15N Nuclear Polarisation in Nitration and Related Reactions. Part 8.[1] The Mechanisms of Rearrangement of 2-Methyl-2-nitrocyclohexa-3,5-dienones

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A kinetic study has been carried out on the regiospecific rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone to 2-methyl-6-nitrophenol in acetic anhydride containing 0.2% sulfuric acid at −27.8 to −6.5 °C. Related studies have been carried out with other concentrations of sulfuric acid and on the effect of the substituents, 3-Me, 4-Me, 5-Me, 6-Me, 4-NO₂ and 6-NO₂. Some of these experiments have been repeated using 15N-labelled compounds. The rearrangement of the unsubstituted dienone gives no significant 15N nuclear polarisation on either the uncatalysed or acid-catalysed paths. However, when the 6-position is blocked by substituents, the nitro group migrates to the 4-position and these rearrangements show the strong 15N nuclear polarisation characteristic of reactions involving an ArO• NO₂• radical pair. Semi-empirical molecular orbital calculations are used to provide information on possible intermediates in reactions involving the radical pair.

2-Methyl-2-nitrocyclohexa-3,5-dienone 1 and other substituted derivatives are known to rearrange rapidly and regiospecifically at low temperatures to form the corresponding 6-nitrophenols[2] (Scheme 1). The first suggestion of this curiously regiospecific rearrangement came from indirect evidence that such intermediates (e.g. 1) when formed, after demethylation, in the ipso-nitration of 2-substituted anisoles give only the 6-nitro isomers on rearrangement.[3] The same regiospecificity is found in the nitro group rearrangements of substituted 2-nitrophenols in trifluoromethanesulfonic acid.[4] These rearrangements presumably occur via the corresponding Wheland intermediates, (e.g. 2, from 3-methyl-2-nitrophenol).


Scheme 1

2 **3**
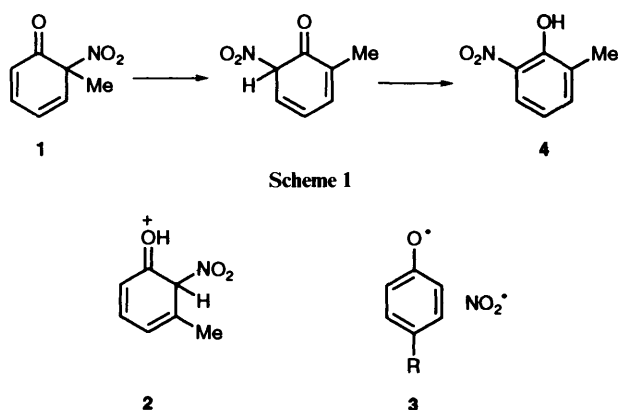
The analogy with the rearrangements of the 4-nitrocyclohexa-2,5-dienones[1,5] suggests a homolytic mechanism for these rearrangements but the regiospecificity of the reactions is not as expected for reaction through a radical pair involving nitrogen dioxide. There is evidence from both the nitrous acid-catalysed nitration of phenol[6] and from the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone[1] that such radical pairs as 3 (R = H or Me) lead to attack at both the ortho and para positions. Explanations of the regiospecificity have therefore involved either a direct [1,5]sigmatropic shift[2] or some interaction of the

nitrogen dioxide radical with the C=O group, possibly involving the formation of an intermediate phenyl nitrate.[3,7]

The kinetics of these reactions have now been investigated and studies have been carried out using 15N labelled compounds to determine whether there is any evidence of radical intermediates from 15N nuclear polarisation.

Results

Preparation.—2-Methyl-2-nitrocyclohexa-3,5-dienone 1 was prepared by the nitration of 2-methylphenyl acetate in acetic anhydride containing 0.2% sulfuric acid at −78 °C. Under these conditions, the reaction was very fast and was essentially complete by the time the first 1H NMR spectrum could be measured. The product analysis was carried out by 1H NMR spectroscopy and the results indicated that the reaction occurred as shown in Scheme 2 with the yields: 1, 65%; 5, 5% and

