THE FORMATION AND REACTIONS OF ADDUCTS FORMED IN THE NITRATION OF *P*-DIETHYLBENZENE

by

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ABSTRACT

Nitration of *p*-diethylbenzene by acetyl nitrate in acetic anhydride at -45°C gives the diastereoisomeric 1,4-diethyl-4-nitrocyclohexa-2,5-dienyl acetates (IA and IB), 1-(*p*-ethylphenyl)-nitroethane (II), and 2,5-diethyl-nitrobenzene (III). The stereochemistry of the acetoxynitro adducts was studied using the n.m.r. shift reagent, tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-d_6-4,6-octane-dionato)-europium. The formation of the dienyl adducts and the side-chain nitro product through the *ipso* attack of nitronium ion at the carbon bearing an ethyl group is discussed. The reactions of the *ipso*-cation, 1,4-diethyl-1-nitrocyclohexa-2,5-dienyl carbonium ion (IV) with water to form the 1,4-diethyl-4-nitrocyclohexa-2,5-dienols (V), with methanol to form the dienyl methyl ethers (VI), and with acetic acid-d_4 to form the trideuterated analogues (VII) of I are presented.

The reactions of I under conditions which promote rearomatisation have been studied and discussed in terms of formation of IV or 1-acetoxy-1,4-diethylcyclohexa-2,5-dienyl cation (VIII). Rearomatisation of I under acidic conditions gives III and *p*-ethylacetophenone (IX) derived from side-chain substituted products. Rearomatisation of I

in aqueous methanol gives 2,5-diethylphenyl acetate (X) and methanolic sodium methoxide solvolysis of I gives V which rearomatises with a 1,2-alkyl shift to give 2,4-diethylphenol (XI).

TABLE OF CONTENTS

ABSTRACT ..... ii-iii
TABLE OF CONTENTS ..... iv-v
LIST OF TABLES vi
LIST OF FIGURES vii
ACKNOWLEDGEMENT viii

I INTRODUCTION. 1

1.1 Introduction 1

1.2 Objectives of Present Work 21

II EXPERIMENTAL. 22

2.1 Instrumentation. 22

2.2 Reagents 23

2.3 Nitration of *p*-Diethylbenzene. 25

2.4 ^{1}H N.M.R. Shift Reagent Study. 29

2.5 Preparation of Authentic Compounds as Comparison Standards. 33

2.6 Exchange Reactions of Dienes 45

2.7 Thermolytic Reactions of Dienes. 60

2.8 Rearomatisation Reactions of Dienes. 61

2.9 Reactions of *p*-Xylene Dienes 65

III DISCUSSION. 70

3.1 Products of Nitration. 70

3.2 Structures of Dienes 73

3.3 Mechanism of Adduct Formation. 79

3.4 Formation of Products Other than 1,4-Adducts. 86

3.5 Reactions of the Adducts 91

3.6 Reactions Under Acidic Conditions. 93

CHAPTER Page

3.7 Base-Catalysed Reactions of Dienes 108

3.8 Pyrolysis and Neutral Solvolysis of Dienes 110

3.9 Conclusion 112

REFERENCES 114

APPENDIX I: REACTIONS OF DIENES 119

APPENDIX II: KEY TO NUMBERED STRUCTURES 125

LIST OF TABLES

TABLE		Page
I.	Aromatic Compounds which have given Diene Adducts on Nitration	11
II.	Gas Chromatographic Data	24
III.	Relative Gradients of Proton Chemical Shifts of Dienes Resulting from Addition of Shift Reagent.	33
IV.	Reaction of Dienes with Sulphuric Acid and Acetic Acid-d_4.	53
V.	Reaction of Diene I with Methanol-d_4 and Trifluoroacetic Acid	58
VI.	Products of the Reaction of Diene I with Methanol-d_4 and Trifluoroacetic Acid.	59
VII.	Reactions of Dienes with Dried Acetic Acid-d_4.	104

LIST OF FIGURES

FIGURE		Page
1.	Proposed Reaction Pathway in Nitration.	4
2.	Typical Reactions of Adducts.	17
3.	Change in Chemical Shift of Protons Plotted Against Weight of Shift Reagent	31
4.	Synthesis of Authentic Compounds.	34
5.	Changes in N.M.R. Spectrum during Solvolysis of Diene IA.	50
6.	Proposed Conformation of Dienes and Shift Reagent	76

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CHAPTER I

INTRODUCTION

1.1

The nitration of aromatic compounds is one of the most widely-studied reactions in organic chemistry. Nitration is of practical importance in the production of nitro-compounds as explosives (e.g., trinitrotoluene) and synthetic intermediates.

Aromatic nitro-compounds are intermediates in the synthesis of phenols, anilines, azo dyes, and the many other compounds which are products of the reduction and diazotisation of the nitro group. In theoretical chemistry, nitration has been extensively studied as the model for the class of reactions known as electrophilic aromatic substitution. In recent years much attention has been focused on products of nitration whose formation does not follow the patterns and mechanisms deduced from the study of the above-mentioned conventional nitrations.

Nitration is typically carried out using solutions of nitric acid in sulphuric acid or oleum, with the concentration of the sulphuric acid being adjusted to produce the desired strength of nitrating mixture (1a,2).

For synthetic work a balance must be achieved among completion of reaction to the desired mononitration product, freedom from side reactions, and the susceptibility of the aromatic substrate to undergo nitration: the familiar activation or deactivation of a compound with respect to benzene. For compounds such as aromatic esters, hydrolysis of the functional group takes place in the mixed acid nitrating mixtures, and for highly activated compounds such as phenols and anilines the oxidising and powerful nitrating properties of nitric acid in sulphuric acid make a less acidic nitrating system desirable. Therefore, nitrating systems involving aqueous nitric acid, nitric acid in inert organic solvents, nitric acid in acetic acid or acetic anhydride, alkyl nitrates in sodium ethoxide solution, and nitronium salts in inert organic solvents, especially sulpholan (3), have been developed (1a). Solutions of nitric acid in acetic acid are frequently used in preparative work; solutions of nitric acid in acetic anhydride form acetyl nitrate and have the advantages of increased solubility of organic substrates compared to aqueous or mixed acid systems and of the relatively mild nitrating properties useful for nitration of highly activated compounds.

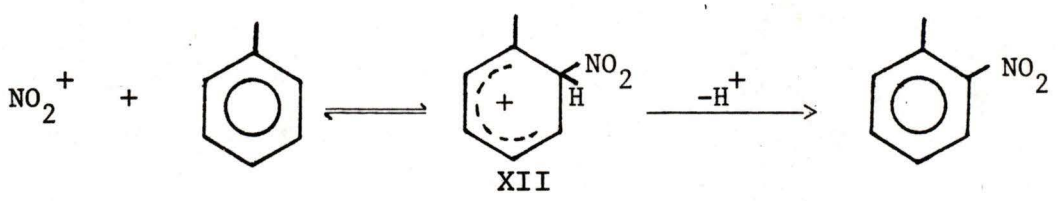
The use of nitrating systems for kinetic and mechanistic studies imposes more stringent requirements upon the system: rates of reaction must be suitable for

measurement, the system should be homogeneous, there should be no doubt as to the nature of the species in solution, and the reaction under study should proceed cleanly, without side reactions. Rates of nitration of aromatic systems more reactive than benzene are too fast to be determined directly so the competitive system developed by Ingold (4) is used to study the relative reactivities of these compounds. Acetic anhydride is not an ideal solvent for kinetic studies of nitration as there is some uncertainty about the actual nature of the electrophile in the solution (1b), although arguments have been advanced recently to show that nitronium ion is the active electrophile as it is in almost all nitrating systems (5). In nitronium salt solutions nitration may occur at the encounter-rate between substrate and nitronium ion: this diffusion-limited reaction does not give reliable kinetic results (1c).

The mechanism of electrophilic aromatic substitution has been elucidated through the study of nitration. The orientation of substitution was determined through analysis of the ratio of isomers formed in mononitration experiments (6), and relative reactivities of the *ortho*-, *meta*-, and *para*-positions have been calculated and explained in terms of electronic and steric effects of substituents. In synthesis of nitro compounds, the desired mononitroaromatic derivatives have often been contaminated with dinitro compounds and, in appropriate systems, with the unexpected

products of non-conventional electrophilic aromatic substitution (7).

Electrophilic aromatic substitution reactions in general, and specifically nitration, have been considered to proceed through the formation of a Wheland intermediate (XII)(8), a cyclohexadienyl cation (also known as a sigma complex or phenonium ion)(6b). For toluene, this process is represented (for *ortho*- substitution) as:



XII

In solutions of nitronium salts (3) and in aqueous sulphuric acid solutions of nitric acid (9), where reaction occurs at the encounter rate between the activated aromatic compounds and the electrophile, the occurrence of rate-limiting formation of a π-complex rather than the σ-complex (XII) has been proposed (3). The reaction profile would then be a curve with three minima (Fig. 1).

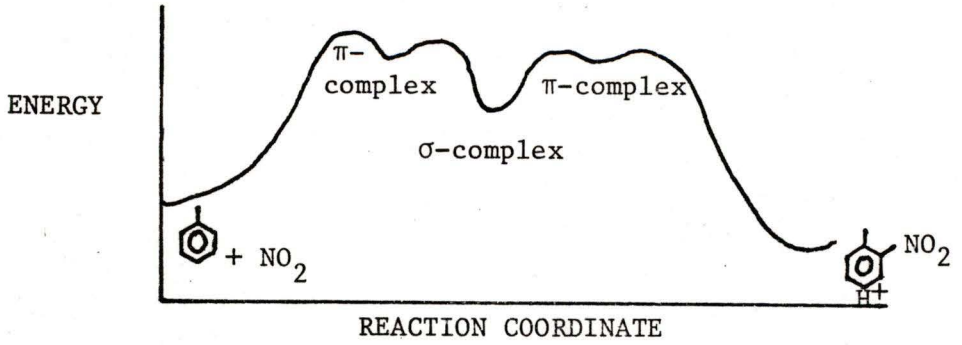
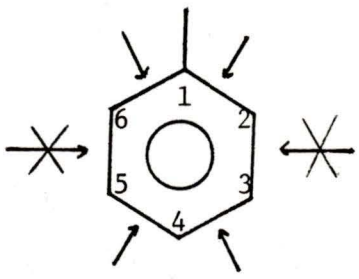


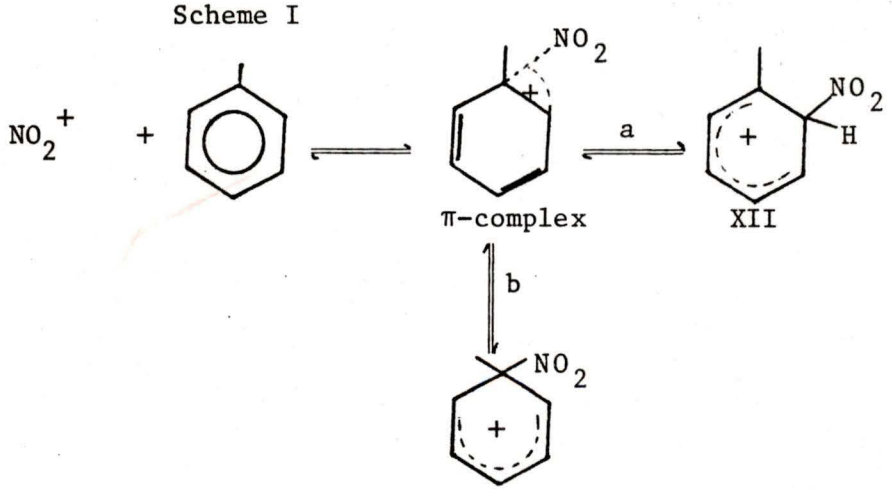
Fig. 1. Proposed Reaction Pathway in Nitration (3)

In this approach, Olah (10) has invoked molecular orbital theory to explain the orientation of substitution. The formation of the π-complex must take place with the highest occupied molecular orbital and at bonds bearing the same sign as (the lowest unoccupied molecular orbital of) the nitronium ion--in toluene this means the C1-C2, C1-C6, C3-C4, or C4-C5 bonds but not the C2-C3 or C5-C6 bonds.



Thus XII is formed according to the following scheme:

Scheme I



Formation of the *meta*- and *para*-cyclohexadienyl cations would require the formation of the isomeric π-complex. Schofield and his collaborators have shown that positional selectivity in nitration is maintained even when substrate selectivity

is lost (9). This occurs in the situation where the substrates are so reactive that they react at the encounter-controlled limit. This observation requires the existence of an "encounter-pair" which may well correspond to Olah's "π-complex."

The overall kinetic scheme for nitration with nitric acid involves two separate reactions, both of which can be separated into a number of discrete steps. The first part of the reaction, generation of the attacking species (nitronium ion), is not seen in nitronium salt reactions:

$$2\ HNO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O\text{-}NO_2^+ + NO_3^- \qquad (1)$$

$$H_2O\text{-}NO_2^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2O + NO_2^+ \qquad (2)$$

The attack of the electrophile on the aromatic system is composed of the two steps mentioned above:

$$NO_2^+ + ArH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\substack{\pi\text{-complex or}\\ \text{encounter pair}}}{[ArHNO_2]^+} \qquad (3)$$

$$[ArHNO_2]^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Ar^+\!\!<\!\!\begin{matrix} NO_2 \\ H \end{matrix} \qquad (4)$$

σ-complex

Equations (1) - (4) explain the observations of kinetic orders and products of nitration. For values of $k_3 \gg k_{-2}[H_2O]$, which is the case for substrates more reactive than benzene, the rate of nitration is

$$\text{rate} = k_2[H_2ONO_2^+].$$

In this situation the rate-determining step is formation of nitronium ion. When $k_{-2}[H_2O] \gg k_3[ArH]$ the reaction is first-order in aromatic substrate and the rate-determining step is the reaction of the nitronium ion with the substrate. This occurs for deactivated compounds or low concentrations of aromatic.

For reactive substrates in situations where the formation of nitronium ion is fast, the rate is limited by the encounter-rate (equation (3)): the reaction between nitronium ion and substrate is diffusion-controlled. The importance of equations (3) and (4) is that in the diffusion-controlled case equation (3) gives the overall rate of nitration, while (4) gives the isomer distribution among the products (10). Equilibrium (4) is actually the sum of six equilibria (for six-membered ring systems) each of which represents the formation of a particular σ-complex (either a Wheland intermediate or an *ipso*-cation) from the initially formed encounter pair (9). In reactions occurring at a rate much below the diffusion-controlled encounter rate (i.e., for $k_4[Ar^+NO_2] < k_3[ArH][NO_2^+]$) the components of k_4 are rate-determining and product-determining--this is the situation which exists in most electrophilic aromatic substitutions. Under suitable conditions, however, any of steps (2) - (4) may be rate-determining.

In acetic anhydride solutions, equilibria (1) and (2) above are replaced by:

$$Ac_2O + HNO_3 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} AcONO_2 + AcOH \quad (5)$$

$$AcONO_2 + H^+ \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} AcONO_2,H^+ \quad (6)$$

$$AcONO_2,H^+ \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} AcOH + NO_2^+ \quad (7)$$

Encounter-control has also been observed for reactions of reactive substrates (e.g., mesitylene) in acetic anhydride (1b).

The σ-complex in step (4) leads to the products of nitration. In cases where the nitronium ion is geminal to a hydrogen (e.g., XII), the cation is a Wheland intermediate and in the next step it loses the hydrogen as a proton to give the nitrated product. If the nitronium ion is attached to the aromatic nucleus at a position which is substituted by some group other than hydrogen (or one of its isotopes), e.g., XIII, from pathway (b), Scheme I, then the substrate has undergone *ipso*-attack, a term introduced by Perrin & Skinner (11).[1] The cation generated by *ipso*-attack may undergo a wider range of reactions than a Wheland intermediate. Such reactions are (13):

(1) return to encounter pair (π-complex) or starting materials;

---

[1] Pathway (b), formation of the *ipso*-cation, is relatively unimportant in the nitration of toluene (12)--only 3-4% of the aromatic nitro-product from nitration of toluene in acetic anhydride at -30°C was derived from *ipso*-attack, compared with ca. 60% o-nitrotoluene from nitration at 0°C (3a).

(2) loss of the substituent geminal to the electrophile to give an *ipso*-substituted product;

(3) rearrangement by nitro-group migration (usually in a 1-2 fashion) to give a Wheland intermediate or another *ipso*-cation (14);

(4) migration of the geminal substituent and subsequent loss of hydrogen to give a rearranged nitration product;

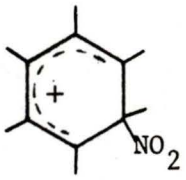
(5) loss of a proton or other leaving group from a substituent remote from the *ipso* position; and

(6) capture by a nucleophile.

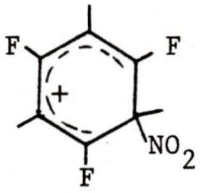
The products of the reactions in groups (2) - (6) above are the products of non-conventional electrophilic substitution (7) and include side-chain substituted compounds, dienones and quinones, rearranged nitro-aromatics, coupled products such as biphenyls and diphenylmethanes, adducts with 1,2- and 1,4-cyclohexadienyl structures (15) and the aromatic acetates and phenols which are decomposition products of such dienyl adducts. It should be re-emphasized that the unifying concept in the production of such a diverse set of compounds is the attack by an electrophile on a substituted position of an aromatic system.

The most direct evidence for the existence of the *ipso*-cation intermediates in electrophilic substitutions would be the isolation of such an ion from a reaction mixture. Olah (16) has prepared the carbonium ions XIV, XV,

XVI, and XVII and obtained their n.m.r. spectra at low



XIV



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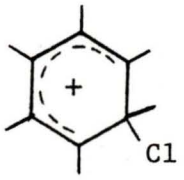

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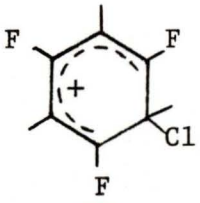


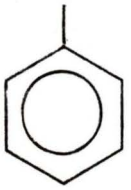
XVII

temperatures. Compounds XIV-XVII have in common the feature that they lack ring substituents which can be easily eliminated and this greatly enhances their stability.

Another approach to the problem of studying unstable species is to trap the desired reactive intermediate. For radical intermediates trapping agents such as phenyl-t-butyl nitrone are used (17). Nucleophiles and nucleophilic solvents have been used to capture carbonium ions (*ipso*-cyclohexadienyl cations) formed in nitration mixtures following the report of the isolation of acetoxynitro-adducts from the nitration of *o*-xylene, *p*-xylene, hemi-mellitene, and 3-bromo-*o*-xylene (18b). Acetoxynitro adducts have been isolated or detected from the nitration of more than twenty-five aromatic systems (Table I) and many of the adducts have been further reacted to give cyclohexadienols, cyclohexadienyl methyl ethers, and chlorocyclohexadienes.

Myhre (14,41,42) and his group, Schofield (43) and co-workers, and Hahn (39,44) have made use of isolable acetoxynitro adducts to generate *ipso*- cyclohexadienyl cations for studies in which Wheland intermediates are not

TABLE I: Aromatic Compounds Which Have Given Diene Adducts on Nitration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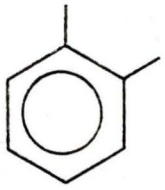
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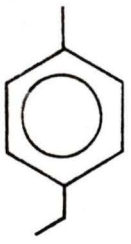
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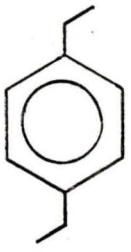
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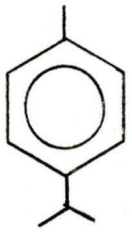
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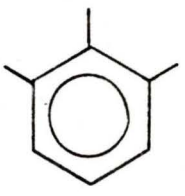
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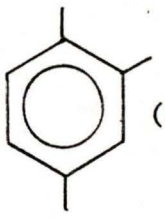
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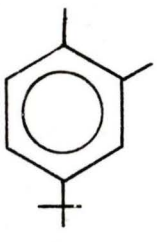
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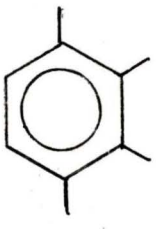
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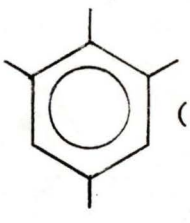
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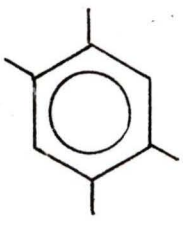
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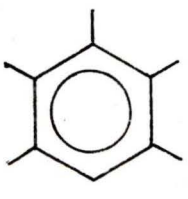
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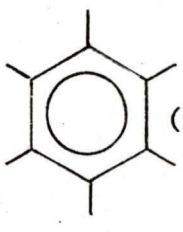
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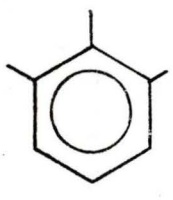
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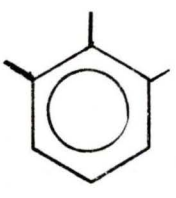
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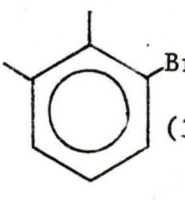

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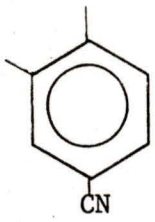

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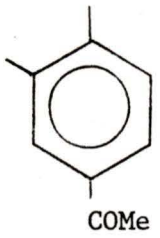

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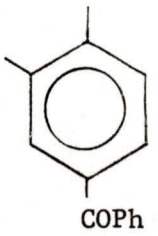

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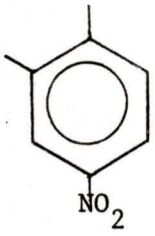

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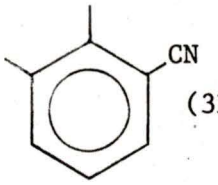

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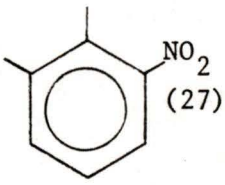

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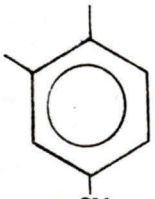

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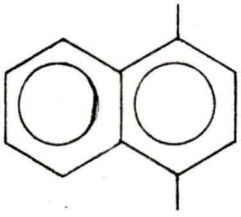

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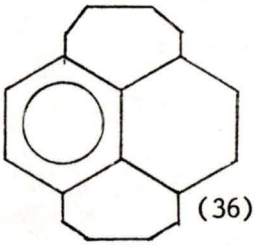

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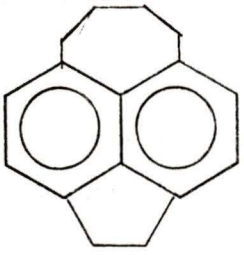

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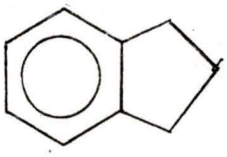

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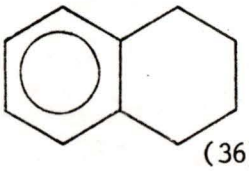

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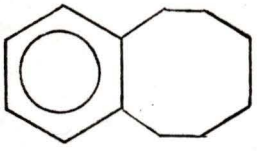

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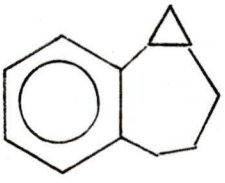

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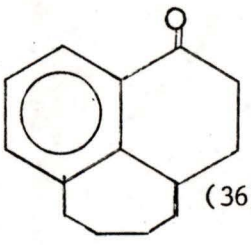

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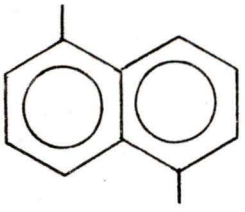

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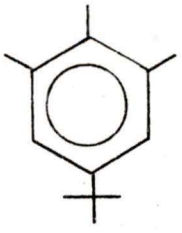

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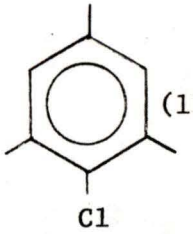
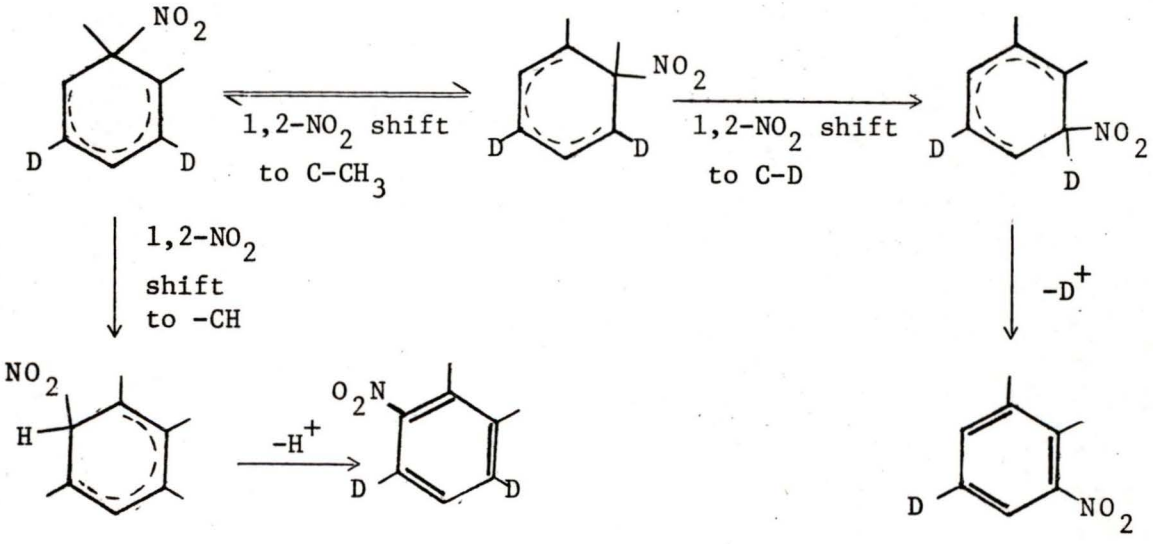


(13)

initially present. Among the interesting results of such studies is Myhre's (14) evidence that the 1,2-nitro shift between adjacent substituted positions is much faster than that between a substituted and unsubstituted position (i.e., interconversion of *ipso*-cations is faster than formation of a Wheland intermediate from an *ipso*-cation) (Scheme 2). If there was no shift between the methylated positions, then the di-deuterated product would be formed quantitatively; with the rate of shift between methylated positions much greater than the rate of migration from a substituted to a hydrogen-bearing carbon, the ratio of mono-:di-deuterated compound would approach 1:1, as was observed.

