Review Article

Reactions of Substituted Phenols with Nitrogen Dioxide;* Rearrangements and Addition Reactions of Nitrodienones

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

In this review are discussed the immediate products of the radical coupling of phenoxy radicals with nitrogen dioxide, namely 4-nitrocyclohexa-2,5-dienones and 6-nitrocyclohexa-2,4-dienones. The rearrangements of these nitrodienones are diverse and include (a) the interconversion of 4-nitrocyclohexa-2,5-dienones and 6-nitrocyclohexa-2,4-dienones, (b) the [1,5]-sigmatropic nitro shift in 6-methyl-6-nitrocyclohexa-2,4-dienones with no substituents at C2, (c) the nitro–nitrito interconversion of 4-nitro(nitrito)-cyclohexa-2,5-dienones and 6-nitro-cyclohexa-2,4-dienones and (d) the rearrangements of 4-nitrocyclohexa-2,5-dienones in the presence of phenols. Finally, the reactions of 4-nitrocyclohexa-2,5-dienones and 6-nitrocyclohexa-2,4-dienones with nitrogen dioxide are discussed.

The reactions of phenols with nitrogen dioxide have a venerable history,[1] but only in the last decade have many of the features of these reactions become clear. However, crucial gaps in our understanding remain and some of these will be highlighted in the following account.

The commonly written description of the reaction of a phenol with nitrogen dioxide is given in Scheme 1.[2] In this reaction scheme the first step is seen as phenolic hydrogen abstraction by nitrogen dioxide to give in an equilibrium the corresponding phenoxy radical and nitrous acid. Subsequent radical coupling of a second molecule of nitrogen dioxide with this phenoxy radical then yields the immediate reaction product(s). For 2,6-di-*tert*-butyl-4-methylphenol (1) as the substrate, nitrous acid and the corresponding phenoxy radical were detected during the formation of 2,6-di-*tert*-butyl-4-

methyl-4-nitrocyclohexa-2,5-dienone (2);[3] earlier this product 2 had been shown to arise from the radical coupling of nitrogen dioxide with the phenoxy radical.[4]
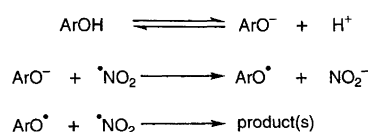

1   2
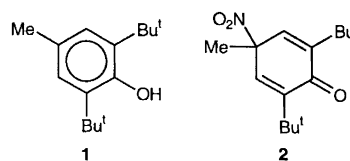
Although it is established that nitrous acid and the phenoxy radical are formed in the reaction sequence, it appears less certain that this reaction involves direct phenolic hydrogen abstraction by nitrogen dioxide. One clear alternative which includes electron transfer from the phenoxide ion to nitrogen dioxide is presented in Scheme 2.

$$ArOH + \cdot NO_2 \rightleftharpoons ArO\cdot + HNO_2$$

$$ArO\cdot + \cdot NO_2 \longrightarrow product(s)$$

Scheme 1.

* Throughout this review we will write nitrogen dioxide as NO_2, although the equilibrium mixture of nitrogen dioxide and dinitrogen tetraoxide is the actual source of NO_2.

$$ArOH \rightleftharpoons ArO^- + H^+$$

$$ArO^- + \cdot NO_2 \longrightarrow ArO\cdot + NO_2^-$$

$$ArO\cdot + \cdot NO_2 \longrightarrow product(s)$$

Scheme 2.

The immediate products of the radical coupling of phenoxy radicals with nitrogen dioxide

The study of the immediate products of radical coupling of phenoxy radicals with nitrogen dioxide is complicated by the marked lability of some of those products. For example, reaction of 2,4-dimethylphenol (3) with nitrogen dioxide in [²H]-chloroform at −60 °C gives 2,4-dimethyl-4-nitrocyclohexa-2,5-dienone (4) (40%), 4,6-dimethyl-6-nitrocyclohexa-2,4-dienone (5) (36%) and 2,4-dimethyl-6-nitrophenol (6) (24%).[5] At −40 °C the 2,4-dienone 5 rearranges rapidly (<45 min) to give the 2,5-dienone 4 (55%) and the nitrophenol 6 (45%), and at ambient temperatures the 2,5-dienone 4 rearranges over 1 h to give the nitrophenol 6.[5] Although not demonstrated directly, nitrophenol 6 undoubtedly arises by keto–enol tautomerism of 2,4-dimethyl-6-nitrocyclohexa-2,4-dienone (7); such tautomerism was seen to occur at −60 °C in the conversion of 2,5-dimethyl-6-nitrocyclohexa-2,4-dienone (8) into the corresponding nitrophenol (9).[5] The 1,3-nitro migrations above, 5→4, 4→7, presumably occur via a homolytic dissociation–recombination mechanism,[6] discussed below.


