IPSO-NITRATION STUDIES

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ABSTRACT

Reaction of pentamethylphenol (19) with nitrogen dioxide in benzene gives the 4-nitrodienone (21), the four isomeric 2,5,6,-trinitrocyclohex-3-enones (23-26), three isomeric 4,5,6-trinitrocyclohex-2-enones (32),(33),[(34) or (35)] and a 2-hydroxy-5,6-dinitrocyclohex-3-enone (36). Nitration of pentamethylphenol (19) with fuming nitric acid in dichloromethane, in contrast, gives no 4-nitrodienone (21) but yields instead the 4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (49-52), in addition to compounds (23),(24),(26),(32) and (36). The 4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (49-52) are formed via the quinonemethide (56).

Reaction of 4-nitrodurenol (58) with nitrogen dioxide in benzene gives the four isomeric 2,4,5,6-tetranitrocyclohex-3-enones (67-70) and hydroxynitrocyclohex-3-enones (71-73) and (77). The mode of formation of the 6-hydroxy ketones (72),(73) and (77) was demonstrated by addition of nitrogen dioxide to the 6-hydroxycyclohexa-2,4-dienone (66). The mode of formation of the above compounds and the acyloin rearrangement products (74-76) are discussed.

Nitration of 4,6-dibromo-2-phenylphenol (105a) and 4-bromo-6-methyl-2-phenylphenol (106a) with fuming nitric acid in acetic acid, results in extensive nitro-debromination. The fuming nitric acid nitration of 6-methyl-4-nitro-2-phenylphenol (106c) gives complex mixtures, but reaction with nitrogen dioxide gives only six compounds, two of which (114,115) were isolated from the reaction mixture. The remaining four compounds (116),(121-123) were identified tentatively by

spectroscopic methods. The mode of formation of compounds (114-116) and (121-123) are discussed.

Reaction of 4-methyl-2,6-diphenylphenol (125) with nitrogen dioxide in benzene gives a complex mixture, from which the cyclohex-2-enones (126-131) were isolated. The mode of formation of these compounds is discussed.

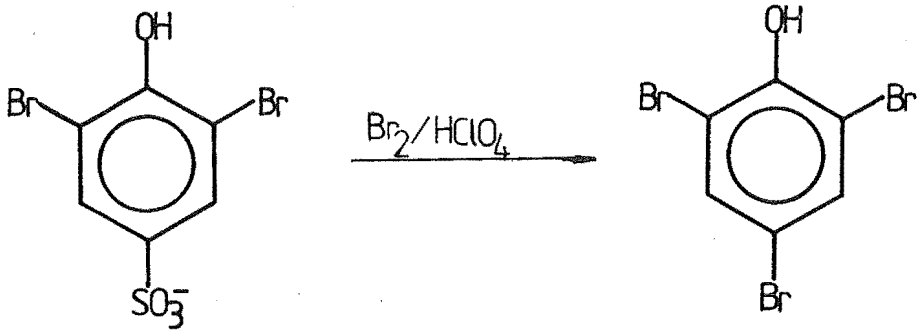
In the above reaction studies, the structures of products were assigned on the basis of their spectroscopic data and single-crystal X-ray analyses of selected compounds. X-ray crystal structures are reported for twenty compounds viz. (23),(24),(25),(32),(33),(36),(49),(67),(68),(71),(72),(74), (77),(114),(115),(126),(127),(128),(130) and (131).

CHAPTER ONE

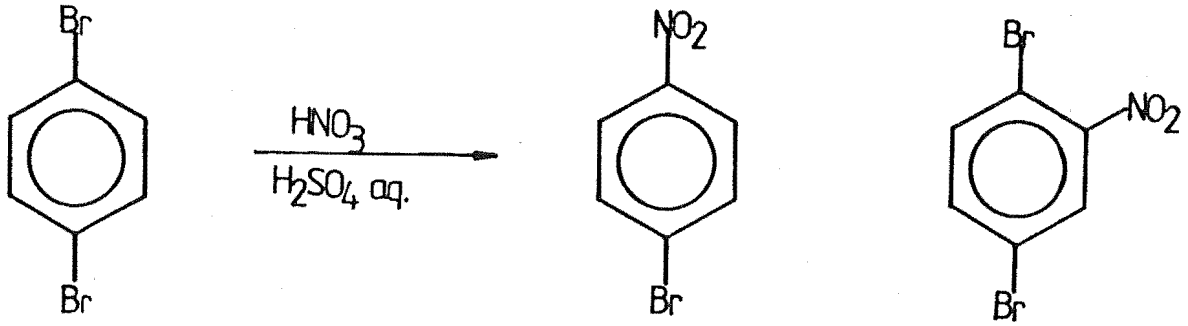
GENERAL INTRODUCTION

1.1 BACKGROUND

The prefix "ipso" was first introduced by Perrin and Skinner[1] to denote attack by a reagent at a substituted position on a benzene ring. This phenomonen has long been known from one of its consequences (ipso substitution) in many electrophilic reactions. For example, the bromination of the 3,5-dibromo-4-hydroxybenzenesulphonate anion,[2] gives 2,4,6-tribromophenol by an ipso substitution process.

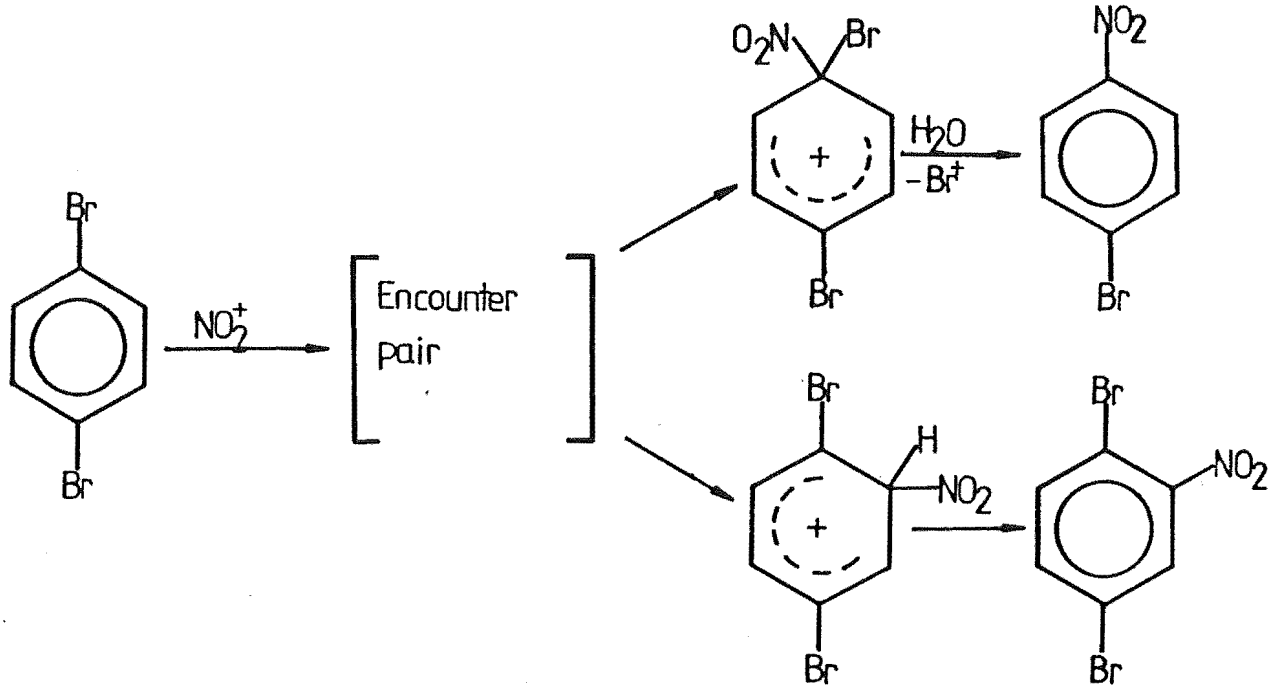


In nitration, ipso substitution and other reactions such as those causing side-chain modification have often been observed and regarded as anomalous or 'non-conventional'. For example, the nitration of 1,4-dibromobenzene in sulphuric acid gives 2,5-dibromonitrobenzene and p-bromonitrobenzene,[3] the product ratio being independent on the acid concentration:



70o\° H_2SO_4	60	34
90o\°	100	0

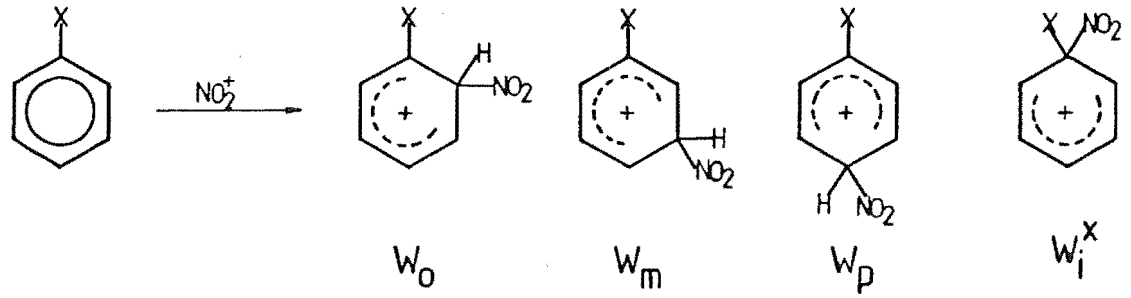
It is only recently that these reactions have been treated as part of an identifiable area of the subject, as being consequences of ipso-attack. For example, in the above reaction, formation of the p-bromonitrobenzene can be rationalised in terms of an ipso-attack of the nitronium ion at the bromine substituted position, followed by loss of bromine from the Wheland intermediate.



1.2 CONSEQUENCES OF ipso ATTACK

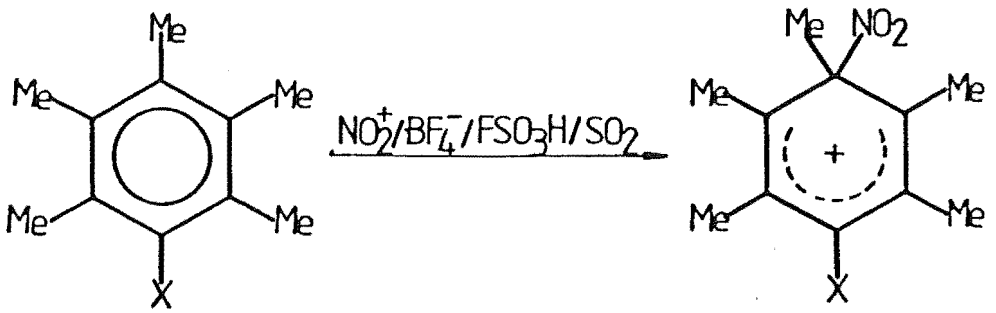
1.2.1 WHELAND INTERMEDIATES FROM ipso ATTACK

The Wheland intermediates (Ws), formed in the electrophilic nitration of mono-substituted benzenes, are of two kinds; those (W_o,W_m,W_p) arising from 'conventional' attack at an unsubstituted position, and that (W_i^X) arising from attack at the substituted position, i.e.:



Direct observation of the first kind of Wheland intermediate have rarely been reported, and generally their chemistry is limited to proton loss.

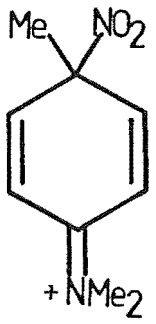
In contrast however, both observation and capture of W_i^X have proved possible in some cases. For example, some hexa-substituted benzenes give cations in conditions where bases or nucleophiles are absent.[4]



X= Me, F, Cl, Br

The structures of these cations were established by ^{1}H, ^{19}F, and ^{13}C n.m.r. spectroscopy.

Particularly stable W_is are to be expected, when stabilising groups are present at the p-position with respect to the ipso position. For example, the nitration of N,N-dimethyl-p-toluidine in 70-77% sulphuric acid at 0^{o}, gives 4-methyl-2-nitro-N,N-dimethylaniline via the stabilised W_i^{Me} cation:[5]

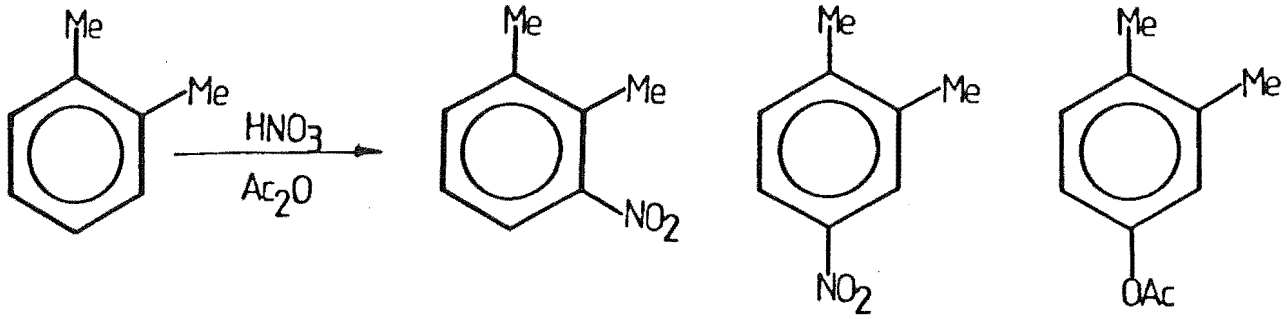


The structure of this cation was established by ^{1}H, and ^{13}C n.m.r. spectroscopy.

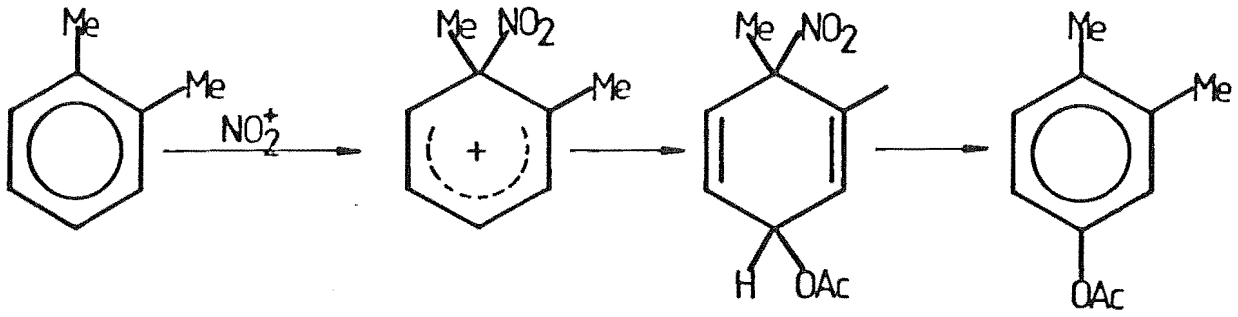
1.3 REACTIONS OF ipso-WHELAND INTERMEDIATES

1.3.1 REACTIONS WITH NUCLEOPHILES

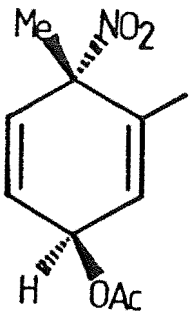
It was this reaction, particularly where the nucleophile is an acetate ion, which was important in drawing attention to ipso-attack in nitration. For example, the nitration of methyl benzenes with nitric acid in acetic anhydride, gave aryl-acetates as well as 'conventional' nitration products.[6] The ratio of nitration to acetoxylation was found to be dependent on the substrate but independent of its concentration:



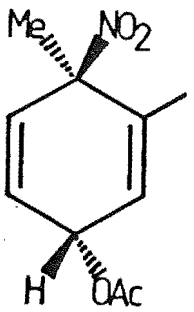
The suggested mechanism for the formation of the acetates, involves an ipso intermediate (W_i^{Me}), which is captured by an acetate ion, followed by elimination of nitrous acid:



This mechanistic proposal was supported by the isolation of the two isomeric adducts (1) and (2), formed during the nitration of o-xylene, and their conversion in aqueous acid into the acetoxyarenes.[7]



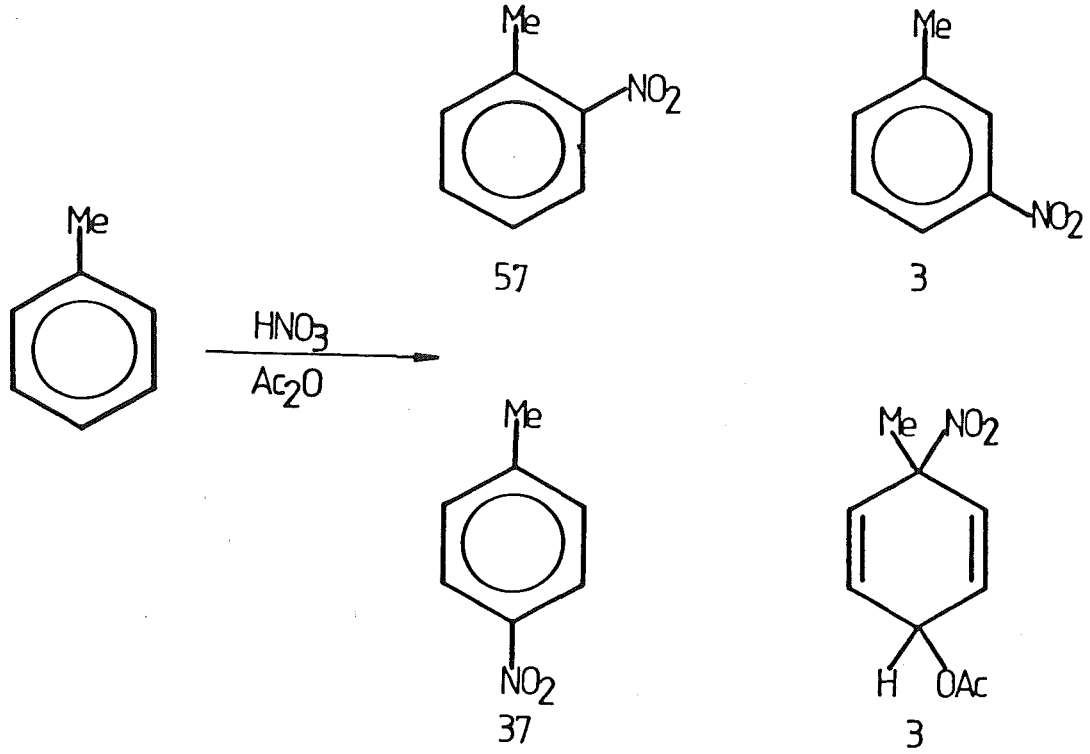
(1)

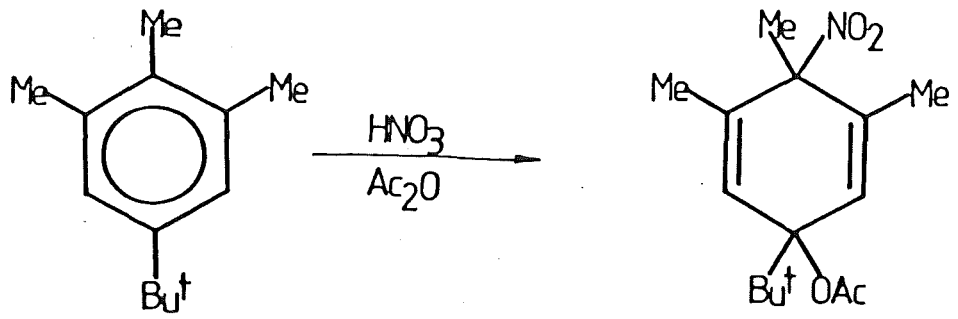


(2)

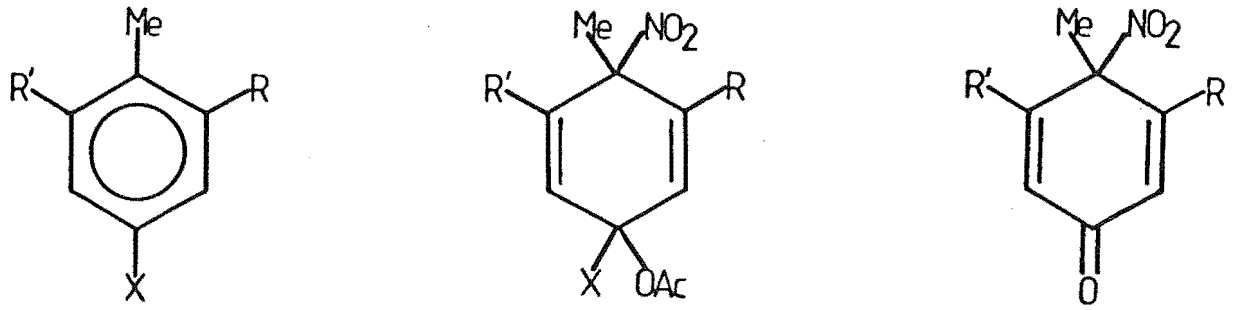
Similar products were obtained from other aromatic substrates under the same conditions, mostly by Fischer and co-workers.

Acetoxynitrodiene formation is usually accompanied by conventional nitration, and the division of the starting material among these different kinds of products gives important information about positional reactivities. For example, the yields of diene-adducts may account for only a few percent of the aromatic as with toluene,[8] or almost all of it, as for 5-tert-butyl-1,2,3-trimethylbenzene.[9]



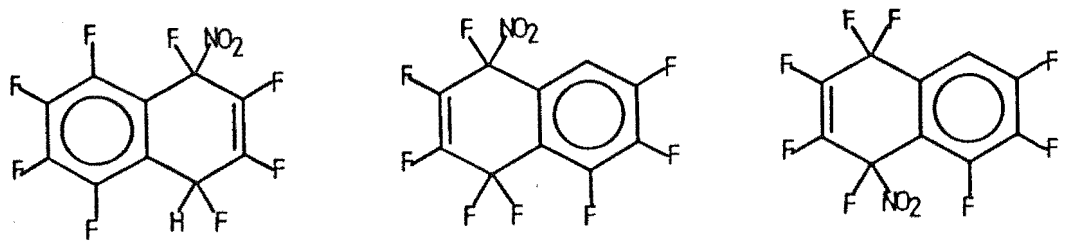


In some cases, the acetoxynitrodienes react further to give dienones. For example:



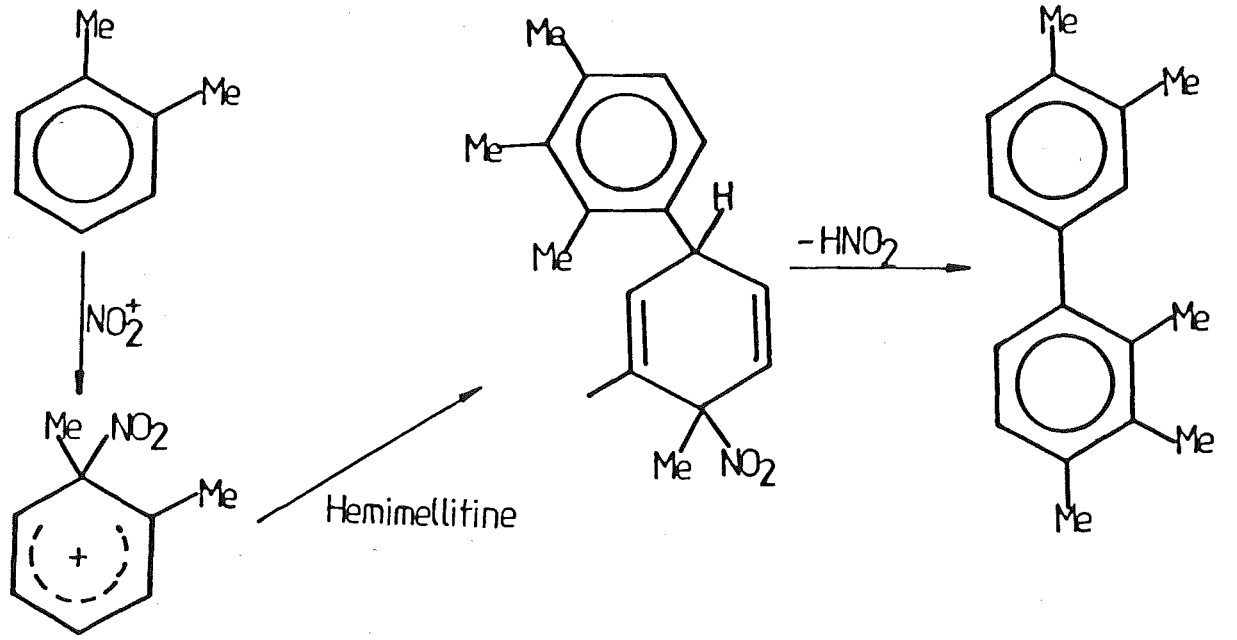
In these reactions the yield of the dienone is dependent on the nature of the substituents X, R and R'.[10]

Nitration of fluorinated aromatics with nitric acid in hydrofluoric acid, can give dienes by ipso-nitration followed by capture of the Wheland intermediate by fluoride ion. Thus 1H-heptafluoronaphthalene gives the following adducts:[11]



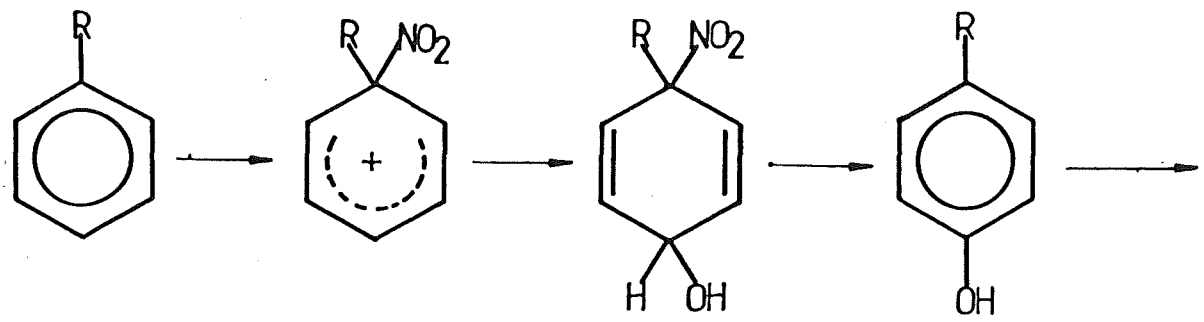
Similar reactions occur with pentafluorotoluene, chloro-, and bromo- pentafluorobenzene, and hexafluorobenzene.[12]

Some aromatic compounds, namely 1,2-dialkyl benzenes, (hemimellitine and prehnitine) give biphenyls as well as conventional nitration products, upon treatment with nitric acid. For example, the addition of nitric acid to a mixture of o-xylene and hemimellitine, gives 2,2',3,4,4'-pentamethyl-biphyenyl.[13]

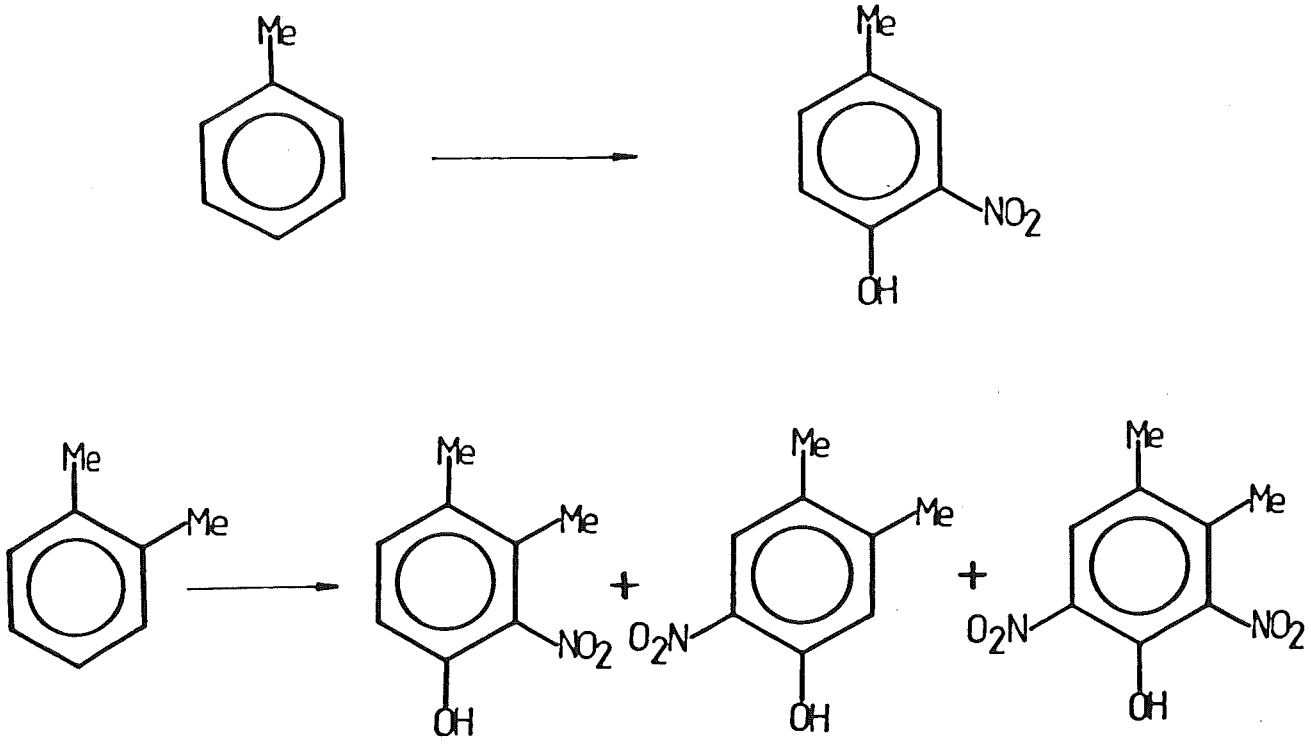


The suggested mechanism, involves the W_i^{Me} intermediates, which react further with the aromatics. This mechanism is supported by the fact that W_i's generated from acetoxynitrodienes react in this way. Thus the 3-chloro-4,5-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate, reacted in trifluoracetic acid with mesitylene to give 3'-chloro-2,4,4',5',6'-pentamethylbiphenyl.[14]

W_i^X's can react with water to give adducts, which rearrange readily to phenols by loss of nitrous acid. These can be nitrated further, and indeed, nitrophenols are common by-products of nitration.[15,16,17]

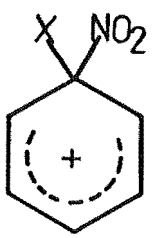


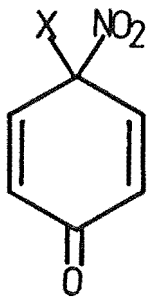
Thus, when nitrations of organic substrates are carried out in aqueous acid, a significant proportion of the W_i^x may be captured by water, resulting in a decreased yield of nitro-aromatic products and a significant formation of nitrophenols. For example, nitration of toluene in 54% sulphuric acid,[15] gives c. 4% of 4-hydroxy-3-nitrotoluene, and o-xylene gives 33% of mono- and dinitro-3,4-dimethylphenols:[16]



1.4 MIGRATION OF THE NITRO GROUP

The Wheland intermediates and dienones, formed in electrophilic ipso-nitration, are capable of rearrangement by migration of the nitro group or less commonly the ipso substituent X.





Based on their differing consequences, three modes of migration of the nitro group can be considered:[18]
(i) intramolecular, (ii) extramolecular and (iii) intermolecular migration.

(i) Intramolecular migration, is characterised by the fact that the nitro group never becomes sufficiently free from the carbon structure to do other than move to a position adjacent to the ipso position, i.e. 1,2-migration occurs.

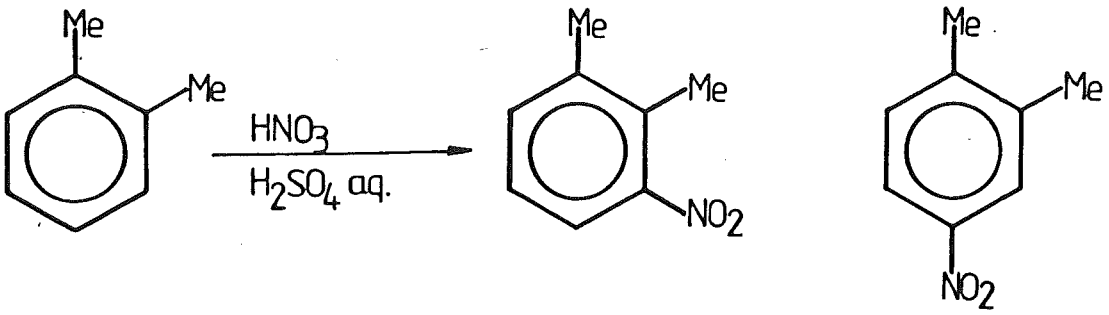
(ii) In extramolecular migration, the nitro group becomes free enough to be able to distinguish and select between the positions in the carbon framework, but it does not leave the "encounter-pair" containing the carbon structure and itself.

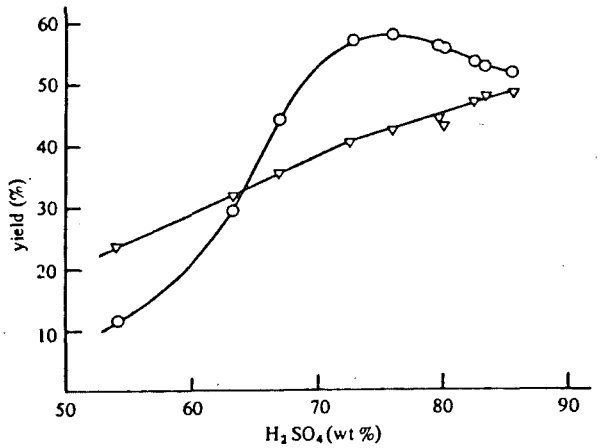
(iii) In intermolecular migration, the ipso nitro group leaves its position, diffuses into the solvent, and may react with carbon structures other than the one it left; this type of migration is often detected using isotope labelling, with the formation of crossover products.

In general extramolecular rearrangement, may occur when the nitration producing the W_i^X, proceeds at the encounter rate, and the intermolecular rearrangement, occurs when the rate of formation of W_i^X is less than the encounter rate.

1.4.1 INTRAMOLECULAR MIGRATION

Intramolecular 1,2-migration, was first proposed by Myhre,[16] to explain the acidity dependence of the ratio of 3- to 4-nitro-o-xylene, produced in the nitration of o-xylene in sulphuric acid.[18]





Nitration of *o*-xylene. Yields of 3-nitro (circles) and 4-nitro-*o*-xylene (triangles) as percentages of the starting material.

The detailed mechanism is illustrated in Scheme 1*. Myhre suggested that W_i^{Me} is captured by water at low acidities, but that with increasing acidity, 1,2-migration becomes increasingly important. In accord with this mechanistic description the solvolysis of the acetoxynitrodiene adducts of the W_i^{Me}, in sulpuric acid of several concentrations, gives only the

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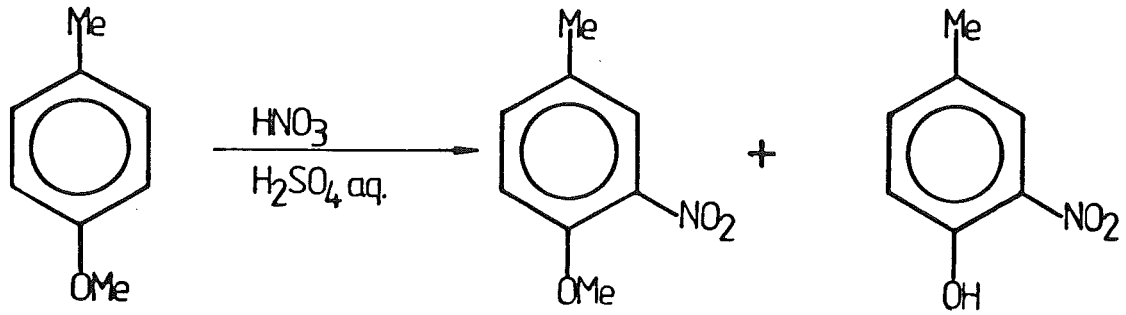
* Schemes 1-6 as foldouts at the end of the General Introduction.

3-nitro-o-xylene and 3,4-dimethylphenol. Thus, return of the W_i^{Me} to the 'encounter-pair' (the step necessary to produce 4-nitro-o-xylene) does not, in this case, compete with nitro migration to produce 3-nitro-o-xylene, or capture by water to produce 3,4-dimethylphenol.

1.4.2 EXTRAMOLECULAR MIGRATION

Extramolcular 1,3-migration of nitro, was invoked to explain the presence of nitrophenols, in the reaction products from the electrophilic nitration of some anisole derivatives.[19] For example, p-methylanisole, upon treatment with nitric acid in sulphuric acid, gave 4-methyl-2-nitroanisole, and 4-methyl-2-nitrophenol in yields that were dependent on the acidity of the medium.[20]

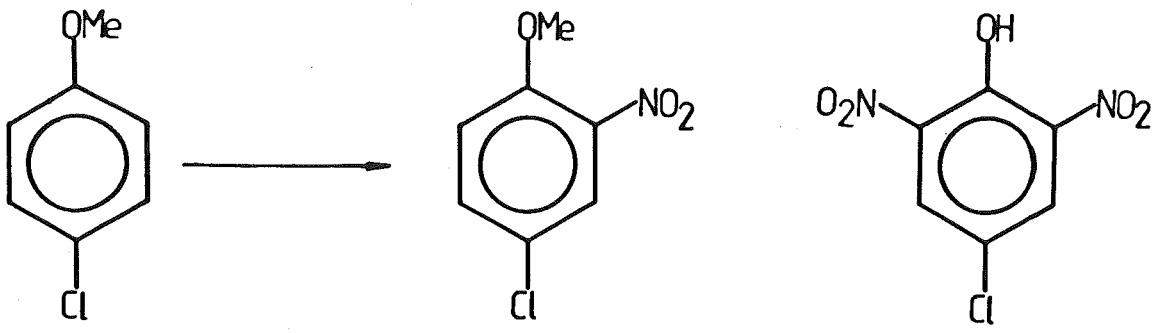


40% H_2SO_4	6	4
60%	8	2

The proposed mechanism is illustrated in Scheme 2. The nitrocyclohexa-2,5-dienone (3), is formed and decays during the reaction. In strong acid, the conjugate acid of the dienone (3) rearranges to give the 4-methyl-2-nitrophenol via dissociation to an encounter complex, followed by rapid recombination. No 4-methylphenol could be detected during the course of this reaction; this is consistent with the kinetic evidence, that p-methylanisole and p-cresol are nitrated at,

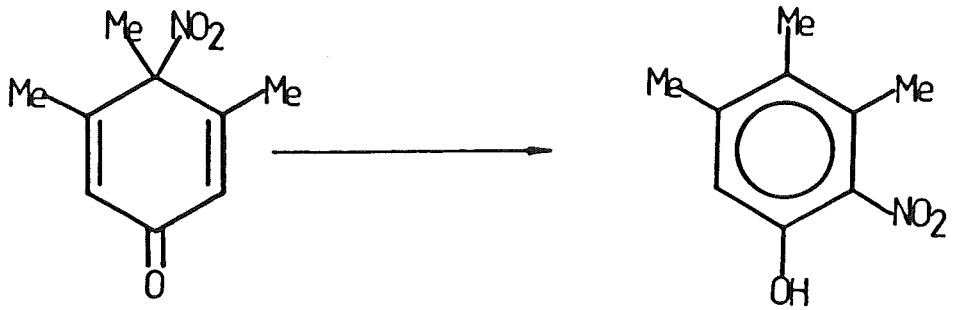
or near the encounter rate, and therefore no significant leakage occurs from the two encounter pairs formed in this mechanism.

Similarly, the nitration of p-chloroanisole, with nitric acid in sulphuric acid,[1,21] gives 4-chloro-2,6-dinitrophenol.



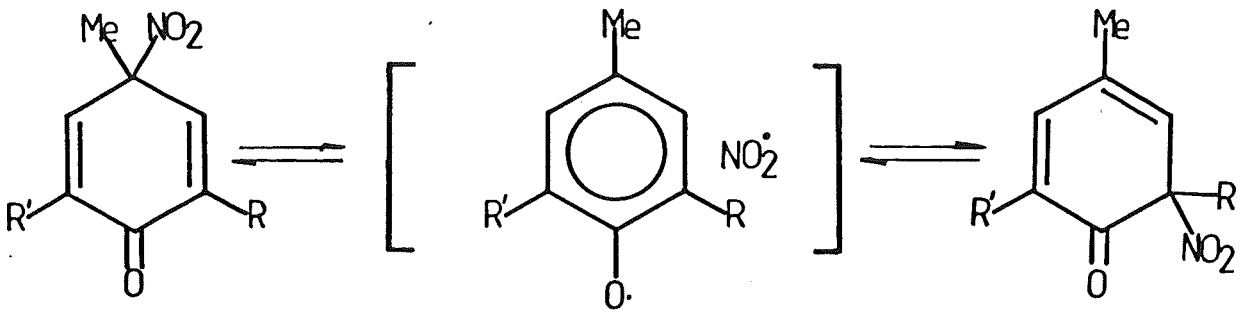
However, in contrast to p-cresol and p-methylanisole, p-chloroanisole does not react at the encounter rate, and during the course of the reaction, p-chlorophenol was detected. This is in accord with the above mechanism, with the acid-catalysed rearrangement of an analogous dienone to the encounter pair, followed by recombination to the 2-nitrophenol, with some leakage from the encounter pair.

The rearrangements of 4-nitrocyclohexa-2,5-dienones is of importance in relation to this present work. These compounds rearrange when the ortho positions are not substituted, to give o-nitrophenols.[22,23] For example, the 3,4,5-trimethyl-4-nitrocyclohexa-2,5-dienone (4), rearranges quantitatively to give the 3,4,5-trimethyl-2-nitrophenol.[24]



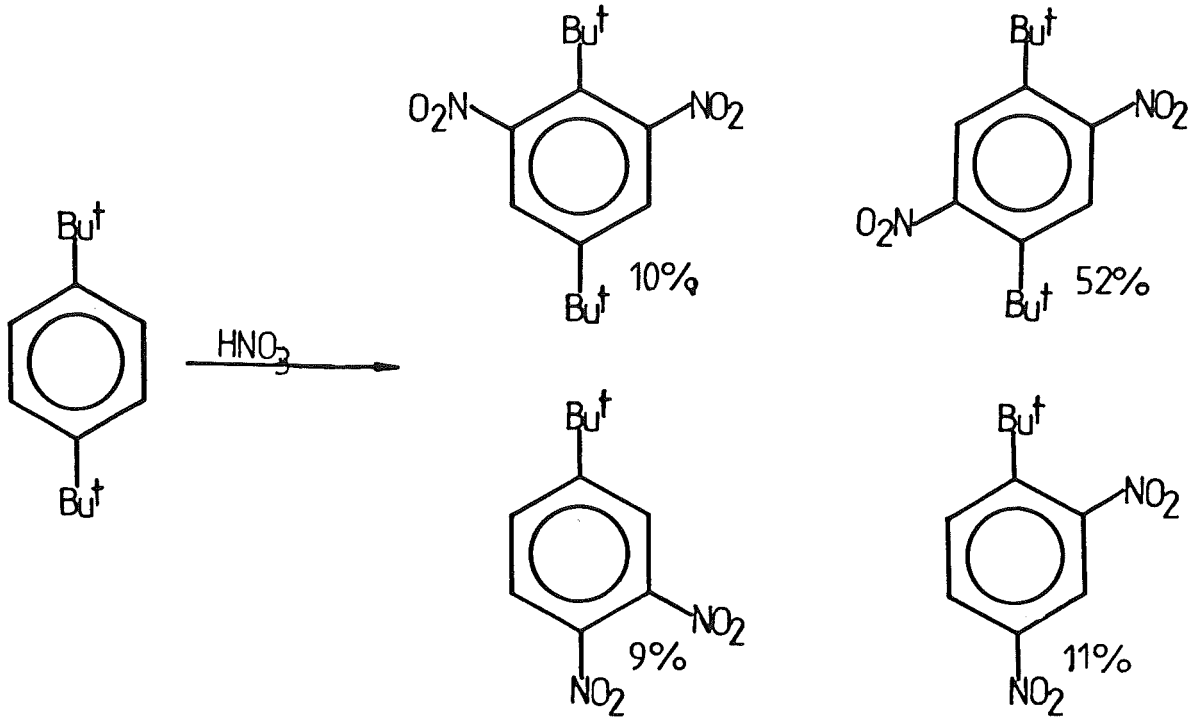
(4)

The conversion of 4-methyl-, 3,4-dimethyl-, and 3,4,5-trimethyl-4-nitrocyclohexa-2,5-dienones, to the corresponding 2-nitrophenols, in hexane, acetic acid, ethanol, water and dimethylsulphoxide have been shown to proceed by a radical dissociation-recombination mechanism, with some leakage of radicals from the solvent cage occurring, as shown in Scheme 3. In more recent work,[25] it is suggested that when the ortho positions are substituted, this radical dissociation-recombination mechanism operates. However, the pathway to 4-nitrophenols is eliminated, and thus an equilibrium between the 4-nitro and 6-nitrocyclohexadienones is established:



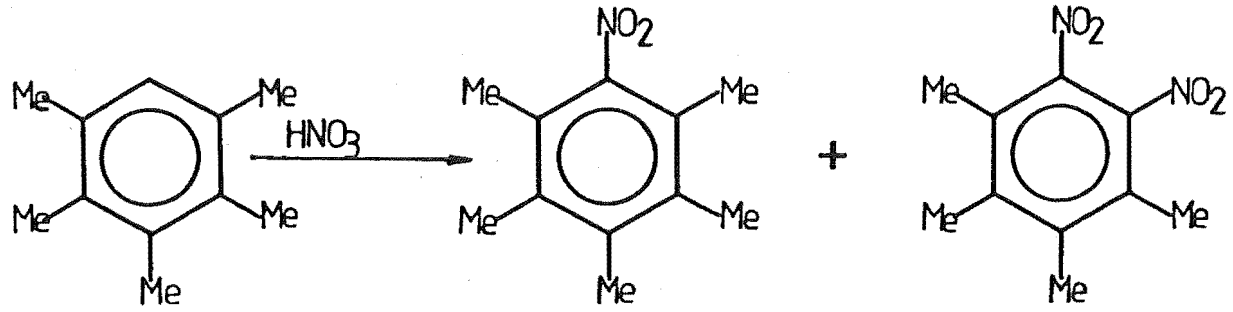
1.5 ipso SUBSTITUTION

ipso-substitution is the longest-known consequence of ipso-attack. It is the main source of the description 'anomalous nitration'.[26] It occurs in cases where the ipso group other than nitro is acyl, alkyl, arylazo, aryloxy, carboxyl, halogen, methoxy, phosphoryl, silyl and sulphonyl. This area is well-represented in the literature, although mechanistic studies are few, and in some cases, uncertainty exists as to the mode of removal, of the non-nitro ipso group. For example, nitration of 1,4-di-t-butylbenzene, gives approximately 20% of the product resulting from nitrode-t-butylation, along with products of conventional nitration.[27]



This process involves the loss of the stable t-butyl cation from the $W_i^{Bu^t}$ as the important step. Not surprisingly, in the nitration of p-ethyltoluene and p-diethylbenzene no de-methylation

or de-ethylation occurs, even though the W_i^{Me} and W_i^{Et} are formed.[28] In contrast, the nitration of pentamethylbenzene gave in addition to nitropentamethylbenzene, dinitroprehritine by an apparent demethylation.[29]



It is unlikely, that a simple displacement of the methyl group as a methyl cation would occur, therefore it is probable that some modification of the methyl group occurs prior to displacement.

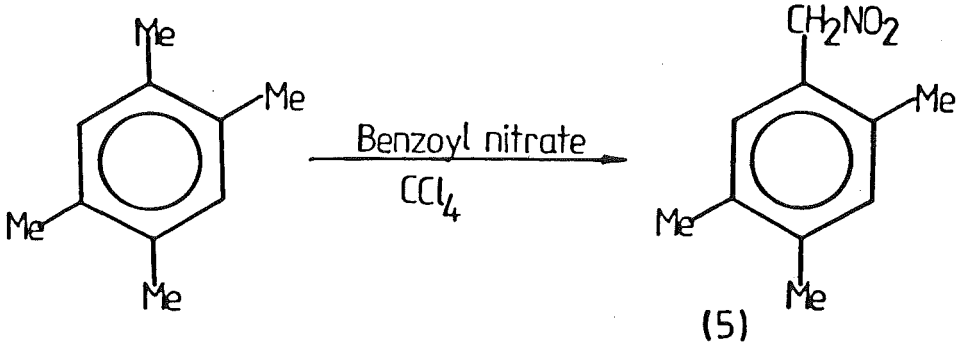
1.6 SIDE-CHAIN MODIFICATION

Examples of electrophilic nitration reactions, giving anomalous products, where alkyl side-chains have been modified, have been well-documented in the literature over the past seventy years. The most important reactions are those of polyalkylbenzenes where benzylnitrites, benzylnitrates and arylnitromethanes are formed.[30,31] Other examples include: side-chain acetoxylation,[32] acetimidation,[33] alkoxylation,[34] arylation[32,35] and hydroxylation.[36] Conversions of side-chain alkyl groups into carboxylic acid, aldehyde or ketone functions are also known.[37]

1.6.1 SIDE-CHAIN NITRATION

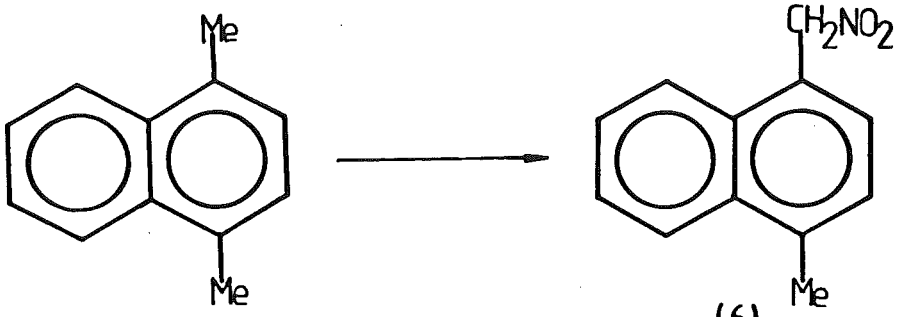
The first reported side-chain nitrations of polymethyl-

benzenes were effected by Willstätter and Kubli[38] in 1909, using benzoylnitrate. For example, durene was treated with benzoylnitrate in carbon tetrachloride to give the side-chain nitro compound (5).



(5)

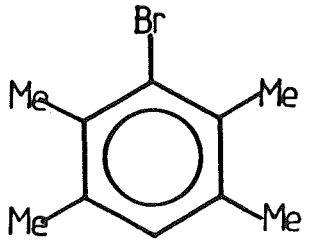
In 1932, Robinson and Thompson[39] treated 1,4-dimethyl-naphthalene with nitric acid in acetic anhydride, to give a high yield of the side-chain nitro compound (6).

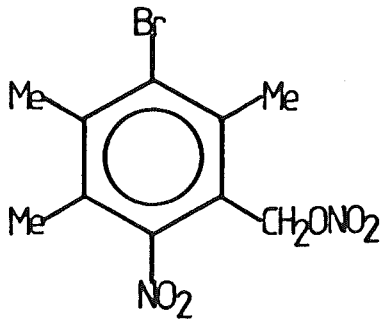


(6)

A more detailed study on polymethylnaphthalene was made by Fischer et al[40] in later years; the results of this are included below.

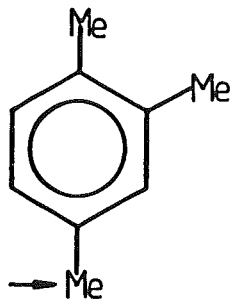
The nitration of 2,3,5,6-tetramethyl-bromobenzene was studied by Smith et al[41] in 1937; this was shown to give the 4-bromo-3,4,6-trimethyl-nitrobenzylnitrate (7).

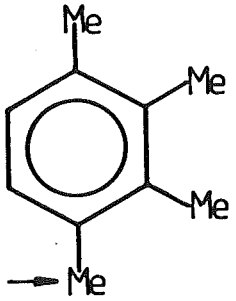


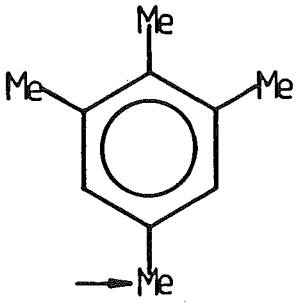


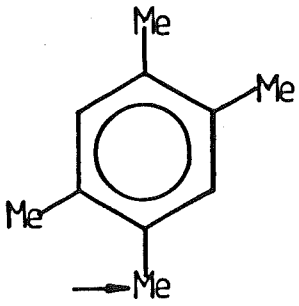
(7)

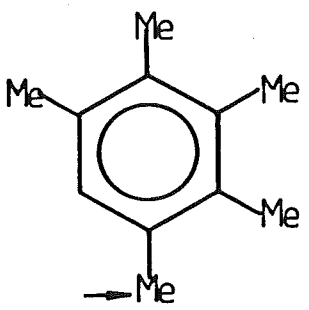
More recent nitrations of polymethylbenzenes have revealed the regiospecificity of side-chain nitration. For example, in the following compounds, the methyl group marked is that which is converted into a side-chain nitro or nitrate.[42,43]

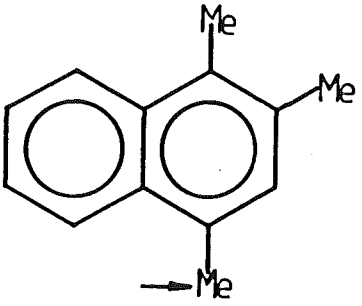






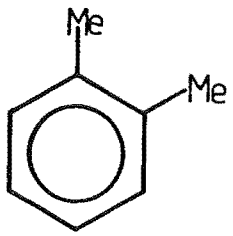


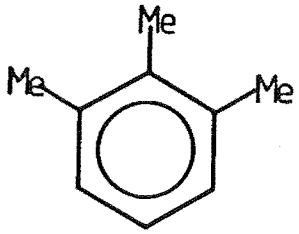


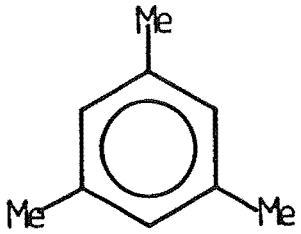


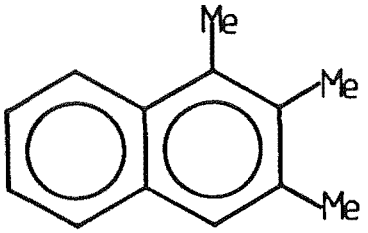
It is apparent that the methyl group attacked is at a <u>para</u> position relative to the most activated <u>ipso</u> ring position.

This p-dimethyl relationship is seen as a requirement for side-chain nitration to occur. In the absence, by the following compounds, side-chain substitution was not observed.[44]







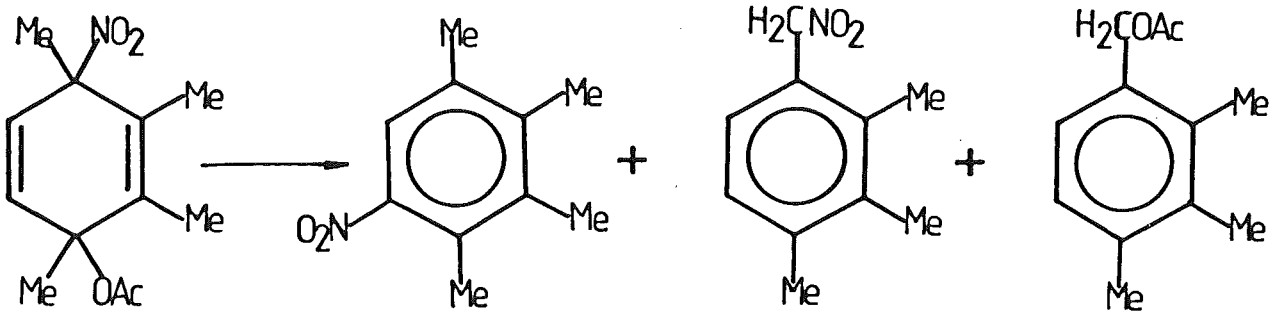


1.6.2 INTERMEDIATES IN SIDE-CHAIN SUBSTITUTIONS

The effect of substituents on side-chain nitration was studied for the following series of compounds: Me_5C_6X where X, = Me, H, Br, NO_2. Kinetically, the times for 10%-completion of side-chain nitration, were determined using nitric acid in nitromethane;[45] the relative reactivities were found to be $1:10^{-2}:10^{-4}:10^{-6}$ respectively. For the nitration of pentamethylbenzene (X=H), added electrolytes generally produced their effects without changing the ratio of side-chain to nuclear nitration. These results suggest that side-chain nitration involves an ionic mechanism and probably a common intermediate (i.e. Wheland intermediate) with that involved in nuclear nitration.

