^{15}N Nuclear Polarisation in Nitration and Related Reactions. Part 7.[1] The Mechanisms of Rearrangement of 4-Methyl-4-nitrocyclohexa-2,5-dienones

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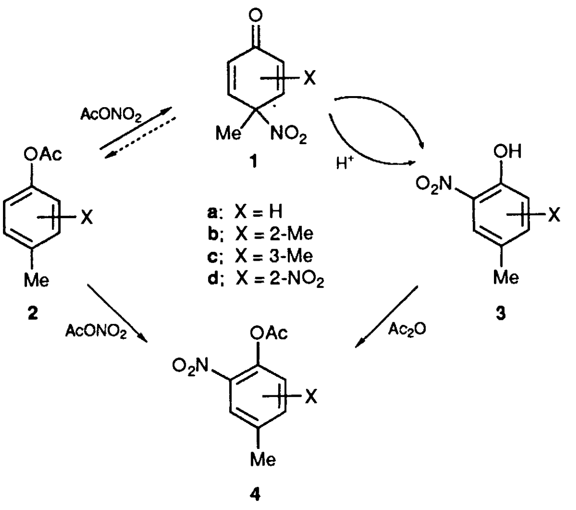
The rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone to 4-methyl-2-nitrophenol has been studied in acetic anhydride at 22–37.5 °C in the presence of varying concentrations of sulfuric acid. Similar studies have been carried out on the ^{15}N labelled compound and on the effects of some substituents (2-Me, 3-Me, 2-NO_2). During reaction, the thermal rearrangement of the labelled compound gives very strongly enhanced ^{15}N NMR absorption signals (enhancement coefficient *ca.* 1000) for both the substrate and the product. For the acid catalysed reaction, the enhancement coefficient of the signals is less (*ca.* 130) but still sufficient to indicate a homolytic reaction path. This interpretation is shown to be consistent with the properties of the radicals involved and with the substituent effects observed.

This work is concerned with the thermal and acid-catalysed rearrangements of the nitrocyclohexadienones **1** (Scheme 1).



Scheme 1

The reactions have been carried out in acetic anhydride as solvent and Scheme 1 includes the subsequent acetylation of the rearranged products **3**.

The work of Barnes and Myhre[2] established that the thermal rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone (**1a**) occurs through the homolytic fission of the C–N bond to form an aryloxy radical and nitrogen dioxide, but the mechanism of the corresponding acid catalysed reaction has not been clearly established. The acidity dependence of the reactions of **1a** and **1** (X = 2-Cl) in aqueous sulfuric acid is consistent with the rearrangement of the conjugate acids of these dienones and the reaction has sometimes been considered to involve the heterolytic fission of the C–N bond in these conjugate acids to form a nitronium ion and the corresponding phenol molecule.[3,4] However, there is also evidence that the acid catalysed decomposition of 2,4,6-trimethyl-4-nitrocyclohexa-2,5-dienone occurs through the homolytic fission of this bond.[5]

The present paper is concerned mainly with the evidence available from ^{15}N nuclear polarisation in the 4-methyl-4-nitrocyclohexa-2,5-dienone rearrangement but the interpretation of the results has required a number of ancillary kinetic studies and some substituent effects have also been determined. The reactions have been followed by ^1H NMR spectroscopy and the experimental technique has involved the formation of the nitrocyclohexa-2,5-dienones in acetic anhydride by nitration of the corresponding aryl acetates followed by the study of the rearrangement reaction in the same solvent. The nitration of 4-methylphenyl acetates under these conditions is known to give good yields of the nitrocyclohexadienone intermediates.[1-6] A preliminary account of the present work has already appeared.[7]

Results

Products.—Under our conditions (see Experimental Section), the nitration of 4-methylphenyl acetate (**2**; X = H) with an equimolar concentration of acetyl nitrate in acetic anhydride occurs rapidly to yield *ca.* 70% of 4-methyl-4-nitrocyclohexa-2,5-dienone and *ca.* 20% of 4-methyl-2-nitrophenyl acetate. The remaining material consists of some unreacted starting material and 2–3% of 2,6-dinitro-4-methylphenol. This product composition refers to the reaction mixture at about 2–3 min after mixing and is based on the integration of the signals in the aromatic region of the ^1H NMR spectrum. The nitrocyclohexadienone then undergoes a further reaction to yield mainly 4-methyl-2-nitrophenol but with a significant back reaction to give more 4-methylphenyl acetate so that the percentage of this species increases from *ca.* 8% to more than 20% during the rearrangement stage. These reactions are shown in Scheme 1 and the ^1H chemical shifts used to identify the species are listed in Table 1. Examples of the NMR spectra in the initial and final stages of the rearrangement are given in Fig. 1.