3　4　5

6　7　8

9
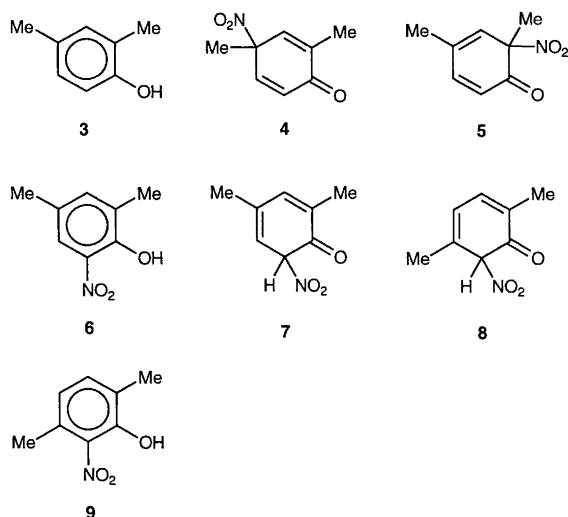
A selection of the results of low temperature (−60 °C) reactions in [²H]-chloroform of nitrogen dioxide with substituted phenols is presented in Table 1.[5,7] These results indicate the diversity in the regiochemistry of the radical coupling of nitrogen dioxide with phenoxy radicals, which is clearly dependent on the nature and pattern of the substituents present. For example, with the increasing size of the 4-substituent, 4-Me → 4-Buᵗ and 4-F → 4-I, coupling of nitrogen dioxide at C4 reduces progressively with a corresponding increase in C2-coupling. The presence of C4-substituents, CN, CHO, CO₂Et and NO₂, leads to exclusive attack of nitrogen dioxide at C2(6). Generally 2-methylphenoxy radicals react with nitrogen dioxide both *ipso* to the 2-methyl group and at C4, and frequently also at C6 in the 2-methylphenoxy radical.[7]

Given the possible complexity of the immediate prod-

10　11　12　13

14　15　16
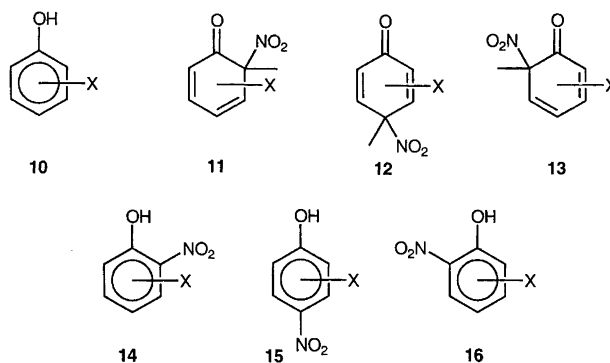
uct mixture, and the potential for their rearrangement to more stable products to be rate-limiting in the reactions of phenols with nitrogen dioxide, it is perhaps not surprising that kinetic studies of the phenol/nitrogen dioxide system are fraught with difficulties.[2,8,9] Indeed, for the reactions of the 2,4,6-trialkylphenols 17 it appears that the reaction rate measured was probably that of the isomerization of 6-nitrocyclohexa-2,4-dienones (18) into 4-nitrocyclohexa-2,5-dienones (19),[2] and for 4-methylphenol (20) the enolization of the 6-nitrocyclohexa-2,4-dienone 21 to give the nitrophenol 22 may become at least partially rate-limiting under some circumstances.[9]

17 a R₁ = Buᵗ, R₂ = Me　18　19
b R₁ = R₂ = Me
c R₁ = R₂ = Buᵗ


20　21　22
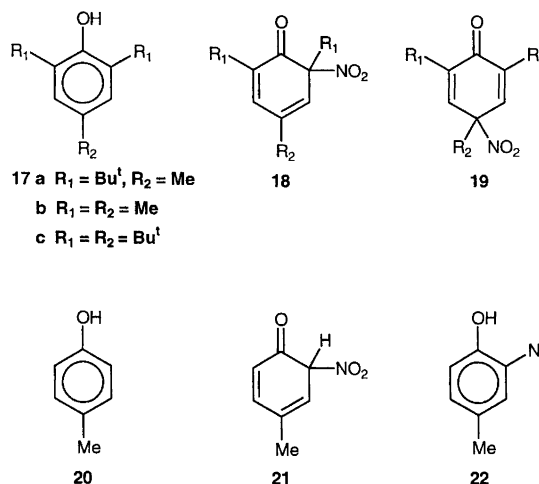
The rearrangements of nitrodienones

The rearrangements of nitrodienones fall into four clear classes of reaction: (a) the interconversion of 4-nitrocyclohexa-2,5-dienones and 6-nitrocyclohexa-2,4-dienones, (b) the [1,5]-sigmatropic nitro shift in 6-methyl-6-nitrocyclohexa-2,4-dienones with no substituents at C2, (c) nitro–nitrito interconversion of 4-nitro(nitrito)-cyclohexa-2,5-dienones and 6-nitrocyclohexa-2,4-dienones and (d) rearrangements of 4-nitrocyclohexa-2,5-dienones in the presence of phenols.