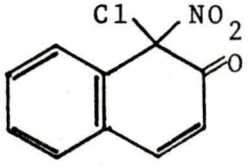


Scheme 2

In this work, and in two previous studies (19,20), the formation of adducts by attack of nitronium ion *ipso* to ethyl groups has been investigated. Products from electro-

philic attack *ipso* to methyl are well-known, and include many 1,4-acetoxynitro adducts, as well as rearomatised products from ions such as the 1,4-diethyl-4-nitrocyclohexadienyl cation, IV, and the 1-acetoxy-1,4-diethylcyclohexadienyl cation, VIII. Attack by nitronium ion *ipso* to isopropyl groups leads to elimination of the isopropyl carbonium ions, giving the dealkylated aromatic products. These studies on ethylbenzenes were initiated in order to determine the behaviour of the ethyl group in *ipso*-nitration. The detection of products from *ipso*-attack on isopropyl groups indicated that the steric hindrance of the ethyl group (in comparison to that of methyl groups) would not prevent *ipso*- attack. However, the greater stability of the secondary isopropyl carbonium ion compared to the primary ethyl carbonium ion indicated that isolation of adducts of ethylbenzenes should be possible.

Perrin (45) established an order of leaving ability for various electrophiles as leaving groups using hydrogen isotope effects and reactions of 1-chloro-1-nitro-2-oxo-1,2-dihydronaphthalene (XVIII). The sequence of increasing



XVIII

leaving ability was: $NO_2^+ < iPr^+ \sim SO_3 < t\text{-}Bu^+ \sim ArN_2^+ < ArCHOH^+ < NO^+$ for S_N1-type reactions, and: $Me^+ < Cl^+ <$

$Br^+ < D^+ \sim RCO^+ < H^+ \sim I^+$ for S_N2-type displacements. Hartshorn (7) combined these orders to give an electrofugal series: $Me^+ < Cl^+ \sim NO_2^+ < iPr^+ \sim SO_3 < Br^+ < t\text{-}Bu^+ \sim D^+ \sim ArN_2^+ \sim RCO^+ < NO^+ \sim H^+ \sim I^+$. Although the order of leaving ability depends on reagents and solvents, the above electrofugal (46) order allows qualitative conclusions and predictions to be made. Unfortunately, the ethyl group has not been studied with respect to its leaving ability, so a prediction before the experiment could not be made. The observation of nitration *ipso* to chlorine (47), methyl, and ethyl and the loss of bromo- (48) and isopropyl (49) substituents on nitration suggest a location for ethyl in the series: in the S_N1 series it must come before isopropyl (which is eliminated) or in the S_N2 series it must come before bromine (which is also eliminated).

The nitration and formation of adducts of toluene, *o*-xylene, *p*-xylene, pseudocumene (1,2,4-trimethylbenzene), and 1,5-dimethylnaphthalene were investigated by Ramsay (23). The rearomatisation reactions of the diene adducts in this series of compounds were split into two groups: toluene and *o*-xylene gave adducts with the acetate group bonded to a secondary carbon while the *p*-xylene and pseudocumene adducts were tertiary acetates. The secondary adducts underwent rearomatisation via 1,4-elimination of nitrous acid, giving aromatic acetates as the products of nitration. These reactions were also reported by Blackstock (18) and the

results used to show the importance of *ipso*-attack in the production of acetates during nitration.

The reactions of the *p*-xylene and pseudocumene adducts which Ramsay studied serve as the model for reactions of tertiary acetate adducts, including the reactions of the dienes from *p*-diethylbenzene. The chemistry is complex and includes exchange of the acetate for other nucleophiles under acid-catalysed conditions, rearomatisation to give side-chain (benzylic) derivations, rearomatisation with migration of the acetate group leading to aryl acetates, migration of the nitro group under strongly acidic conditions to produce nitro-compounds, and hydrolysis of the acetate function under basic conditions to give cyclohexadienols and phenols (Fig. 2).

The symmetry of 1,4-disubstituted compounds such as *p*-xylene and *p*-diethylbenzene tends to obscure the mechanism of rearrangement reactions and migrations of functional groups, as 1,2-processes cannot be distinguished from 1,3-shifts. Studies of pseudocumene, prehnitene (1,2,3,4-tetramethylbenzene) (25), and isodurene (1,2,3,5-tetramethylbenzene) (25) allow the orientation of rearrangements to be deduced. Of especial interest is the formation of benzylic compounds through the postulated trienyl intermediates with an exocyclic methylene structure:

FIGURE 2A

Reactions of
Adducts of *P*-xylene

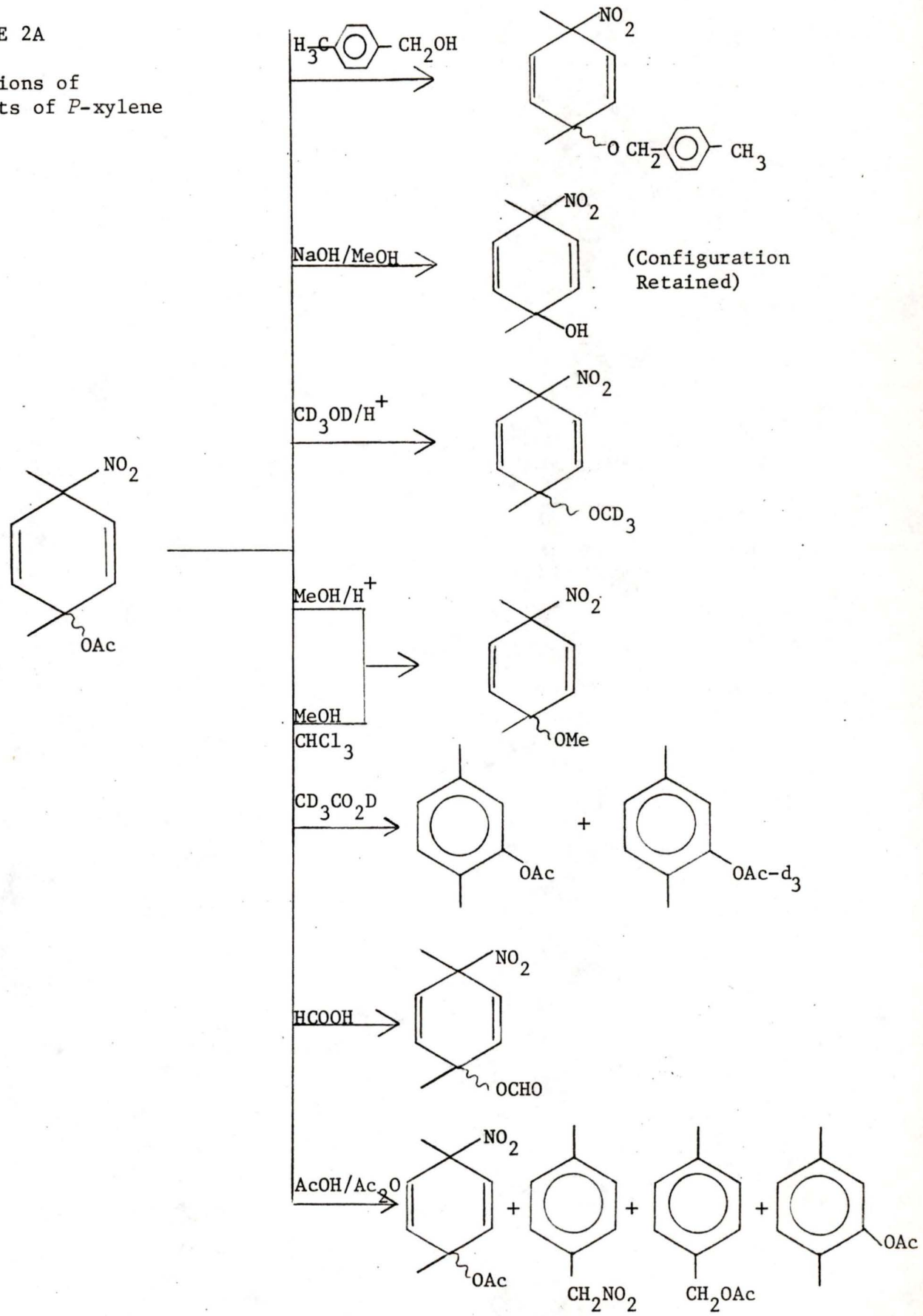
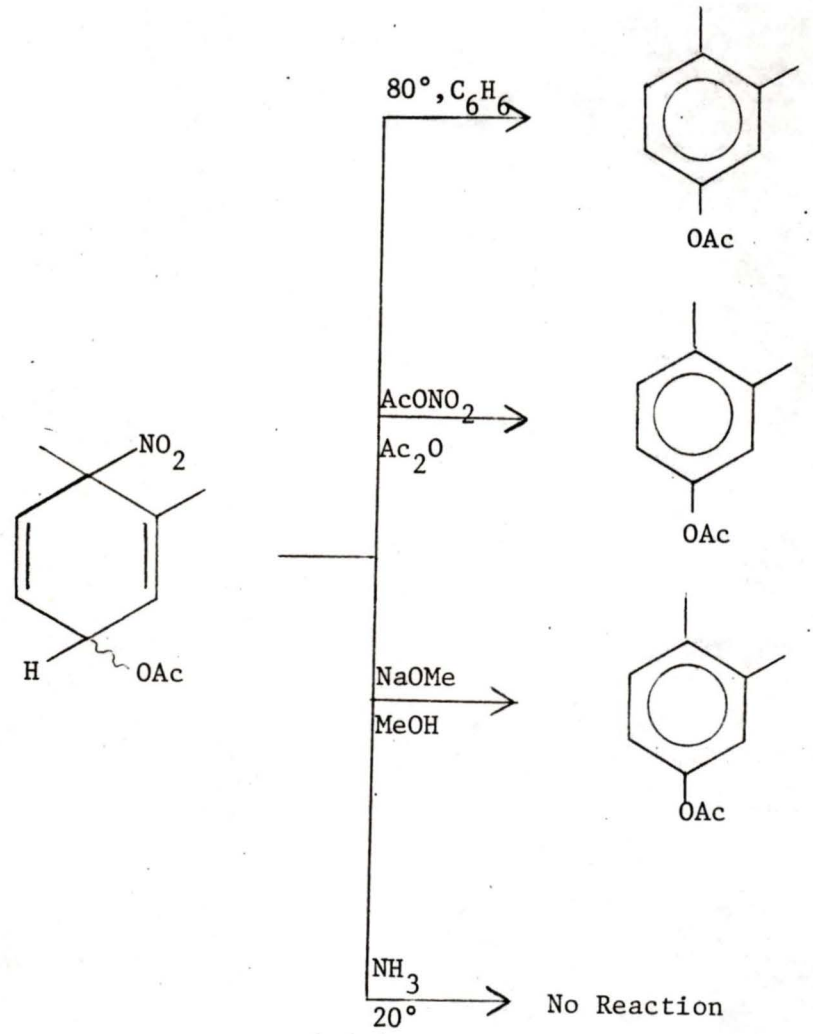
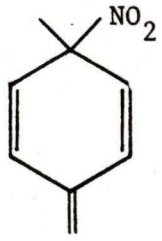


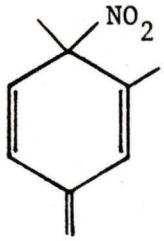
FIGURE 2B

Reactions of Adducts
of *O*-xylene-type Systems





XIX



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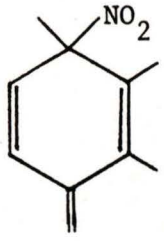
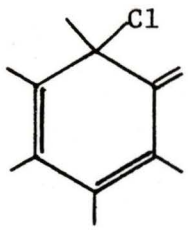


XXI

A common feature of the three intermediates shown above is the *para*-quinoid structure. In chlorinations of hexamethylbenzene, in which the side-chain product is formed, an *ortho*-quinoid structure has been proposed to explain the retention of chlorine in the product (7) (as



opposed to solvolysis to benzylic acetate when the chlorination is carried out in acetic acid). For nitration of a variety of compounds, only products arising from substitution in the alkyl group *para*- to the position most activated towards *ipso*-attack have been found (25).

The foregoing discussion has been concerned with electrophilic aromatic substitution by the nitronium ion, leading to nitro-products. Two other classes of electrophilic reaction are also of interest: nitration via nitrosation and halogenation. Nitrosation is only important

in the nitration of highly activated aromatic compounds, e.g., mesitylene, phenols, and anilines. This reaction is the result of attack by the nitrosonium ion, NO^+, which is formed from nitrous acid in an excess of nitric acid according to the following expression (1d):

$$HNO_3 + HNO_2 \longrightarrow N_2O_4 + H_2O \quad (8)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \quad (9)$$

$$N_2O_4 + ArH \longrightarrow ArNO + HNO_3 \quad (10)$$

$$NO^+ + ArH \longrightarrow ArNO + H^+ \quad (11)$$

$$ArNO + HNO_3 \longrightarrow ArNO_2 + HNO_2 \quad (12)$$

The kinetic form of the reaction has been elucidated, but is rather complex. However, the important point is that nitrous acid is released from nitroacetoxy adducts under various conditions, and when phenols are present (from hydrolysis of aryl acetates) nitrophenols can be expected to be reaction products.

Non-conventional electrophilic aromatic substitution is a feature of halogenation as well as nitration, especially in the reactions of molecular chlorine or bromine in acetic acid (7). Side-chain substitution accompanying halogenation is not a free-radical reaction but is an electrophilic process with a mechanism resembling that of *ipso*-nitration. The formation of the side-chain halides has been claimed to result from an intramolecular rearrangement of the electrophile to the *ortho*-alkyl group, rather than an

intramolecular reaction at the *para*-alkyl group as is seen in nitration. However, the attack of the electrophile at a substituted position is a feature of the halogen reactions.

1.2 Objectives of Present Work

The nitration of *p*-diethylbenzene and the production of compounds derived from *ipso*-attack of nitronium ion from acetyl nitrate at the ethyl-substituted position of the aromatic system was to be studied and related to similar studies of benzenoid (monocyclic aromatic) hydrocarbons. The chemistry of the adducts formed by trapping of acetate by the initially formed nitrocyclohexadienyl cation, IV, is studied under various conditions. A feature of the work which has recently become of interest is the ^{13}C n.m.r. spectra of the various compounds, and these spectra were obtained from dienes formed from *p*-xylene as well as from adducts from *p*-diethylbenzene.

CHAPTER II

EXPERIMENTAL

2.1 Instrumentation

^{1}H n.m.r. spectra were recorded on a Perkin-Elmer R-12-A (60 MHz) spectrometer or a Perkin-Elmer R-32 (90 MHz) spectrometer. Deuterochloroform with 1% v/v tetramethylsilane as reference was used as the solvent for spectra of reaction products and the n.m.r. spectra of fractions obtained from chromatography were measured in carbon tetrachloride. I.r. spectra were recorded on a Perkin-Elmer 337 spectrophotometer calibrated with polystyrene. Spectra of oils were obtained as thin films between sodium chloride plates and solid samples were ground with potassium bromide and pressed into translucent discs. ^{13}C n.m.r. spectra were obtained in deuterochloroform solution with tetramethylsilane as internal standard on a Nicolet TT-14 (15.1 MHz) spectrometer. Mass spectra of authentic samples were obtained as methane chemical ionisation spectra on the Finnegan 3300 system, and g.l.c.-m.s. of product mixtures were run with a 3% S.E.-30 column held at 160°C. G.l.c. analyses were carried out on a Varian Aerograph 2440 gas chromatograph with Westronics recorder and Disc

integrator. Separations were achieved using a 1.3 m X 3 mm column of 3% SE-30 on Chromosorb P 80-100 A.W. at 140°C, or a 3 m X 3mm column of 10% FFAP on Varaport 30 at 160°C. Calibration of the gas chromatograms for retention time and detector response was carried out using *o*-nitrophenol as internal standard (Table II).

2.2 Reagents

p-Diethylbenzene (98%), ethylbenzene (99%), *p*-xylene (99%) were Aldrich; acetic anhydride was certified ACS, Fisher; nitric acid (fuming, Fisher) (300 cm^3) was distilled at 100 Pa from urea (10 g, reagent, Fisher) and sulphuric acid (500 cm^3, reagent A.C.S., Allied) and stored at -25°C; lithium aluminum hydride (95%) was Ventron; aluminum chloride was anhydrous laboratory reagent (B.D.H.); magnesium sulphate powder for drying purposes was anhydrous reagent (M.C. & B.); boron trifluoride etherate was Aldrich; trifluoromethanesulphonic acid was M.C. & B.; trifluoro-acetic acid was Eastman, trifluoroacetic anhydride (99+%) was Aldrich Gold Label; dimethylsulphate was B.D.H. laboratory reagent; methyl iodide was Fischer certified A.C.S.; and ammonia was Linde. Solvents used were methylene chloride (Amachem Reagent), methanol (Amachem anhydrous), ether (Amachem anhydrous) and pentane (technical). Ether was distilled from sodium and stored in glass bottles over molecular sieves, while pentane was distilled from

TABLE II

Gas Chromatographic Data

Compound	SE-30 Retention[1] (min)	FFAP Retention[2] (min)	Detector response
Ethylbenzene	3.0	-	-
p-Diethylbenzene	3.5	1.4	2.15
p-Ethylstyrene	4.0	2.5	2.31
1-(*p*-Ethylphenyl)-ethyl methyl ether	6.13	3.4	1.96
2,5-Diethylanisole	8.4	4.8	0.59
1-(*p*-Ethylphenyl) ethanol	10.0	26.4	1.0
2,5-Diethylphenol	11.6	71.9	0.37
p-Ethylacetophenone	12.6	16.2	1.78
2,5-Diethylphenyl acetate	17.5	16.9	1.57
2,5-Diethylnitrobenzene	20.5	26.1	0.59
1-(*p*-Ethylphenyl)-ethyl acetate	21.4	18.2	0.72
1-(*p*-ethylphenyl)-nitroethane	23.8	-	-
2,5-diethylnitrophenol	34.1	71.9	0.37
2,4-diethylnitrophenol	-	61.9	-

[1]Column temperature: 140°C; carrier flow rate 15 $cm^3 min^{-1}$.

[2]Column temperature: 160°C; carrier flow rate 15 $cm^3 min^{-1}$.

[3]Relative to *o*-nitrophenol which was assigned response 1.0.

phosphorus pentoxide and stored similarly. Deuterated solvents used for n.m.r. experiments were methanol-d_1, methanol-d_4, deuterium oxide (99+%), and acetone-d_6: these were obtained from Merck, Sharp, and Dohme. Basic alumina (Camag, Activity I) for chromatography was deactivated with 3% of an aqueous solution containing 10% glacial acetic acid (reagent A.C.S., Fisher) while neutral alumina (Camag, Activity I) was deactivated with 3% w/w of distilled water. Removal of solvents was carried out under reduced pressure and temperatures were kept below 30°C for solutions which contained adducts.

2.3a Preparation of Adducts from *p*-Diethylbenzene

Para-diethylbenzene was nitrated in acetic anhydride using conditions found by Ramsay (23) to be appropriate for the preparation of adducts from *p*-xylene. In a typical experiment, cold (-78°C) nitric acid (7.1 g, 0.11 mol) was added dropwise to stirred, cold (-78°C) acetic anhydride (21 cm^3). The mixture was warmed to 0°C with an ice bath, to promote the formation of acetyl nitrate, and then placed in a dry-ice cooled pressure-equalised dropping funnel, and added slowly, with stirring, to a solution of *p*-diethylbenzene (9.65 g, 0.072 mol) in acetic anhydride (24 cm^3) at -78°C. After the addition of acetyl nitrate was complete, stirring was continued while the temperature of the reaction mixture was raised to -45°C; this temperature

was maintained for 20 minutes. No difference in the reaction product was observed when a 30 minute reaction time was used.

2.3b Work-up of Nitration Mixture

The reaction mixture was cooled to -78°C and cold (-78°C) ether (200 cm^3) was added. Ammonia was condensed in a dry-ice (solid carbon dioxide) methanol condenser and dropped into the stirred ethereal solution. The temperature was maintained below -60°C during the neutralisation; this was controlled by varying the rate of addition of ammonia. The completion of neutralisation was detected by the drop in temperature of the solution to -75°C and was confirmed using moistened pH paper. Excess ammonia was aspirated and the solution was warmed to 0°C and filtered; the ethereal solution was dried over magnesium sulphate and the solvent evaporated under reduced pressure at 20°C to yield the crude product (10.12 g). Integration of the ^1H n.m.r. spectrum revealed that diene adducts constituted 47% and aromatic compounds 53% of the reaction product.

2.3c Chromatography of the Reaction Mixture

The reaction product was taken up in a minimum volume of ether and pentane (50:50 mixture) and placed on the top of a column of basic alumina deactivated with 3% of 10% aqueous acetic acid. A 40:1 ratio of alumina to

reaction product was used. The column and eluting solvents were cooled to between -20°C and -40°C and the eluting solvent was varied from 100% pentane to 100% ether in a stepwise fashion throughout the separation.

The solvent was forced under pressure (nitrogen at 35 kPa) through the column to minimise the time during which the dienes were in contact with the alumina.

Fractions of 400 cm^3 were collected and the solvent removed under reduced pressure at 25°C. The fractions were weighed. Each fraction was dissolved in carbon tetrachloride and its ^1H n.m.r. spectrum was recorded and integrated. Similar fractions were combined, and their ^1H n.m.r. spectra re-recorded. Although certain reaction mixtures had formed viscous gels when cooled to -40°C alone, and in pentane solution, crystallisation of the dienes was not achieved.

The first column fractions gave aromatic compounds. *P*-Diethylbenzene (2.68 g, 20 mmol) was obtained from the 2.5% ether fractions. ^1H n.m.r. τ(60 MHz, CCl_4) 3.07 (s, 4, 2-H, 3-H, 5-H, 6-H), 7.46 (q, 4, τ = 7.9 Hz, 1-CH_2 and 4-CH_2), 8.81 (t, 6, J = 7.9 Hz, 1- CH_3 and 4-CH_3); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 135 (100, M + 1), 119 (9, M - CH_3).

2,5-Diethylnitrobenzene (1.09 g, 6.1 mmol) was obtained from the 5% ether fractions: b.p. 106-108 at 400 Pa [lit. (50) 137-140° at 1.6 KPa]; i.r. (film) 1532 and

1350 cm^{-1}($-NO_2$); ^1H n.m.r. τ (60 MHz, $CDCl_3$) 2.33 (br. s, 1, H-6), 2.67 (d, 1, J = 7.8 Hz, H-4), 2.79 (d, J = 7.8 Hz, H-3), 7.17 (q, 2, J = 7.0 Hz, 2-CH_2CH_3), 7.36 (q, 2, J = 7.0 Hz, 5-CH_2CH_3), 8.76 (t, 6, J = 7.0 Hz, 2-CH_2CH_3 and 5-CH_2CH_3); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 180 (100, M + 1), 161 (9.5, $M-H_2O$), 133 (9, $M-NO_2$).

The 10% to 15% ether fractions gave 1-(*p*-ethylphenyl)-nitroethane (3.21 g, 17.9 mmol); i.r. (film) 1550, 1360 ($-NO_2$), 1390, 1275 cm^{-1}; ^1H n.m.r. τ(90 MHz, $CDCl_3$) 2.65 (d, 2, J = 8.4 Hz, 2-H and 6-H), 2.75 (d, 2, J = 8.4 Hz, 3-H and 5-H), 4.45 (q, 1, J = 7.6 Hz, $CHCH_3$), 7.36 (q, 2, J = 7.6 Hz, $-CH_2CH_3$), 8.19 (d, 3, J = 7.6 Hz, $CHCH_3$), 8.79 (t, 3, J = 7.6 Hz, CH_2CH_3); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 133 (100, $M-NO_2$).