Kinetics.—The rearrangement reaction has been followed in the same solution as that used to prepare the cyclohexadienones. This is possible because, in the presence of sulfuric acid concentrations $\geq 0.2\%$, the initial nitration is very fast and is complete before the first NMR spectrum can be measured. The initial nitration was carried out at 0 °C and the temperature was then raised to that required for the study of the rearrangement.

The extent of rearrangement has been followed from the

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Table 1 Assignment of the ^1H chemical shifts for the aromatic hydrogen atoms in the nitration of the aryl acetates **2** (Scheme 1) (d = doublet; s = singlet)

	$\delta_H(Ac_2O)$			
Compound	H-2	H-3	H-5	H-6
1a	6.37(d)[a]	7.2(d)[a]	7.2(d)[a]	6.37(d)[a]
2a	7.21(d)	7.01(d)	7.01(d)	7.21(d)
3a	—	7.89(s)[a]	7.45(d)[a]	7.05(d)[a]
4a	—	7.89(s)	7.53(d)	7.19(d)

[a] Ref. 1.

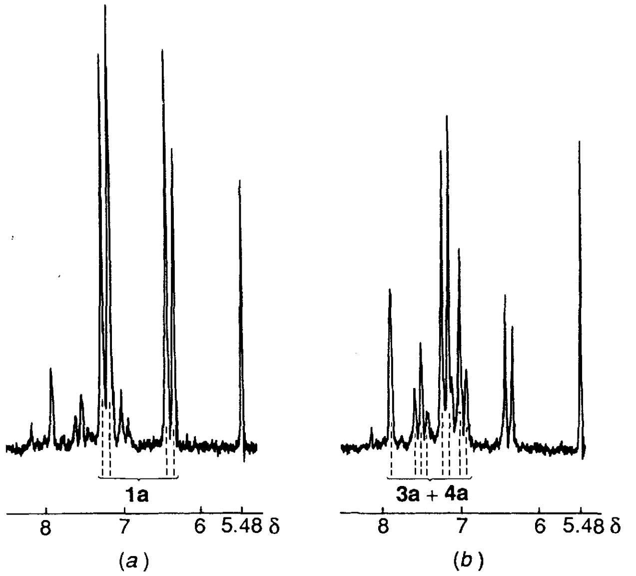


Fig. 1 ^1H NMR spectra taken during the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone (*ca.* 0.7 mol dm^{-3}) in acetic anhydride at 22 °C. The solution contained 0.2% sulfuric acid. Times: (*a*) 8.5 min; (*b*) 146 min. The signals corresponding to the substrate **1a** and the major products **3a**, **4a** are identified. The signal at δ 5.48 is that of the standard (CH_2Cl_2).

Table 2 The variation of the first-order rate coefficient (k_{obs}) for the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone (*ca.* 0.7 mol dm^{-3}) in acetic anhydride with acidity and with temperature

$[H_2SO_4](\%)$	$T/°C$	$k_{obs}/10^{-4}\ s^{-1}$
0.2	22	1.34
0.2	30	3.88
0.2	34	6.69
0.2	36	8.60
0.7	22	2.17
1.1	22	2.70
1.5	22	3.51
2.0	22	4.40
2.5	22	5.52
3.0	22	7.61
3.5	22	9.54
4.0	20	7.74
4.0	22	10.74

