

Dual Reactivity of 2,3,5,6-Tetrabromo-4-methyl-4-nitrocyclohexa-2,5-dienone

Robert G. Coombes

Departments of Chemistry, University College London, 20, Gordon Street, London WC1H 0AJ, UK and Brunel University,† Uxbridge, Middlesex UB8 3PH, UK

2,3,5,6-Tetrabromo-4-methyl-4-nitrocyclohexa-2,5-dienone in acetone solution nitrates 4-methoxyphenol by a radical mechanism, but acts mainly as a brominating agent towards phenol, after rearrangement.

2,3,5,6-Tetrabromo-4-methyl-4-nitrocyclohexa-2,5-dienone (**1**) has been used as a mild nitrating agent for naphthols, phenols and amines and we have recently demonstrated¹ that the nitration of phenol in diethyl ether, the most commonly used solvent, is a radical process involving reaction between the phenoxyl radical and NO_2^\cdot that has escaped from a radical pair in which it was formed by homolytic fission of the C–N bond in **1**. It has been reported² that a change in solvent (to diisopropyl ether, THF, chloroform, hexane or carbon tetrachloride) has little effect on these reactions.

We now report studies involving acetone as solvent, chosen initially because of the high solubility of reactants and products. Information has been obtained partly by using ^{15}N -labelled **1** and searching for chemically induced dynamic polarisation (CIDNP) effects in the ^{15}N NMR spectra during reaction.

Addition of 0.5 cm^3 of a solution of 4-methoxyphenol (1.2 mol dm^{-3}) in dry acetone to 1.5 cm^3 of **1** (0.4 mol dm^{-3}) in the same solvent at -50°C and rapid warming to 30°C led to the formation of 4-methoxy-2-nitrophenol (40%), *p*-benzoquinone (5–8%) and unidentified products, together with 2,3,5,6-tetrabromo-4-methylphenol (70%), the complementary product of nitration reactions, and compound **2** (30%) discussed below. There was less than 6% of any other individual product containing a methoxy group. 4-Methoxy-3-nitrophenol was not detected. Such a reaction with ^{15}N -labelled **1** was carried out within the NMR spectrometer using $[\text{N}^{15}\text{nitrobenzene}]$ in $[\text{H}_6^{15}\text{acetone}]$ as an external reference. A series of ^{15}N spectra taken during the reaction is shown in Fig. 1. Comparison with the noise level and with the signal for the nitrobenzene (S) [too small to be seen with the amplitude settings in spectra (b) and (c)] shows that **1** exhibits enhanced absorption in spectra (b) and (c) and that the 4-methoxy-2-nitrophenol gives a strong emission signal in spectra (b), (c) and (d) with a maximum enhancement factor of >300 . In addition there is a product peak at $\delta -3.1$ which exhibits absorption with a maximum enhancement factor of >150 . The final spectrum (e) shows the unpolarised products at the end of the reaction.

The polarisations of **1** and the 4-methoxy-2-nitrophenol are as expected from the previous study of phenol in diethyl ether and accord with the application of Kaptein's rules³ to the mechanism of Scheme 1. The absorption at $\delta -3.1$ due to compound **2** appears as a singlet in a high resolution proton-coupled ^{15}N NMR spectrum, contrasting with the multiplet from 4-methoxy-2-nitrophenol, and indicating that the nitro group is substituted in an aromatic ring which is fully substituted. This taken with its only ^1H NMR absorption, a singlet at $\delta 2.66$, suggests that compound **2** is a tribromomethyl-nitrophenol. The sign of the polarisation indicates that it is formed by recombination within radical pair A (an S precursor⁴). The inclusion of the 2,4-dienone intermediate in