Scheme 2
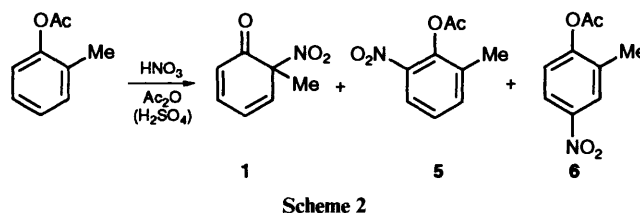
6, 30%. The identity of the species formed was confirmed by 13C NMR spectroscopy. The values of the 1H and 13C chemical shifts are given in the Experimental Section. The yield and chemical shifts for the cyclohexadienone 1 were very similar to those reported previously.[2]
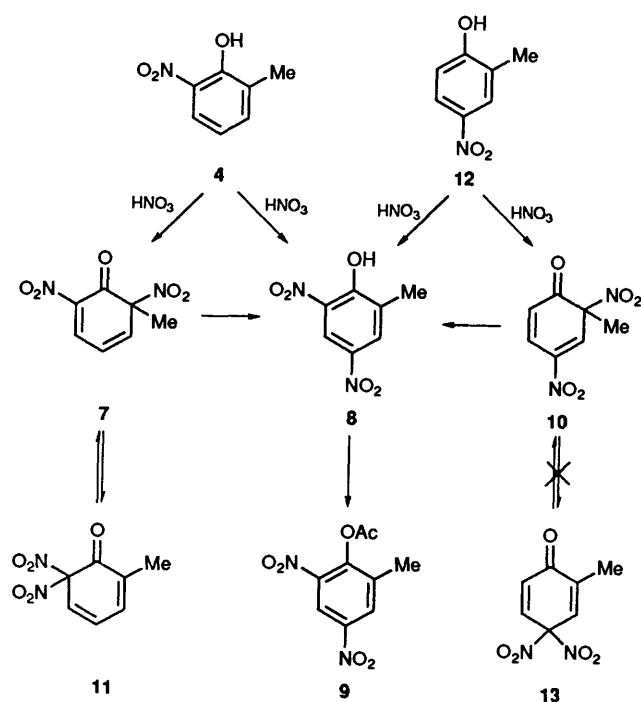
Kinetics.—The kinetics of the rearrangement of the cyclohexadienone 1 (Scheme 1) have been studied using the reaction mixture from the nitration of 2-methylphenyl acetate and have been followed from the variation in the integral for the three most upfield protons of 1 (H-3, H-4, H-6) relative to the integral of the dichloromethane present as a standard (Fig. 1). As reaction proceeds, this ratio decreases and the corresponding ratios for the signals from 2-methyl-6-nitrophenol and 2-methyl-6-nitrophenyl acetate increase: there is no evidence for any formation of 2-methyl-4-nitrophenol or any increase in the signals corresponding to 2-methyl-4-nitrophenyl acetate. How-

Table 1 The variation of the first-order rate coefficient (k_1) for the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone (ca. 1.0 mol dm^{-3}) in acetic anhydride with acidity and with temperature

[H$_2$SO$_4$] (%)	T/°C	k_1/10^{-3} s^{-1}
0.2	−6.5	2.34
0.2	−13.0	0.861
0.2	−22.0	0.180
0.2	−27.0	0.087
2.0	−11.0	2.30
2.0	−16.0	1.11
2.0	−22.0	0.405
4.0	−10.0	5.06
4.0	−15.0	2.19
4.0	−20.0	0.786
4.0	−28.0	0.348
6.0	−14.0	3.89
6.0	−20.0	1.84
6.0	−28.0	0.522

Table 2 Activation parameters for the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone **1** and 2,6-dimethyl-2-nitrocyclohexa-3,5-dienone **14** (X = Me) in acetic anhydride containing varying concentrations of sulfuric acid

Compound	[H$_2$SO$_4$] (%)	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1	0.2	86.7	31
1	2.0	84.5	28
1	4.0	78.3	9
1	6.0	74.0	−4
14 (X = Me)	0.2	118	112

ever, in the presence of a slight excess of nitric acid, there is evidence (see below) that some of the 2-methyl-6-nitrophenol formed undergoes a further reaction to form 2-methyl-4,6-dinitrophenol **8** (Scheme 3). The decrease in the concentration
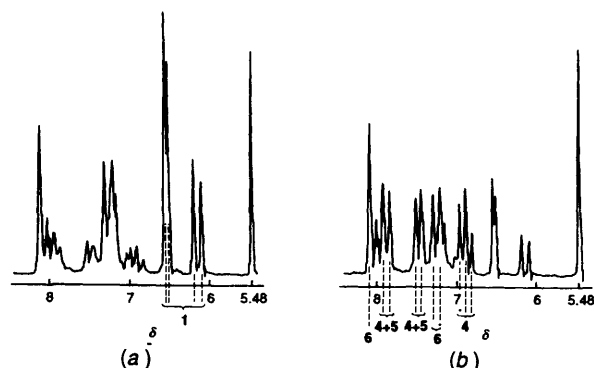

Fig. 1 ^{1}H NMR spectra taken during the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone (ca. 0.65 mol dm^{-3}) in acetic anhydride at −13 °C in the presence of 0.2% sulfuric acid. Times: (a) 7 min 47 s; (b) 26 min 45 s. The most characteristic signals corresponding to the reactant **1** and the compounds **4**, **5** and **6** are identified together with that of the standard (CH$_2$Cl$_2$) at δ 5.48. For chemical shifts see Table 6.