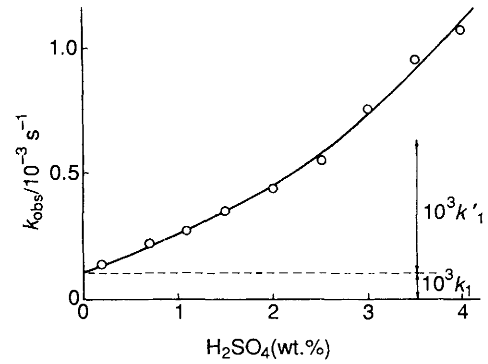


Fig. 2 The variation of the first order rate coefficient (k_{obs}) with the concentration of sulfuric acid for the rearrangement at 22 °C of 4-methyl-4-nitrocyclohexa-2,5-dienone (*ca.* 0.7 mol dm^{-3}) in acetic anhydride containing sulfuric acid (0.2%)

Table 3 Substituent effects on the first-order rate coefficient (k_{obs}) for the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone (*ca.* 0.7 mol dm^{-3}) in acetic anhydride

Substituent	$[H_2SO_4](\%)$	$T/°C$	$k_{obs}/10^{-4}\ s^{-1}$	Relative rate[a]
2-Me	0.2	30	5.25	1.35
2-Me	4.0	20	8.97	1.16
3-Me	0.2	30	1.45	0.37
3-Me	4.0	20	5.06	0.65
2-NO_2	0.2	22	21.7	16.2

[a] Relative to the rate of rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone under the same conditions (Table 2).

integrals of the signals for the cyclohexadienone in the ^1H NMR spectrum. For 4-methyl-4-nitrocyclohexa-2,5-dienone, all of the runs gave good first-order kinetics (correlation coefficient >0.99); further details are available elsewhere.[8] There was no indication of any ^1H nuclear polarisation. The variation of the first-order rate coefficients (k_{obs}) with temperature and with the percentage of added sulfuric acid is shown in Table 2. The variation with temperature gives a good Eyring plot with $\Delta H^\ddagger = 98.4 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = 14 \pm 12$ J K^{-1} mol^{-1}. The variation with acidity gives a curved plot with an intercept corresponding to the uncatalysed reaction (Fig. 2). At the highest acidity used, *ca.* 90% of the reaction is occurring by the acid-catalysed reaction path.

For the analysis of the ^{15}N nuclear polarisation, it is convenient to divide the first order rate coefficients (k_{obs}) into two parts corresponding to the uncatalysed reaction (k_1) and the acid catalysed reaction (k_1') (Fig. 2). At 22 °C, the extrapolated value of k_1 is 9.6×10^{-5} s^{-1}. In the rest of this paper, the kinetic runs carried out at the lowest acidity used (0.2% sulfuric acid) will be taken as those characteristic of the uncatalysed reaction. The value of k_{obs} then obtained at 30 °C (3.88×10^{-4} s^{-1}) is close to that reported[2] for the rearrangement of this compound in acetic acid at this temperature (4.7×10^{-4} s^{-1}).

The rates of reaction of the substituted cyclohexadienones have been followed in the same way and the rate coefficients are listed in Table 3 together with the relative rates of reaction calculated by comparison with the first-order rate coefficients obtained for the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone under the same conditions.

^{15}*N NMR Studies.*—These reactions were carried out under essentially the same conditions as the kinetic studies described above but with the use of ^{15}N labelled nitric acid (99.5%, ^{15}N) to prepare the acetyl nitrate. [^{15}N]Nitrobenzene (*ca.* 0.7 mol dm^{-3}) was also present in the reaction mixture to provide a signal of standard intensity and position (δ_N 370.1 on the liquid ammonia scale). The change in the nucleus studied required a change from the 100 MHz CW NMR instrument to a 200 MHz FT instrument.

The outstanding feature of the runs followed by ^{15}N NMR spectroscopy is the very marked enhancement of the signals for both the starting material and the product. In an uncatalysed

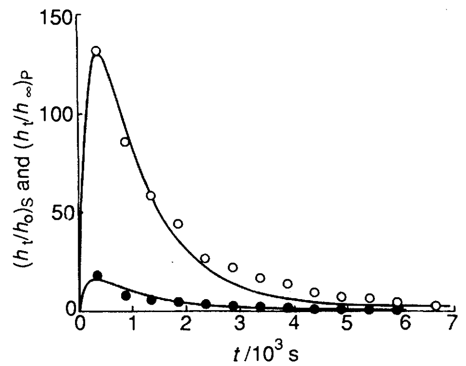


Fig. 3 The relative peak heights for the substrate $[(h_t/h_0)_S]$ (dots) and the product $[(h_t/h_\infty)_P]$ (open circles) in the ^{15}N NMR spectra taken during the uncatalysed rearrangement at 37.5 °C of 4-methyl-4-nitrocyclohexa-2,5-dienone in acetic anhydride containing sulfuric acid (0.2%). The two theoretical curves were calculated taking $k_{obs} = 9.84 \times 10^{-4}$ s^{-1}; $E = 1113$; $R = 0.13$.

