Mechanistic Implications of Nuclear Polarization in the Stevens Rearrangement of *NN*-Dimethyl *p*-Nitrobenzylamine Acetimide

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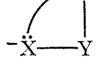
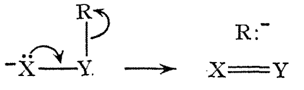
Summary The observation of dynamic nuclear polarisation in the product of a thermal Stevens rearrangement of the title compound leads to the proposal of a homolytic cleavage–recombination pathway.

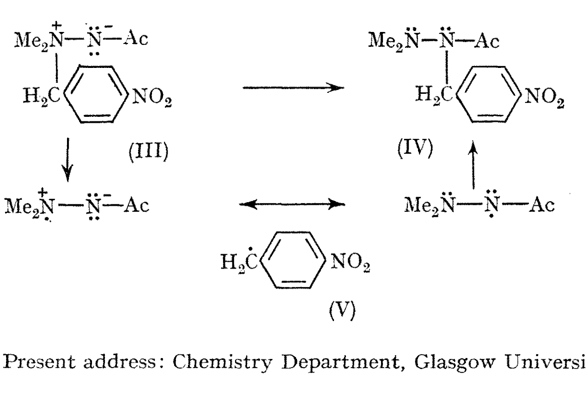
Two main processes have been recognised for 1,2-electrophilic rearrangements, a concerted[1] S_Ni reaction (I) and a non-concerted[2] pathway (II), which is considered to proceed *via* an ion-pair intermediate. In the 1,2-rearrangement of quaternary ammonium ylides (Stevens rearrangement), considerations of orbital symmetry[3] require that in a concerted process inversion of configuration occurs at the migrating centre. Experimentally the rearrangement has been found to proceed intramolecularly[1,2b,2e,4] and with almost complete retention.[1a,1b,2b,4a] and accordingly a tight ion pair in which the migrating group retains chirality has been suggested as an intermediate.



(I)



(II)



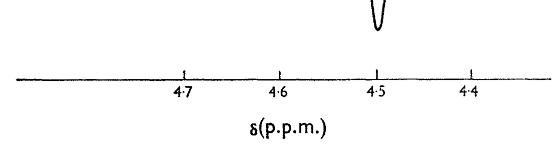


FIGURE. *CIDNP effect observed for the benzylic protons in the rearrangement* (III) → (IV) 100 *sec. after insertion of the sample into probe. The effect was still visible after* 3 *min.*

When *NN*-dimethyl *p*-nitrobenzylamine acetimide (III),[5] m.p. 175—177°, is heated at 180° a 1,2-migration of the *p*-nitrobenzyl group occurs with formation of 1-acetyl-1-*p*-nitrobenzyl-2,2-dimethylhydrazine (IV). We have examined this reaction by n.m.r. at 180° in $[^2\text{H}_5]$-nitrobenzene (100 MHz) when reaction is complete in 10 min. Examination of the benzylic proton region 4·50 p.p.m. downfield from hexamethyldisiloxan revealed a pronounced chemically induced dynamic nuclear polarization[6] (CIDNP) effect (see Figure). The benzylic protons were considered most likely

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to show CIDNP effects since the benzylic carbon is involved in rebonding leading to product formation. The CIDNP effect arises from nuclear spin states of free radicals being populated by relaxations due to magnetic electron–nuclear interactions and the corresponding n.m.r. transitions then show emission or enhanced absorption.

The observation of this effect requires the intervention of a paramagnetic precursor prior to product formation. Hence it is suggested that the *p*-nitrobenzyl group migrates as a *p*-nitrobenzyl radical during this, 1,2-rearrangement which proceeds by a homolytic cleavage–recombination pathway (III) → (V) → (IV). The mechanism of this Stevens rearrangement is thus shown to be similar to those suggested for the Wittig rearrangement,[7] the 1,2-benzyl migration in the rearrangement of methylbenzylphenacylsulphonium ylides,[8] and the benzyne-promoted rearrangement of a methyl group in the adduct with dimethylbenzylamine.[9]

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