Scheme 3
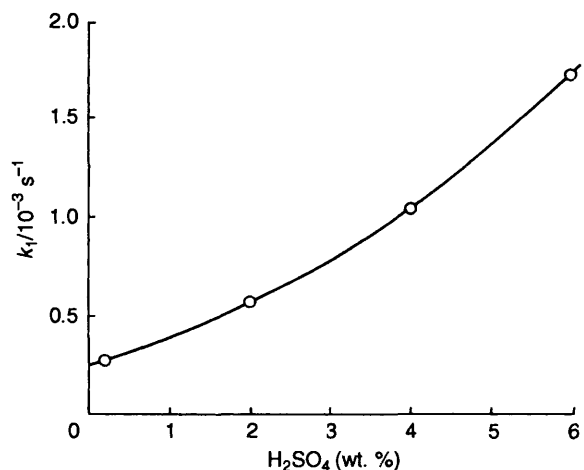
Fig. 2 The variation of the first-order rate coefficient (k_1) with the concentration of sulfuric acid for the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone (ca. 0.65 mol dm^{-3}) in acetic anhydride at −20 °C

of **1** follows good first-order kinetics (correlation coefficient > 0.99) and the resulting first-order rate coefficients (k_1) are given in Table 1 as a function of temperature and acidity. In one run, a small amount of sodium azide was added as a trap for nitrous acid but there was no detectable change in the rate of rearrangement. The activation parameters corresponding to the variation of k_1 with temperature at a given acidity are given in Table 2.

The variation with acidity of the interpolated values of the rate coefficients at −20 °C are shown in Fig. 2. The form of this plot shows that the reaction is proceeding by two reaction paths: a thermal reaction and an acid-catalysed reaction. At the highest acidity used (6.0% H$_2$SO$_4$), ca. 85% of the reaction is taking the acid-catalysed path but, from the NMR spectra, the reaction still appears to show the same regioselectivity as before. The variation in the relative importance of these two pathways

with acidity presumably explains the steady change in the activation parameters listed in Table 2.

Similar experiments have been carried out on the uncatalysed rearrangement of a number of substituted 2-methyl-2-nitrocyclohexa-3,5-dienones and the results are given in Table 3. Because of the wide range of temperatures involved, an attempt has been made to bring the rate ratios to the equivalent values at 0 °C but this is based on the assumption that the substituents act only on the activation energy and so the second set of R values in Table 3 are only an approximation to the relative rates at this temperature. Further details and illustrations of the spectra are available elsewhere.[8] The product obtained from the nitration of 2,4-dimethylphenyl acetate included both of the

Table 3 Substituent effects on the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone in acetic anhydride containing 0.2% sulfuric acid. The ratio R is obtained by dividing the rate coefficient for the rearrangement of the substituted compound (k_1^X) by that calculated for the unsubstituted compound (k_1^0) at the same temperature. The nitro group migrates to the 6-position unless specified otherwise.

Substituent	$T/°C$	$k_1^X/10^{-3}$ s^{-1}	$k_1^0/10^{-3}$ s^{-1}	R	R (0 °C)
3-Me	−9.5	0.246	1.853	0.17	0.18
3-Me	2.0	1.13	7.97	0.14	0.14
4-Me	−35.0	0.901	0.0192	47.0	29
5-Me	2.0	0.675	7.97	0.085	0.084
6-Me[a]	0.0	0.101 [b]	6.0	0.017	0.017
6-Me[a]	2.0	0.149	7.97	0.019	
6-Me[a]	7.0	0.436	15.9	0.027	
6-Me[a]	12.0	0.766	31.1	0.025	
6-Me[a]	22.0	5.73	111	0.052	
4-NO$_2$	−12.5	0.893	0.920	0.97	0.97
6-NO$_2$[a]	−1.0	1.26	5.20	0.24	0.24

[a] Rearrangement to the 4-position. [b] Obtained by extrapolation.

Table 4 Assignment of the ^{15}N chemical shifts for the compounds in Schemes 1–3. The values are on the liquid ammonia scale based on δ_N 370.3 for nitrobenzene.

Compound	Position	δ_N
1		385.0
4		372.5
5		368.3
6		368.7
7	2	380.1
8	4	365.4
	6	368.4
9	4	363.9
	6	363.5
10	2	378.1

possible cyclohexadienone intermediates (deriving from *ipso*-attack at the 2-and 4-positions) but the 2-nitro isomer was very much the more reactive. These results are in general agreement with the qualitative observations reported previously.[2]

The results in Table 3 include the rate coefficients for the rearrangement of two substrates in which the migration of the nitro group to the 6-position is blocked: rearrangement then occurs to the 4-position. With 2,6-dimethyl-2-nitrocyclohexa-3,5-dienone, the NMR spectrum of the product includes an extra signal at δ_H 6.56; this is attributed to the formation of some 2,6-dimethyl-*p*-benzoquinone in accord with earlier work.[2] The nitration of 2-methyl-6-nitrophenol (Scheme 3) in acetic anhydride at −78 °C gives the cyclohexadienone **7** and the dinitrophenol **8** in the ratio 1.4:1; on warming, the cyclohexadienone rearranges smoothly to give the dinitrophenol with very small amounts of a few unidentified sideproducts.

