Kinetics, Isotope Effects, and Mechanism of the Reaction of 1,1,1-Trifluoro-2,2-bis-(4-nitrophenyl)ethane with Piperidine and Pyrrolidine Bases in Dipolar Aprotic Solvents

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The kinetics of the reaction of 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane with piperidine and pyrrolidine bases in a series of solvents [acetonitrile (MeCN), benzonitrile (PhCN), and dimethyl sulphoxide (Me_2SO)] are reported. The reaction is complex, leading to a 1-amino-1-fluoro-2,2-bis-(4-nitrophenyl)ethene as the final product *via* the intermediate 1,1-difluoro-2,2-bis-(4-nitrophenyl)ethene. The reaction is promoted only by primary and secondary amines; tertiary amines appear to be inactive even under reflux conditions. The entropies of activation ($\Delta S^{\ddagger}$/J mol^{-1} K^{-1}) are negative and large (− 183.7 and −162.3) for the reaction with piperidine in PhCN and MeCN; for reaction in Me_2SO the value is only −77.4. The kinetic isotope effects (k_H/k_D) fall between 1.0 and 1.6 at 30 °C. The results obtained are discussed in terms of a multistep mechanism, $(E1cB)_{ip}$, consisting of a pre-equilibrium followed by fast addition–elimination steps.

The reaction of 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) with alkoxide bases exhibits a multistep mechanism, dependent upon the alcohol–alkoxide system.[1,2] It is apparently different from that of the elimination of HCl from 1,1,1-trichloro-2,2-bis-(4-chlorophenyl)ethane,[3–7] 1,1,1-trichloro-2,2-bis-(4-chloro-3-nitrophenyl)ethane,[8] and 1,1,1-trichloro-2,2-bis-(4-nitrophenyl)ethane,[9] which in all cases involves a simple β-elimination with various transition-state structures, producing a stable olefin as the final product. The transition-state structure varies from *E*2H to *E*2H with a contribution of *E*1cB for the elimination of HCl from 1,1,1-trichloro-2,2-bis-(4-chlorophenyl)-ethane promoted by alkoxide bases in the appropriate alcohols.[3,4] The dehydrochlorination of several chloroethanes promoted by strong aliphatic amines also occurs according to the *E*2H mechanism; however in these systems the contribution of the *E*1cB mechanism becomes significantly larger, particularly in the highly polar solvent acetonitrile.[7]

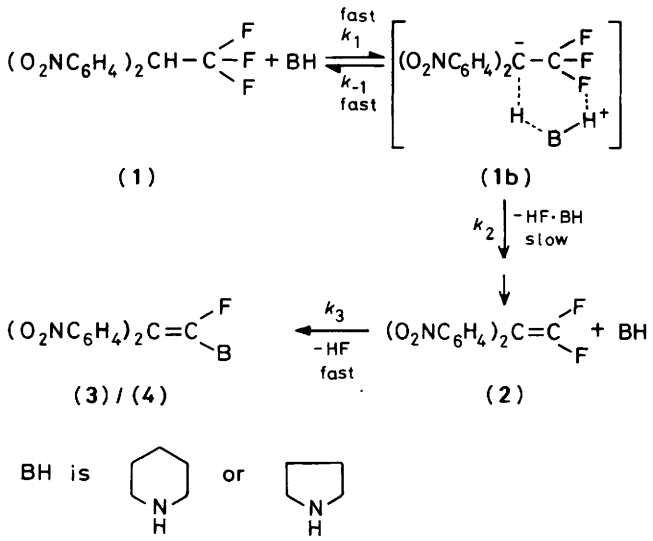
An increase in acidity of the β-hydrogen atom on increasing the number of chloro-substituents[7] or nitro-substituents[8] in the phenyl ring evidently gives a more carbanionic transition state for the β-elimination than would be expected from the results of the experiments carried out with the much stronger alkoxide bases.[4,5] Thus replacement of the chlorine atoms by the more strongly electron-withdrawing nitro groups, as in 1,1,1-trichloro-2,2-bis-(4-nitrophenyl)ethane, results in a mechanism having mainly *E*1cB character, to an extent which varies with the polarity of the solvent used.[9] In the highly polar solvent acetonitrile, the reaction exhibits a large kinetic isotope rate ratio (k_H/k_D), in accord with an apparent $(E1cB)_I$ or *E*2 mechanism. For the less polar solvent tetrahydrofuran the contribution of *E*2H to the overall mechanism becomes larger, and finally for the non-polar solvent hexane there is the greatest contribution of the *E*2H mechanism as indicated by both primary isotope effects and activation parameters.[9] Thus these reactions of chloro- and chloro-nitro-phenyl ethanes in general show *E*2H elimination mechanisms, with various contributions of *E*1cB character in the transition states. The main factors causing change in the reaction mechanism are a different acidity of the β-hydrogen atom, different steric bulk of the reacting molecules,[10] and different expulsion susceptibility of the leaving groups.[11]

