#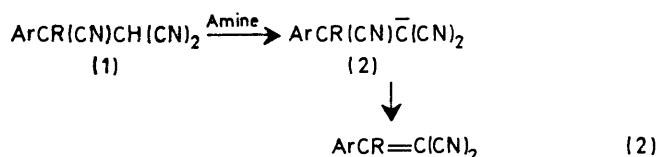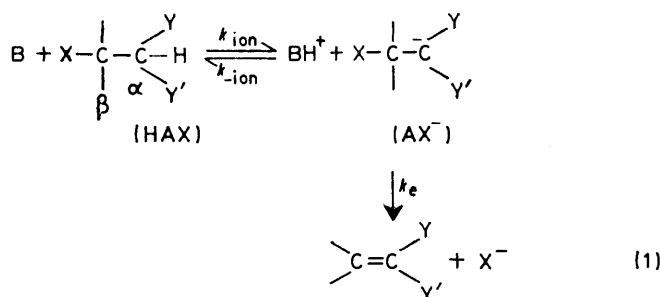 E1cB and E2cB Mechanisms in the Elimination of Trifluoroethoxide Ion from α,α-Dinitro-β,β-diphenyl-β-(trifluoroethoxy)ethanide Anion and the Non-reactivity of the β-Cyano-α,α-dinitro-β,β-diphenylethanide Anion

By **Michael Albeck** * and **Shmaryahu Hoz,** Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel
    Zvi Rappoport, Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

The reaction of α,α-dinitro-β,β-diphenyl-β-(trifluoroethoxy)ethane (5) with the bases (B) pyridine and collidine in acetonitrile gives the corresponding free ammonium ion BH^+ and carbanion (6a). The equilibrium constants (K_{diss}) for the reaction (5) + B $\rightleftharpoons$ (6a) + BH^+ are 0·05 for collidine and 0·00027 for pyridine at 40°. The elimination of $CF_3CH_2O^-$ from (6a) (k_e) to give 1.1-dinitro-2.2-diphenylethylene (3a) is first order in (6a) and in BH^+. and a rate-determining BH^+-assisted expulsion of $CF_3CH_2O^-$ (E2cB mechanism) is suggested. This is verified by the relative reactivities of the BH^+. the reaction in the presence of oxalic acid. and the isotope effects of 1·27 with pyridine and 1·54 with collidine. With Et_3N the elimination is first order in (6a) and unassisted by BH^+: the isotope effect is 1·07. Addition of Et_3N to 3.3-dinitro-2.2-diphenylpropionitrile (4a) and its bis-(p-methoxy)-derivative (4b) gives immediately the corresponding carbanions (6b and c). These carbanions do not eliminate CN^-. and essentially do not exchange their cyano-group with added cyanide ion. thus representing an extreme case of E1cB reactions where the anion which is quantitatively formed is too stable to undergo elimination. The effects of the α-activating groups and the leaving group on the rate of the C–X bond cleavage are discussed.

In the base(B)-catalysed carbanionic elimination (E1cB) from saturated substrates [equation (1)],[1,2] the inter-

$$ B + X-\underset{\underset{\beta}{\overset{|}{C}}}{\overset{\overset{Y}{\diagup}}{\overset{|}{C}}}-H \underset{k_{-ion}}{\overset{k_{ion}}{\rightleftharpoons}} BH^+ + X-\overset{\overset{Y}{\diagup}}{\underset{\underset{Y'}{\diagdown}}{\overset{|}{C}}}-\overset{Y}{\underset{Y'}{\diagup}} $$

$$ (HAX) \qquad\qquad (AX^-) $$

$$ \downarrow k_e $$

$$ \overset{\diagdown}{\underset{\diagup}{}}C=C\overset{\diagup Y}{\underset{\diagdown Y'}{}} + X^- \qquad (1) $$

$$ ArCR(CN)CH(CN)_2 \xrightarrow{\text{Amine}} ArCR(CN)\bar{C}(CN)_2 $$
$$ (1) \qquad\qquad (2) $$
$$ \downarrow $$
$$ ArCR=C(CN)_2 \qquad (2) $$

a; $Ar = 3, 5 - Me_2-4 - NH_2C_6H_2$, $R = CN$

b; $Ar = p - ZC_6H_4(Z=H,Me,or\ MeO), R = Me$

mediate carbanion (AX^-) is usually formed in steady-state concentration. The 'irreversible' and 're-

versible' variants are known for cases where the ionisation (k_{ion}), or the elimination of the leaving group $X^-(k_e)$, are rate determining, respectively.[2] The life-time of AX^- increases by increasing the electron-attracting ability of Y and Y', or by reducing k_e by using a sluggish leaving group X. In the extreme case, which was studied only recently,[3-9] and termed ' E1cB of the second type '[3-5] or ' irreversible first-order carbanion elimination,'[6] the carbanion is formed in a non-steady-state concentration, and reaction of the carbanion to form olefin may be observed directly. Systems activated by nitro,[7] carbonyl,[8] cyano,[4,5] and ethoxycarbonyl[9] groups, where $X = CN$,[4,5] NO_2,[7] and OR[8,9] were investigated.

Our previous work on the amine-catalysed elimination of HCN from the tri- and tetra-substituted ethanes (1a and b) in aprotic solvents [equation (2)][4,5] showed the following characteristics. (a) The carbanions (2a

[1] C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' 1969. Cornell Univ. Press, Ithaca, 2nd edn., pp. 653, 955.
[2] D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490.

[3] Z. Rappoport, *Tetrahedron Letters*, 1968, 3601.
[4] Z. Rappoport and E. Shohamy, *J. Chem. Soc. (B)*, 1971, 2060.
[5] M. Albeck, S. Hoz, and Z. Rappoport, *J.C.S. Perkin II*, 1972, 1248.
[6] F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5945.
[7] A. Berndt, *Angew. Chem. Internat. Edn.*, 1968, **8**, 613.
[8] L. R. Fedor and W. R. Glave, *J. Amer. Chem. Soc.*, 1971, **93**, 285.
[9] T. C. Bruice and R. F. Pratt, *J. Amer. Chem. Soc.*, 1970. **92**, 5956.

and b) are formed in non-steady-state concentrations.[4,5] (b) The reactions are ' catalytic ', i.e., they go to completion even when [HAX] > [B].[4,5] (c) Electron-donating aryl groups increase k_e.[5] k_e, for R = CN is greater than for R = Me.[4,5] (d) $k_{\alpha-H}/k_{\alpha-D}$ values are ca. 1.[4,5] (e) The reaction is faster in chloroform than in acetonitrile.[5]

The kinetic behaviour differs for compounds (1a and b). For example with tri-n-butylamine in chloroform, complete ionisation of (1a) was achieved at low base concentrations,[4] while for (1b) the ionisation is not complete even at high [B],[5] but in both cases the anions AX$^-$ were not observed directly. It was suggested that in the reaction of (1a) with Et$_3$N and Bu$_3$N in chloroform[4] and of (2a) with amines in chloroform, and sometimes in acetonitrile[5] the expulsion of CN$^-$ is electrophilically assisted by the ammonium ion within an ion pair, and the reaction is designated $(E1cB)_{ip}$.[10]

In addition to extending the scope of $E1cB$ reactions,[3] our interest in this reaction is also due to the fact that the k_e step is identical to the last step of nucleophilic vinylic substitutions.[11] In substitution by amines, electrophilic assistance by the ammonium ion in the expulsion of the leaving group was also suggested,[12] but its study is complicated by the multi-step nature of the reaction, and direct measurement of k_e would be beneficial.

