

Evidence from ^{15}N Nuclear Polarisation on the Mechanisms of Rearrangement of Nitrocyclohexadienones

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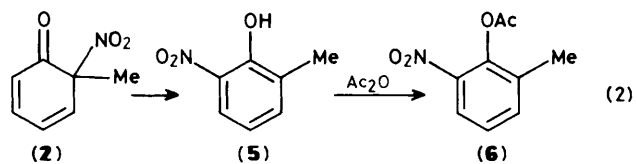
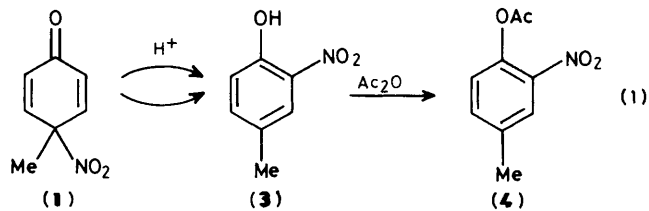
Strong ^{15}N nuclear polarisation is present in both the uncatalysed and acid-catalysed rearrangements of 4-methyl-4-nitrocyclohexa-2,5-dienone but is absent from the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone.

The 1,3-nitro group rearrangements shown in equations (1) and (2) have been discussed by a number of authors.¹⁻⁴ The early work of Barnes and Myhre¹ established that the uncatalysed rearrangement of the 4-nitro compound (1) occurred through homolytic dissociation to form the phenoxy radical and nitrogen dioxide but the mechanisms of the other reactions are less well established. The acid catalysed rearrangement of (1) has been ascribed to dissociation to form the nitronium ion^{2,3} (although there is some evidence to the contrary⁴) and the mechanisms considered for the curiously regiospecific rearrangement of the 2-nitro compound (2) [equation (2)] include homolytic dissociation,³ the formation of an aryl nitrate,³ and a 1,5-sigmatropic migration.⁵

We have investigated these rearrangements using the ^{15}N -labelled nitro compounds in acetic anhydride as solvent[†] and have looked for ^{15}N nuclear polarisation during reaction. As expected, the uncatalysed rearrangement of (1) shows such polarisation: the enhancement of the signals relative to that of the standard (S) present in similar concentration can be seen by comparing the first and third spectrum in Figure 1. The enhancement accords with Kaptein's rules.⁶ After rearrange-

ment, the product (3) becomes acetylated to form the ester (4) and this signal is seen in the third spectrum.

The addition of 6% sulphuric acid to the reaction medium increases the rate of rearrangement by a factor of 5.7 at 22 °C and so, if the acid catalysed reaction were a heterolytic process, we would expect to see a corresponding diminution in the nuclear polarisation observed. An inspection of the



[†] The 4-nitro compound (1) was prepared in the reaction medium by the nitration of *p*-methylphenyl acetate with a 45% solution of aqueous H^{15}NO_3 in acetic anhydride: the medium therefore included acetic acid formed from the water present.