A most dramatic change in reaction mechanism is that previously reported for fluoro-substituted ethanes reacting with alkoxide bases;[1,2] here the reaction has a multistep mechanism dependent upon the alkoxide–alcohol system used. For trifluoroethanes the acidity of the β-hydrogen atom as well as the presence of the much poorer fluorine leaving group causes a multistep process with several intermediates of different reactivities.[1,2] Apparently the rate-determining step for the reaction in lower alcohols with the appropriate alkoxide bases is the first elimination step, forming the olefin 1,1-difluoro-2,2-bis-(4-nitrophenyl)ethane (**2**). In methanol–methoxide the reaction occurs by a pure $(E1cB)_R$ mechanism, whereas in higher alcohols–alkoxides the mechanism appears to be more complex, consisting of $(E1cB)_R$ and $(E1cB)_I$ or *E*2 mechanisms followed by addition–elimination processes giving several intermediates. Kinetic studies[1,2] have defined a clear and self-consistent mechanism of the reaction of (**1**) with alkoxide bases, showing a set of sequential reactions along the reaction pathway. The dependence of this complex mechanism upon the structure of the reacting base prompted us to examine the initial steps of the reaction of (**1**) with amines in the dipolar aprotic solvents acetonitrile (MeCN), benzonitrile (PhCN), and dimethyl sulphoxide (Me_2SO).

Results and Discussion

The effectiveness of aliphatic amines as agents for eliminating HCl from chloroethanes has been discussed previously.[8] The primary, secondary, and tertiary amines used were selected such that their structures were different but possessed similar basicities.[12,13] Generally, we found that the most efficient elimination systems consist of normal primary amines in acetonitrile. In this aprotic differentiating solvent the elimination reactions occur mainly *via* the *E*2H transition state, with a large contribution of *E*1cB resulting from solvation effects.[8] In the case of primary amines, small differences in p*K* values (about 0.2 units) brought about a large change in reaction rate. This was a consequence of the different structures of the amines rather than their basicity. Secondary amines showed a *ca.* 20% decrease in the reaction rate in comparison with primary amines.

The effectiveness of tertiary amines varies with their p*K* values; however their reactivity was almost a power of ten smaller than that for primary amines. In spite of the lower reaction rates of the tertiary amines as a result of their larger steric bulk, we expected that they would react with the fluoro-substituted substrate (**1**) at a rate not very much different from that of primary or secondary amines of similar strength.



Scheme 1.

However it turned out that only primary and secondary amines were reactive; tertiary strong amines of widely different structures (tri-n-propylamine and quinuclidine) were inert. The substrate (**1**) remains unchanged in acetonitrile even after 24 h under reflux with these bases at a 0.1M concentration. Though the tertiary amines themselves do not react with the substrate (**1**), they accelerate the appearance of the products of the reaction with primary or secondary amines when present in the reaction mixture.

In order to determine the intermediates and products of the reaction of the substrate (**1**) with pyrrolidine, piperidine, n-propylamine, and n-butylamine, a complete product analysis was performed. The products were isolated and identified by mass and n.m.r. spectra (Table 4) as 1-fluoro-2,2-bis-(4-nitrophenyl)-1-(pyrrolidin-1-yl)ethene (**3**), 1-fluoro-2,2-bis-(4-nitrophenyl)-1-piperidinoethene (**4**), 2,2-bis-(4-nitrophenyl)-1,1-bis-(propylamino)ethene (**5**), and 1,1-bis-(butylamino)-2,2-bis-(4-nitrophenyl)ethane (**6**). The reactions of the substrate (**1**) with pyrrolidine and piperidine give only the monosubstituted enamines (**3**) and (**4**). However for the reactions with primary amines up to n-propylamine, the doubly substituted enamines (**5**) and (**6**) are also produced. There was no 1,1-difluoro-2,2-bis-(4-nitrophenyl)ethene (**2**) present in the reaction residue owing to its fast reaction in the consecutive addition–elimination steps k_3 (Scheme 1), leading to the appropriate enamines. Its formation in the preceding step involves internal return of the proton within the ion-pair complex in a fast process (k_{-1}) as a pre-equilibrium prior to the slow elimination of HF (k_2) (Scheme 1).