The effects of Y, Y', and X on k_e were little investigated. We decided to use more powerful electron-attracting Y and Y' groups than previously studied, for three reasons. (a) To show experimentally that for the ' $E1cb$ of the second type ' k_e decreases on increasing the electron-attracting ability of Y and Y'. (b) We hoped that complete ionisation would occur, and with sufficiently sluggish X, the anion AX$^-$ could be observed spectroscopically, enabling evaluation of whether free ions or ion pairs are formed.[5] (c) Direct evidence for electrophilic assistance in the expulsion of the leaving group by free ammonium ions may be obtained.
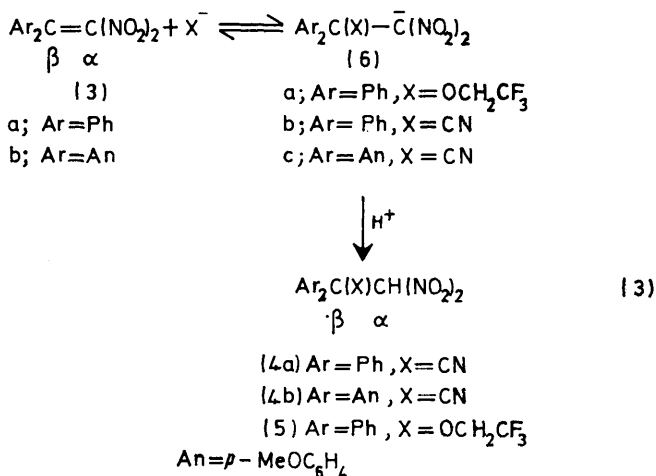
Since the nitro group is one of the best electron-attracting substituents, we had chosen Y = Y' = NO$_2$. For comparison with systems (1a and b), X = CN was studied. As a potentially ' slower ' leaving group we considered an alkoxide ion, and the failure to synthesise stable β-methoxy- and β-ethoxy-α,α-dinitroethanes required instead the use of X = trifluoroethoxy. We therefore studied the amine-catalysed elimination of HX from the β,β-diaryl-β-X-α,α-dinitroethanes (4) and (5). The attempted elimination of HCN from compounds (4) was partially reported in a preliminary communication.[13]

RESULTS

The 1,1-diaryl-2,2-dinitroethanes (4a), (4b), and (5) were prepared by addition of cyanide and trifluoroethoxide ions to the ethylenes (3a and b). The anions (6a—c) are

[10] W. K. Kwok, W. G. Lee, and S. I. Miller, J. Amer. Chem. Soc., 1969, **91**, 468; E. Lord, M. P. Naan, and C. D. Hall, J. Chem. Soc. (B), 1971, 220.

formed immediately, and careful acidification of their solutions gave the substituted ethanes [equation (3)].

$$Ar_2C=C(NO_2)_2 + X^- \rightleftharpoons Ar_2C(X)-\bar{C}(NO_2)_2$$

$$\begin{array}{cc} \beta & \alpha \\ (3) & (6) \end{array}$$

a; Ar=Ph   a; Ar=Ph, X=OCH$_2$CF$_3$

b; Ar=An   b; Ar=Ph, X=CN

                c; Ar=An, X=CN

$$\downarrow H^+$$

$$Ar_2C(X)CH(NO_2)_2 \qquad (3)$$
$$\beta \quad \alpha$$

(4a) Ar=Ph, X=CN

(4b) Ar=An, X=CN
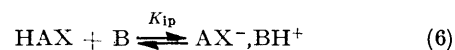
(5) Ar=Ph, X=OCH$_2$CF$_3$

An=p-MeOC$_6$H$_4$

The reaction of (3a) with methoxide ion gave, under similar conditions, only benzophenone dimethyl acetal. When the acidification was conducted at low temperature the adduct Ph$_2$C(OMe)CH(NO$_2$)$_2$ was isolated and identified by n.m.r., but it rapidly decomposed in the slightly aqueous methanolic solution to benzophenone dimethyl acetal. Reaction of ethoxide ion with (3a) gave immediate colouration, but (3a) was recovered unchanged upon acidification.

Ionisation of the Substrate (5).—Addition of triethylamine (TEA), pyridine (Pyr), or 2,4,6-trimethylpyridine (collidine, Coll) to a solution of (5) in acetonitrile resulted in the immediate formation of an absorption maximum at 373 nm, which was.ascribed to the anion (6a). The absorption of (5) at 373 nm is negligible. This was followed by a slow gradual increase in the absorption at 320 nm, ascribed to the formation of the ethylene (3a).

From the initial concentrations of (5) ([HAX]$_0$) and the base ([B]$_0$), and from the spectroscopically determined concentrations of (6a), two equilibrium constants were calculated; one (K_{diss}) for the formation of the free (dissociated) ions [equations (4) and (5)] and one (K_{ip}) for the formation of the ion pair AX$^-$,BH$^+$ [equations (6) and (7)]. The data for various combinations of pyridine,

$$HAX + B \xrightarrow{K_{diss}} AX^- + BH^+ \qquad (4)$$
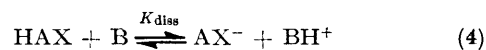
$$K_{diss} = \frac{[AX^-][BH^+]}{([HAX]_0 - [AX^-])([B]_0 - [BH^+])} \qquad (5)$$

$$HAX + B \xrightarrow{K_{ip}} AX^-,BH^+ \qquad (6)$$

$$K_{ip} = \frac{[AX^-,BH^+]}{([HAX]_0 - [AX^-,BH^+])([B]_0 - [AX^-,BH^+])} \qquad (7)$$

collidine and substrate concentrations are presented in

[11] Z. Rappoport, Adv. Phys. Org. Chem., 1969, **7**, 1; G. Modena, Accounts Chem. Res., 1971, **4**, 73.

[12] (a) Z. Rappoport and R. Ta-Shma, J. Chem. Soc. (B), 1971, 1461; (b) Z. Rappoport and P. Peled, J.C.S. Perkin II, 1973, 616; (c) Z. Rappoport and D. Ladkani, ibid., p. 1045.

[13] S. Hoz, M. Albeck, and Z. Rappoport, Tetrahedron Letters, 1972, 3511.

Table 1 and the average values show the much better constancy of the K_{diss} values.

The equilibrium constants for the ionisation in the presence of Et_3N are high, and nearly complete ionisation of (5) occurs even at low base concentrations. For example, addition of $3.56 \times 10^{-5}M$-Et_3N to $8.09 \times 10^{-5}M$-(5) gave $3.47 \times 10^{-5}M$-(6a). Hence, any small error in the determination of the concentration of either species will

the high K_{diss}. In the concentration range $[Et_3N] < [(5)]$, the anion concentration remains reasonably constant, and the initial rate was calculated from equation (9) with $\Delta\varepsilon$ 7200. In this case the reaction rate is nearly zero order

$$\Delta(3a)/\Delta t = \Delta D \text{ (at 320 nm)}/\Delta\varepsilon\Delta t \qquad (9)$$

within a run, and the base serves as a 'catalyst' since the reaction goes to completion even when $[B]_0 < [(5)]_0$.