^{15}N *NMR Studies.*—A number of the above reactions have been followed by ^{15}N NMR spectroscopy using acetyl nitrate prepared from ^{15}N-labelled nitric acid (99.5% [15]N) and with the addition of ^{15}N-labelled nitrobenzene (*ca.* 0.7 mol dm^{-3}) as a standard for measurement of the intensities and positions of the peaks. The conditions were adjusted to bring the half-lives of the reactions to *ca.* 10 min to help the detection of ^{15}N CIDNP effects. The ^{15}N chemical shifts used in the assignment of the peaks are listed in Table 4.

The results indicate that the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone to 2-methyl-6-nitrophenol in acetic anhydride containing 0.2% sulfuric acid gives no obvious ^{15}N nuclear polarisation. Examples of the spectra have been shown previously,[9] and the relative peak heights for a typical run are

Table 5 Comparison of the ^{15}N signals during the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone at −11 °C and 4-methyl-4-nitrocyclohexa-2,5-dienone at 37.5 °C in acetic anhydride containing 0.2% sulfuric acid. The ratio $(h_t/h_0)_I$ refers to the height of the signal for the dienone intermediate at time t divided by that at the start of reaction. The ratio $(h_t/h_\infty)_P$ refers to the height of the signal for the nitrophenol[a] at time t divided by that at the end of reaction. All heights were measured relative to the signal for the standard (Ph[15]NO$_2$).

Time/s	$(h_t/h_0)_I$	$(h_t/h_\infty)_P$	$(h_t/h_0)_I + (h_t/h_\infty)_P$
2-Methyl-2-nitrocyclohexa-3,5-dienone			
225	1	0	1
495	0.84	0.48	1.32
765	0.41	0.62	1.03
1035	0.28	0.77	1.05
4-Methyl-4-nitrocyclohexa-2,5-dienone[b]			
375	17.7	131.5	149.2
880	7.5	85.9	93.4
1355	5.4	58.6	64.0
1865	4.0	44.1	48.1

[a] Including, for the second run, the signal for the acetylated product. [b] Taken from ref 1.

given in Table 5. In the absence of nuclear polarisation, the ratios $(h_t/h_0)_I$ and $(h_t/h_\infty)_P$ should be equal to the fractions of dienone and product present at time t; their sum should therefore be unity. The values found for the sum are in the range 1–1.5 and, given the relatively high experimental error in measuring these small signals, the deviations from unity are probably not significant. Similar results were obtained when the reaction was carried out in acetic anhydride containing 6.0% sulfuric acid. These results are very different from those obtained in the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone (Table 5) where enhancements by a factor of 100 can be observed.

Some ^{15}N nuclear polarisation is however normally present during the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone but it appears in the signals for 2-methyl-2,6-dinitrocyclohexa-3,5-dienone **7** and 2-methyl-2,4-dinitrophenol **8**. The results are not very reproducible and appear to derive from the nitrous acid-catalysed nitration of a small amount of the initial product **4** to form the dienone **7** and the dinitrophenol **8** (Scheme 3). This reaction leads to strong emission signals but the spectra can also be complicated by the subsequent enhanced absorption signals arising from the rearrangement of the dienone **7** to give the dinitrophenol **8**.

To provide further information on this, the further nitration of the unlabelled nitrophenol **4** was studied separately using labelled acetyl nitrate and the resulting spectra are shown in Fig. 3. As expected,[10] the initial nitration at −25 °C leads to strong emission signals [spectrum (*a*)] but, after 2 h at this temperature the normal absorption signals are seen [spectrum (*b*)]. When the temperature is raised to −3 °C, the rate of rearrangement of the dienone **7** becomes significant and the signals for the dienone and the dinitrophenol **8** then show enhanced absorption [spectrum (*c*)]. An interesting feature of the spectrum at the end of reaction [spectrum (*d*)] is that the ^{15}N label is found in both the 4- and 6-positions of the dinitrophenol; the rearrangement reaction must therefore be accompanied by the formation of the dinitrodienone **11** (Scheme 3) for, in this molecule, the labelled and unlabelled nitro groups become equivalent.