In order to confirm that the olefin (**2**) is an intermediate we carried out the reaction of the substrate (**1**) with 1,1,3,3-tetramethylguanidine (TMG) base, for which k_2 is similar to k_3.[14] Careful product analysis showed a certain amount of the olefin (**2**) and the appropriate enediamine. Moreover the difluoro-olefin (**2**), prepared by the method previously described,[2] reacts with pyrrolidine and piperidine giving the same products as were obtained in the direct reaction of the substrate (**1**) with these bases (Table 4). These observations and the fact that enamines of this type can be prepared by treating an appropriate olefin with an amine base,[15] indicate that 1,1-difluoro-2,2-bis-(4-nitrophenyl)ethene (**2**) is an intermediate on the reaction pathway (Scheme 1).

The kinetic measurements were carried out for the reactions of (**1**) with piperidine and pyrrolidine in benzonitrile (PhCN), acetonitrile (MeCN), and dimethyl sulphoxide (Me_2SO) under pseudo-first-order conditions with [BH] ≫ [(**1**)]. If we assume that the rate-determining step is formation of the olefin (**2**) in a slow elimination (k_2) of HF from the complex (**1b**), then according to the Scheme, $k_{obs} = (k_1/k_{-1})\,k_2$, where $k_{-1} > k_2$. Since no colour characteristic of the stable ion or ion-pair intermediate is observed,[11] then the pre-equilibrium $K = k_1/k_{-1}$ must be small, suggesting that also $k_{-1} > k_1$. Consequently the pseudo-first-order rate constants (k_1) were determined from runs carried out with at least 30-fold excess of base, in which the change in optical density, at $\lambda_{max.}$ characteristic of the product (**3**) or (**4**), was monitored with time. A good fit to the first-order equation was found for both protonated and deuteriated substrate (**1**). The second-order rate constants are the calculated slopes of plots of k_1 *vs.* [BH]. The first-order rate constants are directly proportional to the base concentration, indicating a second-order elimination reaction.

The second-order rate constants (k) calculated by the method of least-squares for both systems of reactions are collected in Tables 1 and 2, respectively. These rate constants are generally three-fold larger for pyrrolidine than for piperidine. This is contrary to their pK_a values, which are 18.92 and 19.58 in MeCN for piperidine and pyrrolidine, respectively.[12] However this rate ratio holds well for all solvents examined, showing that the influences of strength and structure of the reacting bases on the reaction mechanism are similar. The dielectric constants of these highly polar solvents show more notable effects on the rates and the primary kinetic isotope effects. The rate ratio between the reaction in MeCN and that in PhCN is only *ca.* 3, but the rate for the reaction in Me_2SO is *ca.* 10 times greater than in PhCN. These observations indicate that the ionogenic character of the transition state in both reactions plays an important role. The same conclusion can be drawn from the primary kinetic isotope effects. Although the k_H/k_D values presented in Table 1 and 2 are rather small (1.0—1.6), yet the differences seem to be significant and characteristic of the $(E1cB)_{ip}$ reaction mechanism predicted by Miller.[15] The general tendency indicates that the more polar the solvent, the larger the isotopic rate ratio. The smallest value is found for the reaction of the substrate (**1**) with pyrrolidine, in the least polar solvent PhCN, in which k_H/k_D (1.6) is found for the reaction carried out with piperidine in the most polar solvent Me_2SO. The small kinetic isotope effects (Tables 1 and 2) suggest that the proton transfer is not a rate-determining step, even though the ionogenic character of this complex reaction seems unquestionable. In order to explain the low k_H/k_D values in terms of the $(E1cB)_{ip}$ reaction mechanism predicted by Miller.[16] The general treating the deuteriated substrate [^{2}H]-(**1**) with a deficient amount of piperidine in the ratio 1:1 [the whole reaction involves 3 mol of base for each 1 mol of substrate (**1**) (Scheme 1)]. After the reaction stopped, as a result of exhaustion of the base, mass spectra showed that in the remaining substrate (**1**) there was only 20% of the [^{2}H]-form left. The corresponding relative intensities were 100.0 and 38.3 for m/z 257 ($M^+ - CF_3$) and 258 ($M^+ - CF_3$), respectively. We chose the $M - CF_3$ peaks because of their greater intensities in comparison with the molecular ion peaks M^+.