TABLE 1

Base-catalysed elimination of trifluoroethanol from (5), in acetonitrile

Base	$T/°C$	$10^5[(5)]/M$	$10^5[Base]/M$	$10^5[(6)]/M$	$10^5 k_1/s^{-1}$	$k_2/l\ mol^{-1}\ s^{-1}$	$K_{ip}/l\ mol^{-1}$	$10^4 K_{diss}$
Collidine	40	55	31.6	8.33	11.8	1.42	770	640
		55	94.8	13.2	19.5	1.47	390	510
		55	158.0	15.9	25.0	1.57	280	450
		47.8	88	11.0	15.4	1.40	390	420
		47.8	352	19.2	24.9	1.30	200	390
		14.3	360	18.9	12.5	1.40	470	420
		13	88	5.6	6.7	1.22	950	540
		13	176	6.5	10.1	1.56	590	380
		12.5	151	6.9	8.7	1.27	850	580
		12.5	755	10.2	13.3	1.30	600	600
		14.3	1940	12.8	18.9	1.46	440	570
		14.3 [a]	1940	12.8	18.9	1.46		
		14.3 [b]	1940	12.9	14.8	1.15		
					15.2 ± 5.1 [d]	1.40 ± 0.09 [d]	540 ± 190 [d]	500 ± 80 [d]
	60	13.8	71.5	5.3	24.3	4.60	940	500
		13.8	143	6.9	29.2	4.22	730	510
		13.8	897	11.0	43.8	4.00	440	490
		13.8	1790	12.3	49.8	4.05	460	570
					36.8 ± 10 [d]	4.20 ± 0.20 [d]	643 ± 190 [d]	518 ± 27 [d]
Pyridine	40	35.7	2250	4.3	135	31.5	6.08	2.61
		35.7	3380	5.0	162	32.7	4.80	2.39
		28.6	2360	3.7	126	34.4	6.21	2.27
		14.3	289	1.0	35	35.4	25.8	2.56
		14.3 [c]	473	1.4	46	33.3	22.6	3.13
		14.3 [c]	946	1.85	64	34.5	14.9	2.75
		14.3	1450	2.10	69.5	33.2	11.9	2.50
		14.3	2890	2.93	92	31.4	8.9	2.62
		5.7	2360	1.65	58	35.3	1.76	2.85
		2.9	2360	1.11	35	31.7	2.69	2.99
		14.3	2360	2.94	96	32.6	9.85	2.89
		14.3 [a]	2360 [a]	2.94	96	32.6	9.85	2.89
		14.3 [b]	2360 [b]	2.87	61	21.2	9.55	2.76
					83.5 ± 35.2 [d]	33.2 ± 1.1 [d]	14.1 ± 6.7 [d]	2.69 ± 0.21 [d]

[a] In the presence of $0.049M$-H_2O. [b] In the presence of $0.049M$-D_2O. [c] Average of two experiments. [d] Average on all the experiments in dry acetonitrile.

result in a large error in both K_{diss} and K_{ip}. These values were therefore not calculated, although K_{diss} of 363 was evaluated indirectly (see Discussion section).

Rate Measurements.—In most cases, the elimination reaction from (5) was followed simultaneously at the λ_{max} of the olefin (3a) [320 nm (ε 7200)] and of the carbanion (6a) [373 nm (ε 7500)]. Initial rates (up to 4% reaction) were usually measured and calculated by equation (8), which is based on the above ε values, also takes into account the absorption of (6a) at 320 nm (ε 1950) and of (3a) at 373 nm (ε 5100), and ignores the absorption of (5) (ε 150) at 320 nm.

$$\Delta[3a]/\Delta t = [\Delta D \text{ (at 320 nm)}/5850\ \Delta t] -$$
$$[\Delta D \text{ (at 373 nm)}/22,000\ \Delta t] \qquad (8)$$

When $>90\%$ of the $[(5)]_0$ was converted to (6a) at the beginning of the reaction (mainly with Et_3N), the initial rate was calculated from equation (9) using $\Delta\varepsilon$ 5250 (see above). In the reactions with Et_3N where $[(5)]_0 \geqslant 2$ $[Et_3N]$, the concentration of (6a) is close to $[Et_3N]_0$ due to

For example, with $8.09 \times 10^{-5}M$- of (5) and $3.56 \times 10^{-5}M$-Et_3N, the rates at $40°$ were 5.9×10^{-10}, 5.5×10^{-10}, and $4.9 \times 10^{-10}\ l\ mol^{-1}\ s^{-1}$ at 3, 22, and 52% reaction, respectively.

The first-order rate constants (k_1) for olefin formation were obtained by dividing the initial rates by the initial concentrations of the carbanion $[(6)]_0$. In cases of complete ionisation, and when $[(5)]_0 < [B]$ the computer programme KINDAT [14] was applied for calculating k_1, and the values obtained by both methods were almost identical. Second-order constants (k_2) were obtained by dividing k_1 by the anion concentration. The data presented in Tables 1 and 2 show that the k_1 values are reasonably constant for Et_3N, and that the k_2 values are reasonably constant for collidine and pyridine. The derived activation parameters are summarised in Table 3.

Addition of a rather high concentration (0.09—0.36M)

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

of 2-pyridone to 1·25 × 10⁻⁴M-(5) showed that the anion is not formed. While we were unable to follow the elimination at 320 nm since the amine has high absorption at this

TABLE 2

Et₃N-Catalysed elimination of trifluoroethanol from (5) in acetonitrile

$10^5[(5)]/\text{M}$	$10^5[\text{Et}_3\text{N}]/\text{M}$	$10^5[(6a)]/\text{M}$	$10^5k_1/\text{s}^{-1}$	$10^2k_2/\text{l mol}^{-1}\text{s}^{-1}$
		At 40°		
38·2	89·0	37·3	2·04	5·6
22·0	121·0	21·3	1·58	7·4
22·0	48·5	21·0	1·56	7·4
22·0	24·2	21·0	1·60	7·6
19·2	89·0	18·9 ᵃ	1·48 ᵃ	7·6 ᵃ
19·2	35·6	18·8	1·40	7·0
14·3	45·2	14·3	1·41	10
14·3	18·1	14·3	1·41	10
14·3	9·1		1·41 ᵇ	16 ᶜ
14·3	4·5		1·50 ᵇ	33 ᶜ
14·3	1·8		1·77 ᵇ	98 ᶜ
12·5	38·0		1·66 ᵈ	13 ᵉ
12·5	19·0		1·64 ᵈ	13 ᵉ
8·1	8·9		1·36 ᵈ	15 ᵉ
8·1	3·5	3·5	1·87	54
14·3ᶠ	38·0 ᶠ		2·20	
14·3 ᵍ	38·0 ᵍ		2·06	
		At 60°		
13·8	880		10·8 ᵈ	
13·8	440		10·8 ᵈ	

ᵃ Average of two measurements. ᵇ Calculated by assuming that [(6a)] = [Et₃N]. ᶜ Calculated from k_1/[Et₃N]. ᵈ Calculated by assuming that [(5)] = [(6a)]. ᵉ Calculated from k_1/[(5)]. ᶠ In the presence of 0·049M-H₂O. ᵍ In the presence of 0·049M-D₂O.

wavelength, no change in the absorption at λ 335 nm took place during 150 min at 40°, and the elimination should be very slow.

Reactions in the Presence of Added Acid.—The reaction

with collidine was studied also in the presence of added trichloroacetic or oxalic acid. The k_2 values (Table 4) were calculated by dividing k_1 by the [BH⁺] concentrations which were calculated by equation (10) using K_{diss} 0·05. Trichloroacetic acid had no effect on either k_2 or on the concentration of (6a), while in the presence of oxalic acid the (6a) concentrations decreased, and k_1 increased.

$$[\text{BH}^+] = \frac{K_{\text{diss}}([\text{HAX}]_0 - [\text{AX}^-])[\text{B}]_0}{[\text{AX}^-] + K_{\text{diss}}([\text{HAX}]_0 - [\text{AX}^-])} \quad (10)$$

The conductivities of acetonitrile and of 0·0002M-oxalic acid in acetonitrile at 40° are 0·6 and 1·3 μmho, respectively. The conductivity of collidine (0·0038M) is much higher with added 0·0002M-oxalic acid (22·3 μmho) than with added 0·00018M-trichloroacetic acid (2·0 μmho), suggesting a more dissociated species in the former mixture.