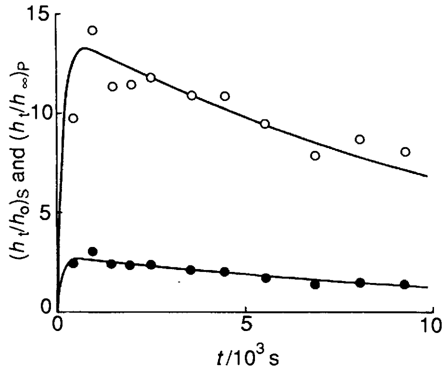


Fig. 4 The relative peak heights for the substrate $[(h_t/h_0)_S]$ (dots) and the product $[(h_t/h_\infty)_P]$ (open circles) in the ^{15}N NMR spectra taken during the uncatalysed rearrangement at 22 °C of 4-methyl-4-nitrocyclohexa-2,5-dienone in acetic anhydride containing sulfuric acid (0.2%). The two theoretical curves were calculated taking $k_{obs} = 0.8 \times 10^{-4}$ s^{-1}; $E = 1030$; $R = 0.126$.

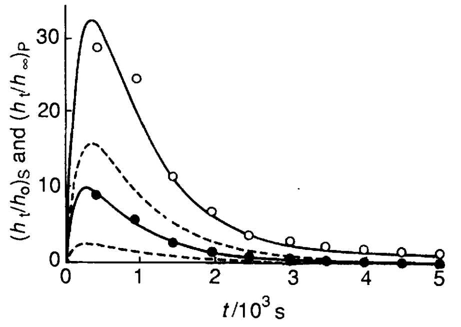


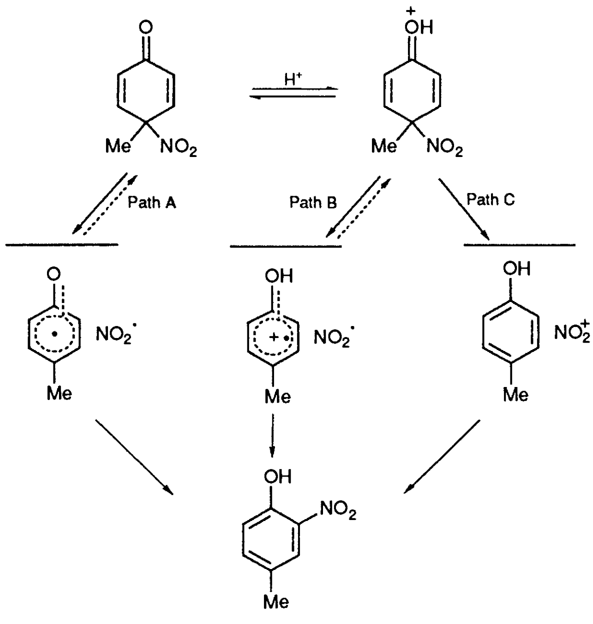
Fig. 5 The relative peak heights for the substrate $[(h_t/h_0)_S]$ (dots) and the product $[(h_t/h_\infty)_P]$ (open circles) in the ^{15}N NMR spectra taken during the acid catalysed rearrangement at 22.3 °C of 4-methyl-4-nitrocyclohexa-2,5-dienone in acetic anhydride containing sulfuric acid (4.0%). The two full theoretical curves were calculated for paths A and B (Scheme 2) taking $k_{obs} = k_1 + k_1' = 1.26 \times 10^{-3}$; $E = 230$; $R = 0.34$. The two broken theoretical curves were calculated for paths A and C taking $k_1 = 1.4 \times 10^{-4}$ s^{-1}; $k_1' = 1.12 \times 10^{-3}$ s^{-1}; $E = 1000$; $R = 0.13$; the upper curve refers to the expected absorption of the product, the lower curve to that of the substrate.

