

## Chemical Polarisation of $^{15}\text{N}$ Nuclei in the Nitramine Rearrangement

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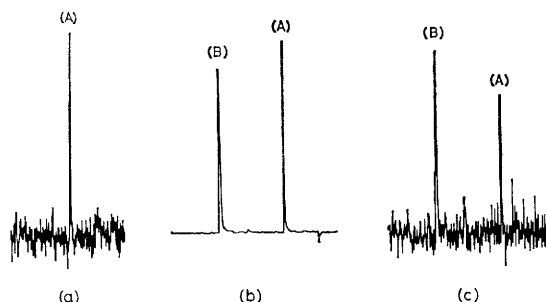
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Strongly enhanced  $^{15}\text{N}$  n.m.r. absorption signals are found for both starting material and products in the acid-catalysed nitramine rearrangements of  $^{15}\text{NO}_2$ -labelled 2,6-dibromo-*N*-nitroaniline and *N*-methyl-*N*-nitroaniline.

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Several mechanisms have been proposed for the nitramine rearrangement but, in recent years, the bulk of the work has supported the intermediate formation of cation radicals as

suggested by W. N. White and his co-workers;<sup>1</sup> however, no direct evidence for such radicals has been obtained from e.s.r. or n.m.r. spectroscopy.<sup>2</sup> Evidence for this mechanism has now



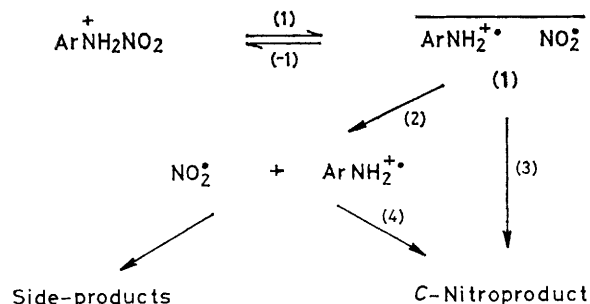
**Figure 1.** (a) The  $^{15}\text{N}$  n.m.r. spectrum of a solution of  $^{15}\text{NO}_2$ -labelled 2,6-dibromo-*N*-nitroaniline ( $0.3 \text{ mol dm}^{-3}$ ) in acetic acid ( $1 \text{ cm}^3$ ). (b) The same, taken during the first minute after the addition of  $1 \text{ cm}^3$  of a mixture of equal volumes of sulphuric acid (98%) and acetic acid. (c) The same taken 15 minutes after mixing. (A) =  $\text{N-}^{15}\text{NO}_2$  peak; (B) =  $\text{C-}^{15}\text{NO}_2$  peak. Pulse angle,  $45^\circ$ ; pulse repetition time 3 s. Spectra (a) and (c), 100 pulses; spectrum (b), 25 pulses. Temperature  $30^\circ\text{C}$ .

been obtained from  $^{15}\text{N}$  n.m.r. spectra taken during the rearrangement of  $^{15}\text{N}$ -labelled nitramines.

The spectra in Figure 1 were taken during the sulphuric-acid-catalysed rearrangement of 2,6-dibromo-*N*-nitroaniline (95%  $^{15}\text{N}$  as  $^{15}\text{NO}_2$ ) in acetic acid as solvent (for details see Figure legend). The great increase in the signal-to-noise (S/N) ratio at the start of the rearrangement is obvious from the spectra [despite the fact that spectrum (b) was taken with fewer pulses and a less concentrated solution than spectrum (a)]. There is probably still some enhancement present after 15 minutes [spectrum (c)] but comparison of the S/N ratios for the three spectra shows that the peaks for both the starting material and the product must be greatly enhanced in spectrum (b). At the end of the reaction, the  $^{15}\text{N}$  and  $^1\text{H}$  n.m.r. spectra are as expected for the 4-nitro-product in accord with earlier work<sup>3</sup> but some  $\text{H}^{15}\text{NO}_2$  and  $\text{H}^{15}\text{NO}_3$  are also present. The results with  $^{15}\text{N}$ -labelled *N*-methyl-*N*-nitroaniline under the same conditions were similar except that the product composition was much more complex.

The simplest interpretation of this enhancement of peaks (A) and (B) involves the nuclear polarisation generated by the partitioning of the radical pair (1) between dissociation [reaction (2)] and recombination at either the amino-group [reaction (-1)] or the 4-position [reaction (3)] (Scheme 1).†

† Although the polarisation provides strong evidence for the reversible formation of the radical pair (1), it is still possible in principle for the polarisation to be carried over from the starting material to the product in some other way. In view of the work of White and his co-workers (refs. 1, 2) it seems unnecessary to postulate such a dual reaction path except perhaps for those nitramine rearrangements near the homolytic-heterolytic borderline (ref. 2).



**Scheme 1**

This interpretation accords with White's mechanism for the rearrangement<sup>1</sup> and the enhancement of the absorption then follows from Kaptein's rules<sup>4</sup> as applied to  $^{15}\text{N}$  nuclei.<sup>5</sup> The appropriate *g*-values have been discussed previously.<sup>6</sup> The argument involves the reasonable assumption that the 4-nitro-product is formed mainly by the intramolecular route‡ and that some of the separated radicals become involved in side-reactions. The interpretation also implies that there is a common process giving rise to the nuclear polarisation observed in the nitramine rearrangement, nitro-group exchange reactions,<sup>6</sup> and nitrous acid catalysed nitration<sup>7</sup> for all appear to depend on partitioning of the radical pairs  $\text{ArNR}_2^+\text{NO}_2^\bullet$  between dissociation and recombination. The fact that this simple process is capable of explaining the different types of spectra observed (emission or enhanced absorption) in these processes provides further support for the correctness of the interpretation.

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‡ From Kaptein's rules, the product from the intermolecular reaction path [reaction (4)] should give an emission spectrum.