The total unreactivity of such strong tertiary amines as quinuclidine towards the substrate (**1**) in dipolar aprotic solvents was shown also by the same exchange experiment: a solution of the substrate (**1**) (15 mmol) was mixed with quinuclidine (9 mmol) in the acetonitrile solvent, and 1.3 mmol of DCl was added to neutralize the base. In the residue of the reaction mixture no deuteriated substrate [^{2}H]-(**1**) was detected (the appropriate mass spectrum showed relative intensities 78.7 and 12.5 for m/z 257 and 258, which are the normal intensities obtained from the natural abundance of ^{13}C). This strongly supports our conclusion that tertiary amines such as quinu-

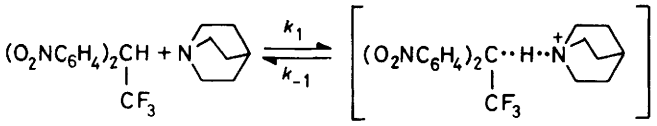
Table 1. Second-order rate constants and isotopic rate ratios for the reactions between 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) and pyrrolidine (BH) in benzonitrile (PhCN), acetonitrile (MeCN), and dimethyl sulphoxide (Me_2SO). Kinetic measurements were completed at wavelengths characteristic of the enamines (**3**). Concentration of (**1**) *ca.* 1×10^{-4} M

[BH]/M	PhCN ($\lambda_{max.}$ 430 nm) (150—300) $\times 10^{-3}$			MeCN ($\lambda_{max.}$ 420 nm) (35—116) $\times 10^{-3}$			Me_2SO ($\lambda_{max.}$ 435 nm) (5—35) $\times 10^{-3}$		
T/°C	$10^3 k_H$ ($dm^3 mol^{-1} s^{-1}$)	$10^3 k_D$	k_H/k_D	$10^2 k_H$ ($dm^3 mol^{-1} s^{-1}$)	$10^2 k_D$	k_H/k_D	k_H ($dm^3 mol^{-1} s^{-1}$)	k_D	k_H/k_D
20							1.09 ± 0.13	0.79 ± 0.05	1.39 ± 0.18
25	3.43 ± 0.18	3.40 ± 0.25	1.00 ± 0.09	1.30 ± 0.01	1.28 ± 0.03	1.02 ± 0.02	1.49 ± 0.20	1.10 ± 0.08	1.38 ± 0.21
30	5.54 ± 0.66	4.99 ± 0.47	1.11 ± 0.17	1.80 ± 0.03	1.71 ± 0.05	1.05 ± 0.04	2.07 ± 0.08	1.39 ± 0.12	1.50 ± 0.14
35	7.35 ± 0.59	7.26 ± 0.83	1.01 ± 0.14	2.31 ± 0.15	2.24 ± 0.03	1.03 ± 0.07	2.74 ± 0.06	1.81 ± 0.12	1.51 ± 0.10
40	9.35 ± 0.83	8.62 ± 0.46	1.08 ± 0.11	3.05 ± 0.16	2.98 ± 0.17	1.02 ± 0.08	4.27 ± 0.12	2.88 ± 0.03	1.48 ± 0.04
45	12.97 ± 2.21	11.48 ± 0.91	1.13 ± 0.21	3.58 ± 0.04	3.31 ± 0.20	1.08 ± 0.07			
50	21.67 ± 1.32	20.04 ± 1.70	1.08 ± 0.11						

Table 2. Second-order rate constants and isotopic rate ratios for the reactions between 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) and piperidine (BH) in benzonitrile (PhCN), acetonitrile (MeCN), and dimethyl sulphoxide (Me_2SO). Kinetic measurements were completed at wavelengths characteristic of the enamines (**4**). Concentration of (**1**) *ca.* 1×10^{-4} M