kinetic run carried out at 37.5 °C, the first spectrum recorded showed an enhancement of the signal for the starting material (δ_N 389.1) by a factor of 17.7 (relative to the initial intensity) and an enhancement of the signal for the product by a factor of 132 (relative to the final intensity). Examples of these enhanced signals were given in our preliminary publication[7] and the variation of the signal intensity with time is shown in Fig. 3. In this and later figures, the height of the product signal is taken as the sum of the heights of the signals for 4-methyl-2-nitrophenol **3** (δ_N 372.1) and its acetylated derivative **4** (δ_N 363.8) since some acetylation of the product occurs during the kinetic run.

Experiments were also carried out with uncatalysed reactions at lower temperatures but the corresponding enhancements are then much less although more persistent (Fig. 4). The ratio of the enhancement of the product signal to that for the starting material is unchanged. At a given temperature, the effect of acid catalysis is to increase the initial enhancement of both signals (compare the results in Figs. 4 and 5) but to increase the enhancement in the signal for the starting material by more than that for the product.

Discussion

The mechanisms to be considered are shown in Scheme 2. Path A corresponds to the original mechanism of Barnes and Myhre[2] (with the addition of some return of the radical pair to the starting material), Path B corresponds to the possible acid catalysed homolytic rearrangement and Path C to the proposed rearrangement through the nitronium ion.[3,4] Qualitatively, it is clear that the large enhancement observed with the uncatalysed rearrangement (Figs. 3 and 4) accords with the mechanism of Barnes and Myhre[2] because it is consistent with Kaptein's rules[9] given the negative hyperfine coupling constant for this nucleus in nitrogen dioxide[10] and known difference between the *g*-values of nitrogen dioxide (2.0000)[11] and the 4-methylphenoxy radical (2.004 32).[12] However, an understanding of the effect of acidity on this reaction requires a more detailed analysis of the nuclear polarisation in terms of the enhancement coefficient *E* (the factor by which the NMR signal is enhanced at the time of formation of the polarised material).[13]



Scheme 2

For this purpose, it is necessary to distinguish between the unpolarised substrate and product (S, P), and the corresponding polarised materials (S*, P*). The polarised materials are generated by the homolysis and then decay to the unpolarised substrate and product with a first-order rate coefficient β given by the reciprocal of the relaxation time T_1 of the ^{15}N nucleus in the nitro group (here taken to be 170 s).[14] The observed enhancements of the signals for the substrate and product are related to the concentrations of the polarised and unpolarised species by eqns. (1) and (2), respectively. The enhancement

$$(h_t/h_o)_S = ([S] + E[S^*])_t/[S]_{t=0} \qquad (1)$$

$$(h_t/h_\infty)_P = ([P] + E[P^*])_t/[P]_{t=\infty} \qquad (2)$$

coefficient (E) has been assumed to have the same value for both polarised materials since the two are formed by different ways of recombination of the same radical pair.† The reactions determining how the concentrations of S, S*, P and P* vary with time are shown in Scheme 3, Path A. In Scheme 3, k_1 is the observed first-order rate coefficient for the rearrangement and the rate coefficient for the conversion of S to S* is written as Rk_1 where R is a measure of the number of radical pairs reforming the substrate as a fraction of those forming the product. The concentrations of S, S*, P and P* as a function of time and the best values of E and R can then be calculated by numerical integration of eqns. (3)–(6) and fitting the resulting values of

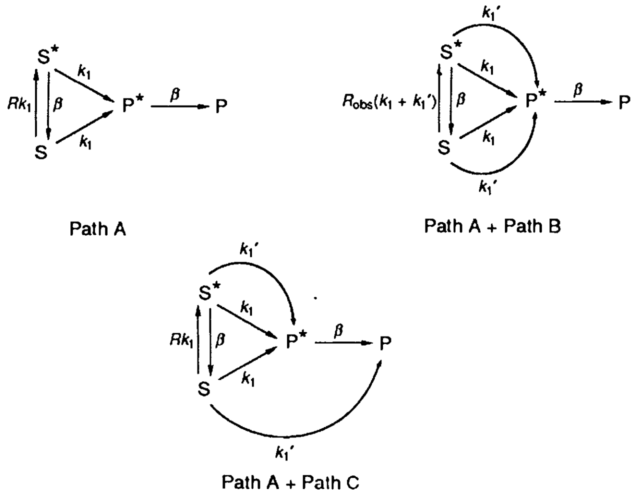
$$d[S]/dt = -k_1[S] - Rk_1[S] + \beta[S^*] \qquad (3)$$