Studies have also been carried out on the reaction of unlabelled 2-methyl-4-nitrophenol **12** with labelled acetyl nitrate in acetic anhydride containing 4.0% sulfuric acid. The initial nitration leads to the expected emission signals in the dienone **10** and the dinitrophenol **8** but there is no obvious nuclear polarisation in the subsequent rearrangement of the
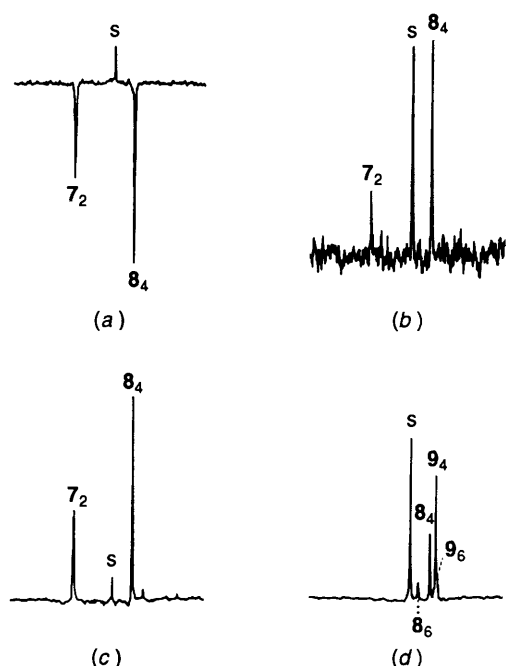
Scheme 4

Fig. 3 ^{15}N NMR spectra taken during the nitration of 2-methyl-6-nitrophenol 4 (0.5 mol dm^{-3}) with ^{15}N-labelled acetyl nitrate (0.5 mol dm^{-3}) in acetic anhydride in the presence of 0.2% sulfuric acid (Scheme 3). Times: (a) 9–13.5 min at −25 °C; (b) after 2 h at −25 °C; (c) 8–12.5 min after bringing to −3 °C; (d) after complete reaction. The assignment is indicated by the relevant structure number with a subscript indicating the position of the label. The signal of the NMR standard (p-dinitrobenzene) is shown as S. For ^{15}N chemical shifts, see Table 4.

dienone to the dinitrophenol. The final spectrum also gave no indication of any exchange reaction with the nitro group at the 4-position and so the dienone 13 (Scheme 3) is presumably not formed. In another reaction carried out using 1% sulfuric acid, a peak in the correct position for the 4-[15]NO$_2$-labelled dinitrophenol could just be detected but the extent of any such exchange must be very small.

Discussion

This discussion is concerned mainly with the four reaction paths shown in Scheme 4 and particularly with the mechanisms of Paths A and B. The rates of proton loss from the four products on the right hand side of Scheme 4 are assumed to be fast.

The CIDNP results above show that the 2-methyl-2-nitrocyclohexa-3,5-dienones rearrange in two apparently separate ways. If the 6-position is free, the nitro group migrates to that position in a relatively rapid step without any significant nuclear polarisation (Path A). If rearrangement to the 6-position is blocked, the nitro group migrates to the 4-position in a slower step involving strong nuclear polarisation (Path C).

Mechanism of Paths B and C.—Although the extent of reaction along Path B has not yet been directly measured, the mechanism will be assumed to be the same as that in the 6-substituted compounds (Path C). This mechanism is not in doubt. From the CIDNP effects, it must involve a radical pair and, from the phase of the polarisation, it appears entirely analogous to the rearrangement of the 4-methyl-4-nitrocyclohexa-2,5-dienones [1] (Path D). These two reactions would be expected to have the same reaction path from the principle of microscopic reversibility.[11] The reaction will therefore be considered to involve a radical pair of the type shown in structure 3. The phase of the polarisation implies that reaction occurs predominantly by recombination within the radical pair.
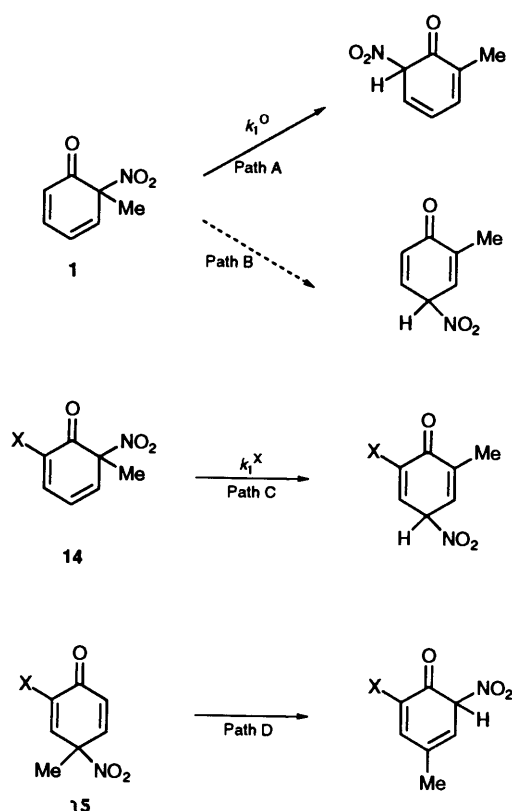
There are, however, three points worth noting. First, for a given substituent X, the rate of reaction on Path C is considerably faster than that on Path D. Thus, at 22 °C, the first-order rate coefficient for the rearrangement of the dienone 14 (X = Me) is 5.73 × 10^{-3} s^{-1}. From our earlier results,[1] the corresponding rate coefficient for the rearrangement of 15 (X = Me) would be 1.8 × 10^{-4} s^{-1}. A similar conclusion could be drawn from the results for X = NO$_2$. These results refer to low concentrations of added acid and hence to the uncatalysed reaction path. The nitro-3,5-dienones 14 appear therefore to undergo homolysis more readily than the nitro-2,5-dienones 15. Secondly, since the migration of the nitro group from the 4-position to the 2-position is subject to strong acid catalysis,[1] the same should be true for the reverse migration (Path C), for the 2-nitrodienones are unlikely to be significantly protonated under the conditions studied. Finally the dienone 14 (X = Me) gives some of the corresponding p-benzoquinone during rearrangement;[2] this can be understood in terms of the attack of the nitrogen dioxide radical via oxygen but the factors determining the mode of addition of this radical are not understood.