Isotope Effects.—The isotope effects k_D/k_H were evaluated by comparing the elimination rates in acetonitrile containing 0·049M-H₂O and -D₂O. These conditions were used since H–D exchange with the solvent is expected to be rapid, and at the 10⁻⁴M concentrations used an α-deuteriated substrate (and ammonium ion) may rapidly exchange with adventitious water. Control experiments show that these water concentrations only slightly affect the reaction rate (Tables 1 and 2). The isotope effect with Et₃N (1·07) is unity within the experimental error, while the higher isotope effects with pyridine and collidine (Table 3) show that hydrogen–deuterium exchange indeed took place under these conditions.

Attempts to Eliminate HCN *from* (4a) *and* (4b).—Addition of one equivalent of Et₃N to either (4a or b) (2·10⁻⁴—3·10⁻⁵M) in acetonitrile resulted in complete ionisation. The spectra observed are ascribed to the anions (6b and c) [λ_max. (MeCN) 372 nm (ε 8700) and 373 nm (ε 8300), respectively]. Further addition of Et₃N caused no spectral changes. When these mixtures were kept for 17 h at 40°, there was no evidence for the formation of (3a and b),

TABLE 3

Kinetic and equilibrium data for the reaction of (5) with amines

Amine	$T/°\text{C}$	pK_a (MeCN)	K_{diss}	$10^5k_e/\text{s}^{-1}$	$k_e'/\text{l mol}^{-1}\text{s}^{-1}$	k_H/k_D	$\Delta H^{\ddagger}/\text{kcal mol}^{-1}$	$\Delta S^{\ddagger}/\text{cal mol}^{-1}\text{K}^{-1}$
Et₃N	40	18·46	363	1·58 ± 0·15		1·07		
	60			10·8			19·4 ᵉ	−19 ᶜ
Collidine	40	14·6 ᵇ	0·050 ± 0·008	(−0·32 ± 1·2) ᵃ	1·44 ± 0·10	1·27		
	60		0·052 ± 0·003	(4·6 ± 1·3) ᵃ	3·62 ± 0·11		9·0 ᵈ	−30 ᵈ
Pyridine	40	12·33	(2·69 ± 0·21) × 10⁻⁴	(2·85 ± 2·3) ᵃ	31·8 ± 0·8	1·54		

ᵃ From the intercepts of Figure 1 (see text). ᵇ Calculated from K_{ion} of (5), and K_{diss} for the reaction of (5) with collidine. ᶜ Based on k_e. ᵈ Based on k_e'.

TABLE 4

Reaction of 1·4 × 10⁻⁴M-(5) with collidine (B) in the presence of carboxylic acids in acetonitrile at 40°

$10^5[\text{Acid}]/\text{M}$	$10^5[\text{B}]/\text{M}$	$10^5[(6a)]/\text{M}$	$10^5[\text{BH}^+]/\text{M}$ ᵃ	$10^5k_1/\text{s}^{-1}$	$k_2/\text{l mol}^{-1}\text{s}^{-1}$ ᵇ	$k_2/\text{l mol}^{-1}\text{s}^{-1}$ ᶜ
1·05-Trichloroacetic	464	10·0	9·6	12·2	1·27	1·22
5·26-Trichloroacetic	464	10·0	9·6	12·2	1·27	1·22
5·26-Trichloroacetic	928	11·6	10·6	12·5	1·18	1·08
6·68-Oxalic	464	8·5	15	18·5	1·23	2·18
33·4-Oxalic	464	6·2	27·9	32·8	1·17	5·29
33·4-Oxalic	928	8·5	30·0	31·8	1·06	3·74
13·4-Oxalic	682	9·5	16·7	19·8	1·19	2·09
26·7-Oxalic	1360	10·8	21·3	25·6	1·20	2·37
40·1-Oxalic	2730	11·9	26·7	35·3	1·32	2·97

ᵃ The [BH⁺] is calcuated by using equation (10) and K_{diss} = 0·05. ᵇ From k_1/[BH⁺]. ᶜ From k_1/[AX⁻].

and (4a and b) were recovered unchanged upon acidification. Similar results were obtained with 1.85×10^{-4}M-(4a) and $6\cdot10^{-5}$M-Et$_3$N, where any cyanide ion formed would be rapidly protonated by the excess of (4a) and presumably becomes ineffective in the reverse reaction.

Reaction of 10^{-4}M-(4a) with $1—2\cdot15 \times 10^{-2}$M-collidine resulted in incomplete formation of (6b), but no elimination was observed during 6 days at $40°$.

Attempted Exchange of (4a) *and* (4b) *with* CN$^-$.—A mixture of $0\cdot048$M of ^{14}CN-labelled (4a) [which was prepared from (3a) and K^{14}CN], $0\cdot053$M-Et$_3$N, and $0\cdot0143$M-KCN was kept for 20 h at $40°$ in acetonitrile. Reisolation of [^{14}CN]-(4a) showed 7% loss in its radioactivity. This is within the rather high experimental error, since a small difference between the two large countings, at the beginning and the end of the reaction, is measured.

When a mixture of $0\cdot027$M of unlabelled (4b), $0\cdot02$M-Et$_3$N, and $0\cdot01$M-K^{14}CN was kept for 5 h at $40°$ in MeCN, the reisolated (4b) was at most $0\cdot32\%$ labelled. From this value, the upper limit for the first order rate constant for exchange with the excess of K^{14}CN is $6\cdot10^{-7}$ s^{-1}.
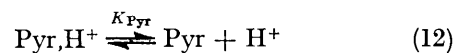
DISCUSSION

The nature of X, Y, and Y$'$ [equation (1)] and analogy with the elimination of HCN from (1a and b) where the carbanions (2a and b) are intermediates[4,5] strongly suggest a carbanionic process for the base-catalysed elimination of trifluoroethanol from (5). The fast ionisation of (1a) and Et$_3$N, coupled with the much higher acidity of dinitromethane [$pK_a(H_2O)$ $3\cdot57$][15] as compared to that of malononitrile [$pK_a(H_2O)$ $11\cdot1$][15] predicts a rapid formation of the anion (6a). The absorption maximum at 373 nm which formed immediately upon addition of base to (5) is therefore ascribed to the anion (6a). The reaction thus involves two stages: the formation of (6a) and subsequent elimination from the anion.

Formation of the Anion. Ionisation and Acidity of (5) *in Acetonitrile.*—The nature and the concentration of the species involved in the carbanionic elimination are determined by one of the two equilibrium constants K_{ip} or K_{diss} [equations (4) and (6)] which show whether the ionisation leads to an ion pair or to free ions. The almost complete ionisation in the presence of Et$_3$N is similar to that of (1a),[4] but in contrast to that of (1b),[5] showing that (5) is a stronger acid than (1b). However, this behaviour precludes decision whether K_{ip} or K_{diss} applies. The data of Table 1 show that when the concentrations of the anions are used, a much better constancy for K_{diss} is found than for K_{ip} in pyridine and in collidine. The free ion (6) is therefore the species involved in the elimination with these bases, and presumably also with Et$_3$N. The data for the reactions of pyridine and 2,6-lutidine with (1a) in chloroform,[4] combined with the relationship, $K_{ip}(MeCN) > K_{ip^-}$ (chloroform) for (1b),[5] indicates that $pK_a(5) < pK_a$ (1a).