$$d[S^*]/dt = -k_1[S^*] - \beta[S^*] + Rk_1[S] \qquad (4)$$

$$d[P^*]/dt = -\beta[P^*] + k_1[S] + k_1[S^*] \qquad (5)$$

$$d[P]/dt = \beta[P^*] \qquad (6)$$

$(h_t/h_o)_S$ and $(h_t/h_\infty)_P$ to the experimental results. The theoretical curves in Figs. 3 and 4 have been drawn by this numerical integration although in the initial calculation of E and R it was found more convenient to calculate E by using an explicit solution[13] for the concentrations of P and P* and then to use this value in a similar calculation of R.



Path A

Path A + Path B

Path A + Path C

Scheme 3

The theoretical curves provide a good fit to the experimental data for both fast and slow kinetic runs with no significant variation of E and R over the temperature range studied. Thus, for the run at 37.5 °C in Fig. 3, E = 1113 and R = 0.13; for the run at 22 °C in Fig. 4, E = 1030 and R = 0.126.

It is now possible to see to what extent the results for the acid catalysed runs accord with the suggested mechanisms. The relevant reactions for concurrent homolytic and heterolytic processes (Path A + Path C) are included in Scheme 3. In this diagram, S and S* stand for the normal and polarised substrates irrespective of the degree of protonation. The lower curved arrow corresponds to the acid catalysed conversion of the normal substrate to the normal product and the upper curved arrow to the acid catalysed conversion of the polarised substrate to the polarised product (both of these steps are considered as heterolytic processes). When these reactions are added, eqns. (3)–(6) take the form of eqns. (7)–(10). In these equations, the

$$d[S]/dt = -k_1[S] - k_1'[S] - Rk_1[S] + \beta[S^*] \qquad (7)$$

$$d[S^*]/dt = -k_1[S^*] - k_1'[S^*] - \beta[S^*] + Rk_1[S] \qquad (8)$$

$$d[P^*]/dt = -\beta[P^*] + k_1[S] + k_1[S^*] + k_1'[S^*] \qquad (9)$$

$$d[P]/dt = \beta[P^*] + k_1'[S] \qquad (10)$$

assumption is made that the extent of protonation is slight since there is no sign that the plot in Fig. 2 is reaching a plateau; the homolytic process is therefore considered to continue as before.

For a given run, all of the rate coefficients in these equations are known and so theoretical curves can be obtained by numerical integration and compared with the experimental results. Examples of such theoretical curves are provided by the broken lines in Fig. 5: for the product, the observed polarisation is greater than expected by a factor of *ca.* two and, for the starting material, the corresponding factor is *ca.* four. It appears, therefore, that the observed results cannot be explained by the incursion of a heterolytic process. The discrepancies would be even greater if the extent of protonation of the cyclohexadienone **1a** were assumed to be sufficient to reduce the rate of the uncatalysed reaction.

The full lines in Fig. 5 have been calculated on the assumption that the acid catalysed reaction of the substrate is homolytic Scheme 3 (Path A + Path B). In principle, separate values of E and R should be considered for the uncatalysed and acid catalysed reaction paths but a simpler method of analysis has been chosen first in which the acid catalysis is considered to effectively increase the rate coefficient k_1 for Path A. The values of E_{obs} and R_{obs} thereby obtained are the weighted averages for the two reaction paths. The form of the curves is clearly correct but, to fit the experimental results, the effective enhancement factor E_{obs} must be taken as 230 and the effective value of R_{obs} as 0.34. Similar results have been obtained in other kinetic runs involving acid catalysis.[8] When these results are analysed in terms of the separate contributions of the thermal and acid-catalysed reaction paths, the values for the acid catalysed path are E' = 130 and R' = 0.37. These results indicate that the acid catalysed homolytic reaction leads to much less polarisation and to much greater return of the radical pair to the substrate.