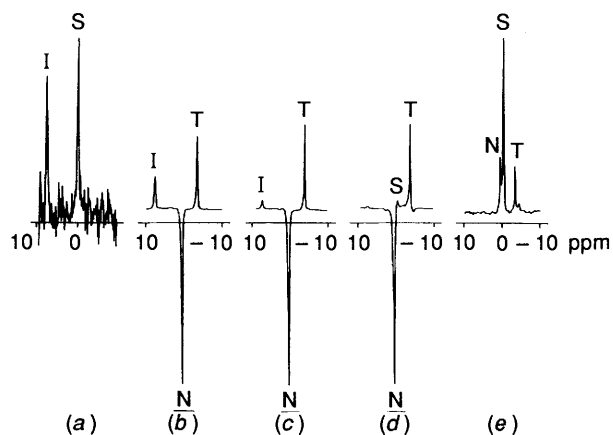
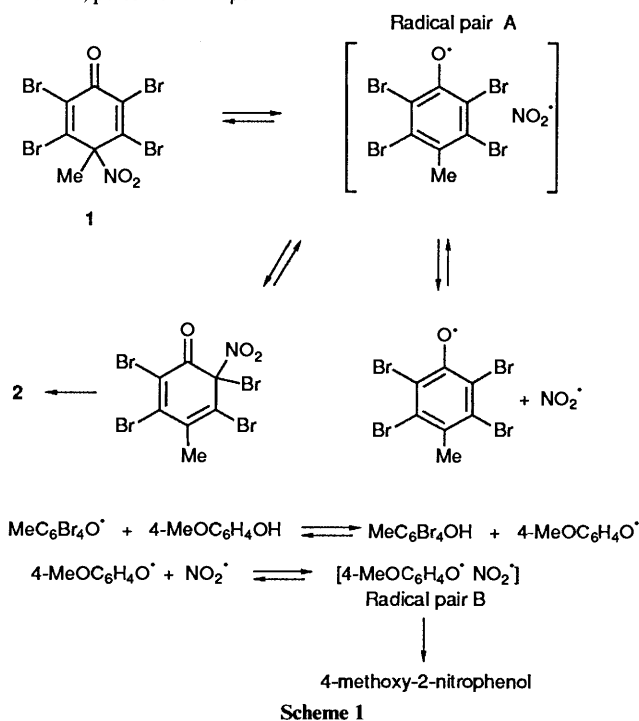


Fig. 1 ^{15}N NMR spectra taken during the nitration of 4-methoxyphenol by the ^{15}N -labelled dienone (**1**) under the conditions described in the text: (a) before addition of the 4-methoxyphenol solution; (b) 7–11 min after addition; (c) 12–16 min after addition; (d) 17–21 min after addition; (e) at the end of reaction. Peaks: S, standard ($\text{Ph}^{15}\text{NO}_2$); I, the cyclohexadienone (**1**); N, 4-methoxy-2-nitrophenol; T, compound **2** (see text). The spectra involved 24 pulses [(e), 4321 pulses], pulse repetition time 10 s, pulse width 20 μs .



Scheme 1 is discussed below. The persistence of the polarisation of **2** over that of **1** is due to the fact that **1**, a reactant, is disappearing and **2**, a product, is being formed.

† Present address.

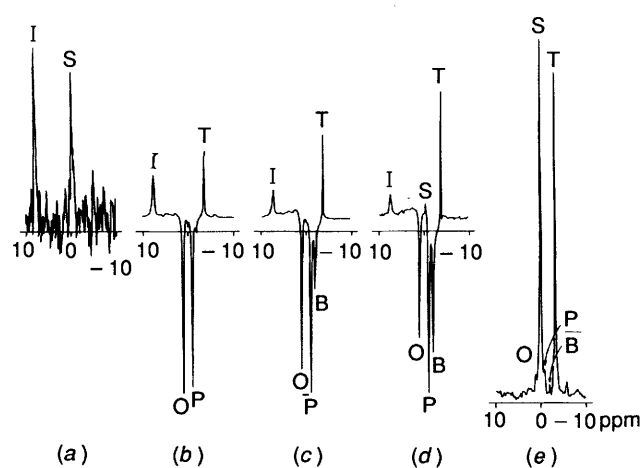


Fig. 2 ^{15}N NMR spectra taken during the reaction of phenol with the ^{15}N -labelled dienone (**1**) under the conditions described in the text: (a) before addition of the phenol solution; (b) 4–8 min after addition; (c) 9–13 min after addition; (d) 14–18 min after addition; (e) at the end of the reaction. Peaks: S, I, T as in Fig. 1; O, 2-nitrophenol; P, 4-nitrophenol; B, 4-bromo-2-nitrophenol. Spectral parameters as in Fig. 1 except that (e) involved 4223 pulses.