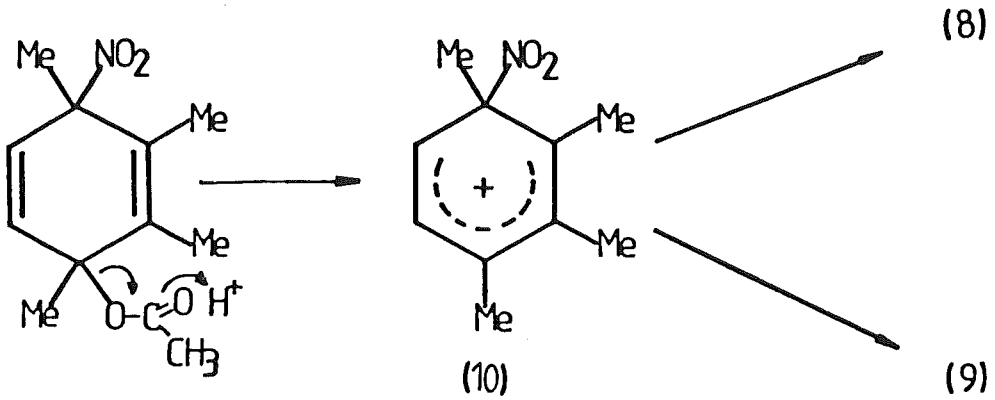
The acetoxynitrodienes produced in nitrations in acetic

anhydride have been shown to give side-chain nitro compounds when treated with various acids.[46] For example, the 1,4-nitro-acetate adduct of prehnitine, upon treatment with sulphuric acid in acetic anhydride,[47] gives the side-chain nitro compound (8) and the acetate (9), along with ring nitration.

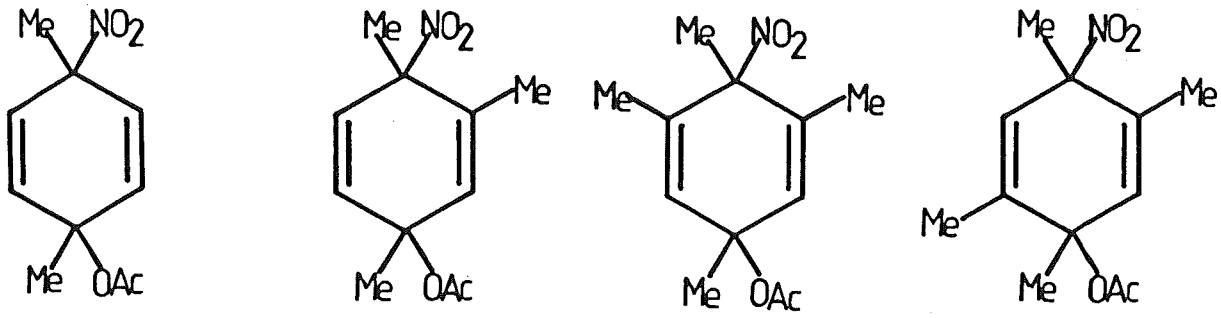


(8) (9)

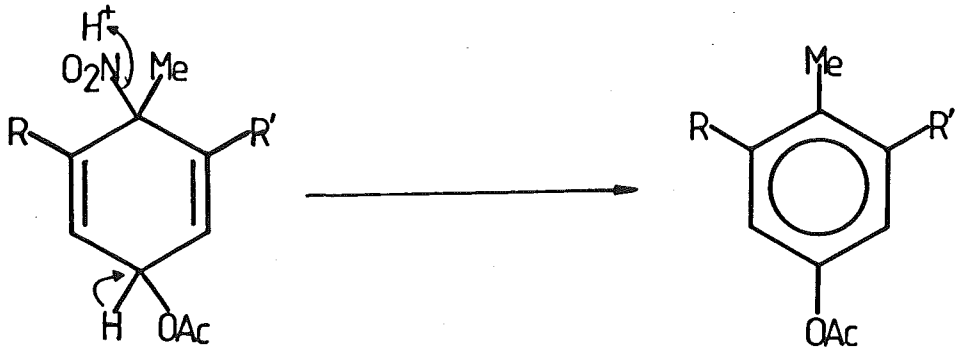
The mechanism for the formation of the side-chain substituted products, outlined below, is likely to involve the ipso Wheland intermediate (10), formed by an acid-catalysed loss of acetate:



The following acetoxynitrodienes also show this behaviour.[46]



Acetoxynitrodienes having a hydrogen at the 4-position, rearrange to acetoxyarenes, by the more facile loss of nitrous acid:[6]

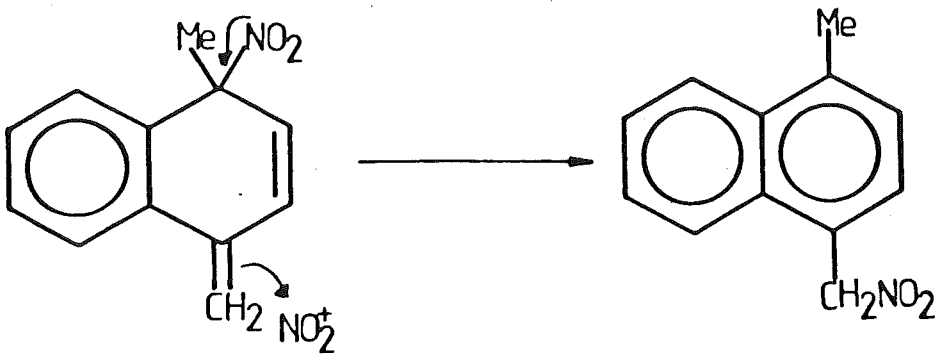


These results clearly indicate that the pathway for formation of side-chain substitution products involves an initial attack of NO_2^+ to give an ipso-Wheland intermediate, with incorporation of the resulting side-chain group at the methyl group para to this position.

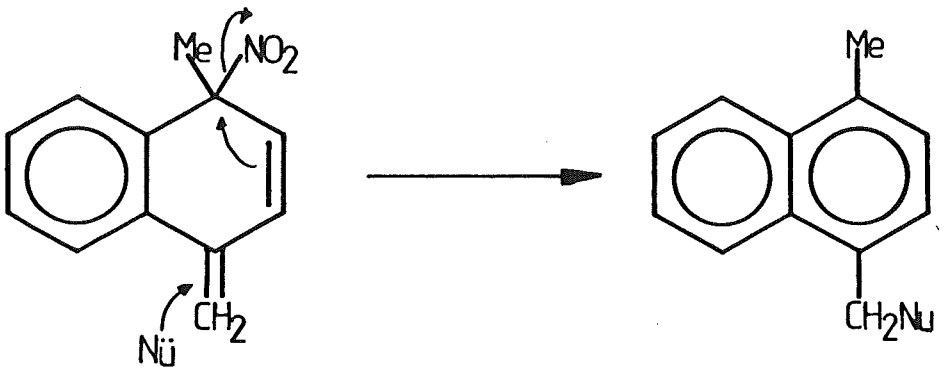
1.6.3 MECHANISMS OF SIDE-CHAIN SUBSTITUTION

The likely mechanism of side-chain substitution is shown in Scheme 4. The key step involves the W_i^{Me}, which may lose a proton from the methyl group para to the ipso position to

give the methylenecyclohexadiene (11). The methylenecyclohexadiene can be attacked by nitronium ion, to give a side-chain nitro compound. For example, the nitration of 1,4-dimethylnaphthalene to give the side-chain nitro compound,[39,40] is thought to involve this process.

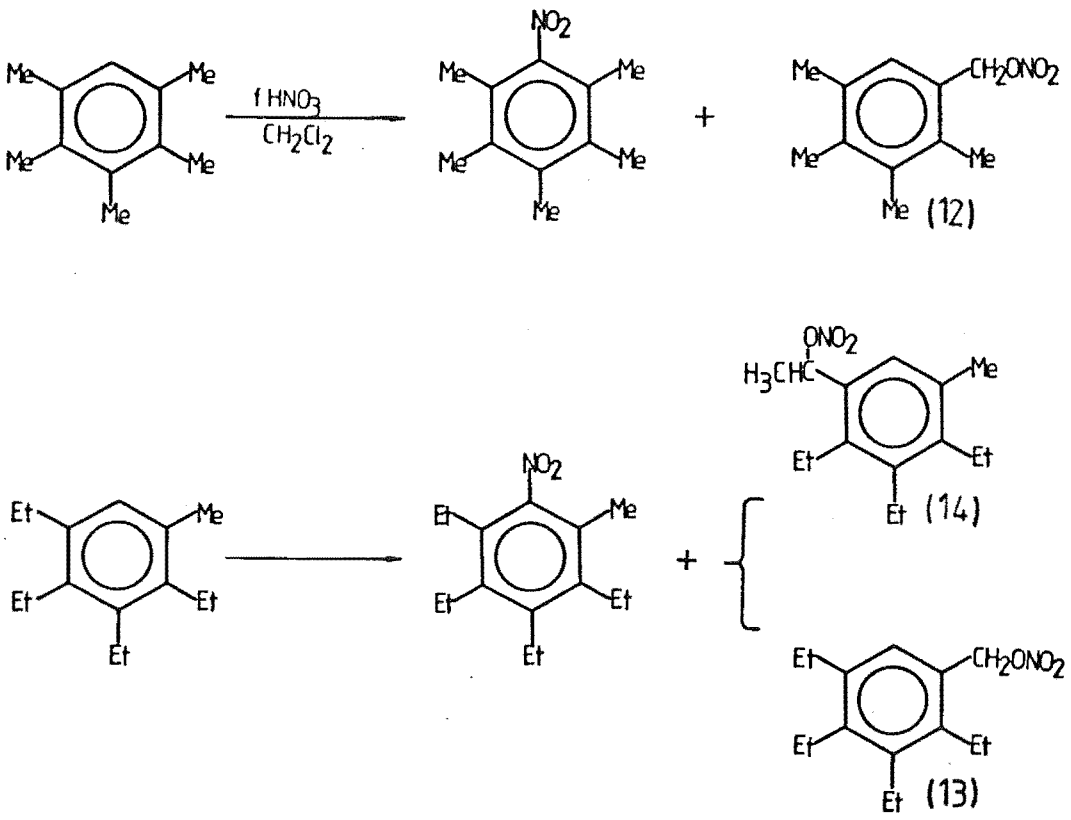


Attack on this diene by nucleophiles would rationalise the formation of side-chain substitution products such as nitrates or acetates.



A contrasting mechanism was proposed by Suzuki and Nakamura[48] to explain the products obtained from the nitration of pentamethylbenzene and 2-methyl-pentaethylbenzene. The nitration of pentamethylbenzene, gives the pentamethylnitrobenzene, and 2,3,4,5-tetramethylbenzylnitrate (12), while the nitration of 2-methyl-tetraethylbenzene gave 2,3,4,5-tetraethyl-

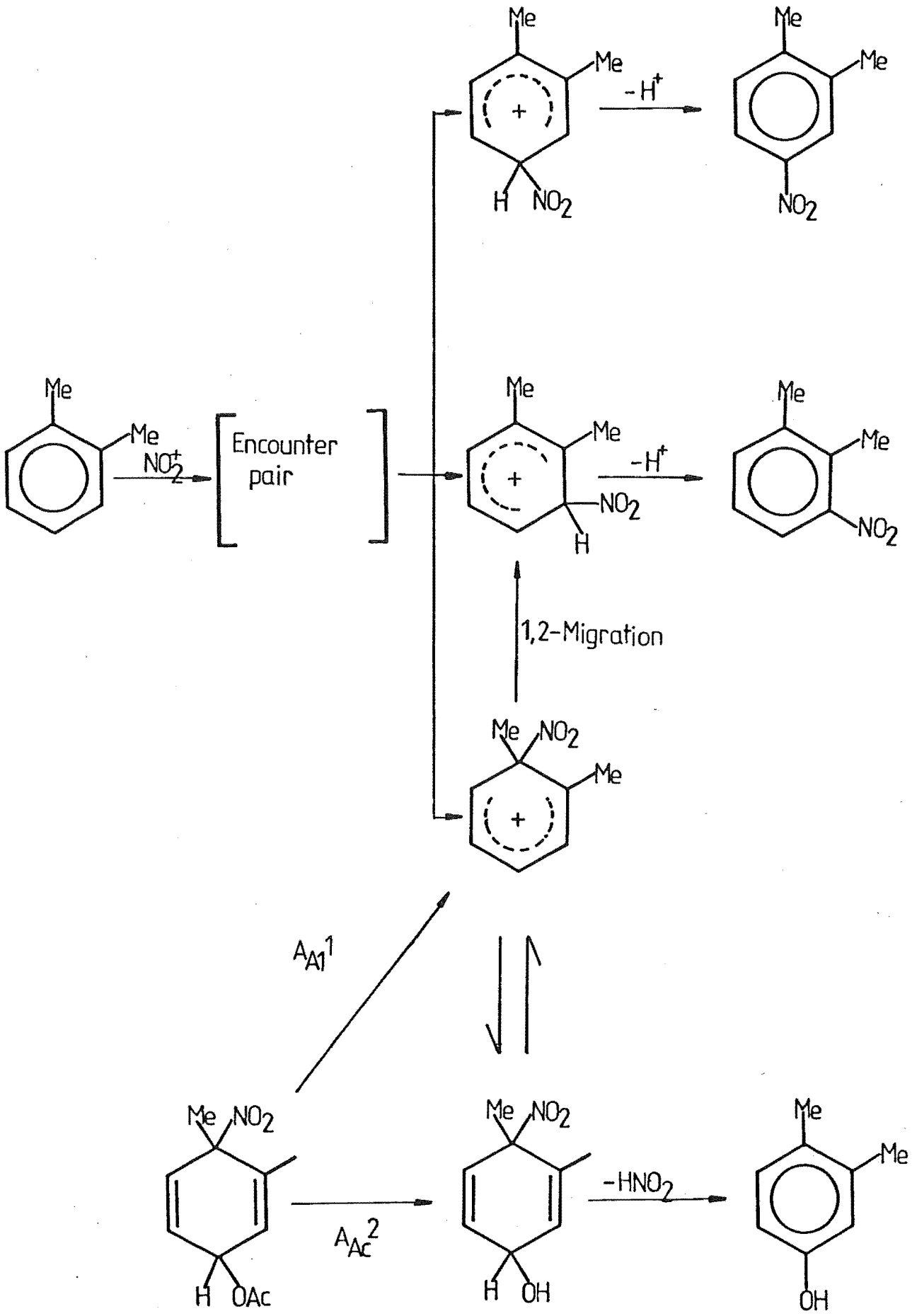
6-methylnitrobenzene, with the 2,3,4,5-tetraethylbenzylnitrate (13) and 2,3,4-triethyl-5-methyl-α-methylbenzylnitrate (14), in comparable yields:



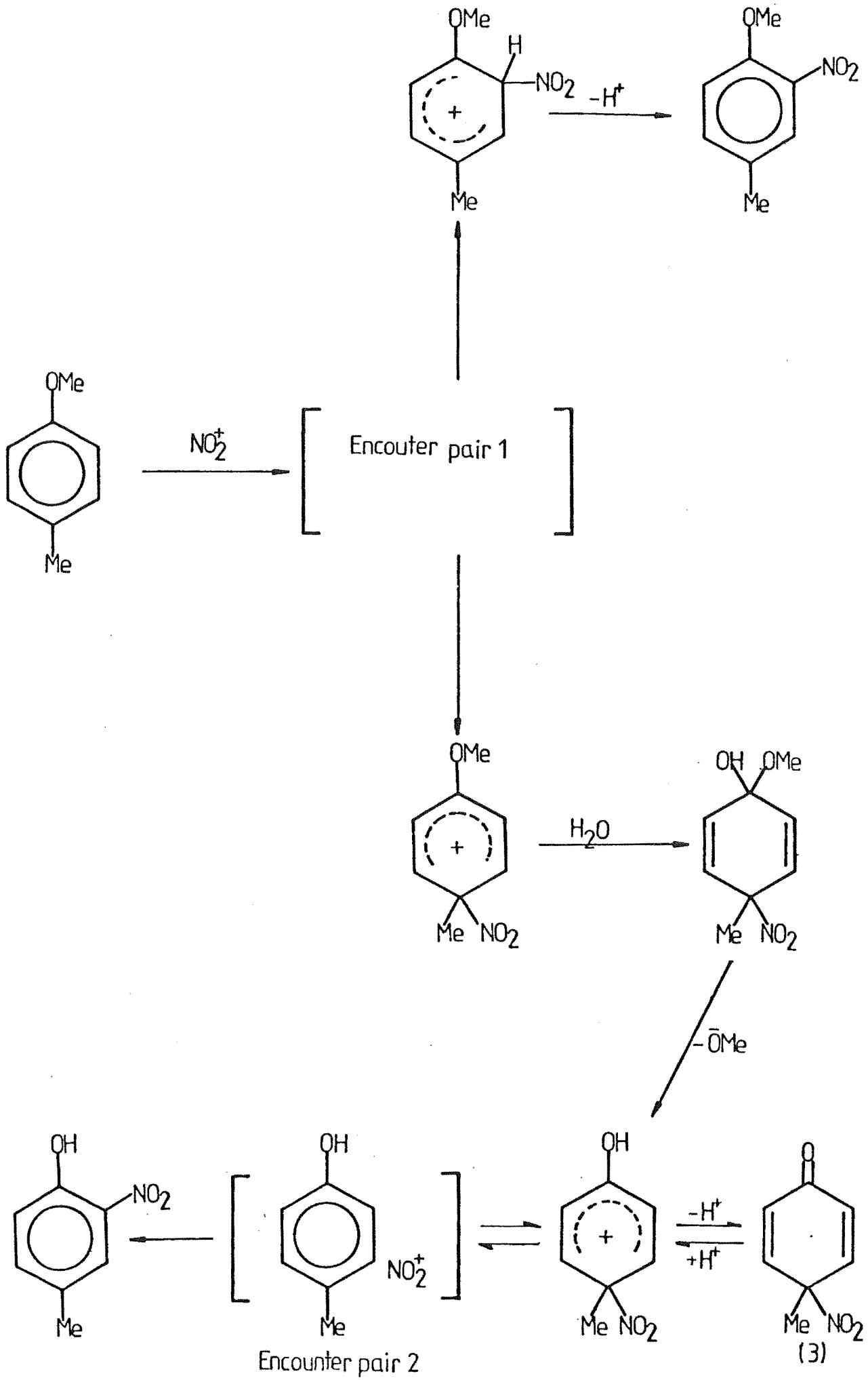
The reaction mechanism proposed by Suzuki and Nakamura[48] is outlined in Scheme 5, and involves the conventional Wheland intermediate (15), which may lose a proton from the alkyl group ortho to this position. Intramolecular rearrangement gives the side-chain nitrite (16), which is assumed then, to be oxidised to isolated nitrate.

A more likely mechanism, based on the above evidence, is outlined in Scheme 6. This scheme involves two types of attack - (i) at the vacant position to give the conventional nitration product, and (ii) at the most activated ipso position to give the ipso Wheland intermediate (17). Proton loss from the methyl group para to the site of ipso attack, would give the

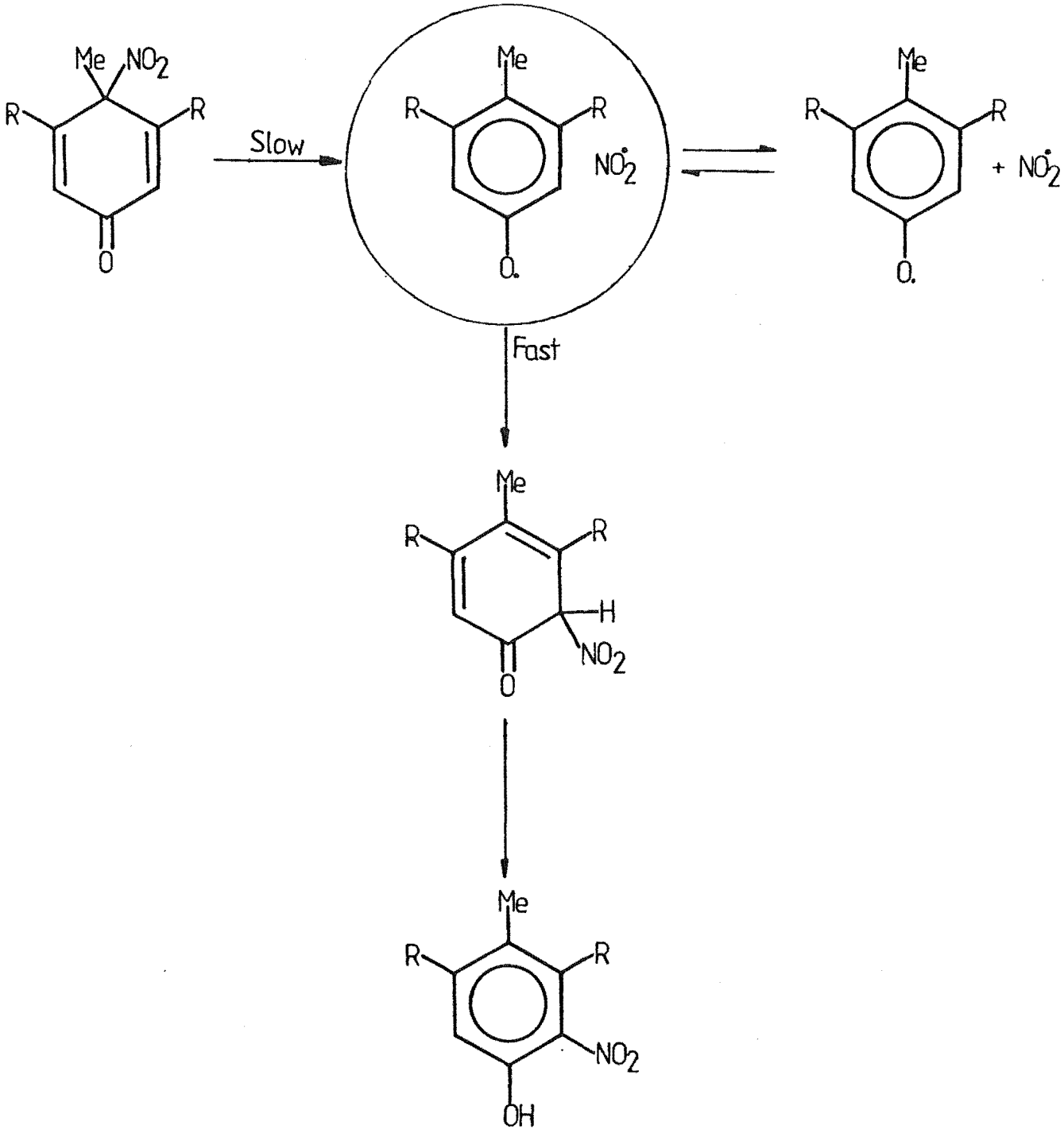
methylenecyclohexadiene (18). Attack on this by nitrate ion, would give the observed products.


Me
Me
NO_2^+
Encounter pair
$-H^+$
NO_2
H
1,2-Migration
A_{A1}^1
A_{Ac}^2
OAc
OH
$-HNO_2$

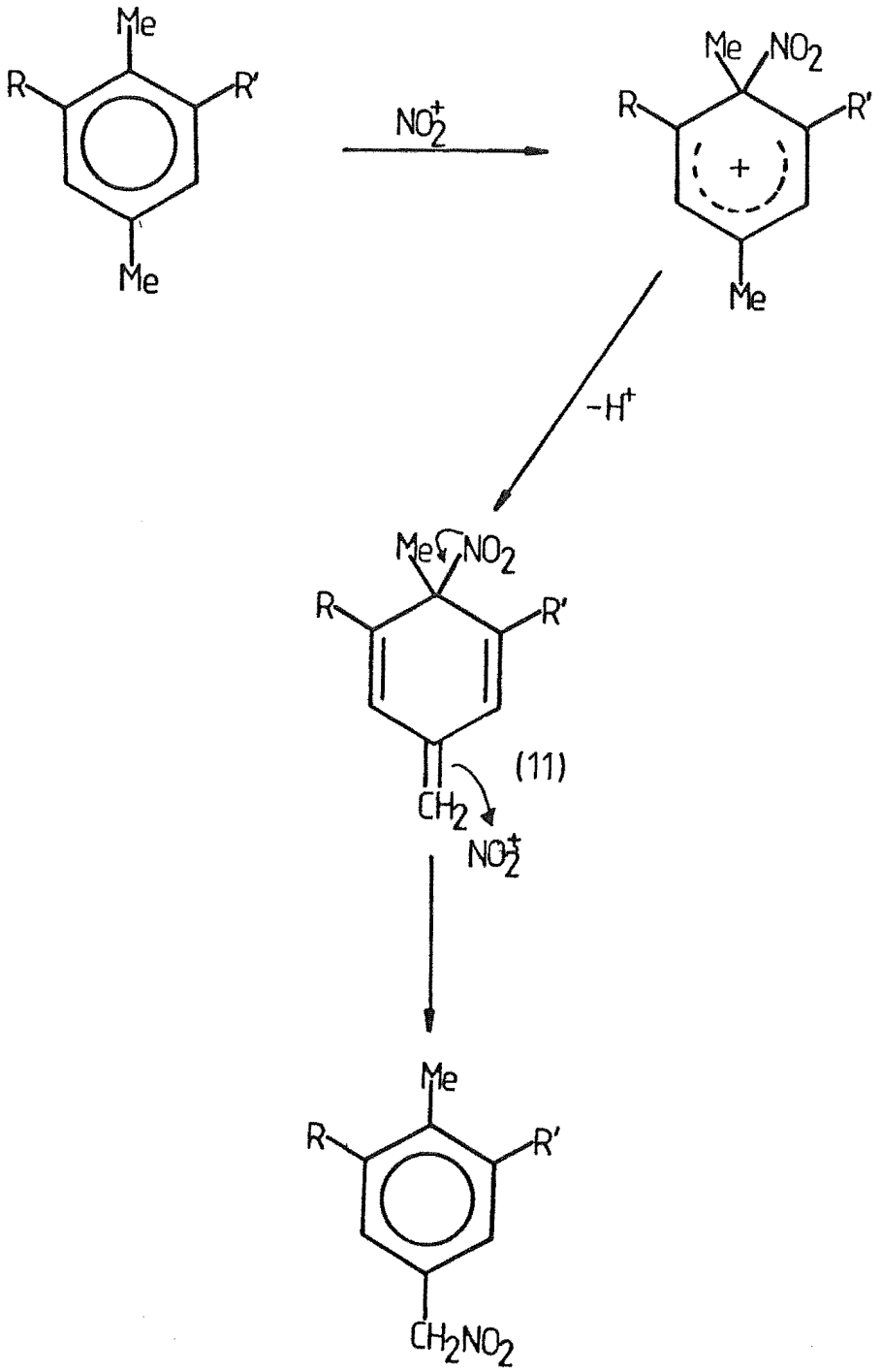
SCHEME 1



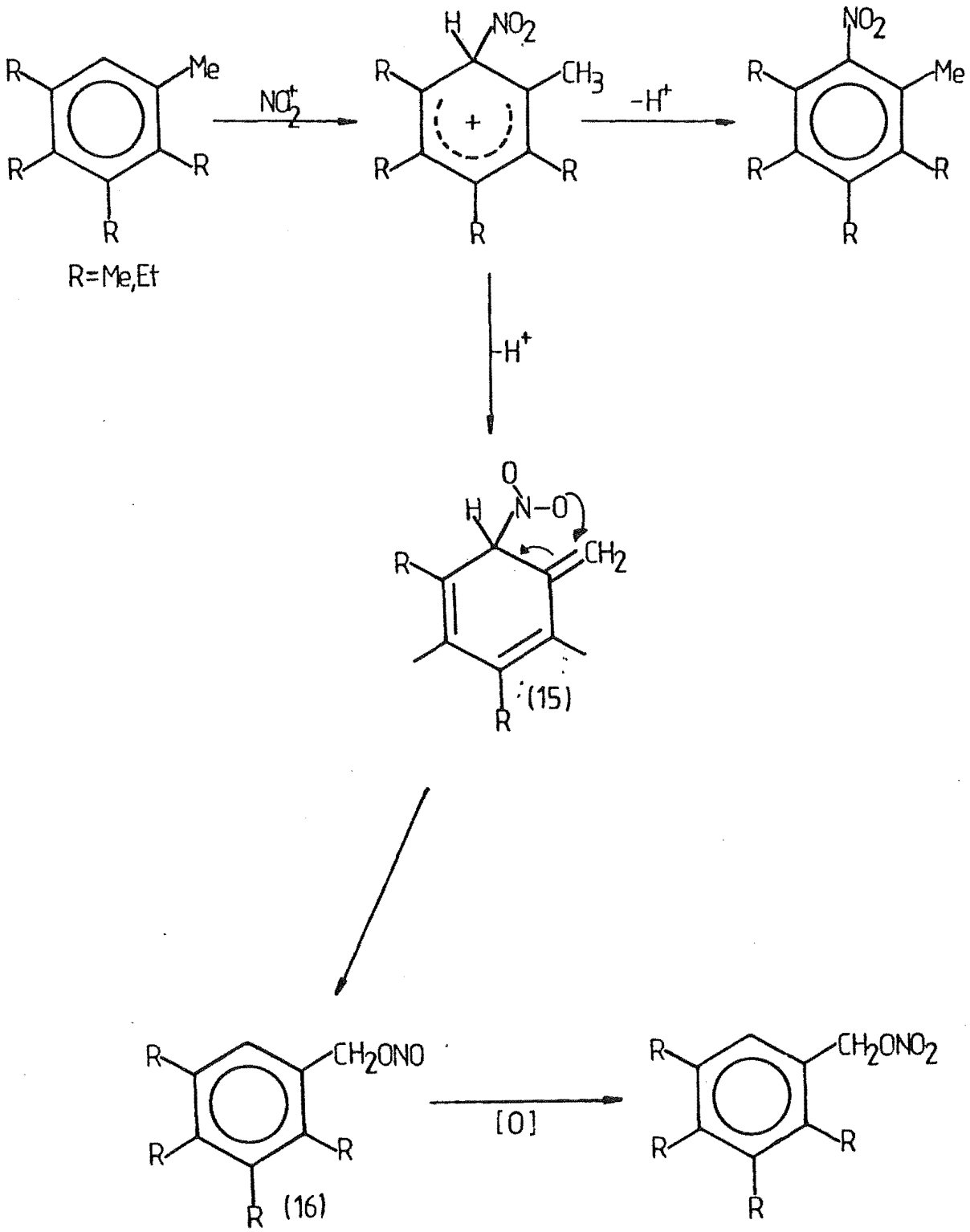
SCHEME 2


Me
NO2
R
R
O
Slow
Me
R
R
NO2
O.
Me
R
R
+ NO2
O.
Fast
Me
R
R
H
NO2
O
Me
R
R
NO2
OH

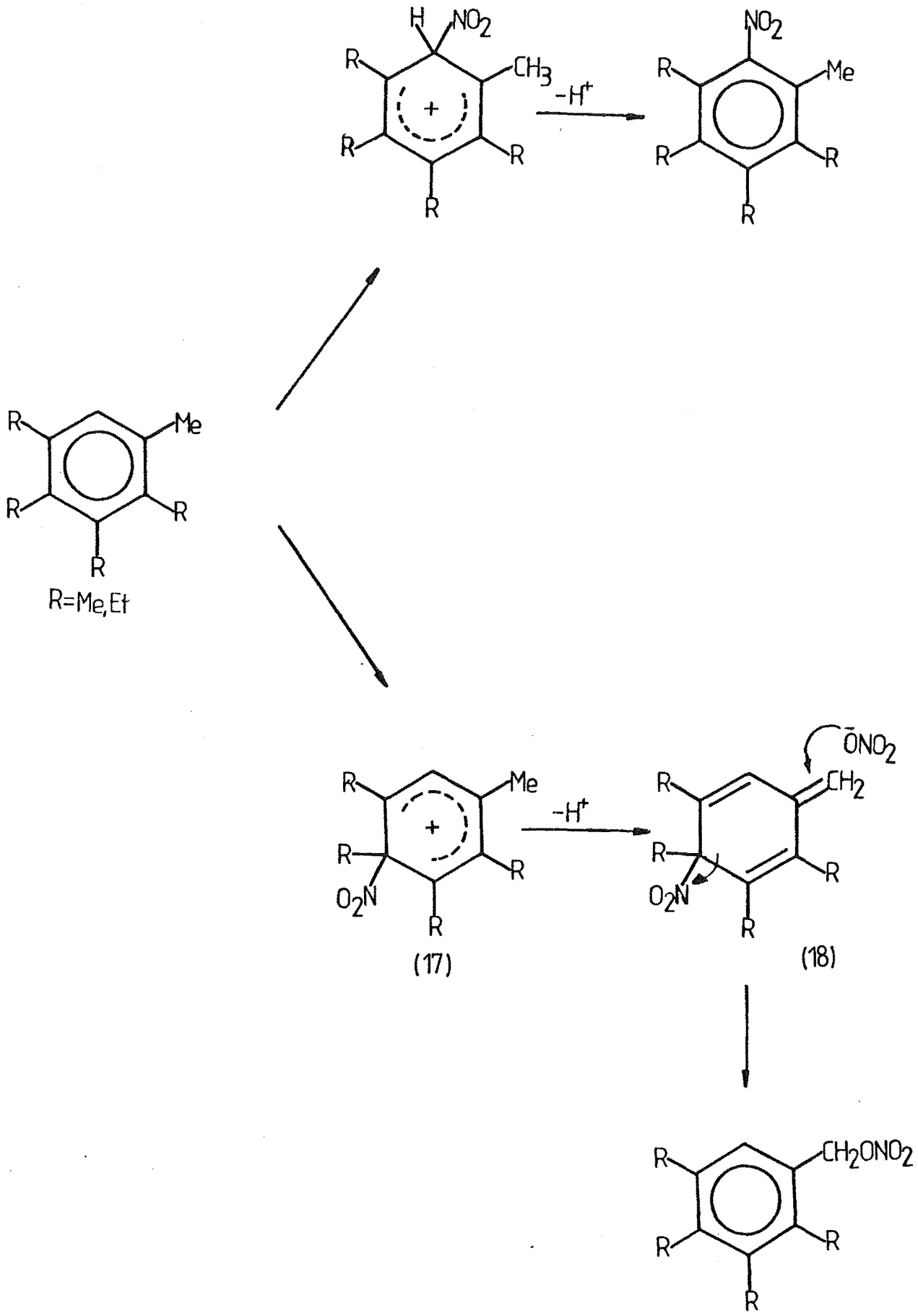
SCHEME 3



SCHEME 4


R
Me
R
R
R
R=Me,Et
NO_2^+
H
NO_2
CH_3
+
$-H^+$
NO_2
$-H^+$
O
N–O
H
CH_2
(15)
CH_2ONO
(16)
[O]
CH_2ONO_2

SCHEME 5



SCHEME 6

CHAPTER TWO

THE NITRATION OF PENTAMETHYLPHENOL (17)

2.1 INTRODUCTION

In 1971 Suzuki and Nakamura[49] reported the nitration of some substituted pentamethylbenzenes on brief reaction with fuming nitric acid in dichloromethane at -10^{o} to -5^{o}. For the nitration of pentamethylphenol (19)* (20 minute reaction) the only product identified, after quenching the reaction with water, was the 4-hydroxy-2,3,4,5,6-pentamethylcyclohexa-2,5-dienone (20), a compound assumed to be formed from the corresponding 4-nitrodienone (21). However, the ^{1}H n.m.r. spectrum of the crude nitration product showed a signal characteristic of a benzylic nitrate group at δ 5.21 ($\underline{CH_2}ONO_2$) and the infrared spectrum had bands at 845, 1270 and 1630 cm^{-1}, characteristic of an organic nitrate ester. Although this compound was not isolated, the m-nitratomethylphenol structure (22) was proposed for it.[49]

On the basis of the evidence from the work of Suzuki and Nakamura,[49] it appears that some side-chain nitrate ester formation occurs during the nitration of pentamethylphenol. Further, it seems likely that the 4-hydroxydienone (20) is a short-term reaction product. However, because of the possibility of formation of nitrate esters, it seemed likely that a long-term reaction of pentamethylphenol with nitric acid in dichloromethane might be complex, with potentially two series of products being possible, i.e. one series of products derived directly from pentamethylphenol and a second

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* Diagrams of compounds in block A at end of this thesis.

series of products from a tetramethyl-nitratomethylphenol. It was decided, therefore, to study first the reaction of pentamethylphenol (19) with nitrogen dioxide in benzene, and then to examine the products from the nitration with fuming nitric acid in dichloromethane.

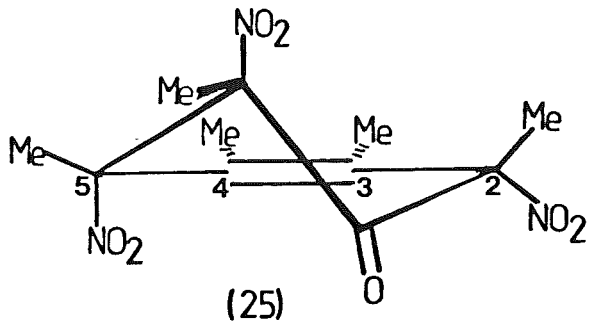
2.2 REACTION OF PENTAMETHYLPHENOL (19) WITH NITROGEN DIOXIDE IN BENZENE

Reaction of pentamethylphenol with nitrogen dioxide in benzene gave a crude product, shown by its infrared spectrum to be a mixture of non-conjugated carbonyls ca. 1755 cm^{-1}, conjugated carbonyls 1710 cm^{-1}, and a broad absorption at 1590-1540 cm^{-1}, indicated the presence of nitro groups. The ^1H n.m.r. spectrum showed a complicated pattern of signals from δ c. 1.8-2.2 p.m.m.; no signals at 5-6 p.m.m., indicative of side-chain nitration, were observed. The composition of the crude product was essentially independent of the reaction time used, within the range of time 2 min to 90 h. The components of the crude product were separated by a combination of fractional crystallization using dichloromethane/pentane solvent mixtures, and by chromatography on a Chromatotron silica gel plate. The yields recorded represent the estimated composition of the crude product.

(a) 2,5,6-Trinitrocyclohex-3-enones (23),(24),(25) and (26)

From the crude product were isolated the four possible 2,5,6-trinitrocyclohex-3-enones (23),(24),(25) and (26) the structures of which were determined unambiguously from their spectroscopic data combined with single-crystal X-ray structure determination for three of them: (23),(24) and (25). The perspective drawing of 2,3,4,5,6-pentamethyl-r-2,t-5,t-6-

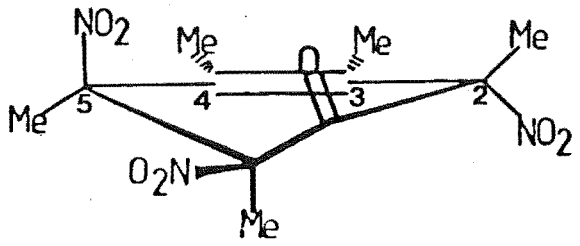
trinitrocyclohex-3-enone (23), $C_{11}H_{15}N_3O_7$, m.p. 124-126° (dec.) is presented in Figure (1) with the corresponding fractional coordinates in Table (1). Similar information is presented for 2,3,4,5,6-pentamethyl-r-2,t-5,c-6-trinitrocyclohex-3-enone (24), $C_{11}H_{15}N_3O_7$, m.p. 114-115° (dec.), (Fig (2) and Table (2)), and for 2,3,4,5,6-pentamethyl-r-2,c-5,t-6-trinitrocyclohex-3-enone (25), $C_{11}H_{15}N_3O_7$, m.p. 116-118° (dec.), (Fig (3) and Table (3)). The ring conformation in each of these compounds can be defined by a consideration of the torsional angles C(4)-C(3)-C(2)-C(1) and C(3)-C(4)-C(5)-C(6), as presented in Table (8). For example, for the <u>cis</u>-2,5-dinitro compound (25) the ring conformation in the solid state as represented in Fig (3), is best described as a flattened half-chair, with the 5-NO_2 group pseudoaxial.



(25)

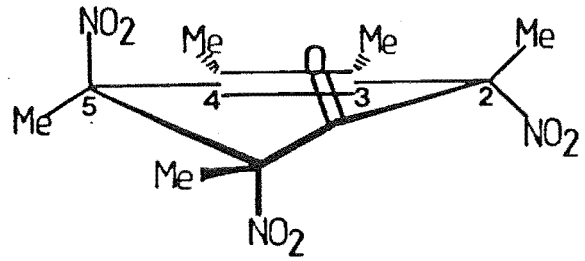
C(3)-C(4)-C(5)-C(6)	19.7°
C(4)-C(3)-C(2)-C(7)	12.9°

In contrast the two compounds having the <u>trans</u>-2,5-dinitro stereochemistry (23) and (24), as shown in Figs (1) and (2), exist in the solid state in a skew-boat conformation with the 5-NO_2 group in a flagpole orientation.



(23)

C(3)-C(4)-C(5)-C(6)	-31.3°
C(4)-C(3)-C(2)-C(1)	11.2°



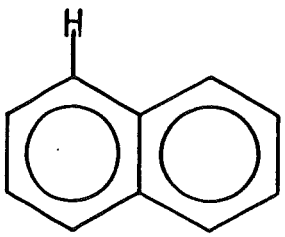
(24)

C(3)-C(4)-C(5)-C(6)	-35.7°
C(4)-C(3)-C(2)-C(1)	15.9°

Notable in the structures of compounds (23),(24) and (25) (Figs 1,2, and 3) are the various orientations of the nitro groups relative to the ring carbon atoms, or the geminal methyl carbons. For example, for the trans-5,6-dinitro compounds (24) and (25), in addition to the ring conformation difference, noted above, there are differences in the orientations of the 5-NO_2 and 6-NO_2 nitro groups relative to the ring carbons. In compound (24) the planes of the 5-NO_2 and 6-NO_2 groups are nearly aligned with the C(5)-C(6) bond. [torsion angles: C(5)-C(6)-N(6)-O(61) -1.0(7)°; C(6)-C(5)-N(5)-O(52) 17.9(7)°]. However, for compound (25), while the plane of the 6-NO_2 group is nearly aligned with the C(5)-C(6) bond [torsion angle: C(5)-C(6)-N(6)-O(61) -10.4(3)°], the plane of the 5-NO_2 group is closely aligned with the C(5)-C(10)

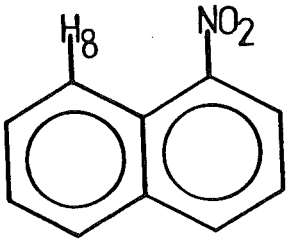
bond, [torsion angle: C(10)-C(5)-N(5)-O(52) 8.6(4)°]. For both these compounds, the 2-NO_2 group is closely aligned with the C(2)-C(7) bond. In contrast, for compound (23) the planes of the 2-NO_2, 5-NO_2 and 6-NO_2 groups, are more substantially displaced from alignment with the C(2)-C(7) [-33.1(4)°], C(5)-C(10) [20.6(4)°] and C(6)-C(11) [-32.0(4)°] bonds respectively.

The effect of the orientation of a nitro group on the ^1H n.m.r. chemical shifts of neighbouring protons, has been studied by Wells and Alcorn[50] using some substituted nitronaphthalene derivatives. The ^1H n.m.r. spectra of 1-nitronaphthalene (27) and some methyl substituted 1-nitronaphthalenes were recorded in dimethylacetamide solution. The important feature of these spectra, is the chemical shift value of the hydrogen at the <u>peri</u>- position to the nitro group, as shown below:



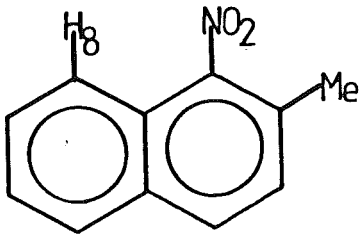
(28)

H_α δ 7.95



(27)

H_8 δ 8.36

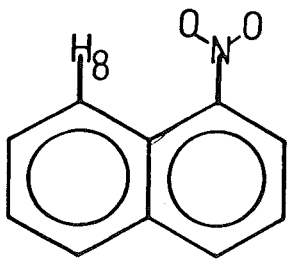


(29)

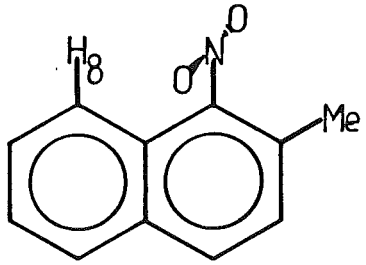
H_8 δ 7.68

For 1-nitronaphthalene (27), the chemical shift of H(8), is moved downfield by 0.41 p.p.m. relative to the corresponding proton signal for the unsubstituted naphthalene (28). In

contrast, the chemical shift of H(8) for 1-nitro-2-methyl-naphthalene (29) is upfield, relative to the naphthalene position, by 0.27 p.p.m. These effects were rationalised in terms of the orientation of the nitro group relative to H(8). In 1-nitronaphthalene the nitro group is essentially coplanar with the plane of the naphthalene ring system and the H(8) resonance reflects the deshielding effect of the proximate nitro oxygen atom. In 2-methyl-1-nitronaphthalene, non-bonded interactions between the adjacent nitro and methyl groups force the nitro group to adopt an orientation essentially perpendicular to the plane of the ring system.



(27)



(29)

Because of the anisotropy of the nitro group, H(8) for this compound has a resonance upfield from that of the unsubstituted naphthalene system.

Thus, for structures (23),(24),(25) and (26), the extent of the variation in the orientations of the nitro groups in the solid state, makes the assignment of the ^{1}H n.m.r. spectra particularly hazardous. Also, to this must be added the necessary assumption that these molecules exist in the same conformation in solution and in the solid state.

However, for compounds (23),(24),(25) and (26), some limited assignment of the ^{1}H n.m.r. spectra is possible. In

the ^{1}H n.m.r. spectra of all four compounds, evidence of 3-Me/4-Me coupling is apparent, either as peak broadening [(23),(24) and (26)] or as the appearance of the two methyl signals as quartets (25). By comparison of the ^{1}H n.m.r. spectra for compounds (23),(24),(25) and (26) with those for the closely related 4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (49),(50),(51) and (52), it was possible to assign signals due to the 3-Me and 4-Me groups in compounds (23),(24), (25) and (26). Notable in the ^{1}H n.m.r. spectra of the trans-5,6-dinitro compounds (24) and (25) is the presence of a methyl signal at c. δ 2.12 - the most deshielded methyl signal in the cis-5,6-dinitro compounds (23) and (26) appears at δ 2.04.

In relation to the established stereochemistry of these 2,5,6-trinitrocyclohex-3-enones (23),(24),(25) and (26), it is interesting to note the relationship between the stereochemistry of these compounds and their relative order of elution from a Chromatotron silica gel plate. The observed order of elution is: r-2,t-5,c-6; c-5,t-6; t-5,t-6; c-5,c-6. Similar stereochemistry/elution order patterns have been noted for related 2,5,6-trinitrocyclohex-3-enones (30) and (31).[51]

(b) 4,5,6-Trinitrocyclohex-2-enones (32),(33), [(34) or (35)]

Three 4,5,6-trinitrocyclohex-2-enones (32),(33) and [(34) or (35)] were isolated from the crude product. For two compounds (32) and (33), the structures and stereochemistry were determined by single-crystal X-ray analysis, but for the third compound, (34) or (35), crystals of adequate quality could not be obtained, and so the stereochemistry at C4, remains uncertain. The spectroscopic data for the three compounds (32), (33), and [(34) or (35)] were consistent with the assigned structures. A perspective drawing of 2,3,4,5,6-pentamethyl-r-4,t-5,t-6-trinitrocyclohex-2-enone (32), $C_{11}H_{15}N_3O_7$, m.p. 124-126^{o} (dec.) is presented in Fig (4) with corresponding fractional coordinates in Table (4). Corresponding information is presented for 2,3,4,5,6-pentamethyl-r-4,c-5,c-6-trinitrocyclohex-2-enone (33), $C_{11}H_{15}N_3O_7$, m.p. 116-118^{o} (dec.) (Fig (5) and Table (5)). From an inspection of the appropriate torsion angles (Table (8)), it is clear that compound (32) exists in the solid state, in a skew-boat conformation [torsion angles: C(2)-C(3)-C(4)-C(5) 3.9(3)^{o}; C(3)-C(2)-C(1)-C(6) -18.0(3)^{o}], with the C(5)-N(5) bond close to perpendicular to the rough plane of the ring atoms. In contrast, the ring system of compound (33) exists in the solid state, in a modified [C(1), Sp^2] half-chair conformation [torsion angles: C(2)-C(3)-C(4)-C(5) -13.3(4)^{o}; C(3)-C(2)-C(1)-C(6) 14.6(4)^{o}] with the 5-NO_2 group axial.

In the absence of an X-ray structure determination on the third 4,5,6-trinitrocyclohex-2-enone, m.p. 88-89^{o} (dec.), it is not possible to define the stereochemistry of the compound, and its structure, (34) or (35) remains uncertain.

(c) r-2-Hydroxy-2,3,4,5,6-pentamethyl-t-5,t-6-dinitrocyclohex-3-enone (36)

A minor product (36) was isolated from the crude product above, and its structure was determined by single-crystal X-ray analysis. A perspective drawing of the hydroxy dinitro ketone (36), $C_{11}H_{16}N_2O_6$, m.p. 165-165.5° is presented in Fig (6) with corresponding fractional coordinates in Table (6). The spectroscopic data for the hydroxy dinitro ketone (36) were in accord with its established structure. The ring system of compound (36) exists in a skew-boat conformation [torsion angles (table 8): C(4)-C(3)-C(2)-C(1) -6.1(7)°; C(3)-C(4)-C(5)-C(6) 26.6(6)°] with the 5-NO_2 group in the flagpole orientation [torsion angle: C(3)-C(4)-C(5)-N(5) -90.3(5)°]. The H(2) to O(1) distance is 2.82 Å, ruling out the presence of intramolecular hydrogen bonding.

The structure of the hydroxy dinitro ketone (36) was novel, all previously isolated hydroxydinitrocyclohex-3-enones having the 6-hydroxy-2,5-dinitro substitution pattern (37).[52,53] Unfortunately the hydroxy dienone (38) could not be prepared by standard methods, and therefore the addition of nitrogen dioxide to this compound (38) could not be attempted.

(d) Other products

Apart from the minor product, 2,3,5,6-tetramethyl-1,4-benzoquinone (39) (c. 1%),[54] the only other product isolated was 2,3,4,5,6-pentamethyl-4-nitrocyclohexa-2,5-dienone (21) (38%). The spectroscopic data for the latter compound (21) were in accord with the structure assigned, the 4-nitrocyclohexa-2,5-dienone structure being indicated by the relative simplicity of the ^1H n.m.r. spectrum, the appearance of seven carbon resonances in the ^{13}C n.m.r. spectrum, and the ultraviolet

spectrum (λ_{max} 247 nm). The 4-nitrodienone (21) is unusual; its isolation from the reaction of nitrogen dioxide with pentamethylphenol, and its essentially quantitative recovery, after treatment with nitrogen dioxide in benzene, clearly show that it does not rearrange to give the 6-nitrocyclohexa-2,4-dienone (40) under these conditions. A ^{1}H n.m.r. time-scan in deuteriochloroform showed no change in its spectrum after 24 hours. In contrast, the 3,4,5-tribromo-2,6-dimethylcyclohexa-2,5-dienone (41) readily interconverts with the 6-nitrocyclohexa-2,4-dienone (42).[53]

2.2.1 A MECHANISM FOR THE FORMATION OF (23),(24),(25),(26), (32),(33), [(34) or (35)],(21),(36).

The formation of the observed products can be rationalised as shown in the reaction scheme outlined in Scheme (7)*. In the initial step (1), the phenolic hydrogen atom is abstracted by nitrogen dioxide, to give the phenoxy radical (43), a reaction accompanied by the formation of nitrous acid. In step (2) this phenoxy radical undergoes radical-coupling with nitrogen dioxide either at the 4- position to give the 4-nitrodienone (21), or at the 6- position to give the intermediate 6-nitrodienone (40).

The first step, the formation of the phenoxy radical, is analogous to that demonstrated by Brunton et al,[55] for the 2,6-di-t-butyl-4-methylphenol (44). Short-term treatment of this phenol (44) with nitrogen dioxide in petroleum ether gave the corresponding phenoxy radical (45), which was detected by e.s.r. spectroscopy. The coupling reaction

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* Reaction Schemes as foldouts at the end of this thesis.

between the phenoxy radical (43) and nitrogen dioxide (step 2) is also known: Cook and Woodworth[56] reacted the 2,4,6-tri-t-butylphenoxy radical (46) with nitrogen dioxide, to give a quantitative yield of the 4-nitro-2,4,6-t-butylcyclohexa-2,5-dienone (47).

As has been shown, above, the 4-nitrodienone (21) is unreactive under the reaction conditions, and is isolated as a major product. Therefore, the formation of the 4,5,6-trinitrocyclohex-2-enones (32),(33) and [(34) or (35)] must arise by 4,5-addition of nitrogen dioxide to the 6-nitrodienone (40). In principle, the 2,5,6-trinitrocyclohex-3-enones (23),(24), (25) and (26) could arise from the 6-nitrodienone (40) by either 2,3- or 2,5- addition of nitrogen dioxide. While this uncertainty can not be resolved on the basis of the information available, it seems likely that attack by nitrogen dioxide on the diene system of the 6-nitrodienone (40) is initiated at C5 to give the resonance-stabilised radical (48), as shown in step 3. Thus the formation of 4,5,6-trinitrocyclohex-2-enones (32),(33) and [(34) or (35)] would result from attack of NO_2 on the radical (48) at C4, and the formation of 2,5,6-trinitrocyclohex-3-enones (23)→(26) arise from attack of NO_2 at C2. The r-2-hydroxy-dinitrocyclohex-3-enone (36), as will become clear later, is likely to have arisen from attack on the resonance-stabilised radical (48) at C2 by an oxygen-centred radical form of nitrogen dioxide (ONO), followed by hydrolysis.

2.3 THE REACTION OF PENTAMETHYLPHENOL WITH EXCESS FUMING NITRIC ACID IN DICHLOROMETHANE

Pentamethylphenol was reacted initially at -10 to -5° with c. 1 mole fuming nitric acid, which was added carefully as a

dilute solution in dichloromethane. After this addition, further fuming nitric acid (neat) was added dropwise, and the mixture stirred at 20° for 90 h. Removal of the nitric acid, and solvent under reduced pressure gave a crude product, which had absorptions in its infrared spectrum characteristic of non-conjugated carbonyl c. 1755 cm^{-1}, conjugated carbonyl c. 1710 cm^{-1}, and nitrate ester functions. c. 1630, 1260, 850 cm^{-1}. The ^1H n.m.r. spectrum had, in addition to a complicated pattern of signals due to methyl groups from c. 1.8-2.2 p.p.m., signals at c. 5.2-5.6 p.p.m. due to $-CH_2ONO_2$ groups. The components of this crude product were separated by a combination of fractional crystallization and chromatography.

(a) 2,3,5,6-Tetramethyl-4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (49)(50)(51) and (52)

From the crude product were isolated the four possible 4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (49)(50)(51) and (52). The structure of one of these compounds, (49), was determined by single-crystal X-ray analysis; a perspective drawing of this compound, 2,3,5,6-tetramethyl-4-nitratomethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (49), $C_{11}H_{14}N_4O_{10}$, m.p. 135-136° (dec.), is presented in Fig (7) with corresponding fractional coordinates in Table (7). The spectroscopic data for compound (49) were in accord with its established structure. Compound (49), in the solid state, exists in a skew-boat conformation [torsion angles: C(4)-C(3)-C(2)-C(1) -11.9(4)°; C(3)-C(4)-C(5)-C(6) 32.5(4)°]. Comparison of these torsion angles with those for the 2,5,6-trinitrocyclohex-3-enone (23), reveal that, in the solid state at least, the ring conformations of the two compounds are essentially identical. Further, the orientations of the nitro groups in these two compounds (23) and (49) are

also very similar (see Table (8).