The properties of the radicals involved accord with these differences between the two reaction paths. From the g values of the 4-methylphenoxyl radical (2.004 32)[12] and its conjugate acid (2.003 17),[12] it is clear that the value of Δg must be less for the acid catalysed path; this is one factor in determining the intensity of the nuclear polarisation observed.[16] Protonation of the 4-methylphenoxyl radical[12] also reduces the hyperfine coupling constant at the 2-position from 6.1×10^{-4} to 4.5×10^{-4} T and increases the hyperfine coupling constant for the 4-methyl group from 12.7×10^{-4} to 15.1×10^{-4} T; the implied change in the spin distribution should favour the recombination of the radical pair at the 4-position.

The homolytic interpretation of the acid catalysed reaction also implies that electron withdrawal from the aromatic ring favours the homolysis of the C–N bond. This is consistent with earlier kinetic studies of the effect of a 2-chloro substituent,[3,4] and with the present studies on the 2-nitro substituent (Table 3). Even 4-methyl-4-nitro-2,3,5,6-tetrabromocyclohexa-2,5-dienone is now known to act as a homolytic nitrating agent.[17] The homolytic interpretation of the acid catalysed reaction is also consistent with the similar substituent effects of

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† This may be an oversimplification, for the rearrangement may occur through a succession of distinct radical pairs.[15]

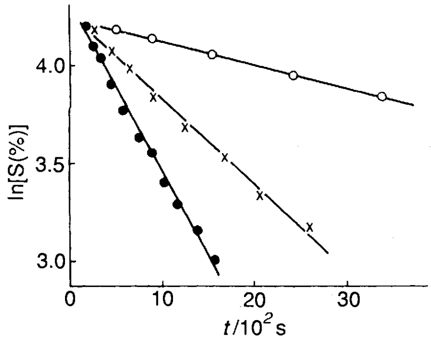

Fig. 6 Examples of first-order plots for the rearrangement of the *ipso*-intermediate **1** (X = H) in acetic anhydride. Open circles, at 22 °C with 0.2% sulfuric acid; crosses, at 22 °C with 2% sulfuric acid; dots, at 36 °C with 0.2% sulfuric acid. Only half of the first run is shown in the Figure.

methyl groups on the uncatalysed and acid catalysed reaction paths (Table 3).

In conclusion, the studies of ^{15}N nuclear polarisation are entirely consistent with the interpretation of Barnes and Myhre[2] for the uncatalysed rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone but add to this interpretation the evidence for significant return of the radical pair to the initial cyclohexadienone. For the acid catalysed reaction, the present work indicates that an acid catalysed homolytic reaction is present and that there is no evidence to require the incursion of a heterolytic reaction. The present work cannot, however, exclude the possibility that a heterolytic process makes some contribution to the reaction rate.

Experimental

Materials.—4-Methylphenol, 4-methylphenyl acetate, 2,4-dimethylphenol, 3,4-dimethylphenol, and 4-methyl-2-nitrophenol were obtained from Aldrich in grades of the highest purity available. All gave the expected ^1H NMR spectra and were used without further purification. Acetic anhydride was obtained from BDH and was purified by distillation (b.p. 138–140 °C). Sulfuric acid (98%) was AnalaR grade and was used as supplied. Nitric acid (100%) was prepared by distillation under reduced pressure (1 mmHg) of a 1:1 v/v mixture of AnalaR fuming nitric acid (d. 1.5) and AnalaR sulfuric acid (98%) at 0 °C. [^{15}N]Nitric acid (100%, 99% ^{15}N] was prepared in a similar way except that, as it was supplied as a 45% aqueous solution by MSD isotopes, the ratio of sulfuric acid to nitric acid was changed to 2.3:1. [^{15}N]Nitrobenzene was prepared as described previously.[18]