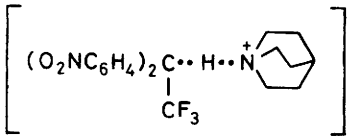
[BH]/M	PhCN ($\lambda_{max.}$ 408 nm) (231—950) $\times 10^{-3}$			MeCN ($\lambda_{max.}$ 400 nm) (41—90) $\times 10^{-3}$			Me_2SO ($\lambda_{max.}$ 416 nm) (4—28) $\times 10^{-3}$		
T/°C	$10^3 k_H$ ($dm^3 mol^{-1} s^{-1}$)	$10^3 k_D$	k_H/k_D	$10^3 k_H$ ($dm^3 mol^{-1} s^{-1}$)	$10^3 k_D$	k_H/k_D	$10^3 k_H$ ($dm^3 mol^{-1} s^{-1}$)	$10^3 k_D$	k_H/k_D
20							276 ± 13	153 ± 7	1.81 ± 0.12
25	1.46 ± 0.06	1.46 ± 0.10	1.00 ± 0.08	4.35*	3.23*	1.35*	486 ± 28	304 ± 2	1.60 ± 0.09
30	2.08 ± 0.01	1.86 ± 0.08	1.12 ± 0.05				725 ± 48	449 ± 7	1.61 ± 0.10
35	2.47 ± 0.12	2.27 ± 0.06	1.09 ± 0.06	7.01 ± 1.03	5.57 ± 0.21	1.26 ± 0.19	914 ± 28	571 ± 11	1.60 ± 0.06
40	3.42 ± 0.16	2.98 ± 0.08	1.15 ± 0.06	10.22 ± 1.05	8.09 ± 0.77	1.26 ± 0.17	1 189 ± 97	784 ± 25	1.52 ± 0.13
45	3.90 ± 0.16	3.32 ± 0.14	1.18 ± 0.10	12.74 ± 2.12	10.18 ± 0.42	1.25 ± 0.21			
50	4.67 ± 0.15	4.24 ± 0.29	1.10 ± 0.08	14.48 ± 1.30	11.08 ± 1.35	1.31 ± 0.19			
55				19.69 ± 2.63	17.60 ± 2.83	1.12 ± 0.23			

* Data obtained from extrapolation of the kinetic results.



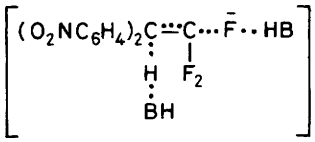
where $k_1 << k_{-1}$

Scheme 2.



(**1a**)

clidine form very stable complexes with the substrate (**1**) [of the type (**1a**)], which are negligibly dissociated, but internal return of the protium takes place in a fast process. With an excess of quinuclidine in the latter reaction mixture, the equilibrium of Scheme 2 is valid. Addition of DCl to this system changes the equilibrium position: the quinuclidine reacts with DCl, pushing the reaction to the left with complete reconstitution of the original substrate (**1**) by the internal return process. This also proves our assumption that the complex (**1a**) is negligibly dissociated. On the other hand addition of the tertiary amine to a reaction system containing primary or secondary amines accelerates the reaction of the latter with the substrate (**1**) when [HB] ≃ [quinuclidine] = 10[(**1**)]. At first sight this seems to be a result of additional formation of the ion-pair intermediate (**1a**), which can react in a consecutive step with the primary or secondary amine, abstracting the fluorine atom by formation of a hydrogen bond, giving (**1c**).[17]



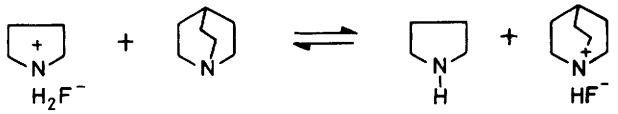
(**1c**)

In order to explain the role of tertiary amines as catalysts we performed another exchange experiment in which 1.6 mmol of deuteriated substrate [^{2}H]-(**1**) and 0.7 mmol of both pyrrolidine and quinuclidine were mixed. The experiment shows a 10% increase in the exchange of deuterium by protium. The only self-consistent explanation of both the acceleration and the larger exchange is that the additional amount of strong quinuclidine base removes HF molecules in the second and third steps of the reaction (Scheme 1). Hence the presence of the quinuclidine in the reaction mixture restores the pyrrolidine or piperidine according to Scheme 3. Therefore we have in the reaction mixture an additional amount of piperidine or pyrrolidine which is normally combined with HF.