The remaining three 4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (50),(51) and (52) also gave spectroscopic data in accord with their gross structure. The assignment of stereochemistry to these compounds was based (i) on the comparison of selected features of their ^{1}H n.m.r. spectra with those of the 2,5,6-trinitrocyclohex-3-enones (23),(24),(25) and (26), and (ii) on the order of elution of these nitrates (49),(50),(51) and (52) from the chromatotron, using ether/petroleum ether as eluents. It was noted, above, that the ^{1}H n.m.r. spectra of the trans-5,6-dinitro compounds (24) and (25) each exhibit a methyl resonance at δ c. 2.12, but the most deshielded methyl signal in the cis-5,6-dinitro compounds (23) and (26) appears at δ 2.04. By analogy, the nitrato-compounds (50) and (51), which have methyl signals at δ c. 2.18 are assigned trans-5,6-dinitro structures. Compounds (49) and (52), having the most deshielded methyl signal at δ c. 2.10, are thus cis-5,6-dinitro compounds; as the structure of compound (49) has been determined by X-ray crystal structure analysis, compound (52) is assigned the r-2,c-5,c-6-trinitro by exclusion. Comparison of the ^{1}H n.m.r. spectra of the 2,5,6-trinitrocyclohex-3-enones (23),(24),(25) and (26) with those for the 4-nitratomethyl derivatives (49),(50),(51) and (52), allows the identification of the signal due to the 3-Me group as the most upfield signal. On the basis of the frequency of this signal for compounds (24) (δ 1.77), (25) (δ 1.84) (50) (δ 1.88) and (51) (δ 1.92), the stereochemistry of compounds (50) and (51) were assigned as indicated. With the assignments made on the basis of ^{1}H n.m.r. comparisons, it is notable that the order of elution of these compounds

from a Chromatotron silica gel plate, is the same order observed for the 2,5,6-trinitrocyclohex-3-enones (23),(24), (25) and (26), and the related sets of 2,5,6-trinitrocyclohex-3-enones (30) and (31).[51]

(b) Other products

In addition to the 4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (49),(50),(51) and (52), five further compounds were isolated from the reaction of pentamethylphenol (19) with fuming nitric acid in dichloromethane. These compounds were the three 2,5,6-trinitrocyclohex-3-enones (23),(24) and (26), the 4,5,6-trinitrocyclohex-2-enone (32), and the unusual hydroxy dinitro ketone (36). Each compound was identified by comparison with authentic material.

2.4 REACTION OF NITRO DIENONE (21) WITH FUMING NITRIC ACID IN DICHLOROMETHANE

Treatment of the 4-nitrodienone (21) with fuming nitric acid in dichloromethane, as for pentamethylphenol (19) above, gave a crude product that had essentially the same composition as that from the reaction of pentamethylphenol (19) with fuming nitric acid; the same products were also isolated from this mixture.

There are two important features of this reaction: (i) the formation of products, shown from the reaction of pentamethylphenol with nitrogen dioxide, to arise from the addition to nitrogen dioxide to the 6-nitrodienone, and (ii) the formation of 4-nitratomethyl ketones (49),(50),(51) and (52).

(i) The 4-nitrodienone (21) as described above, is stable in organic solvents, and does not interconvert with the 6-nitrodienone (40), the intermediate to the formation of the

compounds (23),(24),(26),(32),(36). However, this result suggests that in the strongly acidic conditions of the above reaction, the 4-nitrodienone (21) is in rapid equilibrium with the 6-nitrodienone (40). Thus, it is clear that this interconversion of the 4- and 6- nitrodienones in fuming acid, is acid-catalysed. A possible mechanism for this conversion, as outlined in Scheme (8), involves protonation of the 4-nitrodienone (21) to give its conjugate acid (53). This can dissociate to give the species (54),[57] which may recombine at the C4 position, and go back to (53), or at the C6 position to give the conjugate acid of the 6-nitrodienone (55).

(ii) The formation of the 4-nitrato ketones (49),(50), (51) and (52), in the reaction of the 4-nitrodienone (21) with fuming nitric acid, is also likely to be an acid-catalysed process. It is possible that under these conditions, the 4-nitrodienone (21) may undergo an acid-catalysed elimination of nitrous acid to give the tetramethyl-p-quinonemethide (56) (Scheme 9). This species would be expected to be susceptible to attack by nucleophiles present in the system. It appears, therefore, that the 4-nitratomethyl compounds arise by attack of nitrate ion on the methylene-carbon atom of the p-quinonemethide (56), giving the 4-nitratophenol (57) Scheme (10).

2.5 PREPARATION OF p-QUINONEMETHIDE (56), AND ITS REACTION WITH FUMING NITRIC ACID IN DICHLOROMETHANE

A solution of the p-quinonemethide (56) in dichloromethane was prepared from pentamethylphenol (19) by a modification of the procedure of Dyall and Winstein.[58] Treatment of this solution of the p-quinonemethide [^{1}H n.m.r. (CH_2Cl_2) δ 1.96, 2.13;

integrals c. 1:1] with fuming nitric acid, as for pentamethylphenol (19), above, gave a crude product, from which the tetramethyl-1,4-benzoquinone (39) and the four possible 4-nitratomethyl-2,5,6-trinitrocyclohex-3-enones (49),(50),(51) and (52) could be isolated. It is notable that the relative yields for these nitratoketones are very similar to those from (i) the nitration of pentamethylphenol (19), and (ii) the nitration of the 4-nitrodienone (21).

These results suggest that the formation of the 4-nitratomethyl ketones (49),(50),(51) and (52) in the fuming nitric acid nitration, of pentamethylphenol (19), involve the 4-nitrodienone (21) and the p-quinonemethide (56) as intermediates.

2.6 A MECHANISM FOR THE REACTION OF PENTAMETHYLPHENOL (19) WITH FUMING NITRIC ACID IN DICHLOROMETHANE

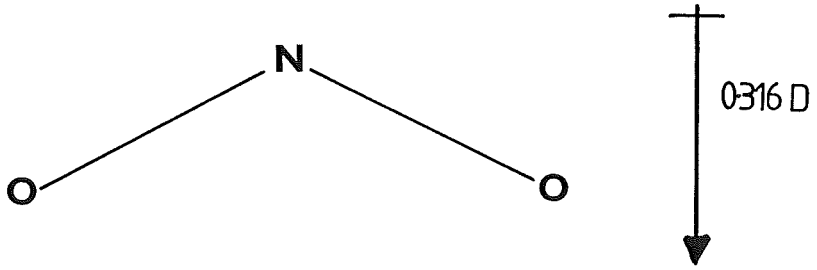
The reaction sequence described in Scheme (11), involves the initial formation of the 4-nitrodienone (21) and the 6-nitrodienone (40), which are in rapidly attained equilibrium. Thus, the reaction of the 6-nitrodienone (40) with nitrogen dioxide to give the products (23),(24),(26),(32) and (36) (step 2), is in competition with the acid-catalysed elimination of nitrous acid from the 4-nitrodienone (21) (step 3) to give the p-quinonemethide (56). 1,6-Addition of nitric acid to the p-quinonemethide (step 4) gives the 4-nitratomethylphenol (57), which can then react analogously to pentamethylphenol (19) to give the nitrato ketones (49),(50),(51) and (52).

CHAPTER THREE

THE REACTION OF 2,3,5,6-TETRAMETHYL-4-NITROPHENOL (58) WITH NITROGEN DIOXIDE IN BENZENE

3.1 INTRODUCTION

The monomeric form of nitrogen dioxide, which has an unpaired electron, has been a topic of much study using electron spin resonance spectroscopy. Solution studies[74] in non-polar non-coordinating solvents, such as cyclohexane have shown that the unpaired electron is distributed about the molecule with c. 50% of the spin density centred on the nitrogen, leaving about 25% on each of the oxygen atoms. Further, these studies have calculated the O-N-O bond angle to be 132-134°. An important feature of nitrogen dioxide, is the presence of a significant dipole moment of 0.316D,[75] as compared with that of water (1.85 D), the more electro-positive element, nitrogen, being the positive end of the dipole.



The reaction of 2,4,5-tribromo-3,6-dimethylphenol (59a)[25] with fuming nitric acid in acetic acid, gives the all cis-hydroxy-dinitrocyclohex-3-enone (60a)(Scheme 12), with no observed formation of 2,5,6-trinitrocyclohex-3-enones. In

contrast the nitration of 2,4-dibromo-3,5,6-trimethylphenol (59b) gave a 2,5,6-trinitrocyclohex-3-enone (61) of unknown stereochemistry and in yields up to 26%, in addition to the C2-epimeric 6-hydroxy-2,5-dinitrocyclohex-3-enones (60b) and (62)[53] (Scheme 13). The structures of the two phenols (59a) and (59b) differ only at C5, with the replacement of the C5-bromine in phenol (59a) with a C5-methyl group in phenol (59b).

The division of products, into those from addition of nitrogen dioxide to the 6-nitrodienone (63), and those from addition of nitrogen dioxide to the 6-hydroxydienone (64) (Scheme 13), depend on the relative rates, of the conversion of the 6-nitrodienone (63) into the 6-hydroxydienone (64) (presumably via a nitro-nitrito rearrangement), and the rate of addition of nitrogen dioxide to the 6-nitrodienone (63). Thus, the increase in trinitro ketone formation, in going from a C5-bromine (59a) to a C5-methyl group (59b), may be rationalised either by the promotion of addition of the electrophilic nitrogen dioxide to the 6-nitrodienone (63) at C5, by the electron-donating methyl group, or less likely by reducing the rate of conversion of the 6-nitrodienone (63) into the corresponding 6-hydroxydienone (64) (Scheme 13).

The reaction of pentamethylphenol (19) with nitrogen dioxide in benzene, gives the 4-nitrodienone (21) and products arising from addition of nitrogen dioxide to the 6-nitrodienone (40). No 6-hydroxy-2,5-cyclohex-3-enones (37) were isolated from this reaction in which the products, above, account for 97% of the pentamethylphenol reacted.

It was decided, therefore, to examine the reaction of 2,3,5,6-tetramethyl-4-nitrophenol (58)* with nitrogen dioxide

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* Diagrams in Block B at the end of this thesis.

in benzene solution. For this substrate (58) the potential intermediate 6-nitrodienone (65), differs in structure from 6-nitrodienone (40), formed from pentamethylphenol (19), only in the presence of the electron-withdrawing nitro group at C4 instead of a methyl group. Thus it would be of interest to determine whether the reaction products were formed either by nitrogen dioxide addition to the 6-nitrodienone (65) to give tetranitrocyclohexenones and/or by conversion of the 6-nitrodienone (65) into the 6-hydroxydienone (66) (cf Scheme 13), followed by nitrogen dioxide addition to give 6-hydroxy-2,4,5-trinitrocyclohex-3-enones.

3.2 REACTION OF 2,3,5,6-TETRAMETHYL-4-NITROPHENOL (58) WITH NITROGEN DIOXIDE IN BENZENE

Reaction of 2,3,5,6-tetramethyl-4-nitrophenol (58) with nitrogen dioxide in benzene gave a crude product, the infrared spectrum of which exhibited absorptions due to hydroxy groups 3525 cm^{-1}, non-conjugated carbonyl groups 1760-1750 cm^{-1}, and a broad absorption at 1590-1540 cm^{-1} due to nitro groups. The ^{1}H n.m.r. spectrum showed a complicated pattern of peaks at c. δ 1.8-2.3 p.p.m. with highfield signals at c. δ 1.54 p.p.m. The components of this crude product were separated by a combination of fractional crystallization using dichloromethane/pentane solvent mixtures, and chromatography on a Chromatotron silica gel plate. Some of the compounds isolated were formed during the chromatographic separations; these will be indicated, and their mode of formation identified.

(a) 2,3,5,6-Tetramethyl-2,4,5,6-tetranitrocyclohex-3-enones (67),(68),(69) and (70)

From the crude product were isolated the four possible

2,4,5,6-tetranitrocyclohex-3-enones (67),(68),(69) and (70), the structures of two of which were determined by single-crystal X-ray structure analysis, below. Unfortunately, tetranitroketones (69) and (70) did not give crystals of a satisfactory quality for X-ray structure analysis. The spectroscopic data for all four compounds were in accord with their gross structure. A perspective drawing of 2,3,5,6-tetramethyl-r-2,4,t-5,c-6-tetranitrocyclohex-3-enone (67), $C_{10}H_{12}N_4O_9$, m.p. 118-119° (dec.) is presented in Fig (8) with corresponding fractional coordinates in Table (9). Similar information is presented for 2,3,5,6-tetramethyl-r-2,4,c-5,t-6-tetranitrocyclohex-3-enone (68), $C_{10}H_{12}N_4O_9$, m.p. 118-119° (dec.) (Fig (9) and Table (10)). From an inspection of the appropriate torsion angles (Table (8)) it is clear that, in the solid state, the trans-5,6-dinitro compounds (67) and (68), exist with the ring in a skew-boat conformation, for (67) [torsion angles; C(4)-C(3)-C(2)-C(1) -8.4(5)°: C(3)-C(4)-C(5)-C(6) 24.5(4)°], and (68) [torsion angles; C(4)-C(3)-C(2)-C(1) -8.6(4)°: C(3)-C(4)-C(5)-C(6) 20.3(4)°]. (These are similar to the ring conformation for the related trans-5,6-dinitro compounds (24) and (25) (See Table (8)) from pentamethylphenol (19)). For both these compounds (67) and (68) the 5-NO_2 group is in a flagpole orientation: (67) [torsion angle: C(3)-C(4)-C(5)-N(5) -84.9(4)°], and (68) [torsion angle: C(3)-C(4)-C(5)-N(5) -91.6(4)°]. This conformational similarity extends to the orientations of the 4-NO_2 and 5-NO_2 groups [for (67) C(3)-C(4)-N(4)-O(42) -68.2(5)°; C(9)-C(5)-N(5)-O(52) 3.1(5)°: for (68) C(3)-C(4)-N(4)-O(42) -76.6(4)°; C(9)-C(5)-N(5)-O(52) -4.2(4)°]. The differences in orientation of the 2-NO_2 and 6-NO_2 groups are more marked, particularly for the 6-NO_2 groups [for

(67) O(21)-N(2)-C(2)-C(3) 27.0(5)°; O(62)-N(6)-C(6)-C(5) -3.8(5)°: for (68) O(21)-N(2)-C(2)-C(3) -11.0(4)°; O(62)-N(6)-C(6)-C(5) 97.0(3)°].

The stereochemistry of the remaining two tetranitroketones (69) and (70) could not be determined using X-ray crystal-structure analysis. Furthermore no ^{1}H n.m.r. correlations could be made with the four isomeric 2,3,5,6-pentamethyl-2,5,6-trinitrocyclohex-3-enones (23),(24),(25) and (26) of known stereochemistry. The probable reason for this difficulty with ^{1}H n.m.r./stereochemistry correlations, as outlined in chapter two, arises from the variation in the orientations of the nitro groups in these compounds. However, the elution order/stereochemistry relationship, observed for the related sets of isomeric 2,4,6-trinitrocyclohex-3-enones: (23)-(26), (30) and (31)[51] using as eluents ether/petroleum ether solvent mixtures which is: r-2,t-5,c-6-; r-2,c-5,t-6-; r-2,t-5,t-6-; r-2,c-5,c-6, allows the assignment of stereochemistry to the tetranitroketones (69) and (70). For the tetranitrocyclohex-3-enones (67),(68),(69) and (70), the elution order was (67),(68),(69),(70). Compounds (67) and (68) whose structures have been determined above, have the r-2,t-5,c-6- and r-2,c-5,t-6- stereochemistry respectively; thus compounds (69) and (70) are assigned the r-2,t-5,t-6- and r-2,c-5,c-6- stereochemistry respectively.

(b) Hydroxynitrocyclohex-3-enones (71),(72) and (73).

Three hydroxynitrocyclohex-3-enones (71),(72) and (73) were isolated from the crude product by separation on a Chromatotron silica gel plate. The 2-hydroxy-4,5,6-trinitrocyclohex-3-enone (71) is stable under these chromatographic conditions. However, the 6-hydroxy-2,4,5-trinitro- (72) and the 2,6-dihydroxy-4,5-

dinitro- (73) are partially converted into mixtures of substituted cyclopentenols under these conditions, as shown by control studies; for compounds (72) and (73) the yields isolated represent the minimum amount present in the crude product.

The structures of two of these compounds, (71) and (72), were determined by single-crystal X-ray structure analysis; the structure of the third compound, (73) was assigned on the basis of the structure of one of its acyloin rearrangement products (74), determined below. The spectroscopic data for these compounds were in accord with the assigned structures. A perspective drawing of r-2-hydroxy-2,3,5,6-tetramethyl-4,t-5,t-6-trinitrocyclohex-3-enone (71), $C_{10}H_{13}N_3O_8$, m.p. 167-167.5°, is presented in Fig (10) with corresponding fractional coordinates in Table (11). Similar information is presented for c-6-hydroxy-2,3,5,6-tetramethyl-r-2,4,c-5-trinitrocyclohex-3-enone (72), $C_{10}H_{13}N_3O_8$, m.p. 129.5-130.5° (dec.), is presented in Fig (11) and Table (12). From inspection of the appropriate torsion angles (Table (8)) it is clear that, in the solid state, the 2-hydroxy compound (71) exists in a skew-boat conformation with the 5-NO_2 group in a flagpole orientation, while the 6-hydroxy compound (72) has a half-chair conformation with the 5-NO_2 group pseudoaxial. The absence of intramolecular hydroxyl-carbonyl group hydrogen bonding in compound (71) is clear from the perspective drawing (Fig 10); this is supported by the O(1)-H(2) distance of 2.94 Å. In contrast, the O(1)-H(6) distance for (72) is 2.19 Å, and the O(1)-C(1) and C(6)-O(6) bonds are close to coplanar [torsion angle: O(1)-C(1)-C(6)-O(6) 17.7(7)°], consistent with intramolecular hydrogen-bonding in the compound (72).

(c) Cyclopentenol Derivatives (75) and (76)

These compounds (75) and (76) were isolated in only low yield (<1% each) by crystallizations of Chromatotron fractions (which were mixtures) from the crude product. Although it is not possible to prove that they were not present in the crude product prior to separation, it is believed that they are acyloin rearrangement products of the C2-epimeric -6-hydroxy-2,4,5-trinitrocyclohex-3-enones (72) and (77). In accord with this interpretation, the 6-hydroxy-2,4,5-trinitrocyclohex-3-enones (72) and (77) are significant components of the crude product. [(72), c. (10%); (77), c. 15%] (^{1}H n.m.r.), and have been shown to undergo acyloin rearrangement on a chromatotron silica gel plate (control experiments). The spectroscopic data for compounds (75) and (76) were in accord with their assigned general structures; argument in support of the stereochemical assignments will be presented later, below.

3.3 FORMATION OF 2,3,5,6-TETRAMETHYL-4,6-DINITROCYCLOHEXA-2,4-DIENONE (65) AND 6-HYDROXY-2,3,5,6-TETRAMETHYL-4-NITROCYCLOHEXA-2,4-DIENONE (66)

Reaction of 2,3,5,6-tetramethyl-4-nitrophenol (58) with fuming nitric acid in acetic acid, followed by the addition of water, gave a crude product which was recrystallised at low temperature from dichloromethane/pentane to yield the 6-nitrodienone (65). This compound was unstable in deuteriochloroform (^{1}H n.m.r.) and rearranged rapidly to give first a further unstable compound, probably the corresponding 6-nitritodienone (78), which decayed to yield the 6-hydroxydienone (66). The structural assignment for the nitrodienone (65) is based on the ^{13}C n.m.r. spectrum of the compound at -60°, which

exhibited ten carbon resonances of appropriate chemical shifts.

The instability of the 6-nitrodienone (65) in chloroform was exploited for the preparation of the 6-hydroxydienone (66). Nitrogen gas was bubbled through a solution of the 6-nitrodienone (65) in chloroform to give, on removal of the solvent under reduced pressure an essentially quantitative yield of the 6-hydroxydienone (66).

3.4 REACTION OF THE 6-HYDROXY-2,3,5,6-TETRAMETHYL-4-NITRO-CYCLOHEXA-2,4-DIENONE (66) WITH NITROGEN DIOXIDE IN BENZENE

Reaction of the 6-hydroxydienone (66) with nitrogen dioxide, as for 2,3,5,6-tetramethyl-4-nitrophenol (58), above, gave a crude product, which was shown (^{1}H n.m.r.) to be a mixture c. 3:2:5 of compounds (72),(73) and (77). Each of these compounds was isolated by fractional crystallization of the crude product, using dichloromethane/pentane solvent mixtures. The residues from these crystallizations were subjected to chromatography on a Chromatotron silica gel plate and gave a further compound, the cyclopentenediol (74). This compound (74) was not present in the material absorbed onto the Chromatotron silical gel plate (^{1}H n.m.r.), and was shown (control experiment) to arise by rearrangement of the 2,6-dihydroxycyclohex-3-enone (73).

The structures of compounds (77) and (74), were determined by single-crystal X-ray analysis. A perspective drawing of t-6-hydroxy-2,3,5,6-tetramethyl-r-2,4,t-5-trinitrocyclohex-3-enone (77), $C_{10}H_{13}N_3O_8$, m.p. 118-120^o (dec.), is presented in Fig (12) with corresponding fractional coordinates in Table (13). Similar information is presented for 1-acetyl-2,3,5-trimethyl-4,c-5-dinitrocyclopent-3-ene-r-1,t-2-diol (74), $C_{10}H_{14}N_2O_7$, m.p.

120-121° (dec.) (Fig (13) and Table (14)). The spectroscopic data for these compounds were in accord with the structures determined above.

In the solid state, the trans-2,5-dinitro compound (77) exists with the ring in a skew-boat conformation (torsion angles, Table 8) with the 5-NO_2 group in a flagpole orientation [torsion angle: C(3)-C(4)-C(5)-N(5) -86.5(6)°], in contrast to the cis-2,5-dinitro compound (72) shown, above, to exist in a half-chair conformation. For the trans-2,5-dinitro compound (77) the O(1)-H(6) distance is 2.29 Å and the C(1)-O(1) and C(6)-O(6) bonds are close to coplanar [torsion angle O(1)-C(1)-C(6)-O(6) 22.0(7)°], consistent with intramolecular hydroxyl-carbonyl group hydrogen-bonding in the molecule.

For the cyclopentenediol (74), the two highest peaks in the final difference-Fourier map were in chemically reasonable positions for the two hydroxy group hydrogen atoms, but these did not refine. However, the presence of intramolecular hydroxyl-hydroxyl or hydroxyl-carbonyl group hydrogen-bonding can be excluded, on the basis of the O(1)-O(2) distance (3.71 Å), the O(2)-O(6) distance (3.17 Å), and the torsion angle O(1)-C(1)-C(6)-O(6) = 166.2(8)°. Notable in the structure of the cyclopentenediol (74) is the near-eclipsing of the plane of the 5-NO_2 group with the C(5)-C(4) bond [torsion angle: C(4)-C(5)-N(5)-O(52) -11(1)°].

On the basis of this established 2,5-stereochemistry of the cyclopentenediol (74), the structure of its precursor, 2,6-dihydroxycyclohex-3-enone (73) can be defined. The acyloin rearrangement of 2,6-dihydroxycyclohex-3-enone (73) does not affect the relative stereochemistry at C2 and C5; thus the r-2,t-5 stereochemistry of the 2,6-dihydroxycyclohex-3-enone (73) is established. The additions of nitrogen dioxide to

6-hydroxy-6-methylcyclohexa-2,4-dienones (79) are known to involve initial attack of nitrogen dioxide at C5 to yield exclusively cis-6-hydroxy-5-nitro compounds (ref 53 and other references cited within). Therefore the 2,6-dihydroxycyclohex-3-enone (73) is also assigned the cis-6-hydroxy-5-nitro- stereochemistry.

3.5 BASE-CATALYSED ACYLOIN REARRANGEMENT OF c-6-HYDROXY-2,3,5,6-TETRAMETHYL-r-2,4,c-5-TRINITROCYCLOHEX-3-ENONE (72)

When a two phase system of dilute aqueous sodium bicarbonate and a dichloromethane solution of the hydroxy trinitro ketone (72) was shaken vigorously for 5 min., the product was shown (^{1}H n.m.r.) to be a mixture (c. 2:1) of the two cyclopentenols (75) and (80), although the minor component (80) could not be obtained in a pure state. However, these two cyclopentenols (75) and (80), being derived from the cis-2,5-dinitrocyclohex-3-enone (72) must also have the cis-2,5-dinitro- stereochemistry.

From studies of related pairs of cyclopentenols,[53] it has been shown that the stereochemistry at C1 can be determined from the relative chemical shift values in the ^{1}H n.m.r. spectrum, of the acetyl methyl group. For example, the pair of C1 epimeric cyclopentenols (81) and (82)* derived from the 2,4,5-tribromo-c-6-hydroxy-r-2,c-5-dinitrocyclohex-3-enone (83) have distinctive chemical shift values for the acetyl methyl groups, for (81) δ 2.37 p.p.m. and (82) 2.64 p.p.m. Thus the chemical shift for the acetyl- methyl which is trans to the C2 and C5 nitro groups, is downfield c. 0.3 p.p.m.

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* Cyclopentenols (80) and (81) with relevant ^{1}H n.m.r. data are presented in Figure (14).

relative to an acetyl- methyl group which is cis to the C2 and C5 nitro groups. A similar downfield shift of the acetyl methyl protons (Δ0.13-0.21) is observed for the trans-2,5-dinitro- cyclopentenol derivatives (88) and (89),(90) and (91) when the acetyl group is trans- rather than cis- to the C2 nitro function, see Fig (14). Another notable feature of the ^{1}H n.m.r. spectra of the cyclopentenols in Fig (14), is seen for those cyclopentenols having a C2-methyl group (84),(85), (86),(87),(88),(89),(90) and (91) where the chemical shift of this C2-methyl group is dependent on whether it is cis- (c. δ 1.9-1.97) or trans- (δ 1.74-1.78) to the C1-hydroxyl group.

The stereochemistry at C1 for the cyclopentenols (75) and (80) is thus established, on the basis of the chemical shifts of the acetyl methyl protons, see Fig (15) for ^{1}H n.m.r. data for the trinitrocyclopentenols.

3.6 BASE-CATALYSED ACYLOIN REARRANGEMENT OF t-6 HYDROXY-2,3,5,6-TETRAMETHYL-r-2,4,t-5-TRINITROCYCLOHEX-3-ENONE (77)

Treatment of the second C6-hydroxy trinitro ketone (77), as above, gave a complex mixture of products in which the cyclopentenol (76) was the major component; fractional crystallization gave pure cyclopentenol (76). This compound (76) must have the trans-2,5-dinitro- stereochemistry. The stereochemistry at C1 can be assigned by considering the ^{1}H n.m.r. shift data for this compound (76) (Fig (15)). The assignment of the acetyl methyl proton to the signal at δ 2.23 compares with other trans-2,5-dinitro-cyclopentenols- (Fig (14)). The δ 1.53 p.p.m. signal can only be assigned reasonably to the C2-methyl group, this relatively highfield value for the C2-methyl group suggests that this group is trans to the C1 hydroxyl group, thus the stereochemistry at C1 for (75) is assigned.

3.7 BASE-CATALYSED ACYLOIN REARRANGEMENT OF r-2,t-6-DIHYDROXY-2,3,5,6-TETRAMETHYL-4,t-5-DINITROCYCLOHEX-3-ENONE (73)

Treatment of a dichloromethane solution of the 2,6-dihydroxycyclohex-3-enone (73) with aqueous sodium bicarbonate, as above, gave a mixture (c 2:1) of the C1-epimeric cyclopentenols (74) and (92). Only the major component could be isolated by fractional crystallization.

3.8 REACTION PATHWAYS IN THE REACTION OF 2,3,5,6-TETRAMETHYL-4-NITROPHENOL (58) WITH NITROGEN DIOXIDE IN BENZENE

The primary products formed in the reaction of 2,3,5,6-tetramethyl-4-nitrophenol (58) can be accommodated in the reaction sequence outlined in Scheme (14). The formation of the 6-nitrodienone (65), as for pentamethylphenol (19), probably involves the initial formation of the phenoxy radical (93), followed by radical-coupling at the C6 position. The first and major partitioning of the reacting material occurs at this 6-nitrodienone (65) stage. Immediate reaction of this 6-nitrodienone (65) with NO_2 at C5 would give the delocalised radical (94), which then reacts either with NO_2 to give the tetranitroketones (67),(68),(69) and (70) or with ONO to give, after hydrolysis, the 2-hydroxy-5,6-dinitro compound (71). These products, all of which were stable under the chromatographic separation procedure used, were isolated in a total yield of 56%.

Conversion of the 6-nitrodienone (65) into the 6-hydroxydienone (66), via the nitrito ketone (78), represents the initial stage of the second reaction sequence arising from the 6-nitrodienone (65). Reaction of the 6-hydroxydienone (66)

with nitrogen dioxide would give the delocalised radical (95), with the cis-6-hydroxy-5-nitro- stereochemistry.[53] Subsequent reaction of the delocalised radical (95) would give the observed products, hydroxytrinitroketones (72) and (77) by reaction with NO_2 and the dihydroxycyclohex-3-enone (73) by reaction with ONO followed by hydrolysis.

Because of the instability of the products (72),(73) and (77) under the chromatographic separation conditions employed, and the consequent difficulty of isolation of compounds from complex mixtures of the reaction products (72)(73) and (77) and their derived acyloin products, the yields of material isolated, (72),(73),(75) and (76), do not give a true indication of the yields of the primary products (72),(73) and (77) in the initial mixture. However, separate reaction of the 6-hydroxydienone (66) with nitrogen dioxide gives the products (72)(73) and (77) in a ratio 3:2:5, and the reaction of the phenol (58) with nitrogen dioxide gave estimated yields (^{1}H n.m.r. of the crude product) (72) (c. 10%) and (77) (c. 15%). In the light of these results, and the yields of material actually isolated, it appears that the phenol (58) nitrogen dioxide reaction yields 6-hydroxycyclohex-3-enones (72) [10%] (73) [6%] and (77 [15%]; these yields are believed to reflect more accurately the actual yield of each compound in the crude product.

From the above estimates, the ratio of 6-nitro-:6-hydroxy-cyclohex-3-enones formed in the reaction of 2,3,5,6-tetramethyl-4-nitrophenol (58) with nitrogen dioxide is c. 55:30. This result is in contrast to the reaction of pentamethylphenol (19) with nitrogen dioxide, which gave only 4-nitrodienone (21) and the 6-nitrocyclohexenones (23),(24),(25),(26),(32),

(33)(34 or 35) and (36).

The effect on the product ratios, in going from a C4-methyl group for pentamethylphenol (19) to a C4-nitro group in 4-nitrodurenol (58) is best rationalised by looking at the corresponding 6-nitrodienones (40) and (65), formed during the reaction of these phenols with Nitrogen dioxide. Thus, the replacement of the C4-methyl group in 6-nitrodienone (40) with a C4-nitro group in the 6-nitrodienone (65), has the effect of allowing the rearrangement of the 6-nitrodienone (65) to 6-hydroxydienone (65), to compete with nitrogen dioxide addition to the 6-nitrodienone (65). This is best interpreted as the electron withdrawing nitro group at C4 making the 6-nitrodienone (65) less susceptible to attack by the electrophilic nitrogen dioxide, thus allowing the alternative reaction, rearrangement of the 6-nitrodienone (65) to 6-hydroxydienone (66) to compete.

CHAPTER FOUR

THE NITRATION OF 4,6-DISUBSTITUTED 2-PHENYLPHENOLS

4.1 INTRODUCTION

There have been very few reported examples in the literature, where nitration of substituted aromatics has resulted in attack ipso to a phenyl substituent. In one example, the nitration of 9-acetoxy-10-phenylanthracene (96)* [59] with fuming nitric acid in acetic acid gives the nitro diacetate (97), 10-acetoxy-10-phenylanthrone (98), 10-hydroxy-10-phenylanthrone (99), via an initial attack ipso to the acetate group. However, a further product isolated is the 10-nitro-10-phenylanthrone (100), a compound envisaged as arising initially from nitronium ion attack ipso to the 10-phenyl group.

In contrast, the reaction of the substituted biphenyls [60] (101),(102),(103) and (104) gave exclusively, products from attack of the nitro group at the unoccupied ring positions. It was decided, therefore to examine the reactions of 4,6-disubstituted-2-phenylphenols with fuming nitric acid in acetic acid, and with nitrogen dioxide in benzene solution. Of particular interest, was whether attacks on these phenolic systems occurred ipso to the phenyl substituent, and if so, what were the subsequent reactions of the product of initial attack. Of the phenols studied, the nitration of the bromophenols (105a),(105b) and (106a) resulted in nitro-debromination giving the corresponding nitrophenols (105c) and (106c). The dinitrophenol (105c) was unreactive under the conditions

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* Refer block C diagrams as foldouts at the end of this thesis.

employed, whereas the nitration of the nitrophenol (106c) did lead to attack ipso to the phenyl substituent; however this attack appears to occur as part of the addition of nitrogen dioxide to the diene system of the initially-formed 6-nitro-dienone (107) and to the 6-hydroxydienone (108).

4.2 DISCUSSION

4.2.1 Nitration of 4,6-Dibromo-2-phenylphenol (105a)

Reaction of the 4,6-dibromo-2-phenylphenol (105a) with fuming nitric acid (d 1.5; 1.1 mole) in acetic acid gave the 6-bromo-4-nitro-2-phenylphenol (105b) (67%), but no further reaction products could be isolated. The structure of this phenol was assigned on the basis of its elemental analysis, and by comparison of its ^{1}H n.m.r. spectroscopic data with those of the related compounds (105a) and (105c).

Nitration of 4,6-dibromo-2-phenylphenol with excess fuming nitric acid in acetic acid resulted in extensive nitro-debromination, the 4,6-dinitro-2-phenylphenol (105c) being isolated in c. 70% yield. Earlier McOmie et al[61] reported the formation of the dinitrophenol (105c) in c. 80% yield on reaction of an ethanolic solution of the dibromo phenol (105a) with nitric acid (d 1.42).

From the above results, it appears that the reaction of 4,6-dibromo-2-phenylphenol (105a) with nitric acid in acetic acid, giving the 4,6-dinitrophenol (105c), follows the reaction sequence outlined in Scheme (15). Initial attack of nitronium ion occurs ipso to the C4-bromine atom to give the 4-nitrodienone (109). Acid-catalysed elimination of Br^{+} from this 4-nitrodienone (109) (step 2) gives the 4-nitrophenol (105b), which would undergo further nitro-debromination at C6.

Attempted reaction of the dinitrophenol (105c) with either fuming nitric acid in acetic acid for two weeks, or with nitrogen dioxide in benzene for 3h. resulted in the recovery of the dinitrophenol (105c) in essentially quantitative yield.

4.2.2 Nitration of 4-Bromo-6-methyl-2-phenylphenol (106a)

As a result of the facile displacement of bromine during the nitration of the dibromophenol (105a), and the lack of reactivity of the dinitro phenol (105c) under the normal nitration conditions (see above), it was decided then, to study the nitration reactions of the 4-bromo-6-methyl-2-phenylphenol (106a). This substrate was prepared by bromination of 6-methyl-2-phenylphenol (106b). The nitration of 4-bromo-6-methyl-2-phenylphenol (106a) with fuming nitric acid in acetic acid resulted in a high yield of the 4-nitro-6-methyl-2-phenylphenol (106c)(77%) by nitro-debromination, two minor components of the crude product, which was separated by silica gel column chromatography, were both 1,4-benzoquinones, 2-bromo-3-methyl-5-phenyl-1,4-benzoquinone (110)(c. 8%) and 2-methyl-6-phenyl-1,4-benzoquinone (111)(c. 9%). The structures of the two 1,4-benzoquinones (110) and (111) were assigned on the basis of the elemental analysis and spectroscopic data for the compounds. In the ^{1}H n.m.r. of the quinone (111) the C3-vinylic proton appeared as a doublet of quartets, with coupling to the C2-methyl group, and to the C5-vinylic proton. The structure for the 2-bromo-3-methyl-5-phenyl-1,4-benzoquinone (110) is indicated by the appearance of the C6-vinylic proton as a singlet, and by the significant deshielding of the C3-methyl resonance due to the proximate C2-bromine atom, compared with the C6-methyl group for the quinone (111).

Some mechanistic comment is necesary, as to the mode of formation of the quinones (110) and (111) and the nitrophenol (106c). It seems likely that there is a common intermediate to all three products which is the 4-nitrodienone (112). The nitrophenol (106c) might then be envisaged as arising from an acid-catalysed elimination of Br^+ from this nitrodienone (106c), see Scheme (16). Alternatively the 4-nitrodienone (112) may undergo a nitro-nitrito rearrangement to give the 4-nitrito dienone (113) (step 3). Loss of the elements NOBr from this nitrito dienone would give the 2-methyl-6-phenyl-1,4-benzoquinone (111). The formation of the 2-bromo-3-methyl-5-phenyl-1,4-benzoquinone (110) could then arise by addition of HBr to the quinone (111), followed by oxidation (step 4).[61]

4.2.3 Nitration of 6-Methyl-4-nitro-2-phenylphenol (106c) with Fuming Nitric Acid

Reaction of 6-methyl-4-nitro-2-phenylphenol (106c) with fuming nitric acid in acetic acid gave a mixture of at least ten components [^{1}H n.m.r.]. The infrared spectrum of this crude product had absorptions characteristic of hydroxyl (3500), carbonyl (1750) and nitro (1590-1530 cm^{-1}) functions. However, none of these components could be separated by fractional crystallization, and unfortunately, attempts at separating this mixture on a Chromatotron silica gel plate resulted in extensive decomposition of the material.

4.2.4 Reaction of 6-Methyl-4-nitro-2-phenylphenol (106c) with Nitrogen Dioxide

Reaction of 6-methyl-4-nitro-2-phenylphenol (106c) with nitrogen dioxide in benzene gave a crude product shown to

consist of six components (^{1}H n.m.r.); the methyl resonances of these products in deuteriochloroform were observed at δ 1,20 (c. 17%), 1.39 (c. 3%), 1.62 (c. 12%), 1.75 (c. 28%), 1.90 (c. 26%) and 2.19 (c. 12%). Fractional crystallization of the crude product using dichloromethane/pentane gave the compound (114) (^{1}H n.m.r. δ 1.75, methyl), the structure of which was determined by single-crystal X-ray structure analysis. A perspective drawing of r-2-t-6-dihydroxy-6-methyl-4,t-5-dinitro-2-phenylcyclohex-3-enone (114), $C_{13}H_{12}N_2O_7$, m.p. 142-143° (dec.) is presented in Fig (16) with corresponding fractional coordinates in Table(15). The spectroscopic data for this dihydroxy ketone (114) were in accord with its established structure. In the solid state, the alicyclic ring system for (114) exists in a flattened half-chair conformation [torsion angles: C(4)-C(3)-C(2)-C(1) 3.9(9)°; C(3)-C(4)-C(5)-C(6) 20.9(9)°] with the 5-NO_2 group in a pseudoaxial orientation [torsion angle: C(3)-C(4)-C(5)-N(5) -99.0(8)°]. In compound (114) the planes of the 4-NO_2 and 5-NO_2 groups are close to alignment with the C(3)-C(4) and C(5)-C(6) bonds respectively [0(41)-N(4)-C(4)-C(3) -6.3(8)°; (0.52)-N(5)-C(5)-H(5) -1(3)°]. The 0(1)-H(6) distance for compound (114) is 2.29 Å, and the C(1)-0(1) and C(6)-0(6) bonds are close to coplanar [torsion angle: 0(1)-C(1)-C(6)-0(6) -10.6(9)°], consistent with weak intramolecular HO(6)-carbonyl group hydrogen bonding in the compound (114). The 0(1)-H(2) distance was 2.66 Å and the torsion angle 0(1)-C(1)-C(2)-0(2) -95.0(7)°. In the compound (114) the 2-OH group is pseudoaxial with the 6-Me group 1:3-syn-axial to it.

No other components could be obtained by fractional crystallization, and as above, the material was unstable on a chromatotron silica gel plate. However, HPLC separation of the

mixture gave a pure compound (115) (^{1}H n.m.r. δ 1.90, methyl) and an impure sample (c. 90% purity) of a further compound (^{1}H n.m.r. δ 1.20, methyl) which was tentatively assigned the dihydroxy structure (116). The structure of compound (115) was determined by single-crystal X-ray structure analysis; a perspective drawing of r-2-hydroxy-6-methyl-4,c-5,t-6-trinitro-2-phenylcyclohex-3-enone (115), $C_{13}H_{11}N_3O_8$, m.p. 115-116° (dec.) is presented in Figure (17), with corresponding fractional coordinates in Table (16). The spectroscopic data for this hydroxy trinitro ketone (115) were in accord with its established structure. In the solid state, the alicyclic ring system for (115), exists in a flattened half-chair conformation [torsion angles: C(4)-C(3)-C(2)-C(1) 2.9(3)°; C(3)-C(4)-C(5)-C(6) 24.1(3)°] which closely resembles that for the dihydroxy ketone (114). Again, the 5-NO_2 group exists in a pseudoaxial orientation [torsion angle: C(3)-C(4)-C(5)-N(5) -94.0(2)°]. The similarity with compound (114) extends to the orientations of the planes of the 4-NO_2 and 5-NO_2 groups [torsion angles: C(3)-C(4)-N(4)-O(41) -0.1(3)°; O(52)-N(5)-C(5)-H(5) 4(1)°]; the plane of the 6-NO_2 is close to alignment with the C(5)-C(6) bond [torsion angle: C(5)-C(6)-N(6)-O(62) 14.9(2)°]. In compound (115) the O(1)-H(2) distance (2.67 Å) and the torsion angles O(1)-C(1)-C(2)-O(2) 30.9(3) and C(1)-C(2)-O(2)-H(2) 49(2)° rule out the possibility of intramolecular hydroxyl-carbonyl group hydrogen bonding. Notable in the structure (115) is the pseudoaxial orientation of the 2-phenyl group, the plane of which is close to alignment with the C(3)-C(2) bond [torsion angle: C(3)-C(2)-C(7)-C(71) 15.6(2)°].

4.2.5 Reaction Pathways to Compounds (114) and (115)

The formation of the compounds (114) and (115) can be envisaged as arising by the reaction pathways outlined in Scheme (17). Although the 6-nitrodienone (107) and the corresponding 6-hydroxydienone (108) were not stable enough to be isolated, it has already been shown that the 4,6-dinitro-dienone (65) and 6-hydroxy-4-nitro dienone (66) (see chapter three) are key intermediates in the analogous reaction of 2,3,5,6-tetra-4-nitrophenol (58) with nitrogen dioxide. Addition of nitrogen dioxide on the 6-nitrodienone at C5 to give the delocalised radical (117) is in competition with nitro-nitrito rearrangement of the 6-nitrodienone (117) followed by hydrolysis to give the 6-hydroxydienone (108). Addition of nitrogen dioxide to the 6-hydroxydienone (108) would give the delocalised radical (118). Whereas addition of nitrogen dioxide to the 6-nitrodienone (107) at C5 can give both cis and trans delocalised radicals (117), additions of nitrogen dioxide to the related 6-hydroxydienone (118) would be expected to give solely the cis-6-hydroxy-5-nitro delocalised radical as based on previous work.

On the basis of the established structures (114) and (115) it is clear that further reaction of the delocalised radicals (117) and (118), with nitrogen dioxide results in carbon-oxygen bond formation at C2, via the 2-nitrito compounds (119) and (120). The two compounds (114) and (115) which are both 2-hydroxy-2-phenylcyclohex-3-enones account for c. 54% of the 6-methyl-4-nitro-2-phenylphenol (106c) reacted, assuming that three further stereoisomers of (115) and the C2 epimer of compound (114) are also present in the crude product, then it appears that the reactions of the delocalised radicals (117) and

(118) occur with a high yield of C2-O bond formation, if not exclusively, to give 2-hydroxycyclohex-3-enones as the only products.

The identification of the remaining four compounds, which were not isolated in a pure state, can be made to a limited extent. Firstly if the assumption is made that all four compounds are 2-hydroxycyclohex-3-enones, then it remains to identify which compound is the C2-epimer of the established C6-hydroxy compound (114). Unfortunately the 6-hydroxydienone (108) could not be prepared, above, and therefore its reaction with nitrogen dioxide could not be studied directly. However it could be studied indirectly; the 6-nitrodienone (107) was generated in benzene solution by addition of two moles of nitrogen dioxide to the phenol (106c) in benzene. This solution was stirred at 5^{o} for 1 h while any NO_2 present was removed in a stream of nitrogen. Under these conditions it was envisaged that the formation of the delocalised radical (117) would be suppressed and the 6-nitrodienone (107) would yield the 6-hydroxydienone (108). The reaction mixture, assumed to contain the 6-hydroxydienone (108), and unreacted 6-nitrodienone (107) was then reacted with excess nitrogen dioxide. The ^{1}H n.m.r. of the crude material exhibited the six methyl resonances found for the crude product from the normal phenol (106c)/nitrogen dioxide reaction. However, the signal intensities were significantly different: δ 1.20 (c. 28%), 1.39 (c. 1-2%), 1.62 (c. 5%), 1.75 (c. 40%) 1.90 (c. 10%) and 2.19 (c. 4%). It is clear that in the above reaction, the pathway involving the 6-hydroxy dienone (108) is favoured, and furthermore that this has led to an enhanced yield of the dihydroxy compound (114) and a second compound (δ 1.20). This

second compound which was isolated in only 90% purity is therefore tentatively assigned as the C2-epimer of the dihydroxy ketone (116).

The marked difference in the ^{1}H n.m.r. methyl signals for compounds (114) and (116) can be rationalised if certain assumptions on the conformations of these two compounds in solution are made. The dihydroxy ketone (114) exists in the solid state, with the C6-Me and the C2-OH groups in a 1:3-syn-axial relationship, which if it persisted in solution would lead to a deshielding of the C6-methyl protons.[62] If the C2-epimer (116) adopted the same ring conformation as compound (114), and the pseudoaxial phenyl group adopted the same orientation as in compound (114) (Fig 16), then the 6-Me protons would be markedly shielded due to the anisotropy of the 1,3-syn-axial phenyl group.

Associated with the enhanced yields of the two compounds (114) and (116) in the above experiment, there is a proportionate decrease in the yields of the other four components in the crude product, the 2-hydroxy trinitro ketone (115) (δ 1.90) and the three compounds having methyl resonances at δ 1.39, 1.62 and 2.19. Given the structure of the compound (115), it seems likely that the other three compounds are the four possible stereoisomers of (115). Now if it is assumed that the alicyclic ring conformations of these three isomers are similar to that for compound (115) in solution, then their ^{1}H n.m.r. methyl resonances can be related to their stereochemistry as in Fig (18). The significant deshielding of the methyl protons for (123) δ 2.19 could be due to the 1,3-syn-axial relationship of the 6-Me and 2-OH groups, while in structure (121) δ 1.39 the methyl group protons could be shielded by the

1,3-syn-axial phenyl group, given the established structure for compound (115), then the structure (122) is defined by exclusion.

If the above assignments are valid, then the reaction of 6-methyl-4-nitro-2-phenylphenol (106c) (see Scheme 17) is partitioned into c. 53% of products arising from immediate reaction of the initially formed 6-nitrodienone (107) with nitrogen dioxide, and 45% of products coming from the nitro-nitrito rearrangement, of the 6-nitrodienone to the 6-hydroxy-dienone (108). Furthermore, the addition of NO_2 to the intermediate delocalised radicals (117) and (118) results in the exclusive formation of C2-hydroxy compounds.

In view of the interpretation of this result-exclusive formation of C2-O bond formation - three points must be taken into consideration: (i) in reaction of the analogous 2,6-dimethyl-4-nitrophenol (124), all the products isolated accounting for > 90% of the crude product were C2-nitro compounds.[63] (ii) On the basis of the reaction of 4-methyl-2,6-diphenylphenol (125) with nitrogen dioxide in benzene (below), where a high proportion of the products have a nitro group ipso to the phenyl group, it seems unlikely that this is a steric effect of the C2-phenyl group allowing ONO attack to compete with NO_2 attack. (iii) The delocalised radicals (117) and (118), are highly resonance stabilised. It is inviting, therefore to postulate that these C2-hydroxy cyclohex-3-enones (114),(115),(116),(121),(122) and (123) arise by a nitro-nitrito rearrangement of initially formed C2-nitro compounds via the delocalised radicals (117) and (118), see Scheme (18).

4.2.6 Reaction of 4-Methyl-2,6-diphenylphenol (125) with Nitrogen Dioxide in Benzene

The reaction of 4-methyl-2,6-diphenylphenol (125) with nitrogen dioxide in benzene solution gave a complex mixture of at least ten components (^{1}H n.m.r.), the infrared spectrum of which indicated the presence of hydroxy (3550), conjugated-carbonyl (1720,1705) and nitro functions (1590-1550 cm^{-1}). Four compounds (126),(127),(128) and (129) were separated from the crude product by fractional crystallization. The structures of three of these (126),(127) and (128) were established by single-crystal X-ray structure analysis. A perspective drawing of r-4-hydroxy-4-methyl-c-5,c-6-dinitro-2,6-diphenylcyclohex-2-enone (126), $C_{19}H_{16}N_2O_6$, m.p. 170-171° (dec.) is presented in Fig (19) with corresponding fractional coordinates in Table (17). Similar information is presented for r-4-hydroxy-4-methyl-c-5,c-6-dinitro-2-(2'-nitrophenyl)-6-phenylcyclohex-2-enone (127), $C_{19}H_{15}N_3O_8$, m.p. 168.5-169° (dec.) (Fig(20) and table (18)) and 4-methyl-r-4,c-5,c-6-trinitro-2,6-diphenylcyclohex-2-enone (128) (Fig(21) and Table (19)). The spectroscopic data for (126),(127) and (128) were in accord with their established structures, and the spectroscopic data for the fourth compound, tentatively assigned the structure (129), below, are in accord with its gross structure.

In the solid state the alicyclic ring system for the 4-hydroxy compound (126) exists in a flattened half-chair conformation [torsion angles: C(3)-C(2)-C(1)-C(6) 12.9(9)°; C(2)-C(3)-C(4)-C(5) 11.9°] with the 5-NO_2 group in a pseudo-axial orientation [torsion angle: C(3)-C(4)-C(5)-N(5) 80.9(6)°]. In compound (126) the planes of the 5-NO_2 and 6-NO_2 groups are aligned with the C(5)-H(5) and C(5)-C(6) bonds respectively

[O(52)-N(5)-C(5)-H(5) -20.2(23)°, O(62)-N(6)-C(6)-C(5) -4.6(8)°]. Notable in compound (126) is the pseudoaxial orientation of the 6-phenyl group [torsion angle: C(2)-C(1)-C(6)-C(9) 82.7(6)°]; furthermore the plane of the 6-phenyl group is aligned with the C(1)-C(6) bond [torsion angle: C(1)-C(6)-C(9)-C(95) 1.2(8)°]. The 4-methyl group is in a 1,3-syn-axial relationship with the 6-phenyl group (see Fig (19)) [torsion angle: C(6)-C(5)-C(4)-C(8) 83.6(6)°].

The 4-hydroxy-2'-nitrophenyl compound (127) exists in the solid state in a conformation which is almost identical with that for the 4-hydroxy compound (126). The alicyclic ring system for compound (127) exists in a flattened half-chair conformation [torsion angles: C(3)-C(2)-C(1)-C(6) 13.5(1.7)°; C(2)-C(3)-C(4)-C(5) 11.0(1.9), cf with compound (126), above] with the 5-NO_2 group in a pseudoaxial orientation [torsion angle: C(3)-C(4)-C(5)-N(5) 82.7(1.2)°]. The similarity between compound (126) and compound (127) extends to the orientations of the various substituents about the alicyclic ring. For compound (127) the planes of the 5-NO_2 and 6-NO_2 groups are aligned with the C(5)-H(5) and C(5)-C(6) bonds respectively [O(51)-N(5)-C(5)-H(5) -15.0(5.1)°; O(61)-N(6)-C(6)-C(5) -2.1 (1.5)°]. In compound 127) the 6-phenyl group is in a pseudoaxial orientation with the plane of the phenyl ring aligned with the C(1)-C(6) bond [torsion angles: C(2)-C(1)-C(6)-C(9) 82.9(1.2)°; C(1)-C(6)-C(9)-C(91) -8.5(1.1)°]. As in compound (126), the 4-methyl group for compound (127) is pseudoaxial [torsion angle: C(6)-C(5)-C(4)-C(8) 87.4(1.2)] and exists in a 1,3-syn-axial relationship to the 6-phenyl group. Furthermore, the 4-methyl group lies in a position perpendicular to the plane of the 6-phenyl ring; if this arrangement persisted in solution it would lead to a shielding of the 4-methyl group in the ^1H n.m.r.

spectrum.

The plane of the 2-phenyl group is significantly rotated from planarity with the C(2)-C(3) bond torsion angle: C(3)-C(2)-C(7)-C(75) -59.2(1.8)^{o} .

The alicyclic ring system for the trinitro ketone (128) also exists in the solid state in a flattened half-chair conformation [torsion angles:* C(2)-C(3)-C(4)-C(5) 22.6(6)^{o}; C(3)-C(2)-C(1)-C(6) 10.0(6)^{o}] with the 5-NO_2 group in a pseudoaxial orientation [torsion angle: C(3)-C(4)-C(5)-N(5) 72.8(4)^{o}]. The plane of the 6-NO_2 group is closely aligned with the C(6)-C(5) bond [C(5)-C(6)-N(6)-O(62) 5.2(5)^{o}], however, the planes of the 4-NO_2 and 5-NO_2 groups for this compound (128) are not so closely aligned with the C(3)-C(4) and C(5)-H(5) bonds [C(3)-C(4)-N(4)-O(42) -21.2(5)^{o}; H(5)-C(5)-N(5)-O(51) 25.3(2.3)^{o}]. As for the compounds (126) and (127) the 6-phenyl substituent is in a pseudoaxial orientation [torsion angle: C(2)-C(1)-C(6)-C(9) 90.5(4)^{o}] with the 4-methyl 1,3-<u>syn</u>-axial to it. Further, the plane of the 6-phenyl group is again aligned with the C(1)-C(6) bond [torsion angle C(1)-C(6)-C(9)-C(91) 5.8(6)^{o}]. The 2-phenyl substituent is significantly displaced from alignment with the C(3)-C(2) bond [C(3)-C(2)-C(7)-C(71) -49.4(6)^{o}].

Two further compounds (130) and (131), were obtained from the residues from the above crystallizations by separation on a Chromatotron silica gel plate. The structures of these were established by single-crystal X-ray crystal structure analysis. A perspective drawing of the 4-methyl-r-4,t-5,t-6-trinitro-2,6-diphenylcyclohex-2-enone (130), $C_{19}H_{15}N_3O_7$, m.p. 137.5-138.5^{o} (dec.) is presented in Figure (22) with corresponding fractional coordinates in Table (20). Similar information is presented for the two independent molecules of

* For the enantiomer of the drawing in Fig 21.

t-6-hydroxy-4-methyl-r-4,t-5-dinitro-2,6-diphenylcyclohex-2-enone (131), $C_{19}H_{16}N_2O_6$, m.p. 135-136.5° (dec.) (Figs (23) and (24), and Table 21)).

From an examination of the appropriate torsion angles, it is clear that in the solid phase, the alicyclic ring system for compound (130) exists in a flattened half-chair conformation [torsion angles:* C(2)-C(3)-C(4)-C(5) 4.4°; C(3)-C(2)-C(1)-C(6) 19.7°], with the 5-NO_2 group in a pseudoaxial orientation [torsion angle: C(3)-C(4)-C(5)-N(5) 86.1°]. The planes of the 4-NO_2, 5-NO_2 and 6-NO_2 groups are close to alignment with the C(3)-C(4), C(5)-H(5) and C(5)-C(6) bonds respectively [torsion angles: C(3)-C(4)-N(4)-O(42) -11.4°; H(5)-C(5)-N(5)-C(51) 21.4°; C(5)-C(6)-N(6)-O(61) 13.6°]. Similar to compounds (126),(127) and (128), the 6-phenyl substituent for compound (130) is in a pseudoaxial orientation [torsion angle: (C(2)-C(1)-C(6)-C(9) 74.3°] with the plane of the 6-phenyl group aligned with the C(1)-C(6) bond [torsion angle: C(1)-C(6)-C(9)-C(95) 0.9°]. The plane of the 2-phenyl substituent is significantly out of alignment with the C(2)-C(3) bond [torsion angle: C(3)-C(2)-C(7)-C(75) 39.3°].

Compound (131) exists in the solid state as two independent molecules. The alicyclic ring conformation for molecule one (Fig (23)) is best described as a flattened half-chair [torsion angles: C(2)-C(3)-C(4)-C(5) 3.7(6)°; C(3)-C(2)-C(1)-C(6) 12.9 (6)°], again, the 5-NO_2 group is in a pseudoaxial orientation [torsion angle: C(3)-C(4)-C(5)-N(5) 87.4(4)°], the planes of the 4-NO_2 and 5-NO_2 groups are closely aligned with the C(3)-C(4) and H(5)-C(5) bonds respectively [torsion angle: C(3)-C(4)-N(4)-O(41) -5.2(6)°; H(5)-C(5)-N(5)-O(52) 1.8(2.3)°].