Trans-1,4-diethyl-4-nitrocyclohexa-2,5-dienyl acetate, IA, (1.92 g, 8.0 mmol) was eluted in the 30% and 40% ether fractions: i.r. (CCl_4) 1755 and 1255 ($-OCOCH_3$), 1555 ($-NO_2$), 1020, and 815 cm^{-1}; ^1H n.m.r., τ(90 MHz, $CDCl_3$): 3.90 (broad s, 4, 2-H, 3-H, 5-H, and 6-H), 7.86 (q, 2, J = 7.6 Hz, 4-CH_2CH_3), 8.03 (s, 3, $-OCOCH_3$), 8.13 (q, 2, J = 7.6 Hz, 1-CH_2CH_3), 9.08 (t, 3, J = 7.6 Hz, 4-CH_2CH_3), 9.24 (t, 3, J = 7.6 Hz, 1-CH_2CH_3); ^{13}C n.m.r. ($CDCl_3$) δc (TMS): 7.5 (1-CH_2CH_3), 8.2 (4-CH_2CH_3), 21.6 ($OCOCH_3$), 32.3 (1-CH_2CH_3), 32.6 (4-CH_2CH_3), 77.0 (C-1), 88.3 (C-4),

126.1 (C-2 and C-6), 133.8 (C-3 and C-5), 169.4 ($OCOCH_3$).

From the 50% ether fractions a mixture (1.25 g, 5.2 mmol) of the dienes was obtained, in approximately equal proportions, as judged from the dienyl signals of the ^1H n.m.r. spectrum. This mixture was used without further separation of the components in pyrolysis and rearomatisation experiments.

Elution with 75% ether and 100% ether gave the diastereoisomeric diene, *cis*-1,4-diethyl-4-nitrocyclohexa-2,5-dienyl acetate, IB, (2.31 g, 9.7 mmol) as a yellow oil: i.r. (CCl_4) 1745 and 1240 ($OCOCH_3$), 1550 cm^{-1} (NO_2); ^1H n.m.r. τ(90 MHz, $CDCl_3$) 3.78 (d, 2, J = 10.6 Hz, 3-H and 5-H), 3.90 (d, 2, J = 10.6 Hz, 2-H and 6-H), 7.95 (q, 2, J = 7.5 Hz, 4-CH_2CH_3), 8.05 (s, 3, -$OCOCH_3$), 8.17 (q, 2, J = 7.5 Hz, 1-CH_2CH_3), 9.10 (t, 3, J = 7.5 Hz, 4-CH_2CH_3), 9.16 (t, 3, J = 7.5 Hz, 1-CH_2CH_3); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 7.8 (1-CH_2CH_3), 8.3 (4-CH_2CH_3), 21.7 (-$OCOCH_3$), 32.2 (1-CH_2CH_3), 34.1 (4-CH_2CH_3), 76.2 (C-1), 86.5 (C-4), 126.8 (C-2 and C-6), 132.5 (C-3 and C-5), 169.3 ($OCOCH_3$).

2.4 ^1H N.M.R. Shift Reagent Study of Acetoxy Dienes

The lanthanide shift reagent *tris*(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-d_6-4,6-octanedionato-d_3) europium ($Eu(fod)_3$-d_{27}) was used in an experiment to assign the stereochemistry of the acetoxy dienes and to allow the assignments of the signals in the ^1H n.m.r. spectra of the

dienes to be confirmed. Small, carefully weighed increments of shift reagent (7-20 mg) were added to solutions (350 mm^3) of the diene adducts (ca. 50 mg) dissolved in deuterochloroform, with tetramethylsilane as internal standard. Changes in volume of the solution due to the addition of the shift reagent were ignored. The position of the acetate methyl signal for each combination of shift reagent and diene was measured, and the slope of the change of chemical shift against weight of added shift reagent was calculated for each isomer. The positions of the other signals in the spectra were found and the slope of the change of the shift of the signals against the change in shift of the methyl singlet was calculated for every signal of each isomer. The linearity of the relationship of shift reagent added to change in field of the signal was checked using a linear least-squares programme for the Monroe calculator (Fig. 2 and Table III).

Figure 3A: Change in Chemical Shift of the Protons of Diene IA Plotted Against Weight of Shift Reagent

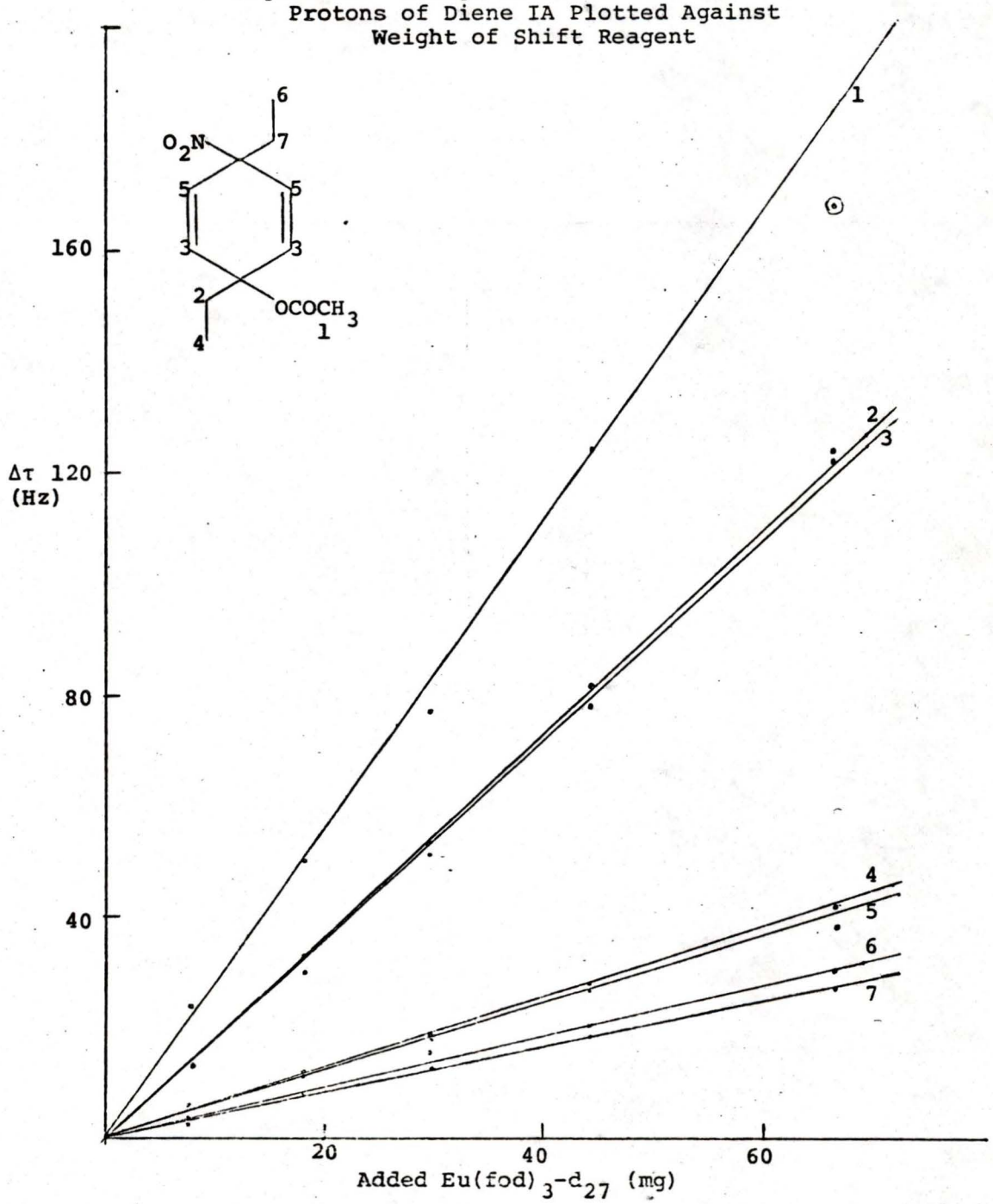


Figure 3B: Change in Chemical Shift of the Protons of Diene IB Plotted Against Weight of Shift Reagent

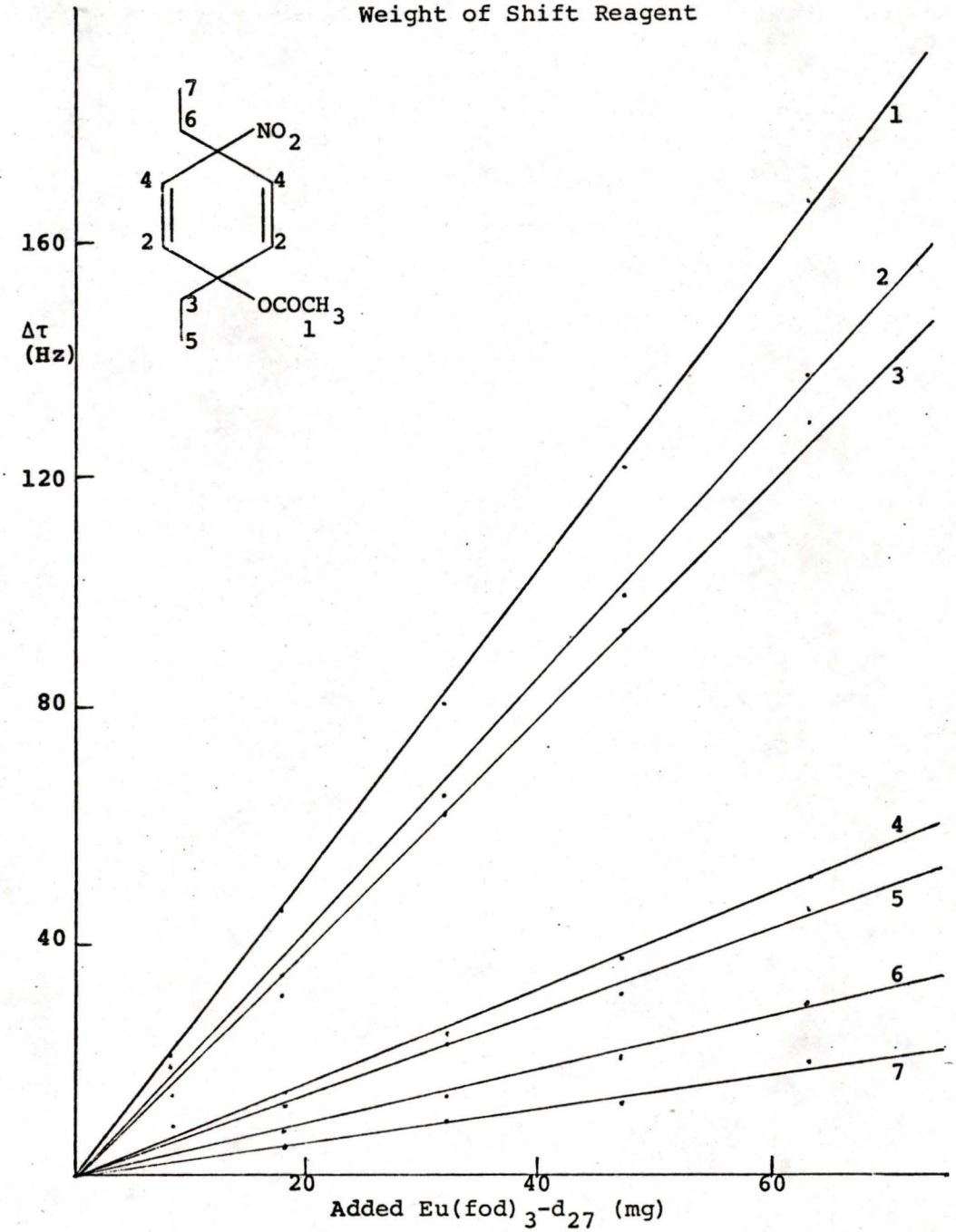


TABLE III

Relative Gradients of Proton Chemical Shifts of Dienes IA and IB Resulting from Addition of $Eu(fod)_3$-d_{27}

Relative Shift	IA	IB
$-OCOC\underline{H}_3$	1.00	1.00
2-$\underline{H}$ and 6-$\underline{H}$	0.76	0.82
3-$\underline{H}$ and 5-$\underline{H}$	0.22	0.30
$1\text{-}C\underline{H}_2CH_3$	0.74	0.78
$1\text{-}CH_2C\underline{H}_3$	0.26	0.28
$4\text{-}C\underline{H}_2CH_3$	0.17	0.18
$4\text{-}CH_2C\underline{H}_3$	0.18	0.12

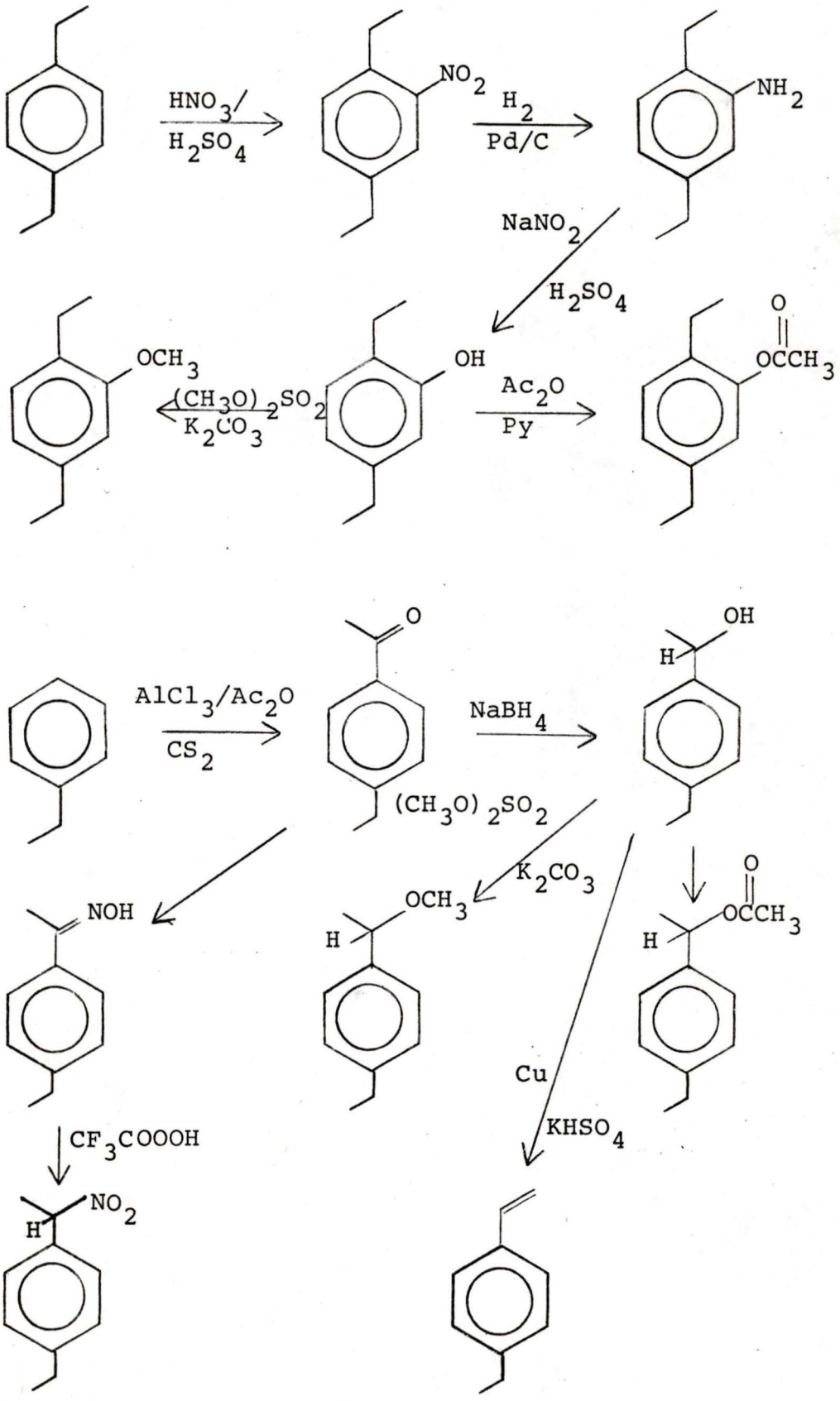
2.5 Preparation of Authentic Samples as Comparison Standards

Two series of authentic compounds were used for comparison with products of rearomatisation reactions of the dienes, as well as with the aromatic products of the nitration reaction. The first series consisted of derivatives of 2,5-diethylnitrobenzene and the second series was derived from 1-(*p*-ethylphenyl)-ethanol or *p*-ethylacetophenone (see Fig. 4).

2.5a 2,5-Diethylnitrobenzene from *p*-Diethylbenzene (2)

A nitrating mixture was prepared from nitric acid (8g, 0.13 mol) and concentrated sulphuric acid (10 cm^3) by

FIGURE 4. Synthesis of Authentic Compounds



cooling both reagents to -5°C and slowly adding the nitric acid to the sulphuric acid. A solution of *p*-diethylbenzene (10 g, 0.075 mol) in acetic acid (10 cm^3) and concentrated sulphuric acid (10 cm^3) was cooled to -5°C, and stirred. The cooled nitrating mixture was added to the *p*-diethylbenzene solution during 35 min. and the reaction mixture was stirred at -5°C for a further 45 min. The product was poured into ice (150 g) and sodium carbonate was added to the ice slurry until a neutral solution was obtained. The organic products were separated by extraction with methylene chloride (3 X 100 cm^3), the combined extracts were washed with water and dried over anhydrous magnesium sulphate. After removal of solvent a ^1H n.m.r. spectrum of the crude product (6.1 g, 0.034 mol) was obtained: this compound was identical with 2,5-diethylnitrobenzene isolated from nitration of *p*-diethylbenzene in acetic anhydride on ^1H n.m.r. and gas chromatographic analysis.

2.5b 2,5-Diethylaniline from 2,5-Diethylnitrobenzene (51)

2,5-Diethylnitrobenzene (6.7 g, 0.037 mol) and 10% palladium on charcoal catalyst were placed in a reaction bottle with ethanol (75 cm^3). The solution was connected to a Parr hydrogenator at room temperature with a hydrogen gas pressure of 200 kPa. After 3 hours, the pressure was 150 kPa and after a further 3 hours with no drop in the pressure, the mixture was filtered and the solvent removed to give

2,5 diethylaniline (5.4 g, 0.036 mol): ^{1}H n.m.r. τ(60 MHz, $CDCl_3$), 3.05 (d, 1, J = 8.0 Hz, 3-H), 3.43 (d, 1, J = 8.0 Hz, 4-H), 3.51 (s, 1, 6-H), 6.65 (broad s, 2, $-NH_2$, disappears on shaking with D_2O), 7.47 and 7.53 (overlapping quartets, 4, J = 7.0 Hz, 2-CH_2CH_3 and 5-CH_2CH_3), 8.78 and 8.80 (overlapping triplets, 6, J = 7.0 Hz, 2-CH_2CH_3 and 5-CH_2CH_3), mass spectrum (chemical ionisation, methane) m/e (relative intensity) 150 (100, M + 1), 134 (13, M-CH_3).

2.5c 2,5-Diethylphenol from 2,5-Diethylaniline (52)

Sulphuric acid (2.5 g) was added to water (10 cm^3) being cooled in an ice-bath. Diethylaniline (1.75 g, 0.012 mol) was added to the diluted sulphuric acid, and more water (10 cm^3) was added. To this cold solution, sodium nitrite (0.9 g, 0.013 mol) dissolved in water (2 cm^3) was added dropwise. Starch-iodide test paper was used to check the reaction for completion. The reaction mixture was stirred and allowed to reach room temperature where it was held for 30 minutes, then heated to 55°C for one hour in a water bath. The reaction mixture was cooled and the product extracted with ether (3 X 25 cm^3) and the combined extracts were washed with water. The ethereal solution of product was shaken with potassium hydroxide solution (2N, 3 X 25 cm^3) and the combined aqueous extracts were acidified with concentrated hydrochloric acid. The free phenols were extracted from the acidic aqueous solution using methylene

chloride (3 X 50 cm^3) and the solvent was removed.

The crude product was put on a column of neutral alumina deactivated with 3% water and eluted with ether-pentane (1:1). Thin-layer chromatography of the column fractions allowed the identical samples to be identified and combined, giving 2,5-diethylphenol (0.50 g, 0.0033 mol): i.r. (film) 3700-3100 (ArOH), 1430, 1120 cm^{-1} (-OH); ^1H n.m.r. τ (60 MHz, $CDCl_3$) 2.95 (d, 1, J = 8 Hz, 3-H), 3.28 (d, 1, J = 8 Hz, 4-H), 3.33 (broad s, 1, 6-H), 5.34 (broad s, 1, ArOH) (disappears after shaking with D_2O), 7.43 (broad q, 4, J = 7 Hz, 2-CH_2CH_3 and 5-CH_2CH_3), 8.79 (t, 6, J = 7 Hz, 2-CH_2CH_3 and 5-CH_2CH_3); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 151 (100, M + 1), 135 (15, M-CH_3), 133 (15, M-OH).

2.5d 2,5-Diethylanisole from 2,5-Diethylphenol

2,5-Diethylphenol (0.50 g, 3.3 mmol), anhydrous potassium carbonate (0.250 g, 1.6 mmol), dimethylsulphate (0.22 g, 1.75 mmol), and reagent grade acetone (1.5 cm^3) were mixed and refluxed for eight hr. After this time, the acetone was removed and water was added to the mixture. The solution was extracted with ether (3 X 5 cm^3) and the ethereal extract was washed with water and dried over anhydrous magnesium sulphate. The solvent was removed to give 2,5-diethylanisole, pure by g.l.c.: i.r. (film) 1460 (-OCH_3), 1265 cm^{-1} (OAr); ^1H n.m.r. τ (60 MHz, $CDCl_3$) 2.98

(d, 1, $\underline{J}$ = 8.0 Hz, 3-$\underline{H}$), 3.30 (broad d, 1, $\underline{J}_{34}$ = 8.0 Hz, 4-$\underline{H}$), 3.36 (s, 1, 6-$\underline{H}$), 6.25 (s, 3, -OC$\underline{H}_3$), 6.59 (q, 2, $\underline{J}$ = 6.7 Hz, 2-C$\underline{H}_2$CH$_3$), 7.40 (q, 2, $\underline{J}$ = 7.0 Hz, 5-C$\underline{H}_2$CH$_3$), 8.77 (t, 3, $\underline{J}$ = 6.7 Hz, 2-CH$_2$C$\underline{H}_3$), 8.82 (t, 3, $\underline{J}$ = 7.0 Hz, 5-CH$_2$C$\underline{H}_3$); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 165 (100, M + 1), 149 (5, M-CH$_3$).

2.5e 2,5-Diethylphenylacetate from 2,5-Diethylphenol

A mixture of 2,5-diethylphenol (0.095 g, 0.63 mmol), pyridine (0.5 cm^3), and acetic anhydride (1.5 cm^3) was stirred for 30 min. The solution was then refluxed for 30 min., cooled to 0°C, and water (5 cm^3) was added. After stirring for 15 min., the cold solution was extracted with ether (4 X 5 cm^3) and the combined ethereal extracts were washed with water. The ethereal extracts were dried over anhydrous magnesium sulphate and the solvent was removed, giving 2,5-diethylphenylacetate: i.r. (film) 1765 and 1206 cm^{-1} (OCOCH$_3$); ^{1}H n.m.r. τ (90 MHz, CDCl$_3$) 2.85 (d, 1, $\underline{J}$ = 8.0 Hz, 3-$\underline{H}$), 2.99 (broad d, 1, $\underline{J}$ = 8.0 Hz, 4-$\underline{H}$), 3.18 (broad s, 1, 6-$\underline{H}$), 7.37 (q, 2, $\underline{J}$ = 7.0 Hz, -C$\underline{H}_2$CH$_3$), 7.51 (q, 2, $\underline{J}$ = 7.0 Hz, -C$\underline{H}_2$CH$_3$), 7.72 (s, 3, -OCOC$\underline{H}_3$), 8.78 (t, 3, $\underline{J}$ = 7.0 Hz, -CH$_2$C$\underline{H}_3$), 8.83 (t, 3, $\underline{J}$ = 7.0 Hz, -CH$_2$C$\underline{H}_3$); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 193 (39, M + 1), 150 (100, M-CH$_2$CO).