In the light of these facts it becomes evident that the tertiary amines with no hydrogen on the sp^2-hybridized nitrogen atom are not able to react according to the $(E1cB)_{ip}$ mechanism in which the substrate (**1**) gives the ion-pair complex (**1a**). In fact during the possible collapse of the ion pair (**1a**) to the final

Table 3. Activation parameters for the reactions of 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) with piperidine (B^1) and pyrrolidine (B^2) bases in benzonitrile (PhCN), acetonitrile (MeCN), and dimethyl sulphoxide (Me_2SO)

		PhCN (ε 24)		MeCN (ε 37)		Me_2SO (ε 42)	
		B^1	B^2	B^1	B^2	B^1	B^2
$\Delta H^{\ddagger}$ / kJ mol^{-1}	^1H	34.3 ± 2.5	52.3 ± 3.6	38.1 ± 2.1	37.7 ± 2.1	51.9 ± 5.4	48.5 ± 2.5
	^2H	33.5 ± 2.1	50.2 ± 4.2	41.4 ± 2.9	36.4 ± 2.9	57.3 ± 6.7	44.8 ± 3.8
$\Delta H^{\ddagger}(^2H) - \Delta H^{\ddagger}(^1H)$		−0.8 ± 3.3	−2.1 ± 5.4	3.3 ± 3.8	−1.3 ± 3.8	5.4 ± 8.8	−3.8 ± 4.6
$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	^1H	−183.7 ± 7.5	−116.3 ± 11.3	−162.3 ± 6.3	−154.0 ± 6.7	−77.4 ± 18.0	−79.1 ± 8.8
	^2H	−187.0 ± 7.1	−123.8 ± 13.0	−154.0 ± 9.6	−159.4 ± 9.2	−64.0 ± 22.6	−94.6 ± 8.8
$\Delta S^{\ddagger}(^2H) - \Delta S^{\ddagger}(^1H)$		−3.4 ± 10.5	−7.5 ± 17.2	+8.4 ± 11.3	5.4 ± 11.3	13.4 ± 28.9	−15.5 ± 12.6
$\Delta G^{\ddagger}$ / kJ mol^{-1}	^1H	89.1 ± 3.3	87.0 ± 5.0	86.6 ± 2.9	83.7 ± 2.9	74.9 ± 7.5	72.0 ± 3.8
	^2H	89.3 ± 2.9	87.0 ± 5.4	87.2 ± 4.2	83.7 ± 4.0	76.1 ± 9.6	72.8 ± 4.6



Scheme 3.

products, attraction between the positive pole and the incipient negative charge of the leaving fluoride ion could take place causing the removal of an HF fragment as already suggested.[10] The fact that the tertiary amines are totally inert to the substrate (**1**) and the results of the exchange experiments excluded this possibility.

The primary and secondary amines can react with the substrate (**1**) *via* the ion-pair complex (**1b**) as an intermediate, and the abstraction of $B^+H_2F^-$ within the ion pair occurs as the rate-determining step (Scheme 1). A similar mechanism involving electrophilic assistance by potassium ion within the ion pair was suggested for the $(E1cB)_{ip}$ eliminations of HF from 1,1,1-trifluoro-2-phenylpentane[18] and of methanol from 1-methoxyacetophenone.[19]

The involvement of ion pairs in the pre-equilibrium *E*1cB mechanism was suggested by Miller[16] to account for the low values (near unity) of isotope effects and exchange. For all our reactions k_H/k_D fell between 1.0 and 1.6, confirming a fast pre-equilibrium of the ammonium NH protons with the β-^2H of [^2H]-(**1**) before appreciable elimination takes place. This is also supported by the large 80% exchange of deuterium by protium in the exchange experiment.

The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, collected in Table 3, fit the suggested mechanism (Scheme 1), showing large negative entropies of activation. The most negative $\Delta S^{\ddagger}$ value (−183.7 J mol^{-1} K^{-1}) is found for the reaction carried out in the least polar solvent, PhCN. The negative and relatively large $\Delta S^{\ddagger}$ values are compatible with considerable change in the charges between the ground and the transition states. This is consistent with earlier observations[20,21] and similar to the $(E1cB)_{ip}$ or ion-assisted elimination mechanisms of HCN where the appropriate $\Delta S^{\ddagger}$ values are −55 and −125 J mol^{-1} K^{-1} respectively. Generally the $\Delta S^{\ddagger}$ values are more negative for the bimolecular process where BH_2^+ participates in the transition state.