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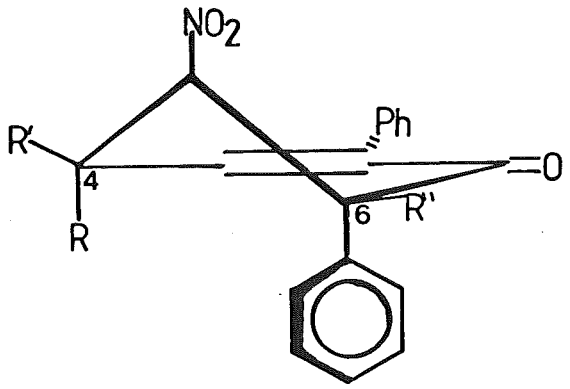
* For the enantiomer of the molecule in Fig 22.

The 6-phenyl substituent is in a pseudoaxial orientation with the plane of the phenyl group closely aligned with the C(1)-C(6) bond, [torsion angles; C(2)-C(1)-C(6)-C(9) 82.8(5)°; C(1)-C(6)-C(9)-C(95) 3.2(6)°]. In compound (31), molecule one, the H(6)-O(1) distance (2.09 Å) and the near planarity of the O(1)-C(1) and C(6)-O(6) bonds [torsion angle; O(1)-C(1)-C(6)-O(6) 24.6(5)°] indicate the presence of intramolecular hydroxylcarbonyl group hydrogen bonding between OH(6) and O(1).

A comparison between the two molecules of compound (131) in the solid state, using the program XFIT,[64] which involves the superposition of the two molecules, is shown by the computer-generated drawing in Fig (25). As can be seen from this drawing, the most significant difference between the two molecules is in the orientation of the 6-phenyl groups. This difference is associated with a slightly different alicyclic ring conformation for molecule two, which is best described as a skew-boat [torsion angles; C(11)-C(12)-C(13)-C(14) -0.5(6)°; C(12)-C(11)-C(10)-C(15) 16.8(6)°, (see Fig (24)]. For molecule two, the presence of intramolecular hydroxyl-carbonyl group hydrogen bonding is indicated by the H(6')-O(1') distance of 2.08 Å and the torsion angle; O(1')-C(10)-C(15)-O(6') 16.5(6)°. This conformation difference between the two molecules of compound (131) is best interpreted as a packing effect, with the differing environments of the two molecules resulting in slightly different ring conformations.

Notable in the infrared spectrum of compound (131) in the solid state, is the presence of two distinct hydroxyl functions. It is interesting to note that in a packing diagram for compound (131) (Fig (26)), there are two clearly distinguishable environments of the H(6) hydroxy protons.

For all the structures established by X-ray crystallography, in the solid state the 6-phenyl substituent exists in a pseudoaxial orientation, with the plane of the phenyl ring, in each case, aligned with the C(1)-C(6) bond. Furthermore, for all compounds, there exists a near 1,3-syn-axial relationship between the 6-phenyl and the 4-substituent which is cis to the 6-phenyl group. Thus the 4-substituent cis to the 6-phenyl group, would be facing the plane of the phenyl ring.



It is interesting to note, therefore, that for those compounds (126),(127) and (128), having a cis-4-methyl-6-phenyl-pattern, the ^{1}H n.m.r. spectrum exhibits a signal due to the methyl protons at a highfield frequency (126)(δ 0.89), (127) (δ 0.93) and (128)(δ 1.2) relative to those compounds (130) (δ 1.90) and (131)(δ 1.87) having the trans-4-methyl-6-phenyl substitution pattern. It seems likely therefore, that the conformations of compounds (126),(127) and (128) (at least), in solution, are similar to their solid state conformations: the relatively highfield signals for the 4-methyl protons in these compounds (126),(127) and (128) can thus be interpreted as being due to the shielding of the 4-methyl protons by the

6-phenyl group.

Two further major components, present in the crude material, above (^{1}H n.m.r.) (δ 1.28 14%) and (δ 1.78 12%) could not be isolated in a pure state; on chromatography on a Chromatotron silica gel plate they were eluted in complex mixtures of other compounds present initially, and their decomposition products. The possible structure of these compounds and that of the minor product (129) isolated above, will be discussed below.

At this point, very little mechanistic comment can be made, as to the mode of formation of the products (126),(127),(128), (129),(130) and (131) from the reaction of 4-methyl-2,6-diphenylphenol (125) with nitrogen dioxide. It is uncertain whether the formation of the 4-hydroxy-dinitro compound (126) arises from the 6-nitrodienone (132), by addition of NO_2 at C5 followed by C-O bond formation at C4 (Scheme (19)) or alternatively by addition of nitrogen dioxide to the 4-hydroxy-dienone (133). If the latter explanation is true, then it is likely that the trinitro ketones (128) and (130), and the hydroxy dinitro ketone (131), arise from addition of nitrogen dioxide to the corresponding 4-nitrodienone (134). No comment will be made at this stage with respect to the 4-hydroxy-2'-nitrophenyl ketone (127).

4.2.7 Formation of 4-Methyl-4-nitro-2,6-diphenylcyclohexa-2,5-dienone (134) and 4-Hydroxy-4-methyl-2,6-diphenyl-cyclohexa-2,5-dienone (133)

Reaction of 4-methyl-2,6-diphenylphenol (125) with fuming nitric acid in acetic acid, followed by the addition of water, gave a crude product which was recrystallized at low temperature to yield the 4-nitrodienone (134). The structural

assignment for the 4-nitrodienone (134) is based on its ^{1}H n.m.r. spectrum, and its ^{13}C n.m.r. spectrum of the compound at -50^{o}, which exhibited nine carbon resonances of appropriate chemical shifts.

Treatment of this 4-nitrodienone (134) with an acetic acid/sodium acetate buffer system, under a constant stream of nitrogen gas, gave a crude product which was separated on a Chromatotron silica gel plate. The major product isolated was the 4-acetoxymethyl-2,6-diphenylphenol (135) (c. 50%), with the 4-hydroxydienone being isolated in c. 30% yield. A third compound (see experimental), which was isolated in c. 18% yield by weight, could not be identified by standard spectroscopic techniques (^{1}H n.m.r., ^{13}C n.m.r.(SFORD), infrared and ultraviolet). The elemental analysis for this compound was in accord with a molecular formula: $C_{18}H_{16}O_4$ but unfortunately, crystals of a quality necessary for an X-ray study could not be obtained.

The 4-acetoxymethyl phenol (135) is an expected by-product of this reaction, with analogous acetoxymethyl phenol (136) being formed from buffer treatment of the 4-methyl-4-nitrodienone (137).[65] However, the yield of the 4-acetoxymethyl phenol (135) is large relative to the formation of the analogous acetate above. The likely precursor to the 4-acetoxymethyl phenol (135) is the p-quinone methide (138), which is susceptible to attack by nucleophiles on the C-terminal of the diene system.

4.2.8 Reaction of 4-Hydroxy-2,6-diphenylcyclohexa-2,5-dienone (133) with Nitrogen dioxide

In order to investigate the mechanism of formation of the 4-hydroxy ketone (126) the reaction of the

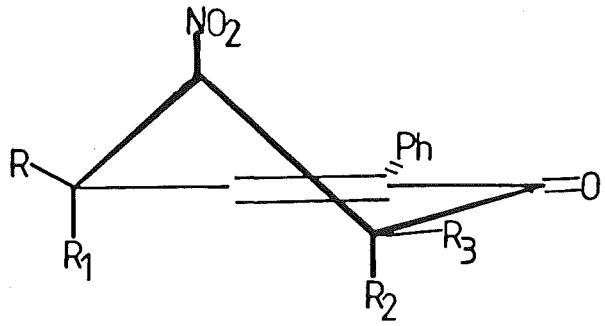
4-hydroxydienone (133) with nitrogen dioxide was examined. Reaction of the 4-hydroxydienone (133) with nitrogen dioxide, gave a crude product which was separated by a combination of fractional crystallization using dichloromethane/pentane solvent mixtures, and chromatography on a Chromatotron silica gel plate. The products isolated, were the same as those isolated from the reaction of 4-methyl-2,6-diphenylphenol (125) with nitrogen dioxide, but the relative yields were significantly different. The yield of the 4-hydroxy ketone (126)(25%) is enhanced relative to the phenol (125)/nitrogen dioxide reaction. Whereas the yields of the other five compounds were correspondingly decreased; trinitro ketone (128)(25 → 10%), trinitro ketone (130) (11 → 3%), 4-hydroxy-2'-nitrophenyl ketone (127) (4 → 1%), 6-hydroxy ketone (131) (11 → 3%) the minor product (129) from the phenol (125)/nitrogen dioxide reaction was not detected. The other two compounds, which were major components of the phenol (125)/nitrogen dioxide reaction ^{1}H n.m.r. (δ 1.28) and (δ 1.78), were also formed in proportionately decreased yield (^{1}H n.m.r.).

The above results suggest that the 4-hydroxydienone (133) reacts with nitrogen dioxide to give the 4-hydroxy ketone (126). Surprisingly 4-nitro compounds (127),(130) and (131) were formed in this reaction of the 4-hydroxydienone (133) with nitrogen dioxide. However, a similar reaction has been observed recently in the reaction of the 4-hydroxydienone (139) with nitrogen dioxide when the 4-nitrodienone (140) was formed in high yield. This type of reaction does not extend, however, to the reaction of nitrogen dioxide with 4-hydroxy-2,3,4,5,6-pentamethylcyclohexa-2,5-dienone (20). This compound was stable under these reaction conditions. A

possible reaction mechanism for the conversion of the 4-hydroxy-dienones (133) and (139) into the corresponding 4-nitrodienones (134) and (140) will be discussed later.

In light of the differences in product yields between the reactions of the phenol (125) and the 4-hydroxydienone (133) with nitrogen dioxide, some comment can be made with regard to the structural assignment of the minor product (129) from the phenol (125)/nitrogen dioxide reaction, and to the possible structures of the two compounds having methyl resonances (δ 1.28) and (δ 1.78).

The ketones (126),(127),(128),(130) and (131), established by X-ray crystallography all exist in the solid state with the alicyclic ring system in a half-chair conformation, with the 5-NO_2 group in a pseudoaxial orientation [although compound (131) molecule two, is by definition a skew-boat, the differences in the orientation of substituents about the ring, as compared with molecule one, are not significant]. Furthermore, from the ^1H n.m.r. evidence, above, it seems likely that the solid state conformations of these compounds (126),(127),(128), (130) and (131) are the conformations adopted in solution. Given the necessary assumption that all the substituted cyclohex-2-enones formed in the above reaction exist in a half-chair conformation, with the 5-NO_2 group in a pseudoaxial orientation, then the alicyclic ring systems for all compounds can be described in the diagram below:



Thus the structure of the minor product (129) is assigned on the basis of:

(i) its ^{1}H n.m.r. spectrum with a methyl group chemical shift δ 1.48 suggesting a 1,3-syn-axial relationship between the 4-methyl group and 6-phenyl group;

(ii) the appearance of the aromatic phenyl protons as a c. 9H multiplet suggests some substitution in a phenyl ring;

(iii) the appearance of nitro functions in the infrared spectrum at c. (1580-1560) indicative of nitro groups bonded to sp^3 centres, and 1530 cm^{-1} indicating an sp^2 nitro group.

If it is assumed that the two major components, which could not be isolated, are substituted cyclohex-2-enones, it appears they must be 4-nitrosubstituted compounds. Thus, for the compound having the ^{1}H n.m.r. methyl frequency δ 1.28, the syn-1,3-diaxial relationship between the 4-methyl and 6-phenyl groups is suggested, i.e. R=NO_2, R_1=Me and R_2=phenyl (see the above diagram). However the all cis trinitro ketone (128) has been isolated; it must be assumed, therefore, that R_3=OH. On this basis the compound with a methyl resonance in the ^{1}H n.m.r. at δ 1.28 p.p.m. can be tentatively assigned the c-6-hydroxy-4-methyl-r-4,c-5-dinitrocyclohex-2-enone (141)

structure. No such argument is possible concerning the structure of the compound (142) (δ 1.78) and its structure remains unknown.

4.2.9 The Mechanism of the Reaction of 4-Methyl-2,6-diphenylphenol (125) with Nitrogen Dioxide

The reaction sequence for the reaction of the 4-methyl phenol (125) with nitrogen dioxide, as described in Scheme (20), involves the initial formation of the phenoxy radical (143) (step 1a). Radical-coupling between this radical (143) and NO_2 occurs preferentially at C4 giving the 4-nitrodienone (134). The 4-nitrodienone (134) could rearrange to give the 4-hydroxydienone (133) (step 2a) (presumably *via* the nitrito dienone (144)). Addition of NO_2 at C5 of the 4-hydroxydienone (133) would give the resonance stabilised radical (145), which on further reaction with NO_2 at C6 would then give the 4-hydroxy ketone (126). An alternative reaction fate for the 4-nitrodienone (134) is the immediate addition of NO_2 at C5 to give the resonance stabilised radical (146) (step 3a). Subsequent reaction of this resonance stabilised radical (146) at C6 with NO_2 would give the trinitro ketones (128) and (130); corresponding reaction with ONO would yield the 6-hydroxy ketones (131) and (141).

A minor reaction pathway involves the formation of the 2'-nitrophenylphenol (147), a process assumed to occur *via* the aryl nitrate (148) (step 1b). Intramolecular transfer of NO_2 from the C1 oxygen to the 2'-position of the immediately adjacent phenyl substituent would give the biradical intermediate (149). Intramolecular hydrogen atom transfer from C2' to the C1 oxygen atom would yield the 2'-nitrophenol (147). Reaction of the 2'-nitrophenylphenol (147) in an

analagous way to the 4-methyl phenol (125) would give rise to the compounds (127) and (129).

The formation of 4-nitro ketones (127),(130) and (131) in the reaction of the 4-hydroxydienone (133) with NO_2 suggests that the 4-nitrodienone (134) to 4-hydroxydienone (133) reaction (step 2a) above is reversible under these reaction conditions. The mechanism of the interconversion of the 4-hydroxydienone (134) and the 4-nitrodienone (133) is not certain. However, a possible reaction sequence is outlined in Scheme (21). The important step in this reaction involves nitrosation of the 4-hydroxydienone (133) by one of the possible forms of dinitrogen tetraoxide, leading to the 4-nitrito dienone (144). Nitrito-nitro rearrangement of this 4-nitrito dienone would give the 4-nitrodienone (134). An analogous nitrito-nitro rearrangement was observed for the nitrito compound (150) on its storage in methanol solution.[66]

CHAPTER FIVE

EXPERIMENTAL METHODS

APPARATUS, MATERIALS AND INSTRUMENTATION

Infrared spectra were recorded on a Shimadzu IR-27G spectrophotometer for liquid films and nujol malls. Ultraviolet absorption spectra were determined on Varian superscan 3 or Varian DMS 100 spectrophotometers.

Routine ^{1}H n.m.r. spectra were obtained for deuteriochloroform, deuterioacetonitrile and deuteriodimethylsulphoxide solutions, with tetramethylsilane as an internal reference on a Varian T60 spectrometer. ^{1}H n.m.r. and ^{13}C n.m.r. Fourier Transform spectra were recorded on a Varian CFT-20 Fourier Transform spectrophotometer for deuteriochloroform and deuterioacetone solutions with tetramethyl silane as an internal reference. All chemical shifts are expressed as parts per million (ppm) downfield from TMS and are quoted as position (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), relative integral and coupling constants (J, Hz).

Microanalyses were carried out by Professor A.D. Campbell and associates, University of Otago.

Melting points were determined in open capillaries and are uncorrected.

Preparative scale chromatography was routinely carried out using a Chromatotron (Model 7924, Harrison Research Inc.) equipped with rotors coated with Silica gel PF-254 (with $CaSO_4.\frac{1}{2}H_2O$ type 60 for TLC, Merck: E.M Laboratories Incorporated, item number 7749) of various thicknesses (generally 2mm).

All solvents used were either of analytical grade (AR) or were purified and dried according to standard procedures.[67]

"Ether" refers to commercial diethyl ether distilled off sodium hydride, and "Petroleum ether" refers to petroleum ether (50-70^{o}C distilled off phosphorus pentoxide.

The nitrogen dioxide used, was prepared by the method described by Kevin Sutton (Ph.D thesis: University of Canterbury).

EXPERIMENTAL RELATING TO CHAPTER TWO

THE PREPARATION OF PENTAMETHYLPHENOL (19)

(a) Preparation of Bis (chloromethyl) mesitol (151)

Hydrogen chloride gas, was bubbled through a stirred solution of mesitol (20 g), in acetic acid (270 ml) and aqueous formaldehyde (30% w/v; 80 ml), for 3 h at 20°. During this time, a pink precipitate developed. The resulting mixture was heated at 60° for a further 4 h. The precipitate was then filtered off, giving a white powder (40 g) which was recrystallized from ether/petroleum-ether to give the 2,4,6-trimethyl-3,5-bis-chloromethylphenol (151) (35 g), m.p. 134-135° (lit[68] 144°). ν_{max}(Nujol) 3400 cm^{-1}, OH. ^1H n.m.r. ($CDCl_3$) δ 2.33, 6H o-methyls; 2.43, 3H, p-methyl; 4.7, 4H, chloromethyls; 4.62, OH.

(b) Hydrogenation of Bis (chloromethyl) mesitol (151)

A solution of the phenol (151) (24 g) in dry methanol (100 ml), with 10% palladium-charcoal catalyst (2 g), was shaken under an atmosphere of hydrogen for 30 min. The catalyst was removed by filtration, and the solvent removed under reduced pressure, to give a white solid (15 g). This was recrystallized from methanol, giving the pentamethylphenol (19) (11 g) as white needles, m.p. 126-126.5 (lit[68] 128°). ν_{max}(Nujol) 3550 cm^{-1}, OH. ^1H n.m.r. ($CDCl_3$) δ 2.20, 15H, Me's; 3.5, OH.

REACTION OF PENTAMETHYLPHENOL (19) WITH NITROGEN DIOXIDE IN BENZENE

A solution of pentamethylphenol (19) (520 mg) in dry benzene (15 ml) was deoxygenated by a stream of nitrogen.

Nitrogen dioxide was bubbled through the stirred solution at 5° for 30 s.; for total reaction times of 2 min. the nitrogen dioxide flow was continued for a further 90 s., but for extended reaction times, the reaction mixture was stirred under an atmosphere of nitrogen dioxide for a period of time (2 h. or 90 h.). The excess nitrogen dioxide was then removed in a stream of nitrogen, and the benzene solvent removed under reduced pressure to give a residue (1.52 g) which retained some benzene solvent. The components of the crude product were separated by a combination of fractional crystallization (dichloromethane/pentane) and chromatographic separation on a Chromatatron silica gel plate. The product yields were found to be independent of the reaction time used above. The products isolated in the given yields:

2,3,4,5,6-Pentamethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (23). - (15%) m.p. 124-126° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1755, α,α'-dinitro ketone; 1640, C=C; 1575-1555 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.88, br s, 3-Me; 1.98, br s, 6H, Me's; 2.02, Me; 2.04, Me.

2,3,4,5,6-Pentamethyl-r-2,t-5,c-6-trinitrocyclohex-3-enone (24). - (9%), m.p. 114-115° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1748, α,α'-dinitro ketone; 1655, C=C; 1580-1550 cm^{-1}, NO_2. (CD_3SOCD_3) δ 1.77, br s, 3-Me; 1.90, Me; 1.94, Me; 2.03, br s, 4-Me; 2.13, Me.

2,3,4,5,6-Pentamethyl-r-2,c-5,t-6-trinitrocyclohex-3-enone (25). - (10%). m.p. 116-118° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1755, α,α'-dinitro ketone; 1660, C=C; 1580-1560 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.84, q, J 1 Hz, 3-Me; 1.92, Me; 1.94, Me; 2.03, q, J 1 Hz, 4-Me; 2.12, Me.

2,3,4,5,6-Pentamethyl-r-2,c-5,c-6-trinitrocyclohex-3-enone (26). - (7%), m.p. 132-132.5 (Found: C, 43.7; H, 5.0; N, 13.6. $C_{11}H_{15}N_3O_7$ requires C, 43.9; H, 5.0; N, 13.95%). ν_{max}(Nujol) 1755, α,α'-dinitro ketone; 1655, C=C; 1575, 1555 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.79, br s, 3-Me; 1.89, Me; 1.93, br s, 4-Me; 2.02, Me; 2.04, Me.

2,3,4,5,6-Pentamethyl-r-4,t-5,6-6-trinitrocyclohex-2-enone (32). - (5%), m.p. 124-126° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1705, conjugated ketone; 1575-1560 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.79, 6H; 1.97, 9H; ($CDCl_3$) δ 1.78, 1.80, 1.99, each 3H; 1.93, br s 3-Me; 2.08, br s, 2-Me. λ_{max} ($CHCl_3$) 246 nm (ε 12500).

2,3,4,5,6-Pentamethyl-r-4,c-5,c-6-trinitrocyclohex-2-enone (33). - (3%), m.p. 116-118° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1710, conjugated ketone; 1650, C=C; 1570,1560,1550 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.93, 6H; 1.97, 3H; 2.06, 3H; 2.08, 3H: ($CDCl_3$) δ 1.92, br s, 3-Me; 2.02, 6H, Me's; 2.07, 6H, Me's. λ_{max}($CHCl_3$) 247 nm (ε 10,000).

2,3,4,5,6-Pentamethyl-r-4,5,6-trinitrocyclohex-2-enone (34) or (35). - (6%), m.p. 88-89° (dec.) (Found: C, 43.9; H, 5.2; N, 13.7. $C_{11}H_{15}N_3O_7$ requires: C, 43.9; H, 5.0; N, 13.95%). ν_{max}(Nujol) 1705, conjugated ketone; 1650, C=C; 1580-1550 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.93, 6H; 1.97, 3H; 2.06, 3H; 2.08, 3H: ($CDCl_3$) δ 1.92, br s, 3-Me; 2.02, 6H, Me's; 2.07, 6H, Me's. λ_{max}($CHCl_3$) 247 nm (ε 10,000).

r-2-Hydroxy-2,3,4,5,6-pentamethyl-t-5,t-6-dinitrocyclohex-3-enone (36). - (3%), m.p. 165-165.5° (X-ray crystal structure determined, below) ν_{max}(Nujol) 3525, OH; 1735, α-nitro ketone;

1660, C=C; 1565, 1555 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.70, 3H, Me; 1.85, 6H, Me's; 1.93, 3H, Me; 1.99, 3H, Me; c. 2.35, OH.

2,3,4,5,6-Pentamethyl-4-nitrocyclohexa-2,5-dienone (21). - (38%), m.p. 15-16° (Found: C, 63.5; H, 7.6; N, 6.4. $C_{11}H_{15}NO_3$ requires C, 63.1; H, 7.2; N, 6.7%). ν_{max}(Nujol) 1672, conjugated carbonyl; 1645, C=C; 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.82, 3H, 4-Me; 1.92, 2-, 3-, 5-, and 6- methyls. ^{13}C n.m.r. ($CDCl_3$) 1165, 15.18, 23.06, 92.77, 133.41, 145.01, 183.95. λ_{max}($CHCl_3$) 247 nm (ε 10,000).

2,3,5,6-Tetramethyl-1,4-benzoquinone (39). - (1%) m.p. 110-111° (lit[54] m.p. 110-111°), ν_{max}(Nujol) 1638 cm^{-1}, C=O. ^1H n.m.r. ($CDCl_3$) δ 2.02, Me's. λ_{max}($CHCl_3$) 262, 268 nm (ε 25,000 24,500).

REACTION OF PENTAMETHYLPHENOL (19) WITH FUMING NITRIC ACID IN DICHLOROMETHANE

To a solution of pentamethylphenol (2.12 g) in dichloromethane (16 ml) at -10° to -5°, was added dropwise over 20 min., a solution of fuming nitric acid (0.8 ml; d 1.5) in dichloromethane (6 ml). Further fuming nitric acid (3 ml; d 1.5) was added dropwise over 20 min. to the cooled (-10° to -5°), stirred solution, and the resulting solution was stirred for 90 h at 20°. During this time a white precipitate formed. The solvent and nitric acid were removed under reduced pressure at 20° to give a yellow residue (c. 5.3 g).

Addition of dichloromethane to the crude product and filtration gave 2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,c-5,c-6-trinitrocyclohex-3-enone (52). - (21%) m.p. 135-135.5°

(Found: C, 36.59; H, 4.28; N, 14.99. $C_{11}H_{14}N_4O_{10}$ requires: C, 36.5; H, 3.90; N, 15.47%). ν_{max}(Nujol) 1755, α,α'-dinitro ketone; 1660, C=C; 1635,1265,855, $-ONO_2$; 1580, 1570, 1555 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.96, 3H, Me; 2.08, 6H, Me's; 2.09, 3H, Me; 5.36, 2H, $C\underline{H}_2ONO_2$.

The residue, after removal of the dichloromethane, was separated into its components, by a combination of fractional crystallization (dichloromethane/pentane) and chromatographic separations on a Chromatotron silica gel plate, yielding:

2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (49). - (15%) m.p. 135-136° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1755, α,α'dinitro ketone; 1655, C=C; 1645,1260,855, $-ONO_2$; 1555-1580 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 2.00, 6H, Me's; 2.10, 6H, Me's, 5.43, 2H, $C\underline{H}_2ONO_2$.

2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,c-5,t-6-trinitrocyclohex-3-enone (51). - (2%) m.p. 99-99.5° (Found: C, 36.4; H, 3.9; N, 15.1. $C_{11}H_{14}N_4O_{10}$ requires C, 36.5; H, 3.9; N, 15.5%) ν_{max}(Nujol) 1755, α,α'-dinitro ketone; 1660, C=C; 1650,1265, 850, $-ONO_2$; 1580-1560 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.92, 3H, Me; 1.98, 3H, Me; 2.10, 3H, Me; 2.18, 3H, Me; 5.49, 2H $C\underline{H}_2ONO_2$.

2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,t-5,c-6-trinitrocyclohex-3-enone (50) - (7%) m.p. 123-124° (Found: C, 36.7; H, 4.0; N, 15.0. $C_{11}H_{14}N_4O_{10}$ requires C, 36.5; H, 3.9; N, 15.5%). ν_{max}(Nujol) 1750, α,α'-dinitro ketone; 1660, C=C; 1650,1265,850, $-ONO_2$; 1560,1570 cm^{-1}, NO_2. ^1H n.m.r. (CD_3SOCD_3) δ 1.88, 3H, Me; 1.97, 3H, Me; 2.00, 3H, Me; 2.18, 3H, Me; 5.42, 2H, $C\underline{H}_2ONO_2$.

2,3,4,5,6-Pentamethyl-r-2,c-5,c-6-trinitrocyclohex-3-enone (26). - (7%) m.p. and mixed m.p. 132-132.5°, spectroscopic data identical with those of an authentic sample, above.

2,3,4,5,6-Pentamethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (23). - (8%) m.p. and mixed m.p. 124-126°, spectroscopic data identical with those of an authentic sample, above.

2,3,4,5,6-Pentamethyl-r-2,t-5,c-6-trinitrocyclohex-3-enone (24). - (6%) m.p. and mixed m.p. 114-115°, spectroscopic data identical with those of an authentic sample, above.

2,3,4,5,6-Pentamethyl-r-4,t-5,t-6-trinitrocyclohex-2-enone (32). - 7%) m.p. and mixed m.p. 124-126° (dec.), spectroscopic data identical with those for an authentic sample above.

r-2-Hydroxy-2,3,4,5,6-pentamethyl-t-5,t-6-dinitrocyclohex-3-enone (36). - (3%) m.p. and mixed m.p. 165-165.5°, spectroscopic data identical with those for an authentic sample, above.

ATTEMPTED REACTION OF 2,3,4,5,6-PENTAMETHYL-4-NITROCYCLOHEXA-2,5-DIENONE (21) WITH NITROGEN DIOXIDE IN BENZENE SOLUTION

A solution of the 4-nitrodienone (21) (385 mg) in dry benzene (10 ml) was deoxygenated by a stream of nitrogen. Nitrogen dioxide was bubbled through the stirred solution at 5° for 3 min., and the excess nitrogen dioxide was then removed in a stream of nitrogen. The benzene solvent was removed under reduced pressure to give a residue (380 mg), the infrared and ^{1}H n.m.r. spectra were identical with those of an authentic sample of the 4-nitrodienone (21), above; no evidence was found for the presence of trinitro ketones in this residue.

REACTION OF 2,3,4,5,6-PENTAMETHYL-4-NITROCYCLOHEXA-2,5-DIENONE (21) WITH FUMING NITRIC ACID IN DICHLOROMETHANE

Fuming nitric acid (0.5 ml; d 1.5) was added dropwise over 20 min to a stirred solution of the 4-nitrodienone (21) (391 mg) in dichloromethane (4 ml) at -10°. The mixture was then stirred at 20° for 90 h, during which time a white precipitate developed. The dichloromethane solvent and nitric acid were removed under reduced pressure to give a residue (640 mg). The composition of this residue was essentially the same as that obtained from the reaction of pentamethylphenol (19) with fuming nitric acid in dichloromethane.

PREPARATION OF TETRAMETHYL-p-QUINONEMETHIDE (56) AND ITS REACTION WITH FUMING NITRIC ACID IN DICHLOROMETHANE

A mixture of pentamethylphenol (19) (230 mg), silver oxide (1 g) and dichloromethane (5 ml) was shaken at 20° for 5 min. The solution of the p-quinonemethide (56) [^{1}H n.m.r. (CH_2Cl_2) δ 1.96, 2.13; integrals ~1:1] was decanted from the silver oxide, cooled to 5°, and fuming nitric acid (0.4 ml; d 1.5) added with stirring. The mixture was stirred at 20° for 90 h, and then the solvent and nitric acid were removed under reduced pressure to give a residue (461 mg). This mixture was separated into its components by chromatography (Chromaton silical gel plate) and fractional crystallization from dichloromethane/pentane to give:

2,3,5,6-Tetramethyl-1,4-benzoquinone (39) (4%).

2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,c-5,c-6-trinitrocyclohex-3-enone (52) (29%).

2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (49) (27%).

2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,t-5,c-6-trinitrocyclohex-3-enone (50) (14%).

2,3,5,6-Tetramethyl-4-nitratomethyl-r-2,c-5,t-6-trinitrocyclohex-3-enone (51) (6%).

EXPERIMENTAL RELATING TO CHAPTER THREE

PREPARATION OF 2,3,5,6-TETRAMETHYL-4-NITROPHENOL (58)

(a) Preparation of 2,3,5,6-Tetramethylphenylacetate (152)

A solution of 2,3,5,6-tetramethylphenol (19 g) in acetic anhydride (30 ml) was heated under reflux for 3.5 h. The excess acetic anhydride was then removed by distillation under reduced pressure (c. 5 mm Hg.), and the resulting brown solid was recrystallised from aqueous acetic acid to give the acetate (152) as a white powder (16 g) m.p. 76-77° (lit[69] m.p. 78-79°). ν_{max} (Nujol) 1750 ester carbonyl; 1620 phenyl; 1225 cm^{-1} acetate. ^1H n.m.r. ($CDCl_3$) δ 2.01 6H, methyls; 2.22 6H, methyls; 2.33 3H, acetate methyl; 6.85 1H.

(b) Reaction of 2,3,5,6-Tetramethylphenylacetate (152) with Fuming Nitric Acid in Acetic Anhydride

Fuming nitric acid (4.25 ml; d 1.5) was added dropwise to a cooled (-5°-0°), stirred solution of the acetate (152) (14 g) in acetic anhydride (30 ml). The resulting solution was stirred at 0° for a further 15 min, and then at 20° for 1 hr. The orange solution was poured into water (300 ml), sodium bicarbonate was added until the solution was neutral, and extracted with diethyl ether (200 ml). The ether layer was washed twice with water (100 ml), dried over magnesium sulphate, and the solvent removed under reduced pressure to give a yellow solid (14 g). This crude product was separated into its components by silica gel column chromatography to give: 2,3,4,6-Tetramethyl-1,4-benzoquinone (39) (3.1 g) m.p. 110-111° (lit[54] m.p. 110-111°), spectroscopic data identical with those of an authentic sample, above. 2,3,5,6-Tetramethyl-4-nitrophenol (58) (9.8 g), m.p. 123-124° (lit[70] m.p. 123-124°).

ν_{max}(Nujol) 3670 OH; 1520 cm^{-1} NO_2. ^1H n.m.r. ($CDCl_3$) δ 2.17 12H, methyls; 4.87 1H, OH.

Reaction of 2,3,5,6-Tetramethyl-4-nitrophenol (58) with Nitrogen Dioxide

A solution of the nitrophenol (58) (500 mg) in dry benzene (10 ml) was deoxygenated by a stream of nitrogen. Nitrogen dioxide was bubbled through the stirred solution at 5° for 30 s, and the resulting mixture was stirred at 20° under an atmosphere of nitrogen dioxide for 3 h. The excess nitrogen dioxide was then removed under reduced pressure to give a residue (998 mg) which retained some benzene solvent. ν_{max} (smear) 3525 OH; 1760-1750 ketones; 1590-1540 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.51, 1.54, 1.84, 1.88, 1.90, 1.97, 2.02, 2.08, 2.10, 2.16, 2.22, 2.23, 3.83, 3.95. The components of this crude product were separated by a combination of fractional crystallisation (dichloromethane/pentane and ether/pentane) and on a Chromatotron silica gel plate. The yields given are those for the material isolated:

2,3,5,6-Tetramethyl-r-2,4,t-5,c-6-tetranitrocyclohex-3-enone (67). - (17%), m.p. 118°-119° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1755, α,α'-dinitro ketone 1670, C=C; 1590-1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.88, Me; 2.02, Me; 2.09, Me; 2.23, Me.

2,3,5,6-Tetramethyl-r-2,4,c-5,t-6-tetranitrocyclohex-3-enone (68). - (17%) m.p. 118°-119° (dec.) (X-ray crystal structure determined, see below). ν_{max} (Nujol) 1755, α,α'-dinitro ketone; 1655, C=C; 1595, 1585, 1555 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.88, Me; 1.89, Me; 2.12, Me; 2.17, Me.

2,3,5,6-Tetramethyl-r-2,4,t-5,t-6-tetranitrocyclohex-3-enone (69). - (12%) m.p. 119.5-120° (dec.), (Found: C, 35.9; H,

3.6; N, 16.7. $C_{10}H_{12}N_4O_9$ requires C, 36.1; H, 3.6; N, 16.9%). ν_{max}(Nujol) 1760) 1760, α,α'-dinitro ketone; 1640, C=C; 1590, 1580, 1570, 1540 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.88, Me; 2.00, Me; 2.12, Me; 2.24, Me.

2,3,5,6-Tetramethyl-r-2,4,c-5,c-6-tetranitrycyclohex-3-enone (70). - (8%) m.p. 140-140.5° (dec.) (Found: C, 36.3; H, 3.5; N, 16.6. $C_{10}H_{12}N_4O_9$ requires C, 36.1; H, 3.6; N, 16.9%). ν_{max}(Nujol) 1760, α,α'-dinitro ketone; 1665, C=C; 1595, 1590, 1570, 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.88, Me; 2.02, Me; 2.04, Me; 2.15, Me.

r-2-Hydroxy-2,3,5,6-tetramethyl-4,t-5,t-6-trinitrocyclohex-3-enone (71). - (2%) m.p. 167-167.5° (X-ray crystal structure determined, below). ν_{max}(Nujol) 3550, OH; 1755, α-nitro ketone; 1660, C=C; 1580, 1560 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.83, Me; 1.88, Me; 2.08, Me; 2.10, Me; 3.35, OH.

c-6-Hydroxy-2,3,5,6-tetramethyl-r-2,4,c-5-trinitrocyclohex-3-enone (72). - (8%) m.p. 129.5-130.5 (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 3500, OH; 1750, α-nitro ketone; 1565-1540 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.53, Me; 1.83, Me; 1.98, Me; 2.10, Me; 3.96, OH.

r-2, t-6-Dihydroxy-2,3,5,6-tetramethyl-4,t-5-dinitrocyclohex-3-enone (73). - (1%) m.p. 114-115° (dec.) (Found: C, 43.8; H, 5.1; N, 10.2%). ν_{max}(Nujol) 3525 sh, OH; 3400, br, OH; 1735, C=O; 1565, 1530 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.53, Me; 1.81, Me; 1.84, Me; 2.08, Me; 2.38, OH; 3.88, OH.

1-Acetyl-2,3,5-trimethyl-t-2,4,t-5-trinitrocyclopent-3-en-r-1-ol (75). (<1%) m.p. 155-156° (dec.) (Found: C, 39.5; H, 4.3; N, 13.5. $C_{10}H_{13}N_3O_8$ requires: C, 39.6; H, 4.3; N, 13.9%).

ν_{max}(Nujol) 3550, OH; 1720, C=O; 1665, C=C; 1560, 1530 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.87, Me; 2.12, 6H, Me's; 2.45, Me; 5.09, OH.

1-Acetyl-2,3,5-trimethyl-c-2,4,t-5-trinitrocyclopent-3-en-r-1-ol (76). - (<1%) m.p. 139-140° (dec.) (Found: C, 39.7; H, 4.3; N, 13.5. $C_{10}H_{13}N_3O_8$ requires: C, 39.6; H, 4.3; N, 13.9%). ν_{max}(Nujol) 3450, OH; 1720, C=O; 1660, C=C; 1580, 1550, 1540 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.53, Me; 2.15, Me; 2.18; Me; 2.23, Me; OH signal not visible in spectrum of a low concentration solution.

Preparation of 2,3,5,6-Tetramethyl-4,6-dinitrocyclohexa-2,4-dienone (65).

Fuming nitric acid (d 1.5, 0.65 ml) was added dropwise to a solution of 2,3,5,6-tetramethyl-4-nitrophenol (58) (3.12 g) in acetic acid (30 ml) at 5°. The resulting mixture was stirred for 10 min., excess water added, and the crude product (3.2 g) isolated by filtration. Recrystallization of this material from dichloromethane/pentane at <5° gave pure 2,3,5,6-tetramethyl-4,6-dinitrocyclohexa-2,4-dienone (65) m.p. 64-65° (dec.) (Found: C, 50.3; H, 5.0; N, 11.8. $C_{10}H_{12}N_2O_6$ requires C, 50.0; H, 5.0; N, 11.7%). ν_{max}(Nujol) 1680, conjugated ketone; 1640, C=C; 1560-1540 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$; -60°) δ 1.93, 6H, Me's; 2.05, Me; 2.10, Me. ^{13}C n.m.r. ($CDCl_3$; -50°) δ 11.9, 13.7, 16.2, 23.1, 93.7, 130.0, 132.6, 140.8, 148.5, 190.5.

Preparation of 6-Hydroxy-2,3,5,6-tetramethyl-4-nitrocyclohexa-2,4-dienone (66)

Nitrogen was bubbled for 10 h through a solution of

2,3,5,6-tetramethyl-4,6-dinitrocyclohexa-2,4-dienone (65) (3.2 g) in chloroform (70 ml). Removal of the solvent under reduced pressure gave a yellow solid, which on crystallization from ether/petroleum ether gave 6-hydroxy-2,3,5,6-tetramethyl-4-nitrocyclohexa-2,4-dienone (66) (2.01 g), m.p. 88-88.5°, (Found: C, 56.9; H, 6.4; N, 6.5. $C_{10}H_{13}NO_4$ requires C, 56.9; H, 6.2; N, 6.6%) ν_{max}(Nujol) 3475, OH; 1665, conjugated ketone; 1650, C=C; 1545 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.43, 6-Me; 1.99, 9H, Me's; 3.50, OH. ^{13}C n.m.r. ($CDCl_3$) δ 11.5, 12.9, 15.5, 28.9, 76.9, 128.5, 139.7, 142.2, 146.2, 203.4. λ_{max} (cyclohexane) 304 nm (ε 3600). Further hydroxydienone (66) (604 mg) was obtained from the mother liquor from the above crystallization by separation on a Chromatotron silica gel plate.

Reaction of 6-Hydroxy-2,3,5,6-tetramethyl-4-nitrocyclohexa-24-dienone (66) with Nitrogen Dioxide

A solution of the hydroxydienone (66) (980 mg) in dry benzene (20 ml) was deoxygenated by a stream of nitrogen. Nitrogen dioxide was bubbled rapidly through the stirred solution at 5° for 30 s, and the resulting mixture was stirred at 20° under an atmosphere of nitrogen dioxide for 1 h. The excess nitrogen dioxide was then removed in a stream of nitrogen, and the benzene solvent removed under reduced pressure to give a white solid residue (1.46 g) which retained some benzene solvent. The crude product was shown (^1H n.m.r.) to be a mixture of compounds (77), (73) and (72) in the ratio c. 5:2:3 respectively. Fractional crystallization of this crude material from dichloromethane/pentane and ether/pentane gave the following compounds:

c-6-Hydroxy-2,3,5,6-tetramethyl-r-2,4,c-5-trinitrocyclohex-3-enone (72). - (30%) m.p. 129.5-130.5° m.m.p. 129-130° (dec.), spectroscopic data identical with those of an authentic sample.

t-6-Hydroxy-2,3,5,6-tetramethyl-r-2,4,t-5-trinitrocyclohex-3-enone (77). - (30%) m.p. 118-120° (dec.) (X-ray crystal structure determined, below) ν_{max}(Nujol) 3500, OH; 1750, α-nitro ketone; 1670, C=C; 1570, 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$ δ 1.54, Me; 1.83, Me; 2.03, Me; 2.22, Me; 3.83, OH.

r-2,t-6-Dihydroxy-2,3,5,6-tetramethyl-4,t-5-dinitrocyclohex-3-enone (73). - (10%) m.p. 114-115°, m.m.p. 114-115° (dec.), spectroscopic data identical with those of an authentic sample.

The mixture of compounds, which remained after the above separation by crystallisation, were subjected to chromatography on a Chromatatron silica gel plate and gave a further identifiable material:

1-Acetyl-2,3,5-trimethyl-4,c-5-dinitrocyclopent-3-ene-r-1,t-2-diol (74). - (10%) m.p. 120-121° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 3525, sh, OH; 3400, br, OH; 1723, 1717, C=O; 1653, C=C; 1555 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.54, Me; 2.29, Me; 2.47, Me; 2.18, OH; 4.80, OH.

Base-catalysed Acyloin Rearrangement of c-6-Hydroxy-2,3,5,6-tetramethyl-r-2,4,c-5-trinitrocyclohex-3-enone (72).

A two-phase system consisting of a solution of the hydroxy trinitro ketone (72) (416 mg) in dichloromethane (15 ml) and aqueous sodium bicarbonate (0.7% w/v; 10 ml) was agitated vigorously for 5 min. The organic layer was separated, dried with magnesium sulphate, and evaporated at 20° to give a residue (419 mg), shown by its ^1H n.m.r. spectrum to be a

mixture (c. 2:1) of 1-acetyl-2,3,5-trimethyl-t-2,4,t-5-trinitrocyclopent-3-en-r-1-ol (75) and probably its C1 epimer, cyclopentenol (80) [^{1}H n.m.r. ($CDCl_3$) δ 1.82, Me; 1.97, Me; 2.40, Me; 2.45, Me; by subtraction of ^{1}H n.m.r. spectrum for (75)]. Fractional crystallization of the crude product from dichloromethane/pentane gave pure cyclopentenol (75) (130 mg) m.p. 155-156°, identical (^{1}H n.m.r. and infrared spectra) with authentic material; the second component of the mixture could not be obtained in a pure state.

Base-catalysed Acyloin Rearrangement of t-6-Hydroxy-2,3,5,6-tetramethyl-r-2,4,t-5-trinitrocyclohex-3-enone (77)

Treatment of the hydroxy ketone (77) (390 mg) in dichloromethane (10 ml) with aqueous sodium bicarbonate (0.7% w/v; 10 ml) for 10 min, as above, gave a crude product (375 mg), shown by its ^{1}H n.m.r. spectrum to be a complex mixture. Fractional crystallization of this mixture from dichloromethane/pentane gave 1-acetyl-2,3,5-trimethyl-c-2,4,t-5-trinitrocyclopent-3-en-r-1-ol (76) (60 mg), m.p. 139-140° (dec.), identical (^{1}H n.m.r. and infrared spectra) with authentic material.

Base-catalysed Acyloing Rearrangement of r-2,t-6-Dihydroxy-2,3,5,6-tetramethyl-4,t-5-dinitrocyclohex-3-enone (73)

Treatment of the dihydroxy ketone (73) (100 mg) in dichloromethane (5 ml) with aqueous sodium bicarbonate (0.7% w/v; 5 ml) for 5 min, as above, gave a crude product (95 mg), shown by its ^{1}H n.m.r. spectrum to be a mixture (c. 2:1) of 1-acetyl-2,3,5-trimethyl-4,c-5-dinitrocyclopent-3-ene-r-1,-t-2-diol (74) and a second compound, presumably the C1-epimeric cyclopentenediol (82) [^{1}H n.m.r. ($CDCl_3$) δ 1.34, Me; 1.53, Me;

2.19, Me; 2.23, Me]. Fractional crystallization of the crude product from dichloromethane/pentane gave the pure major component, cyclopentenediol (74), m.p. 120-121° (dec.), identical (^{1}H n.m.r., infrared spectra) with authentic material.

EXPERIMENTAL RELATING TO CHAPTER FOUR

PREPARATION OF 4,6-DIBROMO-2-PHENYLPHENOL (105a)

The phenol (105a), was prepared from o-hydroxybiphenyl by the method of Auwers and Wittig.[71]

NITRATION OF 4,6-DIBROMO-2-PHENYLPHENOL (105a) WITH FUMING NITRIC ACID IN ACETIC ACID

(a) With 1.1 Moles of Fuming Nitric Acid:- To a slurry of the phenol (105a)(1g) in acetic acid (1 ml) at 5° was added dropwise over 2 min. a solution of fuming nitric acid (0.15 ml; d 1.5) in acetic acid (1 ml). The phenol (105a) dissolved during the addition of the fuming nitric acid, and a yellow compound which precipitated was shown to be 6-bromo-4-nitro-2-phenylphenol (105b)(423 mg) m.p. 113.5-114° (Found: C, 48.8; H, 3.0; Br, 27.1; N, 4.5. $C_{12}H_8BrNO_3$ requires C, 49.0; H, 2.7; Br, 27.2; N, 4.8%) ν_{max}(Nujol) 3425, OH; 1520, NO_2; 705, C-Br. ^1H n.m.r. ($CDCl_3$) δ 6.33, OH; 7.53, 5H, phenyl protons; 8.22, d, J 3Hz, H3; 8.34, d, J 3Hz, H5. ^{13}C n.m.r. ($CDCl_3$) δ 154.8, 141.5, 134.9, 129.7, 129.0, 128.3, 127.1, 125.6, 110.8.

The above filtrate, gave a further crop of crystals (180 mg), shown (^1H n.m.r., infrared spectra) to be the bromo nitro phenol (105b). No further compounds could be isolated from the residue.

(b) With Excess Fuming Nitric Acid:- To a stirred solution of the phenol (105a)(2 g) in acetic acid (6 ml) at 5° was added fuming nitric acid (d 1.5; 4 ml) dropwise over 20 min. The resulting mixture was stored at 10° for 30 min. and the crystalline material which deposited was identified

as 4,6-dinitro-2-phenylphenol (105c) (470 mg), m.p. 209-210° (lit[61] 201-203°) (Found: C, 55.0; H, 3.1; N, 10.7. $C_{12}H_8N_2O_4$ requires C, 55.4; H, 3.1; N, 10.8%) ν_{max}(Nujol) 1560, 1510 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 2.60, OH; 7.55, 5H, phenyl protons; 8.52, d, J 3Hz, H3; 9.08, d, J 3Hz, H5.

Addition of water to the mother liquor, above, gave further dinitro phenol (105c) (500 mg). This latter filtrate was diluted with dichloromethane, washed with water and dried with magnesium sulphate. The residue, after removal of the solvent under reduced pressure, was absorbed onto silica gel. Elution with petroleum ether and petroleum ether/ether mixtures gave further dinitro phenol (105c) (300 mg) (total yield 71%).

Attempted Nitration of 4,6-Dinitro-2-phenylphenol (105c) with Fuming Nitric Acid in Acetic Acid

Fuming nitric acid (d 1.5, 1 ml) was added dropwise over 10 min. to a stirred suspension of the phenol (105c) (500 mg) in acetic acid (2 ml) at 5°, and the resulting solution stirred at 20° for two weeks. The mixture was diluted with chloroform, the solution washed repeatedly with water, dried with magnesium sulphate and the solvent removed under reduced pressure. The yellow residue (480 mg) was identical (infrared, ^1H n.m.r. spectra) with authentic 4,6-dinitro-2-phenylphenol (105c).

Attempted Reaction of 4,6-Dinitro-2-phenylphenol (105c) with Nitrogen Dioxide in Benzene Solution

A solution of the phenol (105c) (125 mg) in dry benzene (5 ml) was deoxygenated by a stream of nitrogen. Nitrogen dioxide was bubbled through the solution for 30 s, and the

resulting mixture stirred under an atmosphere of nitrogen dioxide for 3 h. The excess nitrogen dioxide was then removed in a stream of nitrogen and the solvent removed under reduced pressure to give a yellow solid (140 mg) which retained some benzene solvent. After drying under high vacuum this material was identical (infrared, ^{1}H n.m.r. spectra) with authentic 4,6-dinitro-2-phenylphenol (105c).

2-Methyl-6-phenylphenol (106b)

The phenol (106b) was prepared from 6-phenylsalicyclic acid by the method of Jensen and Lofgren.[72]

4-Bromo-6-methyl-2-phenylphenol (106a)

A solution of bromine (2.9 g) in carbon tetrachloride (5 ml) was added to a stirred solution of 6-methyl-2-phenylphenol (106b) (3 g) in carbon tetrachloride (5 ml) in a darkened reaction vessel. The resulting mixture was stirred at 20^o for 30 min, and the solvent then removed under reduced pressure to give as a residue an orange oil (4.95 g). This material was purified on a silica gel Chromatographic column to give 4-bromo-6-methyl-2-phenylphenol (106a) (4.88 g) as an oil (Found: C, 59.4; H, 4.0; Br, 30.3. $C_{13}H_{11}BrO$ requires: C, 59.3; H, 4.2; Br, 30.4%). ν_{max} (liquid film) 3575, OH; 715 cm^{-1}, C-Br. ^{1}H n.m.r. ($CDCl_3$) δ 2.25, Me; 5.20, OH; 7.15, bs, 2H, H3, H5; 7.50, 5H, phenylprotons.

Nitration of 4-Bromo-6-methyl-2-phenylphenol (106a) with Fuming Nitric Acid in Acetic Acid

Fuming nitric acid (d 1.5, 2.1 ml, 1.1 moles) was added dropwise over 20 min to a stirred solution of the phenol (106a) (12 g) in acetic acid (40 ml) at 5^o, and the resulting mixture

stirred at 20° for 30 min. The reaction mixture was diluted with ether, the ether solution washed with water and dried. Removal of the solvent under reduced pressure gave a yellow solid residue (10 g) which was adsorbed onto a silica gel (300 ml) chromatographic column.

Elution with petroleum ether gave 2-bromo-3-methyl-5-phenyl-1,4-benzoquinone (110) (1.0 g), m.p. 97-98° (Found: C, 56.4; H, 3.3; Br, 29.3. $C_{13}H_9BrO_2$ requires: C, 56.4; H, 3.3; Br, 28.8%). ν_{max}(Nujol) 1655 cm^{-1}, C=O. ^1H n.m.r. ($CDCl_3$) δ 2.31, Me; 6.96, H6; 7.43, phenyl protons. λ_{max} (cyclohexane) 227,255,313 nm (ε 23500, 11300, 11000).

Elution with petroleum ether/ether (100:1) gave 2-methyl-6-phenyl-1,4-benzoquinone (111) (800 mg), m.p. 45-46° (Found: C, 79.0; H, 5.0. $C_{13}H_{10}O_2$ requires: C, 78.8; H, 5.1%). ν_{max} (Nujol) 1655,1650 cm^{-1}, C=O. ^1H n.m.r. ($CDCl_3$) δ 2.13, d, J 2Hz, Me; 6.67, dq, $J_{3,Me}$ 2Hz, $J_{3,5}$ 3Hz, H3; 6.80, d, $J_{5,3}$ 3Hz, H5; 7.47, phenyl protons. λ_{max} (cyclohexane) 229, 248, 288, 364 nm (ε 15300, 12000, 4100, 1500).

Elution with petroleum ether/ether (95:5) gave 6-methyl-4-nitro-2-phenylphenol (106c) (8 g), m.p. 92-93° (Found: C, 68.2; H, 4.9; N, 6.0. $C_{13}H_{11}NO_3$ requires: C, 68.1; H, 4.8; N, 6.1%). ν_{max}(Nujol) 3500, OH; 1515 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 2.36, Me; 5.90, OH; 7.45, 5H, phenylprotons; 7.99, 2H, H3,H5. ^{13}C n.m.r. ($CDCl_3$) δ 16.3, 123.7, 125.9, 126.0, 129.0, 129.05, 129.1, 129.9, 134.9, 141.0, 156.3.

Reaction of 6-Methyl-4-nitro-2-phenylphenol (106c) with Fuming Nitric Acid in Acetic Acid.

Fuming nitric acid (d 1.5, 2 ml) was added dropwise over 20 min to a stirred suspension of the phenol (106c) (1 g) in

acetic acid (3 ml) at 5°. The resulting mixture was stored at 10° for 8 h, but no crystalline material deposited. The reaction mixture was then diluted with dichloromethane (50 ml) and the solution washed with water and dried. Removal of the solvent under reduced pressure gave a brown oil (1.41 g), shown (^{1}H n.m.r.) to be a mixture of c. ten components. The crude mixture gave ν_{max} (liquid film) 3500, OH; 1750, C=O; 1590-1530 cm^{-1}, NO_2. Attempted separation of the components of this mixture on a silica gel Chromatotron plate resulted only in extensive decomposition of the material.

Reaction of 6-Methyl-4-nitro-2-phenylphenol (106c) with Nitrogen Dioxide in Benzene Solution

A solution of the phenol (106c) (507 mg) in dry benzene (5 ml) was deoxygenated by a stream of nitrogen. Nitrogen dioxide was bubbled through the stirred solution at 5° for 30 s and the resulting mixture stirred under an atmosphere of nitrogen dioxide for 2 h. The excess nitrogen dioxide was then removed in a stream of nitrogen and the solvent removed under reduced pressure to give a brown oil (800 mg), ν_{max} (liquid film) 3500, OH; 1745, C=O; 1570-1540 cm^{-1}, NO_2. In the ^{1}H n.m.r. ($CDCl_3$) spectrum of the brown oil six distinct methyl resonances were apparent: δ 1.20 (c. 17%), 1.39 (c. 3%), 1.62 (c. 12%), 1.75 (c. 28%), 1.90 (c. 26%), 2.19 (c. 12%). Attempted separation of the components in the brown oil on a Chromatotron silica gel plate resulted in extensive decomposition of the material.

Fractional crystallization of the crude product from dichloromethane/pentane gave r-2,t-6-dihydroxy-6-methyl-4,t-5-dinitro-2-phenylcyclohex-3-enone (114) (100 mg), m.p. 142-143°

(dec.) (X-ray crystal structure determined, below). ν_{max} (Nujol) 3525, 3500, OH; 1740, C=O; 1675, C=C; 1590, 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.75, Me; 4.07, OH; 6.67, d, $J_{5,3}$ 1Hz, H5; 7.52, 5H, phenylprotons; 7.75, d, $J_{3,5}$ 1Hz, H3. No further components could be obtained by fractional crystallization.

The above residue was subjected to HPLC separation on a Shimadzu LC4 using a Sorbex CN-propyl column (25 cm X 4.6 mm) and chloroform/petroleum ether mixtures and gave:

(a) r-2-hydroxy-6-methyl-4,c-5,t-6-trinitro-2-phenylcyclohex-3-enone (115), m.p. 115-116° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 3550, OH; 1755, C=O; 1675, C=C; 1570, 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.90, Me; 3.25, OH; 6.70, d, $J_{5,3}$ 1Hz, H5; 7.43, 5H, phenyl protons; 7.97, d, $J_{3,5}$ 1Hz, H3.

(b) a compound, isolated only at c. 90% purity, tentatively assigned the structure - r-2,c-6-dihydroxy-6-methyl-4,c-5-dinitro-2-phenylcyclohex-3-enone (116) ν_{max} (liquid film) 3500, OH; 1745, C=O; 1680, C=C; 1575, 1545 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.20, Me; 6.07, d, $J_{5,3}$ 1Hz, H5; 7.49, 5H, phenyl protons; 8.13, d, $J_{3,5}$ 1Hz, H3.

