdots H\cdots B]^{\ddagger} \longrightarrow A + XH + B$$

SCHEME 3
X = CN

Scheme 3 accommodates also the ' catalytic ' nature of the elimination. As discussed earlier,[4] the reaction will proceed to completion when [B] < [HAX] whenever $pK_a(HAX) \ll pK_a(HX)$: the base B is not neutralised by the formed HX but it continues the reaction by deprotonation of the unchanged HAX. When X^- is a sluggish leaving group and HX is a weak acid, both the *E*1cB of the second type and the ' catalysis ' are favoured by the same structural factors.

Evidence for Carbanion Formation.—Compounds (II) are sufficiently activated by the three cyano-groups for an easy formation of carbanions, and the ' catalsyis ' shows that they are more acidic than HCN. The pK_a values of $ArC(Me)(CN){\cdot}CH(CN){\cdot}CO_2Et$ in 40% EtOH are 8·58, 8·78, and 8·84 for Ar = Ph, Tol, and An, respectively.[14] Since ethyl cyanoacetate is somewhat less acidic than malononitrile [as judged from indirect kinetic evidence,[15a] since an accurate pK_a value for $CH_2(CN){\cdot}CO_2Et$ is not available [15b]] it suggests pK_a values of 7·5—8·5 for (IIa)—(IIc) in water. Further, the pK_a values of compound (II) in acetonitrile may well be *ca.* 7·5—8·5, since the pK_a of malononitrile is similar in water and in dimethyl sulphoxide.[16]

Experimental evidence for the formation of carbanions (and high k_{ion}) is the fast exchange of the α-proton of compound (IIa) under homogeneous ($MeCN-D_2O$) and heterogeneous [($C_6H_6-D_2O$), ($CHCl_3-D_2O$)] conditions, and the α-D exchange of the deuteriated (IIa) in wet chloroform. Formation of the anion can also be inferred from the spectral changes observed on addition of Bu^n_3N to solutions of compounds (IIa)—(IIc), although quantitative determination of $[AX^-]$ is difficult (see Experimental section).

The Elimination Mechanism.—The appearance of a plateau in the plots of k_1 against [Base] at high base concentrations suggests a saturation effect which is expected if the ionisation of HAX is complete. At the plateau region $k_1^{pl} = k_{el}$ and the C–CN bond cleavage is rate-determining. Consequently, the reaction is of the first order in AX^- (*i.e.*, in HAX) within a kinetic run, zeroth order in the amine, and nearly independent of the nature of the amine (Et_3N or Bu^n_3N). In view of the fast H–D exchange and the absence of deuterium isotope effect, the predictions (a)—(e) for the *E*1cB of the second type [7] brought above are realised in our system. At low base concentrations the deprotonation of HAX is incomplete, and the concentration of AX^- in different runs is governed by the equilibrium constant for the acid–base reaction. However, within a kinetic run the reaction should be of zeroth order in $[AX^-]$, as observed, since $[AX^-]$ remains virtually constant owing to the ' catalysis ' by the amine.[4,7]

The involvement of ion pairs in the ' pre-equilibrium ' *E*1cB was suggested on the basis of isotope effects and exchange [8] and the absence of common-ion rate depression.[8,9] For *E*1cB of the second type the latter criterion suggested an ion-pair mechanism or electrophilic assistance by free (or dissociated) BH^+ ions during the expulsion of the cyanide ion from (I).[4] In the present case, the differentiation between the intermediacy of ion pairs and dissociated ions is being assessed by the use of the stoicheiometric concentrations of the anion (III) (Tables 1 and 2). Both K_{ip} and K_{diss} were calculated from equations (2) and (4) and their average values are given in Table 3. In view of the approximations and extrapolations introduced into their calculations the constancy of the K_{ip} values in chloroform is rather good, while the corresponding K_{diss} cover a much larger range. This is demonstrated with compound (IIa) for which the range of (III) studied is higher than that for the other compounds: K_{ip} is changed by ±20% when K_{diss} changes 250-fold. Moreover, the K_{ip} values for (IIa), (IIb), and (IIc) in chloroform are rather similar, although that for the phenyl compound (IIc) is somewhat higher, as expected for a process where electron-donation reduces K_{ip}.

In acetonitrile K_{ip} for (IIa) seems to fit better the data at 25 °C, and K_{diss} at 40 °C. K_{diss} seems to fit better the data for (IIc). The error associated with both K_{ip} and K_{diss} is rather large, especially for the tolyl compound (IIb).