Mechanism of Path A.—Before considering the possible mechanisms for this reaction path, it is helpful to look at the relative rates of rearrangement to the 6- and 4-positions.

With 2-methyl-2-nitrocyclohexa-3,5-dienone, the only evidence is that the nitro group migration to the 6-position appears to be regiospecific[2] (Scheme 4, Path A); the rate ratio between Paths A and B is therefore at least 50. Other evidence comes from the use of the 6-substituted dienones 14 as a model for Path B, Scheme 4. With X = Me, the activation parameters in Table 2 show that the rate coefficient ratio $k_1^0/k_1^X = 59$ at 0 °C (Scheme 4). Since an *ortho* methyl group has very little effect on the rate of migration of the nitro group from the 4- to the 2-position (the substituent factor is 1.35 at 30 °C,[1] it is unlikely to have much effect on the reverse reaction; the factor of 59 is therefore a reasonable approximation to the relative rates of
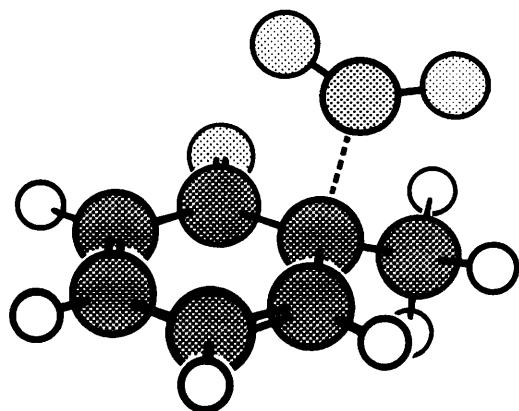
Fig. 4 The calculated transition state structure for the homolysis of the C–N bond in 2-methyl-2-nitrocyclohexadienone

Table 6 Heats of formation of chemical species involved in the uncatalysed and acid-catalysed rearrangement of 2-methyl-2-nitro-cyclohexadienone. The figures in the 'Conjugate acids' column refer to chemical species protonated on what is initially the carbonyl oxygen atom. The values in parentheses are based on the observed heat of formation of nitrogen dioxide (see Experimental Section).

| | $\Delta H_f^0/kJ\ mol^{-1}$ | |
| | Neutral | Conjugate |
Chemical species	species	acids
2-Methyl-2-nitrocyclohexadienone 1	− 52.68	708.1
Transition state for homolysis of 1	39.75	761.37
Radical pair ArO˙ NO₂˙ from 1	− 34.53	684.46
	(6.47)	(725.46)
Nitrate ester from 1	− 22.06	703.47
Peroxynitrite ester from 1	168.38	670.31
2-Methyl-6-nitrocyclohexadienone	− 74.98	683.41

Paths A and B in Scheme 4. This argument is supported by the corresponding values for X = NO₂ (Table 3). The rate coefficient ratio is then only 4.0 at 0 °C but a 6-nitro group is known to increase the rate coefficient for migration of the *ipso*-nitro group from the 4- to the 2-position (Path D) by a factor of 16 at 22 °C and hence, if the same factor operates in the reverse direction, the rates for Paths A and B in Scheme 5 would differ by a factor of *ca.* 64.

With one substrate, 2-methyl-2,6-dinitrocyclohexa-3,5-di-enone 7 (Scheme 3) labelled with ¹⁵N at the 2-position, evidence for the concurrent operation of Paths A and B can be obtained directly since rearrangement to the 6-position has an even chance of leading to exchange between the labelled and unlabelled nitro groups. Such exchange is not apparent in the first spectrum of the run [spectrum (*c*), Fig. 3] but, after complete reaction, the signal corresponding to isotopic exchange at the 6-position is clearly seen [spectrum (*d*), Fig 3]. Unfortunately, the initial presence of a considerable amount of the product 8 labelled in the 4-position (formed in the nitration process) and the polarisation of the 4-labelled product during the run complicate the quantitative assessment of these results.