Reaction of 6-Methyl-4-nitro-2-phenylphenol (106c) with 2 Moles of Nitrogen Dioxide, Followed by Excess Nitrogen Dioxide

A solution of the phenol (106c) (499 mg) in dry benzene (5 ml) was deoxygenated by a stream of nitrogen. A solution of nitrogen dioxide (110 mg; 2 moles) in dry benzene (0.6 ml) was added dropwise over 20 min. The resulting solution was stirred at 5° for 1 h. while a stream of nitrogen was bubbled through it.

Excess nitrogen dioxide was bubbled through the stirred solution for 30 s and the resulting mixture stirred under an atmosphere of nitrogen dioxide for 1.5 h. The excess nitrogen dioxide was then removed in a stream of nitrogen, and the solvent removed under reduced pressure to give a brown oil (800 mg), which retained some benzene solvent. In the ^{1}H n.m.r. ($CDCl_3$) spectrum of the brown oil two major methyl resonances were apparent: δ 1.20 (c. 28%) and 1.75 (c. 40%), and four minor methyl resonances: δ 1.39 (c. 1-2%), 1.62 (c. 5%), 1.90 (c.10%), 2.19 (c. 4%).

Fractional crystallization of the mixture from dichloromethane/pentane gave r-2,t-6-dihydroxy-6-methyl-4,t-5-dinitro-2-phenylcyclohex-3-enone (114) (50 mg), identical with authentic material.

Further fractional crystallization of the residue from the above crystallization gave material (116) of c. 90% purity, ν_{max} (liquid film) 3500, OH; 1745, C=O; 1680, C=C; 1575, 1545 cm^{-1}, NO_2. ^{1}H n.m.r. ($CDCl_3$) δ 1.20, Me; 6.07, d, $J_{5,3}$ 1Hz, H5; 7.49, 5H, phenyl protons; 8.13, d, $J_{3,5}$ 1Hz, H3.

4-Methyl-2,6-diphenylphenol (125)

Hydrogen chloride was bubbled through a stirred solution of 2,6-diphenylphenol (10 g) in acetic acid (150 ml) and aqueous formaldehyde (30%; 6 ml) at 20° for 3 h, and the resulting solution stirred at 20° for a further 10 h. Isolation by means of ether gave the crude 4-chloromethyl-2,6-diphenylphenol (153) as a red oil. This red oil was dissolved in dry methanol (150 ml) and reacted with hydrogen in the presence of a palladium/charcoal catalyst (5%; 1g) for 4 h. The catalyst was removed by filtration, and the solvent removed

under reduced pressure to give a clear oil. Purification by means of chromatography on a silica gel column and crystallization from ether/light petroleum gave pure 4-methyl-2,6-diphenylphenol (125) (7 g), m.p. 79-80° (Found: C, 87.4; H, 6.2. $C_{19}H_{16}O$ requires: C,87.7; H, 6.2) ν_{max} (Nujol) 3550 cm^{-1}, OH. ^1H n.m.r. ($CDCl_3$) δ 2.34, Me; 5.18, OH; 7.05, H3, H5; 7.45, 10H, phenyl protons. ^{13}C n.m.r. ($CDCl_3$) δ 20.45, 127.45, 128.6, 128.7, 130.4, 137.8, 147.1.

Reaction of 4-Methyl-2,6-diphenylphenol (125) with Nitrogen Dioxide in Benzene Solution

A solution of the phenol (125) (1.01 g) in dry benzene (20 ml) was deoxygenated by a stream of nitrogen. Nitrogen dioxide was bubbled through the stirred solution at 5° for 30 s, and the resulting mixture was stirred at 20° for 2.5 h under an atmosphere of nitrogen dioxide. During this time a colourless precipitate was deposited. Removal of the excess nitrogen dioxide by a stream of nitrogen, followed by filtration gave a solid (101 mg) shown (^1H n.m.r.) to be a mixture (c 1:1) of two compounds. These components were separated by chromatography on a Chromatotron silica gel plate to give in order of elution:

r-4-Hydroxy-4-methyl-c-5,c-6-dinitro-2,6-diphenylcyclohex-2-enone (126) m.p. 170-171° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 3550, OH; 1703, α'-nitro-conjugated ketone; 1570, 1560 cm^{-1}, NO_2. ^1H n.m.r. (CD_3CN) δ 0.89, Me; 4.62, OH; 6.21, d, $J_{5,3}$ 1.8 Hz, H5; 6.57, d, $J_{3,5}$ 1.8 Hz, H3; 7.57, 10H, phenyl protons. UV λ_{max} (CH_3CN) 218, 272 nm (ε 16,500, 3000)

r-4-Hydroxy-4-methyl-c-5,c-6-dinitro-2-(2'-nitrophenyl)-6-phenylcyclohex-2-enone (127), m.p. 168.5-169° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol 3525, OH; 1703, α'-nitro-conjugated ketone; 1650, C=C; 1575, 1555, 1520 cm^{-1}, NO_2. ^1H n.m.r. (CD_3CN) δ 0.93, Me; 4.56, OH; 6.22, d, $J_{5,3}$ 2Hz, H5; 6.57, d, $J_{3,5}$ 2Hz, H3; 7.20-7.67, total 9H, 2'-nitrophenyl and phenyl protons, UV λ_{max}(CH_3CN) 218,272 nm (ε 16500,3000).

Removal of the benzene solvent from the filtrate, above, under reduced pressure gave a residue which, on fractional crystallization from dichloromethane/pentane, gave further samples of hydroxy ketones (126) (total yield 6%) and (127) (total yield 4%).

Further fraction crystallization gave a nitro ketone, tentatively assigned the structure (129), m.p. 136-137° (dec.) ν_{max}(Nujol) 1730 α'-nitro-conjugated ketone; 1650, C=C; 1580, 1560, 1530 cm^{-1} NO_2. ^1H n.m.r. (CD_3CN) δ 1.48, 3H, Me; 7.0, d, $J_{5,3}$ 2Hz, $H5_j$ 7.2, d, $J_{3,5}$ 2Hz, H3; 7.55, m, 9H.

Finally, fractional crystallization gave 4-methyl-r-4,c-5,c-6-trinitro-2,6-diphenylcyclohex-3-enone (128) (200 mg), m.p. 121-122° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1710, α'-nitro-conjugated ketone; 1640, C=C; 1580, 1560-1540 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.20, Me; 6.47, d, $J_{5,3}$ 2Hz, H5; 6.88, d, $J_{3,5}$ 2Hz; 7.53, phenyl protons. UV λ_{max} (CH_3CN) 221, 283 nm (30,000, 6000).

The combined residue from the above fractional crystallizations was shown (^1H n.m.r.) to be a mixture of at least seven compounds giving rise to methyl resonances, ^1H n.m.r. ($CDCl_3$) δ 1.20 (c. 15%), 1.28 (c. 17%), 1.70 (c. 3%), 1.78

(c. 12%), 1.87, 1.90 (total c 31%), 2.25 (c. 4%). Attempted chromatographic separation of this residue on a Chromatotron silica gel plate gave the following pure compounds, in order of elution:

t-6-Hydroxy-4-methyl-r-4,t-5-dinitro-2,6-diphenylcyclohex-2-enone (131) (11%), m.p. 135-135.5° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 3500, 3450, OH; 1710, br, conjugated carbonyl; 1620, C=C, 1565 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) 1.87, Me; 4.42, OH; 6.33, d, $J_{5,3}$ 2Hz, H5; 6.79, d, $J_{3,5}$ 2Hz, H3; 7.34, s, 5H, phenyl protons; 7.67, m, 5H, phenyl protons, UV λ_{max} (CH_3CN) 221,278 nm (30,000, 6000).

4-Methyl-r-4,t-5,t-6-trinitro-2,6-diphenylcyclohex-2-enone (130) (11%), m.p. 137.5-138.5° (dec.) (X-ray crystal structure determined, below). ν_{max}(Nujol) 1730, α'-nitro-conjugated ketone; 1575, 1565 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1.90, Me; 6.62, d, $J_{5,3}$ 2Hz, H5; 6.80, d, $J_{3,5}$ 2Hz, H3; 7.20-7.50, m, 5H, phenyl protons; 7.55, s, 5H, phenyl protons, UV λ_{max} (CH_3CN) 217,287 nm (ε 20,000, 4000).

Further 4-methyl-r-4,c-5,c-6-trinitro-2,6-diphenylcyclohex-2-enone (128) (total yield 25%), m.p. 121-122° (dec.), identical with authentic material, above.

The remaining material eluted from the Chromatotron silica gel plate was complex mixtures of the compounds initially adsorbed together with decomposition products.

The overall yields of products isolated were (126) (6%), (127) (4%), (128) (25%), (130) (11%) and (131) (11%).

4-Methyl-4-nitro-2,6-diphenylcyclohexa-2,5-dienone (134)

Fuming nitric acid (0.37 ml; d 1.5) was added dropwise to a stirred solution of 4-methyl-2,6-diphenylphenol (125) (1.6 g)

in acetic acid (30 ml) at 6°, and the resulting solution was stirred at 20° for 10 min. Water was then added and the colourless solid (c 1.6 g) which precipitated recrystallized from dichloromethane/pentane at 5° to give 4-methyl-4-nitro-2,6-diphenylcyclohexa-2,5-dienone (134), m.p. 81-83° (Found: C, 74.6; H, 4.9; N, 4.3. $C_{19}H_{15}NO_3$ requires: C, 74.7; H, 4.95; N 4.6%). ν_{max}(NUjol) 1665, 1645, conjugated ketone; 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 2.05, Me; 7.17, H3, H5; 7.47, 10H, phenyl protons. ^{13}C n.m.r. ($CDCl_3$; -50°) δ 26.3, 84.6, 128.3, 128.6, 128.9, 133.7, 138.9, 140.15, 182.0.

4-Hydroxy-4-methyl-2,6-diphenylcyclohexa-2,5-dienone (133)

A stream of nitrogen was passed through a stirred solution in a darkened flask at 20° of the 4-nitro dienone (134) (1.6 g) and sodium acetate (2 g) in acetic acid (30 ml) for 12 h. The crude product (1.2 g), isolated by means of ether, was adsorbed onto a Chromatotron silica gel plate; elution gave the following compounds:

4-Acetoxymethyl-2,6-diphenylphenol (135) (516 mg), m.p. 97.5-98° (Found: C, 79.2; H, 5.7. $C_{21}H_{18}O_3$ requires: C, 79.2; H, 5.7%). ν_{max}(Nujol) 3425, OH; 1720, 1250 cm^{-1}, acetate. ^1H n.m.r. ($CDCl_3$) δ 2.06, Me; 5.10, $-CH_2OA_c$; 5.40, OH; 7.26, H3, H5; 7.50, 10H, phenyl protons. ^{13}C n.m.r. ($CDCl_3$) δ 20.7, 66.0, 127.75, 128.1, 128.8, 129.0, 129.3, 130.3, 137.2, 149.6, 170.85.

4-Hydroxy-4-methyl-2,6-diphenylcyclohexa-2,5-dienone (133) (295 mg), m.p. 70-71° (Found: C, 82.45; H, 5.8. $C_{19}H_{16}O_2$ requires: C, 82.6; H, 5.8%). ν_{max}(Nujol) 3450, OH; 1660, 1640, 1625 cm^{-1}, conjugated carbonyl. ^1H n.m.r. ($CDCl_3$) δ 1.63, Me; 1.82, OH; 6.95, H3, H5; 7.40, 10H, phenol protons. ^{13}C n.m.r.

($CDCl_3$) δ 27.5, 67.4, 128.1, 128.2, 129.0, 135.25, 137.7, 148.1, 183.2. λ_{max} (cyclohexane) 220, 279 nm (ε 5000, 1000).

A third compound which was not identified was isolated in the yield (190 mg) m.p. 113-114°. (Found c, 73.02; H, 5.37. $C_{18}H_{16}O_4$ requires: C, 73.02; H, 5.42) ν_{max}(Nujol) 3450, OH; 1760, 1748, C=O, ^{1}H n.m.r. ($CDCl_3$) δ 2.13 6H; 5.53 1H, OH (exchanged D_2O); 7.43, 7.50 10H, 7.67 1H. ^{13}C n.m.r. 20.93(2), 89.69(d), 128.01(d), 128.37(d), 128.95(d), 129.33(d), 136.89(s), 150.52(s), 168.78(s), λ_{max} (cyclohexane) [0.045 mg/ml] 213.7 nm (A, 3.46%), 237.6 (A, 3.34%), 296.2 (A, 0.63%).

Reaction of 4-Hydroxy-4-methyl-2,6-diphenylcyclohexa-2,5-dienone (133) with Nitrogen Dioxide in Benzene

A solution of the 4-hydroxy dienone (133) (290 mg) in dry benzene (5 ml) was deoxygenated by a stream of nitrogen. Nitrogen Dioxide was bubbled through the solution for 30 s, and the resulting mixture was stirred under an atmosphere of nitrogen dioxide for 2 h. During this time a colourless precipitate formed. The excess nitrogen dioxide was removed by a stream of nitrogen, and the solvent removed under reduced pressure. The solid residue was triturated with dichloromethane and filtered to give a colourless powder (35 mg), shown [^{1}H n.m.r. (CD_3CN)] to be a mixture (c. 2:1 of the 4-hydroxy-5,6-dinitro ketone (126) and the 4-hydroxy-2',5,6-trinitro ketone (127) (estimated yield c. 2%). The filtrate, above, gave a residue on removal of solvents which on crystallization yielded further 4-hydroxy-5,6-dinitro ketone (126) (45 mg).

The residue from the above crystallization was adsorbed onto a Chromatotron silica gel plate and elution gave the following identifiable material in order of elution.

t-6-Hydroxy-4-methyl-r-4,t-5-dinitro-2,6-diphenylcyclohex-2-enone (131) (3%).

4-Methyl-r-4,t-5,t-6-trinitro-2,6-diphenylcyclohex-2-enone (130) (3%).

4-Methyl-r-4,c-5,c-6-trinitro-2,6-diphenylcyclohex-2-enone (128) (10%).

r-4-Hydroxy-4-methyl-c-5,c-6-dinitro-2,6-diphenylcyclohex-2-enone (126) (total yield 25%).

These products were identical (m.p.; infrared, ^{1}H n.m.r. spectra) with authentic material.

APPENDIX

The data sets used for the X-ray crystal structure analyses in this thesis were collected on two different instruments. For the 4-nitrato ketone (49) (Chapter 1), crystal data, established from precession photographs and measured accurately, by using a Hilger & Watts four-circle diffractometer, are presented below. Ni-filtered Cu Kα X-radiation [λ(Cu Kᾱ) 1.5418 Å] and the θ/2θ scan technique were used to collect reflection intensities out to a Bragg angle, given below. The space group was determined unambiguously as a result of the structure analysis reported below but initially indicated by systematic absences of appropriate reflections. The cell parameters were determined by least-squares refinement, using the setting angles of 25 accurately centred reflections ($40^{o}<2\theta<65^{o}$) being used.

Crystal data for 2,3,5,6-tetramethyl-4-nitratomethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (49). - $C_{11}H_{14}N_4O_{10}$, M 362.25, orthorhombic, space group $P\,2_12_12_1$, a 11.05(1), b 15.461(1) c 8.774(1), U 1506.44 Å^3, D_m 1.59 g cm^{-1}, Z 4, μ(Cu Kᾱ) 12.03 cm^{-1}. The crystal was colourless and of approximate dimensions 0.5 mm by 0.6 mm by 0.05 mm. Number of reflections measured 1216, number with $I > 3\sigma(I)$ 1093, maximum bragg angle θ 57°; g 0.0005; R-factor 0.042; wR 0.046; absorption correction, maximum 1.682, minimum 1.067.

Intensity data were processed by means of a Burroughs B6930 computer and programs HILGOUT (based on DRED by J.F. Blount and PICKOUT by R.J. Doedens) and ABSORB (a major revision, by L.K. and D. Templeton, of the program AGNOST installed on local Burroughs hardware by A. Zalkin).

For the remaining compounds whose structures were determined by X-ray crystal structure analysis (compounds (23),(24),(25),(32),(33),(36),(67),(68),(71),(72),(74),(77), (114),(115),(126),(127),(128),(130) and (131)), crystal data established from precession photographs and measured accurately, by using a Nicolet XRD P3 four-circle diffractometer, are given below. Molybdenum X-radiation [λ(Mo K$\bar{\alpha}$) 0.71069 Å] from a graphite crystal monochromater and either the $\theta/2\theta$ or W scan technique were used to collect reflection intensities out to a Bragg angle θ, given below. The space group was, in each case determined unambiguously as a result of the structure analyses reported below but initially indicated by systematic absences of appropriate reflections. The cell parameters were determined, in each case, by least-squares refinement, the setting angles of 25 accurately centred reflections ($20^{o}<2\theta<30^{o}$) being used. Absorption corrections were neither warranted or applied.

Crystal data for 2,3,4,5,6-Pentamethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (23). - $C_{11}H_{15}N_3O_7$, M 301.25, monoclinic, space group $P2_1/n$ a 7.774(2), b 16.427(4), c 11.198 (2) Å, β 106.27(2)^{o}, U 1372.77 Å^3, D_m 1.46 g cm^{-3}, D_c 1.46 g cm^{-3}, Z 4, μ(Mo Kα) 1.15 cm^{-1}. The crystal was colourless and of approximate dimensions 0.3 by 0.5 by 0.6 mm Number of independent reflections measured 1631, number with $I > 3\sigma(I)$ 1343; maximum bragg angle θ 25^{o}; g 0.00044; R-factor 0.049 wR 0.057.

Crystal data for 2,3,4,5,6-Pentamethyl-r-2,t-5,c-6-trinitrocyclohex-3-enone (24). - $C_{11}H_{15}N_3O_7$, M 301.25, monoclinic, space group $P2_1/c$, a 9.045(2), b 10.920(3), c 14.429(7) Å,

β 103.26(3)°, U 1387.06 Å^3, D_m 1.43 g cm^{-3}, D_c 1.44 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.14 cm^{-1}. The crystal was colourless and of approximate dimensions 0.5 by 0.5 by 0.25 mm. Number of independent reflections measured 1402, number with $I > 3\sigma(I)$ 806; maximum Bragg angle θ 22.5°; g 0.00120; R-factor 0.057; wR 0.060.

Crystal data for 2,3,4,5,6-Pentamethyl-r-2,c-5,t-6-trinitrocyclohex-3-enone (25). - $C_{11}H_{15}N_3O_7$, M 301.25, triclinic, space group $P\bar{1}$, a 6.555(1), b 8.710(2), c 12.473(2) Å, α 87.71(1)°, β 81.31(1)°, γ 71.96(1)°, U 669.43 Å^3, D_m 1.48 g cm^{-3}, D_c 1.49 g cm^{-3}, Z 2, μ(Mo Kᾱ) 1.18 cm^{-1}. The crystal was colourless and of approximate dimensions 0.7 by 0.6 by 0.2 mm. Number of independent reflections measured 2358, number with $I > 3\sigma(I)$ 1965; maximum Bragg angle θ 25°; g 0.0005; R-factor 0.057; wR 0.072.

Crystal data for 2,3,4,5,6-Pentamethyl-r-4,t-5,t-6-trinitrocyclohex-2-enone (32). - $C_{11}H_{15}N_3O_7$, M 301.25, monoclinic, space group $P2_1/n$, a 9.374(1), b 11.248(2), c 13.040(2) Å, β 98.52(1)°, U 1359.77 Å^3, D_m 1.46 g cm^{-3}, D_c 1.47 g cm^{-3}, Z 4, μ(Mo Kᾱ), 1.16 cm^{-1}. The crystal was colourless and of approximate dimensions 0.3 by 0.3 by 0.5 mm. Number of independent reflections measured 2157, number with $I > 3\sigma(I)$ 1758; maximum Bragg angle θ 25°; g 0.00068; R-factor 0.052; wR 0.06.

Crystal data for 2,3,4,5,6-Pentamethyl-r-4,c-5,c-6-trinitrocyclohex-2-enone (33). - $C_{11}H_{15}N_3O_7$, M 301.25, monoclinic, space group $P2_1/c$, a 6.982(1), b 14.973(3), c 13.081(3), β 96.32(2), U 1357.35 Å^3, D_m 1.49 g cm^{-3}, D_c 1.49 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.16 cm^{-1}. The crystal was colourless and of approximate dimensions 0.2 by 0.2 by 0.4 mm. Number of

independent reflections measured 1765, number with $I > 3\sigma(I)$ 1320; maximum Bragg angle θ 22.5°; g 0.0002; R-factor 0.045; wR 0.049.

Crystal data for r-2-Hydroxy-2,3,4,5,6-pentamethyl-t-5,t-6-dinitrocyclohex-3-enone (36). - $C_{11}H_{16}N_2O_6$, M 272.25, monoclinic, space group $P2_1/c$ a 6.119(1), b 13.814(4), c 16.621(4) Å, β 100.82(2)°, U 1379.87 Å^3, D_m 1.39 g cm^{-3}, D_c 1.40 g cm^{-3}, Z 4, μ(Mo K$\bar{\alpha}$) 1.01 cm^{-1}. The crystal was colourless and of approximate dimensions 0.7 by 0.3 by 0.2 mm. Number of independent reflections measured 1500, number with $I > 2\sigma(I)$ 1239; maximum Bragg angle θ 22.5°; g 0.00037; R-factor 0.069; wR 0.071.

Crystal data for 2,3,5,6-Tetramethyl-r-2,4,t-5,c-6-tetranitrocyclohex-3-enone (67). - $C_{10}H_{12}N_4O_9$, M 332.23, orthohombic, space group P $ca2_1$, a 13.143(4), b 8.537(2), c 12.669(3) Å, U 1420 Å^3, D_m 1.54 g cm^{-3}, D_c 1.55 g cm^{-3}, Z 4, μ(Mo K$\bar{\alpha}$) 1.30 cm^{-1}. The crystal was colourless and of approximate dimensions 0.6 by 0.5 by 0.3 mm. Number of independent reflections measured 1820, number with $I > 3\sigma(I)$ 1333; maximum Bragg angle θ 29°; g 0.00054; R-factor 0.051; wR 0.057.

Crystal data for 2,3,5,6-Tetramethyl-r-2,4,c-5,t-6-tetranitrocyclohex-3-enone (68). - $C_{10}H_{12}N_4O_9$, M 332.23, monoclinic, space group P $2_1/c$, a 13.478(3), b 6.341(2), c 16295(5) Å, β 95.51(2)°, U 1387 Å^3, D_m 1.57 g cm^{-3}, D_c 1.59 g cm^{-3}, Z 4, μ(Mo K$\bar{\alpha}$) 1.33 cm^{-1}. The crystal was colourless and of approximate dimensions 1.2 by 0.3 by 0.15 mm. Number of independent reflections measured 1711, number with $I > 3\sigma(I)$ 1511; maximum Bragg angle θ, 22.5°; g 0.00074; R-factor 0.053; wR 0.061.

Crystal data for r-2-Hydroxy-2,3,5,6-tetramethyl-4,t-5,t-6-trinitrocyclohex-3-enone (71). - $C_{10}H_{13}N_3O_8$, M 303.23, monoclinic, space group $P2_1/c$, a 6.628(1), b 8.402(1), c 23.941(4) Å, β 96.23(1)°, U 1325 Å^3, D_m 1.52 g cm^{-3}, D_c 1.52 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.25 cm^{-1}. The crystal was colourless and of approximate dimensions 0.8 by 0.1 by 0.2 mm. Number of independent reflections measured 1557, number with $I > 3\sigma(I)$ 1341; maximum Bragg angle θ, 22.5°, g 0.00050; R-factor 0.040; wR 0.045.

Crystal data for c-6-Hydroxy-2,3,5,6-tetramethyl-r-2,4,c-5-trinitrocyclohex-3-enone (72). - $C_{10}H_{13}N_3O_8$, M 303.23, orthorhombic, space group P na2_1, a 15.635(5), b 6.132(2), c 13.981(4) Å, U 1342 Å^3, D_m 1.49 g cm^{-3} g cm^{-3}, Dc 1.50 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.23 cm^{-1}. The crystal was colourless and of approximate dimensions 0.5 by 0.5 by 0.08 mm. Number of independent reflections measured 1491, number with $I > 3\sigma(I)$ 984; maximum Bragg angle θ, 28°, g 0.00069; R-factor 0.046; wR 0.051.

Crystal data for t-6-Hydroxy-2,3,5,6-tetramethyl-r-2,4,t-5-trinitrocyclohex-3-enone (77). - $C_{10}H_{13}N_3O_8$, M 303.23, monoclinic, space group $P2_1/c$, a 10.648(2), b 15.206(3), c 8.363(3) Å, β 95.95(2)°, U 1347 Å^3, D_m 1.50 g cm^{-3}, Dc 1.49 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.23 cm^{-1}. The crystal was colourless and of approximate dimensions 0.12 by 0.12 by 0.65 mm. Number of independent reflections measured 1506, number with $I > 3\sigma(I)$ 1112; maximum Bragg angle θ, 22.5°; g 0.00037; R-factor 0.061; wR 0.065.

Crystal data for 1-Acetyl-2,3,5-trimethyl-4,c-5-dinitrocyclopent-3-ene-r-1,t-2-diol (74). - $C_{10}H_{14}N_2O_7$, M 274.23, triclinic, space group $P\bar{1}$, a 6.100(3), b 8.031(4), c 13.619(8) Å, α 74.06(3)°, β 83.52(2)°, γ 70.79(3)°, U 608.5 Å^3, D_m 1.49 g cm^{-3}, Dc 1.50 g cm^{-3}, Z 2, μ(Mo Kᾱ) 1.20 cm^{-1}. The crystal was colourless and of approximate dimensions 0.38 by 0.025 by 0.088 mm. Number of independent reflections measured 1165, number with $I > 3\sigma(I)$ 589; maximum Bragg angle θ, 24°; g 0.00000; R-factor 0.070; wR 0.053.

Crystal data for r-2,t-6-Dihydroxy-6-methyl-4,t-5-dinitro-2-phenylcyclohex-3-enone (114). - $C_{13}H_{12}N_2O_7$, M 303.25, monoclinic, space group $P2_1/c$, a 10.749(4), b 21.165(5), c 6.075(2) Å, β 105.05(3)°, U 1334.2 Å^3, D_m 1.52 g cm^{-3}, Dc 1.53 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.19 cm^{-1}. The crystal was colourless and of approximate dimensions 0.7 by 0.2 by 0.1 mm. Number of independent reflections measured 1323, number with $I > 3\sigma(I)$ 859; maximum Bragg angle θ, 22.5°; g 0.0008; R-factor 0.055; wR 0.056.

Crystal data for r-2-Hydroxy-6-methyl-4-c-5,t-6-trinitro-2-phenylcyclohex-3-enone (115). - $C_{13}H_{11}N_3O_8$, M 337.24, monoclinic, space group $P2_1/n$, a 9.184(3), b 6.917(4), c 22.984(7) Å, β 96.78(2)°, U 1449.4 Å^3, D_m 1.52 g cm^{-3}, Dc 1.54 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.23 cm^{-1}. The crystal was colourless and of approximate dimensions 0.9 by 0.8 by 0.6 mm. Number of independent reflections measured 1875, number with $I > 3\sigma(I)$ 1717; maximum Bragg angle θ, 23°; a 0.00066; R-factor 0.042; wR 0.049.

Crystal data for 4-4-Hydroxy-4-methyl-c-5,c-6-dinitro-2,6-diphenylcyclohex-2-enone (126) - $C_{19}H_{16}N_2O_6$, M 368.344, monoclinic, space group $P2_1/c$, a 7.354(2), b 13.823(4), c 17.779(6) Å, β 99.24(2)°, U 1783.9 Å^3, D_m 1.38 g cm^{-3}, Dc 1.37 g cm^{-3}, Z 4, μ(Mo Kᾱ) 0.97 cm^{-1}. The crystal was colourless and of approximate dimensions 0.7 by 0.1 by 0.05 mm. Number of independent reflections measured 1450, number with $I > 3\sigma(I)$ 1026; maximum Bragg angle θ, 22.5°; g 0.00045, R-factor 0.055; wR 0.058.

Crystal data for r-4-Hydroxy-4-methyl-c-5,c-6-dinitro-2-(2'-nitrophenyl)-6-phenylcyclohex-2-enone (127).- $C_{19}H_{15}N_3O_8$, M 413.342, orthorhombic, space group P bca, a 14.841(4), b 13.951(3), c 17.554(6) Å, U 3634.5 Å^3, D_m 1.50 g cm^{-3}, Dc 1.51 g cm^{-3}, Z 8, μ(Mo Kᾱ) 1.13 cm^{-1}. The crystal was colourless and of approximate dimensions 0.10 by 0.09 by 0.05 mm. Data were collected as above, but at -100°C. Number of independent reflections measured 1429, number with $I > 2\sigma(I)$ 1049; maximum Bragg angle θ, 22.5°; g 0.00087; R-factor 0.10; wR 0.099.

Crystal data for 4-Methyl-r-4,c-5,c-6-trinitro-2,6-diphenylcyclohex-2-enone (128).- $C_{19}H_{15}N_3O_7$, M 397.343, orthorhombic, space group $Pna2_1$, a 9.202(2), b 14.736(2), c 13.688(3) Å, U 1856.1 Å^3, D_m 1.42 g cm^{-3}, Dc 1.42 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.04 cm^{-1}. The crystal was colourless and of approximate dimensions 0.6 by 0.4 by 0.3 mm. Number of independent reflections measured 1670, number with $I > 3\sigma(I)$ 1330; maximum Bragg angle θ 24°; g 0.00028; R-factor 0.046; wR 0.051.

Crystal data for 4-Methyl-r-4,t-5,t-6-trinitro-2,6-diphenylcyclohex-2-enone (130). - $C_{19}H_{15}N_3O_7$, M 397.343, monoclinic, space group $P2_1/c$, a 13.621(1), b 13.498(5), c 10.885(3) Å, β 112.90(1)°, U 1843.5 Å^3, D_m 1.41 g cm^{-3}, Dc 1.43 g cm^{-3}, Z 4, μ(Mo Kᾱ) 1.04 cm^{-1}. The crystal was colourless and of approximate dimensions 0.6 by 0.7 by 0.05 mm. Number of independent reflections measured 1930, number with $I > 3\sigma(I)$ 1226; maximum Bragg angle θ 22.5°; g 0.0005; R-factor 0.039; wR 0.039.

Crystal data for t-6-Hydroxy-4-methyl-r,t-5-dinitro-2,6-diphenylcyclohex-2-enone (131). $C_{19}H_{15}N_2O_6$, M 368.344, monoclinic, space group $P2_1/c$, a 7.725(1), b 27.317(3), c 16.844(2) Å, β 97.77(1)°, U 3521.8 Å^3, D_m 1.38 g cm^{-3}, Dc 1.39 g cm^{-3}, Z 8, μ(Mo Kᾱ) 0.98 cm^{-1}. The crystal was colourless and of approximate dimensions 0.38 by 0.25 by 0.18 mm. Number of independent reflections measured 2965, number with $I > 3\sigma(I)$ 2594; maximum Bragg angle θ, 22.5°; g 0.00085; R-factor 0.055; wR 0.058.

The structure consists of two, well separated, crystallographically independent molecules.

Intensity data were processed and structure solution and refinement were carried out using a Data General Nova 4X computer and the SHELXTL^{64}(G. Sheldrick) system of programs (designed specifically for minicomputer use). Diagrams for structures (49) (23) and (32) were produced using ORTEP II (C.K. Johnson), all others were produced using the SHELXTL graphics program XP and a Tektronix 4113A colour graphics unit and Tektronix 4662 plotter.

All of the structures determined were solved by using direct-methods and difference Fourier syntheses. Blocked

cascade least-squares refinements were employed, reflection weights $1/[\sigma^2(F) + g(F^2)]$. being used. The function minimized was $\Sigma w(|Fo|-|Fc|)^2$. Anomalous dispersion corrections were from Cromer and Limerman.[73] Methyl and methylene hydrogens were included as rigid groups pivoting about their carbon atoms, phenyl hydrogen atoms were refined with idealised coordinates calculated geometrically from the phenyl carbon coordinates and a C-H bond length of 0.96 Å. For compounds (49),(23),(24),(25),(32),(33),(36),(67),(68),(71),(72),(77) and (115) all non-hydrogen atoms were assigned anisotropic thermal parameters. For compound (74) the alicyclic ring atoms were refined with isotropic temperature factors. For structures (126),(128),(130) and (131) the phenyl carbon atoms were refined with isotropic temperature factors, and for compound (114) the phenyl group was refined isotropically as a rigid regular hexagon (C-C 1.395 Å, C-H 0.96 Å), with fixed temperature factors for the hydrogen atoms. For compound (127), the only atoms refined anisotropically were the substituent nitro-and hydroxyl- groups. Final Fourier syntheses showed no significant residual electron density and there were no abnormal discrepancies between observed and calculated structure factors.

Further, more comprehensive material regarding the structural information for the above structures (temperature factors, structure factor amplitudes, interatomic distances, bond angles and torsional angles) is deposited with the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Victoria 3002, Australia.

TABLE 1. Fractional coordinates for non-hydrogen atoms in 2,3,4,5,6-pentamethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (23), $C_{11}H_{15}N_3O_7$

Atom	$10^4X/a$	$10^4X/b$	$10^4Z/c$	10^3U*
C(1)	7605(4)	6069(2)	3239(3)	39(1)
C(2)	6624(4)	5246(2)	3028(3)	44(1)
C(3)	4631(4)	5305(2)	2425(3)	39(1)
C(4)	3728(4)	6004(2)	2280(3)	36(1)
C(5)	4645(4)	6828(2)	2678(3)	37(1)
C(6)	6570(4)	6797(2)	2533(3)	38(1)
C(7)	7091(5)	4747(2)	4225(4)	65(1)
C(8)	3687(5)	4501(2)	2075(4)	58(1)
C(9)	1718(4)	6042(2)	1759(4)	60(1)
C(10)	3634(5)	7562(2)	2028(4)	54(1)
C(11)	6525(4)	6755(2)	1156(3)	49(1)
N(2)	7517(4)	4810(2)	2108(4)	61(1)
N(5)	4757(4)	6876(2)	4080(3)	53(1)
N(6)	7668(4)	7542(2)	3091(3)	54(1)
O(1)	9132(3)	6127(2)	3857(3)	62(1)
O(21)	8921(4)	4467(2)	2541(4)	97(2)
O(22)	6783(6)	4867(2)	1014(4)	94(2)
O(51)	5865(3)	6448(2)	4783(2)	59(1)
O(52)	3699(5)	7297(3)	4401(3)	100(2)
O(61)	7305(4)	7886(2)	3959(2)	71(1)
O(62)	8879(4)	7738(2)	2675(3)	89(1)

* For anisotropic atoms, the equivalent isotropic temperature factor (U) is defined as one-third of the trace of the orthogonalised U_{11} tensor.

TABLE 2. Fractional coordinates for non-hydrogen atoms in 2,3,4,5,6-pentamethyl-r-2,t-5,c-6-trinitrocyclohex-3-enone (24), $C_{11}H_{15}N_3O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	2641(7)	1165(5)	1059(4)	35(2)
C(2)	4267(7)	987(6)	1660(5)	38(3)
C(3)	4483(7)	1135(6)	2720(4)	37(3)
C(4)	3329(7)	1122(6)	3146(5)	40(3)
C(5)	1692(7)	918(6)	2581(5)	49(3)
C(6)	1397(7)	1511(6)	1592(5)	45(3)
C(7)	4954(8)	-182(7)	1382(5)	58(3)
C(8)	6145(8)	1254(7)	3264(5)	60(3)
C(9)	3540(9)	1155(8)	4220(5)	77(4)
C(10)	447(8)	1175(7)	3108(6)	67(3)
C(11)	-196(7)	1309(7)	958(6)	65(3)
N(2)	5113(6)	2088(6)	1302(4)	46(2)
N(5)	1637(6)	-512(5)	2375(4)	52(2)
N(6)	1575(6)	2941(5)	1734(4)	49(2)
O(1)	2388(5)	1099(4)	210(4)	56(2)
O(21)	4785(6)	3101(5)	1542(4)	64(2)
O(22)	6003(6)	1889(5)	812(4)	74(3)
O(51)	1512(6)	-1163(5)	3036(4)	81(2)
O(52)	1770(6)	-884(4)	1604(4)	77(2)
O(61)	1871(5)	3364(4)	2524(3)	58(2)
O(62)	1363(6)	3514(5)	998(4)	74(2)

TABLE 3. Fractional coordinates for no--hydrogen atoms in 2,3,4,5,6-pentamethyl-r-2,c-5,t-6-trinitrocyclohex-3-enone (25), $C_{11}H_{15}N_3O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	574(3)	3814(3)	6528(2)	35(1)
C(2)	1373(4)	4943(3)	7147(2)	37(1)
C(3)	2155(4)	4248(3)	8196(2)	37(1)
C(4)	2535(3)	2691(3)	8458(2)	37(1)
C(5)	2049(4)	1472(3)	7775(2)	41(1)
C(6)	1821(3)	2000(3)	6579(2)	36(1)
C(7)	3060(5)	5529(3)	6398(2)	52(1)
C(8)	2628(5)	5447(3)	8886(2)	56(1)
C(9)	3414(5)	2034(4)	9485(2)	56(1)
C(10)	3504(7)	360(3)	7858(3)	76(1)
C(11)	862(4)	987(3)	5955(2)	50(1)
N(2)	-677(4)	6404(3)	7429(2)	52(1)
N(5)	-313(4)	1516(3)	8281(2)	58(1)
N(6)	4080(3)	1856(2)	5944(2)	45(1)
O(1)	-885(3)	298(2)	6010(2)	53(1)
O(21)	-796(5)	7663(3)	6941(3)	90(1)
O(22)	-2085(4)	6214(3)	8108(2)	72(1)
O(51)	-1758(3)	2737(3)	8166(2)	78(1)
O(52)	-554(6)	335(5)	8740(4)	130(2)
O(61)	5613(3)	1613(3)	6427(2)	78(1)
O(62)	4177(4)	2026(3)	4975(2)	71(1)

TABLE 4. Fractional coordinates for non-hydrogen atoms in 2,3,4,5,6-pentamethyl-r-4,t-5,t-6-trinitrocyclohex-2-enone (32), $C_{11}H_{15}N_3O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	5643(3)	-2826(2)	3713(2)	42(1)
C(2)	4280(3)	-2501(2)	4073(2)	37(1)
C(3)	3441(3)	-1662(2)	3644(2)	34(1)
C(4)	3686(3)	-986(2)	2657(2)	35(1)
C(5)	5090(3)	-1382(2)	2196(2)	35(1)
C(6)	6261(3)	-1874(2)	3061(2)	35(1)
C(7)	3904(3)	-3234(3)	4972(2)	54(1)
C(8)	2078(3)	-1282(3)	4056(2)	52(1)
C(9)	2333(3)	-1059(3)	1834(2)	51(1)
C(10)	5705(3)	-445(3)	1543(2)	50(1)
C(11)	6958(3)	-934(2)	3819(2)	47(1)
N(4)	3865(2)	373(2)	2929(2)	42(1)
N(5)	4547(3)	-2439(2)	1469(2)	51(1)
N(6)	7471(3)	-2454(2)	2567(2)	52(1)
O(1)	6333(2)	-3714(2)	3981(2)	67(1)
O(41)	4261(2)	649(2)	3819(2)	58(1)
O(42)	3553(2)	1072(2)	2221(2)	63(1)
O(51)	4177(2)	-3337(2)	1881(2)	63(1)
O(52)	4477(3)	-2298(2)	544(2)	83(1)
O(61)	7161(3)	-3123(2)	1850(2)	74(1)
O(62)	8672(3)	-2255(3)	2913(3)	122(2)

TABLE 5. Fractional coordinates for non-hydrogen atoms in 2,3,4,5,6-pentamethyl-r-4,c-5,c-6-trinitrocyclohex-2-enone (33), $C_{11}H_{15}N_3O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	6790(4)	7646(2)	2158(2)	39(1)
C(2)	8007(4)	7475(2)	3143(2)	35(1)
C(3)	8073(4)	6671(2)	3591(2)	35(1)
C(4)	6935(4)	5865(2)	3134(2)	35(1)
C(5)	6032(4)	5972(2)	1974(2)	35(1)
C(6)	5231(4)	6931(2)	1811(2)	37(1)
C(7)	9164(5)	8270(2)	3588(3)	53(1)
C(8)	9250(5)	6522(2)	4625(2)	55(1)
C(9)	5446(5)	5547(2)	3836(3)	54(1)
C(10)	4544(5)	5252(2)	1624(3)	51(1)
C(11)	3462(4)	7152(2)	2375(3)	54(1)
N(4)	8492(4)	5090(2)	3143(2)	46(1)
N(5)	7781(4)	5871(2)	1322(2)	42(1)
N(6)	4608(4)	7089(2)	647(2)	55(1)
O(1)	6830(3)	8341(1)	1688(2)	60(1)
O(41)	10165(4)	5301(2)	3040(2)	60(1)
O(42)	7922(4)	4332(2)	3241(2)	77(1)
O(51)	8865(3)	6513(2)	1281(2)	50(1)
O(52)	8002(4)	5152(2)	0929(2)	64(1)
O(61)	5291(4)	6636(2)	0016(2)	73(1)
O(62)	3481(4)	7700(2)	0422(2)	101(1)

TABLE 6. Fractional coordinates for non-hydrogen atoms in r-2-hydroxy-2,3,4,5,6-pentamethyl-t-5,t-6-trinitrocyclohex-3-enone (36), $C_{11}H_{16}N_2O_6$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	711(7)	3413(3)	350(3)	45(2)
C(2)	1854(7)	3907(3)	1198(3)	49(2)
C(3)	3348(7)	3236(3)	1822(3)	43(2)
C(4)	3518(7)	2282(3)	1698(3)	40(2)
C(5)	2281(7)	1780(3)	879(3)	44(2)
C(6)	1849(7)	2496(3)	118(3)	42(2)
C(7)	97(9)	4377(4)	1627(4)	76(2)
C(8)	4624(9)	3750(3)	2609(3)	72(2)
C(9)	4803(8)	1615(3)	2380(3)	63(2)
C(10)	3376(8)	855(3)	643(3)	65(2)
C(11)	4043(8)	2792(4)	-172(3)	63(2)
N(5)	28(7)	1508(3)	1125(3)	59(2)
N(6)	313(8)	2067(4)	-682(3)	69(2)
O(1)	-826(5)	3768(2)	-143(2)	63(1)
O(2)	3302(6)	4615(2)	919(2)	68(1)
O(51)	-1255(5)	2182(3)	1178(2)	69(2)
O(52)	-363(6)	675(3)	1296(3)	93(2)
O(61)	-1136(7)	1512(3)	-550(3)	87(2)
O(62)	540(8)	2344(4)	-1394(3)	112(2)

TABLE 7. Fractional coordinates for non-hydrogen atoms in 2,3,5,6-tetramethyl-4-nitratomethyl-r-2,t-5,t-6-trinitrocyclohex-3-enone (49), $C_{11}H_{14}N_4O_{10}$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	5460(3)	3486(2)	1645(4)	37(1)
C(2)	5773(3)	4342(2)	2472(4)	36(1)
C(3)	5432(3)	5157(2)	1639(4)	37(1)
C(4)	4715(3)	5155(2)	413(4)	34(1)
C(5)	4179(3)	4338(2)	-255(4)	38(1)
C(6)	5056(3)	3573(2)	-26(4)	35(1)
C(7)	5303(3)	4315(2)	4110(4)	51(1)
C(8)	5899(4)	5972(2)	2353(5)	56(1)
C(9)	4374(3)	6007(2)	-313(4)	43(1)
C(10)	3781(4)	4417(3)	-1900(4)	60(1)
C(11)	6168(3)	3680(2)	-1024(4)	52(1)
N(2)	7195(3)	4315(2)	1540(4)	49(1)
N(5)	3029(3)	4158(2)	738(3)	46(1)
N(6)	4476(3)	2700(2)	-447(4)	51(1)
N(9)	2739(3)	7014(2)	-181(3)	47(1)
O(1)	5621(3)	2806(1)	2237(3)	58(1)
O(21)	7730(2)	4616(2)	1480(4)	74(1)
O(22)	7665(3)	4011(3)	3658(4)	83(1)
O(51)	2046(2)	4320(2)	217(3)	66(1)
O(52)	3213(2)	3906(2)	2031(3)	59(1)
O(61)	5129(3)	2136(2)	-874(4)	85(1)
O(62)	3402(3)	2626(2)	-303(5)	84(1)
O(91)	3196(2)	6211(1)	303(3)	45(1)
O(92)	1759(3)	7156(2)	295(4)	71(1)
O(93)	3375(3)	7443(2)	-991(3)	63(1)

TABLE 8. Selected torsion angles for substituted cyclohexenones from Chapters 2 and 3

	Atoms		
Angles	C(4)-C(3)-C(2)-C(1)	C(3)-C(4)-C(5)-C(6)	C(3)-C(4)-C(5)-N(5)
(23)	11.2(5)	-31.3(4)	-84.4(5)
(24)[A]	15.9(9)	-35.7(9)	-76.0(8)
(25)	12.9(3)	19.7(3)	-92.1(2)
(36)	-6.1(7)	26.6(6)	-90.3(5)
(49)[B]	-11.9(4)	32.5(4)	-82.9(4)
(67)	-8.4(4)	24.5(4)	-84.9(4)
(68)	-8.6(4)	20.3(4)	-91.6(4)
(71)	6.8(3)	-29.2(3)	85.1(3)
(72)	-3.1(6)	-22.3(6)	90.3(6)
(77)	8.5(6)	-25.6(7)	-86.5(6)[o]
	C(2)-C(3)-C(4)-C(5)	C(3)-C(2)-C(1)-C(6)	C(3)-C(4)-C(5)-N(5)
(32)	-3.9(3)	18.0(3)	88.9(2)
(33)	13.3(4)	14.6(4)	75.1(3)

A - For the enantiomer in Fig (2)

B - For the enantiomer in Fig (7)

TABLE 9. Fractional coordinates for non-hydrogen atoms in 2,3,5,6-tetramethyl-r-2,4,t-5,c-6-tetranitrocyclohex-3-enone (67), $C_{10}H_{12}N_4O_9$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	2227(3)	7185(4)	4178(4)	49(1)
C(2)	2039(3)	5905(4)	5013(3)	46(1)
C(3)	1254(3)	6292(4)	5823(3)	41(1)
C(4)	864(3)	7734(4)	5872	31(1)
C(5)	1085(3)	9119(4)	5177(3)	39(1)
C(6)	1479(3)	8568(4)	4077(3)	43(1)
C(7)	3051(4)	5386(7)	5501(6)	85(2)
C(8)	978(4)	5024(5)	6616(4)	67(2)
C(9)	248(3)	10361(5)	5125(4)	58(1)
C(10)	1917(3)	9869(4)	3403(3)	53(1)
N(2)	1605(3)	4539(4)	4324(3)	67(1)
N(4)	183(3)	8123(4)	6759(3)	52(1)
N(5)	2061(2)	9920(4)	5653(3)	51(1)
N(6)	559(3)	7831(4)	3464(3)	64(1)
O(1)	2921(3)	7084(4)	3582(4)	102(2)
O(21)	704(3)	4419(5)	4244(4)	98(2)
O(22)	2209(4)	3656(5)	3942(5)	142(3)
O(41)	498(3)	9102(5)	7378(3)	74(1)
O(42)	-650(3)	7504(5)	6808(4)	94(2)
O(51)	2815(2)	9103(4)	5700(3)	64(1)
O(52)	2021(3)	11271(4)	5938(4)	91(2)
O(61)	738(4)	7493(6)	2564(4)	122(2)
O(62)	-255(3)	7702(5)	3885(3)	81(1)

TABLE 10. Fractional coordinates for non-hydrogen atoms in 2,3,5,6-tetramethyl-r-2,4,c-5,t-6-tetranitrocyclohex-3-enone (68), $C_{10}H_{12}N_4O_9$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	1330(2)	1245(5)	2879(2)	34(1)
C(2)	2089(2)	879(4)	2245(2)	36(1)
C(3)	3085(2)	3(4)	2598(2)	35(1)
C(4)	3290(2)	-130(5)	3409(2)	32(1)
C(5)	2653(2)	378(4)	4093(2)	31(1)
C(6)	1530(2)	384(4)	3770(2)	33(1)
C(7)	1587(3)	-362(6)	1516(2)	49(1)
C(8)	3789(3)	-686(6)	1992(2)	51(1)
C(9)	2895(2)	-995(5)	4851(2)	41(1)
C(10)	865(2)	1492(6)	4334(2)	45(1)
N(2)	2305(2)	3120(4)	1909(2)	46(1)
N(4)	4302(2)	-753(5)	3725(2)	34(1)
N(5)	2862(2)	2716(4)	4335(2)	41(1)
N(6)	1221(2)	-1954(4)	3715(2)	39(1)
O(1)	568(2)	2158(4)	2689(1)	54(1)
O(21)	3115(2)	3877(4)	2083(2)	71(1)
O(22)	1626(2)	3966(4)	1476(2)	65(1)
O(41)	4826(2)	635(6)	4035(2)	81(1)
O(42)	4550(2)	-2566(6)	3672(2)	90(1)
O(51)	2714(2)	3987(4)	3783(2)	57(1)
O(52)	3111(2)	3153(4)	5048(2)	71(1)
O(61)	1411(2)	-2904(3)	3104(2)	50(1)
O(62)	821(2)	-2721(4)	4277(2)	65(1)

TABLE 11. Fractional coordinates for non-constrained atoms in r-2-hydroxy-2,3,5,6-tetramethyl-4,t-5-trinitrocyclohex-3-enone (71), $C_{10}H_{13}N_3O_8$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	3905(4)	3422(3)	634(1)	32(1)
C(2)	3917(4)	4879(3)	1024(1)	31(1)
C(3)	2861(4)	4569(3)	1549(1)	30(1)
C(4)	2229(4)	3122(3)	1665(1)	30(1)
C(5)	2345(4)	1619(3)	1322(1)	30(1)
C(6)	2256(4)	2172(3)	701(1)	32(1)
C(7)	6058(4)	5496(4)	1168(1)	45(1)
C(8)	2581(5)	5990(3)	1912(1)	50(1)
C(9)	785(4)	361(3)	1423(1)	42(1)
C(10)	171(4)	2856(4)	490(1)	42(1)
N(4)	1324(4)	2874(3)	2195(1)	42(1)
N(5)	4519(4)	939(3)	1505(1)	41(1)
N(6)	2666(4)	777(3)	313(1)	46(1)
O(1)	4989(3)	3341(2)	264(1)	47(1)
O(2)	2659(3)	6035(2)	708(1)	43(1)
O(41)	-343(4)	3444(3)	2235(1)	68(1)
O(42)	2295(4)	2097(3)	2554(1)	71(1)
O(51)	5926(3)	1755(3)	1386(1)	56(1)
O(52)	4689(3)	-293(3)	1764(1)	64(1)
O(61)	1989(4)	890(3)	-178(1)	70(1)
O(62)	3655(4)	-335(3)	513(1)	67(1)
H(2)	3364(57)	6503(46)	538(17)	

TABLE 12. Fractional coordinates for non-constrained atoms in c-6-hydroxy-2,3,5,6-tetramethyl-r-2,4,c-5-trinitrocyclohex-3-enone (72), $C_{10}H_{13}N_3O_8$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	6833(3)	7455(8)	-198(4)	38(1)
C(2)	5974(3)	6282(8)	62(4)	38(1)
C(3)	5932(3)	5576(7)	1099(3)	35(1)
C(4)	6603(3)	5891(7)	1665	31(1)
C(5)	7449(3)	6896(7)	1456(4)	35(1)
C(6)	7644(3)	6802(7)	354(4)	35(1)
C(7)	5802(4)	4420(11)	-630(4)	62(2)
C(8)	5121(4)	4519(10)	1406(4)	51(2)
C(9)	8188(3)	5956(9)	2025(4)	43(2)
C(10)	7909(4)	4543(8)	23(4)	52(2)
N(2)	5303(3)	8072(8)	-92(4)	57(2)
N(4)	6513(3)	5295(8)	2690(3)	46(2)
N(5)	7391(3)	9390(6)	1665(3)	45(1)
O(1)	6860(2)	8723(7)	-852(3)	62(1)
O(21)	5105(3)	9193(7)	590(4)	72(2)
O(22)	5013(3)	8274(10)	-886(4)	101(2)
O(41)	6440(3)	3434(7)	2925(3)	72(2)
O(42)	6523(4)	6795(8)	3253(3)	91(2)
O(51)	7918(3)	10204(6)	2202(4)	68(1)
O(52)	6833(3)	10351(5)	1231(3)	52(1)
O(6)	8284(2)	8345(7)	169(3)	47(1)
H(6)	8207(40)	8502(107)	-421(54)	

TABLE 13. Fractional coordinates for non-constrained atoms in t-6-hydroxy-2,3,5,6-tetramethyl-r-2,4,t-5-trinitrocyclohex-3-enone (77), $C_{10}H_{13}N_3O_8$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	2737(5)	9737(3)	1178(6)	39(1)
C(2)	2517(4)	9072(3)	2510(5)	38(1)
C(3)	2342(5)	9483(3)	4126(5)	36(1)
C(4)	2229(4)	10348(3)	4222(5)	33(1)
C(5)	2284(4)	11032(3)	2939(6)	37(1)
C(6)	3076(5)	10684(3)	1620(6)	39(1)
C(7)	1459(5)	8448(4)	1924(7)	55(2)
C(8)	2199(6)	8870(4)	5502(6)	57(2)
C(9)	2715(6)	11932(3)	3558(6)	56(2)
C(10)	4481(5)	10709(4)	2198(7)	61(2)
N(2)	3763(4)	8532(3)	2727(6)	57(2)
N(4)	1916(7)	10724(3)	5791(5)	82(2)
N(5)	927(5)	11112(4)	2078(5)	56(2)
O(1)	2692(4)	9500(2)	-202(4)	61(2)
O(21)	4557(4)	8743(3)	3780(6)	85(2)
O(22)	3900(5)	7952(4)	1792(7)	122(3)
O(41)	2766(5)	10738(3)	-3103(5)	77(2)
O(42)	852(5)	11001(4)	5823(6)	100(2)
O(51)	446(4)	10444(3)	1531(5)	76(2)
O(52)	425(5)	11826(3)	1994(6)	99(2)
O(6)	2844(4)	11233(2)	283(4)	73(2)
H(6)	2684(49)	11002(33)	-441(62)	

TABLE 14. Fractional coordinates of non-hydrogen atoms in 1-acetyl-2,3,5-trimethyl-4,c-5-dinitrocyclopent-3-ene-r-1,t-2-diol (74) $C_{10}H_{14}N_2O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	1708(17)	3026(13)	2094(8)	23(3)
C(2)	1682(18)	2201(13)	3262(8)	26(3)
C(3)	2197(17)	3619(13)	3672(8)	34(3)
C(4)	1713(16)	5205(13)	2987(7)	23(3)
C(5)	1068(16)	5121(12)	1981(7)	25(3)
C(6)	5363(18)	2329(14)	1719(7)	33(5)
C(7)	4972(18)	854(14)	1162(8)	47(7)
C(8)	1926(18)	6173(13)	979(7)	43(6)
C(9)	2968(19)	3156(15)	4735(7)	44(6)
C(10)	-663(18)	1949(13)	3683(8)	40(6)
N(4)	1719(15)	6914(11)	3131(6)	45(5)
N(5)	-1633(14)	5931(10)	1900(7)	45(5)
O(1)	399(12)	2487(8)	1517(5)	32(4)
O(2)	3495(13)	511(9)	3547(6)	40(4)
O(41)	844(18)	8293(11)	2492(7)	78(5)
O(42)	2581(14)	6913(10)	3901(6)	58(5)
O(51)	-2539(12)	6256(9)	1081(5)	58(4)
O(52)	-2803(12)	6218(10)	2689(6)	66(5)
O(6)	5733(12)	2907(9)	1959(5)	50(4)