2.5f *p*-Ethylacetophenone from Ethylbenzene (53)

To a solution of ethylbenzene (99 g, 0.89 mol) in carbon disulphide (300 cm^3) anhydrous aluminum chloride (266 g, 2.0 mol) was added. The solution was heated to a gentle reflux and acetic anhydride (72.2 g, 0.71 mol) was added slowly over a period of 20 min. The carbon disulphide was distilled off and the product poured into a mixture of ice and hydrochloric acid. The aqueous solution was extracted with ether (3 X 200 cm^3), and the combined extracts were washed with 10% sodium hydroxide solution (300 cm^3) and water (2 X 300 cm^3). The ether was removed and the product distilled under reduced pressure. *p*-Ethylacetophenone (62.8 g, 0.41 mol) was collected at 72°C/50 Pa: i.r. (film) 1680 (-CO), 1275 cm^{-1}; ^1H n.m.r. τ(60 MHz, $CDCl_3$) 2.17 (d, 2, $\underline{J}$ = 8.4 Hz, 2-$\underline{H}$ and 6-$\underline{H}$), 2.77 (d, 2, $\underline{J}$ = 8.4 Hz, 3-$\underline{H}$ and 5-$\underline{H}$), 7.33 (q, 2, $\underline{J}$ = 7.7 Hz, 4-$C\underline{H}_2CH_3$), 7.45 (s, 3, $COC\underline{H}_3$), 8.76 (t, 3, $\underline{J}$ = 7.7 Hz, 4-$CH_2C\underline{H}_3$); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 15.2 ($ArCH_2\underline{C}H_3$), 26.3 ($ArCO\underline{C}H_3$), 28.9 ($Ar\underline{C}H_2CH_3$), 128.0 (<u>C</u>-3 and <u>C</u>-5 or <u>C</u>-2 and <u>C</u>-6), 128.6 (<u>C</u>-2 and <u>C</u>-6 or <u>C</u>-3 and <u>C</u>-5), 135.0 (<u>C</u>-1), 149.8 (<u>C</u>-4), 197.1 (-$\underline{C}OCH_3$); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 149 (100, M + 1), 133 (9, M-CH_3).

2.5g 1-(*p*-Ethylphenyl)ethanol from *p*-Ethylacetophenone (54)

p-Ethylacetophenone (40.07 g, o.27 mol) was added slowly, with stirring, to a solution of sodium borohydride

(3.42 g, 0.09 mol) in ethanol (95%; 75 cm^3). The temperature of the reaction mixture was maintained below 50°C. After standing for 15 min., the reaction mixture was carefully treated with 10% hydrochloric acid solution to dissolve a white precipitate which had formed. The ethanol was removed, the aqueous layer was extracted with ether (3 X 50 cm^3), and the combined ethereal extracts were dried over anhydrous magnesium sulphate. The crude product was distilled under reduced pressure from anhydrous potassium carbonate (8 g) and 1-(*p*-ethylphenyl)ethanol (28.8 g, 0.19 mol) was collected at 85-93°C/50 Pa: i.r. (film) 3600-3150 (-OH), 1095 cm^{-1}; ^1H n.m.r. τ(60 MHz, $CDCl_3$) 2.85 (broad s, 4, Ar$\underline{H}$), 5.32 (q, 1, $\underline{J}$ = 6.5 Hz, -C$\underline{H}$OHCH_3), 7.43 (q, 2, $\underline{J}$ = 7.3 Hz, -C$\underline{H}_2$CH_3), 8.58 (d, 3, $\underline{J}$ = 6.5 Hz, -CHOHC$\underline{H}_3$), 8.80 (t, 3, $\underline{J}$ = 7.3 Hz, -CH_2C$\underline{H}_3$); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 15.6 (-CH_2C$\underline{H}_3$), 25.1 (-CHOHC$\underline{H}_3$), 28.6 (-C$\underline{H}_2$CH_3), 69.8 (-C$\underline{H}$OHCH_3), 125.5 (C-2′ and C-6′), 127.8 (C-3′ and C-5′), 143.0 (C-1′ or C-4′), 143.4 (C-4′ or C-1′); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 149 (5.5, M-1), 132 (100, M-H_2O), 106 (45, M-C_2H_4O).

2.5h 1-(*p*-Ethylphenyl)-nitroethane from *p*-Ethylacetophenone (55)

In this two-step preparation, *p*-ethylacetophenone was first converted to its oxime, which was oxidized with peroxytrifluoroacetic acid to the required nitroethane.

p-Ethylacetophenone (5g, 0.034 mol) was dissolved in ethanol (95%, 20 cm^3) and added to a solution of hydroxylamine hydrochloride (3.7 g, 0.054 mol) in 5% sodium hydroxide (12 cm^3) solution. The solution was heated to 100°C for 10 minutes, then cooled (0°C), and crystallised. *p*-Ethylacetophenone oxime: m.p. 80-82°C (Lit. (56) 82-83°C); ^1H n.m.r. τ (60 MHz, $CDCl_3$) 2.50 (d, 2, J = 8.0 Hz, 2-H and 6-H), 2.87 (d, 2, J = 8.0 Hz, 3-H and 5-H), 7.40 (q, 2, J = 7.6 Hz, 4-CH_2CH_3), 7.82 (s,3,C(NOH)CH_3), 8.80 (t, 3, J = 7.6 Hz, 4-CH_2CH_3).

A solution of pertrifluoroacetic acid was prepared by the careful addition of 90% hydrogen peroxide solution (900 mm^3) to a solution of trifluoroacetic anhydride (5.3 cm^3) in acetonitrile (7.8 cm^3). This solution was dropped over a period of 15 minutes into a solution of *p*-ethylacetophenone oxime (2.5 g, 15.5 mmol), urea (0.33 g, 5.5 mmol), and dibasic sodium phosphate dissolved in acetonitrile (35 cm^3). The reaction mixture was refluxed for one hour, then cooled and poured into water (20 cm^3). On extraction with methylene chloride (3 X 20 cm^3), the mixture formed an emulsion which was broken with filtration through Celite. The combined extracts were washed with brine, dried over anhydrous magnesium sulphate, and the solvent was removed. The product was distilled, giving a clear liquid, b.p. 119°C at 400 Pa.

Investigation of the product by thin layer

chromatography showed that it was composed of two major components. Dry-column chromatography of 350 mg of product on a column of silica (Woelm) using ether-pentane (1:24) as solvent gave two segments from which 1-(*p*-ethylphenyl)-nitroethane (200 mg, 1.1 mmol) was obtained, and two segments from which starting material (*p*-ethylacetophenone) was recovered. 1-(*p*-ethylphenyl)-nitroethane: i.r. (film) 1550, 1275 cm^{-1} (NO_2); ^1H n.m.r. τ (90 MHz, $CDCl_3$) 2.65 (d, 2, $\underline{J}$ = 8.4 Hz, 2′-$\underline{H}$ and 6′-$\underline{H}$), 2.75 (d, 2, $\underline{J}$ = 8.4 Hz, 3′-H and 5′-$\underline{H}$), 4.45 (q, 1, $\underline{J}$ = 7.5 Hz, $-CHNO_2C\underline{H}_3$), 7.36 (q, 2, $\underline{J}$ = 6.5 Hz, $-C\underline{H}_2CH_3$), 8.19 (d, 3, $\underline{J}$ = 7.5 Hz, $-CHNO_2C\underline{H}_3$), 8.79 (t, 3, $\underline{J}$ = 6.5 Hz, $-CH_2C\underline{H}_3$); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 133 (100, $M-NO_2$).

2.5i 1-(*p*-Ethylphenyl)-ethyl methyl ether from 1-(*p*-Ethylphenyl)-ethanol

To a solution of 1-(*p*-ethylphenyl)-ethanol (5 g, 0.033 mol) in dry tetrahydrofuran (100 cm^3, distilled from lithium aluminum hydride) an excess of sodium hydride (4.8 g, 0.2 mol) was added. The resulting mixture was refluxed for two hr. under an atmosphere of dry nitrogen. A test sample was withdrawn and treated with methyl iodide (250 mm^3), then filtered, diluted with acetone, and injected into a gas chromatograph to evaluate the progress of the reaction. The reaction mixture was removed from the heat and methyl iodide

(28 g, 0.2 mol) was added over 20 min. The mixture was stirred and refluxed for 30 min., cooled, and diluted with ether (100 cm^3). The ethereal solution was washed with brine (2 X 100 cm^3) and water (2 X 100 cm^3), dried over anhydrous magnesium sulphate, and the ether was evaporated. The 1-(*p*-ethylphenyl)-ethyl methyl ether had: i.r. (film) 1460, 1265, 1046 cm^{-1}; ^1H n.m.r. τ(60 MHz, $CDCl_3$) 2.84 (s, 4, Ar$\underline{H}$) 5.80 (q, 1, $\underline{J}$ = 6.3 Hz, -C$\underline{H}$(OCH_3)CH_3), 6.85 (s, 3, -CH($O\underline{CH_3}$)CH_3), 7.39 (q, 2, $\underline{J}$ = 7.8 Hz, -$\underline{CH_2}CH_3$), 8.59 (d, 3, $\underline{J}$ = 6.3 Hz, -CH(OCH_3)$\underline{CH_3}$), 8.78 (t, 3, $\underline{J}$ = 7.8 Hz, -$CH_2\underline{CH_3}$); ^{13}C n.m.r. ($CHCl_3$) δc (TMS) 15.6 (-$CH_2\underline{CH_3}$), 24.0 (-CH(OCH_3)$\underline{CH_3}$), 28.7 (-$\underline{CH_2}CH_3$), 56.1 (-CH($O\underline{CH_3}$)CH_3), 79.6 (-$\underline{CH}$(OCH_3)CH_3), 126.2 ($\underline{C}$-2′ and $\underline{C}$-6′), 127.9 ($\underline{C}$-3′ and $\underline{C}$-5′), 140.9 ($\underline{C}$-1′), 143.2 ($\underline{C}$-4′); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 163 (9, M-H), 149 (20, M-CH_3), 133 (100, M-OCH_3). The ether contained about ten per cent of the starting alcohol as an impurity.

2.5j *p*-Ethylstyrene from 1-(*p*-Ethylphenyl)-ethanol (54)

1-(*p*-Ethylphenyl)-ethanol (5.0 g, 0.033 mol), potassium hydrogen sulphate (0.3 g), and copper powder (0.3 g) were heated to 200° and the distillate was collected. The crude product was taken up in ether (50 cm^3) and dried over anhydrous magnesium sulphate. The product was distilled giving *p*-ethylstyrene: b.p. 72°C/2kPa; i.r.

(film) 1630, 1405, 835 cm^{-1}; ^{1}H n.m.r. (60 MHz, $CDCl_3$) (57) 2.70 (d, 2, J = 7.6 Hz, 2-H and 6-H), 2.87 (d, 2, J = 7.6 Hz, 3-H and 5-H), 3.32 (double d, 1, J = 17.3 Hz and J = 10.9 Hz, ArCH = CH_2), 4.38 (double d, 1, J = 17.3 Hz and J = 1.3 Hz, *cis*- ArCH = CHH), 4.87 (double d, 1, J = 10.9 Hz and J = 1.3 Hz, *trans*- ArCH = CHH), 7.40 (q, 2, J = 7.6 Hz, $-CH_2CH_3$), 8.80 (t, 3, J = 7.6 Hz, $-CH_2CH_3$); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 133 (100, M + 1), 103 (5, $M-CH_2CH_3$).

2.5k 1-(*p*-Ethylphenyl)-ethyl acetate from 1-(*p*-ethylphenyl)-ethanol

A solution of 1-(*p*-ethylphenyl)-ethanol (2.5 g, 0.017 mol), acetic anhydride (25 cm^3), and pyridine (10 cm^3) was stirred for half an hour, refluxed for half an hour, cooled to 0°C, and diluted with water (50 cm^3). The aqueous solution was extracted with ether (3 X 50 cm^3) and the combined extracts were washed with water. After drying over anhydrous magnesium sulphate and removal of the solvent, 1-(*p*-ethylphenyl)-ethyl acetate was obtained: i.r. (film) 1745 (-CO), 1370, 1240 cm^{-1}; ^{1}H n.m.r. τ(60 MHz, $CDCl_3$) 2.82 (broad s, 4, ArH), 4.16 (q, 1, J = 6.5 Hz, $CH(OCOCH_3)CH_3$), 7.40 (q, 2, J = 7.4 Hz, $-CH_2CH_3$), 7.98 (s, 3, $-OCOCH_3$), 8.49 (d, 3, J = 6.5 Hz, $-CH(OCOCH_3)CH_3$), 8.78 (t,3, J = 7.4 Hz, $-CH_2CH_3$); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 15.6 ($-CH_2CH_3$), 21.1 ($-OCOCH_3$), 22.1 ($-CH(OCOCH_3)CH_3$), 28.6

($\underline{C}H_2CH_3$), 76.1 (-$\underline{C}H(OCOCH_3)CH_3$), 126.3 ($\underline{C}$-2′ and $\underline{C}$-6′), 128.0 ($\underline{C}$-3′ and $\underline{C}$-5′), 139.2 ($\underline{C}$-1′), 143.8 ($\underline{C}$-4′), 169.8 (-O$\underline{C}OCH_3$); mass spectrum (chemical ionisation, methane) m/e (relative intensity) 191 (2.3, M-H), 177 (1.1, M-CH_3), 150 (1.9, M-$COCH_2$), 132 (100, M-$HOCOCH_3$).

2.6 Exchange Reactions of Dienes

2.6a Preparation of 1,4-diethyl-4-nitrocyclohexa-2,5-dienols (V)

Both isomeric acetoxynitro dienes were reduced to their corresponding alcohols ("hydroxy dienes") by aluminum hydride (58). Aluminum hydride was prepared and used as a solution in tetrahydrofuran: aluminum chloride (835 mg, 6.3 mmol) was added to a stirred mixture of lithium aluminum hydride (730 mg, 19.2 mmol) in tetrahydrofuran (60 cm^3). After fifteen minutes of stirring, the insoluble materials were filtered from the aluminum hydride reagent.

To aluminum hydride reagent (30 cm^3) at 0°C, a solution of acetoxy diene (IA) (200 mg, 0.84 mmol) in dry tetrahydrofuran (1 cm^3) was added and stirred. After fifteen minutes, water was dropped into the reaction mixture to decompose the excess aluminum hydride reagent. Ether (25 cm^3) followed by brine (25 cm^3) was added to the tetrahydrofuran solution; the ether layer was separated, the aqueous layer was extracted with more ether (3 X 25 cm^3), and the combined ethereal solution was dried over anhydrous

sodium sulphate. On removal of the solvent, *trans*-1,4-diethyl-4-nitrocyclohexa-2,5-dienol, VA (115 mg, 0.58 mmol) was obtained. On recrystallisation from ether-pentane the hydroxy diene gave white needles: m.p. 64.5-65.5°C; i.r. (KBr) 3530-3150 (-OH), 1540 ($-NO_2$), 1017 and 811 cm^{-1}; ^1H n.m.r. τ(60 MHz, $CDCl_3$) 4.0 (s, 4, 2-H, 3-H, 5-H, 6-H), 6.30 (s, 1, -OH), 7.91 (q, 2, J = 7.3 Hz, 4-CH_2CH_3), 8.35 (q, 2, J = 7.8 Hz, 1-CH_2CH_3), 9.12 (t, 3, J = 7.3 Hz, 4-CH_2CH_3), 9.26 (t, 3, J = 7.8 Hz, 1-CH_2CH_3); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 8.2 (1-CH_2CH_3), 8.5 (4-CH_2CH_3), 32.9 (1-CH_2CH_3), 33.4 (4-CH_2CH_3), 68.9 (C-1), 87.7 (C-4), 125.4 (C-2 and C-6), 137.3 (C-3 and C-5).

2.6b Preparation of *cis*-1,4-diethyl-4-nitrocyclohexa-2,5-dienol

Cis-1,4-diethyl-4-nitrocyclohexa-2,5-dienol, VB (70 mg, 0.36 mmol) was prepared in the same manner as hydroxy diene VA, starting from acetoxynitro adduct 1B. VB was crystallised to white needles from ether-pentane: m.p. 52-53°C; i.r. (KBr) 3500-3100 (-OH); 1540 ($-NO_2$), 1010 and 812 cm^{-1}; ^1H n.m.r. τ(60 MHz, $CDCl_3$) 3.95 (s, 4, 2-H, 3-H, 5-H, 6-H), 6.35 (broad s, 1, -OH), 7.91 (q, 2, J = 7.3 Hz, 4-CH_2CH_3), 8.38 (q, 2, J = 7.8 Hz, 1-CH_2CH_3), 9.14 (t, 3, J = 7.3 Hz, 4-CH_2CH_3), 9.20 (t, 3, J = 7.8 Hz, 1-CH_2CH_3); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 8.3 (1-CH_2CH_3 and 4-CH_2CH_3), 33.3 (1-CH_2CH_3), 33.4 (4-CH_2CH_3), 68.1 (C-1), 87.7 (C-4), 125.4 (C-2 and C-6), 136.7 (C-3 and C-5).

2.6c Reaction of Diene IA with 0.1% Sulphuric Acid in Methanol-d_4

Acid-catalysed exchange reactions of the acetoxy dienes with nucleophilic solvents were studied using ^1H n.m.r. spectrometry. After the reactions were complete, the mixture was diluted with ether (5 cm^3), cooled to -78°C, and neutralised with ammonia. After filtration of the neutral solution, the product was dried over anhydrous magnesium sulphate, the solvent removed, and the products were analysed by g.l.c., g.l.c.-m.s., and ^1H n.m.r.

Acetoxy diene IA (35 mg, 0.15 mmol) was dissolved in methanol-d_4 (315 mm^3). To this was added a solution (35 mm^3) of 1% w/v sulphuric acid in methanol. The progress of the reaction at 35°C was monitored using ^1H n.m.r. The signal at τ 3.88 p.p.m. due to the vinyl protons of the acetoxy diene decayed from 100% of the signal between τ 3.5 and τ 4.5 p.p.m. at the start of the experiment, to 70% after ten minutes, to 20% after 30 minutes, and to zero after 110 minutes. Broad singlets at τ 3.65 and 3.80 p.p.m., and doublets at τ 4.05 and 4.23 p.p.m. appeared and increased in intensity during the course of the experiment. These were the peaks of the vinyl quartets of the methoxyl adducts (VI A and VI B). By the time that the starting diene had been replaced by methoxy diene, rearomatisation had occurred to the extent of ca 20%.

The reaction was repeated using diene 1A (50 mg,

.21 mmol), 1% sulphuric acid in methanol solution (35 mm^3), with methanol-d (CH_3OD) (315 mm^3) as solvent. After 50 min. at 35°C, the singlet signal in the 90 MHz ^1H n.m.r. spectrum due to the vinyl protons of the acetoxy diene had disappeared and been replaced by a pair of AB quartets, one at τ 3.73 p.p.m. and τ 4.13 p.p.m. (J = 10 Hz) and one at τ 3.74 p.p.m. and τ 4.09 p.p.m. (J = 10 Hz). Methoxyl peaks at τ 6.95 and 6.94 corresponded in intensity to the sets of dienyl protons: the isomers were present in a ratio of 9:5.

Rearomatisation to the extent of ca 20% had occurred. This prevented the assignment of the signals from the ethyl groups of the methoxy dienes. The aromatic compound appeared to be a mixture of 2,5-dimethylanisole and 2,5-diethylnitrobenzene.

2.6d Reaction of Diene IA with 5% Deuterium Oxide in Methanol-d_4

Diene IA (100 mg, 0.42 mmol) was dissolved in a solution of methanol-d_4 (950 mm^3) and deuterium oxide (50 mm^3) in an n.m.r. tube and the ^1H n.m.r. spectrum was recorded at various times until the signals near τ 4 p.p.m. due to vinyl protons had disappeared and been replaced by signals between τ 2 and τ 3 p.p.m. from aromatic protons.

To monitor the progress of the reaction, 60 MHz ^1H n.m.r. spectra were recorded at the time of mixing and at 15 minutes, 35 minutes, 70 minutes, 115 minutes, 18.5 hours,

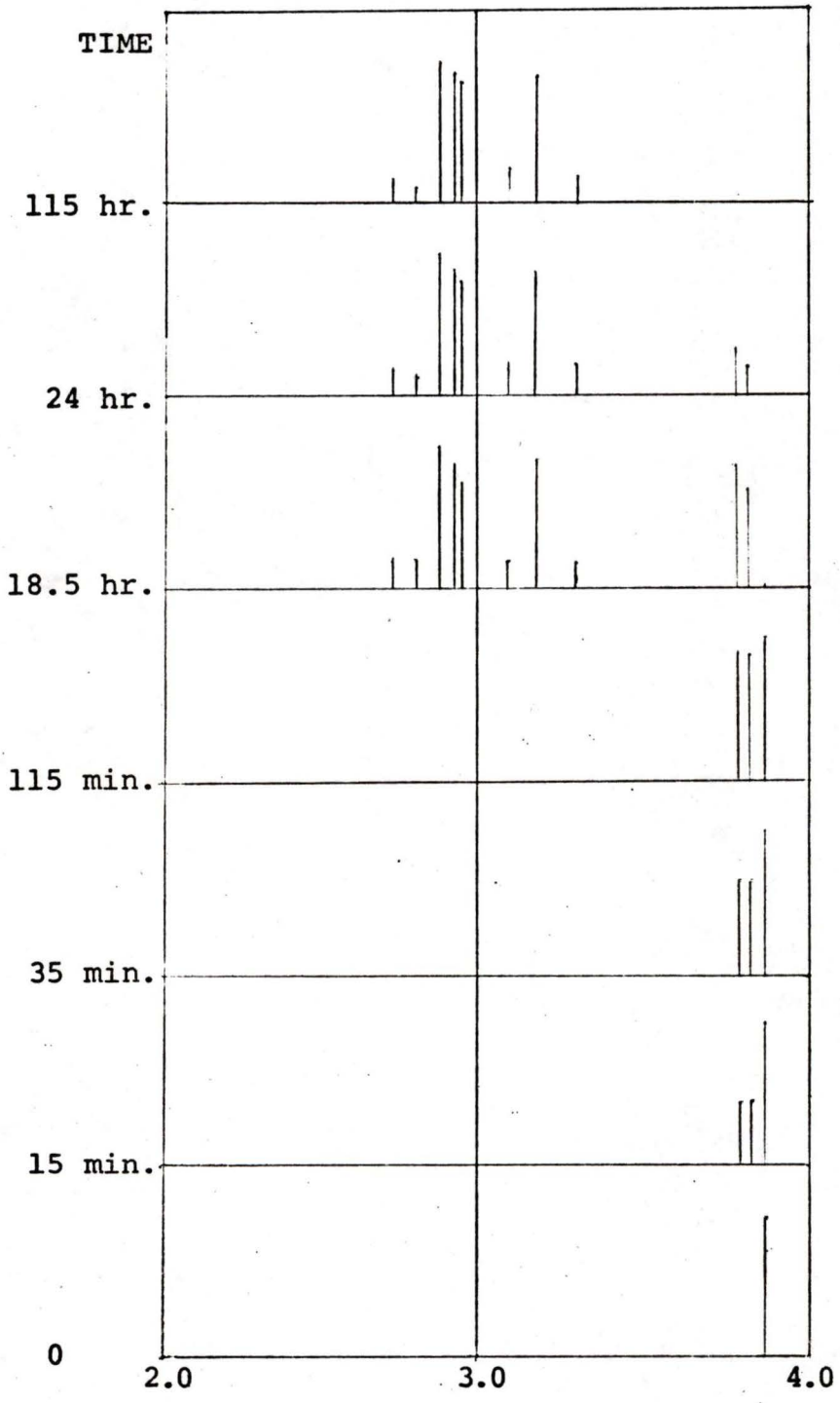
24 hours, and 115 hours after the time of mixing. In the methanol-water solvent, the vinyl protons of Diene IA gave a single signal at τ 3.85 p.p.m. After fifteen minutes, the dienyl region of the spectrum contained three well-resolved signals between τ 3.65 and τ 4.0 p.p.m. (Figure 5). The appearance of signals in the aromatic region was detected by integration after thirty-five minutes, and signals were observed after seventy minutes. After 115 minutes the ratio of the integral of the aromatic to the dienyl region was 2:9; the ratio was 5:2 after 18.5 hours, 3:1 after 24 hours, and the dienes had completely rearomatised after 115 hours.

Gas chromatographic and combined gas chromatographic-mass spectrometric analysis of the aromatic products showed the presence of four major components, eluted in the order: *p*-ethylstyrene (m/e (M + 1) 133, 6.4%); 2,5-diethylanisole-d_3 (m/e (M + 1) 168, 12.0%); 2,5-diethylphenol (m/e (M + 1) 151, 1.3%); 2,5-diethylphenyl acetate (m/e (M + 1) 193, (M-$COCH_3$) 151, 80.3%). Very small amounts (less than 1%) of 2,5-diethylbenzene (m/e (M + 1) 135) and 2,5-diethylnitrobenzene (m/e (M + 1) 180) were identified by the combined gas chromatographic-mass spectrometric technique.

2.6e Reaction of Dienes IA and IB with Deuterium Oxide and Acetic Acid-d_4

A mixture of acetoxy dienes IA and IB (50 mg, mmol) was cooled to -78°C in an n.m.r. tube. Acetic acid-d_4

Figure 5. Dienyl and Aromatic Region of 60 MHz N.M.R. Spectrum Changes During Solvolysis of Diene IA in Methanol-d_4 and Deuterium Oxide (5%) at 35°C



(300 mm^3) was added to the cold dienes followed by deuterium oxide (15 mm^3) and tetramethylsilane (2 drops). This procedure produces a layered mixture in the tube, and the dienes do not come in contact with water until the tube is heated. The reaction was observed at 35°C using n.m.r. techniques. Rearomatisation of the dienes was 90% complete after 325 min. The resolution of the dienyl region of the spectrum at 60 MHz in this solvent was not high enough to permit observation of changes in the dienes before rearomatisation. Work-up and gas chromatographic analysis showed the presence of four components of the product which were identified by g.l.c. and g.l.c.-m.s.: 1-(*p*-ethylphenyl) ethanol (m/e (M-OH) 133, 10%); 2,5-diethylphenol (m/e (M + 1) 151, 16%); 2,5-diethylphenyl acetate and 2,5-diethylphenyl acetate-d_3 (m/e (M + 1) 193 and 196, 43%) with a ratio of 3:1 respectively; and an isomer of 2,5-diethylnitrophenol (m/e (M + 1) 196, 31%).

