The Mechanism of the Stevens Rearrangement: a Quantitative CIDNP Study

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Summary Quantitative CIDNP measurements have been made on the Stevens rearrangements of the ylides (**1a**—**e**); the experimental enhancement factors (V_{exp}) are 25% or less than would be expected for a reaction proceeding only by a free radical pathway.

The observation of CIDNP signals during the course of the Stevens rearrangement led to the postulate of a radical pair mechanism for the reaction.[1] However, it is conceivable that the rearrangement actually proceeds by a dual mechanism with only a fraction of the reaction giving radical pairs. We report the results of a quantitative CIDNP study designed to test this possibility.[2]

Table

Average experimental (V_{exp}) and calculated (V_{theo}) enhancement factors for the CIDNP spectra (90 MHz) for the rearrangement (**1a**) → (**2a**).

	H_X[a]	H_A, H_B[a]	NMe_2
V_{exp}	58	− 91[b]	− 31
V_{theo}	245	−357	−121
V_{exp}/V_{theo} ..	0·24	0·25	0·26

[a] Signals of ABX system [$-CO-CH_X(NMe_2)-CH_AH_B-Ph$]. [b] Enhancement factor obtained by averaging all eight transitions of the diastereotopic protons (H_A, H_B).

The crystalline ylides (**1a**—**e**)[3] were dissolved in $CDCl_3$ (0·1 M) at 0°. The solutions were then transferred to a preheated (59°) n.m.r. spectrometer probe and 90° pulse spectra were determined at 5 second intervals. Each free induction decay (F.I.D.) was stored on a disk immediately after the F.I.D. had been accumulated. The spectra were processed after completion of the run and a typical run is shown in the Figure. The first-order rate constant, *k*, at each instant of the 90° pulse was evaluated by monitoring the integrated intensities of the starting material transitions correcting for incomplete relaxation between pulses. After the reaction had come to completion pseudo-T_1 values for each transition in the rearrangement products (**2a**—**e**) were determined *via* the standard 180–*t*–90° pulse experiments.† Experimental enhancement factors (V_{exp}) for the transitions originating from the indicated protons (see Table) were then calculated[4]‡ from the reaction rate constants, pseudo-T_1 values,† the pulse repetition rate, τ, and the intensities of the CIDNP spectra of the products (**2**) measured at the times of the various pulses and after the rearrangements (**1** → **2**) were complete.§

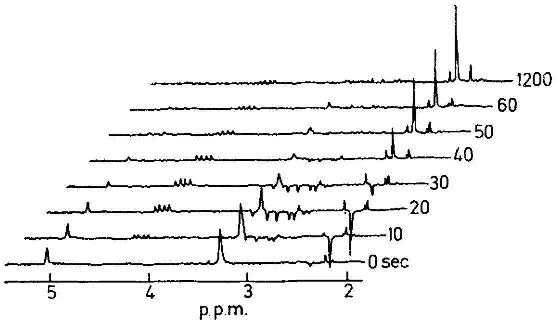
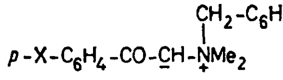
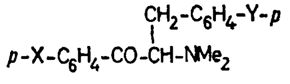


Figure. Single pulse Fourier transform spectra at 90 MHz during the thermal transformation of the ylide (**1a**) in $CDCl_3$ as a function of time. The singlets (δ 5·02, 3H) and (δ 3·28, 6H) are assignable to the ylide (**1a**: $-CO-\overset{-}{CH}-\overset{+}{N}Me_2-CH_2Ph$) and the multiplets centred at (δ 4·4 and 3·2) to the ABX system and the NMe_2 group (δ 2·38) of the product (**2a**).



$$p\text{-}X\text{-}C_6H_4\text{-}CO\text{-}\underset{-}{C}H\text{-}\overset{\displaystyle CH_2\text{-}C_6H_4\text{-}Y\text{-}p}{\underset{+}{N}}Me_2$$

(1)



$$p\text{-}X\text{-}C_6H_4\text{-}CO\text{-}\overset{\displaystyle CH_2\text{-}C_6H_4\text{-}Y\text{-}p}{C}H\text{-}NMe_2$$

(2)

	X	Y
a	H	H
b	H	Br
c	H	OMe
d	Br	H
e	NO_2	H

$Ph\text{-}CO\text{-}\dot{C}H\text{-}NMe_2$

(3)

The enhancement factors (V_{exp}) thus determined should be compared (Table) with those calculated (V_{theo}) from the radical pair theory assuming freely diffusing radical pairs. The magnetic parameters of the dimethylaminophenacyl radical (**3**) ($g = 2{\cdot}0039$; $a_{C-H} = -12$ G; $a_{NMe_2} = 6$ G)¶ were obtained by adjusting these parameters until a reasonably good fit was obtained for the relative intensities of the CIDNP obtained during rearrangements (**1a** → **2a**) and (**1b** → **2b**) using the known parameters for benzyl and *p*-bromobenzyl radicals.[5] The diffusion parameter, *m*,[6] was adjusted to $1{\cdot}25 \times 10^{-6}$, a value which gives good results for *bona fide* free radical reactions[7] such as the decomposition of α-phenylazotoluene in the presence of free radical scavenger.[8] Using these parameters and estimating the degree of random pairing from the yield of bibenzyl (5%) theoretical enhancement factors (V_{theo}) were calculated for the radical pair mechanism of the rearrangements (**1** → **2**, **a**—**e**) and are listed in the Table.

A comparison of the experimental (V_{exp}) with the theoretical (V_{theo}) enhancement factors shows that the experimental values for (**2a**) are smaller (*ca.* 25%) than expected by theory for an exclusive (100%) free radical process. Similar ratios (V_{exp}/V_{theo}) were obtained for (**2b**), 0·13; (**2c**), 0·20; (**2d**), 0·16; and (**2e**), 0·10. The error

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† In principle, the relaxation behaviour of spin coupled multiplets cannot be described by a single T_1. In practice the deviation from exponential decay was found to be within experimental error of the measurement and the time constant of this experimentally determined relaxation rate. This is here referred to as a pseudo-T_1.

‡ Extracting enhancement factors from pulse Fourier transform spectra is considerably more complicated than from continuous wave spectra. A description of the mathematical derivation is lengthy and will be published elsewhere.

§ It can be shown that averages of the individual transitions within a spin–spin splitting multiplet are less affected by the simplifications of treating relaxation with a pseudo-T_1 than are the individual transitions.

¶ An INDO calculation gave the values −9·5 and 3 G, respectively.

limits of these ratios are hard to estimate because of the substantial simplification inherent in the model. However, we believe that the uncertainty *in these ratios* (V_{exp}/V_{theo}) are $< 50\%$ and that their absolute and relative values are certainly meaningful.

It is possible to equate the ratio (V_{exp}/V_{theo}) with the *fraction of the reaction proceeding by a radical pair mechanism*, implying a dual mechanism with the major pathway being presumably a concerted reaction. Recent theoretical studies lend support to this view.[9,10]

Alternatively, it is possible that the major fraction of the radical pairs ($>80\%$) combine without separation on a time scale too short for evolution of the spin wavefunction. Complementary experimental evidence on loss of optical activity of the migrating group suggests that the lifetime of the major fraction of the pairs would have to be short even relative to rotational correlation times.[11] The distinction between a concerted pathway and the interaction *of radical pairs which do not separate or even rotate* is difficult.

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