TABLE 15. Fractional coordinates for non-constrained atoms in r-2,t-6-dihydroxy-6-methyl-4,t-5-dinitro-2-phenylcyclohex-3-enone (114) $C_{13}H_{12}N_2O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	6689(6)	4517(3)	-3565(12)	35(3)
C(2)	5820(5)	4059(3)	-2686(10)	29(2)
C(3)	6593(5)	3554(3)	-1198(10)	31(3)
C(4)	7872(6)	3541(3)	-631(10)	30(2)
C(5)	8740(6)	4018(3)	-1261(11)	32(3)
C(6)	8019(6)	4644(3)	-1912(11)	36(3)
C(71)	3533(4)	3707(2)	-4375(6)	40(2)
C(72)	2599(4)	3391(2)	-6037(6)	53(2)
C(73)	2936(4)	3099(2)	-7859(6)	49(2)
C(74)	4206(4)	3123(2)	-8019(6)	53(2)
C(75)	5140(4)	3438(2)	-6357(6)	47(2)
C(7)	4803(4)	3730(2)	-4535(6)	30(2)
C(8)	7895(6)	4991(3)	229(10)	45(3)
O(1)	6354(4)	4797(2)	-5338(8)	42(2)
O(2)	5260(4)	4428(2)	-1195(7)	39(2)
O(41)	7843(4)	2623(2)	1448(7)	53(2)
O(42)	9688(4)	2968(2)	1103(8)	59(2)
O(51)	8377(4)	3712(2)	-5080(7)	52(2)
O(52)	10361(5)	3742(3)	-3054(9)	73(2)
O(6)	8776(4)	5021(2)	-3004(8)	49(2)
N(4)	8520(5)	2996(2)	752(8)	41(2)
N(5)	9202(5)	3795(3)	-3307(9)	43(2)
H(2)	4791(47)	4746(24)	-1945(82)	
H(3)	6092(46)	3254(24)	-561(83)	
H(5)	9465(47)	4070(24)	-82(85)	
H(6)	8293(56)	5151(29)	-4374(104)	

TABLE 16. Fractional coordinates for non-constrained atoms in r-2-hydroxy-6-methyl-4,c-5,t-6-trinitro-2-phenylcyclohex-3-enone (115) $C_{13}H_{11}N_3O_8$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	2389(2)	2430(3)	8279(1)	35(1)
C(2)	829(2)	1648(3)	8296(1)	36(1)
C(3)	741(2)	368(3)	8825(1)	38(1)
C(4)	1829(2)	29(3)	9233(1)	34(1)
C(5)	3352(2)	776(3)	9236(1)	35(1)
C(6)	3398(2)	2626(3)	8867(1)	36(1)
C(7)	-206(2)	3382(3)	8310(1)	34(1)
C(71)	-807(2)	3923(3)	8808(1)	42(1)
C(72)	-1725(2)	5515(4)	8796(1)	48(1)
C(73)	-2057(2)	6538(4)	8293(1)	55(1)
C(74)	-1450(3)	6033(4)	7795(1)	58(1)
C(75)	-530(2)	4451(3)	7802(1)	47(1)
C(8)	4942(2)	3270(4)	8782(1)	52(1)
N(4)	1577(2)	-1213(2)	9736(1)	45(1)
N(5)	4255(2)	-746(3)	8964(1)	44(1)
N(6)	2765(2)	4239(3)	9214(1)	45(1)
O(1)	2830(2)	2851(3)	7827(1)	56(1)
O(2)	366(2)	596(2)	7780(1)	49(1)
O(41)	361(2)	-1883(2)	9755(1)	57(1)
O(42)	2623(2)	-1490(3)	10102(1)	72(1)
O(51)	3906(2)	-1093(2)	8448(1)	58(1)
O(52)	5239(2)	-1538(3)	9273(1)	78(1)
O(61)	2441(2)	5714(2)	8946(1)	60(1)
O(62)	2633(3)	3992(3)	9724(1)	85(1)
H(2)	934(24)	-128(40)	7729(9)	
H(3)	-226(19)	-243(30	8846(8)	
H(5)	3789(18)	915(26)	9623(8)	

TABLE 17. Fractional coordinates for non-constrained atoms in r-4-hydroxy-4-methyl-c-5,c-6-dinitro-2,6-diphenylcyclohex-2-enone (126) $C_{19}H_{16}N_2O_6$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	-602(8)	77(4)	7125(3)	42(2)
C(2)	-2333(8)	340(4)	6638(3)	39(2)
C(3)	-2937(8)	1251(4)	6622(3)	43(3)
C(4)	-2001(10)	2105(4)	7030(3)	39(3)
C(5)	29(10)	1861(4)	7368(3)	38(3)
C(6)	220(10)	840(4)	7730(3)	36(3)
C(7)	-3402(8)	-440(4)	6175(3)	40(2)
C(71)	-2566(10)	-1024(4)	5701(3)	58(2)
C(72)	-3600(9)	-1726(4)	5252(4)	62(2)
C(73)	-5400(9)	-1807(4)	5286(4)	63(2)
C(74)	-6302(12)	-1219(5)	5720(4)	79(2)
C(75)	-5242(9)	-522(4)	6178(4)	63(2)
C(8)	-3101(9)	2482(4)	7625(4)	52(3)
C(9)	-676(8)	776(4)	8449(3)	38(2)
C(91)	-28(9)	1405(4)	9045(3)	53(2)
C(92)	-790(10)	1368(5)	9704(4)	66(2)
C(93)	-2121(10)	723(5)	9778(4)	73(2)
C(94)	-2750(10)	90(5)	9196(4)	68(2)
C(95)	-1994(8)	109(4)	8523(3)	49(2)
O(1)	123(6)	-706(3)	7115(2)	62(2)
O(4)	-1965(6)	2827(3)	6454(2)	57(2)
O(51)	1187(7)	1271(3)	6299(3)	84(2)
O(52)	1984(6)	2723(3)	6690(3)	77(2)
O(61)	2658(6)	=138(3)	8329(3)	64(2)
O(62)	3419(8)	1173(4)	7827(4)	99(3)
N(5)	1164(8)	1949(3)	6738(3)	61(3)
N(6)	2280(7)	608(4)	7977(3)	51(2)
H(5)	438(48)	2314(23)	7727(18)	
H(3)	-4012(57)	1435(28)	6299(23)	
H(4)	-1778(76)	3351(37)	6722(31)	

TABLE 18. Fractional coordinates for non-constrained atoms in r-4-hydroxy-4-methyl-c-5,c-6-dinitro-2-(2'-nitrophenyl)-6-phenylcyclohex-2-enone (127) $C_{19}H_{15}N_3O_8$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	4220(9)	364(8)	12158(7)	24(3)
C(2)	5599(8)	98(7)	11532(8)	21(3)
C(3)	5946(8)	-770(8)	11503(8)	22(3)
C(4)	5741(8)	-1579(8)	12013(7)	23(3)
C(5)	4889(9)	-1384(8)	12541(9)	25(3)
C(6)	4856(8)	-356(7)	12815(7)	18(3)
C(71)	5374(9)	1464(8)	10565(8)	27(4)
C(72)	5727(9)	2192(8)	10133(8)	30(4)
C(73)	6649(9)	2449(9)	10211(8)	35(4)
C(74)	7138(9)	1917(8)	10714(8)	34(4)
C(75)	6805(8)	1188(8)	11119(7)	24(3)
C(7)	5920(8)	906(8)	11058(7)	25(3)
C(8)	6550(7)	-1859(8)	12515(7)	26(4)
C(91)	6297(6)	465(5)	13283(4)	32(4)
C(92)	6983(6)	553(5)	13821(4)	32(4)
C(93)	6964(6)	-4(5)	14481(4)	34(4)
C(94)	6260(6)	-648(5)	14602(4)	41(4)
C(95)	5574(6)	-736(5)	14063(4)	33(4)
C(9)	5592(6)	-179(5)	13404(4)	24(3)
N(5)	4054(7)	-1621(8)	12060(6)	36(4)
N(6)	3957(7)	-162(9)	13252(6)	30(4)
N(71)	4428(7)	1208(7)	10452(5)	33(4)
O(1)	4522(5)	1125(6)	12130(4)	27(3)
O(4)	5526(5)	-2375(6)	11529(5)	28(3)
O(51)	3709(6)	-2392(7)	12131(5)	46(4)
O(52)	3777(5)	-977(6)	11634(5)	39(3)
O(61)	3418(6)	-814(7)	13293(6)	46(4)
O(62)	3887(6)	625(7)	13517(5)	36(4)
O(71)	4203(6)	378(6)	10496(5)	37(3)
O(72)	3918(6)	1872(7)	10301(6)	56(4)
H(5)	4789(70)	-1913(45)	12880(43)	
H(4)	5597(76)	-2930(39)	11783(57)	

TABLE 19. Fractional coordinates for non-constrained atoms in 4-methyl-r-4,c-5,c-6-trinitro-2,6-diphenylcyclohex-2-enone (128) $C_{19}H_{15}N_3O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(5)	1341(4)	6499(3)	2535(3)	32(1)
C(4)	1339(4)	5853(3)	1641(3)	36(1)
O(1)	-1136(3)	5288(2)	4121(3)	53(1)
N(4)	1219(4)	6475(2)	741(3)	44(1)
C(9)	2354(4)	5395(3)	3782(3)	35(1)
C(2)	-712(4)	5006(3)	2442(3)	34(1)
C(91)	2175(5)	4493(3)	4047(4)	43(1)
C(71)	-2979(5)	4480(3)	1646(4)	50(1)
C(6)	1051(4)	5974(3)	3485(3)	32(1)
C(8)	2733(5)	5319(3)	1504(4)	43(1)
C(3)	55(5)	5234(3)	1653(4)	38(1)
O(51)	503(4)	7909(2)	1979(3)	58(1)
C(75)	-2018(5)	3590(3)	2952(4)	51(1)
C(7)	-1941(4)	4352(3)	2363(3)	35(1)
O(61)	644(4)	6405(2)	5132(3)	60(1)
C(95)	3739(5)	5782(3)	3806(4)	43(1)
N(6)	903(4)	6678(2)	4323(3)	40(1)
N(5)	162(4)	7209(2)	2395(3)	41(1)
C(94)	4928(5)	5265(3)	4060(4)	53(1)
C(1)	-376(4)	5414(3)	3420(4)	36(1)
C(93)	4753(5)	4380(3)	4325(4)	56(1)
O(62)	1133(4)	7474(2)	4126(3)	62(1)
C(92)	3403(5)	3992(3)	4318(4)	53(1)
C(72)	-4064(5)	3835(4)	1502(4)	59(1)
C(73)	-4093(6)	3066(4)	2058(5)	65(1)
O(41)	2338(4)	6846(2)	460(3)	65(1)
C(74)	-3094(6)	2943(4)	2798(4)	63(1)
O(52)	-1062(3)	7037(2)	2689(3)	54(1)
O(42)	42(4)	6585(2)	370(3)	62(1)
H(5)	2222(37)	6834(21)	2529(26)	
H(3)	-149(50)	4929(29)	1070(38)	

TABLE 20. Fractional coordinates for non-constrained atoms in 4-methyl-r-4,t-5,t-6-trinitro-2,6-diphenylcyclohex-2-enone (130) $C_{19}H_{15}N_3O_7$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(6)	2199(3)	171(3)	2834(4)	42(2)
O(1)	2794(2)	1451(2)	4494(2)	58(1)
C(4)	889(3)	-1030(3)	3165(4)	46(2)
C(7)	2626(3)	181(3)	6557(4)	41(2)
O(41)	1070(2)	-2287(2)	1736(3)	66(1)
O(51)	-564(2)	498(2)	971(3)	87(2)
C(91)	3023(3)	-1102(3)	1829(4)	47(2)
O(61)	1536(3)	1335(2)	1067(3)	90(2)
C(71)	2741(3)	1125(3)	7113(4)	54(2)
O(62)	3233(2)	1281(2)	2166(3)	69(1)
N(6)	2333(3)	1001(2)	1937(3)	56(2)
C(5)	1068(3)	-259(3)	2235(5)	47(2)
O(52)	387(2)	1167(2)	2871(3)	84(2)
N(4)	1356(2)	-2027(2)	2896(3)	51(1)
C(3)	1449(3)	-772(3)	4600(4)	47(2)
C(2)	2103(3)	5007(3)	105(4)	40(2)
C(9)	3041(3)	-604(3)	2954(4)	41(2)
N(5)	230(3)	548(3)	1999(4)	66(2)
O942)	1931(2)	-2494(2)	3862(3)	73(1)
C(95)	3873(3)	-807(3)	4177(4)	47(2)
C(92)	3800(3)	-1789(3)	1920(4)	57(2)
C(75)	3009(3)	-616(3)	7417(4)	63(2)
C(1)	2388(3)	652(3)	4191(4)	43(2)
C(93)	4610(3)	-1989(3)	3132(4)	60(2)
C(72)	3230(3)	1254(3)	8479(4)	61(2)
C(8)	-287(3)	-1271(3)	2832(4)	74(2)
C(94)	4641(3)	-1499(3)	4252(4)	56(2)
C(74)	3496(4)	-482(3)	8781(4)	84(3)
C(73)	3596(4)	456(3)	9307(4)	75(2)
H(3)	1295(22)	-1204(20)	5213(28)	
H(5)	937(21)	-514(21)	1386(28)	

TABLE 21. Fractional coordinates for non-constrained atoms in C-6-hydroxy-4-methyl-r-4,t-5-dinitro-2,6-diphenylcyclohex-2-enone (131) $C_{19}H_{16}N_2O_6$

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
C(1)	-411(5)	812(2)	697(3)	34(2)
C(2)	-2316(5)	855(2)	721(2)	30(2)
C(3)	-2867(5)	1047(2)	1373(3)	36(2)
C(4)	-1740(6)	1276(2)	2063(2)	36(2)
C(5)	207(6)	1309(2)	1959(3)	36(2)
C(6)	844(5)	885(2)	1481(3)	35(2)
C(7)	-3541(5)	714(2)	4(2)	32(1)
C(71)	-4972(6)	1013(2)	-241(3)	40(1)
C(72)	-6133(7)	893(2)	-910(3)	53(1)
C(73)	-5879(7)	475(2)	-1342(3)	53(1)
C(74)	-4482(6)	177(2)	-1109(3)	46(1)
C(75)	-3299(6)	294(2)	-439(3)	40(1)
C(8)	-2499(6)	1764(2)	2293(3)	49(2)
C(9)	1055(6)	421(2)	1991(3)	36(1)
C(91)	2183(7)	440(2)	2711(3)	55(1)
C(92)	3452(8)	18(2)	3180(4)	70(2)
C(93)	1634(7)	-408(2)	2929(3)	73(2)
C(94)	577(7)	-436(2)	2208(3)	64(2)
C(95)	269(6)	-15(2)	1745(3)	45(1)
C(10)	4954(6)	1978(2)	6552(3)	36(2)
C(11)	6800(6)	1814(2)	6602(3)	35(2)
C(12)	7418(6)	1687(2)	5928(3)	39(2)
C(13)	6497(6)	1747(2)	5093(3)	38(2)
C(14)	4673(6)	1973(2)	5057(3)	38(2)
C(15)	3735(6)	1857(2)	5784(3)	38(2)
C(16)	7925(6)	1816(2)	7391(3)	36(1)
C(161)	3680(6)	1939(2)	7429(3)	47(1)
C(162)	10753(7)	1955(2)	8151(3)	62(2)
C(163)	10089(7)	1850(2)	8860(3)	53(1)
C(164)	8365(6)	1723(2)	8823(3)	50(1)
C(165)	7274(6)	1709(2)	8104(3)	43(1)
C(17)	7666(6)	2017(2)	4577(3)	55(2)
C(18)	3190(6)	1316(2)	5773(3)	39(1)
C(181)	2083(6)	1148(2)	5117(3)	53(1)
C(182)	1551(7)	655(2)	5081(3)	67(2)

TABLE 21 (Cont.)

Atom	10^4X/a	10^4Y/b	10^4Z/c	10^3U
C(183)	2139(7)	341(2)	5689(3)	67(2)
C(184)	3214(7)	518(2)	6341(3)	65(2)
C(185)	3733(6)	995(2)	6387(3)	52(1)
N(4)	-1803(6)	948(2)	2811(2)	45(2)
N(5)	510(5)	1780(1)	1529(3)	46(2)
N(4')	6217(6)	1230(2)	4705(3)	54(2)
N(5')	4811(5)	2523(1)	4988(2)	50(2)
O(1)	221(4)	717(1)	92(2)	47(1)
O(41)	-2792(5)	591(1)	2738(2)	67(2)
O(42)	-906(5)	1060(1)	3436(2)	61(1)
O(51)	-219(5)	1843(1)	850(2)	64(2)
O(52)	1515(5)	1071(1)	1893(2)	72(2)
O(6)	2506(4)	1030(1)	1273(2)	48(1)
O(1')	4395(4)	2201(1)	7086(2)	53(1)
O(41')	5380(5)	1212(1)	4040(2)	73(2)
O(42')	6911(6)	886(1)	5067(2)	77(2)
O(51')	4268(5)	2709(1)	4350(2)	74(2)
O(52')	5473(5)	2753(1)	5576(2)	70(2)
O(6')	2211(4)	2148(1)	5721(2)	53(1)
H(3)	-4105(43)	1074(12)	1374(19)	
H(3')	8665(50)	1594(14)	5922(22)	
H(5')	4051(42)	1875(11)	4585(19)	
H(5)	919(46)	1359(12)	2475(20)	
H(6')	2381(61)	2330(17)	6156(27)	
H(6)	2479(71)	939(20)	829(33)	

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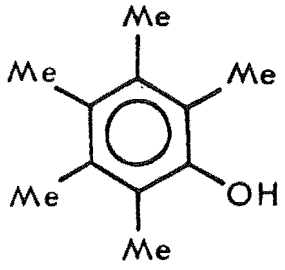

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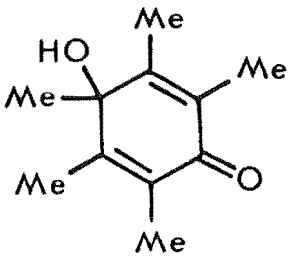

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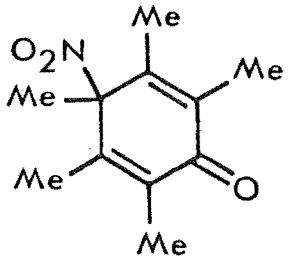

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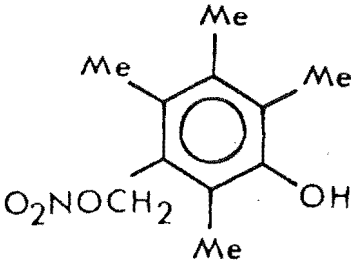

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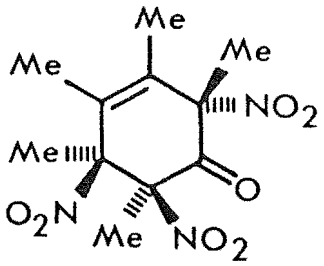

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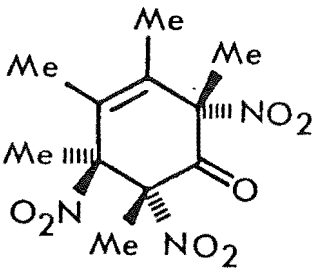

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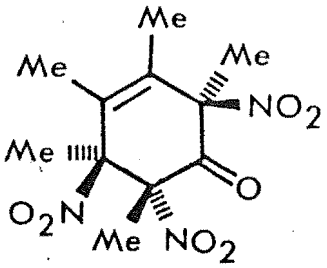

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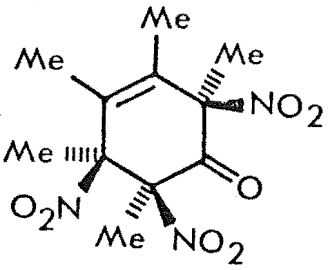

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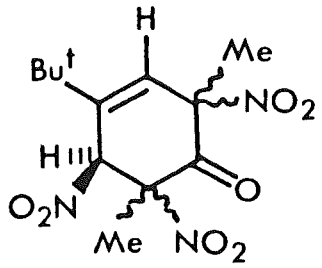

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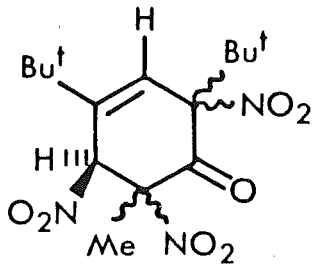

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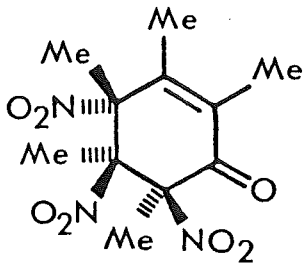

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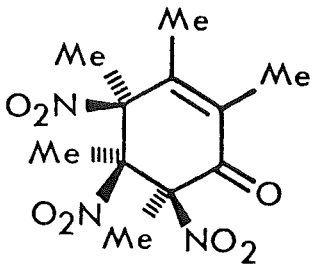

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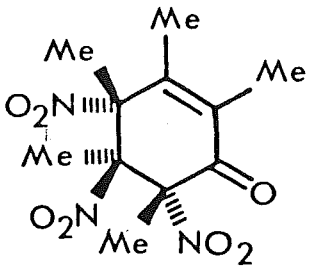

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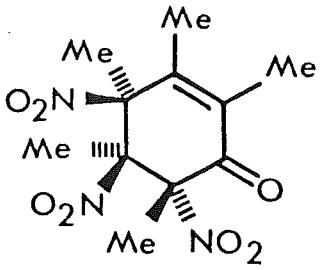

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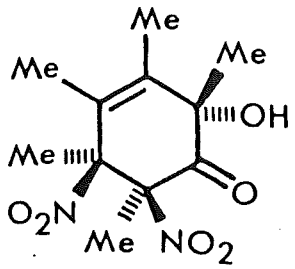

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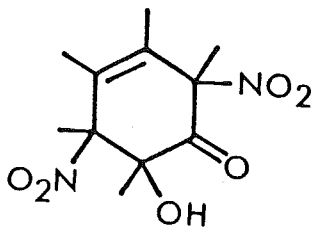

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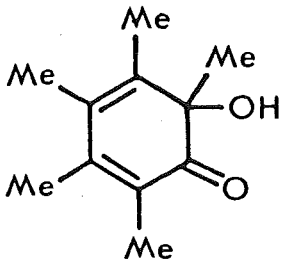

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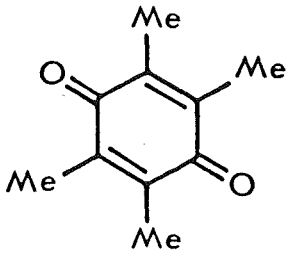

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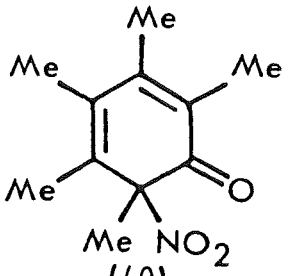

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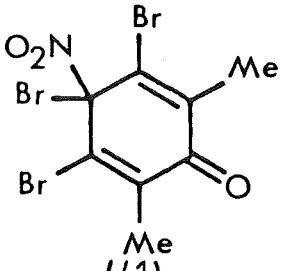

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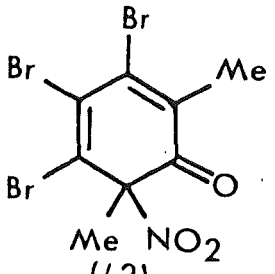

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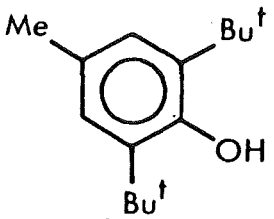

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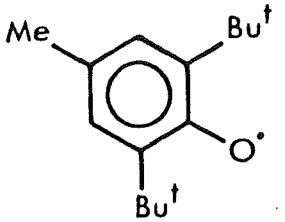

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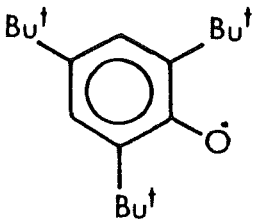

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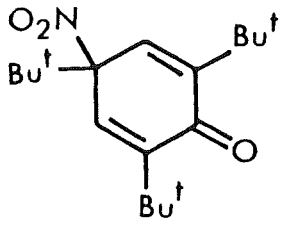

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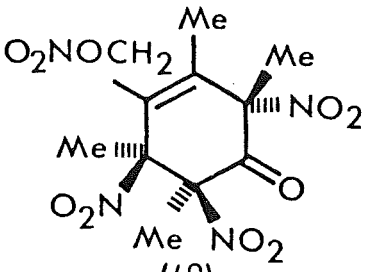

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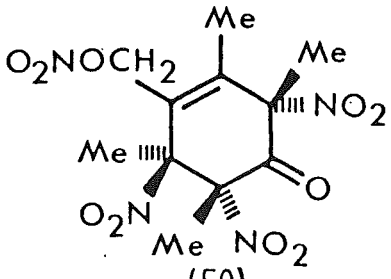

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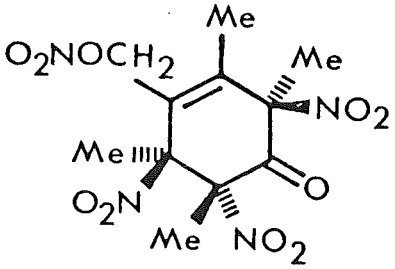

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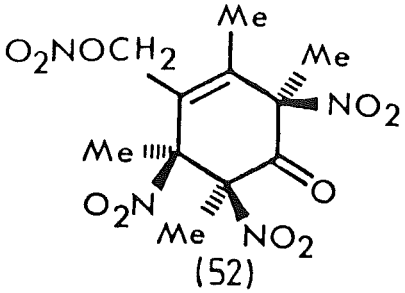

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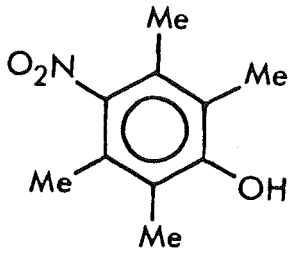
BLOCK B.



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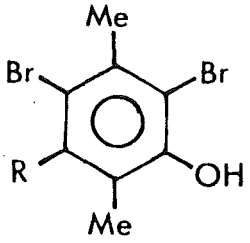
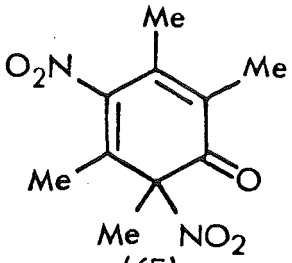


(59)

(a) R = Br

(b) R = Me



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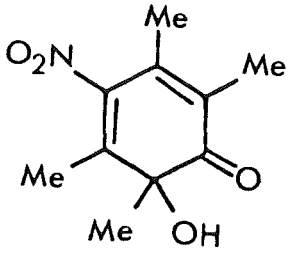

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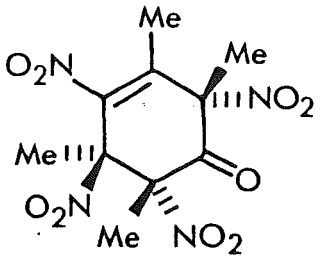

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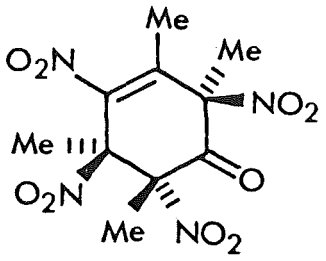

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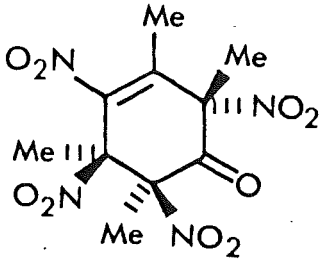

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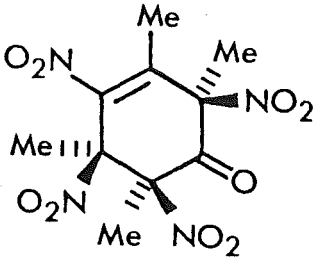

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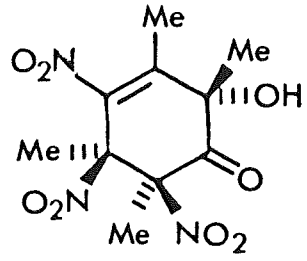

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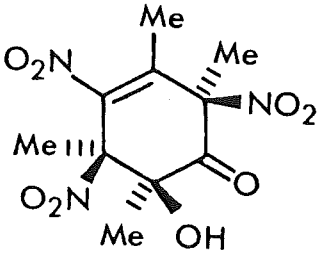

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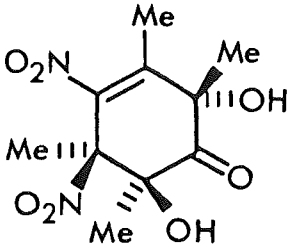

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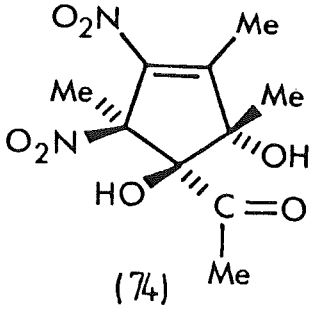

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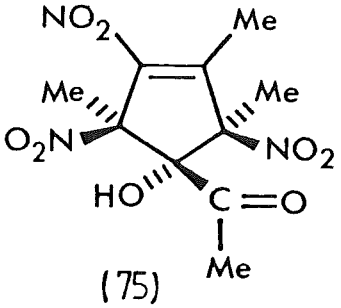

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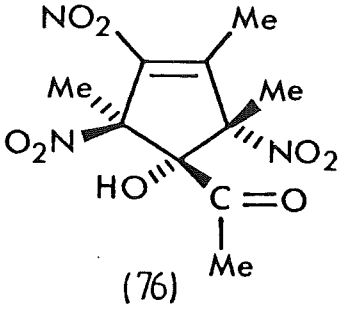

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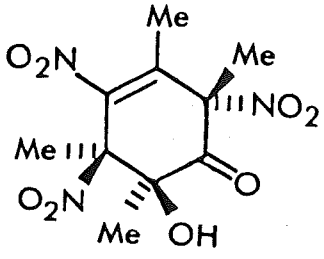

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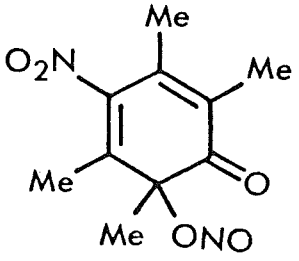

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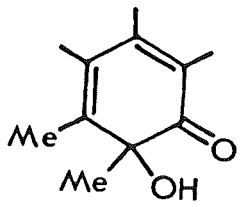

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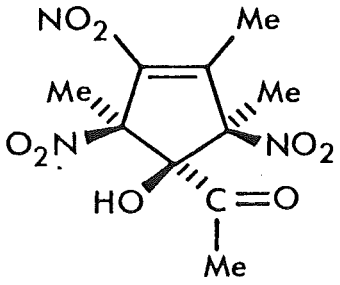

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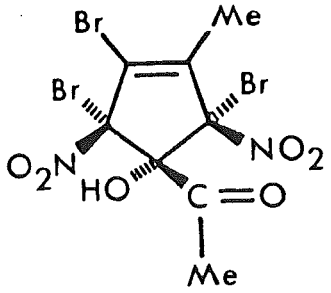

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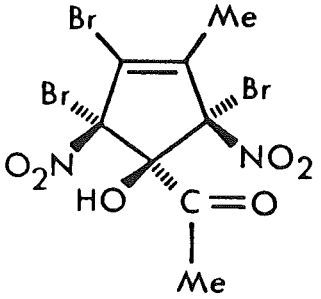

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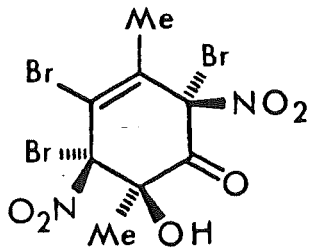

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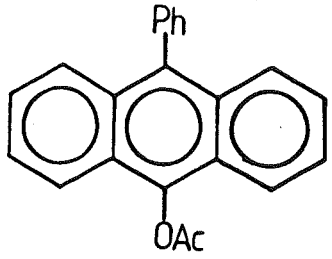
BLOCK C.



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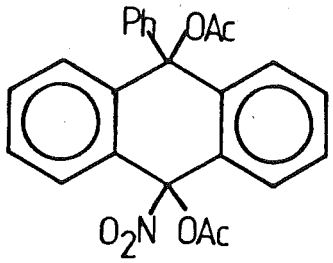

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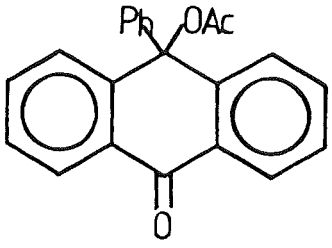

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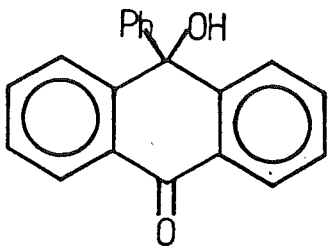

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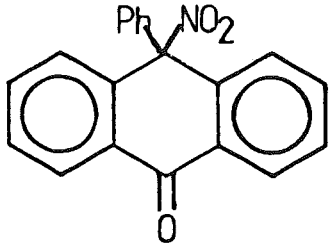

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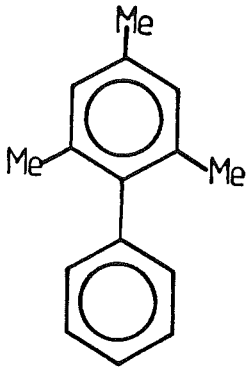

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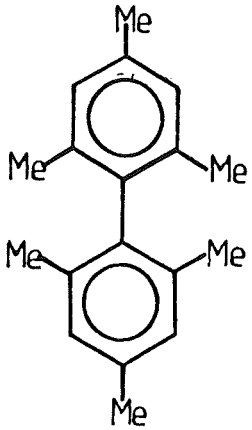
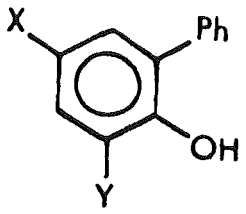


(102)

(103)

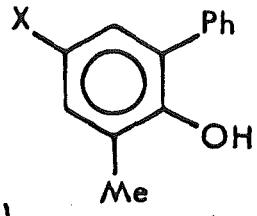
BLOCK C cont.

(104)



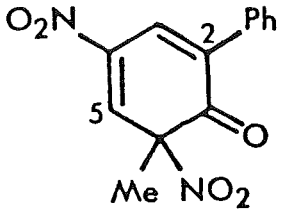
(105)

(a) X = Y = Br
(b) X = NO_2 , Y = Br
(c) X = Y = NO_2



(106)

(a) X = Br
(b) X = H
(c) X = NO_2



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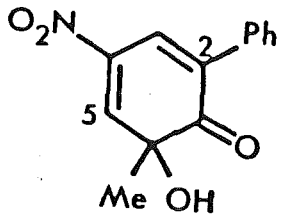

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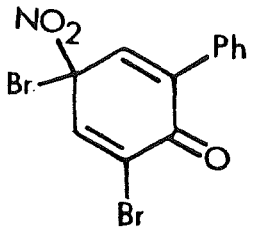

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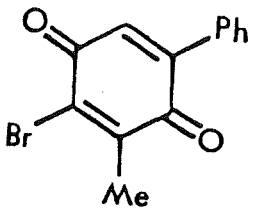

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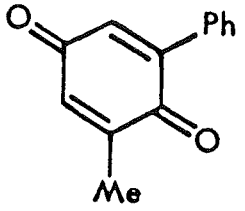

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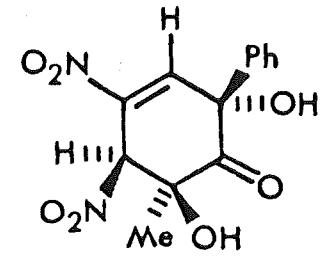

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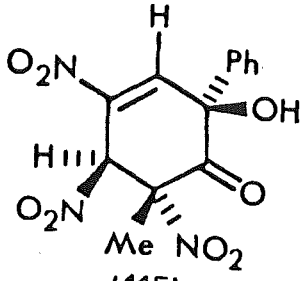

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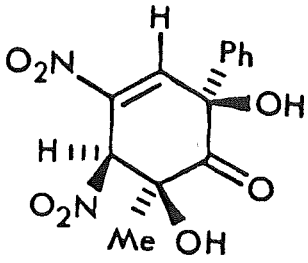

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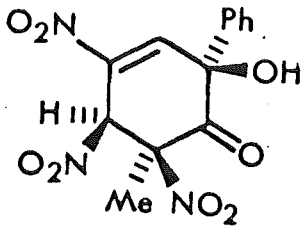

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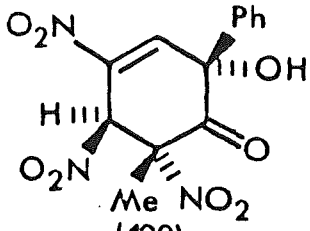

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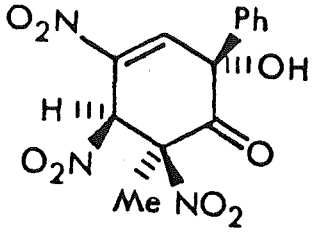

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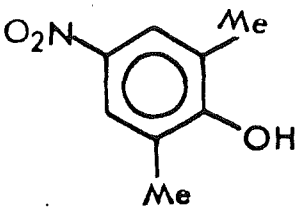

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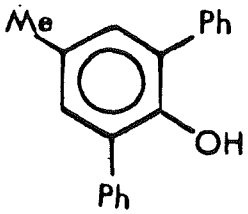

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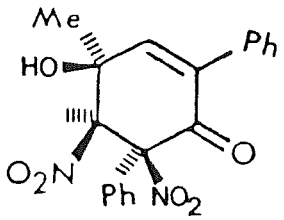

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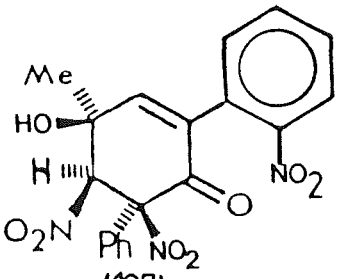

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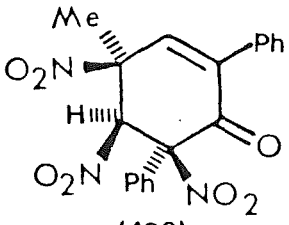

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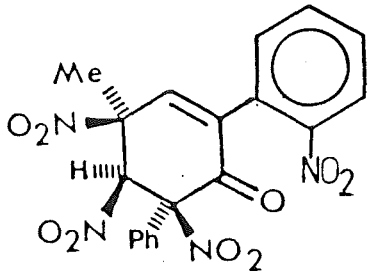

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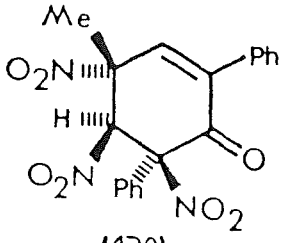

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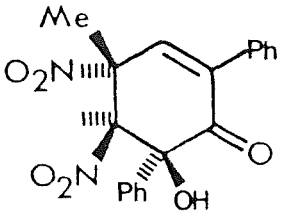

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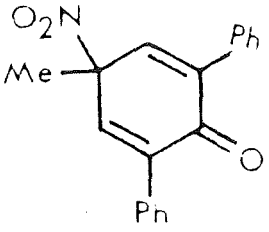

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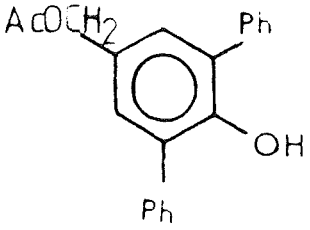

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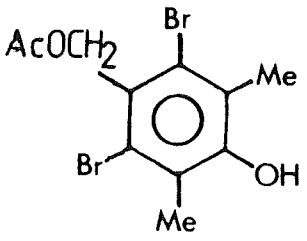

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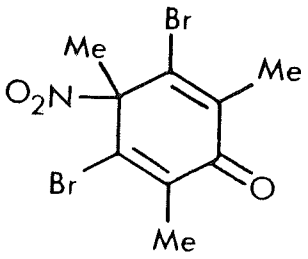

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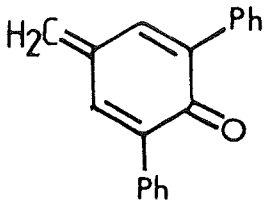

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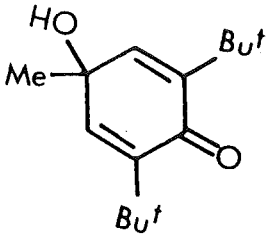

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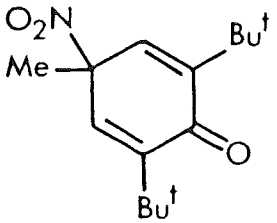

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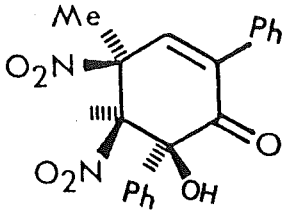

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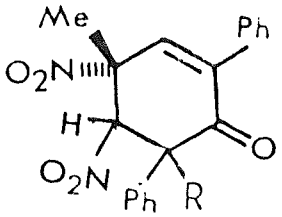

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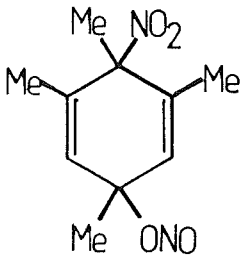

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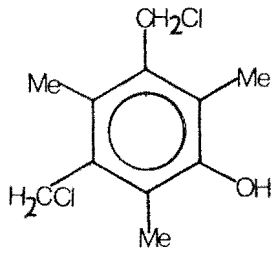

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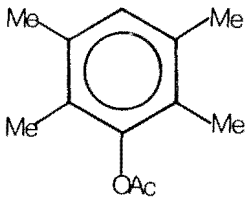

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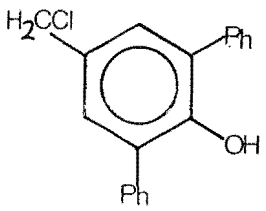

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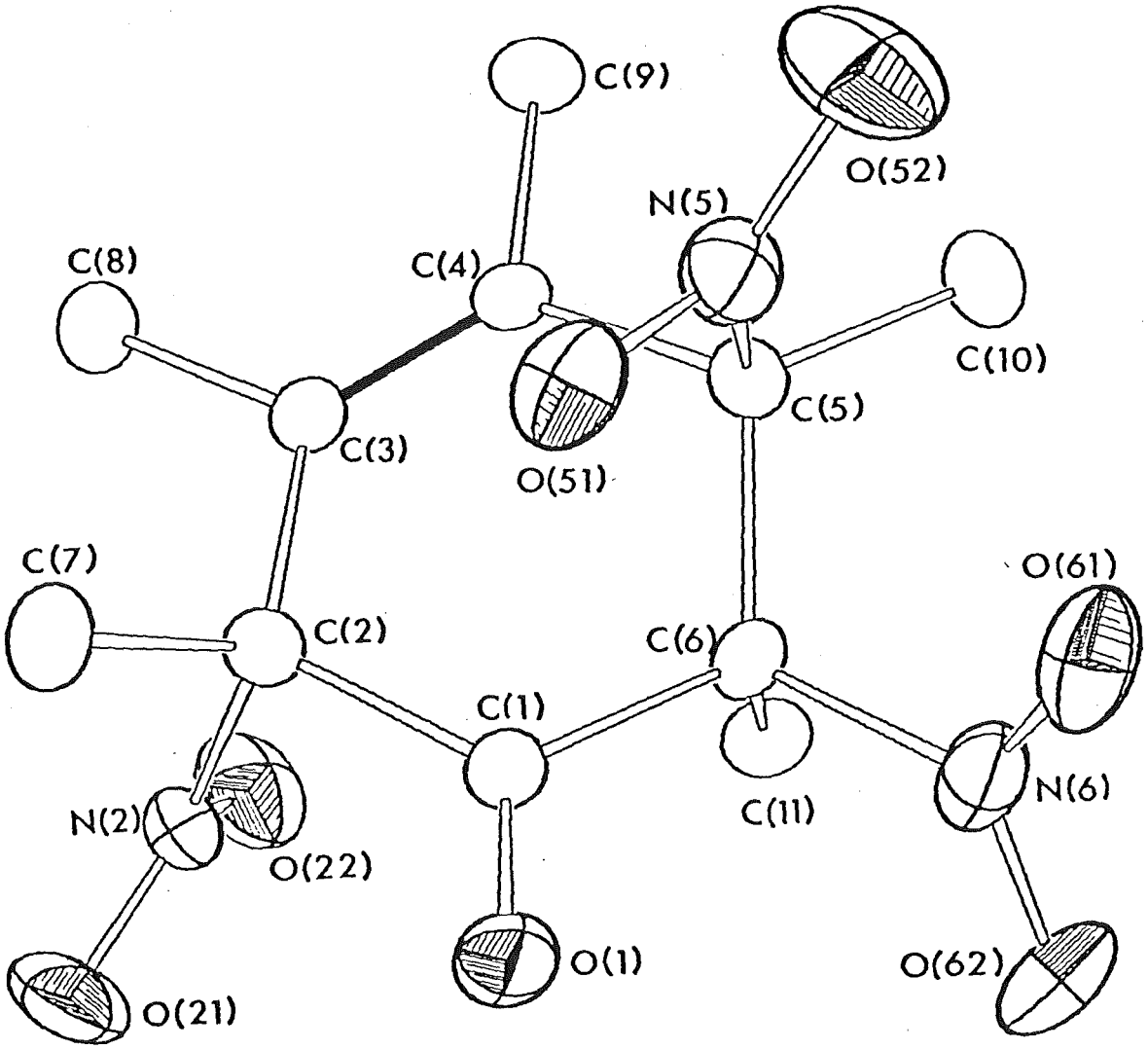


FIGURE 1.

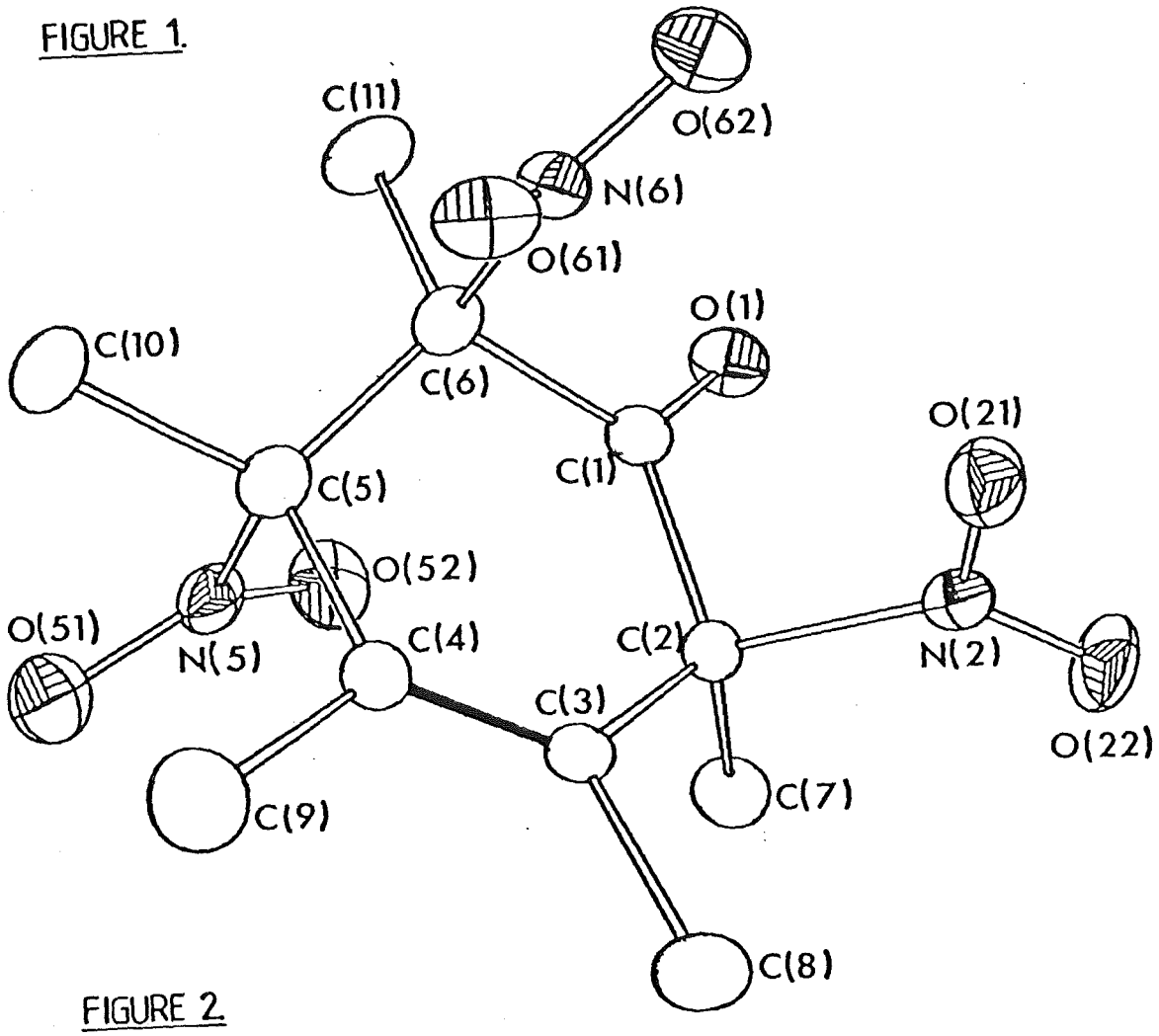


FIGURE 2.

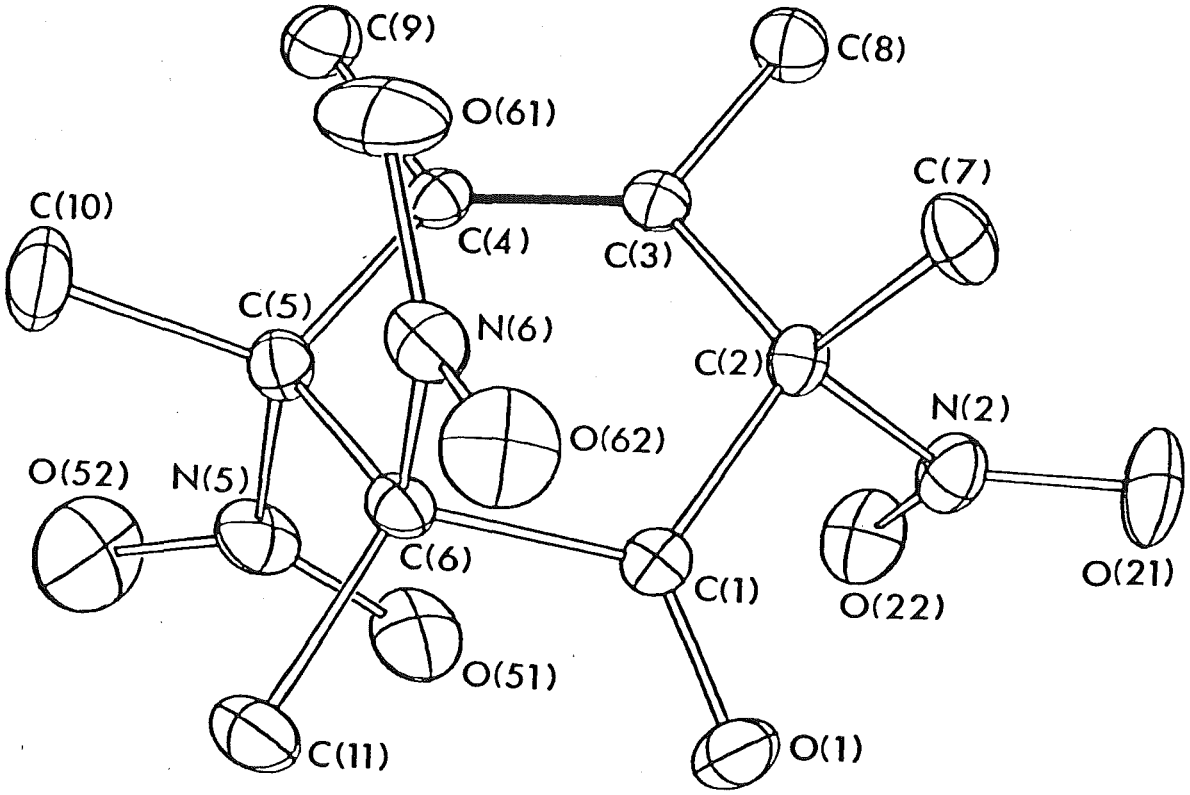


FIGURE 3.

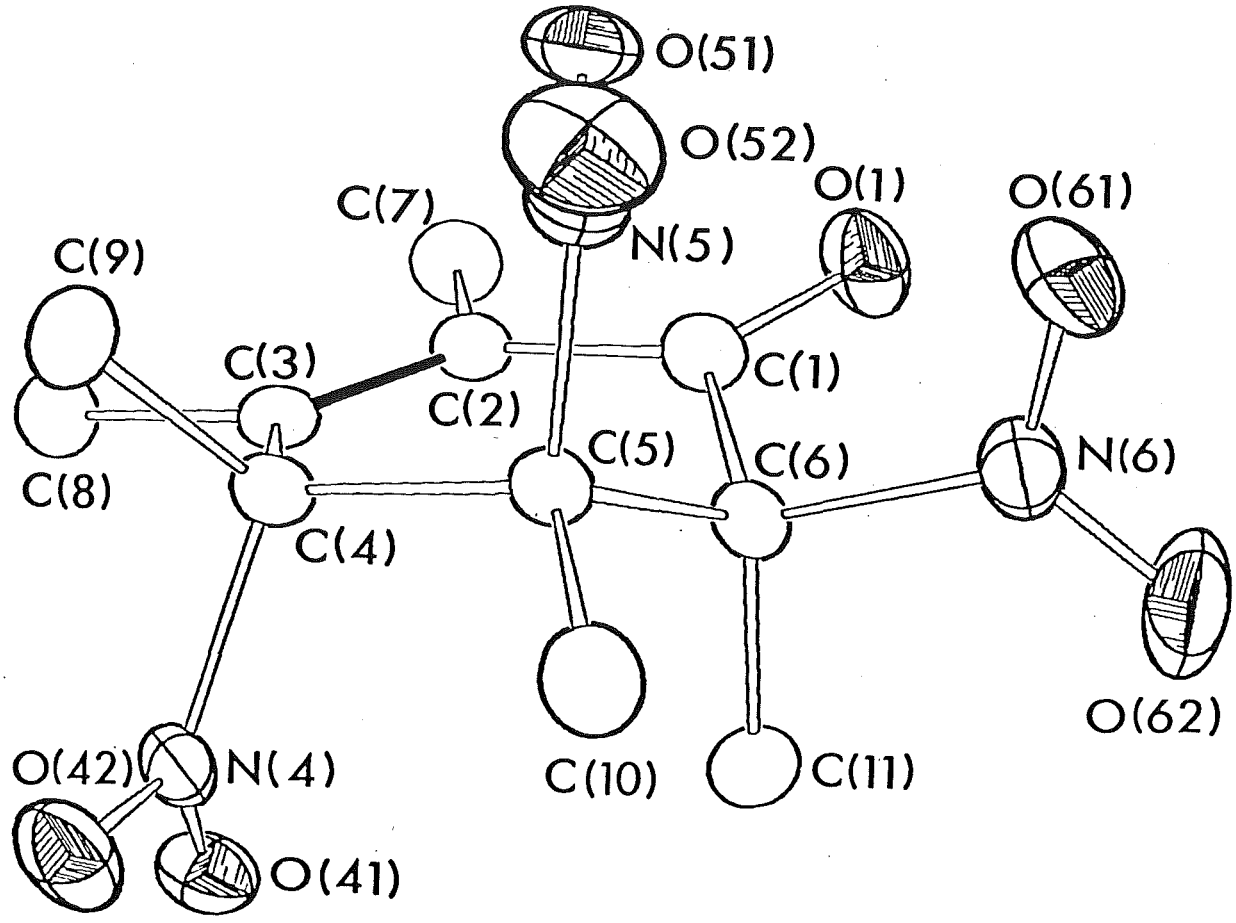


FIGURE 4.