The largest enthalpy of activation, $\Delta H^{\ddagger}$ = 51.9 kJ mol^{-1}, is found for the reaction of the substrate (**1**) with piperidine in the most polar solvent Me_2SO. This value matches that (52.7 kJ mol^{-1}) found for HCN elimination[21] in chloroform and is smaller than the 84 kJ mol^{-1} found for $(E1cB)_{ip}$ elimination of HCN in acetonitrile. The enthalpies of activation (Table 3) are not very different for pyrrolidine and for piperidine bases; they fall in the range of 34—52 kJ mol^{-1}, indicating a similar reaction mechanism. For HF elimination promoted by alkoxide bases there was a much wider range (27—82 kJ mol^{-1}), reflecting the change of mechanism from $(E1cB)_I$ to $(E1cB)_R$.[2] The higher value of $\Delta H^{\ddagger}$ for the secondary amines is characteristic of proton-abstraction reactions.[2,22] The enthalpy value of *ca.* 40 kJ mol^{-1} found for the present reaction is reasonable for C–F bond cleavage from the ion pair intermediate (**1b**).

The activation parameters, as well as the small kinetic isotope effects (k_H/k_D) and the extensive exchange of deuterium by protium, and also the lack of reactivity of tertiary amines, support the proposed Scheme 1 for the reaction, suggesting that the rate-determining step is the abstraction of the heavy leaving fluoride anion with the formation of the olefin (**2**), which is converted in a fast step into the final enamines (**3**) and (**4**).

In the fast step (k_3) there is a certain amount of base catalysis in the reaction pathway. However the high concentrations of the amines used to produce pseudo-first-order conditions prevented any observation of catalysis.

Experimental

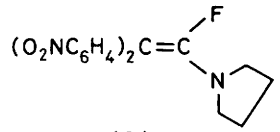
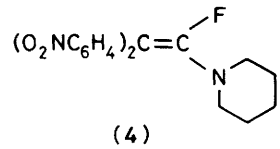
Materials.—1,1,1-Trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) and its deuteriated analogue [^2H]-(**1**) were prepared by reduction of α,α,α-trifluoroacetophenone (Aldrich; b.p. 165—166 °C) in dry ether by $LiAlH_4$ or $LiAlD_4$; after normal work-up the alcohol obtained was dissolved in a four-fold molar excess of benzene and cooled to 0 °C. Then 2% oleum was added dropwise with vigorous stirring and finally the product 1,1,1-trifluoro-2,2-diphenylethane was isolated. Nitration of the phenyl groups was accomplished according to the method of Skerret[23] by means of fuming nitric acid at −30 °C. The crude 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) was recrystallized from methanol to yield light yellow crystals, m.p. 117 °C.

The olefin 1,1-difluoro-2,2-bis-(4-nitrophenyl)ethene (**2**) was isolated from the reaction of the substrate (**1**) with a three-molar excess of Pr^iO^- in Pr^iOH. The products of the reaction were purified by t.l.c. [aluminium sheets covered with silica (Silica-gel 60 F 254; Merck); benzene as eluant]. Mass spectra and $\lambda_{max.}$ have been reported.[2]

Piperidine and pyrrolidine (Merck) were dried over potassium hydroxide pellets, filtered off, and distilled fractionally in an apparatus flushed with dry, CO_2-free nitrogen. The b.p.s were 106 and 88 °C, respectively. Only the middle fraction was collected and used.

Reagent grade acetonitrile (Aldrich) was purified by the method of O'Donnell *et al.*[24] with a final fractional distillation over P_2O_5. Reagent grade benzonitrile (Aldrich) was purified by the method of Coetzee *et al.*[25] by drying with CaH_2 followed by fractional distillation at reduced pressure over a small amount of P_2O_5. Reagent grade dimethyl sulphoxide (Merck) was

Table 4. Mass spectral and n.m.r. data for the products of the reaction of 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) with pyrrolidine, piperidine, propylamine, and butylamine