Kinetic Runs.—Acetic anhydride was added slowly to nitric acid (100%) at 0 °C to give a solution (2 mol dm^{-3}) of acetyl nitrate. Dichloromethane was added to provide a reference signal and the solution was allowed to stand for 20 min at 0 °C to ensure complete formation of the acetyl nitrate. This solution was then added to an equal volume of a solution of 4-methylphenyl acetate (2 mol dm^{-3}) in acetic anhydride at 0 °C. At least 0.2% (w/w) sulfuric acid was also present in the final reaction mixture. Part of the reaction mixture was then brought to the required temperature in the probe of an NMR spectrometer. After 5 min, to ensure that the initial nitration was complete, the ^1H NMR spectrum was scanned at intervals using a JEOL JS-100 CW spectrometer and the relative concentrations of the main components (the cyclohexadienone **1a**, 4-methylphenyl acetate, 4-methyl-2-nitrophenol, 4-methyl-2-nitrophenyl acetate, 2,6-dinitro-4-methylphenol, and 2,6-dinitrophenyl acetate) were determined by integration based on the chemical shifts shown in Table 1 (see Fig. 1). Rate coefficients were calculated from a first-order plot of the percentage of the cyclohexadienone **1a** present (Fig. 6). The rate coefficients had standard errors of *ca.* 3% but the error estimates in the activation parameters are based on an error of 5% to allow for other factors that may be involved. At the end of a typical kinetic run, the products were isolated, separated by HPLC and identified by ^1H NMR spectroscopy and mass spectrometry; only 4-methylphenyl acetate, 4-methyl-2-nitrophenyl acetate, and 4-methyl-2,6-dinitrophenyl acetate were found to be present.[8]

The other substrates were studied in a similar way although the corresponding acetates were prepared *in situ* from the reaction of the phenols with the acetic anhydride.

Studies of Nuclear Polarisation.—The runs followed by ^{15}N NMR spectroscopy were carried out in a similar way but using a Varian XL200 spectrometer and [^{15}N]nitrobenzene as the standard. To ensure equivalent conditions for the ^1H and ^{15}N NMR studies, each run followed by ^{15}N NMR spectroscopy was preceded by a kinetic run followed by ^1H NMR spectroscopy using the same broadband probe and the rate coefficient from the first run was used in the analysis of the polarisation found in the second. In determining the extent of polarisation, the height of the signal for the cyclohexadienone **1a** and the sum of the heights of the signals for 4-methyl-2-nitrophenol and 4-methyl-2-nitrophenyl acetate were normally measured relative to the height of the signal for the standard. These ratios were then divided by the corresponding ratios at the start and end of reaction to determine the quantities $(h_t/h_o)_S$ and $(h_t/h_\infty)_P$ used in eqns. (1) and (2). Where the intensity of the product signals prevented the direct determination of the above ratios, the height of the product signals were first measured relative to that of the cyclohexadienone and the spectrum was then replotted on a greater scale so that the latter signal could be compared with that of the standard.

Calculations.—The models used as a basis for the calculations (Scheme 3) do not allow for some return to the original substrate **2** during the rearrangement but this should not be a serious defect since the value of the ratio $(h_t/h_\infty)_P$ is unchanged if both P_t and P_∞ are reduced by the same factor. Another weakness is that the same enhancement coefficient is assigned to the formation of P* from S and the formation of P* from S* but the resulting errors should not be significant since the calculations suggest that only *ca.* 2% of the reaction takes the latter route. The numerical integrations for eqns. (3)–(10) used a simple computer program with intervals of *ca.* 0.1 s. For the formation of P from S according to Path A (Scheme 3), an explicit solution also exists[13] and the two methods gave identical results within the accuracy required for plotting. The enhancement coefficient (E') and R-value (R') for the acid catalysed pathway were derived from the equations: $k_{obs}E_{obs} = k_1E + k_1'E'$; $k_{obs}R_{obs} = k_1R + k_1'R'$.

A more detailed analysis of some of the above results has been carried out using the KINETIC program;[19] this allowed for some return to 4-methylphenol during the rearrangement and for the subsequent nitration of some of this material. 4-Methylphenol is known to react with nitrogen dioxide to form some 4-methyl-4-nitrocyclohexadienone.[20] As might be expected, the more detailed analysis gave a better fit to data for the kinetic runs (Fig. 6) and the polarisation plots (Fig. 3) but did not lead to any change in the above conclusions.

Acknowledgements

One of us (S. T.) thanks the SERC for a studentship.

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Paper 2/02785B
Received 28*th May* 1992
Accepted 8*th June* 1992