(a) *The interconversion of 4-nitrocyclohexa-2,5-dienones and 6-nitrocyclohexa-2,4-dienones.* The aromatization of

Table 1. Yields of products of reaction of nitrogen dioxide with substituted phenols 10 in [^{2}H]-chloroform at $-60\,^\circ$C.[5,7]

	Products						
	Nitrodienones			Nitrophenols			
10	11	12	13	14	15	16	Other
3-Bu^t	24	40	—	—	—	36	—
4-Me	—	43	—	57	—	—	—
4-Et	—	37	—	63	—	—	—
4-Pr^i	—	25	—	75	—	—	—
4-Bu^t	—	18	—	82	—	—	—
2,3-Me$_2$	22	31	—	—	16	18	13
2,4-Me$_2$	36	40	—	—	—	24	—
2,5-Me$_2$	24	42	10	—	7	4	13
2,6-Me$_2$	52	37	—	—	11	—	—
3,4-Me$_2$	—	52	—	16	—	32	—
3,5-Me$_2$	—	8	—	54	23	—	15
2-Bu^t-5-Me	—	31	31	—	18	—	20
2,4-Bu$^t_2$	—	33	48	—	—	19	—
2,6-Bu$^t_2$	47	53	—	—	—	—	—
3,5-Bu$^t_2$	65	35	—	—	—	—	—
2,3,5-Me$_3$	31	32	Trace	—	11	26	—
2,3,6-Me$_3$	26	44	30	—	—	—	—
2,4,5-Me$_3$	26	26	24	—	—	24	—
2,4,6-Me$_3$	50^a	50^a	—	—	—	—	—
3,4,5-Me$_3$	—	55	—	45	—	—	—
2,3,5,6-Me$_4$	52	48	—	—	—	—	—
2,3,4,5,6-Me$_5$	52	48	—	—	—	—	—
4-F	—	39	—	61	—	—	—
4-Cl	—	34	—	66	—	—	—
4-Br	—	28	—	72	—	—	—
4-I	—	—	—	95	—	—	5
4-CN	—	—	—	100	—	—	—
4-CHO	—	—	—	100	—	—	—
4-CO$_2$Et	—	—	—	100	—	—	—
4-Ph	—	34	—	66	—	—	—
4-NO$_2$	—	—	—	100	—	—	—
2,6-Br$_2$	—	—	—	—	100	—	—
2,6-Cl$_2$	—	—	—	—	100	—	—
2,6-Me$_2$-4-NO$_2$	100	—	—	—	—	—	—

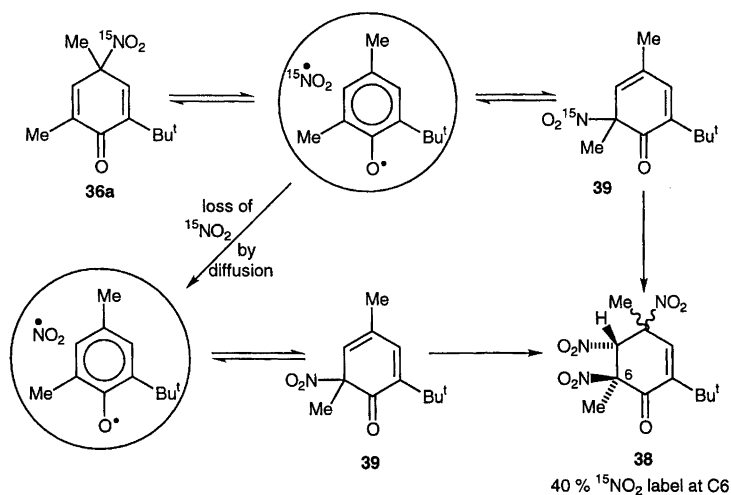^{a}A ratio 11:12 of 55:45 has also been reported.[2]
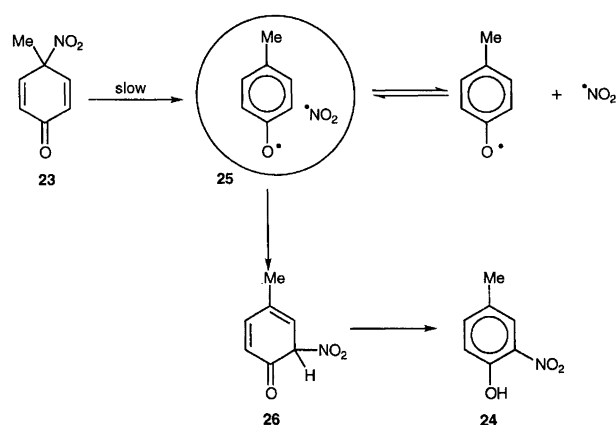
Scheme 3.

Scheme 4.

4-methyl-4-nitrocyclohexa-2,5-dienone (23) with a 1,3-shift of the nitro group to give 4-methyl-2-nitrophenol (24) has been shown to occur via a homolytic dissociation–recombination mechanism (Scheme 3).[6] The initial
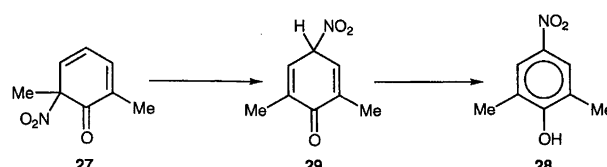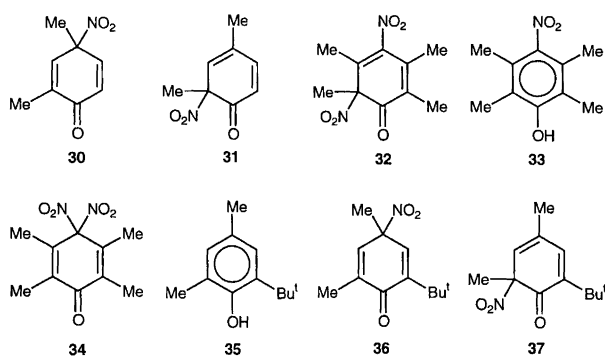
dissociation to give the nitrogen dioxide/phenoxy radical pair within the solvent cage 25 was rate-limiting, and labelling studies demonstrated that the rate of recombination of this radical pair to form the isomeric 6-nitrocyclohexa-2,4-dienone (26) was comparable with the rate of diffusion of the radical pair from the solvent cage. Enolization of this 6-nitrocyclohexa-2,4-dienone 26 to give the 2-nitrophenol 24 is the final irreversible process. Although detailed mechanistic studies were not possible because of the lability of the reactants, it seems certain that the rearrangement of 2,6-dimethyl-6-nitrocyclohexa-2,4-dienone (27) to give 2,6-dimethyl-4-nitrophenol (28)