We conclude that there is sufficient evidence that the reaction in chloroform involves rate-determining C–CN bond cleavage within an $\{AX^-BH^+\}$ ion pair. We also

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[12] S. Patai and Z. Rappoport, *J. Chem. Soc.*, 1962, 383, 392.

[13] R. Breslow, *Tetrahedron Letters*, 1964, 399.

[14] R. Carrié, *Bull. Soc. sci. Bretagne*, 1962, **37**, 99.

[15] (*a*) S. Patai and Y. Israeli, *J. Chem. Soc.*, 1960, 2020; S. Patai and Y. Zabicky, *ibid.*, p. 2030; (*b*) R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

[16] C. D. Ritchie in ' Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, ch. 4.

speculate that in the more dissociation-inducing acetonitrile the reaction involves both free ions and ion pairs. Indeed, the more acidic compound in chloroform (IIc) seems to be more dissociated in acetonitrile.

If the role of the BH^+ is to supply electrophilic assistance to the expulsion of the cyanide ion, an elimination *via* dissociated ions may be accelerated by the addition of external BH^+. That addition of trichloroacetic acid does not affect the rate in acetonitrile may show either that the C–CN bond cleavage does not involve free ions or that electrophilic assistance by dissociated ions is unimportant. The absence of rate acceleration by BH^+ in chloroform fits the absence of a $[BH^+]$ term from the rate equation.

High K_{ip} values are reasonable if $\Delta pK_a = pK_a(Bu^n_3N) - pK_a$ (II) values are sufficiently large. This is probable since the pK_a's of ammonium ions are *ca.* 7 pK_a units higher in acetonitrile than in water[17] and their acidity is reduced more than those of cyanocarbon acids on changing the solvent from water to the dipolar aprotic dimethyl sulphoxide.[17]

TABLE 3

k_1^{pl}, K_{diss}, K_{ip}, and activation parameters for the Bu^n_3N-promoted elimination of HCN from (II)

Compound	Solvent	t/°C	$10^5k_1^{pl}/s^{-1}$	10^2K_{diss}	K_{ip}/l mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$(298 K) cal mol^{-1} K^{-1}
(IIa)	MeCN	25	6·75	43 ± 9	440 ± 60	19·4	−13
	MeCN	40	34	39 ± 12	613 ± 226		
(IIb)	MeCN	25	4·4	49·5 ± 3	550 ± 225	20·0	−12
	MeCN	40	24	36 ± 3	705 ± 295		
(IIc)	MeCN	25	3·6	36 ± 7	1460 ± 1700	20·0	−13
	MeCN	40	19·3	54·7 ± 3·7	854 ± 325		
(IIa)	$CHCl_3$ [a]	30	45	0·33 ± 0·28	12 ± 1		
(IIb)	$CHCl_3$ [a]	30		0·69 ± 0·52	12·6 ± 2·1		
(IIc)	$CHCl_3$ [a]	30		0·15 ± 0·06	16 ± 1·8		

[a] Plateau was not achieved at 40 °C.

The absence of deuterium isotope effects and the magnitude of the activation parameters fit well the $(E1cB)_{ip}$ mechanism. Miller *et al.* had suggested[8] that the $(E1cB)_{ip}$ mechanism provides a rationale for the 'low' isotope effects, and the absence of isotope effects from the $(E1cB)_{ip}$ of the second type was discussed previously.[4] The activation parameters are similar to those found for the C–CN bond cleavage from the conjugate base of (I).

Solvent Effects and Base Dependency.—The *ca.* two orders of magnitude higher K_{ip} (or K_{diss}) in acetonitrile, a solvent of higher dielectric constant, are expected for an ionisation process. The solvent effect on the elimination step is the first one reported for $E1cB$ of the second type. The 5—8 times faster elimination in a solvent of a lower dielectric constant may be due to a lowering of the transition-state energy in chloroform if the $CN^- \cdots HCCl_3$ hydrogen bond is stronger than the (III) $\cdots HCCl_3$ bond, but more probably it reflects a lower polarity of the transition state compared with the ground state. This fits the ion-pair mechanism in which charges are neutralised in the electrophilically-assisted elimination step of Scheme 3.

The results with Et_3N are in line with a higher K_{ip} for the stronger base and with the expected lack of dependence of k_{el} on the base strength.