Product	*m/z* (rel. intensity)	δ_H (60 MHz: solvent $CDCl_3$; standard Me_4Si)
 (**3**)	358 (22.0%), 357 (100.0, M^+), 311 (6.0), 265 (5.9), 222 (6.0), 195 (6.9), 100 (9.8), 98 (10.6), 84 (11.0), 71 (5.8), 70 (12.3), 55 (17.2), 44 (13.0), 43 (17.7), 42 (13.4), 41 (17.1), 28 (11.2)	1.8 (4 H, q, CH_2) 3.1 (4 H, t, NCH_2) 7.0—8.3 (8 H, m, Ar)
 (**4**)	372 (23.1), 371 (100.0, M^+), 370 (11.7), 324 (5.2), 235 (15.6), 234 (11.7), 222 (6.8), 205 (5.7), 190 (5.1), 189 (5.5), 183 (7.4), 182 (7.1), 112 (24.6), 83 (19.5), 69 (16.2), 55 (9.8), 41 (37.5)	1.6 (6 H, q, CH_2) 2.8 (4 H, t, NCH_2) 7.1—8.3 (8 H, m, Ar)
$(O_2NC_6H_4)_2C{=}C(NH[CH_2]_2CH_3)_2$ (**5**)	385 (0.4), 384 (5.2, M^+), 128 (5.7), 99 (10.9), 92 (5.9), 85 (8.4), 71 (6.3), 70 (9.3), 58 (28.5), 44 (27.1), 43 (10.2), 30 (100.0)	0.9, 1.5, 3.2 } 14 H { (t, CH_3); (m, CH_2CH_3); (t, NCH_2) 7.3—8.3 (8 H, m, Ar)
$(O_2NC_6H_4)_2C{=}C(NH[CH_2]_3CH_3)_2$ (**6**)	413 (15.6), 412 (45.6, M^+), 383 (17.8), 370 (10.0), 257 (26.4), 211 (10.0), 193 (16.6), 165 (30.3), 164 (18.6), 163 (27.2), 155 (70.5), 136 (11.5), 99 (88.7), 72 (17.6), 57 (79.1), 44 (91.9), 30 (55.0), 29 (100.0)	0.9, 1.5, 3.2 } 18 H { (t, CH_3); (m, CH_2CH_3); (t, NCH_2) 7.3—8.3 (8 H, m, Ar)
$(O_2NC_6H_4)_2C{=}O$ (**7**)	272 (24.1, M^+), 150 (100.0), 104 (27.6), 76 (25.9)	7.2—8.5 (8 H, m, Ar)

purified by fractional distillation at reduced pressure over a small amount of CaH_2. The middle fraction was collected.

Product Analysis.—2,2-Bis-(4-nitrophenyl)-1-fluoroenamines (**3**)—(**6**) were obtained by treating 1,1,1-trifluoro-2,2-bis-(4-nitrophenyl)ethane (**1**) (30 mg) dissolved in acetonitrile with a ten-fold molar excess of the appropriate amine (pyrrolidine, piperidine, propylamine, or butylamine). There was also a trace of the diaryl ketone (**7**). The reaction mixture was kept overnight at room temperature under nitrogen. Then the solvent and the excess of amine were evaporated off under reduced pressure. The dry residue was subsequently recrystallized from methanol, and separated by preparative t.l.c. [Silica gel 60 F 254 (Merck); solvent benzene]. The mass and n.m.r. spectra were measured with JEOL-D-100 and Varian-60 spectrometers and are collected in Table 4.

Kinetic Measurements.—The initial concentrations of the reacting bases were 1.50×10^{-1} to 3.00×10^{-1}M, 3.5×10^{-2} to 1.16×10^{-1}M, and 0.5×10^{-2} to 3.5×10^{-2}M for the reactions with pyrrolidine in PhCN, MeCN, and MeSO, respectively, and 2.31×10^{-1} to 9.50×10^{-1}M, 4.10 to 9.0×10^{-2}M, and 4.0×10^{-3} to 2.80×10^{-2}M for the reactions with piperidine in PhCN, MeCN, and Me_2SO, respectively. The concentration of the substrate (**1**) was *ca.* 1×10^{-4}M.

The kinetic measurements for the normal (**1**) and the deuteriated substrate [^{2}H]-(**1**) were made with Specord u.v.–visible and stopped-flow spectrophotometers fitted with a constant-temperature bath to control the temperature of the cell block within ± 0.1 °C. The pseudo-first-order rate constants were calculated using the Guggenheim method.

The second-order rate constants were calculated from the plots of the first-order rate constants *vs.* base concentration by the method of least-squares. The activation parameters were evaluated from these by means of a least-squares fit to the transition-state theory equation.

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