Data on the equilibrium constant K_{ion} for the ionisation of (5) in acetonitrile [equation (11)] are not available, but K_{ion} was calculated from equation (12), which is a combination of equations (13) and (1a) for the ionisation of pyridine in acetonitrile and K_{diss} with pyridine. By inserting the values K_{pyr} $4\cdot68 \times 10^{-13}$ l mol^{-1},[16] and K_{diss}

$$\text{HAX} \overset{K_{Ion}}{\rightleftharpoons} \text{AX}^- + \text{H}^+ \qquad (11)$$
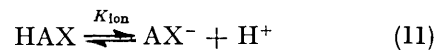
$2\cdot7 \times 10^{-4}$, $K_{ion} = 1\cdot26 \times 10^{-16}$, and $pK_a(5) = 15\cdot9$ in acetonitrile.

$$\text{Pyr,H}^+ \overset{K_{Pyr}}{\rightleftharpoons} \text{Pyr} + \text{H}^+ \qquad (12)$$

$$\text{Pyr} + \text{HAX} \overset{K_{diss}}{\rightleftharpoons} \text{Pyr,H}^+ + \text{AX}^- \qquad (1a)$$

$$K_{ion} + K_{Pyr} \times K_{diss} \qquad (13)$$
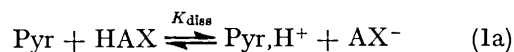
The prediction that (5) would be a strong acid was not realised, since (5) in acetonitrile is $12\cdot3$ pK_a units a weaker acid than dinitromethane in water. This is due to two reasons. First, a change from water to a dipolar aprotic solvent reduces the pK_a, and $pK_a(MeCN) - pK_a(H_2O)$ is $15\cdot3$ for p-nitrobenzoic acid and $13\cdot7$ for salicylic acid,[16] while $pK_a(DMSO) - pK_a(H_2O) = 5\cdot7$ for nitromethane.[17] Although this effect is important, it is doubtful whether the dipolar aprotic DMSO is a good model for acetonitrile, or benzoic acids are good models for (5), since the pK_a of benzoic acid in water ($4\cdot2$) is closer to that in DMSO ($11\cdot0$) than the latter to that in acetonitrile ($20\cdot7$).[16,17] Second, the acidities of substituted nitromethanes $RCH(NO_2)_2$ are similar for different primary R groups, but decrease strongly when the planarity of the anion is distorted when R = isopropyl.[18] Distortion from coplanarity, and a consequent decrease in the acidity, will be much more pronounced for the anion (6a) than for $Me_2CHCH(NO_2)_2$, as shown by models.

From K_{ion} and K_{diss} for the collidine–(5) reaction, a pK_a value of $14\cdot6$ was estimated for collidinium ion in acetonitrile. When equation (13) and the pK_a of Et$_3$N in acetonitrile ($18\cdot46$)[16] were used a K_{diss} value of 363 was calculated for the reaction of (5) with Et$_3$N at $40°$.

The C–X *Cleavage Step.*—The rate-determining step involves the expulsion of $CF_3CH_2O^-$ from the free ion (6a). Two types of kinetic behaviour were observed: with triethylamine, the reaction goes to completion even when [(5)] > [Et$_3$N], and the reaction is first order in the anion (6a) and zero order in the base. With pyridine and collidine, which were always in excess, the reaction is first order in (6a) and first order in BH$^+$. The kinetics are summarised in equation (14), where k_e is the first order constant for the decomposition

[15] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

[16] J. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 45.

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

[18] S. S. Novikov, V. M. Belikov, A. A. Fainzilberg, L. V. Ershova, V. I. Slovetski, and S. A. Shevelev, *Izvest. Akad. Nauk S.S.S.R., Otdel. Chem. Nauk*, 1959, 1855.

of (6a), and k_e' is the constant for the BH^+-assisted process. A plot of k_1 against $[BH^+]$ was indeed linear for the reactions with collidine and pyridine (Figure 1).

$$\text{Rate} = k_1[(6a)] = k_e[(6a)] + k_e'[(6a)][BH^+] \quad (14)$$

The k_e' values which were obtained from the slopes (by a least squares treatment) are given in Table 3 and differ only slightly from the average k_2 values of Table 1. The small k_e values which are obtained from the intercepts differ from k_1 for Et_3N but they have little meaning
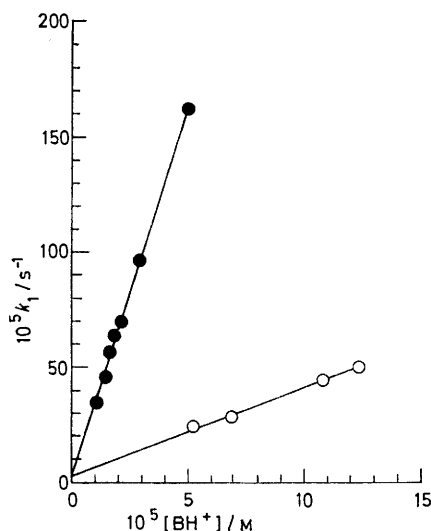
FIGURE 1   Plot of k, against $[BH^+]$ for the reactions of [pyridine] (●) at 40° and [collidine] (○) at 60° in acetonitrile

since they are extremely sensitive to a small error in the slope. The plots suggest that the first term of equation (14) is negligible for pyridine and collidine, and Table 2 shows that the second term is negligible for Et_3N.

The dependence on the BH^+ term suggests electrophilic assistance by the pyridinium ions in the detachment of the CF_3CH_2O group. Electrophilic assistance by potassium ion within an ion pair was suggested in the $(E1cB)_{ip}$ eliminations of HF from 2-phenyl-1,1,1-trifluoropentane,[19] and of methanol from 1-methoxyacenaphthene.[20] Ammonium ion assistance for the expulsion of F^- [21] and CN^- [4,5] within the ion pair was suggested previously in $(E1cB)_{ip}$ eliminations, while assistance by free substituted ammonium ions was found

for the expulsion step of slow leaving groups in nucleophilic aromatic [22] and vinylic substitutions.[12] To the best of our knowledge this is the first example of electrophilic assistance by free cations to the expulsion of a leaving group in elimination from a conjugate base of a carbon acid. We suggest the name $E2cB$ (elimination, bimolecular, from the conjugate base) for this mechanism. A different variant, designated $E_{C=C}2cB$ was suggested earlier [23] for the alkyl-lithium-catalysed elimination of HCl from β-chlorostyrenes. This variant involves a usual $E2$ type elimination of HCl from the lithium salt of the vinyl chloride. It should be noted that the term $E2cB$ was also suggested for the ' irreversible ' $E1cB$ variant, where $k_2 \gg k_{-1}[BH^+]$ of equation (1).[24] However, it seems that this term has not been generally accepted in this sense, as would appear from its absence from a recent book.[25]

The most plausible transition state for the assisted step is (7), where the ammonium ion reacts with the charge-carrying oxygen.

$$Ph_2C-\overset{\frown}{C}(NO_2)_2$$
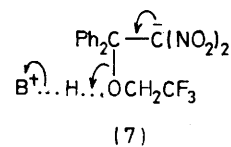$$B^+\cdots H\cdots\overset{\frown}{O}CH_2CF_3$$

(7)

Table 3 shows that the stronger acid, the pyridinium ion, is 22 times more reactive than the collidinium ion. Neglecting steric effects, which probably contribute to this difference, and using the pK_a values in acetonitrile [16] gives a Brønsted α of 0·6. If this value is used to calculate k_e' for Et_3N, assuming that it obeys the same relationship then $k_e' = 6·8 \times 10^{-3}$ l mol^{-1} s^{-1}, and since $k_e/k_e' = 232$, the non-catalysed reaction takes over at our conditions. Similar differences between ' strong ' and ' weak ' bases were previously observed in their reactions with (1a).[4] The high pK_a of (5) precludes catalysis by unchanged (5).