From the above rate coefficient ratios, it seems no longer appropriate to emphasise the magnitude of the rate difference between Paths A and B* and, since both paths appear subject to acid catalysis to about the same extent, it seems unreasonable to postulate completely different mechanisms for these two

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* An early estimate⁹ suggesting a factor of 1000 was based on a comparison of the relative rates of Paths A and D (X = H).

reactions. We suggest, therefore, that both reactions start with the homolysis of the C–N bond to form an aryloxy radical and nitrogen dioxide. This suggestion is supported by semi-empirical molecular orbital calculations using the PM3 method, for these give no indication of any low energy transition state corresponding to a [1,5]sigmatropic rearrangement; instead, as the C–N bond is stretched, the nitrogen atom moves away from the 6-position as shown by the transition state for homolysis in Fig. 4.

This conclusion may seem unexpected in view of the possibility of an allowed [1,5]sigmatropic rearrangement but Houk ¹² has recently emphasised that, with the exception of hydrogen migrations, the energy of such transition states is often comparable to that for stepwise biradical reaction paths. The reaction system considered here (Path A) also differs from one undergoing a conventional [1,5]sigmatropic rearrangement in that the C-1 and C-5 atoms are linked by the C=O group. As a result, the nonsynchronous breaking and formation of the C–N bonds does not necessarily reduce the aromatic stabilisation of the transition state for this then contains an aryloxy radical. Thus, the feature normally favouring a synchronous process is absent.

The interpretation outlined above does, however, leave two major questions unanswered. First, why is the rearrangement of the 2-nitrodienones so regioselective? Secondly, why are no CIDNP effects observed in the 2,6-rearrangements?

In considering the first question, it is significant that the *ortho/para* ratio in the nitramine rearrangement is very sensitive to the viscosity of the medium.¹³ This implies that the radical pair then formed is sufficiently reactive for the selectivity between the *ortho*- and *para*-positions to be determined more by the ease of access to these positions than by the energetics of the two substitution reactions. The aryloxy radicals should be even more reactive towards nitrogen dioxide than the amine cation radicals involved in the nitramine rearrangement and it is clear from the phase of the CIDNP effects ¹ in the rearrangement of the 4-nitrocyclohexa-2,5-dienones that the greater part of the reaction occurs by recombination within the original radical pair. We have therefore to consider the pathways for the relative movement of the radicals within the radical pair.

Our calculations indicate that the direct movement towards the 4-and 6-positions involves higher energy barriers than that towards the oxygen, and that a weak bond is formed between the nitrogen atom and the oxygen atom of the aryloxy radical. Using the observed value for the heat of formation of nitrogen dioxide, the resulting aryl nitrate is of lower energy than the radical pair. A similar interaction occurs with the protonated systems except that the calculations then suggest that the aryl nitrate is not the most stable intermediate and that the interaction of the radicals leads to a protonated peroxynitrite with a particuarly long O–O bond (2.049 Å). The relevant heats of formation are listed in Table 6. As other authors have recognised,³·⁷ interactions of this type could facilitate the 2,6-rearrangement and thus explain the observed regioselectivity.

The absence of any significant CIDNP effects in the 2,6-rearrangement shown as Path A (Scheme 4) does not necessarily imply that this reaction is not homolytic; it is sufficient if very little escape occurs from the radical pair. The argument that the interaction of the nitrogen dioxide with the oxygen atom of the aryloxy radical facilitates the 2,6-rearrangement implies also that this interaction hinders escape from the radical pair. The interaction could also therefore produce the observed difference between the CIDNP effects in the 2,6- and 2,4-rearrangements.

Little significance should be attached to the exact values of the energies listed in Table 6 for these are appreciably different when a different approximation (the AM1 method) is used. Also, the values obviously overestimate the activation energies for the recombination of the radicals, given that recombination

Table 7 Assignment of the ^{1}H chemical shifts for the aromatic hydrogen atoms in the products from the nitration of 2-methylphenyl acetate (Schemes 2 and 3) (s = singlet, d = doublet, t = triplet, m = multiplet)

Compound	$\delta_H(Ac_2O)$			
	H-3	H-4	H-5	H-6
1[a]	6.53 (d)	6.53 (d)	7.27 (m)	6.15 (d)
4	7.50 (d)	6.90 (t)	7.90 (d)	—
5	7.60 (d)	7.35 (t)	7.90 (d)	—
6	8.10 (s)	—	8.06 (d)	7.30 (d)
8	8.34 (s)	—	8.78 (s)	—

[a] The unusual coupling pattern in this substrate (Fig. 1) derives from the virtual coupling of H-5 with the two protons of equal chemical shift (H-3 and H-4).

Table 8 Assignment of the ^{13}C chemical shifts for the aromatic carbon atoms in the products from the nitration of 2-methylphenyl acetate (Schemes 2 and 3)

Compound	$\delta_C(Ac_2O)$					
	C-1	C-2	C-3	C-4	C-5	C-6
1	193.3	92.4	137.6	124.9	143.5	124.9
4	153.8	129.8	138.8	123.1	120.0	133.7
5	146.7	135.0	137.0	126.9	123.8	143.0
6	155.1	133.2	126.7	146.1	123.0	124.0
8	158.1	132.3	131.9	139.8	119.7	133.2

appears to occur mainly before dissociation of the radical pair. However, the pattern of relative energies, the absence of any low energy transition state for the [1,5]sigmatropic rearrangement, and the interaction of the radical pair via what is initially the carbonyl oxygen atom do appear to be independent of the method of approximation. It appears therefore that such interaction provides the best explanation of the observed results.