36a

loss of
$^{15}NO_2$
by
diffusion

39

39

38
40 % $^{15}NO_2$ label at C6

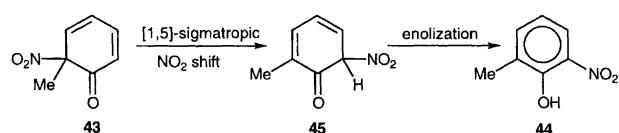*Scheme 5.*

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32

33

34

35

36

37

41

42

40

Scheme 6.

(Scheme 4) also proceeds by a homolytic dissociation–recombination mechanism to give the 4-nitrocyclohexa-2,5-dienone 29; the tautomerization 29 → 28 was demonstrated separately.[5]

The formation of 2,4-dimethyl-4-nitrocyclohexa-2,5-dienone (30) as one of the products of rearrangement of 4,6-dimethyl-6-nitrocyclohexa-2,4-dienone (31)[5] is a clear indication of the greater thermodynamic stability of 4-nitrocyclohexa-2,5-dienones over the corresponding 6-nitrocyclohexa-2,4-dienones when the system is not biased by differences in the nature of the substituents present at C4 and C6. In contrast, 2,3,5,6-tetramethyl-4,6-dinitrocyclohexa-2,4-dienone (32) is the only nitro dienone isolable from nitration of 2,3,5,6-tetramethyl-4-nitrophenol (33),[10] indicating the destabilizing effect of a *gem*-dinitro functionality at C4 in the dinitrocyclohexa-2,5-dienone 34.

Brief treatment of 2-*tert*-butyl-4,6-dimethylphenol (35) with nitrogen dioxide in benzene or nitric acid in acetic acid yields the thermodynamically more stable 2-*tert*-butyl-4,6-dimethyl-4-nitrocyclohexa-2,5-dienone 36, but further reaction of this nitrodienone 36 with nitrogen dioxide proceeds only after its rearrangement to the regioisomeric 6-nitrocyclohexa-2,4-dienone 37. Reaction of the ^{15}N-labelled nitro dienone 36a with excess nitrogen dioxide in benzene gave the epimeric 2-*tert*-butyl-4,6-

dimethyl-4,5,6-trinitrocyclohex-2-enones 38, in which the ^{15}N-label (ca. 40%) was located only at C6.[11] This pattern and extent of ^{15}N-labelling was rationalized in terms of Scheme 5, which involves a homolytic dissociation–recombination sequence with partial exchange of the [^{15}N] nitrogen dioxide with the excess of unlabelled nitrogen dioxide in the system. 4,5-Addition of nitrogen dioxide to the partially labelled 2-*tert*-butyl-4,6-dimethyl-6-nitrocyclohexa-2,4-dienone 39 completed the formation of the trinitro ketones 38. The implication of this observation is that even in such a substituent-unbiased system the thermodynamically less stable nitrodienone 37 may be accessible for further reaction via the homolytic dissociation–recombination rearrangement mechanism. Even more dramatically ^{15}N-labelling studies demonstrated that the formation of the trinitro ketone 40 on reaction of the 4-nitrocyclohexa-2,5-dienone 41 with nitrogen dioxide proceeded via the homolytic dissociation–recombination mechanism to give the sterically compressed 6-nitrocyclohexa-2,4-dienone 42 (Scheme 6); 4,5-addition of nitrogen dioxide to 42 gave trinitro ketone 40.[12]

(b) *The [1,5]-sigmatropic nitro shift in 6-methyl-6-nitrocyclohexa-2,4-dienones with no substituents at C2.* At −20 °C in [^{2}H]-chloroform 6-methyl-6-nitrocyclohexa-2,4-dienone (43) rearranges regiospecifically to give 6-methyl-2-nitrophenol (44),[5] presumably via enolization of the intermediate 2-methyl-6-nitrocyclohexa-2,4-dienone 45 (Scheme 7). A similar rearrangement is seen in the conversion of 5,6-dimethyl-6-nitrocyclohexa-2,4-