Addition of free BH^+ should increase the rate, but this was not observed on addition of trichloroacetic acid to the collidine–(5) reaction. The pK_a of CCl_3CO_2H in acetonitrile is unknown, but we estimated a value of 10·5 from its pK_a in water (0·7) [26] and from the linear dependency which exists between $pK_a(H_2O)$ and pK_a-(MeCN) [16] for benzoic acids (Figure 2). The use of the benzoic acids plot is justified by the resemblance between the ΔpK_a values $[pK_a(DMSO) - pK_a(H_2O)]$ of benzoic and acetic acids.[17] We explain the inefficiency of an acid stronger than collidine ion to reduce the concentration of (6a) and to increase k_1, by the

[19] D. J. Cram and A. S. Wingrove, *J. Amer. Chem. Soc.*, 1964, **86**, 5490.

[20] D. H. Hunter and D. J. Shearing, *J. Amer. Chem. Soc.*, 1971, **93**, 2348; 1973, **95**, 8333.

[21] V. Fiandanese, G. Marchese, and F. Naso, *J.C.S. Chem. Comm.*, 1972, 250.

[22] J. A. Orvik and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1970, **92**, 2417.

[23] M. Schlosser and V. Ladenberger, *Tetrahedron Letters*, 1964, 1945; *Chem. Ber.*, 1967, **100**, 3877, 3893, 3901; W. M. Saunders, jun., and A. F. Cockerill, ' Mechanisms of Elimination Reactions,' Wiley, New York, 1973, p. 521.

[24] (a) S. Oae, ' Elimination Reactions,' Tokyo Kagaku Dojin, Tokyo, 1965, p. 24; (b) Y. Yano and S. Oae, *Tetrahedron*, 1970, **26**, 27; (c) S. Oae, Y. Kadoma, and Y. Yano, *Internat. J. Sulfur Chem.* (A), 1972, **2**, 29.

[25] W. H. Saunders, jun., and A. F. Cockerill, ' Mechanisms of Elimination Reactions,' Wiley, New York, 1973.

[26] G. Kortum, W. Vogel, and K. Andrussow, ' Dissociation Constants of Organic Acids in Aqueous Solutions,' Butterworths, London, 1961.

formation of a collidinium acetate ion pair $CCl_3CO_2^-$,- $H\overset{+}{N}C_5H_2Me_3$, whose cation has much lower catalytic power than the free collidinium ion.

Oxalic acid could be a catalyst in our reaction since internal hydrogen bonding will stabilise the oxalate ion [cf. (8)] and would lead to dissociation of a collidinium oxalate ion pair. Indeed, addition of oxalic acid to the collidine–(5) system reduced the concentration
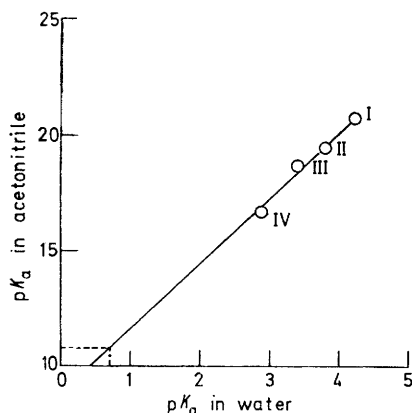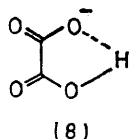

FIGURE 2 A plot of pK_a of benzoic acids in acetonitrile against their pK_a in water: I, $PhCO_2H$; II, m-$BrC_6H_4CO_2H$; III, p-$NO_2C_6H_4CO_2H$; IV, $3,5$-$(NO_2)_2C_6H_3CO_2H$

of (6a) (Table 4) and the k_2 values which were calculated from the new BH^+ concentrations were identical with those obtained for the internally formed BH^+ (Table 2).

(8)

These interpretations are borne out by conductivity experiments. At concentrations similar to those used for the kinetics, the conductivity of a collidinium oxalate mixture is one order of magnitude higher than that of collidinium trichloroacetate, suggesting a higher concentration of dissociated species for collidinium oxalate in acetonitrile.

The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values (Table 4) fit the suggested mechanisms. The $\Delta H^{\ddagger}$ for the unassisted process with Et_3N resembles those found for other ' irreversible first-order carbanionic eliminations,' [6,7] and is ca. 10 kcal mol⁻¹ higher than that for the assisted process with collidine. The $\Delta S^{\ddagger}$ is more negative for the bimolecular process where BH^+ participates in the transition state.

As predicted, no isotope effect was observed for the

* A referee had suggested that isotope effects for proton transfer between oxygen and nitrogen atoms are much smaller than those for proton transfer to and from carbon, and hence an unsymmetrical transition state is not implied. This was based on data on solvent isotope effects which are not directly applicable to our case. The maximum isotope effect for proton transfer between oxygen and nitrogen atoms should be much higher than our observed values.

reaction with Et_3N, since k_e does not involve a proton transfer step. The small isotope effects (k_H/k_D) of 1·27 and 1·54 with collidinium and pyridinium ions, respectively, fit a rate-determining proton transfer k_e' which occurs with an unsymmetrical transition state.[27,*] Note, however, that in our case more than three atoms participate in changes along the reaction co-ordinate. Whether the transition state in this case resembles the reactants or the products is unknown, and the limited data would make a guess which is based on Brønsted's α, highly speculative. Alternately, k_e represents a pre-equilibrium proton transfer from BH^+ to (6a), followed by a slow expulsion of trifluoroethanol from the zwitterion $Ph_2C(\overset{+}{O}HCH_2CF_3)\overset{-}{C}(NO_2)_2$.

The catalytic nature of the reaction shows either that the Et_3N which is consumed by the initial equilibrium is regenerated at a later stage or that the formed $CF_3CH_2O^-$ ionises unchanged (5). Et_3N may be formed directly via transition state (7), or it may be formed in equilibrium (15) which is shifted to the right as judged by the pK_a values of Et_3N and CF_3CH_2OH in water.[28,29]

The overall elimination mechanism is outlined in the Scheme.

$$CF_3CH_2O^- + BH^+ \rightleftharpoons CF_3CH_2OH + B \qquad (15)$$
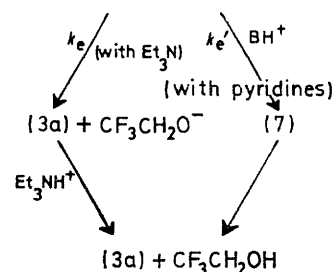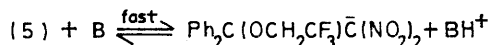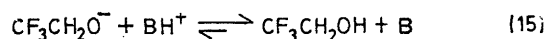
SCHEME

Elimination of CN^- *from* (6b) *and* (6c).—The anions (6b) and (6c) are formed immediately and quantitatively from (4a) and (4b) and Et_3N, but a further elimination of cyanide ion did not take place. The possibility that such elimination is hidden since it is followed by a rapid addition of CN^- to (3a) and (3b) and the (3a) $\rightleftharpoons$ (6b) and the (3b) $\rightleftharpoons$ (6c) equilibria are mainly to the right [equation (16)] was investigated by the exchange experiments. The reaction

$$(3a) \text{ and } (3b) + CN^- \rightleftharpoons (6b) \text{ and } (6c) \qquad (16)$$

of [¹⁴CN]-(6b) with CN^- shows $\leqslant 7\%$ incorporation, but the counting method involves a relatively high

[27] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

[28] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1959, **81**, 1050.