Treatment of phenol under similar conditions to the above, however, gave a different result. The major products of the reaction were 4-bromophenol (40%) with compound **2** (75%). 2-Bromophenol was not positively identified and if present was there to the extent of less than 4%. Nitrophenols [2- (ca. 5%) and 4- (ca. 7%)] and 4-bromo-2-nitrophenol (ca. 4%) could be detected by ^1H and ^{15}N NMR spectroscopy together with 2,3,5,6-tetrabromo-4-methylphenol (25%). A series of ^{15}N NMR spectra taken during a reaction is shown in Fig. 2 and comparisons of signal magnitude can be made as previously. Compound **1** exhibits enhanced absorption in spectra (b), (c) and (d) and strong emission signals are given by 2- and 4-nitrophenols in spectra (b), (c) and (d) with a maximum enhancement factor of ca. 2000. 2-Nitro-4-bromophenol is also formed in emission with a maximum enhancement factor of ca. 600. It is, however, hardly seen in spectrum (b) but increases relative to the nitrophenols in (c) and (d), presumably as 4-bromophenol is formed. Compound **2** is formed with enhanced absorption and a maximum enhancement of ca. 100.

The signs of the polarisations of 1, 2- and 4-nitrophenols and

4-bromo-2-nitrophenol are consistent with the nitro products being formed as expected by mechanisms similar to that in Scheme 1. In this reaction, however, the major pathway is the formation of compound **2**, with enhanced absorption, by recombination of radicals within radical pair A and associated bromination of phenol to give mainly 4-bromophenol. It is reasonable to suggest that 2,3,5,6-tetrabromo-4-methyl-6-nitrocyclohexa-2,4-dienone is a reversibly formed intermediate in the formation of compound **2** and 4-bromophenol. 2,4,4,6-Tetrabromocyclohexa-2,5-dienone is known⁵ to brominate phenol selectively at the 4-position in acetonitrile solution. The reversibility of the 2,4-dienone formation is necessary to explain the fact that the nature of the main products formed depends upon the substrate. Bromination of phenol by the 2,4-dienone must be faster than bromination of 4-methoxyphenol. If 2,3,5,6-tetrabromo-4-methyl-6-nitrocyclohexa-2,4-dienone is the brominating agent arguments concerning regioselectivity due to donor-acceptor and hydrogen bonding interactions used in related systems⁶ are not applicable here.

We conclude that **1** can act as both a nitrating agent and, after rearrangement, as a brominating agent towards phenols and that the balance between the two pathways depends upon the substrate and the solvent.

Acknowledgements

Discussions with Professor J. H. Ridd are gratefully acknowledged.

References

- 1 R. G. Coombes and J. H. Ridd, *J. Chem. Soc., Chem. Commun.*, 1992, 174.
- 2 M. Lemaire, A. Guy, J. Roussel and J.-P. Guetté, *Tetrahedron*, 1987, **43**, 835.
- 3 R. Kaptein, *J. Chem. Soc., Chem. Commun.*, 1971, 732.
- 4 R. Kaptein, *J. Am. Chem. Soc.*, 1972, **94**, 6251.
- 5 V. Calò, F. Ciminale, L. Lopez, G. Pesce and P. E. Todesco, *Chim. Ind. (Milan)*, 1971, **53**, 467.
- 6 A. Guy, M. Lemaire and J.-P. Guetté, *J. Chem. Soc., Chem. Commun.*, 1980, 8; *Tetrahedron*, 1982, **38**, 2339.

Paper 2/02114E

Received 24th April 1992

Accepted 19th May 1992