2.6f Reaction of Dienes IA and IB with Acetic Acid-d_4

Acetic acid was dried by refluxing with 10% (V:V) acetic anhydride. A mixture of dienes IA and IB (50 mg, 0.21 mmol) was cooled to -78°C in a n.m.r. tube. Dry acetic acid-d_4 (450 mm^3) was added to the dienes and the reaction was observed at 35°C by n.m.r. using tetramethylsilane (2 drops) as internal reference. The reaction was essentially complete (93% rearomatisation) after 200 min.

On g.l.c. analysis of the worked-up product, 2,5-diethylphenyl acetate composed 68%, an isomer of 2,5-diethylnitrophenol, 26%, 1-(*p*-ethylphenyl)ethanol, 5%, and *p*-ethylstyrene, 1%, of the reaction product. G.l.c.-m.s. analysis showed that the acetate was an 80:20 mixture of the normal and trideuterated compounds.

2.6g Reactions of Dienes IA and IB with Sulphuric Acid in Acetic Acid-d_4

Four samples of the pair of acetoxy diene isomers IA and IB (50 mg each, 0.21 mmol) were cooled (0°C) in n.m.r. tubes. The samples were reacted with sulphuric acid at various concentrations in 10% acetic anhydride-dried acetic acid-d_4 (Table IV) and were observed by n.m.r. spectrometry at 0°C. Eight components of the reaction mixtures were detected by gas chromatography after work-up. The reactions with 0.05% and 0.5% sulphuric acid gave diene products, and the gas chromatographic analysis does not represent the composition originally present in the reaction mixture.

2.6h Reaction of Diene IB with Sulphuric Acid in Acetic Acid-d_4 and Chloroform-d

In experiment 2.6g(i) there was a change in the dienyl region of the spectrum before rearomatisation took place. The change was thought to result from loss of the *cis*-isomer, diene Ib, from the mixture. After work-up, the n.m.r. spectrum obtained showed a small amount of

TABLE IV

Reaction of Dienes with Sulphuric Acid and Acetic Acid-d_4 at 0°C

Experiment #	2.6g(i)	2.6g(ii)	2.6g(iii)	2.6g(iv)
Sulphuric Acid Concentration (W/V)	0.05%	0.5%	5%	50%
^{1}H n.m.r. time	45 hr.	85 min.	40 min.	< 5 min.
result	mainly dienes no aryl acetate signal	85% dienes no aryl acetate signal	60% aromatic	aromatic only
time	75 hr.			
result	40% aromatic			
G.C. (SE-30)	7 peaks	7 peaks	6 peaks	6 peaks
G.C./M.S.	Deuterated acetate	-	2,5-diethylphenol, nuclear acetate, *p*-ethylacetophenone	2,5-diethylphenol, nuclear acetate and *p*-ethylacetophenone
Products:				
p-Diethylbenzene	2	8		
p-Ethylstyrene	2	1		
p-Ethylacetophenone			32	24
2,5-Diethylphenol	43	61	2	2
2,5-Diethylphenylacetate	18	8	1	
2,5-Diethylnitrobenzene	7	10	65	74
2,5-Diethylnitrophenol	16			
side-chain compound	12	12		

rearomatisation, the presence of the signal at τ 3.98 p.p.m. which is characteristic of the *trans*-diene IA, and the absence of the acetoxy methyl signal at τ 8.0 p.p.m. The conditions of the experiment were chosen to give a reaction in which the *cis*-diene, IB, could be converted to the *trans*-diene, IA, with a minimum amount of rearomatisation.

A solution of acetoxy-diene, IB (50 mg, 0.21 mmol) was dissolved in chloroform-d (150 mm^3) and cooled to 0°C in a n.m.r. tube. Sulphuric acid (0.5% V/V) in dry acetic acid-d_4 (with 10% acetic anhydride) solution (150 mm^3) was cooled to 0°C and added to the diene solution. During the first day of the reaction the changes in the signals due to the dienyl protons were observed using 90 MHz n.m.r. By the fourth day, the starting diene had been replaced by its isomer and the reaction was quenched and worked up. The product was identified as the *trans*-diene IA from its ^1H n.m.r. spectrum.

2.6i Reaction of Diene IA with Methanol and 1% Sulphuric Acid

A stock solution containing sulphuric acid (10.0 g) and methanol was diluted with methanol to 100 cm^3. *trans*-1-Acetoxy-2,5-diethyl-4-nitrocyclohexa-2,5-diene (IA) (50 mg, 0.21 mmol) was dissolved in acetone-d_6 (315 mm^3) and cooled to 0°C. Sulphuric acid solution (35 mm^3) was cooled to 0°C and added to the diene solution. The reaction was observed

by ^{1}H n.m.r. spectrometry for thirty minutes at 0°C; no reaction was detected at that temperature so the solution was warmed to 10°C. After one hour at 10°C the reaction appeared to be complete giving a mixture of dienes. The reaction was quenched by cooling to -20°C, diluting with methylene chloride (5 cm^3), and washing with five per cent sodium bicarbonate solution (3 X 5 cm^3). The product, after drying over magnesium sulphate and removal of solvent, consisted mainly of a pair of isomeric methoxy dienes, as shown by signals in the ^{1}H n.m.r. spectrum at τ 6.94 and τ 6.95 due to the methoxyl methyl protons and pairs of signals in the dienyl region. Approximately twelve per cent of the dienyl signal was due to the starting diene, and 10 per cent of the total product was 2,5-diethylphenyl acetate.

The experiment was repeated using the isomeric *cis*-acetoxy diene (IB) (50 mg, .21 mmol) as starting material. The reaction was followed for two hours at 10°C, and warmed to 35°C before work-up, giving a product with six per cent of the starting material remaining. Integration of the signal from the methoxyl protons indicated a 50:50 ratio of the isomeric methoxy-dienes in the product, although with the small separation the integration is not particularly reliable.

The dienyl region of the spectrum, at 60 MHz, shows two broadened singlets at τ 3.66 and τ 3.83 p.p.m., and two

pairs of doublets, one at τ 4.05 and τ 4.09 p.p.m., and the other at 4.23 and 4.27 p.p.m. Analysis at 90 MHz showed that the dienyl region corresponded to that listed in section 2.6c; however it was not possible to assign a definite stereochemistry to the dienes produced.

2.6j Reaction of Dienes with Water and 1% Sulphuric Acid

A stock solution was prepared by diluting sulphuric acid (10.0 gm) to one hundred cm^3 with water. A solution of *trans*-1-acetoxy-1,4-diethyl-4-nitrocyclohexa-2,5-diene (IA) (50 mg, 0.21 mmol) in acetone-d_6 (315 mm^3) was prepared and cooled to 0°C. Tetramethylsilane (6 drops) was added and the ^1H n.m.r. spectrum was recorded. Sulphuric acid solution (35 mm^3) was added and at various intervals ^1H n.m.r. spectra were obtained, while maintaining the reaction mixture at 0°C. The reaction did not proceed at 0° or 10°, and the solution was noted to have separated into two layers; an excess of TMS was thought to have prevented solution of the water in the organic layer. After standing overnight at room temperature, the reaction mixture was diluted with methylene chloride (5 cm^3), the solution was cooled to -78°C, and ammonia was passed in until the solution was basic. The ^1H n.m.r. spectrum of the product, after drying over magnesium sulphate and solvent removal, showed the presence of the pair of isomeric hydroxy dienes, VA and VB.

2.6k Reaction of Dienes with Methanol-d_4 in Trifluoroacetic Acid

A series of reactions was carried out using methanol-d_4 and trifluoroacetic acid. Samples of either the *cis*- or *trans*- acetoxy dienes (IA or IB) (50 mg, 0.21 mmol for each reaction) were dissolved in measured volumes of methanol-d_4 and cooled to -78°C. Trifluoroacetic acid was cooled to -10°C in an ice-salt bath and was injected into the n.m.r. tubes containing the diene solutions. As the solutions were held at -78°C, the trifluoroacetic acid froze in the tube without reaching the diene solution; to start a reaction the tube was warmed to -10°C and shaken, then monitored by ^1H n.m.r. spectrometry. After rearomatisation was complete (this required about two weeks at room temperature for the reactions with 60% and 40% trifluoroacetic acid) the products were worked up by diluting with methylene chloride (5 cm^3), shaking with sodium bicarbonate solution (3 X 5 cm^3 of 5% solution), washing with water (2 X 5 cm^3), drying over magnesium sulphate, and removal of solvent. The products were analysed by ^1H n.m.r., spectrometry and gas chromatography.

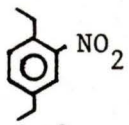
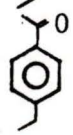
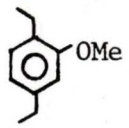
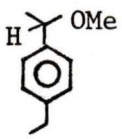
TABLE V

Reaction of Dienes IA and IB with Methanol-d_4 and Trifluoroacetic Acid

Experiment #	2.6k(i)	2.6k(ii)	2.6k(iii)	2.6k(iv)	2.6k(v)
Diene	IA	IB	IA	IB	IA
CD_3OD:					
Vol (mm^3)	35	70	105	140	210
%	10	20	30	40	60
CF_3COOH:					
Vol (mm^3)	315	280	245	210	140
%	90	80	70	60	40
Time (min)	<3	<3	<2	<2	<2
Result	Rearoma-tisation	Rearoma-tisation	Exchange Methoxy Dienes	Partial Exchange Methoxy Dienes	Partial Exchange Methoxy Dienes
Time (min)			25	5	12
Result			Rearoma-tisation	Complete Exchange	75% Ex-change
Time (min)					30
Result					85% Ex-change
Time (Days)				13	13
Result				Rearoma-tisation	Rearoma-tisation

TABLE VI

Products of the Reaction of Acetoxy Dienes IA and IB with Methanol-d_4 and Trifluoroacetic Acid

Experiment	2.6k(i)	2.6k(ii)	2.6k(iii)*	2.6k(iv)*	2.6k(v)*
Starting Diene	IA	IB	IA	IB	IA
% Trifluoroacetic Acid	90	80	70	60	40
% Methanol-d_4	10	20	30	40	60
Products (% by Weight)					
	91.4	94.1	46.3		†3.47
	8.6	5.9	8.3		†0.96
			34.2	96.7	91.26
			7.1	3.3	4.00
			4.1		
					†0.32

*Dienes formed and detected by N.M.R. before rearomatisation.

†Probably due to decomposition of starting diene before reaction.

2.7 Thermolytic Reactions of Dienes

2.7a Pyrolysis of Dienes IA and IB

A solution of acetoxy dienes IA and IB was made up with acetone to give a concentration of diene of about 1%. The solution was injected through an injection port at 200°C onto a 1.3 m column of stainless steel packed with 3% SE-30 which was held at 140°C. The retention times of the decomposition products were compared with the retention times of authentic compounds. The reaction was also performed in the gas chromatography-mass spectrometry instrument to obtain confirmation of the identities of the reaction products.

Seven products were formed in this reaction: *p*-diethylbenzene (16.4%), *p*-ethylstyrene (3.6%), 1-(*p*-ethyl phenyl)ethanol (8.5%), 2,5-diethylphenol (23.5%), 2,5-diethylphenyl acetate (32.9%), 2,5-diethylnitrobenzene (13.4%), and an isomer of 2,5-diethylnitrophenol (1.6%).

2.7b Pyrolysis of Dienes

A 1% solution of hydroxy diene VA in ether was injected through an injection port at 220°C onto an SE-30 column under the conditions listed in 2.7a. The results were similar except for the absence of 2,5-diethylphenyl acetate which was replaced by a larger proportion of 2,5-diethylphenol. *p*-Diethylbenzene (19.2%), *p*-ethylstyrene (4.5%), 1-(*p*-ethylphenyl)ethanol (5.4%), 2,5-diethylphenol

(60.2%), 2,5-diethylnitrobenzene (7.8%), and 2,5-diethylnitrophenol (2.9%) were detected.

2.7c Room Temperature Thermolysis of Diene I

A 1:1 mixture of dienes IA and IB (350 mg, 1.4 mmol) was placed in a n.m.r. tube and held at room temperature for 13 days, with ^1H n.m.r. spectra being obtained at various intervals. No decomposition or rearomatisation occurred during this period.

2.8 Rearomatisation Reactions of Dienes

2.8a Reaction of Diene IB with Boron Trifluoride Etherate

Boron trifluoride etherate (300 mm^3) was cooled to -78°C. Acetoxy diene IB (50 mg, 0.21 mmol) in ether (1:1) was cooled to -78°C and added. The solution was shaken, then warmed to -65°C for ten minutes. The solution was warmed to room temperature and a ^1H n.m.r. spectrum was obtained. Methylene chloride (6 cm^3) was added to the reaction mixture and it was cooled to -78°C and neutralised with ammonia. After filtration and removal of the methylene chloride, the residue was dissolved in pentane (6 cm^3), dried over magnesium sulphate, and filtered. Analysis of the product by ^1H n.m.r. showed it to be mainly 2,5-diethylnitrobenzene with a spectrum similar to that of the authentic compound. Gas chromatography showed the presence of 21% *p*-ethylacetophenone and 79% 2,5-diethylnitrobenzene.

2.8b Reaction of Diene IB with Trifluoromethanesulphonic Acid

The acetoxy diene IB was reacted with trifluoromethanesulphonic acid at -78°C and worked up following the same procedure employed in the reaction with boron trifluoride etherate. The product of the reaction was *p*-ethylacetophenone as indicated by ^{1}H n.m.r. spectrometry and gas chromatography.

The reaction was repeated using a solution of trifluoromethanesulphonic acid (200 mm^3) in methylene chloride. After work-up, the ^{1}H n.m.r. spectrum indicated a minor amount of *p*-ethylacetophenone in the reaction product: the major product was 2,5-diethylnitrobenzene. Gas chromatographic analysis showed 65% 2,5-diethylnitrobenzene, 25% *p*-ethylacetophenone, and 10% 1-(*p*-ethylphenyl)ethyl acetate.

2.8c Reaction of Diene IB with Trifluoroacetic Acid in Trifluoroacetic Anhydride (TFA/TFAA)

A solution of trifluoroacetic acid in trifluoroacetic anhydride (1:1 by volume) was cooled to -55°C. Acetoxydiene IB (50 mg, .21 mmol) was cooled to -78°C and the trifluoroacetic acid solution (300 mm^3) was added to the diene. The reddish-brown mixture which resulted after shaking was held at -65°C for fifteen minutes, with occasional shaking. The reaction mixture was warmed to room

temperature and the ^1H n.m.r. spectrum was obtained. The signal in the dienyl region of the spectrum had disappeared and been replaced by signals between τ 2 and τ 3 p.p.m.

The reaction mixture was diluted with ether (10 cm^3) and washed with 5% sodium bicarbonate solution (3 X 10 cm^3). After drying (magnesium sulphate) and solvent removal, the product was analysed by ^1H n.m.r. and gas chromatography. 2,5-Diethylnitrobenzene was obtained as the only product of the reaction.

A number of repetitions of the above procedure was required before the reaction was observed to proceed cleanly, and various amounts of side-chain compounds were detected by the presence of a doublet signal at lower field than the triplet of the ethyl groups. There was difficulty in achieving precise control of the reaction temperature on mixing.

2.8d Reaction of Diene IB with Methanol and Water

cis-1-Acetoxy-1,4-diethyl-4-nitrocyclohexa-2,5-diene (IB) (80 mg, 0.33 mmol) was dissolved in methanol (2 cm^3) and water (2 cm^3) was added. The addition of water caused the solution to become cloudy, so methanol was dropped into the mixture to remove the cloudiness resulting in a solution that contained ca. 40% water (V/V). The solution was left at room temperature for two days, then worked up. After removal of the methanol, methylene chloride (5 cm^3) was

separated from the organic layer. Drying of the organic layer over magnesium sulphate and solvent removal gave 2,5-diethylphenyl acetate which was pure by ^{1}H n.m.r. and gas chromatographic (FFAP) analysis.

2.8e Reaction of Diene IA with Sodium Methoxide

A stock solution of sodium methoxide was prepared by carefully adding sodium metal (1.80 g, 0.078 mol) in methanol (55 cm^3) to give a solution which was 1.39 M in methoxide.

trans - 1-Acetoxy-1,4-diethyl-4-nitrocyclohexa-2,5-diene (50 mg, 0.21 mmol) was dissolved in sodium methoxide solution (300 mm^3, 0.42 mmol in methoxide) to give a 2:1 excess of base and shaken. The yellow diene gave an orange solution immediately on shaking with the base. ^{1}H n.m.r. spectra recorded up to twenty-five minutes after mixing showed complete rearomatisation. The reaction was worked up by removal of the methanol, addition of ether (5 cm^3) and water (5 cm^3), acidification with concentrated hydrochloric acid solution until the orange colour of the aqueous layer was replaced by a yellow colour in the ether layer, removal of the aqueous layer, and washing with five per cent sodium bicarbonate solution (2 X 5 cm^3), and water (2 X 5 cm^3). After drying over magnesium sulphate and solvent removal, a phenol was obtained which was different than the 2,5-diethylphenol prepared as an authentic compound. The

product was assigned the structure 2,4-diethylphenol by analogy with the reactions of the dienes from *p*-cymene (15) and *p*-ethyltoluene (59).

i.r. (film) 3620-3095 (-OH), 1270 cm^{-1}; ^{1}H n.m.r. τ(90 MHz, $CDCl_3$) 3.19 (s, 1, 3-H), 3.21 (d, 1, J = 8 Hz, 5-H), 3.33 (d, 1, J = 8 Hz, 6-H), 7.40 (q, 2, J = 7.6 Hz, $-CH_2CH_3$), 7.47 (q, 2, J = 7.6 Hz, $-CH_2CH_3$), 8.88 (t, 3, J = 7.6 Hz, $-CH_2CH_3$), 8.91 (t, 3, J = 7.6 Hz, $-CH_2CH_3$). ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 14.1 ($2-CH_2CH_3$), 15.9 ($4-CH_2CH_3$), 23.1 ($2-CH_2CH_3$), 28.1 ($4-CH_2CH_3$), 115.2 (C-6), 126.1 (C-5), 128.8 (C-3), 129.4 (C-2), 136.6 (C-4), 151.3 (C-1).

The ^{1}H and ^{13}C n.m.r. spectra are very similar to those of 4-ethyl-2-methylphenol and 2-ethyl-4-methylphenol (59).

2.9 Reactions of *p*-Xylene Dienes

2.9a Preparation of Acetoxy Dienes

The acetoxy dienes from *p*-xylene were obtained following the procedure of Ramsay (23). The work-up procedure was modified to test the possibility of leaving out the water washing step of the procedure following the procedure described for nitration of *p*-diethylbenzene. This gave an overall yield from the reaction of 87% of the theoretical maximum, and a reaction mixture which was 84% dienes and 16% aromatic compounds as estimated from the n.m.r. integration. After chromatography on 3% aqueous

deactivated neutral alumina, the two isomeric dienes were obtained. *trans*-1,4-Dimethyl-4-nitrocyclohexa-2,5-dienyl acetate, white solid, m.p. 46-47°, ^{1}H n.m.r. τ(60 MHz, CCl_4) 3.99 (s, 4, 2-H, 3-H, 5-H, 6-H), 8.08 (s, 3, $-OCOCH_3$), 8.23 (s, 3, $4-CH_3$), 8.54 (s, 3, $1-CH_3$); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 21.7 ($-OCOCH_3$), 25.1 ($1-CH_3$), 27.0 ($4-CH_3$), 73.2 (1-C), 84.9 (4-C), 126.0 (2-C and 6-C), 135.6 (3-C and 5-C), 169.4 ($-OCOCH_3$). *cis*-1,4-Dimethyl-4-nitrocyclohexa-2,5-dienyl acetate, white solid, m.p. 57-58°C; ^{1}H n.m.r. τ(60 MHz, CCl_4) 3.81 (s, 4, 2-H, 3-H, 5-H, 6-H), 8.08 (s, 3, $-OCOCH_3$), 8.34 (s, 3, $4-CH_3$), 8.49 (s, 3, $1-CH_3$); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 21.7 ($-OCOCH_3$), 26.9 ($1-CH_3$), 27.8 ($4-CH_3$), 72.9 (1-C), 82.3 (4-C), 126.3 (2-C and 6-C), 132.6 (3-C and 5-C), 169.5 ($-OCOCH_3$).

2.9b Sodium Methoxide Hydrolysis of *p*-Xylene Dienes

A solution of sodium methoxide in methanol was prepared by reacting sodium metal (2.13 g, 0.093 moles) with anhydrous methanol (20 cm^3). When hydrogen evolution had ceased the volume of the solution was adjusted to give a concentration of sodium methoxide of 3.09 mmol cm^{-3}. A 1:1 mixture of the *cis*- and *trans*-acetoxy dienes from nitration of *p*-xylene (1.03 g, 4.9 mmol) was dissolved in methanol (5 cm^3) and cooled to 0°C. Sodium methoxide solution (8 cm^3, 24.7 mmol) was cooled to 0°C, then added to the diene solution and stirred at 0°C for ten minutes. The

reaction mixture was neutralised by the addition of ammonium chloride (1.5 gm, 27.0 mmol), methylene chloride (20 cm^3) was added, and the reaction mixture was washed with water (4 X 15 cm^3) to remove salts. After drying over magnesium sulphate, filtration, and removal of solvent, the product was dissolved in deuterochloroform, and its ^1H n.m.r. spectrum was obtained and integrated to show fifteen per cent rearomatisation and eighty-five per cent conversion of starting material to hydroxy dienes. The ratio of isomers was 2:1 with the *trans* isomer predominant. Repetition of the reaction with single isomers of the acetoxy dienes gave the two hydroxy dienes as relatively pure compounds, which were crystallised from carbon tetrachloride. *trans*-1,4-Dimethyl-4-nitrocyclohexa-2,5-dienol: m.p. 112-113°C; ^1H n.m.r. τ(90 MHz, $CDCl_3$) 3.93 (d, 4, 2-H, 3-H, 5-H and 6-H), 8.28 (s, 3, 4-CH_3), 8.63 (s, 3, 1-CH_3); ^{13}C n.m.r. ($CDCl_3$) &c (TMS) 26.8 (1-CH_3), 27.8 (4-CH_3), 65.5 (1-C), 83.9 (4-C), 125.1 (2-C, 6-C), 137.5 (3-C, 5-C).

cis-1,4-Dimethyl-4-nitrocyclohexa-2,5-dienol: m.p. 51-52°; ^1H n.m.r. τ(90 MHz, $CDCl_3$) 3.98 (s, 4, 2-H, 3-H, 5-H, 6-H), 8.32 (s, 3, 4-CH_3), 8.70 (s, 3, 1-CH_3); ^{13}C n.m.r. ($CDCl_3$) &c (TMS) 27.2 (1-CH_3), 28.0 (4-CH_3), 64.8 (1-C), 83.7 (4-C), 125.0 (2-C and 6-C), 136.8 (3-C and 5-C).

2.9c Chloride Exchange with *p*-Xylene Acetoxy Dienes

trans-1-Acetoxy-1,4-dimethyl-4-nitrocyclohexa-2,5-diene (LIA) (.93 g, 4.4 mmol) was dissolved in ether

(100 cm^3). The solution was cooled to -78°C and a fritted glass bubbler was used to pass anhydrous hydrogen chloride gas through the solution for five minutes. The reaction mixture was then stirred while ammonia was condensed into the solution until the acid was neutralised. Excess ammonia was aspirated from the mixture over a two hour period while the mixture was being warmed to 0°C. The residual solids were filtered off, the solution was dried over magnesium sulphate, and the solvent was removed.

Inspection of the ^1H n.m.r. spectrum of the mixture showed the presence of two dienes in different proportions, so the mixture was chromatographed at -20°C on basic alumina (50 g) deactivated with three per cent of ten per cent aqueous acetic acid solution, using ether-pentane mixtures.

From the fractions eluted with 2½, 5, and 7½% ether was obtained *trans*-1-chloro-1,4-dimethyl-4-nitrocyclohexa-2,5-diene, LIIA, a white solid: m.p. 67° (decomposes slowly at room temperature); i.r. (CCl_4) 1550 cm^{-1} ($-NO_2$), ^1H n.m.r. τ(90 MHz, $CDCl_3$) 3.81 (d, 2, J = 10.4 Hz, 3-H and 5-H), 3.95 (d, 2, J = 10.4 Hz, 2-H and 6-H), 8.25 (s, 6, 1-CH_3 and 4-CH_3); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 26.5 (1-CH_3), 31.4 (4-CH_3), 60.6 (1-C), 83.4 (4-C), 125.1 (2-C and 6-C), 135.4 (3-C and 5-C).