[29] Z. Rappoport, ' Handbook of Table for Organic Compounds Identification,' The Chemical Rubber Co., Ohio, 3rd edn., 1967.

error (see Results section). A more accurate method which measures the incorporation of $^{14}CN^-$ into un-labelled (6c) showed only 0·32% incorporation. Since k_e of the 'E1cB of the second type' increases with the electron donation of the β-aryl group,[5] this value is an upper limit for incorporation of *free* cyanide ion into both (6b and c). Assuming that each elimination step leads to exchange, $k_e = 6·10^{-7}$ s^{-1} at 40°.

This k_e for (6c) is at least 560 times lower than k_e of $3·4 \times 10^{-4}$ s^{-1} for the expulsion of CN^- from the anion (2b; $Z = p\text{-MeO}$).[5] The bulky and electron-donating p-methoxyphenyl group of (6c) is expected to enhance k_e at least as much as the methyl group of (2b), and hence, elimination from an α,α-dinitro-carbanion is at least 560 times slower than from an α,α-dicyanocar-banion. This is an outcome of the higher ability of nitro-, compared with a cyano-substituent to disperse a negative charge. This is reflected in the higher σ_I and σ_R values for nitro,[30] and in the high acidity of (4a and b) which completely ionise with equimolar concentrations of Et_3N, whereas much higher concen-trations of Bu_3N are required to completely ionise (1b).[5] There is enough charge on the α-carbon of (2b) to dis-place internally the leaving group. However, so much charge resides on the nitro-groups of (6b and c) that the internal nucleophilicity of the electron pair on the α-carbon is largely reduced and there is not a sufficient driving force to displace the leaving group.

Moving from the 'irreversible' *via* the 'reversible' to the 'second type' E1cB reactions, α-electron-attract-ing groups first increase the overall elimination rate when k_{ion} is rate determining, and then decrease it when k_e becomes rate determining or is the only step measured. The two systems (4) lie at the extreme end of the spectrum of E1cB reactions. The intermediate anion is so stable that it does not expel X^-.

Leaving Group Effects in E1cB *of the Second Type.*— In contrast to the predicted relative reactivities of systems (1b) and (4), the comparison of the behaviour of system (4) and (5) leads to the conclusion that in elimination from carbanions trifluoroethoxy is a better leaving group than cyano. This is somewhat unexpected since the reactivity order of X groups in C–X bond cleavage should roughly follow the acidity of HX, and in the expulsion of X^- from the anions $RCX=N-\bar{N}Ar$ it was estimated that the change in log k_e is approxi-mately half the variation in $pK_a(HX)$.[31] HCN (pK_a 9·21) is a stronger acid in water than trifluoro-ethanol (pK_a 12·37),[28] and the predicted order for k_e is $CN^- > CF_3CH_2O^-$. It is unlikely that a reversal of the pK_a values will occur in acetonitrile, since pK_a-(HCN) = 12·9 in DMSO, and $pK_a(CF_3CH_2OH) = 25 \pm 3$ in DMSO as judged from the pK_a values of other alcohols in DMSO.[17] The only data available for comparison are for substitutions in the compounds $p\text{-Me}_2NC_6H_4$-

$CX=C(CN)_2$ by morpholine in acetonitrile, where there is some indication that the non-catalysed expulsion step of X^- may be faster for $CF_3CH_2O^-$ than for CN^-.[32]

We believe that this reactivity order has, at least in part, a steric origin. Although we were unable to build space-filling models of both (6a and b), the steric congestion may well be higher in (6a) than in (6b and c). This will result in steric acceleration due to the relief of non-bonded interactions, and in a more nucleo-philic α-carbon in the less planar carbanion. Both factors favour the expulsion of the trifluoroethoxy-over the cyano-group.

Conclusions.—The present work describes two new features of the amine-catalysed eliminations from HAX. Electrophilic assistance by *free* BH^+ ions for the detach-ment of the leaving group is observed for system (5), demonstrating an E2cB mechanism, where the anion concentrations were directly measured, System (4) shows an extreme behaviour, where anion formation is complete, but the anion is so stable, that further ex-pulsion of X^- from it is negligible.

EXPERIMENTAL

M.p.s are uncorrected. N.m.r. spectra were recorded on a Varian HA 100 spectrometer and the chemical shifts are given in δ downfield from tetramethylsilane. Mass spectra were taken with a Hitachi–Perkin-Elmer RMU-6-E spectrometer, radioactivity was counted with a Nuclear Chicago planchete counter, and conductivity was measured with a Radiometer conductivity meter equipped with a CDC 104 electrode.

Materials.—Acetonitrile was refluxed for 24 h over P_2O_5 and distilled through a fractionating column. The middle fraction, b.p. 81°, was used. Triethylamine, collidine, and pyridine were spectroscopic or analytic grades (Fluka) and were redistilled before use. Trichloroacetic and oxalic acids (Merck) were analytical samples which were used without further purification. 1,1-Dinitro-2,2-diphenylethylene (3a) was prepared according to Bergmann.[33]

1,1-*Bis*-(p-*methoxyphenyl*)-2,2-*dinitroethylene* (3b). To a stirred suspension of 1,1-bis-(p-methoxyphenyl)ethylene [34] (7 g, 30 mmol) in glacial acetic acid (70 ml), 70% nitric acid (22 ml) was added during 10 min. Short heating of the red solution to 50—60° resulted in a temperature rise to 90°. After rapid cooling (acetone–dry ice), water (100 ml) was added, the organic substrates were extracted with chloroform (3 × 50 ml), separated, washed with water, dried, and the solvent was evaporated. The remaining oil was chromatographed over silica (30—120 mesh; 500 g) with chloroform as eluant, and when a yellow fraction appeared, 700 ml were collected. After evaporation, the residue was crystallised from ligroin, giving 1,1-*bis*-(p-*methoxyphenyl*)-2,2-*dinitroethylene* (0·8 g, 8·3%), m.p. 163° (decomp.), $\lambda_{max.}$ (MeCN) 381 nm (ε 12,800), δ ($CDCl_3$) 3·89 (6H, s, MeO) and 7·55 (8H, centre of AA'BB' q, Ar) (Found:

[30] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, **10**, 1.

[31] A. F. Hegarty, M. P. Cashman, and F. L. Scott, *J.C.S. Perkin II*, 1972, 44.

[32] Z. Rappoport and P. Peled, unpublished results.

[33] E. D. Bergmann and E. Meyer, *Chem. Ber.*, 1932, **65**, 446.

[34] Y. Al-attar and R. Wizinger, *Helv. Chim. Acta*, 1963, **46**, 1286.

C, 58·1; H, 4·4; N, 8·4. $C_{16}H_{14}N_2O_6$ requires C, 58·2; H, 4·25; N, 8·5%).

3,3-*Dinitro-2,2-diphenylpropionitrile* (4a). To 1,1-di-nitro-2,2-diphenylethylene (1·56 g, 56 mmol) in ethanol (25 ml), potassium cyanide (1·15 g, 17·6 mmol) in water (10 ml) was added slowly at 60°. Water (100 ml) was added, the mixture was brought to pH 4 by adding acetic acid, and the white solid was filtered and crystallised from ligroin, giving white needles of 3,3-*dinitro-2,2-di-phenylpropionitrile* (148 mg, 85%), m.p. 132—133°, δ (CDCl₃) 7·13 (1H, s, ∶CH) and 7·41 (5H, s, Ph), *m/e* 297 (*M*, 66%), 251 (*M* — NO₂, 1·5), 220 (*M* — Ph, 21), 205 [*M* — (NO₂)₂, 57], and 192 [*M* — CH(NO₂)₂, 100] (Found: C, 69·35; H, 3·5; N, 14·0. $C_{15}H_{11}N_3O_4$ requires C, 60·6; H, 3·7; N, 14·15%).