Scheme 7.
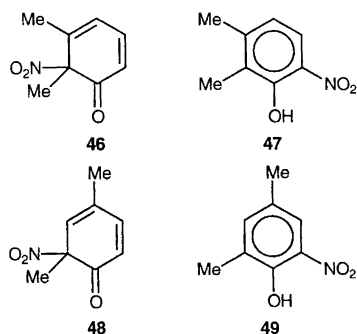
dienone (46) into 2-nitro-5,6-dimethylphenol (47), and as one reaction pathway for the rearrangement of 4,6-dimethyl-6-nitrocyclohexa-2,4-dienone (48) to give the nitrophenol 49.[5] These rearrangements were seen as being analogous to the rearrangements of nitrodienes 50 and 51 to give products 52 and 53 respectively in which the migration of the nitro group occurred both regio- and stereo-specifically (Scheme 8).[13] Given that these latter reactions were thermal and not photochemical reactions, they were seen as involving [1,5]-sigmatropic nitro shifts. By analogy, the rearrangements of nitrodienones 43, 46 and 48 to nitrophenols 44, 47 and 49, respectively, were also described as [1,5]-sigmatropic nitro shifts, followed by enolization.[5]
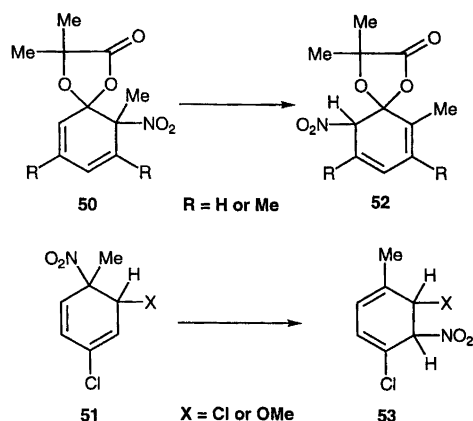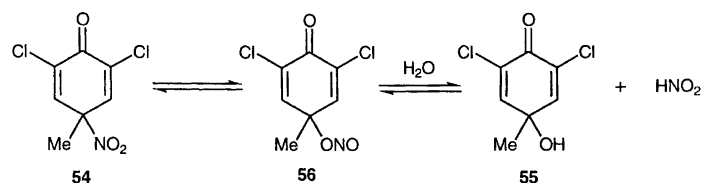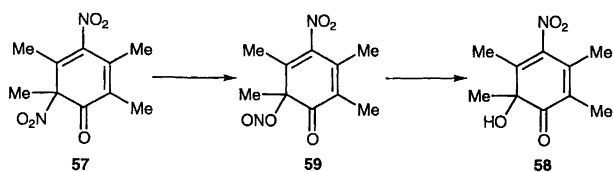

Scheme 8.

(c) *Nitro–nitrito interconversion of 4-nitro(nitrito)-cyclo-hexa-2,5-dienones and 6-nitrocyclohexa-2,4-dienones.* Although the nitration of 2,6-dichloro-4-methylphenol had long been known to yield either the 4-nitrodienone 54 or the 4-hydroxydienone 55 depending on the reaction conditions,[14] it was only in 1986 that Ridd *et al.* provided direct evidence for the nitro–nitrito rearrangement equilibrium (Scheme 9).[15] In this equilibrium the concentrations of the nitrodienone 54 and the nitritodienone 56 are similar (ca. 45:55). The system is unstable, and in the presence of aqueous acid, is converted rapidly into the hydroxydienone 55. Consistent with these observations was the conversion of the 6-nitrodienone 57 into the 6-hydroxydienone 58 via an unstable intermediate on bubbling nitrogen through a solution of 57 in chloroform; this unstable intermediate was undoubtedly the 6-nitrito-dienone 59 (Scheme 10).[10] In the reverse sense, reaction of 4-hydroxydienone 60 with nitrogen dioxide in benzene solution resulted in extensive conversion (>80%) into 4-nitrodienone 61, and reaction of 4-hydroxy-4-methyl-2,6-diphenylcyclohexa-2,5-dienone (62) with excess nitrogen dioxide in benzene resulted in the formation of addition products which could have arisen only by addition of nitrogen dioxide to an intermediate 4-nitro-dienone 63.[16]

In the reactions of a series of polysubstituted phenols 64 with nitrogen dioxide in benzene to give either trinitro ketones and/or 6-hydroxy dinitro ketones, the addition of nitrogen dioxide occurs to the diene system of 6-nitrocyclohexa-2,4-dienones 65 and/or to 6-hydroxy-cyclohexa-2,4-dienones 66. In the present context, it is of interest to note the effect of substituents on the ring system on the reaction pathway(s) followed. For penta-methylphenol (64a) trinitro ketones are formed exclusively by further reaction of the 6-nitro ketone 65a,[17] for 2,3,5,6-tetramethyl-4-nitrophenol 64b via addition to both 6-nitro- 65b and 6-hydroxy- 66b ketones (ratio 55:30),[10] and for 2,6-dimethyl-4-nitrophenol (64c) exclusively via 6-hydroxy ketone 66c.[18] Although it is uncertain whether the 6-nitrito ketone 67 is formed directly by radical coupling of nitrogen dioxide at C6 of the corresponding phenoxy radical with C–ONO bond formation, or by nitro–nitrito rearrangement of an initially formed 6-nitro ketone 64, it is clear that the electron-withdrawing nitro group at C4 promotes C–O bond formation by whatever route, but methyl groups encourage C–N bond formation.

(d) *Rearrangements of 4-nitrocyclohexa-2,5-dienones in the presence of phenols.* The rearrangement of the tetra-


Scheme 9.

Scheme 10.