The fractions eluted with 7½%, 10%, and 15% ether contained 1-chloro-1,4-dimethyl-4-nitrocyclohexa-2,5-diene (LIIB) which was crystallised from ether-pentane to a white

solid: m.p. 105°C; i.r. 1545 cm^{-1} (NO_2); ^1H n.m.r. τ (90 MHz, $CDCl_3$) 3.78 (s, 4, 2-H, 3-H, 5-H, and 6-H), 8.20 (s, 6, 1-CH_3 and 4-CH_3); ^{13}C n.m.r. ($CDCl_3$) δc (TMS) 28.0 (1-CH_3), 31.9 (4-CH_3), 60.5 (1-C), 82.3 (4-C), 124.7 (2-C and 6-C), 134.9 (3-C and 5-C).

CHAPTER III

DISCUSSION

3.1 Products of Nitration

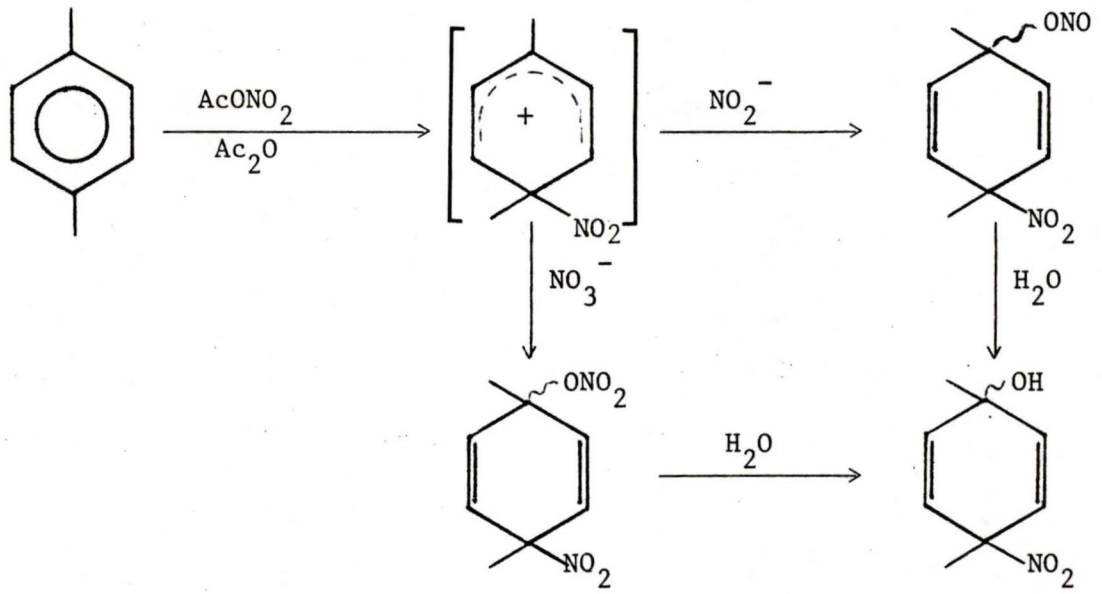
Nitration of *p*-diethylbenzene in acetic anhydride gave unreacted hydrocarbon (30%), 1-(*p*-ethylphenyl)nitroethane (27%); 2,5-diethylnitrobenzene (9%), and the *cis*- and *trans*- adducts 1,4-diethyl-4-nitrocyclohexa-2,5-dienyl acetate, I (34%).

Conditions which promote the complete reaction of *p*-xylene (23) and *p*-ethyltoluene (19) to nitro-compounds and acetoxynitrocyclohexadienyl adducts are not sufficiently vigorous to ensure complete reaction of *p*-diethylbenzene, although small-scale reactions appeared to have progressed to completion. The reactivity of ethylbenzene towards conventional nitration in various solvent systems is appreciably less than that of toluene (60) despite the larger inductive effect of the ethyl group (61a). Measurement of the partial rate factors for nitration of toluene and ethylbenzene (6b) reveals that substitution is actually faster in the *para* position of ethylbenzene than in the *para* position of toluene, but that this is more than offset by a reduced ratio of *ortho* substitution, presumably a reflection

of greater steric hindrance by ethyl than by methyl. In the nitration of *p*-ethyltoluene (19) the ratio of partial rate factors (f^R) for nitration *ipso* to methyl and ethyl was found to be 1.0:0.4. The ethyl group presumably exhibits greater steric inhibition of *ipso*-attack than does methyl. Given this ratio of reactivities it may be estimated that the reaction of *p*-diethylbenzene at the *ipso*-positions with acetyl nitrate under the nitrating conditions would be about one-third as fast as the reaction of *p*-xylene under the same conditions, and the recovery of some unreacted *p*-diethylbenzene in conditions under which *p*-diethylbenzene is completely reacted is not surprising.

Combining the yields of adducts (34% of the starting material on a molar basis) and side-chain nitro-compound (27%) shows that 61% of the starting material was nitrated at the *ipso*-position, or 87% of the hydrocarbon which actually reacted.

In the nitration of *p*-xylene the isomeric *cis*- and *trans*-hydroxy dienes were produced as well as the acetoxy dienes (23). The hydroxy compounds were thought to arise from hydrolysis of nitrate or nitrite adducts of the initially formed nitrocyclohexadienyl cation:



A dry work-up was employed in the nitration of *p*-diethylbenzene so the final step in the production of hydroxydienes was not possible. In the nitration of tetramethylbenzenes (25) nitro-nitrito dienes were eluted from alumina columns before the acetoxynitro dienes, but decomposed on heating. In hydrocarbon systems, acetoxy dienes are eluted before hydroxy dienes, and by analogy with the isodurene example, nitro-nitrito dienes, if formed from *p*-diethylbenzene, would be eluted before the acetoxy dienes. Neither nitrito-nitro nor hydroxy-nitro adducts were obtained. It is possible that hydroxy-nitro dienes were formed but not recovered, but nitrito-nitro adducts, if formed, would have been isolated. The factors which result in the formation of nitrito-nitro dienes with some substrates but not with others have not yet been elucidated.

3.2 Structure of Dienes

3.2 Structure of Diene I

The acetoxynitro adducts from *p*-diethylbenzene were obtained as oils. Because they could not be crystallised and were too thermally unstable to be distilled, elemental analyses and measurements of ultraviolet absorptions were not carried out. Structural assignments are based on ^{1}H and ^{13}C n.m.r. spectra; infrared spectra and results of gas chromatographic and gas chromatographic-mass spectrometric pyrolysis experiments. The results of work on other systems, especially *p*-xylene and *p*-ethyltoluene, were used for comparison with the *p*-diethylbenzene studies, making use of the powerful chemical tool of reasoning by analogy.

Infrared absorption at 1755 and 1250 cm^{-1} reveal the presence of the acetoxy groups in diene IA, while the band at 1555 cm^{-1} confirms the presence of the nitro group. The isomeric diene IB has a similar spectrum with absorptions at 1745, 1240, and 1550 cm^{-1}.

The symmetry of the cyclohexadienyl adducts is evident from the ^{13}C n.m.r. spectra, in which each twelve carbon compound gives rise to ten signals. The 1,4-cyclohexadienyl structure has the required symmetry: a 1,3-cyclohexadienyl compound with nitro- and acetoxy-substituents would give signals for each of the twelve carbon atoms. The assignment of the signals is facilitated by the use of gated spectra so the acetoxy methyl carbon (a quartet) is easily

distinguished from the methylene carbons (triplets of quartets), and from the ethyl methyl carbons (quartets of triplets). The gated spectra reveal that the four vinylic carbons each have an attached proton. This plus the requirement of accommodating the two original ethyl groups, whose presence is confirmed in the ^{13}C n.m.r. spectra of the adducts, and the nitro and acetate functions, together with the symmetry requirement completely determines the structures as those depicted as IA and IB. Unfortunately, the overlap of the ethyl methyl signals did not allow the methylene and methyl coupling constants to be measured with certainty. The downfield methylene groups are assigned as those geminal to the nitro group, while the upfield methylenes are on C-1 in each isomer. There is some doubt as to the assignment of the methyl groups, but the same pattern is assumed, with the downfield pair of signals assigned to the 4-ethyl group and the upfield signals assigned to the 1-ethyl group. The vinyl pairs of carbons are assigned with the nitro-group adjacent to the downfield pair, i.e., C-3 and C-5, and the upfield pair to C-2 and C-6.

The ^{1}H n.m.r. spectra confirm the assigned structure: the four vinyl protons, two ethyls, and an acetoxy methyl group are clearly evident. Specific absorptions are assigned using the spectra obtained from the lanthanide shift reagent ($Eu(fod)_3$-d_{27}) studies (23). The shift studies, combined with model-building exercises, allow the

unambiguous assignment of the stereo-chemistry of the diastereo isomeric dienes. Diene IA is assigned the *trans*-adduct configuration because the relative shifts of the ethyl signals are in the order 1-CH_2 > 1-CH_3 > 4-CH_3 > 4-CH_2 while diene IB had relative shifts 1-CH_2 > 1-CH_3 > 4-CH_2 > 4-CH_3. Since the shift induced in the resonance position of a proton by the shift reagent is a function $\left(\frac{1}{r^3}\right)$ of the time-averaged distance, r, from the metal to the proton (62), the 4-methyl group in diene IA must be able to approach the europium atom more closely than the 4-methylene group, and in diene IB the 4-methyl group must be further from the metal than the 4-methylene. The figure (Fig. 5) shows that only in the *trans*- isomer can the 4-methyl group be closer to the europium than the 4-methylene when the lanthanide is complexed to the acetoxy group (63). This argument varies from that presented elsewhere (19), in which the assignment of the stereochemistry is based on the relative shifts of the methyl triplet signals at the 4-positions: since the relative gradient is higher for the methyl triplet in IA than IB, IA must have the 4-ethyl group on the same face of the cyclohexadienyl ring as the acetoxy group and must therefore have the *trans*-adduct configuration.

Assignment of the other signals in the spectra is relatively straightforward. The acetoxy methyl is shifted the most in each case, as the shift reagent complexes with the acetoxy group and is therefore closer to the acetate

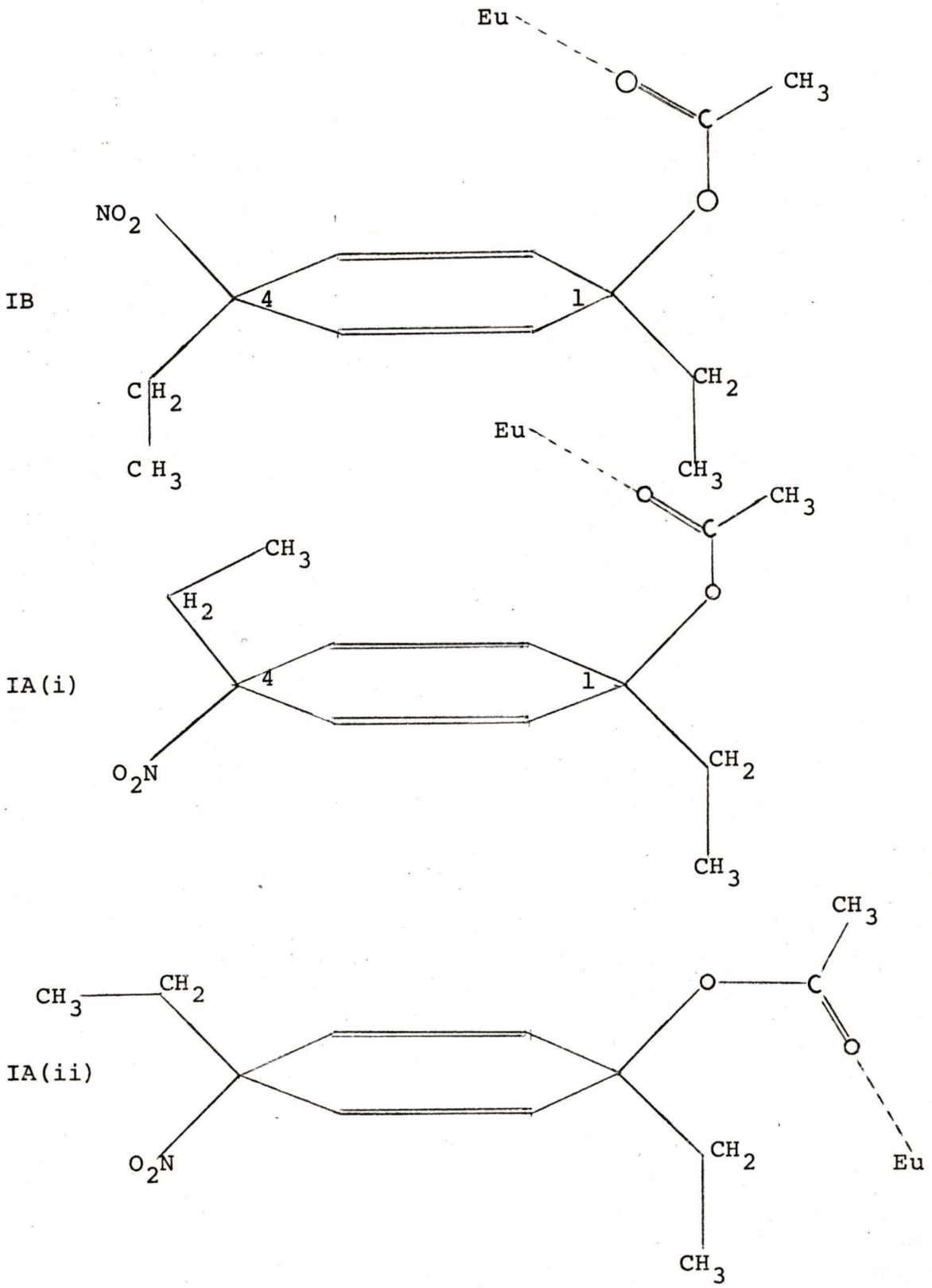


Fig. 6 Proposed Conformation of Dienes and Shift Reagent

methyl protons than to other protons. The 2- and 6-protons of the cyclohexadienyl ring are closer to the acetoxy-group than are the 3- and 5-protons and are therefore shifted downfield by the reagent much more than are the latter. The peaks of the 2- and 6-protons pass through those of the 3- and 5-protons on the addition of shift reagent since the latter, due to their proximity to the nitro group, were originally downfield. The ethyl groups at C-1 of each diene are shifted significantly more than the ethyl groups at C-4: rotation of the acetoxy group to a position as shown in Figure 5, IA(ii) emphasises the proximity of the geminal ethyl group to the shift reagent.

3.2a Structures of Hydroxy Dienes

The hydroxy dienes, *cis*- and *trans*-1,4-diethyl-1-hydroxy-4-nitrocyclohexa-2,5-diene, were prepared as pure isomers from the respective acetoxy dienes by reductive cleavage with aluminum hydride (24). This $B_{AC}2$ hydrolysis proceeds without cleavage of the ring to oxygen bond and must result in retention of the original stereochemistry.

3.2b Structures of *p*-Xylene Adducts

The diastereoisomeric pairs of acetoxy-, LI, and hydroxy-, LIII, dienes from *p*-xylene were characterised by Ramsay (23). The nitration product obtained in the present work did not contain hydroxy-nitro adducts when a dry work-up

was employed. This indicates that the hydroxy dienes that Ramsay found were the result of hydrolysis during work-up, rather than a necessary product of acetyl nitrate nitration.

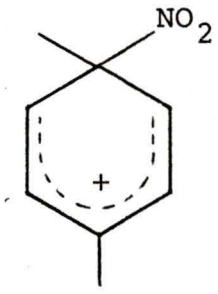
The preparation of *p*-xylene hydroxy dienes, LIII, from the acetoxy dienes through sodium methoxide-catalysed solvolysis confirms the $B_{Ac}2$ mechanism suggested by Ramsay. The ratio of base to diene used was 5:1, where, with sodium hydroxide, Ramsay found that when a base:diene ratio of greater than 1:1 was used rearomatisation of the acetoxy diene was extensive. The observations made in the present study suggest that the rearomatisation should be attributed to some factor other than the base:diene ratio. Dienols can be obtained by methoxide solvolysis or by reduction with aluminum hydride. The aluminum hydride method is milder and more rapid. It is therefore the preferred method of obtaining dienols.

3.2d Chloro-dienes from *p*-Xylene

A pair of isomeric 1-chloro-1,4-dimethyl-4-nitro-cyclohexa-2,5-dienes were prepared from the reaction of anhydrous hydrogen chloride in ether with the *trans*-nitroacetoxy adduct of *p*-xylene. The stereochemistry of the chloronitro dienes was not investigated, but was assigned on the basis of order of elution from the column: the first eluted isomer has *trans* stereochemistry in the acetoxy diene from *p*-xylene, so the first chloro diene was assigned the

trans - stereochemistry. The hydroxy-dienes do not follow this pattern, probably because the hydroxyl hydrogen is available for hydrogen bonding.

The reaction to produce the isomeric chloronitro-adducts must proceed through the cation,

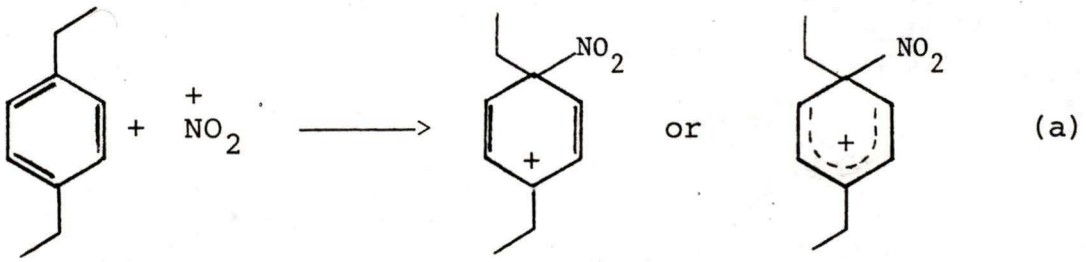


produced by protonation and loss of the acetoxy group as acetic acid. This S_N1-type mechanism, which parallels the mechanism of $A_{Al}1$ hydrolysis, follows an initial pathway similar to that of other reactions carried out in highly acidic but poorly ionising media, such as reactions with boron trifluoride etherate (2.8a). The ability of the nucleophilic chloride ion to trap the cation formed results in an exchange (substitution) reaction rather than the rearrangement or other reaction of the cyclohexadienyl cation.

3.3 Mechanism of Adduct Formation

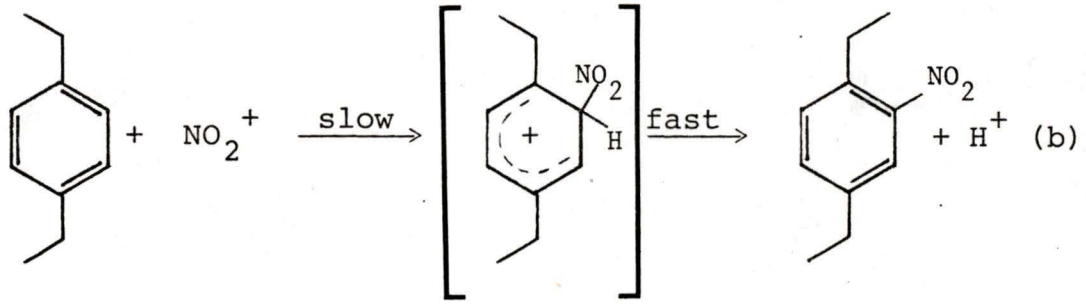
The diastereoisomeric *cis*- and *trans*-2,5-diethyl-4-nitrocyclohexa-2,5-dienyl acetates, IA and IB, are formed in a two-step reaction involving the aromatic hydrocarbon and a

nitronium ion formed from acetyl nitrate. The initial step in this reaction must be the formation of the cyclohexadienyl cation, IV, a species which does not decompose or



IV IVa

rearrange immediately. This step should be compared with the initial step in the nitrodeprotonation reaction (conventional electrophilic aromatic substitution), the formation of the Wheland intermediate (6a) (L):

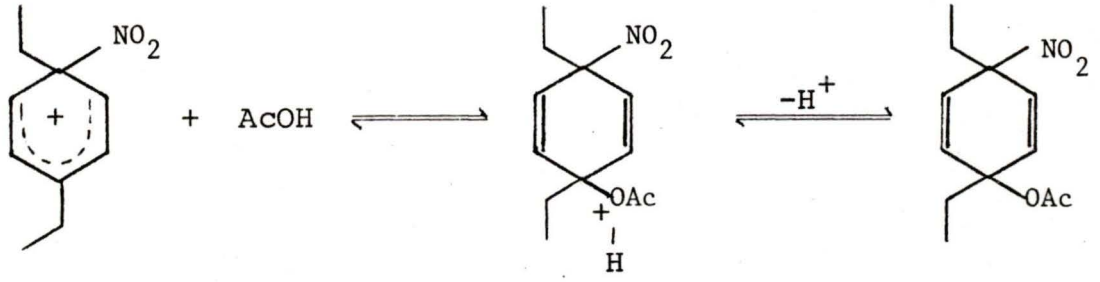


L

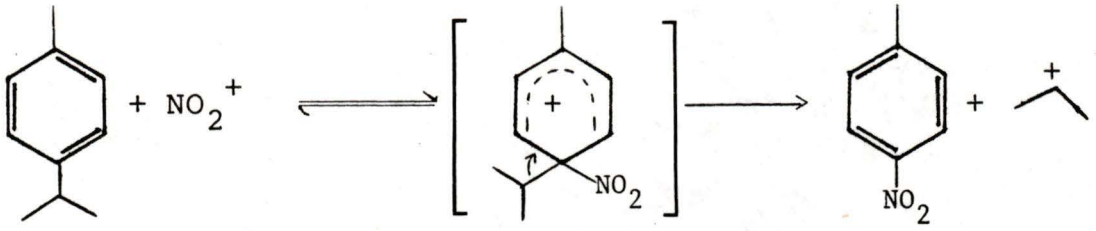
The condition required for *ipso*-attack by the nitronium ion is that the *ipso*-position must be activated to a degree comparable to the activation of the unsubstituted nuclear positions. This condition is fulfilled for *ortho*- and *para*-substituted dialkylbenzenes, but not for *meta*-substituted compounds. In addition, appropriately

substituted chloro-, bromo-, and methoxybenzenes give adducts or decomposition products derived from *ipso*-nitration (47). *p*-Diethylbenzene (like other *p*-dialkyl and *o*-dialkylbenzenes) fulfills the requirements for *ipso*-attack because each ethyl group activates the *ipso*- position of the other.

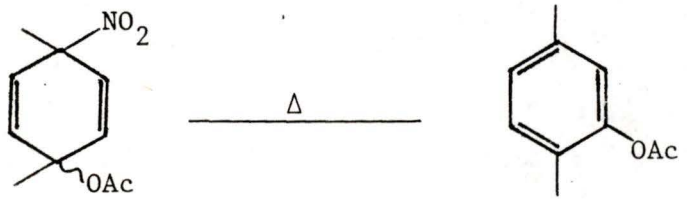
Under suitable conditions, the intermediate, IV, can be trapped. These conditions include low temperature, availability of a nucleophilic species to react with the cation, and low leaving ability of the atom or group geminal to the nitro-group.



When the three conditions are not fulfilled, the *ipso*-intermediate undergoes a variety of other reactions, leading to the products of non-conventional electrophilic aromatic substitution, or the dienyl adduct may be formed and re-aromatised. The nitration of *p*-cymene (21) shows the result of attack *ipso* to a good leaving group (isopropyl, which gives rise to a secondary carbonium ion). No adduct with nitro *ipso* to isopropyl is isolated, but *p*-nitrotoluene is obtained instead.



When temperatures are raised, relatively stable adducts, such as those of *p*-xylene (23) decompose to give products which have been found in nitrations carried out in acetic



anhydride (7). From studies of nitration carried out on various hydrocarbons, and the detection of dienyl products, it can be concluded that certain groups (i.e., hydrogen, isopropyl) when attached to the carbon of an aromatic system which is attacked by an electrophile will be ionised and lost, an aromatic substitution product being formed. Other groups (methyl, ethyl, chloro) form cations less readily; the *ipso*-cyclohexadienyl cation is therefore not rearomatised by loss of the alkyl group but instead is trapped by a nucleophile to form an adduct. Bulky groups, such as *tert*-butyl, prevent the attack of nitronium ion *ipso* to themselves (22).

Evidence for the nature of the attacking electrophile has been discussed in the Introduction. The ratio of

cis- to *trans*- isomers of the dienes obtained (45:55 *cis*: *trans*) is probably not a thermodynamic ratio, as experiments designed to protonate and ionise the acetoxy group, resulting in equilibration of the diastereoisomers (see 2.6h) gave only the *trans*-diene after four days. Experiments on one of the pairs of dienes from *p*-ethyltoluene (59) which involved subjecting each of the dienes separately to the nitrating conditions showed only a small amount (about five per cent) of rearomatisation and a similar amount of isomerisation: the nitration reaction conditions do not result in equilibration of the dienes.

The amount of *ipso*-attack which takes place must be a function of temperature, activity of the electrophile, and activation of the substrate. The yield of products derived from the cation (IV) in both this work and studies of the reaction at 0° indicates that the transition state leading to the *ipso*-cation (IV) must be at a lower energy than the Wheland intermediate (L) for this reaction. This can be shown from the relation:

$$k_i = A_i e^{-Ea_i/RT} \qquad (1)$$

$$\text{and} \quad k_o = 2A_o e^{-Ea_o/RT} \qquad (2)$$

where k_i is the rate constant for *ipso*-attack, R is the gas constant, T is the absolute temperature, A_i is a constant (Arrhenius Factor) for attack at the *ipso*-position, and Ea_i is the energy of activation for the formation of cation IV.