3,3-*Dinitro-2,2-diphenyl*[¹⁴CN]*propionitrile* [¹⁴CN]-(4a). The radioactive compound was prepared in a manner similar to that for unlabelled (4a) excepting that K¹⁴CN (Amersham) with specific activity of 56 mCi mM⁻¹ was used.

2,2-*Bis-(p-methoxyphenyl)-3,3-dinitropropionitrile* (4b). Potassium cyanide (3·5 g, 53·8 mmol) in water (13 ml) was added slowly with stirring to 1,1-bis-(*p*-methoxyphenyl)-2,2-dinitroethylene (0·22 g, 0·67 mmol) in acetonitrile (15 ml). The solution turned dark red immediately. On addition of water (35 ml) and slow acidification (HCl) the colour disappeared. After standing for one week at 5°, white crystals of 2,2-*bis*-(*p-methoxyphenyl*)-3,3-*dinitro-propiontrile* (100 mg, 80%), m.p. 92°, were obtained, δ (CDCl₃) 3·76 (6H, s, MeO), 7·09 (1H, s, ∶CH), and 7·10 (8H, centre of q. Ar), *m/e* 357 (*M*, 16%), 330 (*M* — HCN, 4), 278 (*M* — HNO₂ — NO, 7), 265 [*M* — (NO₂)₂, 17], 252 [*M* — CH(NO₂)₂, 100], and 250 (*M* — *p*-MeOC₆H₄, 18) (Found: C, 57·3; H, 4·25; N, 11·55. $C_{17}H_{15}N_3O_4$ requires C, 57·15; H, 4·25; N, 11·75%).

1,1-*Dinitro-2,2-diphenyl-2-(2,2,2-trifluoroethoxy)ethane* (5). This compound was prepared by two methods. (a) A solution of sodium trifluoroethoxide [35] (58 mmol, 25 ml) was added with stirring to a solution of 1,1-dinitro-2,2-di-phenylethylene (3·8 g, 14 mmol) in dry trifluoroethanol (50 ml). The mixture was heated at 60° for 15 min until a clear red solution was obtained, then cooled with ice-water and acidified with a cold solution of concentrated HCl (19 ml) in water (80 ml). The solution was extracted with chloroform, and the organic layer was washed with water, dried (Na₂SO₄), and evaporated, giving a yellow oil which crystallised after standing for several h, yielding 1,1-*dinitro-2,2-diphenyl-2-(2,2,2-trifluoroethoxy)ethane* (0·014 g, 72%), m.p. 44°, δ (CDCl₃) 3·72 (2H, q, J_{HF} 8 Hz, CH₂), 7·26 (1H, s, ∶CH), and 7·37 (10H, s, Ph), *m/e* 370 (*M*, 11%), 278 [*M* — (NO₂)₂, 2], 270 (*M* — CF₃CH₂OH, 5), and 265 [*M* — CH(NO₂)₂, 100] (Found: C, 52·05; H, 3·6; N, 7·5; F, 15·2. $C_{16}H_{13}F_3N_2O_5$ requires C, 51·9; H, 3·55; N, 7·55; F, 15·4%). (b) Potassium t-butoxide (5·68 g, 76 mmol) was dissolved in trifluoroethanol (40 ml), and 1,1-dinitro-2,2-diphenylethylene (2·55 g, 9·4 mmol) was added to the mixture. A viscous mass was im-mediately formed. Trifluoroethanol (10 ml) was added, the mixture was refluxed for 15 min, and the yellow solid, which consisted of a mixture (2·8 g) of the potassium salt of (6a) and the remaining starting materials, was filtered and stored. Before each set of experiments the salt was dissolved in a cold aqueous 5% K₂CO₃ solution,

washed twice with chloroform, and acidified with dilute hydrochloric acid. The precipitate formed was identical with (5) which was obtained by method (a).

Reaction Between 1,1-Dinitro-2,2-diphenylethylene and Methoxide and Ethoxide Ions.—1,1-Dinitro-2,2-diphenyl-ethylene (0·36 g, 1·3 mmol) and sodium methoxide (0·9 g, 17 mmol) were dissolved with stirring in methanol (30 ml), and water (25 ml) was added to the clear brown-red solution. Slow acidification with dilute HCl at room temperature gave a solid which was filtered, and crystallised from ether, yielding benzophenone dimethyl acetal (0·2 g, 66%), m.p. 105° (lit.,³⁶ 107°), δ (CDCl₃) 3·10 (6H, s, MeO) and 7·33 (10H, m, Ph). When the reaction mixture was acidified at acetone–dry ice temperature, a solid was obtained, which by n.m.r., δ (CDCl₃) 3·07 (3H, s, MeO), 7·30 (1H, s, CH), and 7·38 (10H, s, Ph), was identified as 1,1-dinitro-2,2-diphenyl-2-methoxyethane. The solid is unstable and after two days in the desiccator turns into a green liquid. In reaction with ethoxide ion under the same conditions, the ethane (3a) was recovered unchanged.

Exchange Experiments.—The exchange experiments be-tween cyanide ion and compounds (4a and b) were con-ducted in two ways.

(a) KCN (0·143 mol) was reacted with [¹⁴CN]-(4a) (48 mmol) in the presence of triethylamine (53 mmol). Due to the low solubility of KCN in acetonitrile the solvent used was acetonitrile (10 ml)–water (4 ml). The mixture was kept for 20 h at 40°, chloroform (30 ml)–water (100 ml) were then added, and concentrated HCl was added dropwise until the discharge of the colour. The organic layer was separated, washed thrice with distilled water, and [¹⁴CN]-(4a) [and any (4a) formed] were precipitated by the addition of light petroleum. Attempts to count ¹⁴C by using a liquid scintillation counter were unsuccessful due to the high fluorescence of the material, and a planchete counter was used. A weighed sample was dissolved in analytical acetone on a planchete, and a thin homogeneous film of the material was obtained by evaporating the solvent with a sun-lamp. The counting was sensitive to the thickness of the film, and several planchetes with 0·0023—0·0204 mg of [¹⁴CN]-(4a) were prepared, each was counted thrice for 3 min, and the average reading was taken. The standard deviation in this experiment was ±7%.

(b) A reaction mixture containing K¹⁴CN (10 mmol) with specific activity of 4 mCi mM⁻¹, substrate (4b) (27 mmol), and triethylamine (20 mmol) in acetonitrile (6 ml)–water (2 ml) was kept for 5 h at 40°. The separation, purification, and measurements are identical to those in method (a), except that the counting time of each planchete was 10 min. The standard deviation was ±0·3%.

Kinetic Measurements.—The appropriate volumes of stock solutions of the reactants were mixed at the reaction temperature, and immediately transferred to silica absorp-tion cells in the thermostatted chamber of a Gilford 2400 spectrophotometer. The temperature within the cell was controlled to ±0·1°. The change in the absorption was followed at two wavelengths (see Results section). In the reaction between (5) and the bases, some HF is formed from the decomposition of the trifluoroethanol, and the absorption of the silica cells had to be calibrated before each experiment.

Product Analysis.—In most of the kinetic experiments the u.v. spectrum of the reaction mixture at infinity was

³⁵ E. J. Fear, J. Thrower, and J. Veitch, *J. Chem. Soc.*, 1958, 1322.

³⁶ H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 619.

measured and compared with that of the products. With (4a and b) the m.p. of the solid obtained after work-up of the reaction mixture was taken, and in the reactions of (5) with amines the n.m.r. was measured in chloroform after evaporation of the reactants. In all cases, only the products described above were formed.