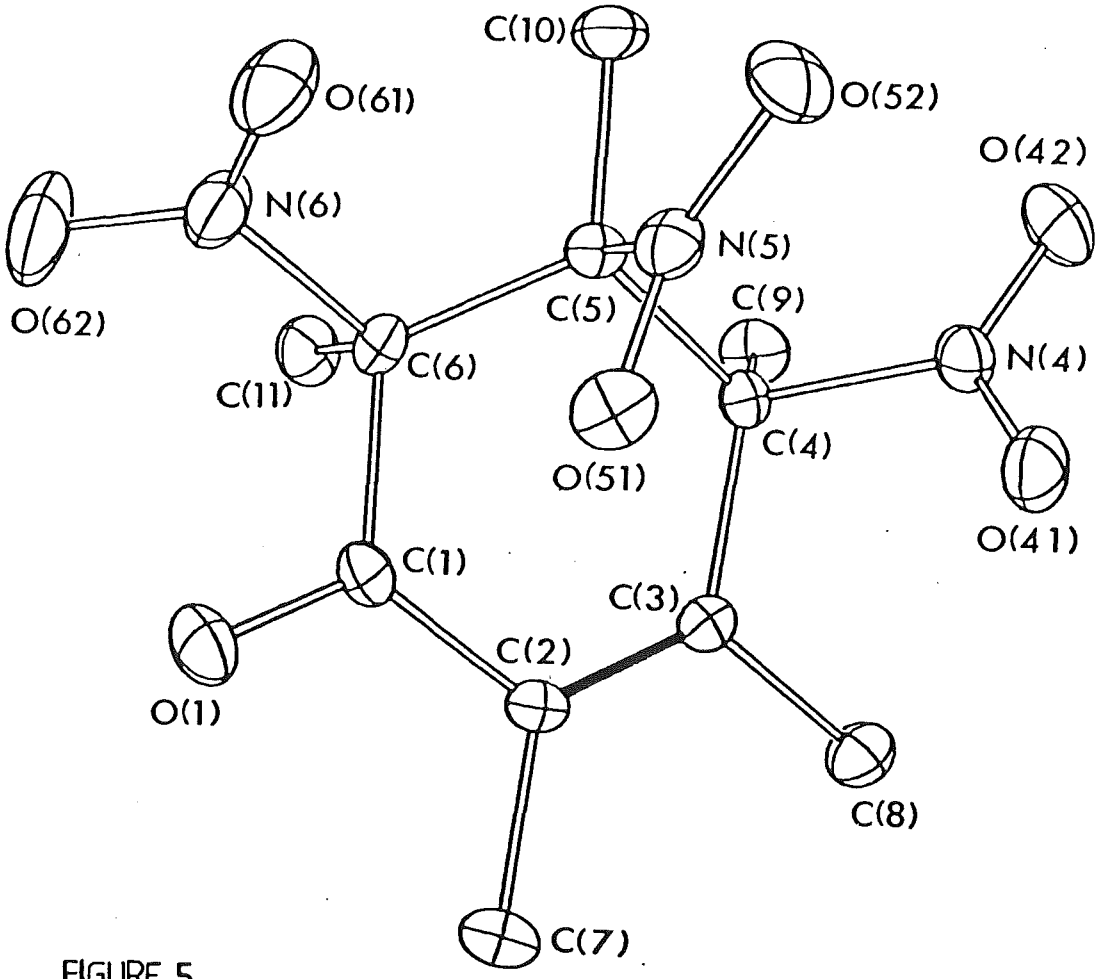


FIGURE 5.

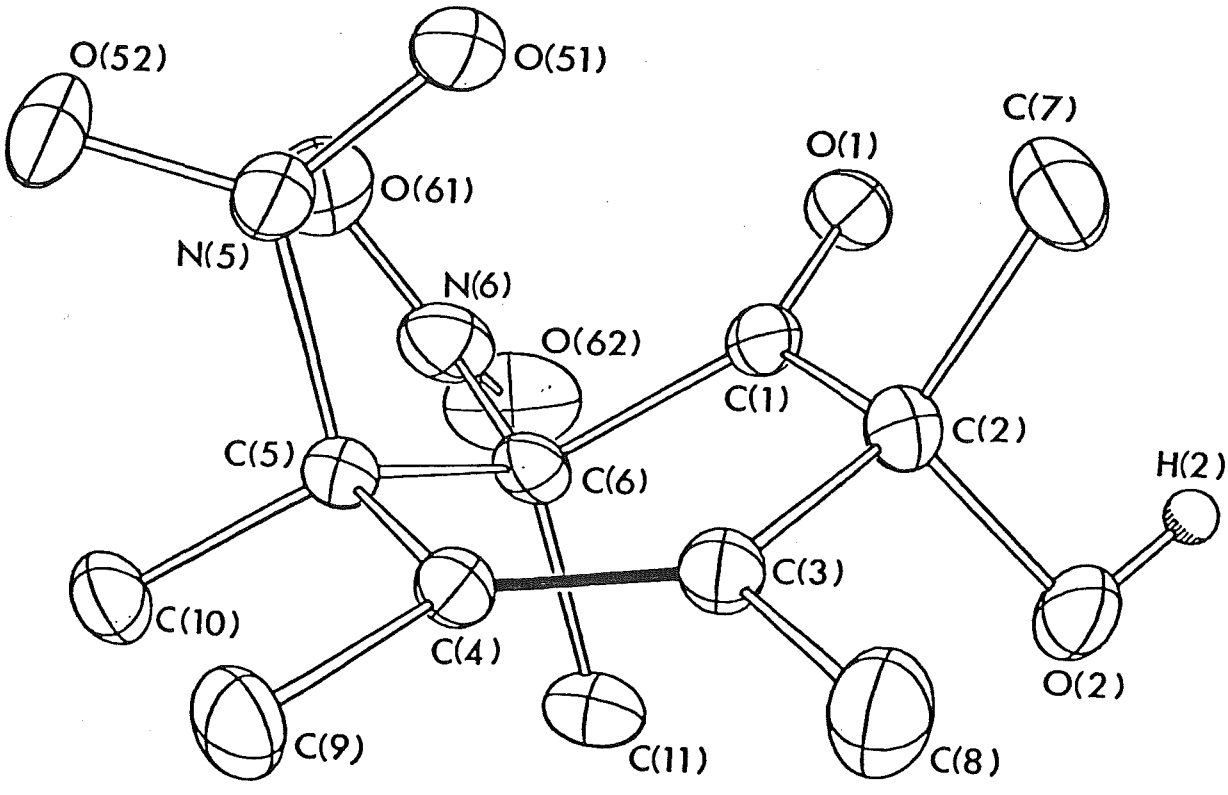


FIGURE 6.

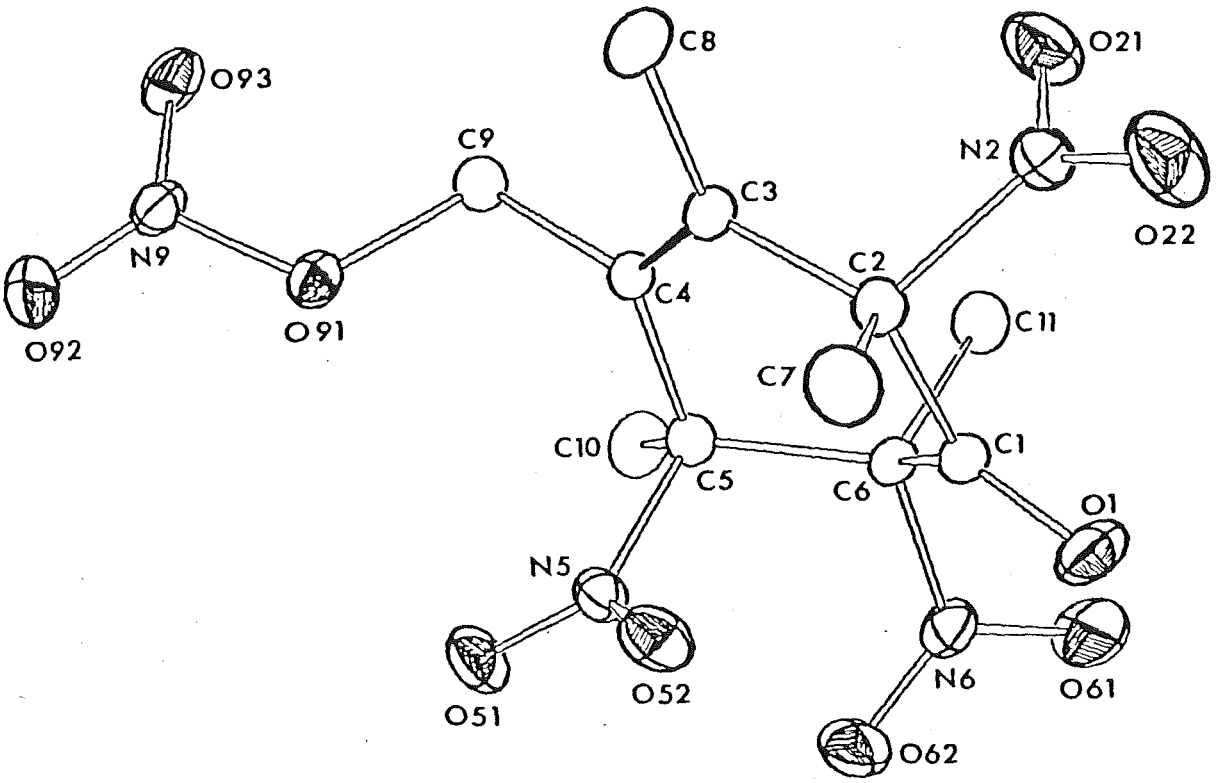
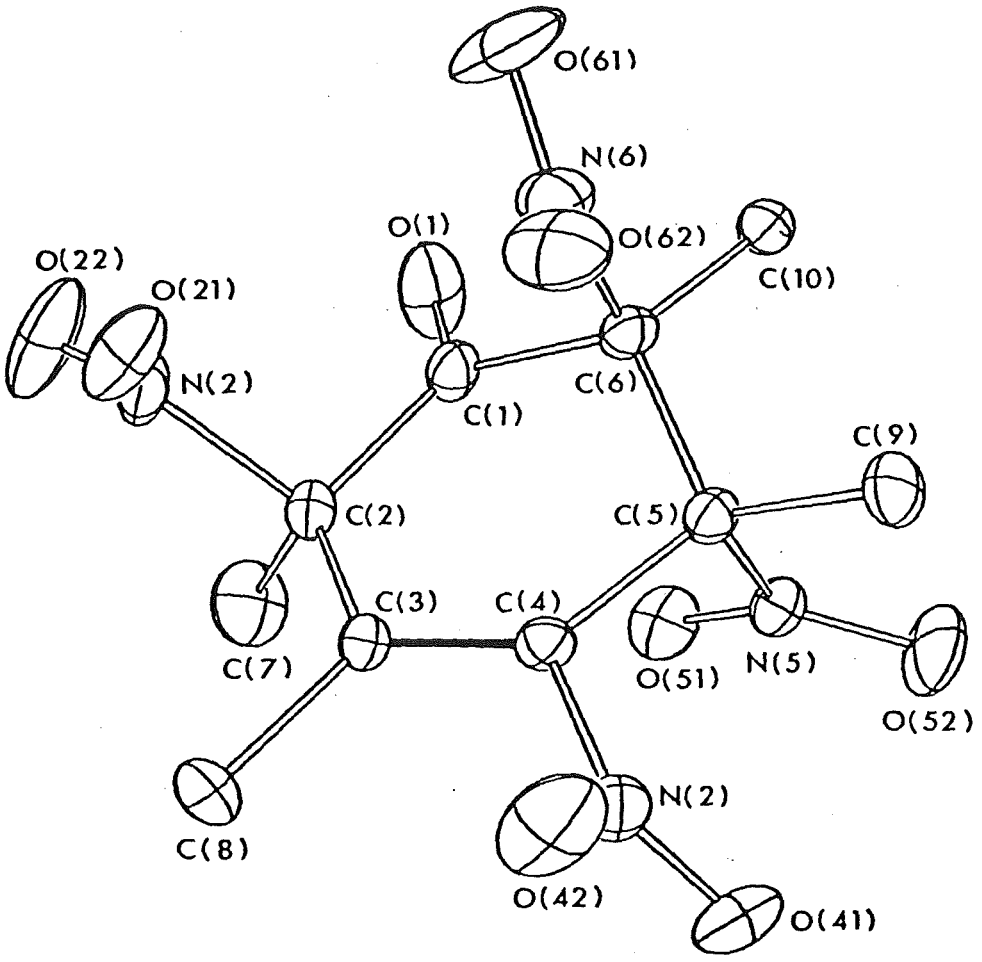


FIGURE 7



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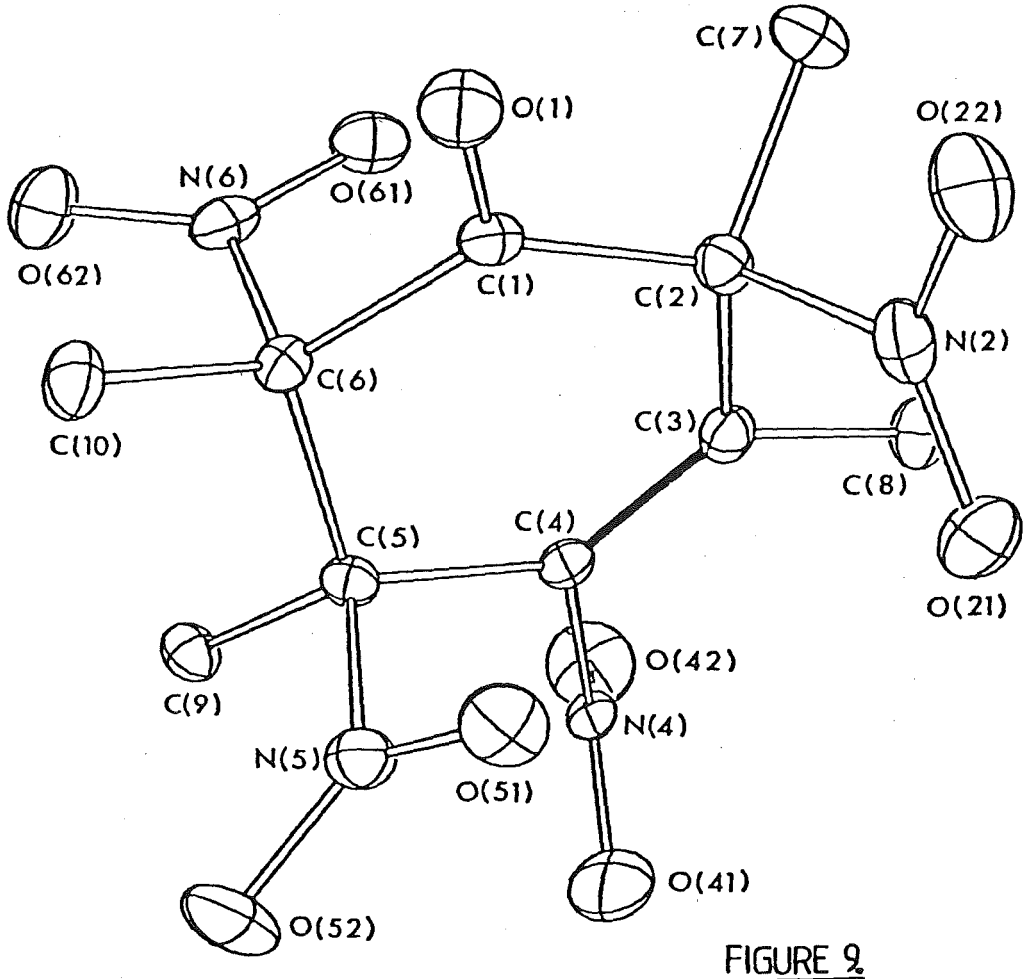

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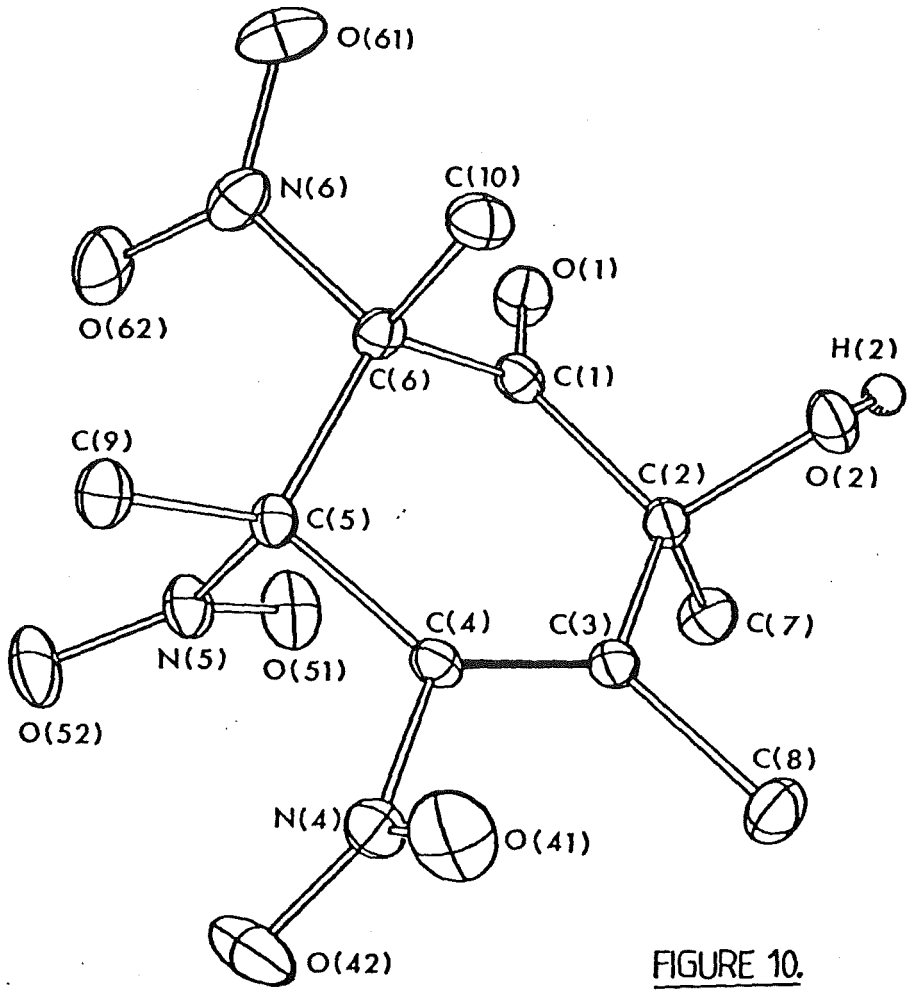
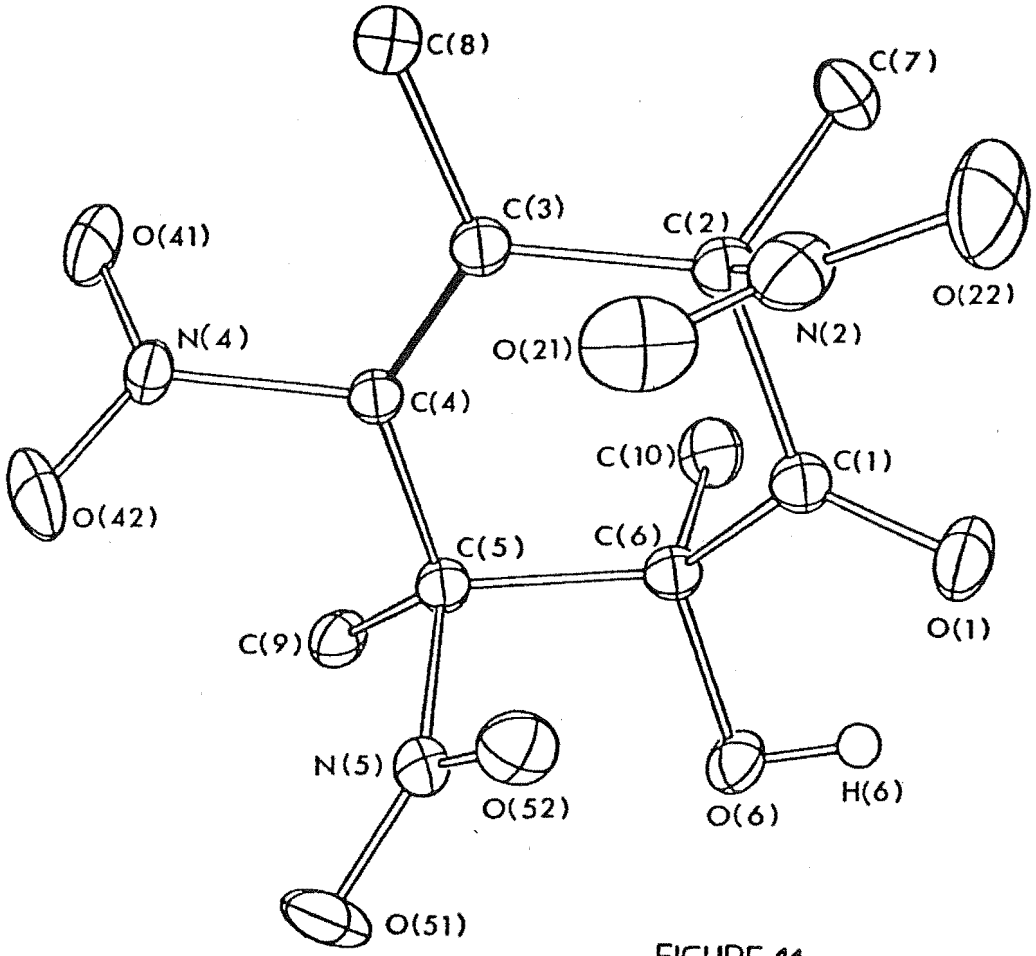


FIGURE 10.



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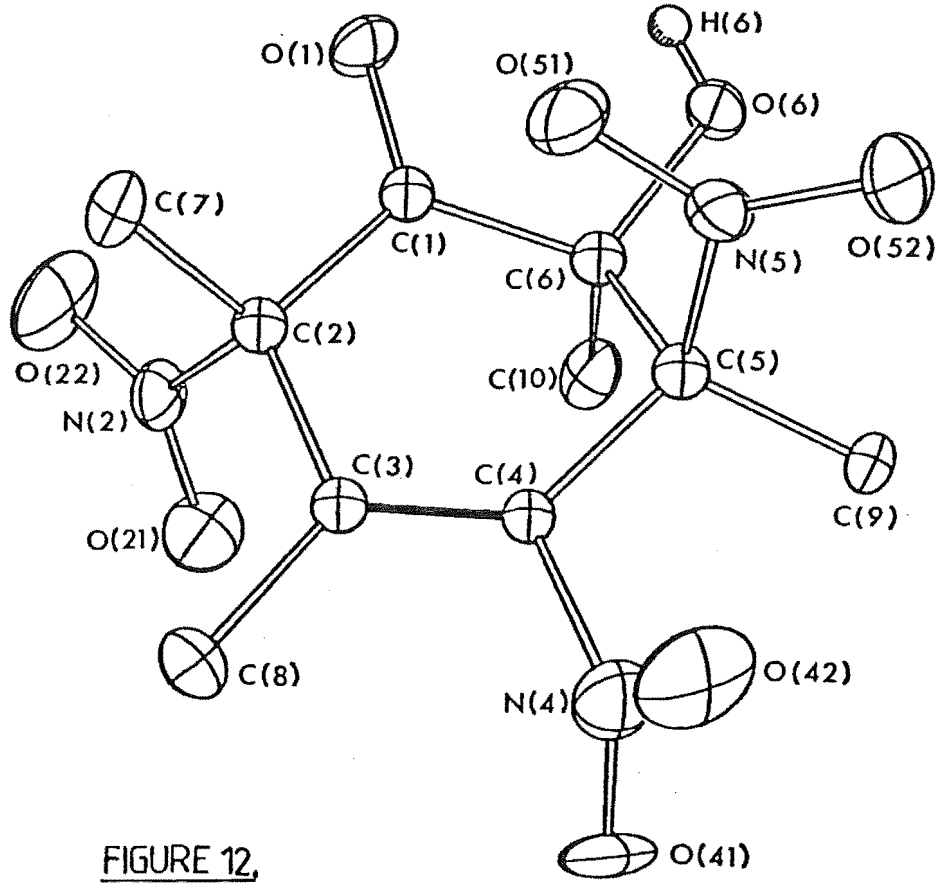

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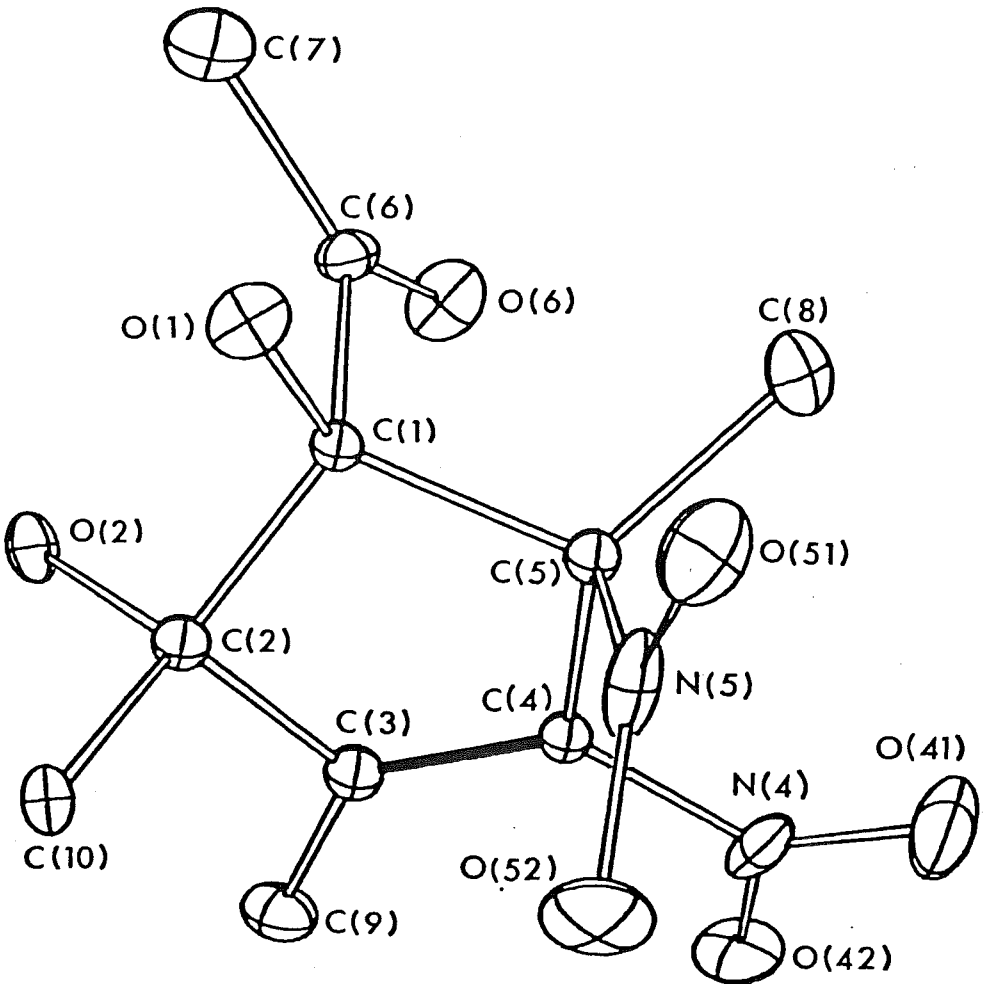

FIGURE 13.

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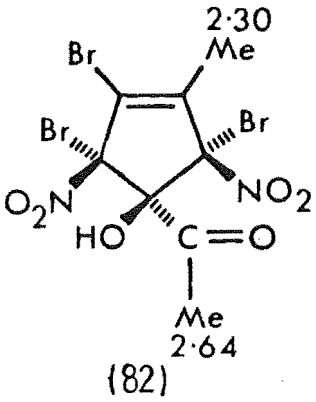

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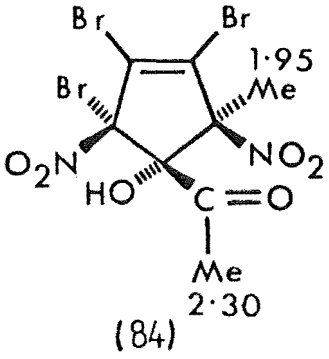

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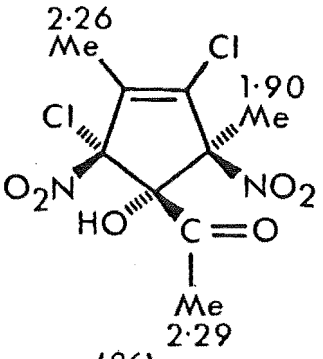

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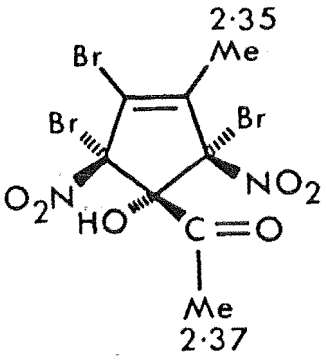

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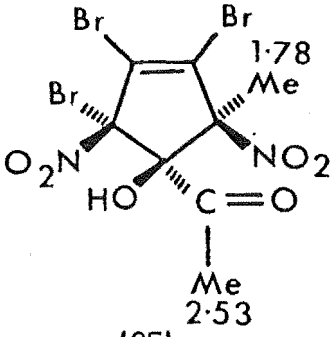

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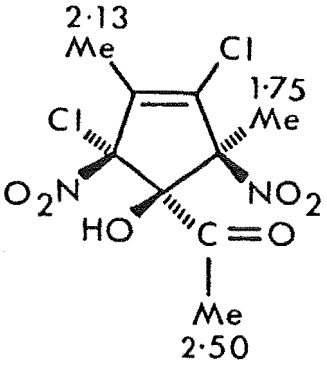

(87)

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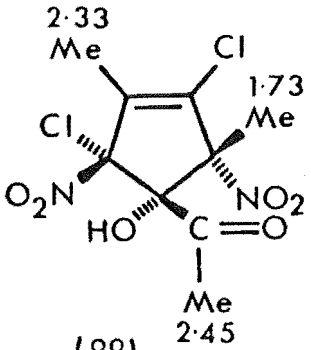

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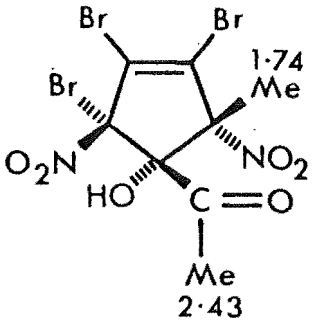

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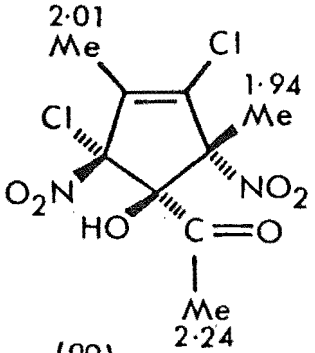
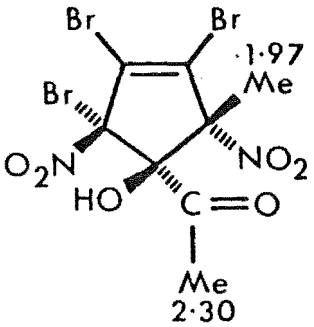


(89)



(91)

FIGURE 14. ^1H n.m.r. ($CDCl_3$) data for selected 2,5-dinitro-cyclopentenols

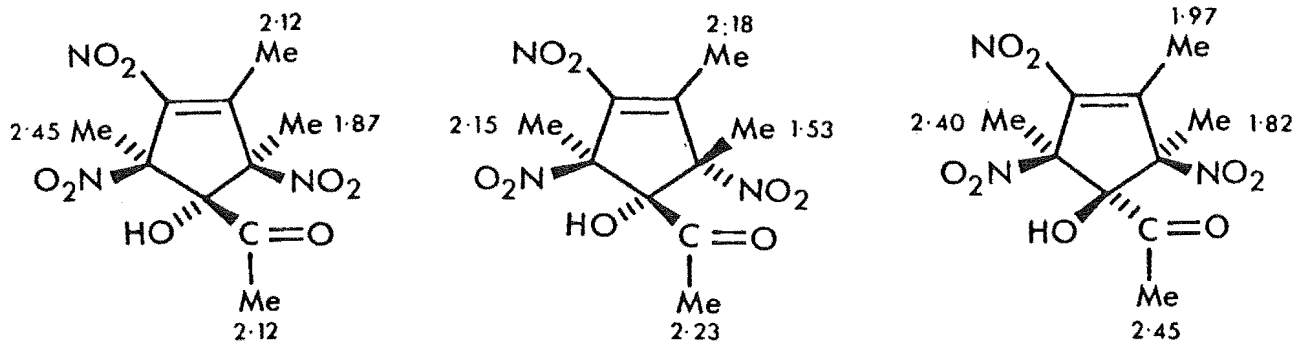


FIGURE 15. ^{1}H n.m.r.($CDCl_3$) data for trinitrocyclopentenols

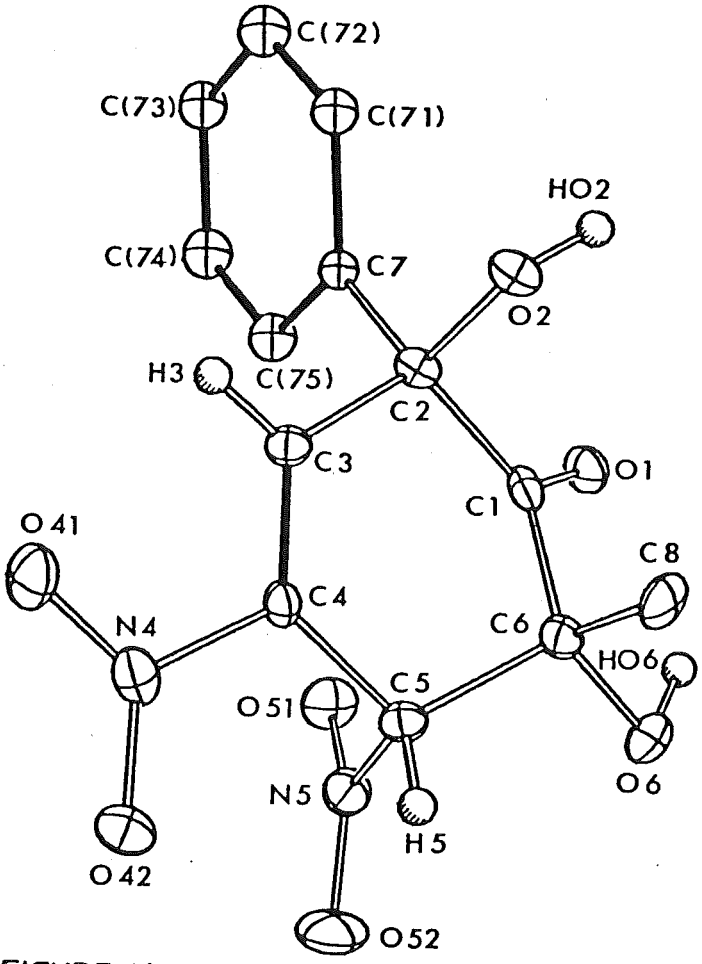


FIGURE 16.

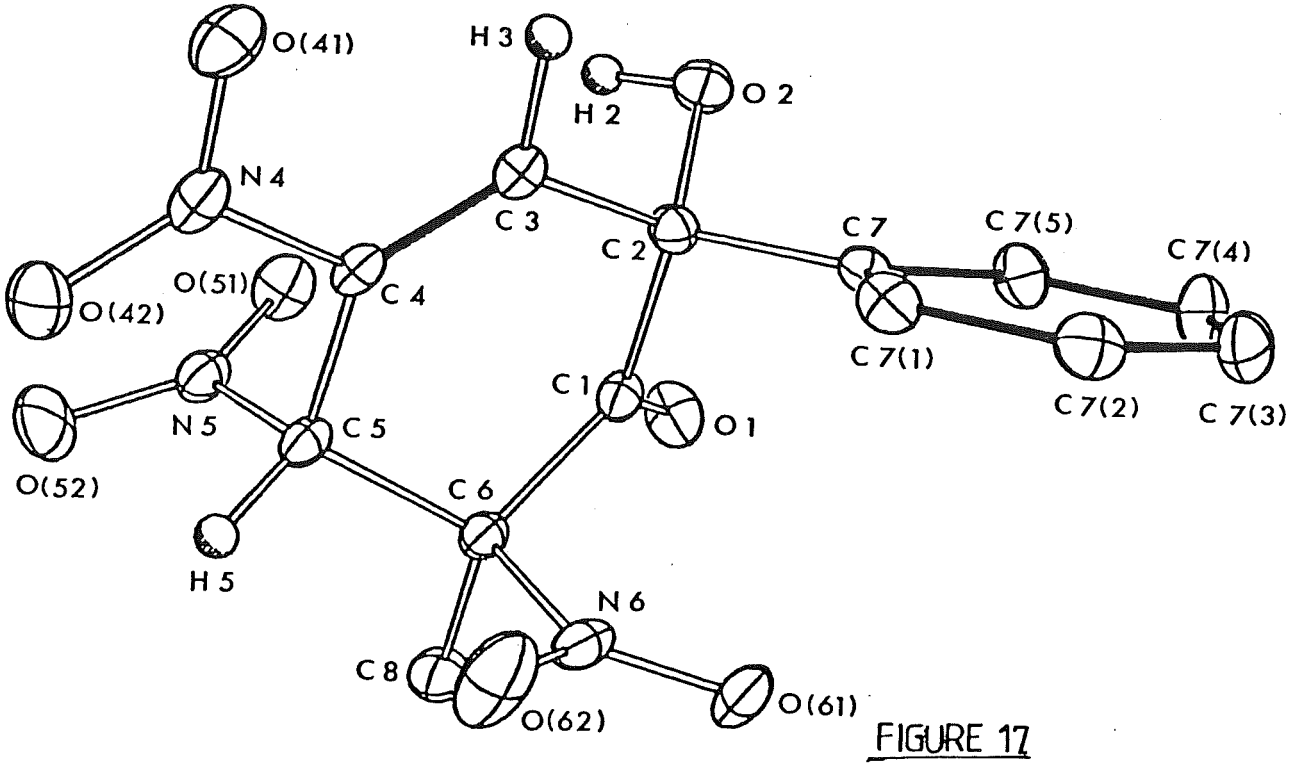
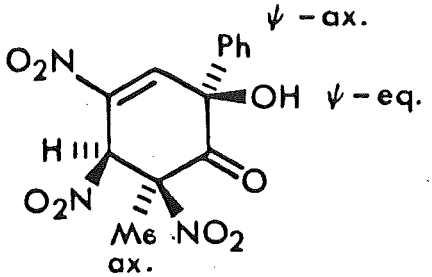
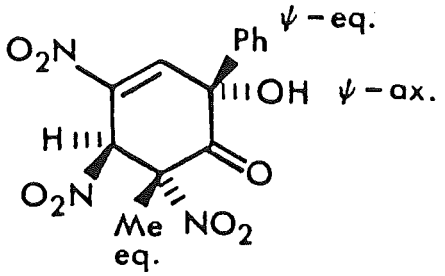


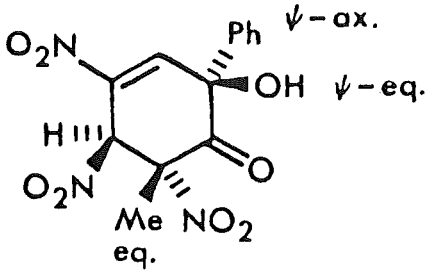
FIGURE 17



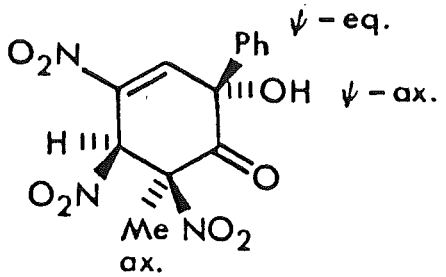
ax.
1·39
(121)



eq.
1·62
(122)



eq.
1·90
(115)



ax.
2·19
(123)

FIGURE 18

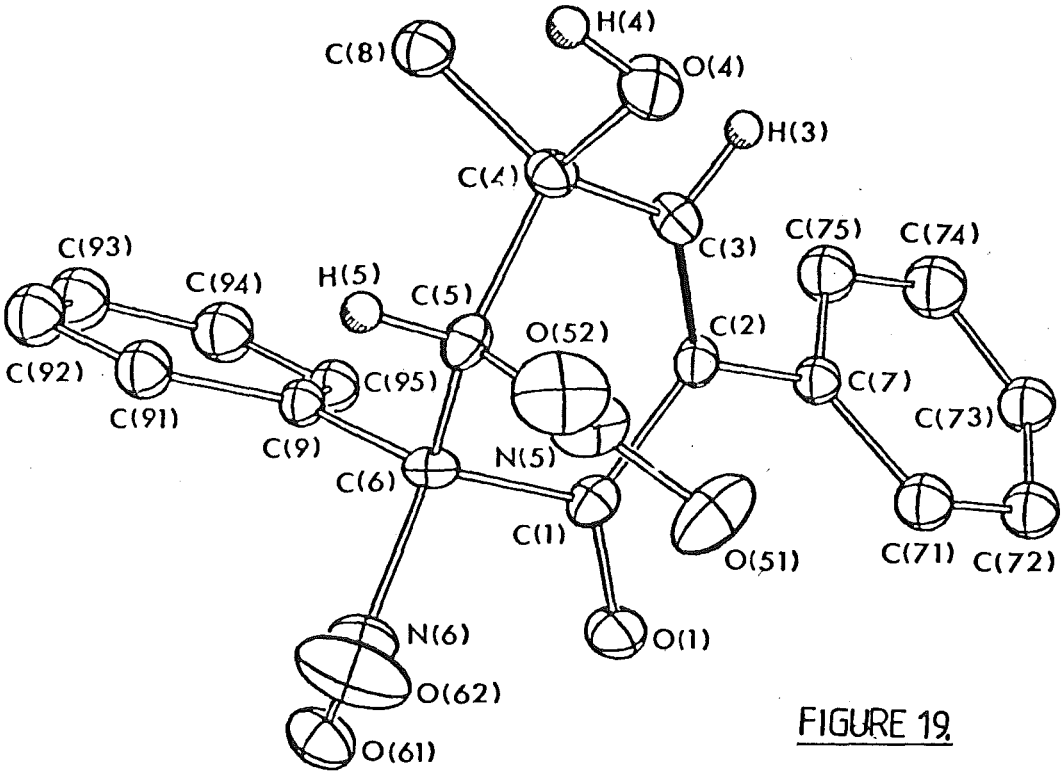


FIGURE 19

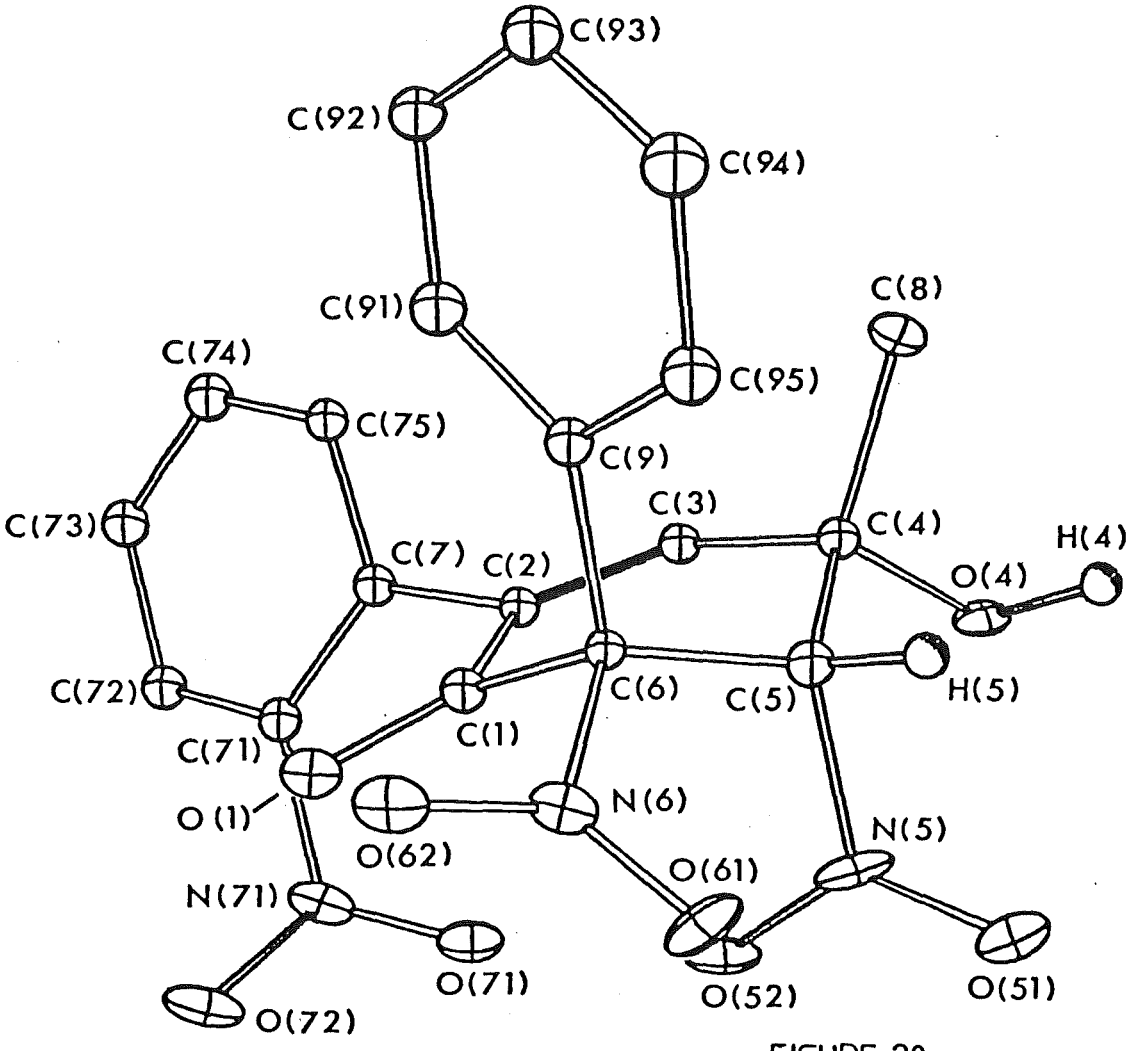


FIGURE 20

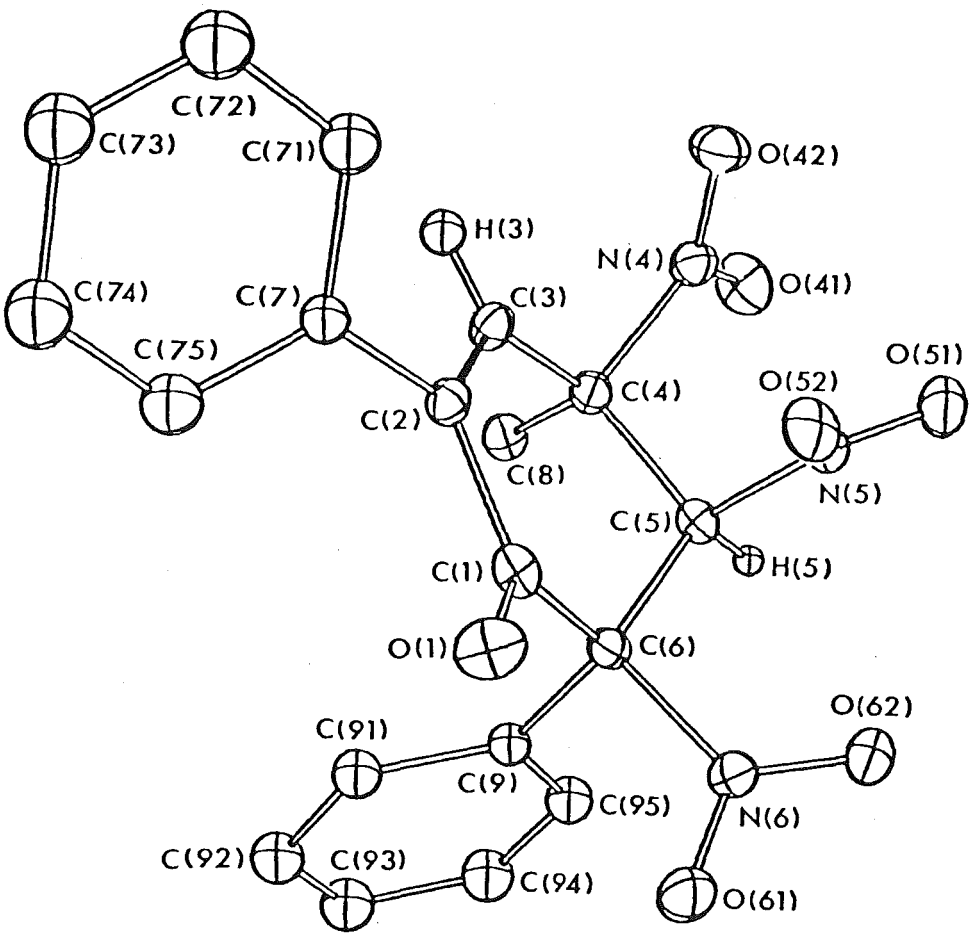


FIGURE 21.

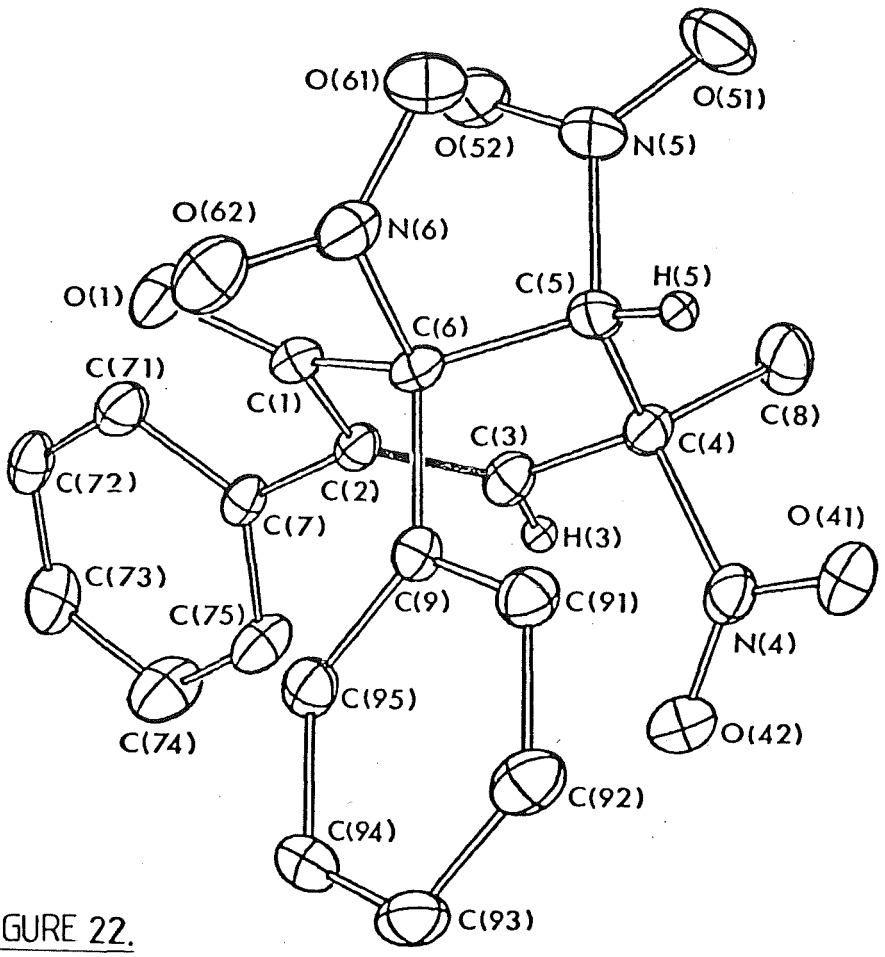


FIGURE 22.

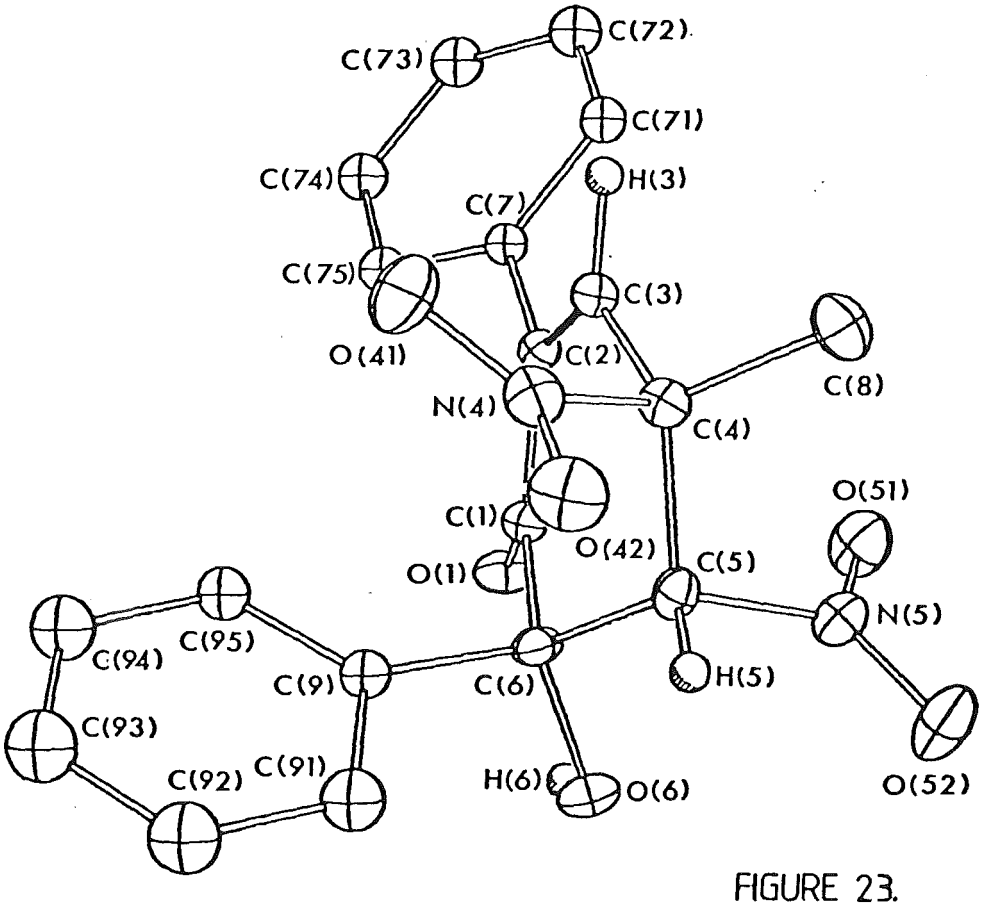


FIGURE 23.

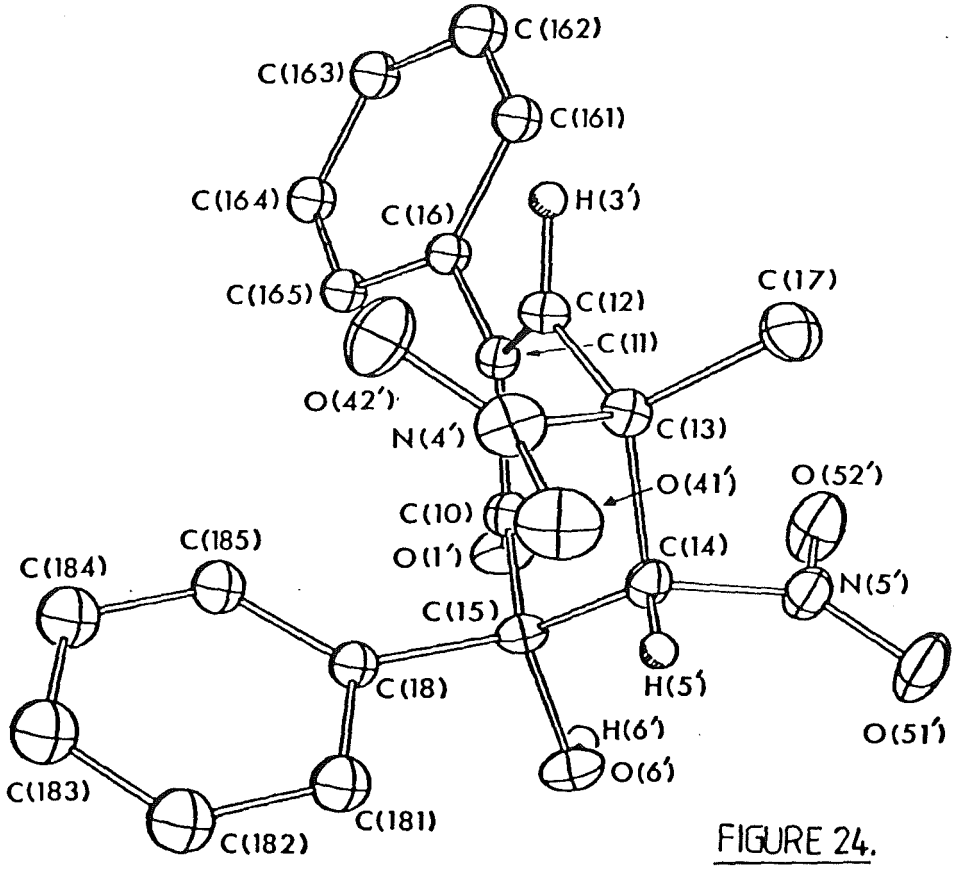


FIGURE 24.