The symbols in equation (2) have the same meaning with the subscript 'o' denoting attack *ortho* to the ethyl groups, and with the factor 2 taken out of A_o to emphasise the proportion of *ortho* to *ipso* positions in *p*-diethylbenzene. Equations (1) and (2) can be combined by assuming that the factors A_i and A_o and Ea_i and Ea_o behave similarly:

$$k_i/k_o = Ce^{-\frac{(Ea_i - Ea_o)}{RT}} \qquad (3)$$

where C is a constant. Now, investigation of equation (3) as the temperature is varied shows that as T increases to a large number, the value of the right side of the equation approaches C, and that the ratio of *ipso*-attack to *ortho*-attack approaches a constant. As the temperature is lowered, the exponent becomes more positive (recall that Ea_o was assumed to be greater than Ea_i) and the ratio of *ipso*-attack to *ortho*-attack increases.

The activation of the aromatic system is composed of a set of positional reactivities which may, in principle, be derived from partial rate factors for the nitration of ethylbenzene (61b):

$$f_p^{Et} = \frac{K_{C_6H_5Et}}{K_{C_6H_6}} \times \frac{\text{fraction } p\text{-substituted product}}{1/6}$$

$$f_o^{Et} = \frac{K_{C_6H_5Et}}{K_{C_6H_6}} \times \frac{(\frac{1}{2}) \text{ fraction } o\text{-substituted product}}{1/6}$$

$$f_m^{Et} = \frac{K_{C_6H_5Et}}{K_{C_6H_6}} \times \frac{(\frac{1}{2}) \text{ fraction } m\text{-substituted product}}{1/6}$$

where the ratio $K_{C_6H_5Et}/K_{C_6H_6}$ is obtained from the reaction of excess benzene and ethylbenzene with an electrophile (6a). Since the fraction of product arising from *ipso*-attack has not been measured for ethylbenzene (it is likely to be quite small, ca. 1%) the f_i^{Et} cannot be derived in this way. It could be derived from the following expression (7):

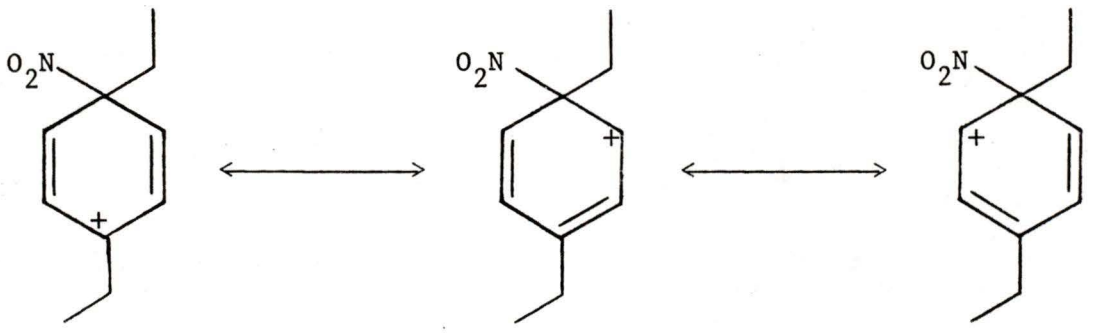
$$f_i^{Et} = \frac{K_{ArEt}}{K_{ArH}} \times \frac{\text{fraction attack at } ipso\text{-position of ArEt}}{\text{fraction attack at corresponding position of ArH}}$$

where ArEt is *p*-diethylbenzene and ArH is ethylbenzene. However, the *p*-diethylbenzene system has not been widely studied, and kinetic values for its nitration are not available. Nevertheless, the ratio $f_i^{Et}:f_o^{Et}:f_m^{Et}:f_p^{Et}$ can be obtained on the assumption that $K_{ArEt}/K_{ArH} = K_{C_6H_5Et}/K_{C_6H_6}$ (which assumes additivity of substituent effects). In *p*-ethyltoluene attack of the nitronium ion *ipso*- to the ethyl group occurs to the extent of about one-third of the amount of attack *ipso* to the methyl group (19). Since $f_p^{Me} = 60$ and $f_p^{Et} = 69.5$, $f_i^{Me}:f_i^{Et} = 1:0.4$. The ratio $f_i^{Me}:f_o^{Me} = 0.1$ has been obtained from the extent of adduct formation in the nitration of toluene (64) and from the known (6c) value of $f_o^{Me} = 49.7$ the value $f_i^{Et} = 0.11 \times 0.4 \times 49.7 = 2.2$ is obtained. This may be compared with the values $f_o^{Et} = 31.4$, $f_m^{Et} = 2.3$, and $f_p^{Et} = 69.5$. An ethyl group activates the *ipso*-

position about as much as the *meta*-position, but is much more activating at the *ortho*- and *para*- positions.

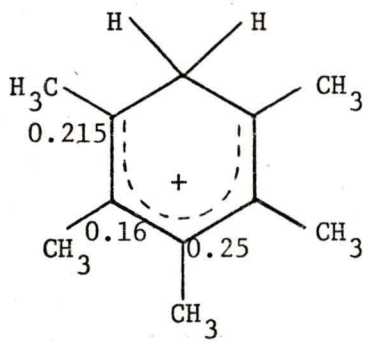
3.4 Formation of Products other than 1,4-Adducts

The cation IV formed in the nitration of *p*-diethylbenzene may be represented, to a first approximation, as a hybrid of three structures with the positive charge equally



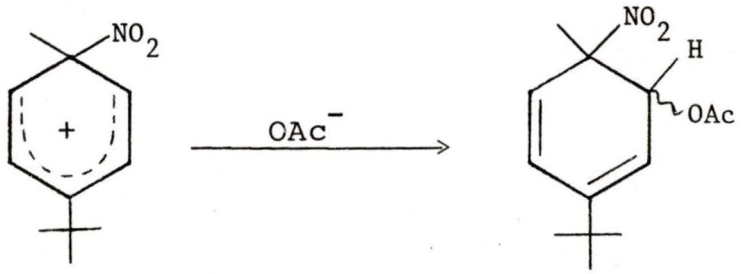
XXIII XXIV XXV

distributed among the *ortho*- and *para*- ring positions. Although little work has been done on ethyl-substituted aromatic systems, an analysis of the pentamethylcyclohexadienyl cation, XXVI shows that the positive charge is

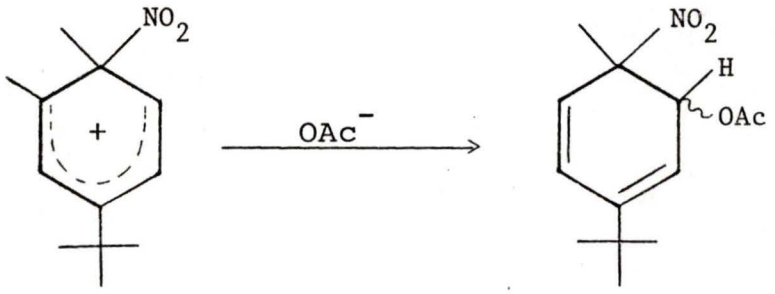


XXVI

concentrated at the *para*-position (65); cation XXIII would be expected to have an even greater concentration of charge at the substituted *para*-position because of the ability of an alkyl group to stabilise the positively-charged centre, with the stability increasing with the size of the alkyl group (61c). The only systems in which a cyclohexadienyl cation is known to trap a nucleophile through structure XXIV are from the *tert*-butyl compounds *p*-*t*-butyltoluene (22) and 4-*t*-butyl-*o*-xylene (24). It would be interesting to investigate

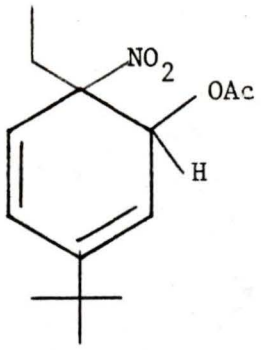


XXVII XXVIII



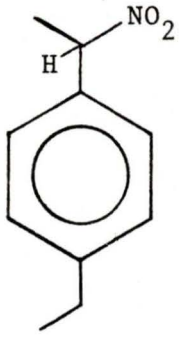
XXIX XXX

the system 4-*t*-butylethylbenzene to determine if the ethyl group was bulky enough to prevent the formation of XXXI.



XXXI

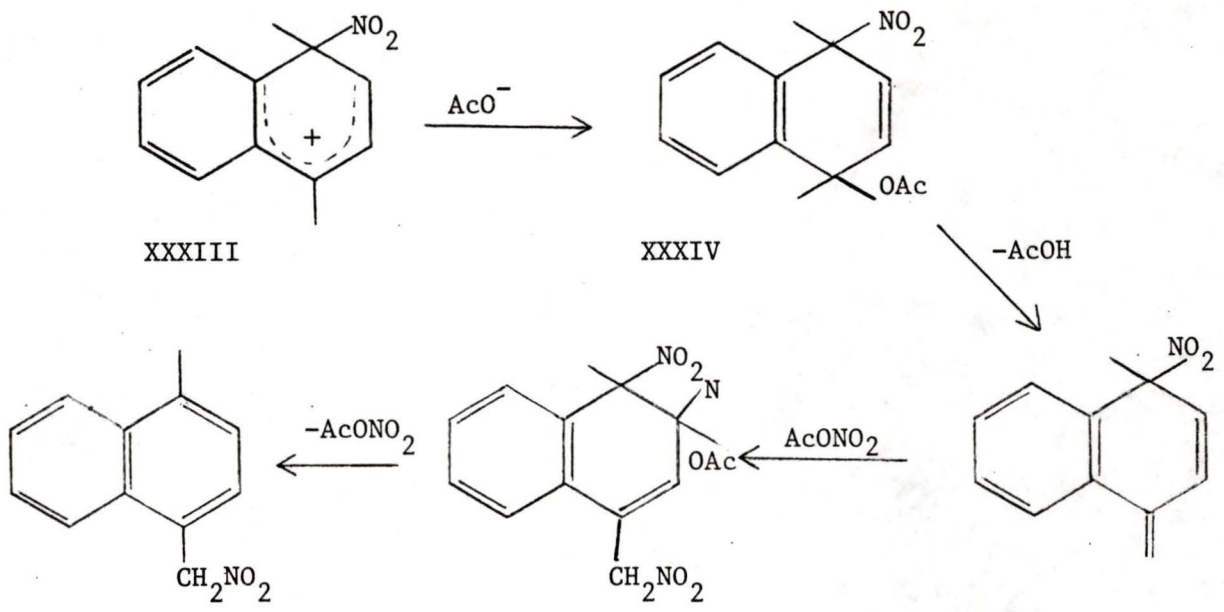
The formation of 1-(*p*-ethylphenyl)nitroethane, XXXII,



XXXII

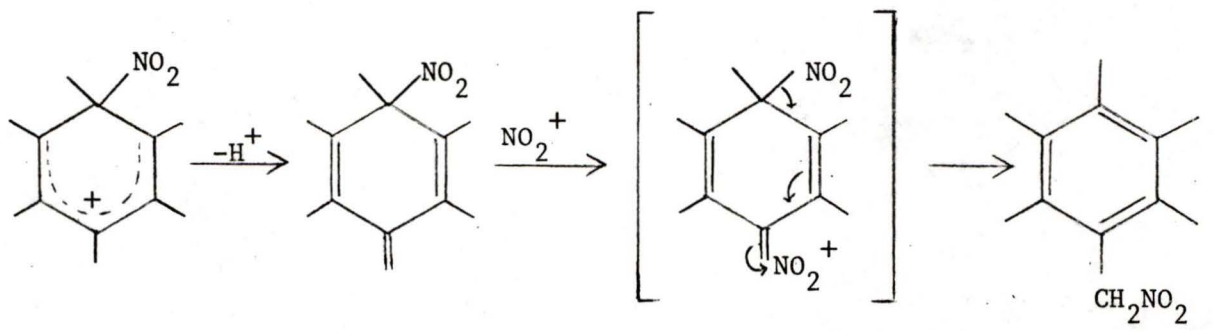
is a consequence of *ipso*-attack. A number of mechanisms have been proposed (7) for the production of side-chain nitro-compounds in various systems (Schemes 3, 4, and 5). Evidence which indicates that the reaction is dependent on the presence of a *para*-methyl group, the availability of a nucleophile, and acid catalysis (12) favours the mechanism of Scheme 6. This mechanism is possible under the reaction conditions where either nitrous acid (formed from acetyl nitrate and/or released in the reaction) or acetate may act as the nucleophile, and where the base is acetate.

Scheme 6 does not specify whether the nucleophile (Y) is added prior to, simultaneously with, or subsequent to the



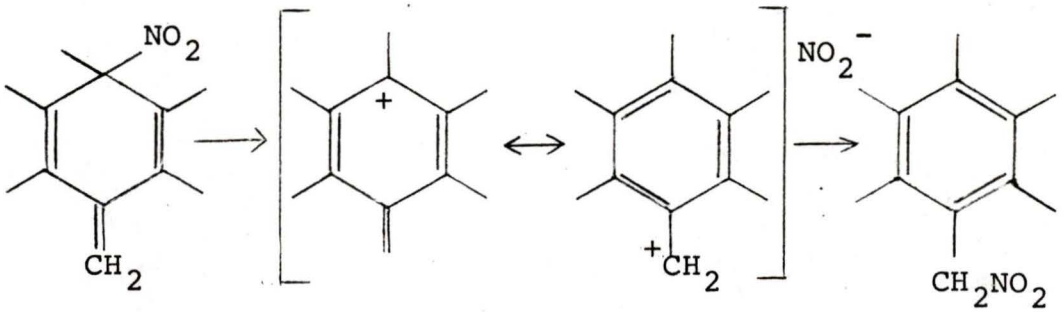
XXXIII XXXIV XXXV XXXVI XXVII

Scheme 3



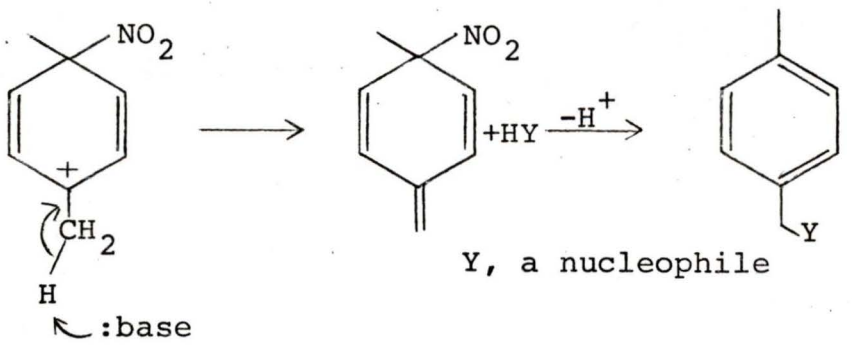
XIV XXXVIII XXXVIIIA XXXIX

Scheme 4



XXXVIII XL XLI XXXIX

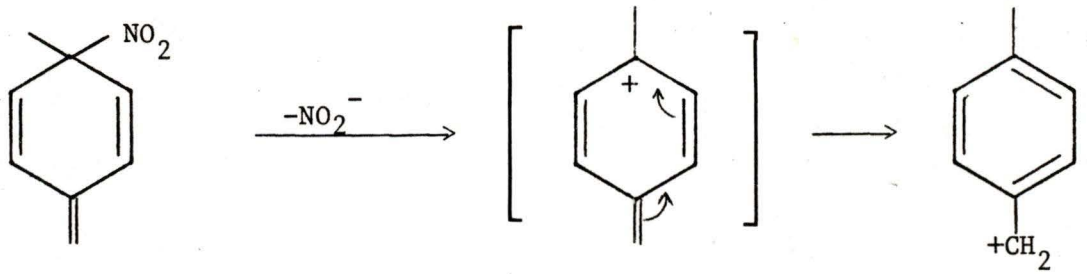
Scheme 5



XLII XIX XLIII

Scheme 6

loss of nitrite. Since it is readily ionised from diene adducts as nitrite anion, it seems most likely that similar ionisation occurs from XIX to generate a benzyl cation which subsequently reacts with a nucleophile. This implies that the reaction is of S_N1' type:

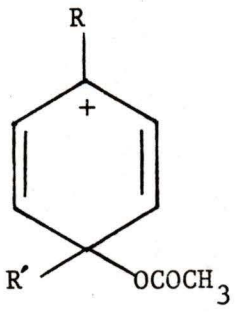


XIX XLIV

Cation XLIV, a benzyl cation, should be relatively stable, but as a carbonium ion it should be a more avid electrophile than the triene XIX, and would be less selective in its reactions. Under various conditions, benzylic nitrites, nitrates, nitro-compounds, acetates, and methyl ethers have been obtained from reaction mixtures in which XLII has been said to exist (23).

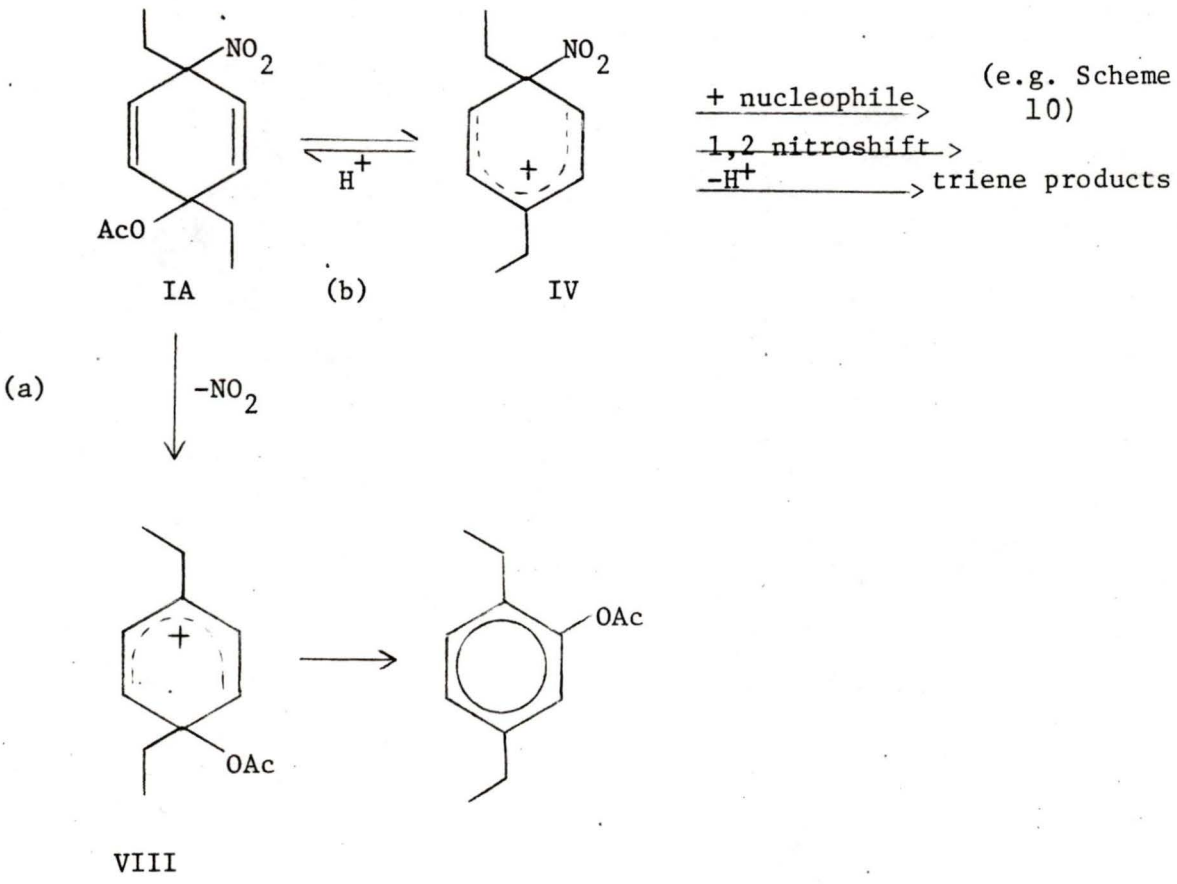
3.5 Reactions of the Adducts

The chemistry of 1-acetoxy-4-nitrocyclohexa-2,5-diene adducts has been extensively investigated. There are two main reaction pathways. Protonation of the acetate group and loss of acetic acid gives the nitrocyclohexadienyl cation, IV. Ionisation of the nitro group as nitrite gives the acetoxycyclohexadienyl cation, VIII:



VIII, R′, R = Et

These cations may react with available nucleophiles to form dienes or they may rearomatise. Rearomatised products may also be obtained from the dienes formed by reaction of IV with other nucleophiles. A prominent reaction in the case of secondary acetate adducts is deprotonation of cation VIII, (R′ = H) to form an aryl acetate. Aryl acetates formed in this way were first detected as the products of non-conventional electrophilic aromatic substitution. In general, acid-catalysed reaction of adducts will involve a partition of the acetoxy diene (or other exchanged diene) through the competing pathways leading to acetoxycyclohexa-2,5-dienyl cation, VIII, or nitrocyclohexa-2,5-dienyl cation, IV (Scheme 7). Pathway (a) is slow, but requires only good ionising conditions. Pathway (b) requires acid catalysis and the presence of good nucleophiles, and may have its rate increased by an increase in acid strength of the reaction medium. The partition of reactions shown (Scheme 7) is general for the reaction of diene adducts of hydrocarbons, and under appropriate conditions the diene can,

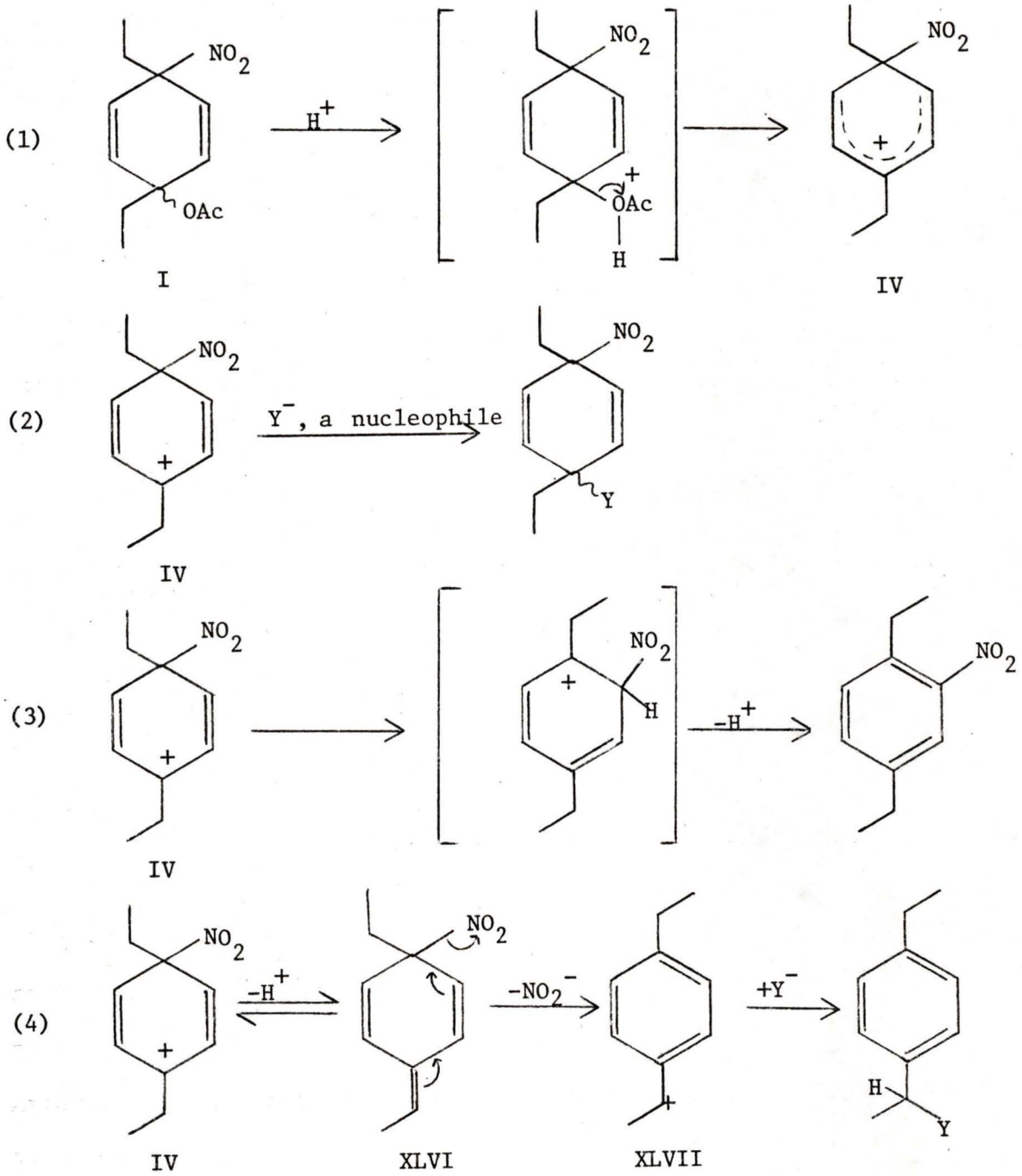


Scheme 7

presumably, be converted quantitatively to products from one of the pathways only.