Substituent Effects.—The data of Tables 1—3 enable the evaluation of substituent effects on both steps of Scheme 3. If $\rho = 0{\cdot}395$ for the pK_a values of $PhCH_2{\cdot}CH(Me){\cdot}NO_2$[18] is taken as an approximation for our compounds {since $pK_a[CH_2(CN)_2] \simeq pK_a(MeNO_2)$[15]} the K_{ip} ratio will be (IIa) 1 : (IIb) 1·17 : (IIc) 1·26. Our K_{ip} values are too rough for detecting such small changes, but we note that K_{ip} (IIc) > K_{ip} (IIb), K_{ip} (IIa).

More interesting are the signs and the magnitudes of the ρ^+ values for the C–CN bond cleavage (—0·36). The sign of ρ in a second-type $E1cB$ elimination was predicted to be negative[7] and ours is the first case where this prediction is demonstrated.* The observation that the (presumably) $E1cB$ elimination from p-$MeNH{\cdot}C_6H_4{\cdot}C(CN)_2{\cdot}CH(CN)_2$ is faster[19] than from (I) is probably due to the same reason.

A low response of k_1^{pl} to the change of the β-aryl group could be ascribed (as in S_N1 and $E1$ reactions) to a small degree of C–CN bond cleavage in the transition state of the elimination. In our opinion the reason is different. In $E1$ reactions the driving force is supplied by spreading the partial positive charge formed in the transition state by the β-aryl groups. In our system this charge is neutralised by the α-electron pair which supplies the main driving force for the C–CN bond cleavage. The inductive effect of the aryl groups and their resonative interaction with the developing double bond are small in comparison.

Relative values of K and k_{el} are now available for $ArCR(CN){\cdot}CH(CN)_2$ for R = CN (I),[4] and R = Me (II). The order of K for R is CN > Me, and is self-explanatory.

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* A Referee has commented that discussion of a ρ value which is based on three substituents only is misleading. We believe that as far as extrapolation to other substituents is not made, such use of the ρ values is justified since in our case it is merely equivalent to the statement 'The rates are slightly enhanced by electron-donating substituents'. We also note that although the correlation with σ^+ seems better, the number of substituents is too small for a clear conclusion. Since ρ is low even for a log k–σ correlation, our conclusion remains valid.

[17] J. F. Coetzee and G. R. Padmanabhan, *J. Amer. Chem. Soc.*, 1965, **87**, 5005.

[18] F. G. Bordwell, W. J. Boyle, jun., and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.

[19] Z. Rappoport and A. Horowitz, *J. Chem. Soc.* (*B*), 1964, 1348.

The elimination from the phenyl compound (IIc) is 20-fold faster than from 1,1,2-tricyano-2-phenylethane in acetonitrile while (I) is 10-times faster in chloroform [4] than (IIa). The low activation by electron-donating substituents ensures that (I) is several times faster than the 4-amino-3,5-dimethyl-substituted compound (II), even when the presence of two potentially leaving cyano-groups in (I) is taken into account. The reactivity order for R in the C–CN bond-cleavage step is CN > Me > H. The Me : H reactivity order is in line with the discussion of substituent effects above, but the order CN > Me is surprising since the β-CN group is electron-attracting compared with β-Me. Models show that there is considerable relief of steric strain during the elimination from (II), and this could be the main reason for the CN : Me reactivity ratio * and may also contribute to the Me : H ratio.

TABLE 4

Physical properties and spectral data for 2-aryl-1,1,2-tricyanopropanes

		Analysis						
		Found (%)				Required (%)		
Compound	M.p. (°C) [a]	C	H	N	Formula	C	H	N
(IIa)	120 (decomp.)	69·15	4·9	19·0	$C_{13}H_4N_3O$	69·3	4·92	18·65
(IIb)	124 (decomp.)	74·75	5·2	20·25	$C_{13}H_{11}N_3$	74·6	5·30	20·1
(IIc)	135 (decomp.)	73·55	4·8	21·3	$C_{12}H_9N_3$	73·8	4·64	21·5

	N.m.r. δ [b]				U.v. spectra [$\lambda_{max.}$/nm (ε)] [c]	
Compound	Aryl	α-H	Me	Miscellaneous	in MeCN	in $CHCl_3$
(IIa)	7·20(q)	4·15(s)	2·06(s)	3·83(s, OMe)	273·5 (1350), 280 (1100)	274 (1500), 281·5 (1300)
(IIb)	7·34(q)	4·17(s)	2·03(s)	2·35(s, Me)	255 (230), 261 (250), 266·5sh (190), 271 (160)	256 (250), 262 (300), 267sh (210), 272 (150)
(IIc)	7·84(m)	4·18(s)	2·09(s)		251 (180), 257 (250), 261 (260), 267·5 (190)	257·5 (280), 262 (300), 269 (230)

[a] Obtained by rapid heating. [b] δ (p.p.m.) in $CDCl_3$ with tetramethylsilane as reference; integration is in line with the assignments. [c] All compounds show fine-structure.