64 X = Y = Me
X = Me, Y = NO$_2$
X = H, Y = NO$_2$

65

66

67

chloro nitrodienone **68** in benzene at 20 °C proceeds by a homolytic dissociation–recombination mechanism to give the 1,2-benzoquinone **69** and the 4-hydroxydienone **70** (ratio ca. 2 : 1) (Scheme 11).[19] The mode of formation of the 6-nitritodienone **71** is uncertain, but the loss of the elements of NOCl from **71** would yield the 1,2-benzoquinone **69**. In the presence of 2,3,5,6-tetrachloro-4-methylphenol (**72**) the yield of 1,2-benzoquinone (**69**) was much reduced, some 4-hydroxydienone (**70**) was formed, but the major products isolated were recovered phenol (**72**) and the nitromethylphenol **73**. The formation of **73** can be accounted for in terms of Scheme 12, in


60

61

62

63
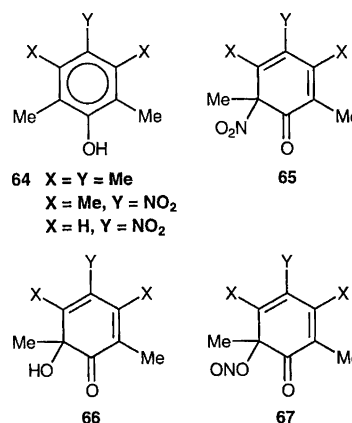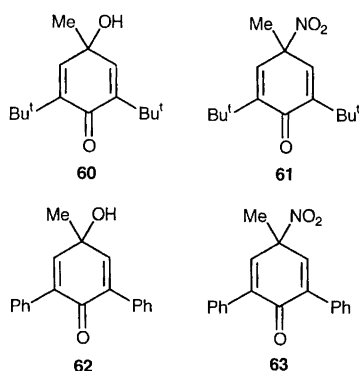
which the crucial reaction step is hydrogen atom transfer from the methyl group to the phenoxy oxygen atom.

The rearrangement of either tetrachloro nitrodienone (**68**) and 3,5-dibromo-2,4,6-trimethylphenol (**74**), or 3,5-dibromo-2,4,6-trimethyl-4-nitrocyclohexa-2,5-dienone (**75**) and tetrachlorophenol (**72**), yielded essentially the same product mixture, namely the tetrachlorophenol **72** and dibromo derivatives **76–78**.[19] These observations can be rationalized in terms of the establishment of a common equilibrium from the two reagent systems (Scheme 13).

The rearrangements of 4-nitrodienones in the presence of phenols[19] had clear implications for the nitration of phenols and amines using 4-nitrodienones under mild conditions. Subsequently such reactions were reported for phenols and naphthols with a variety of 4-nitro-cyclohexa-2,5-dienones.[20] Notwithstanding the well established homolytic reaction pathways in the literature, these authors[20] chose to regard the 4-nitrocyclohexa-2,5-
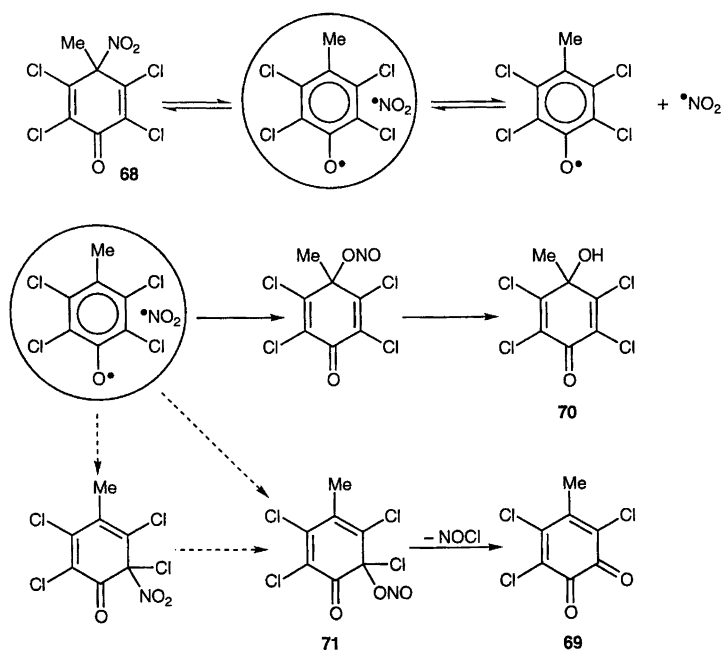
Scheme 11.
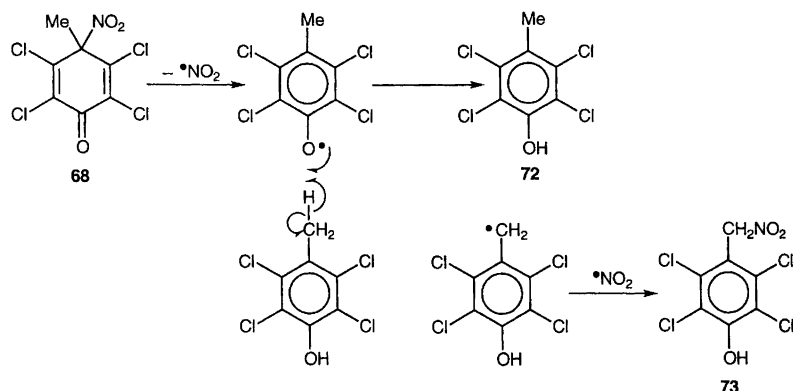
Scheme 12.
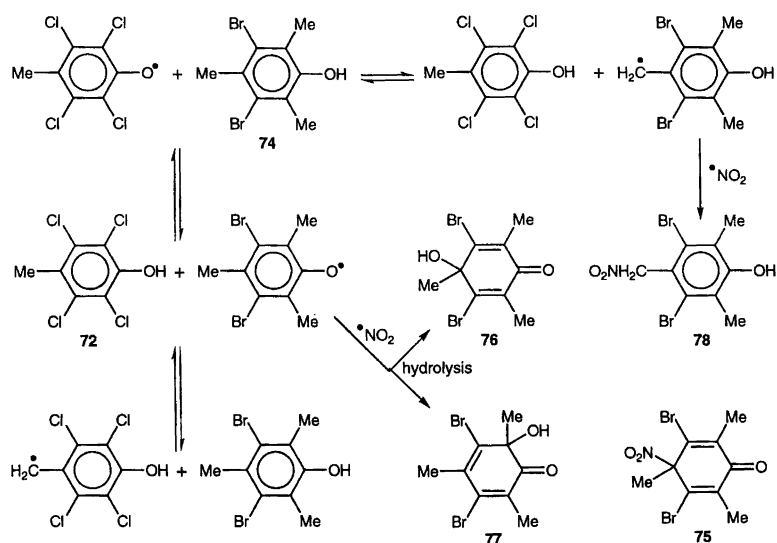
Scheme 13.