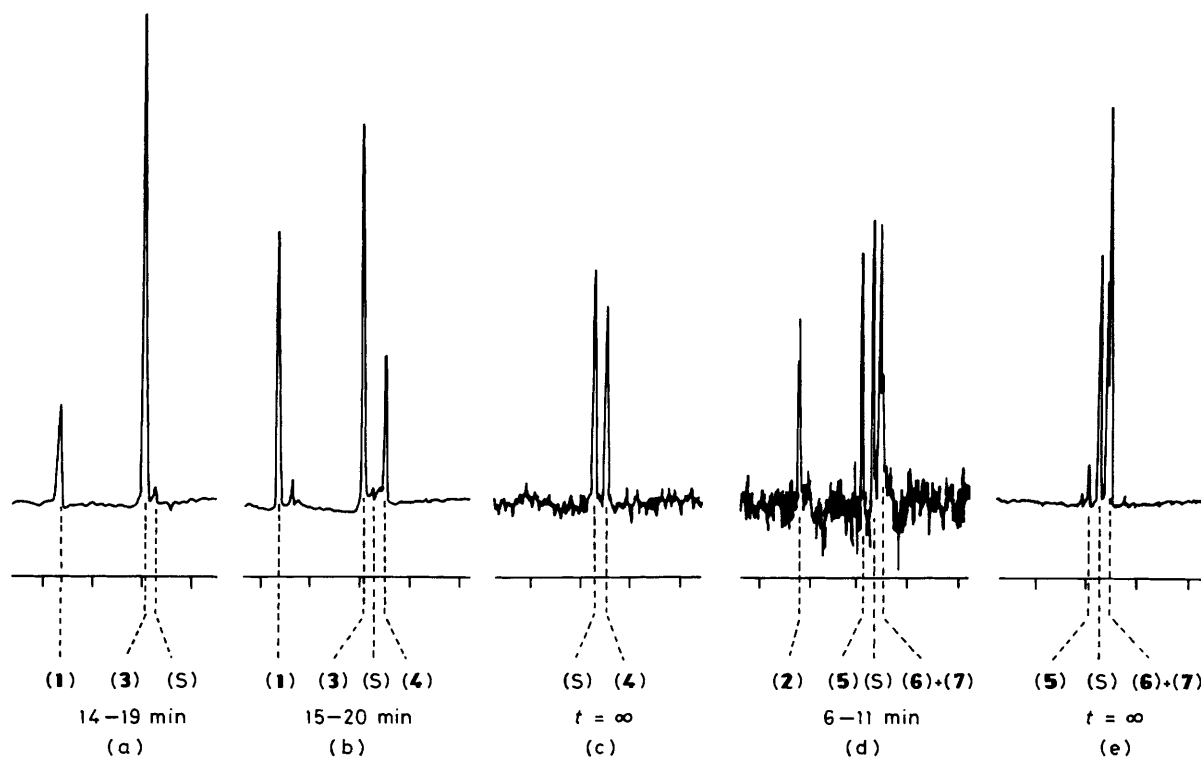


Figure 1. ^{15}N N.m.r. spectra taken at about one half-life during the rearrangement of compounds (1) and (2) in the presence of a standard (S, $\text{C}_6\text{H}_5^{15}\text{NO}_2$): (a), the uncatalysed rearrangement of (1) at 34°C ; (b), the acid catalysed rearrangement of (1) at 23.1°C ; (d), the uncatalysed rearrangement of (2) at -11°C ; (c), (e), the corresponding spectra at $t = \infty$ (see text). The numbers below the spectra indicate the corresponding structures. The nitrocyclohexadienone concentration was 1 mol dm^{-3} (a), (b), or 0.55 mol dm^{-3} (d); in the acid catalysed run, sulphuric acid (6%) was also present. The spectra involved 24 pulses [(e), 3878 pulses], pulse angle 45° , pulse repetition time 10.8 s. The scale divisions are 10 p.p.m., high field on r.h.s.

spectra (b) and (c) in Figure 1 shows that this is not found and a more detailed analysis indicates that the enhancement of the signals is somewhat greater in the acid catalysed run. Some of the ester (4) is then formed during the rearrangement but the final spectrum is essentially the same as that of the uncatalysed run and so only one is shown (c). The acid-catalysed run was carried out at a lower temperature (Figure 1) to make the half-lives of both reactions about 10 minutes.

In contrast, the comparison of peak heights for the standard and the other compounds in spectra (d) and (e) shows that no marked ^{15}N nuclear polarisation is present in the rearrangement of the 2-nitrocompound (2);[‡] a more detailed analysis of the whole run shows that any enhancement of the signals is no more than could arise from experimental error. As before, the infinity spectrum (e) shows that most of the phenol (5) has been converted into the corresponding acetate (6).

The results for the uncatalysed and acid catalysed rearrangements of (1) indicate that both reactions involve a radical pair and the fact that the signals for both the substrate and the product show enhancement indicates that this radical pair is partitioned between dissociation, reaction at the 2-position, and return to the 4-position. The absence of polarisation in the rearrangement of (2) and the known regioselectivity of the reaction⁵ show clearly that a radical pair with that property

cannot be involved in that reaction. At -11°C , the rate of rearrangement of (2) is faster than that of (1) by a factor of *ca.* 1000; the mechanistic change appears therefore to come from the availability of an additional reaction path, rather than from any hindrance to the radical reaction. The details of the additional reaction path are not clear, but it seems probable that considerable charge transfer is involved in the transition state for the introduction of a *p*-methyl group into (2) and this increases the rate of rearrangement by a factor[§] of *ca.* 50 at -35°C .

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References

- 1 C. E. Barnes and P. C. Myhre, *J. Am. Chem. Soc.*, 1978, **100**, 973.
- 2 C. Bloomfield, A. K. Manglik, R. B. Moodie, K. Schofield, and G. D. Tobin, *J. Chem. Soc., Perkin Trans. 2*, 1983, 75.
- 3 R. G. Coombes, J. G. Golding, and P. Hadjigeorgiou, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1451.
- 4 P. C. Myhre, Report 1985, ARO-17572.1-CH-H; *cf. Gov. Rep. Announce Index (U.S.)* 1985, 85(24), Abstr. No. 555-257.
- 5 G. G. Cross, A. Fischer, G. N. Henderson, and T. A. Smyth, *Can. J. Chem.*, 1984, **62**, 1446.
- 6 R. Kaptein, *Chem. Commun.*, 1971, 732.

[‡] Prepared in the reaction medium by the nitration of 2-methylphenyl acetate with 100% H^{15}NO_3 ; a little of (6) and some 2-methyl-4-nitrophenyl acetate (7) was formed at the same time.

[§] This factor comes from our preliminary kinetic studies; it accords with the qualitative observations reported previously.⁵