EXPERIMENTAL

M.p.s were taken with Fischer–Johns apparatus and are uncorrected. N.m.r. was taken with a Varian H/100 instrument.

Materials.—Benzylidenemalononitrile and 1,1,2-tricyano-2-phenylethane were synthesised according to Corson and Stoughton.[21] The 2-aryl-1,1-dicyanoprop-1-enes were prepared according to Mowry.[22] 2-Aryl-1,1,2-tricyanopropanes were prepared by addition of hydrogen cyanide to 2-aryl-1,1-dicyanoprop-1-enes by Corson and Stoughton's method,[21] except that the reaction mixtures were warmed before acidification. The analyses, physical properties, and spectral data are in Table 4.

Solvents.—Chloroform was freshly prepared daily by washing commercial solvent (Frutarom) three times with distilled water, drying (Na_2SO_4), and fractionating. The fraction of b.p. 61—62 °C was used. Acetonitrile was refluxed for 24 h over phosphorus oxide, fractionated, and the middle fraction (b.p. 81 °C) was used.

Labelling Experiments.—Compound (IIa) (0·0004 mol) was shaken for 1 h with 99·5% D_2O (by n.m.r.) (0·45 mol) in anhydrous chloroform, benzene, or acetonitrile (10 ml). Compound (IIa) was then recovered by evaporation of the solvents or by precipitation with CCl_4. The n.m.r. spectrum in our 'kinetic' anhydrous acetonitrile showed complete α-deuteriation, but when commercial $CDCl_3$ was used only a partial H–D exchange (*ca.* 75%) was observed.

Kinetic Procedure.—Stock solutions of the polycyano-compounds and of the amine were prepared daily and kept at the reaction temperature. Aliquot portions were mixed at the reaction temperature and samples were transferred immediately to silica absorption cells (10, 5, and 1 mm) in a thermostatted chamber of a Gilford 2400 spectrophotometer. The increase in the absorption at the $\lambda_{max.}$ of the products was recorded [(IVa) in MeCN, 329 nm (ε 17,500); in $CHCl_3$, 336·5 nm (ε 17,800); (IVb) in MeCN, 302 nm (ε 15,200); in $CHCl_3$, 310 nm (ε 15,300); (IVc) in MeCN, 287 nm (ε 13,500); in $CHCl_3$ 293 nm (ε 14,000)]. The absorption of the products from 1,1,2-tricyano-2-phenylethane first increased but later decreased during the reaction.

On mixing the solutions of (II) and the amine, a small increase in the optical density at wavelengths up to 310 nm was observed and is ascribed to the formation of the anion (III). However, at low wavelengths most of the new absorption is masked by that of the amine while that at higher wavelength is masked after shorter reaction times by that of the products (IV) which have much higher ε.

Product Analysis.—The elimination products (IVa) and (IVc) were isolated from large scale (0·1M) elimination experiments in the presence of a catalytic amount of $Bu^n{}_3N$ in *ca.* 30% yield. Scanning spectra were occasionally taken during the follow-up of the elimination of compounds (IIa)—(IIc) in both acetonitrile and chloroform and showed that only compounds (IVa)—(IVc) are formed. This was verified by t.l.c. (Kieselguhr; 1 : 1 chloroform–CCl_4) which showed that in each reaction only the corresponding elimination product (IV) was formed.

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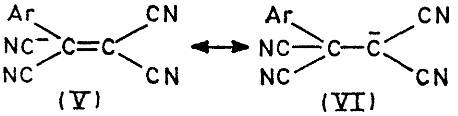
* Another explanation is that a C–CN hyperconjugation in the conjugate base of (I) [(V)—(VI)] increases the elimination rate from (I). A C–CN hyperconjugation was invoked in connection with the unusual u.v. spectrum of (I).[20]



(V) (VI)

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