The main problem remaining concerns the large rate acceleration produced by a *p*-methyl substituent (Table 3). It seems likely that this comes, in part, from the resulting increase in the basicity of the substrate and the basicity of the aryloxy radical;[14] this should increase the importance of the acid-catalysed pathway. Further work is needed on the separate substituent effects on the uncatalysed and acid-catalysed reaction paths.

Experimental

Materials.—2-Methylphenol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, 2,6-dimethylphenol,-2-methyl-4,6-dinitrophenol and 2,6-dimethylbenzoquinone were obtained from Aldrich in grades of the highest purity available. All gave the expected ^{1}H NMR spectra and were used without further purification. 2-Methyl-4-nitrophenol was prepared from 2-methyl-4-nitroaniline following the standard procedure.[15] The product had m.p. 95 °C (lit[16]. 96 °C). 2-Methyl-6-nitrophenol was prepared by the nitration of 2-methylphenol following the procedure[17] for the preparation of 2-nitrophenol from phenol. The product had m.p. 69–70 °C (lit.[16] 70 °C). Both of the above compounds gave satisfactory analyses and ^{1}H NMR spectra; details are available elsewhere.[8] The other reactants and solvents were as described previously.[1]

Kinetic Runs.—The kinetic runs were started by the nitration of the appropriate phenols at −78 °C; phenols without nitro substituents were first converted into the corresponding aryl

acetates by dissolving in acetic anhydride containing 0.2% sulfuric acid at room temperature; phenols with nitro substituents were nitrated as such. The following procedure for the nitration of 2-methylphenol is typical.

2-Methylphenol was dissolved at room temperature in acetic anhydride containing 0.2% sulfuric acid and some dichloromethane to give a solution of 2-methylphenyl acetate (2 mol dm^{-3}). Another portion of the same solvent was cooled to 0 °C and added dropwise to nitric acid (100%, 0 °C) to give a solution of acetyl nitrate (2 mol dm^{-3}). After the second solution had stood for 25 min at 0 °C (to ensure complete conversion of the nitric acid to acetyl nitrate), the two solutions were cooled to −78 °C and mixed. The reaction mixture was then brought to the required temperature in the probe of a JEOL JS-100 CW spectrometer. After 4 min (to ensure temperature control and the completeness of the initial nitration), measurements were made of the ^{1}H NMR integrals for the components of the mixture including the integral for the NMR standard (CH$_2$Cl$_2$) (Fig. 1). The chemical shifts used in the assignment of the signals are listed in Tables 7 and 8. The rate coefficients were calculated from a first-order plot of the ratio of the integral for the three most upfield protons of the dienone 1 and the integral for the standard.

The studies on related substrates were carried out by minor modifications of the above procedure; full details are available elsewhere.[8] In the reactions of the phenols with nitro substituents, the initial solutions were brought rapidly to −78 °C to prevent formation of the corresponding acetates.

Studies of ^{15}N *Nuclear Polarisation.*—The preparation of these reaction solutions were carried out in the same way as for the runs followed by ^{1}H NMR spectroscopy except that labelled nitric acid (100%, 99.5% ^{15}N) was used and the signals were observed using a Varian XL200 spectrometer. All spectra taken during a run involved 24 pulses, pulse angle 45°, pulse repetition time 10.8 s; at the end of reaction, the number of pulses was increased to *ca.* 4000. The chemical shifts used in the interpretation of the spectra are shown in Table 4. To resolve ambiguities in compounds containing two nitro groups, the species labelled in each position were prepared separately using appropriately labelled reagents.

Molecular Orbital Calculations.—All of the calculations listed in Table 6 were carried out by the unrestricted Hartree–Fock approach using the semi-empirical PM3 method in the MOPAC 6.0 program[18] implemented on a Silicon Graphics 4D/320 computer. The calculations for stable molecules were carried out by full optimisation using the keyword PRECISE. The calculations on the transition state for the homolysis reaction (Fig. 4) were carried out by the progressive extension of the C–N bond using the keyword PATH. Since the PM3 method overestimates the stability of nitrogen dioxide (calculated heat of formation −7.94 kJ mol^{-1}, observed heat of formation 33.05 kJ mol^{-1}),[19] the observed heat of formation was used in assessing the evidence for the bonding of the nitrogen dioxide to the oxygen atom of the aryloxy radical. This approach has been used previously in calculations on the thermolysis of molecules containng the NO$_2$ group.[19] A number of the calculations were repeated by the AM1 method under the same conditions as described above.

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