dienones as being a source of nitronium ions. Other authors[21] suggested that the nitration reactions involved ion pairs or a synchronous transfer of the nitro group and a hydrogen atom within a hydrogen-bonded complex formed by the reactants. Finally in 1992 Coombes and Ridd[22] using CIDNP experiments demonstrated that the nitration of phenols by 4-nitrocyclohexa-2,5-dienones did proceed by a homolytic mechanism, as proposed earlier.[6,19]

The reactions of nitrodienones with nitrogen dioxide

The reactions of nitrodienones with nitrogen dioxide involve the stepwise radical addition of nitrogen dioxide to the alkene component of the dienone. For this reason it is not surprising that 6-nitrocyclohexa-2,4-dienones, containing a buta-1,3-diene system, undergo these reactions more readily than 4-nitrocyclohexa-2,5-dienones; indeed, the latter compounds react directly with nitrogen dioxide only in special structural circumstances. The study of the addition reactions of nitrogen dioxide to 6-
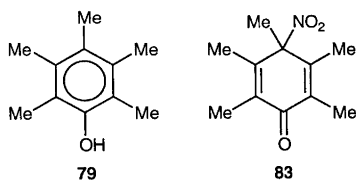
nitrocyclohexa-2,4-dienones is complicated by the fact that these compounds are thermodynamically less stable than the corresponding 4-nitrocyclohexa-2,5-dienones. Thus, 6-nitrocyclohexa-2,4-dienones are transient intermediates and the nature of their addition reactions with nitrogen dioxide can be inferred from: (a) some reactions of polysubstituted phenols with excess nitrogen dioxide in which any 6-nitrocyclohexa-2,4-dienone formed would react with further nitrogen dioxide, and (b) analogy with the reactions of 6-hydroxycyclohexa-2,4-dienones with nitrogen dioxide.

(a) *Some reactions of polysubstituted phenols with excess nitrogen dioxide.* Reaction of pentamethylphenol (79) with excess nitrogen dioxide in benzene gives the four 2,5,6-trinitrocyclohex-3-enones 80, three of the four 4,5,6-trinitrocyclohex-2-enones 81, 2-hydroxy-5,6-dinitrocyclohex-3-enone (82) and the 4-nitrocyclohexa-2,5-dienone 83.[17] Notably the 4-nitrodienone 83 does not react with nitrogen dioxide in benzene, and products 80–82 must therefore arise by further reaction of the

6-nitrodienone **84** with nitrogen dioxide; the suggested reaction pathways are given in Scheme 14.[17]
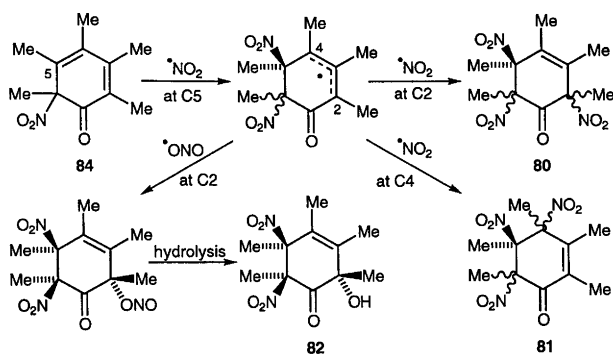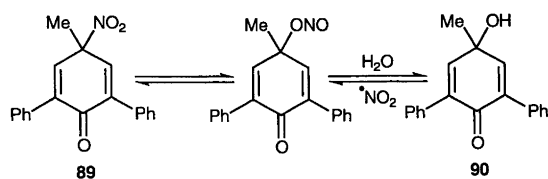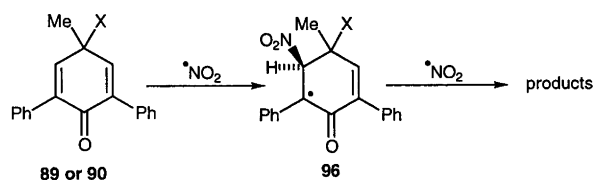

Scheme 14.