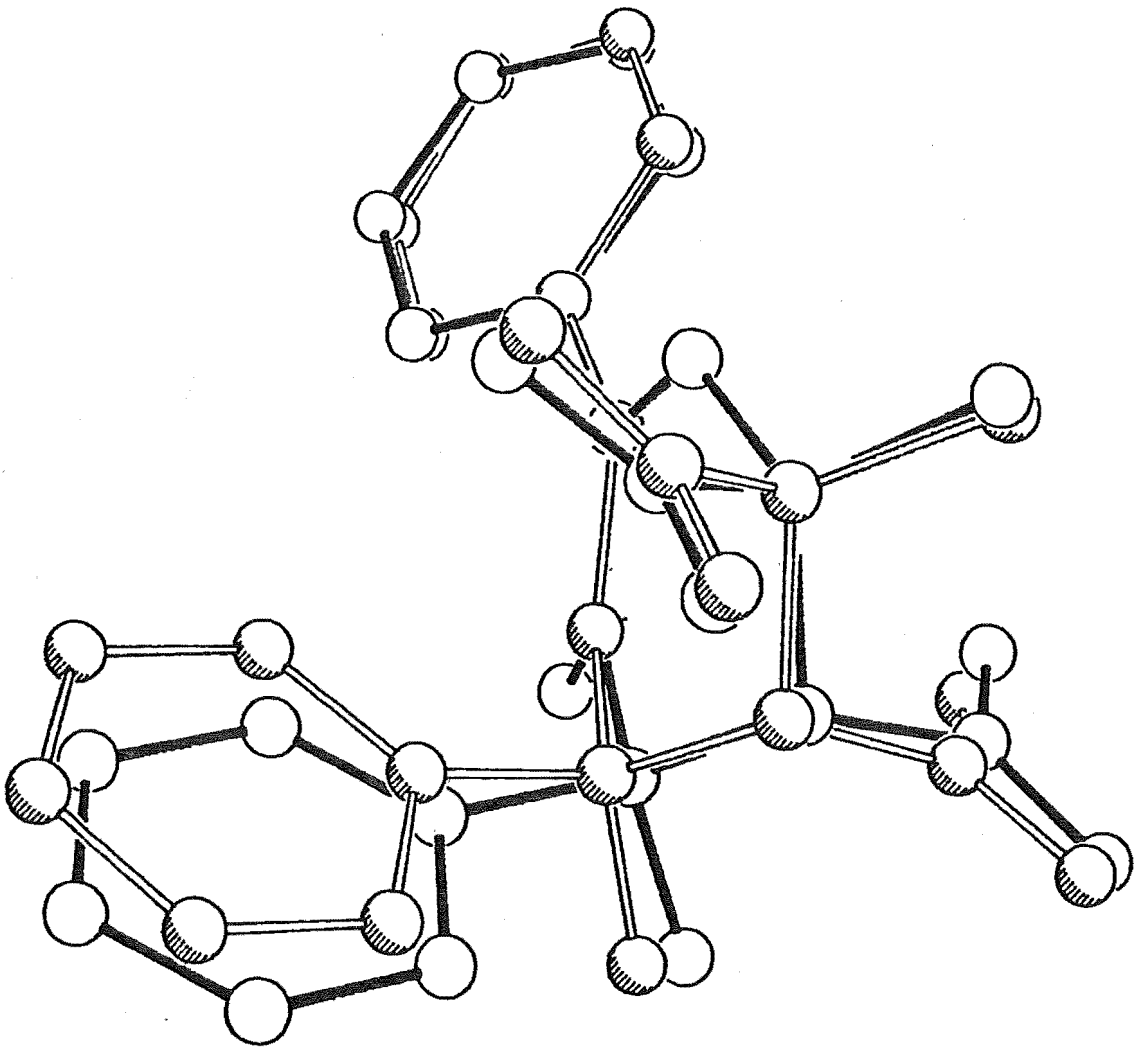


FIGURE 25 Computer generated superposition of the two molecules of compound (131), molecule one is joined by the shaded bonds.

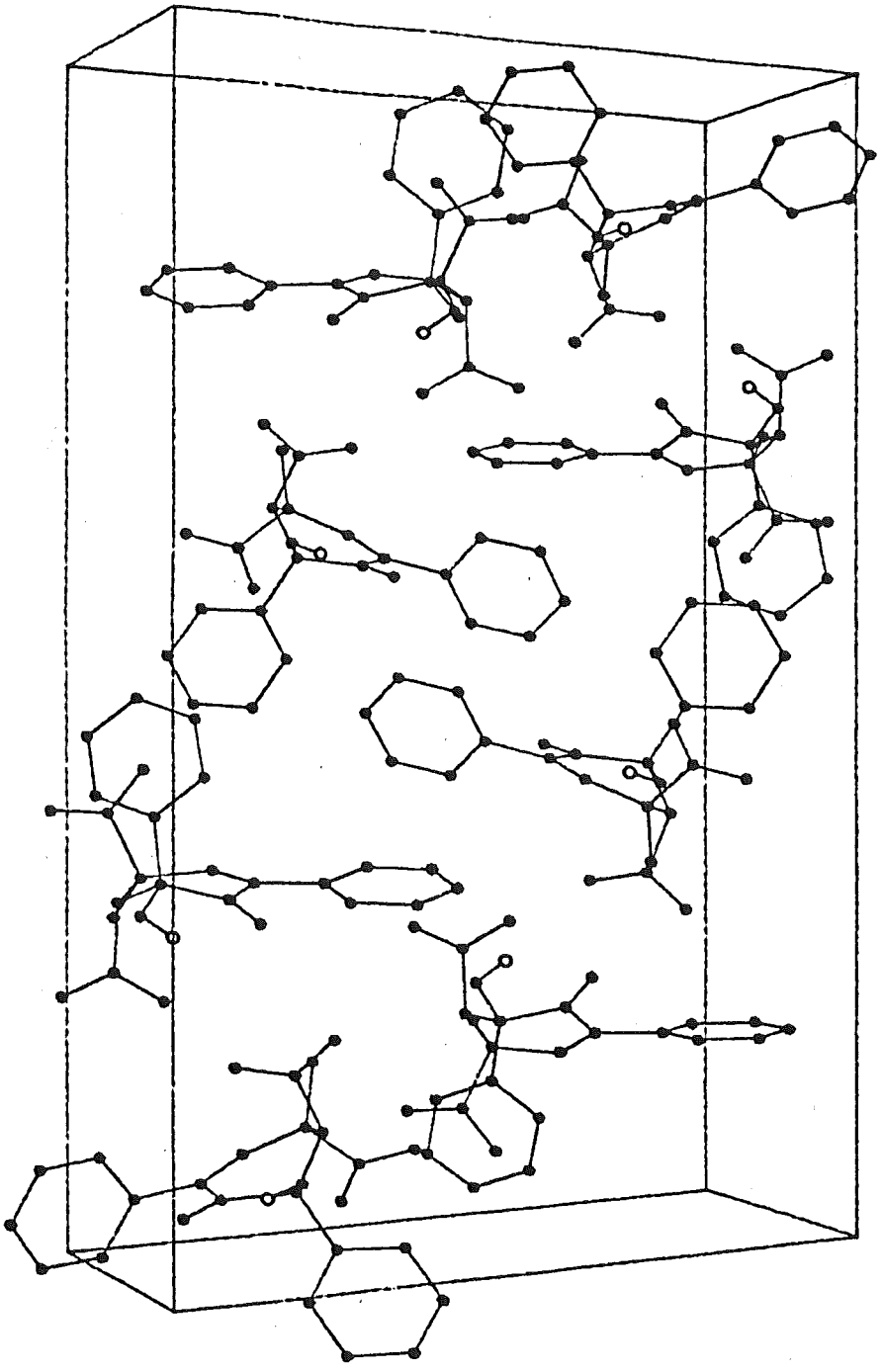
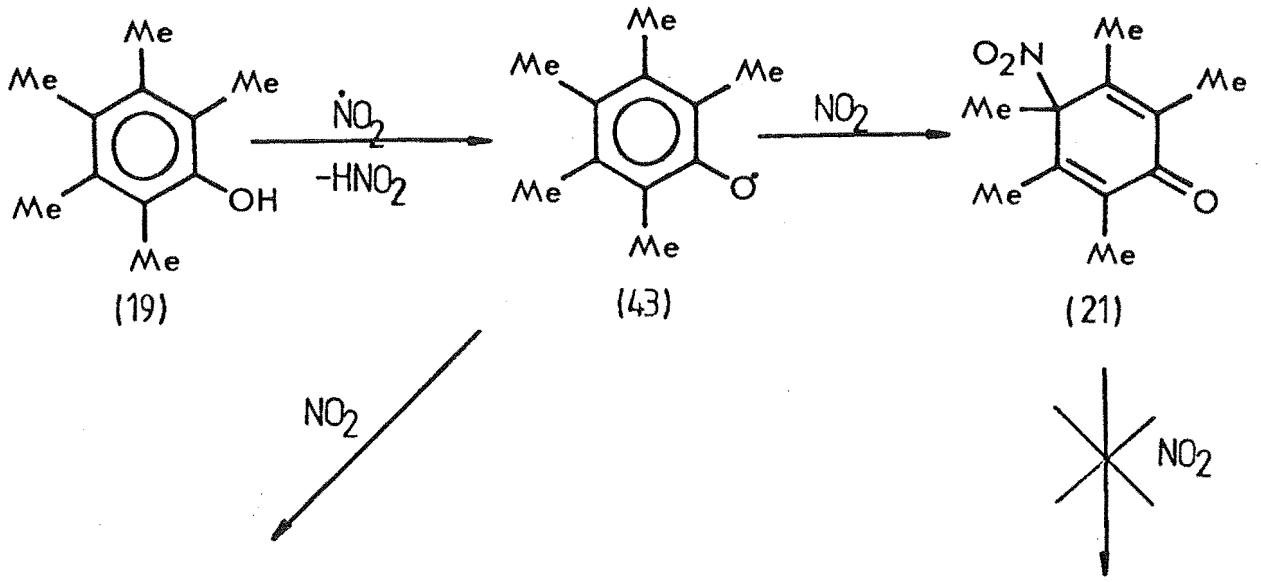
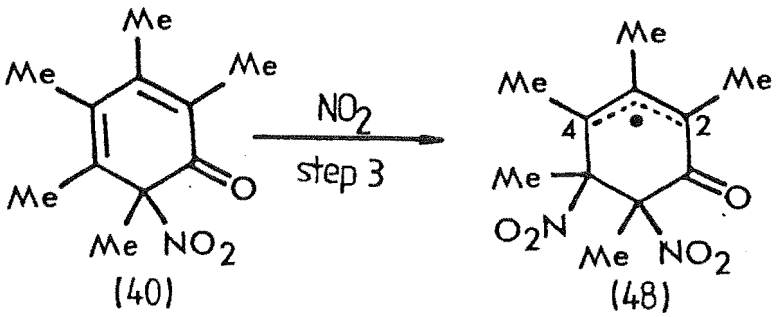
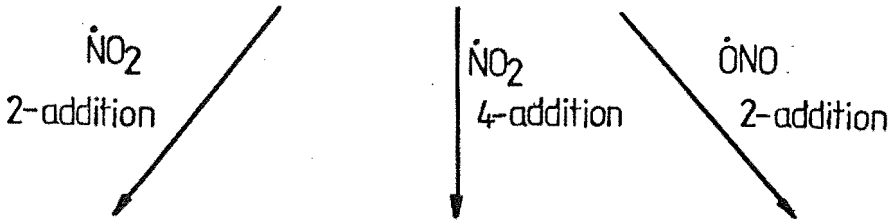
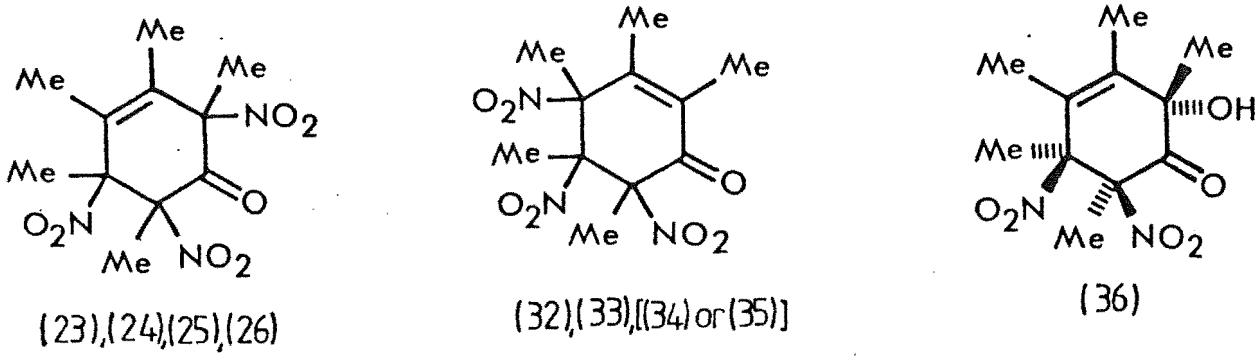


FIGURE 26. Crystal packing diagram for compound (131) the OH hydrogens are represented as open circles.

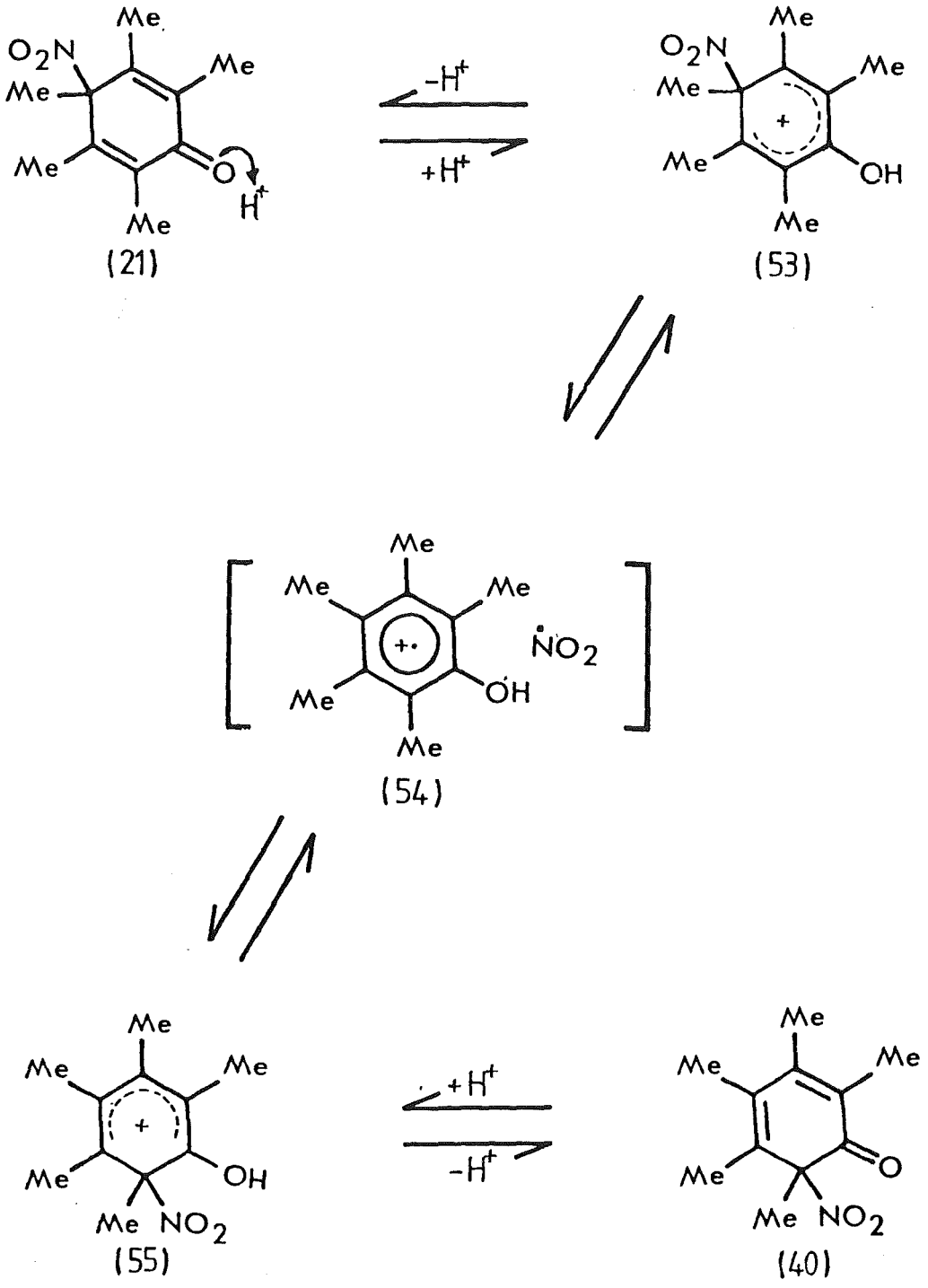

Me
Me
Me
Me
OH
Me
(19)
$\dot{N}O_2$
$-HNO_2$
Me
Me
Me
Me
O
Me
(43)
NO_2
O_2N
Me
Me
Me
O
Me
(21)
NO_2


Me
Me
Me
Me
O
Me
NO_2
(40)
NO_2
step 3
Me
Me
Me
4
2
Me
O
O_2N
Me
NO_2
(48)

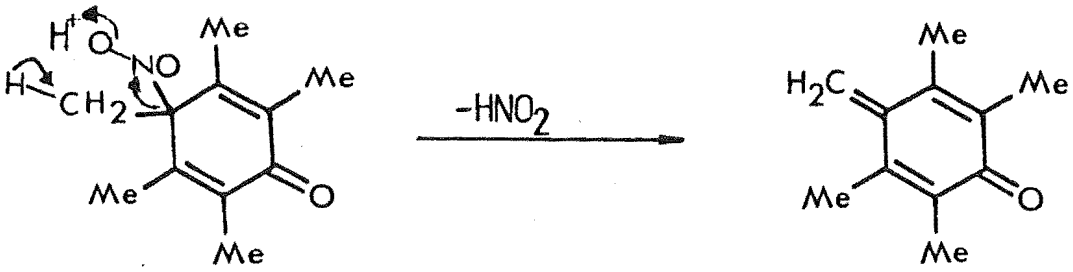

$\dot{N}O_2$
2-addition
$\dot{N}O_2$
4-addition
$\dot{O}NO$
2-addition


Me
Me
Me
NO_2
Me
O_2N
O
Me
NO_2
(23),(24),(25),(26)
Me
Me
Me
Me
O_2N
Me
O_2N
O
Me
NO_2
(32),(33),[(34) or (35)]
Me
Me
Me
OH
Me
O_2N
O
Me
NO_2
(36)

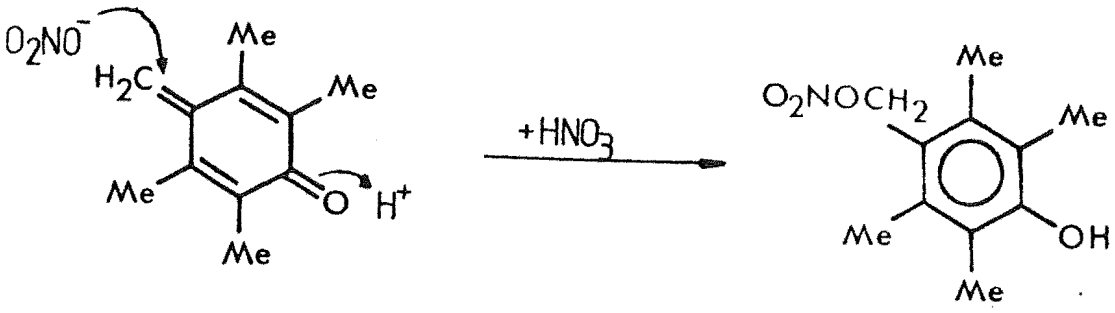
SCHEME 7.


Me
O2N
Me
Me
Me
Me
O
H+
-H+
+H+
Me
O2N
Me
Me
Me
+
OH
Me
(21)
(53)
Me
Me
Me
+·
NO2
Me
OH
Me
(54)
Me
Me
Me
+
Me
OH
Me NO2
(55)
+H+
-H+
Me
Me
Me
O
Me NO2
(40)

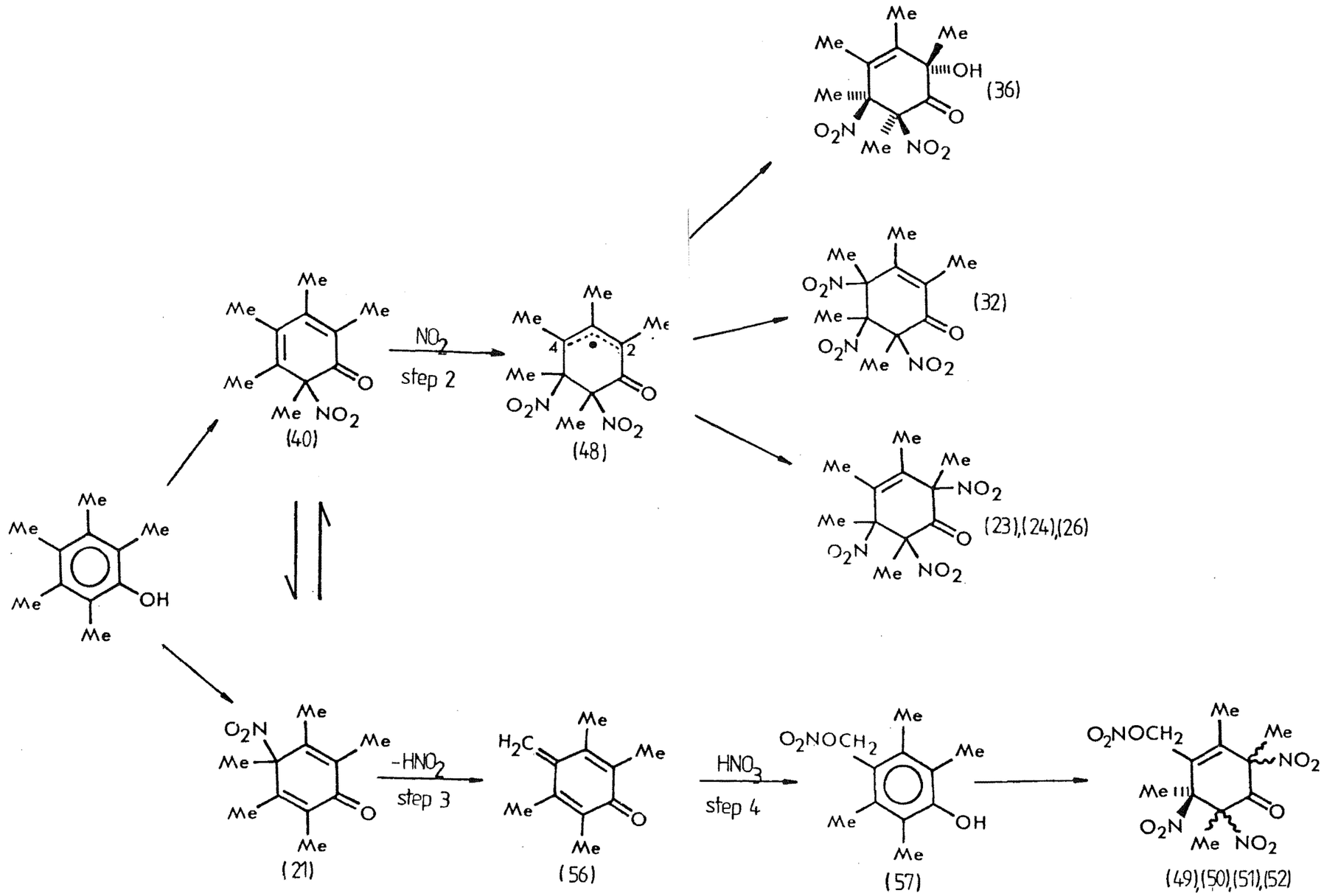
SCHEME 8.



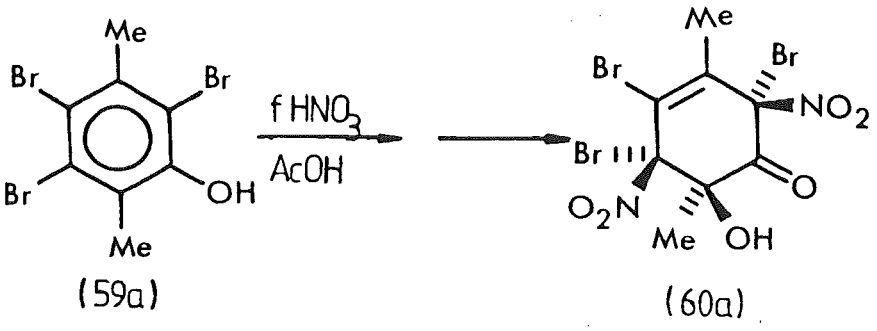
SCHEME 9.



SCHEME 10.

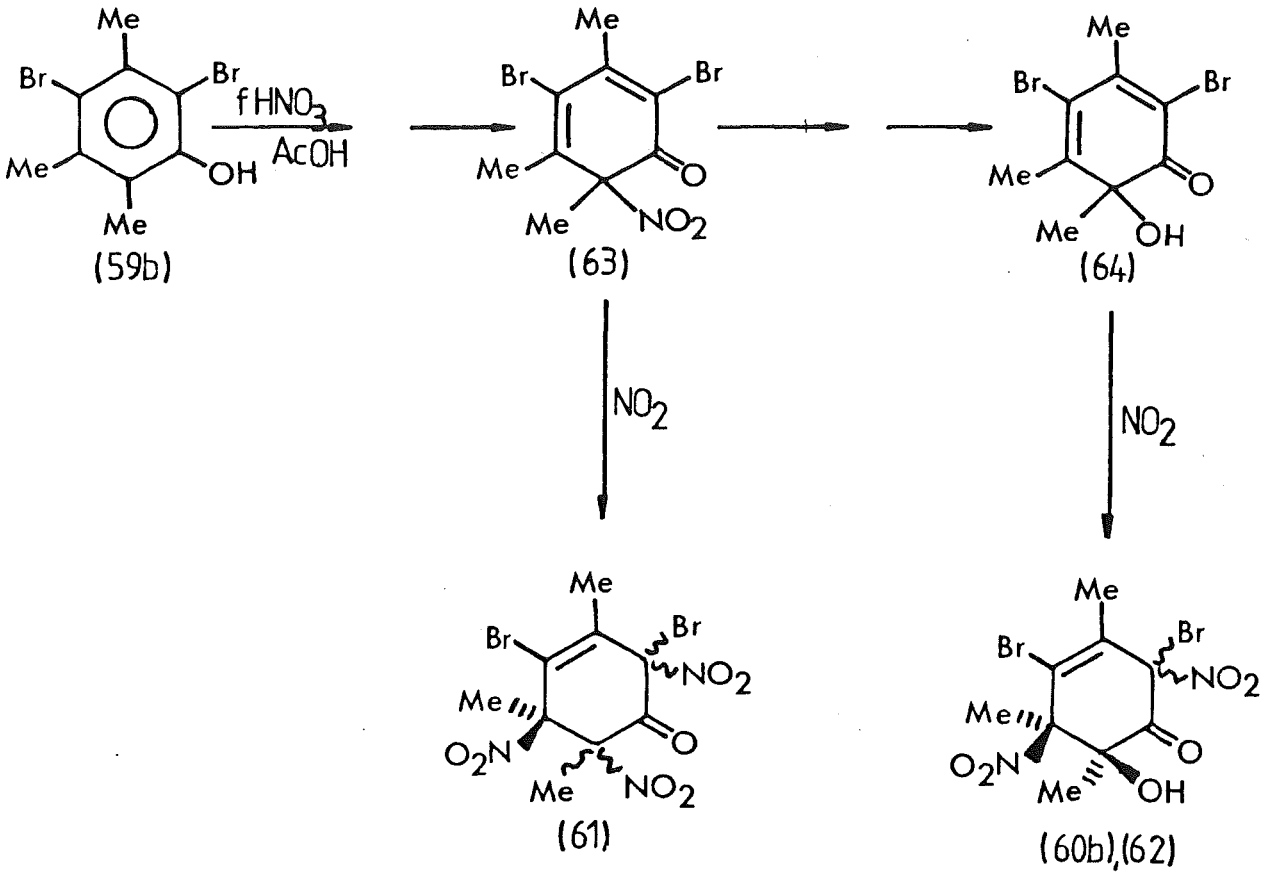

Me
Me
Me
Me
Me
OH
Me
Me
Me
Me
Me
Me
O
Me
NO2
(40)
NO2
step 2
Me
Me
Me
4
2
Me
O2N
O
Me
NO2
(48)
Me
Me
Me
OH
(36)
Me
Me
Me
O2N
Me
O2N
O
Me
NO2
(32)
Me
Me
Me
NO2
Me
O2N
O
Me
NO2
(23),(24),(26)
Me
O2N
Me
Me
Me
Me
O
(21)
-HNO2
step 3
H2C
Me
Me
Me
O
(56)
HNO3
step 4
O2NOCH2
Me
Me
Me
OH
Me
(57)
O2NOCH2
Me
Me
NO2
Me
O2N
O
Me
NO2
(49),(50),(51),(52)

SCHEME 11.

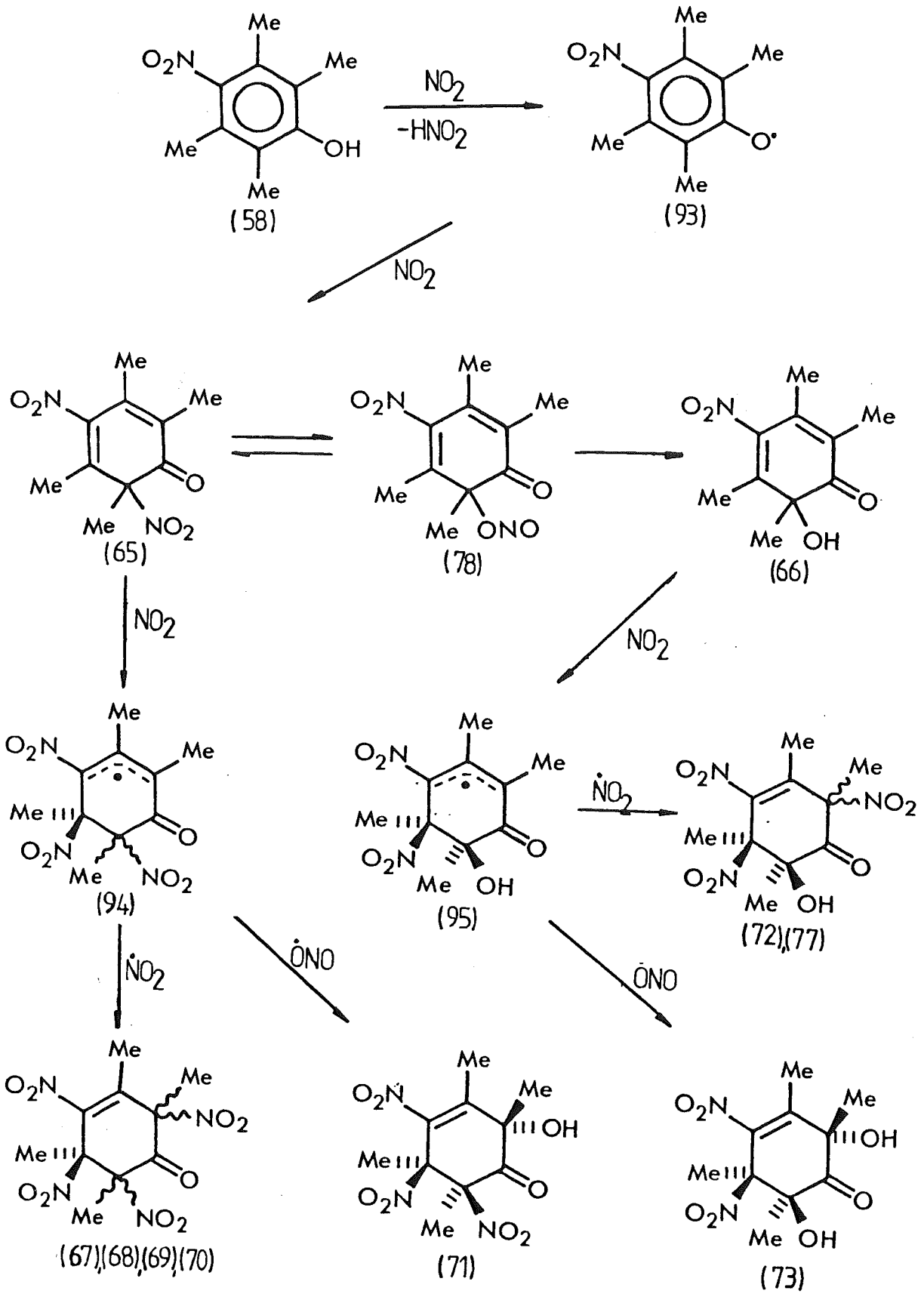


(59a) (60a)

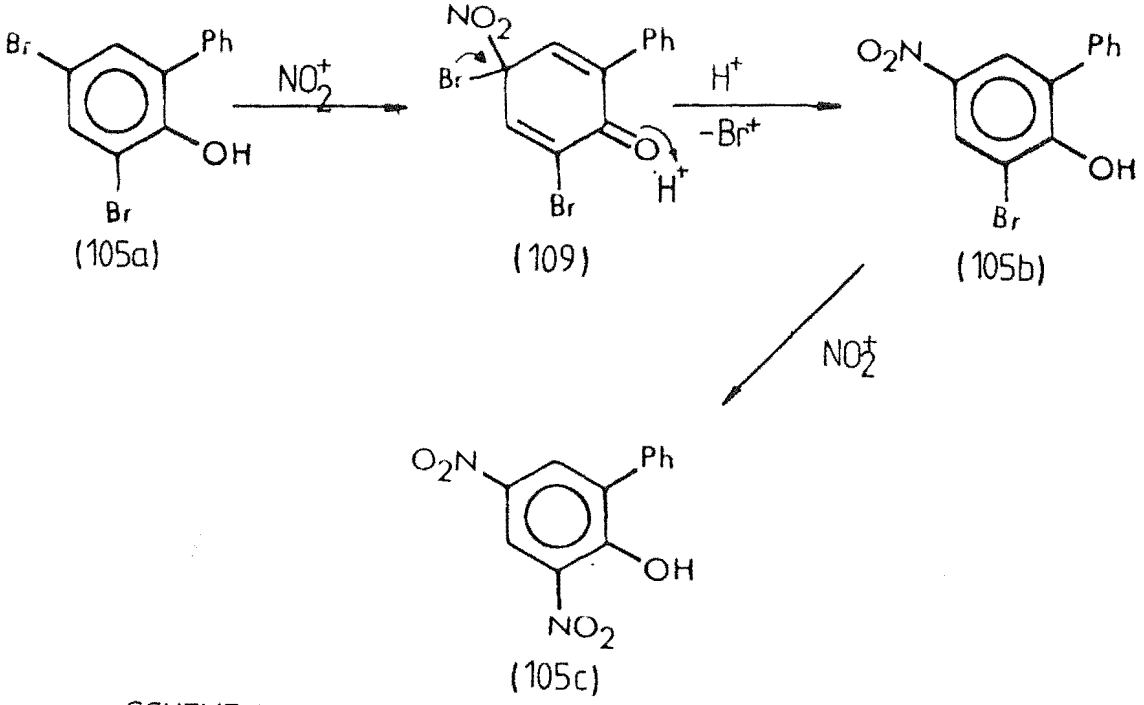
SCHEME 12.



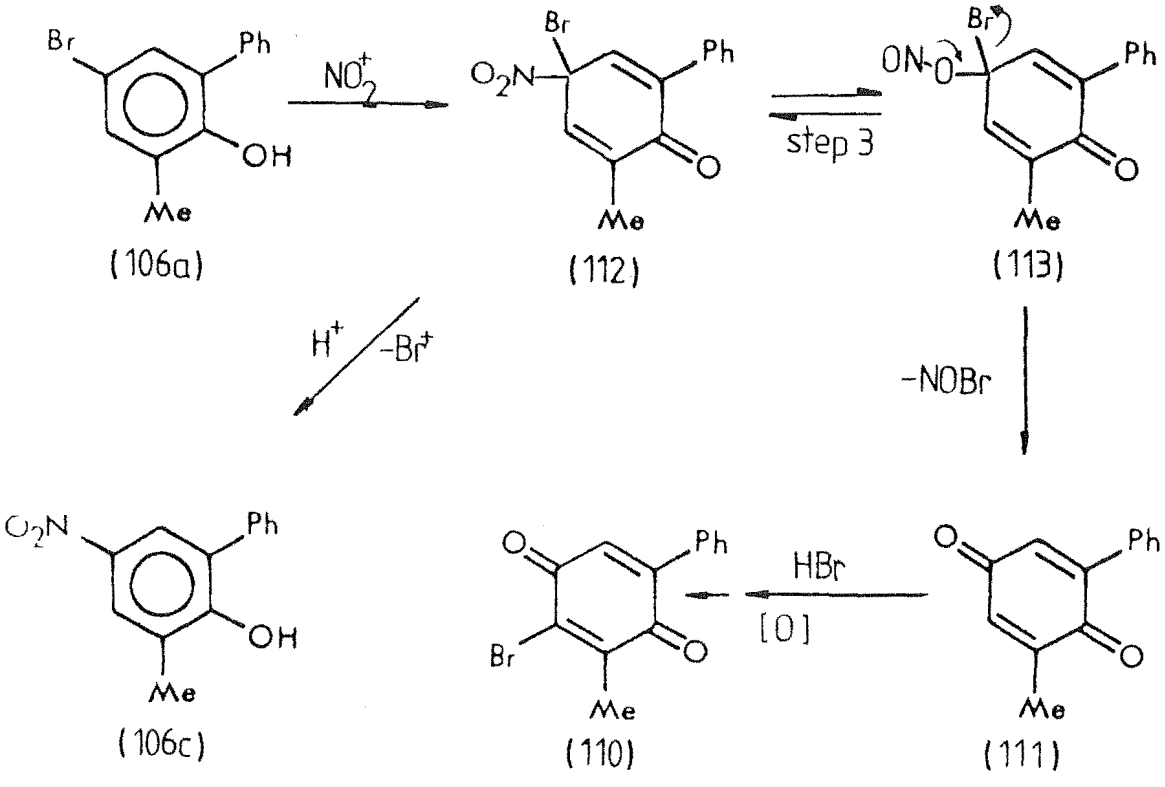
SCHEME 13



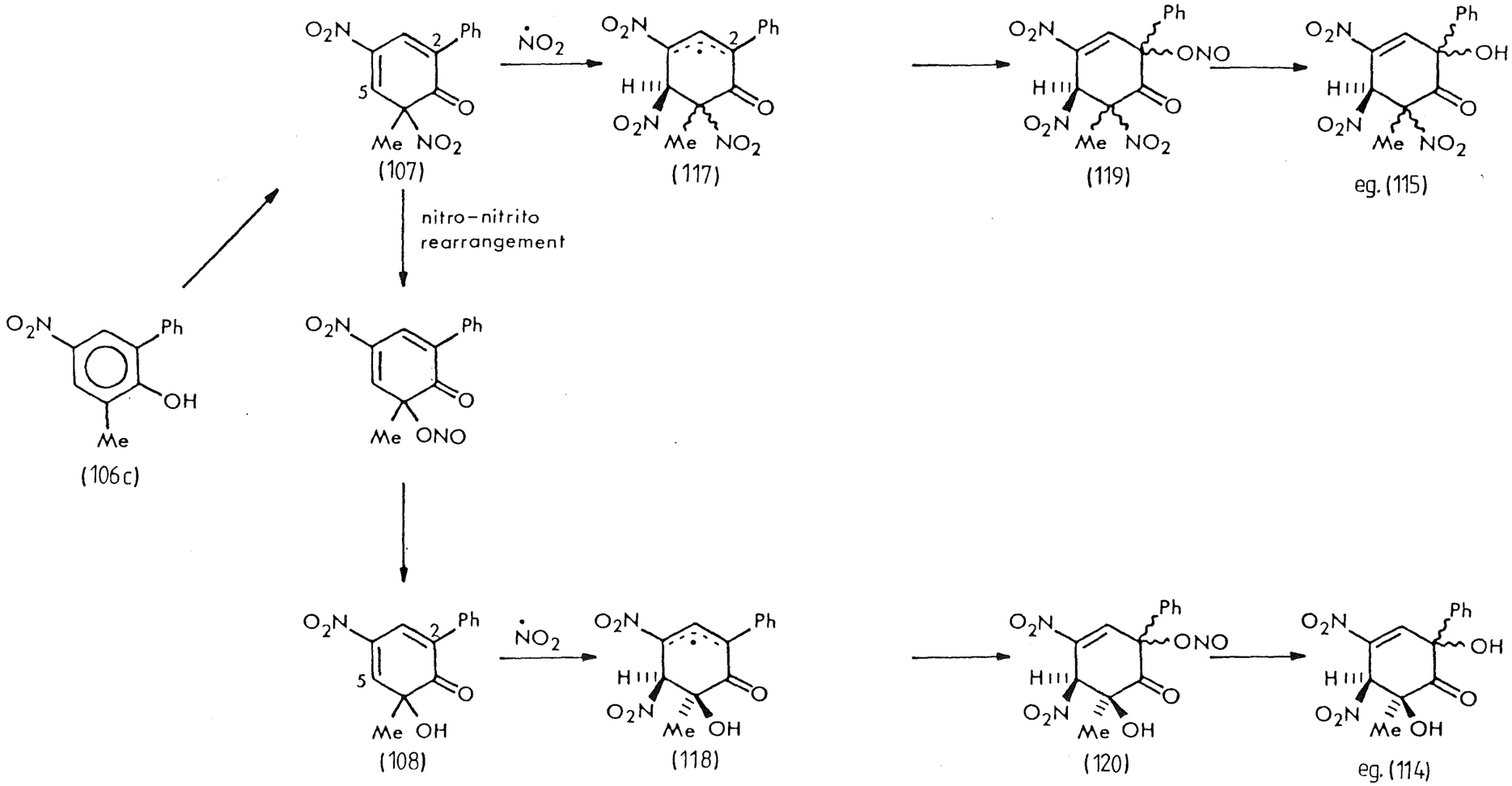
SCHEME 14



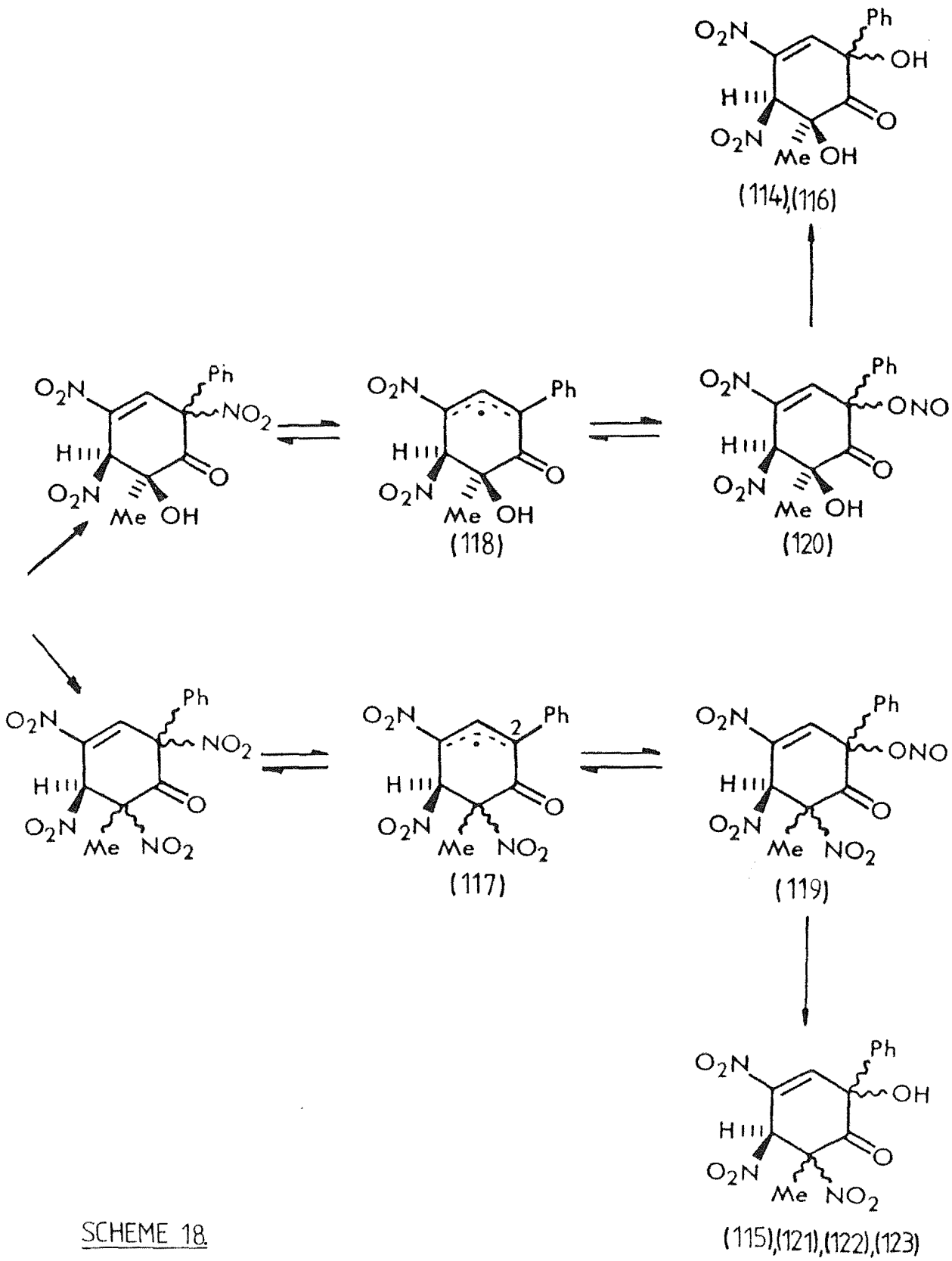
SCHEME 15.



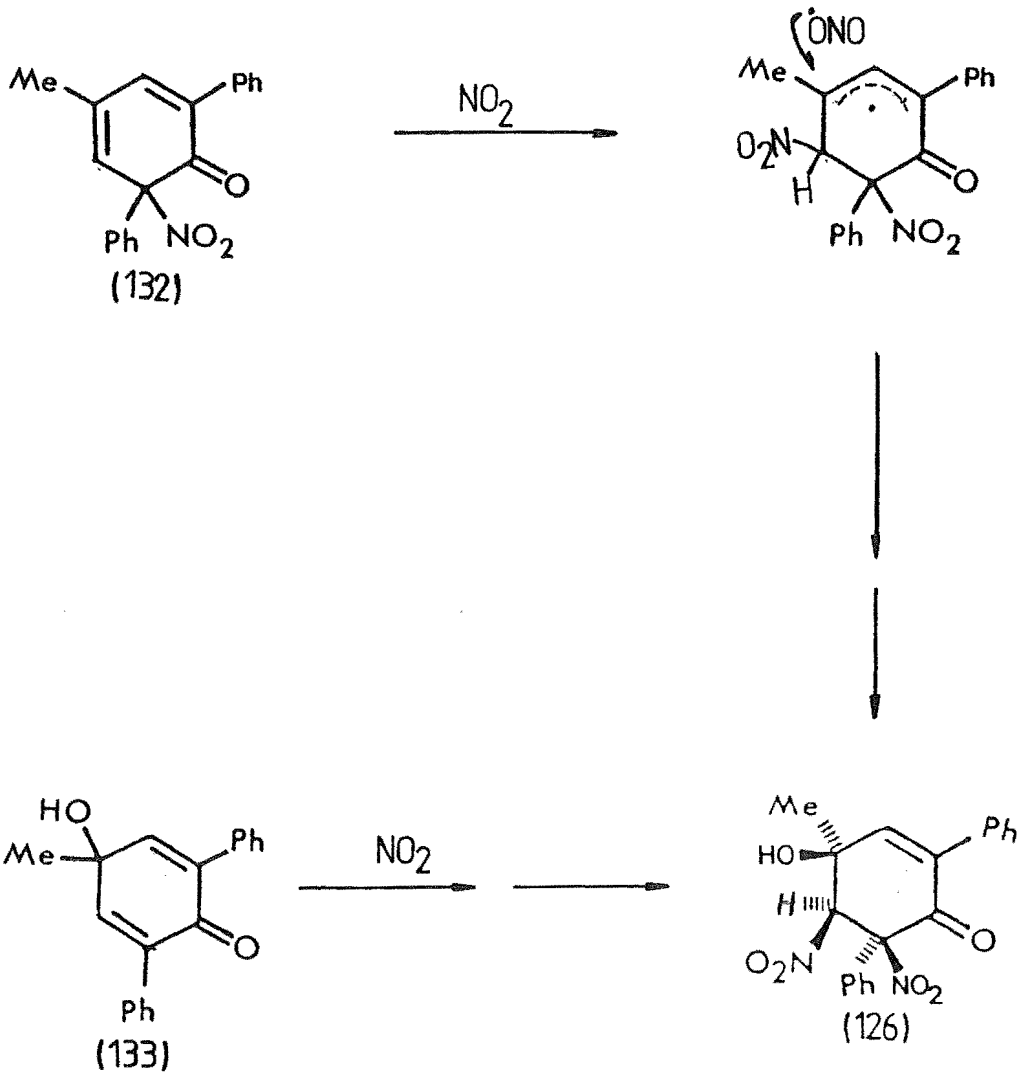
SCHEME 16.


(107)
(117)
(119)
eg. (115)
nitro–nitrito rearrangement
(106c)
(108)
(118)
(120)
eg. (114)

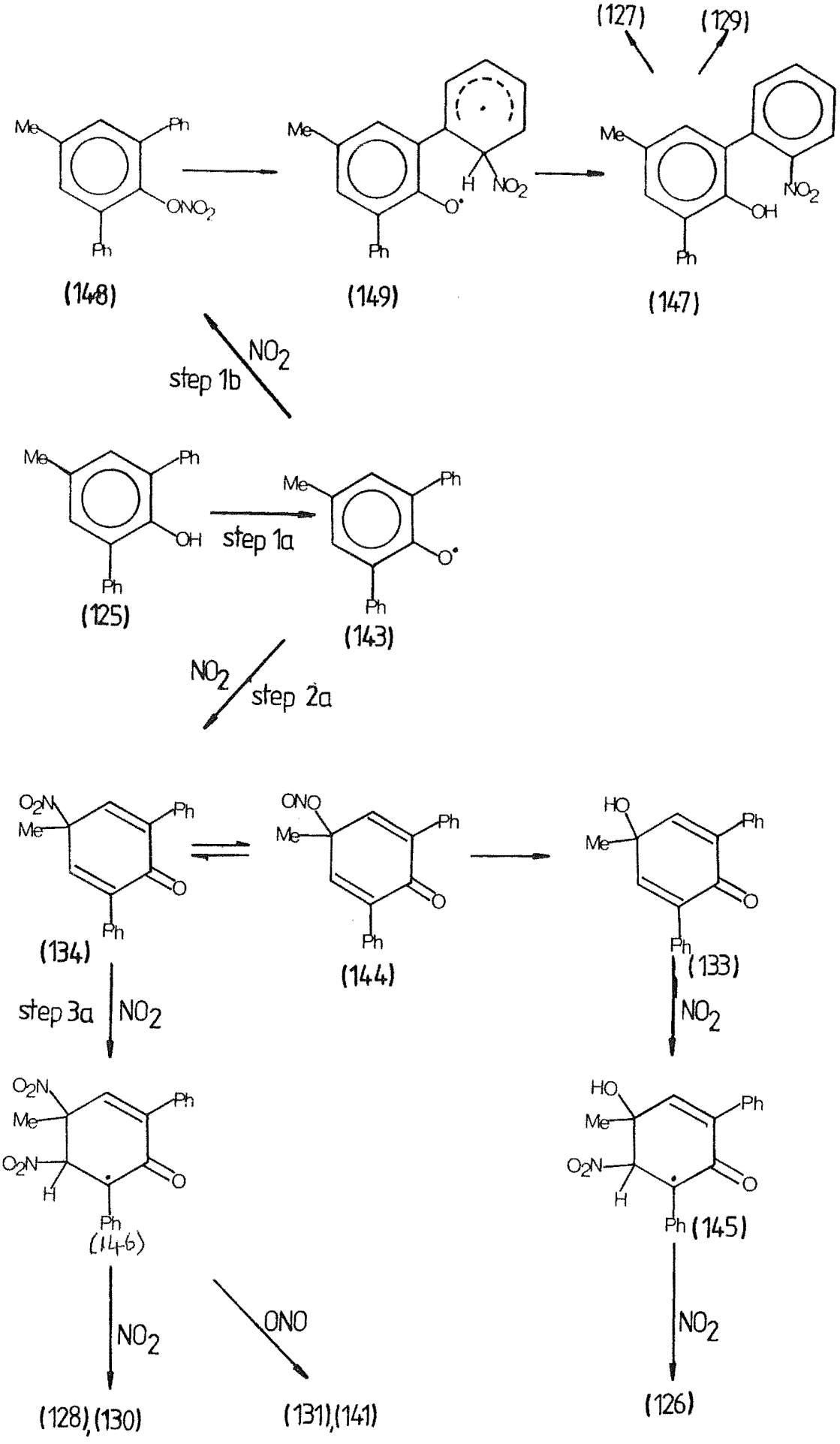
SCHEME 17.



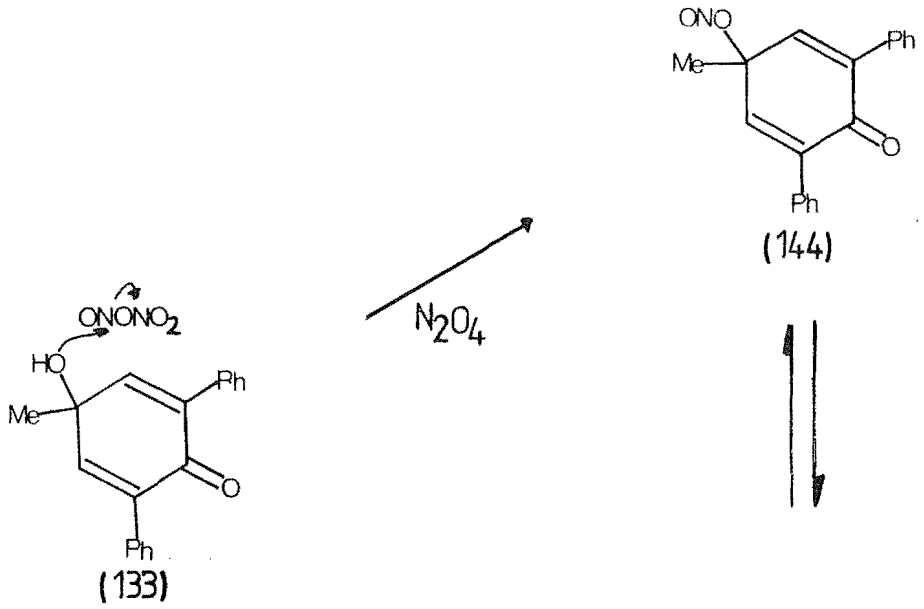
SCHEME 18


Me
Ph
O
Ph
NO2
(132)
NO2
ONO
Me
Ph
O2N
H
O
Ph
NO2
HO
Me
Ph
O
Ph
(133)
NO2
Me
Ph
HO
H
O
O2N
Ph
NO2
(126)

SCHEME 19


(127)
(129)
Me
Ph
ONO2
Ph
(148)
Me
H
NO2
O•
Ph
(149)
Me
NO2
OH
Ph
(147)
step 1b
NO2
Me
Ph
OH
Ph
(125)
step 1a
Me
Ph
O•
Ph
(143)
NO2
step 2a
O2N
Me
Ph
O
Ph
(134)
ONO
Me
Ph
O
Ph
(144)
HO
Me
Ph
O
Ph
(133)
step 3a
NO2
NO2
O2N
Me
O2N
H
Ph
O
Ph
(146)
HO
Me
O2N
H
Ph
O
Ph
(145)
NO2
ONO
NO2
(128),(130)
(131),(141)
(126)

SCHEME 20.



SCHEME 21

ACKNOWLEDGEMENTS

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