Characteristically, the addition of nitrogen dioxide is initiated by attack of nitrogen dioxide at C5 in a 6-nitrocyclohexa-2,4-dienone **85** to give a delocalized carbon radical **86** which may be attacked by a second molecule of nitrogen dioxide at either C2 or C4, dependent on the nature of the substituents R_1 and R_2
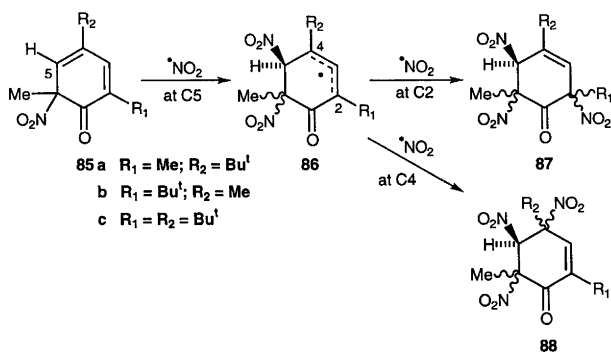

Scheme 15.

Scheme 16.

Scheme 17.

(Scheme 15). For example, in **85a** with a bulky *tert*-butyl substituent at C4, 2,5,6-trinitrocyclohex-3-enones **87a** are the major products,[23] but when the C2-and C4- substituents are interchanged in **85b** 4,5,6-trinitrocyclohex-2-enones **88** are formed.[24] For **85c**, where the C2-and C4-substituents are *tert*-butyl groups, largely 2,5,6-trinitro-cyclohex-3-enones **87c** are formed together with the corresponding 2-hydroxy-5,6-dinitrocyclohex-3-enones.[24] These reaction sequences have been supported the results of reactions ^{15}N-labelled 4-nitrocyclohexa-2,5-dienones with nitrogen dioxide.[11,25]

Only for 4-methyl-4-nitro-2,6-diphenylcyclohexa-2,5-dienone (**89**) and its corresponding 4-hydroxydienone **90** does nitrogen dioxide undergo 2,3-addition to a cross-conjugated dienone system.[16] For these systems **89** and **90** the outcome of the addition of nitrogen dioxide is complicated by the fact that the equilibrium given in Scheme 16 is established during the nitrogen dioxide addition process. Accordingly, in different yields depending on the reactant **89** or **90** used, the same group of five products **91–95** are formed.[16] The initial addition of nitrogen dioxide at C3 in either **89** or **90** would give the benzylic radical **96**; it appears likely that 2,3-addition of nitrogen dioxide to 4-nitrocyclohexa-2,5-dienones the stabilization of the intermediate radical as provided by the phenyl group in **96** (Scheme 17).

(b) *The reactions of 6-hydroxycyclohexa-2,4-dienones with nitrogen dioxide.* The addition of nitrogen dioxide to the 6-hydroxycyclohexa-2,4-dienones **97** occurs via *syn*-addition of nitrogen dioxide at C5, followed by attack of a second molecule of nitrogen dioxide at C2.

97 a R = Br
   b R = Me

98

99

100

101

102
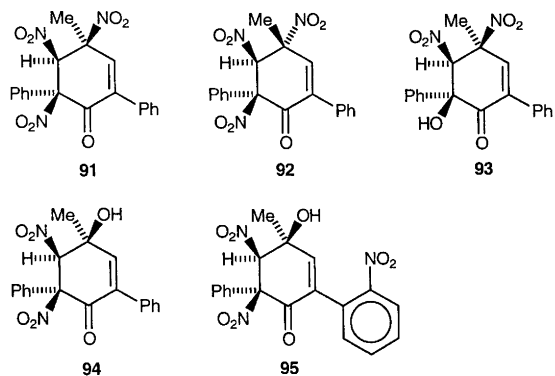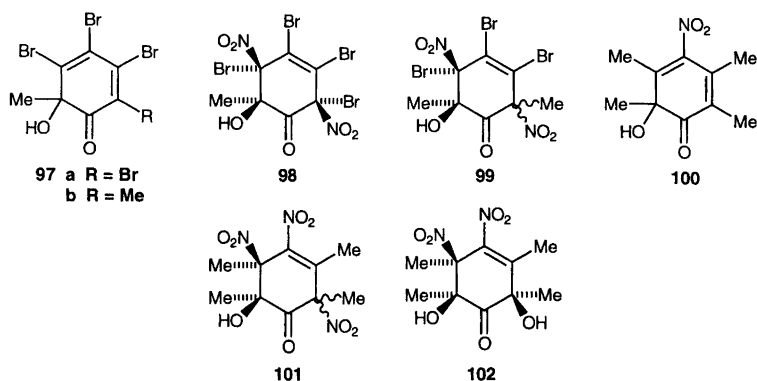
For the tetrabromodienone **97a** only the *cis*-2,5-dinitro compound **98** was formed,[26] but hydroxydienone **97b** gave the epimeric pair **99**.[27] Similarly, reaction of the 6-hydroxydienone **100** with nitrogen dioxide gave exclusively compounds **101** and **102**, each of which contains the *cis*-6-hydroxy-5-nitro system.[10]

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