3.6 Reactions Under Acidic Conditions

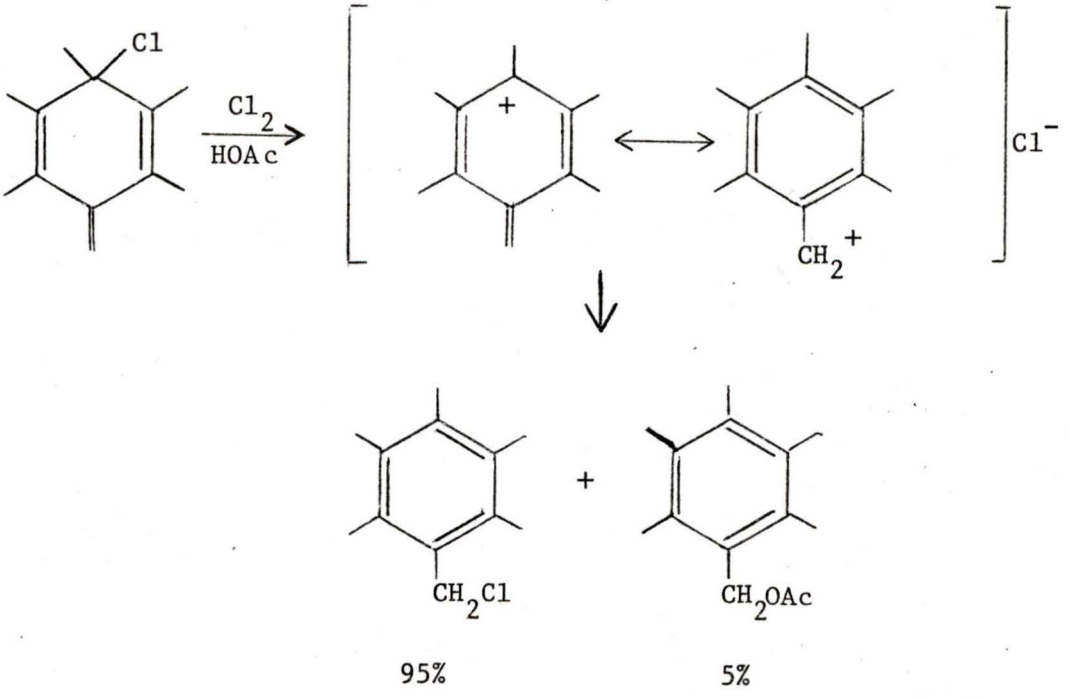
Dienes IA and IB were reacted with acids of varying strengths and concentrations to investigate the spectrum of reactivity of the adducts. A generalisation which explains the products of the reactions, which are summarised in Appendix I, is that the weakly acidic conditions give cation IV which may react with nucleophiles in the solution to give a cyclohexadienyl adduct with epimerisation at C-1 (Reactions 1 and 2, Scheme 8), while strong acids or high


(1)
NO2
OAc
H+
OAc
H
NO2
NO2
I
IV
(2)
NO2
Y−, a nucleophile
NO2
Y
IV
(3)
NO2
NO2
H
−H+
NO2
IV
(4)
NO2
−H+
NO2
−NO2−
+Y−
H
Y
IV
XLVI
XLVII

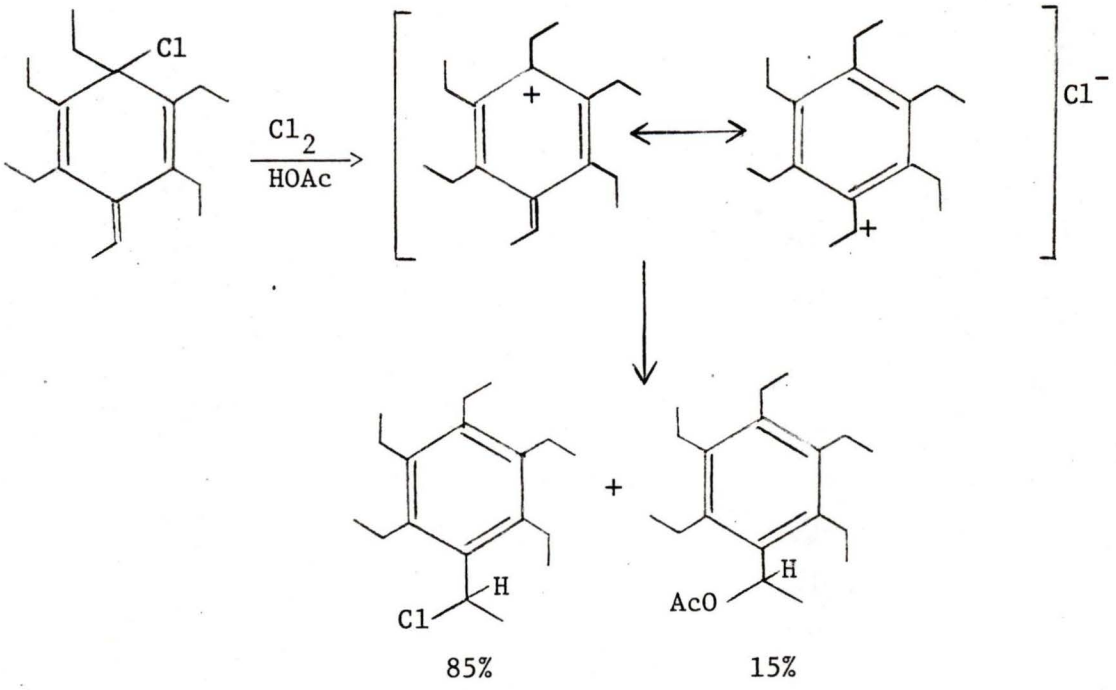
Scheme 8

temperatures cause the initially formed IV to rearomatise through a 1,2-shift of the nitro group (Reaction 3, Scheme 8), or through formation of a triene leading to a side-chain product (Reaction 4). The pathway leading to the formation of side-chain products may conceivably involve the triene and an S_N2' attack by nucleophiles in the solution, but it is more likely that it involves the loss of nitrous acid and trapping of nucleophiles by the benzylic carbonium ion thus formed.

Some evidence in favour of the benzyl cation intermediate is provided by the chlorination of hexa-substituted benzenes (7). The side-chain substitution products are solvolysed to the extent of 5% in the case of hexamethylbenzene and 15% for hexaethylbenzene (Scheme 9).



(a)



(b)

Scheme 9

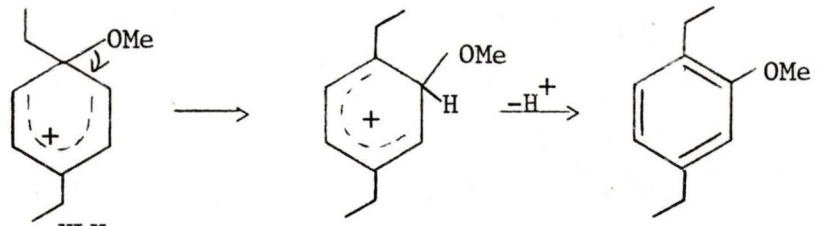
These results are attributed to the greater stability of the secondary carbonium ion formed from an ethyl group as compared to the primary benzylic carbonium ion formed from a methyl group (66).

For a summary of the reactions described below, please refer to Appendix I.

3.6a Reaction of Acetoxy Dienes with Sulphuric Acid and Methanol

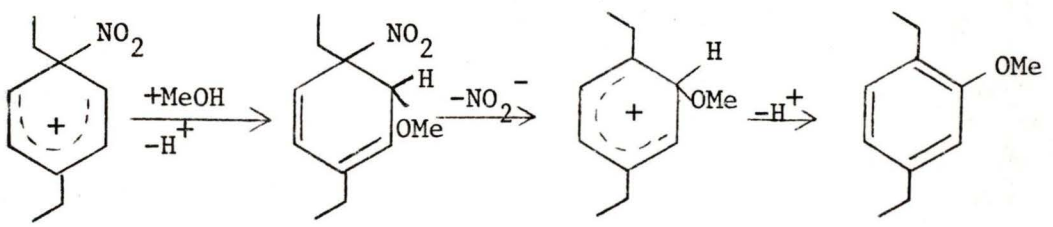
With acid catalysis and a suitable nucleophile, the acetoxy dienes IA and IB can be converted to 1,4-adducts in which the 4-nitro group is retained and the nucleophile at the 1-position has either a *cis*- or a *trans*- relationship to

the nitro-group. Experiments with 0.1% sulphuric acid in methanol-d_3 (2.6c) and 1% sulphuric acid with 10% methanol in acetone-d_6 (2.6i) gave mixtures of the epimeric methoxy (and deuteromethoxy) dienes. The improvement in yield of the dienes with respect to rearomatisation achieved with the higher acid concentration is the result of the more complete protonation of the acetoxy group, allowing less time for the competing rearomatisation reactions which proceed through loss of the nitro group as nitrous acid. It is not known whether the 2,5-diethylanisole obtained as a minor product from this reaction arises by 1,2-shift of the methoxyl group in cation XLV analogously to the formation of 2,5-diethylphenyl acetate (p.111) or whether it is formed from cation



XLV

IV by addition of the methoxyl group at the position adjacent to the nitro-group followed by elimination of nitrous acid:



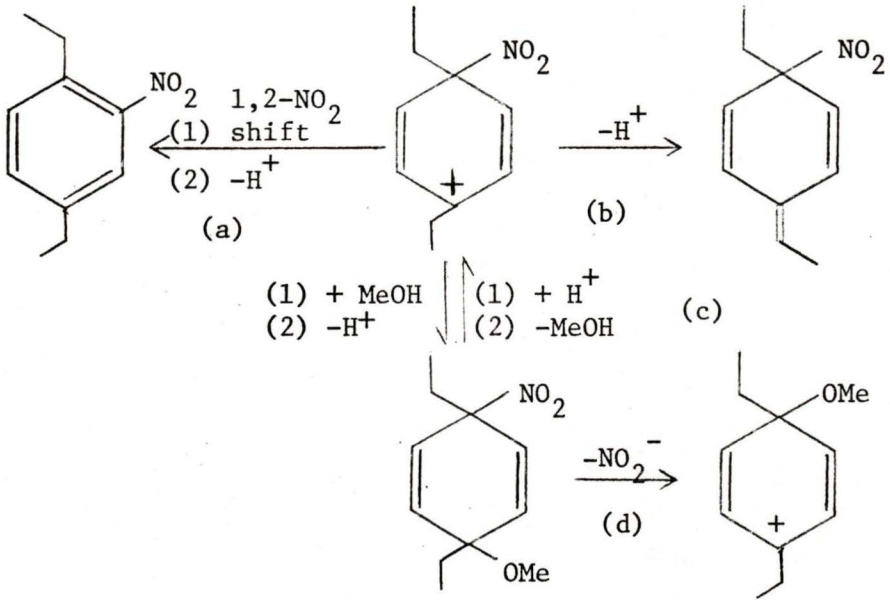
IV

3.6b Reaction with Trifluoroacetic Acid and Methanol

The fate of the cation (IV), despite the uncertainty regarding the nature of the intermediates, is demonstrably affected by the solvent in which it is generated. The results of the series of reactions of Diene I with trifluoroacetic acid (Sec. 2.6k and 2.8c) show that at high acid strength (trifluoroacetic acid in trifluoroacetic anhydride) with a relatively poor nucleophile the 1,2-shift of the nitro group is favoured and is, in fact, quantitative, while at lower acid strength (60% trifluoroacetic acid in methanol) with a strong nucleophile present, the ion is quantitatively converted to methoxy dienes. The methoxy dienes rearomatise to give side-chain and nuclear aromatic methyl ether while at higher acid strength the nucleophilicity of the methanol is in effect reduced and the nitroproducts are formed. Under the conditions of the experiment, it is not possible to determine whether the 2,5-diethylnitrobenzene formed from reaction of the 80% and 90% trifluoroacetic acid mixtures is the product of acetoxy diene reaction, or of methoxy diene, as the reaction is complete by the time the first N.M.R. spectrum can be obtained. With 70% acid solution, the formation and rearomatisation of methoxy dienes can be followed, but the product of the reaction is 46% 2,5-diethylnitrobenzene and 34% 2,5-diethylanisole, which indicates that the methoxy

diene does not react to give methyl ethers exclusively and that it does give the nitroarene at sufficiently high acid concentrations.

The products of the acid-catalysed reactions of the methoxy diene,VI, may be explained by considering the partition of the cation, IV, among three pathways (Scheme 10).

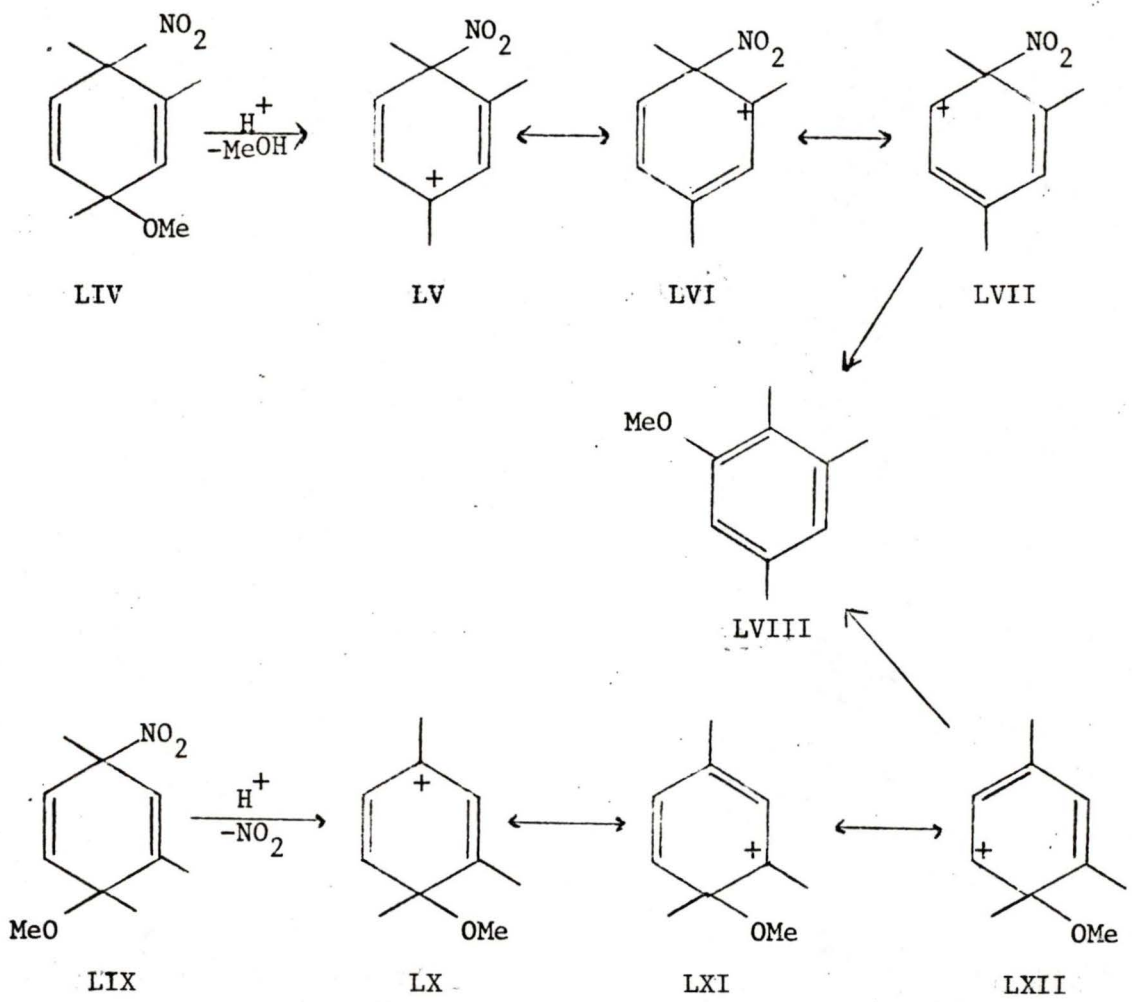


Scheme 10

At low acid concentrations the equilibrium concentration of cation IV is low and correspondingly the rate of formation of 2,5-diethylnitrobenzene is decreased. Reaction by pathway (d) which is independent of acid concentration is then able to compete effectively with (c) and 2,5-diethylanisole is formed in higher yields. Under the highly acidic conditions, cation IV cannot readily lose a proton and is

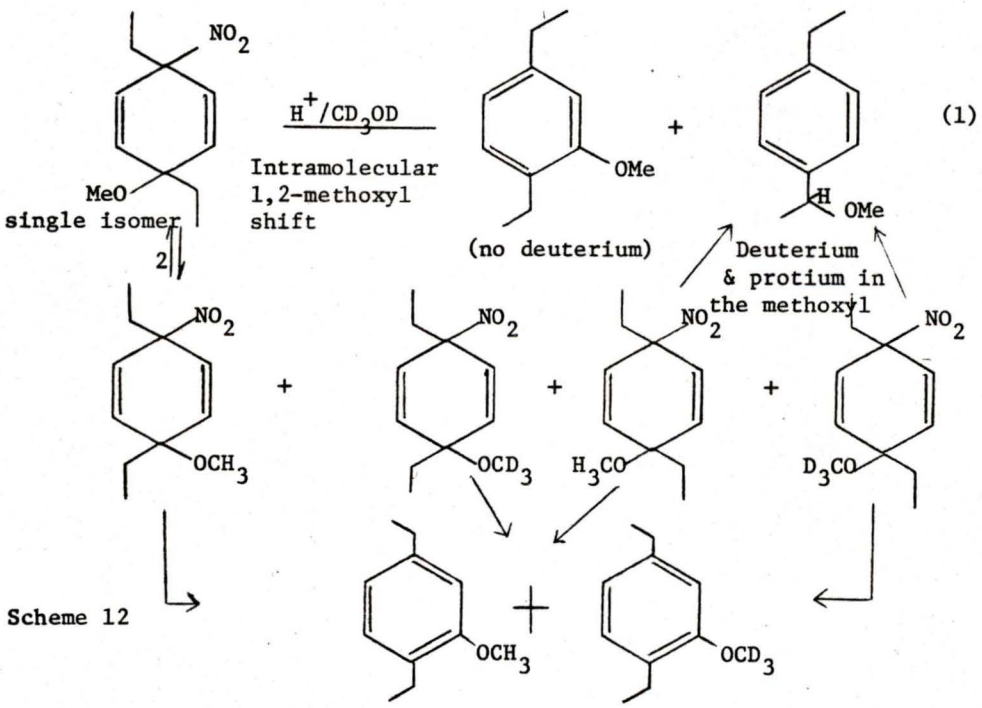
largely constrained to undergoing reaction via pathway (a), although 5-10% of the reaction proceeds through pathway (b) to give side-chain products. The greater nucleophilicity of the solvent with increased methanol allows the cation to be trapped (c).

Ramsay (23) studied the rearomatisation of the methoxy dienes from pseudocumene (Scheme 11). The fine



Scheme 11

balance between loss of the nitro group and loss of the methoxyl group is shown by this reaction, where stabilisation of only one of the canonical forms of the intermediate cation in each case (LVI and LXI) by the adjacent methyl group, can lead to exclusive formation of products from that intermediate. It should be noted that the reaction of LXII to LVIII may be either intermolecular or intramolecular, and this applies to the reaction of the methoxy dienes from *p*-xylene as well. Experiments may be devised which could show if the reaction is intramolecular, but cannot distinguish between intermolecular and intramolecular mechanisms if, as is likely under acidic conditions, exchange takes place before rearomatisation (Scheme 12, Equilibrium 2). The mechanism which Ramsay proposed has the advantage of only requiring one pathway.



Scheme 12

3.6c Reaction of Dienes with Sulphuric Acid and Acetic Acid

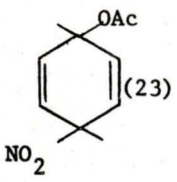
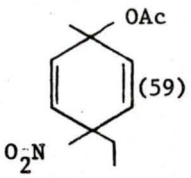
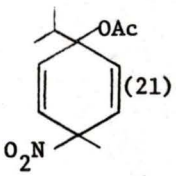
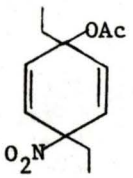
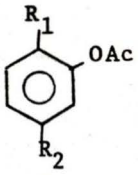
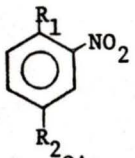
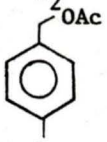
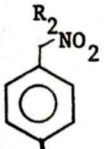
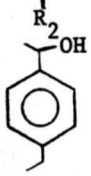
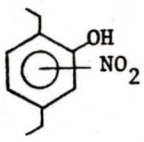
The solvolysis of dienes IA and IB in acetic acid-d_4 (dried by refluxing with 10% of acetic anhydride) was catalysed by sulphuric acid (2.6g). The expected increase in the rate of rearomatisation was observed as the sulphuric acid concentration was increased up to fifty per cent, and exchange of acetate for deuterated acetate was observed in the experiments at lower acid concentration. These reactions proceed through the usual intermediate, nitrocyclohexadienyl cation, IV. When conditions were altered to promote solvolysis, while minimising rearomatisation (viz. 0.25% sulphuric acid, 50% deuterochloroform, 50% dried acetic anhydride (2.6h)) the *cis*-acetoxynitrodiene, IB, was converted entirely to its *trans* diastereoisomer, IA. The greater thermodynamic stability of the *trans*- with respect to the *cis*-isomer has not been observed in other systems in which the acetoxy dienes have been equilibrated. In the reaction of *trans*-1-ethyl-4-methyl-4-nitrocyclohexa-2,5-dienyl acetate with acetic anhydride and trifluoroacetic acid, the diene epimerised to give a 50:50 mixture of the *cis*- and *trans*- dienes in thirty minutes. The significance of the increased thermodynamic stability of the *trans*-diene from *p*-diethylbenzene is the observation that dienes formed in epimeric pairs on nitration of the aromatic substrate in acetic anhydride are formed under conditions of kinetic control.

3.6d Reaction of Diene I with Acetic Acid-d_4

The reaction of the dienes IA and IB with dried acetic acid gave a mixture of hydroxylic products and 2,5-diethylphenyl acetate, with a half-life for the rearomatisation of ca. 50 min. The *p*-ethylstyrene detected by g.l.c. is probably the dehydration product of 1-(*p*-ethylphenyl) ethanol and was not formed during the solvolytic reaction. The reactions of other dienes with dried acetic acid have been studied (Table VII). The deviation from the expected product ratios and the wide difference in the rate of the reaction in the case of *p*-diethylbenzene is probably the result of incomplete drying of the acetic acid. The yield of hydroxylic products also indicates the presence of water in the reaction medium. The nitrophenol is formed by the attack of nitrous acid released from rearomatisation of the diene 2,5-diethylphenol, itself formed by exchange of acetate for hydroxyl via cation IV and subsequent rearomatisation of the hydroxy diene via ionisation of nitrite. Detection of deuterated 2,5-diethylphenyl acetate by g.l.c.-m.s. shows that the acetic acid in this medium is a strong enough acid to protonate the acetoxy group of the starting dienes and to generate cation IV which then traps deuterated acetate from the solvent. However, since only a minor fraction (20%) of the 2,5-diethylphenyl acetate is deuterated it is clear that formation of cation IV and reversion

TABLE VII

Reactions of Dienes With Dried Acetic Acid-d_4

				
$t_{\frac{1}{2}}$	11 hr. (20°C)	20 hr. (35°C)	109 hr. (35°C)	50 min. (35°C)
Aromatic Products				
	51	52	100	68
		3		
	29	38		
	20	7		
				6
				26
Drying Method	18 hr. reflux	no reflux	reflux	1 hr. reflux

to (exchanged) adduct is slower than formation of the acetoxycyclohexadienyl cation, VIII, and migration of the acetate group to form the aryl acetate. This is supported by the fact that only a minor amount of side-chain product, for which cation IV is an essential intermediate, is formed in the reaction. The nitrophenol product is presumably formed by nitration via nitrosation of the phenol.

3.6e Reaction of Diene I with Acetic Acid-d_4 and 5% D_2O

The solvolysis of diene I in acetic acid with added water gave a product ratio very similar to that of the reaction with dry acetic acid (vide supra), giving support to the argument that the acetic acid in the previous experiment was not adequately dried after one hour of reflux with acetic anhydride. The solvolysis of the *p*-xylene adducts under these conditions gave mainly 2-acetoxy-*p*-xylene with about 25% deuterated acetate, while *trans*-1-ethyl-4-methyl-4-nitrocyclohexa-2,5-dienyl acetate gave 58% aryl acetates with 34% deuteration of the acetate. Hydroxy-nitro adducts were observed during the reactions of the *p*-xylene and *p*-ethyltoluene adducts, and the latter yielded 37% of nitrophenols (59).

3.6f Reaction of Diene I with Water and Sulphuric Acid

The solvolysis of the acetoxy diene, IA, gave both of the isomers of the hydroxynitro adduct, V. The reaction

must have proceeded through loss of the protonated acetoxy group to give cation IV, which subsequently trapped the water present in the solution. There is no evidence from this experiment to determine whether the equilibrium mixture of hydroxy dienes was formed.

3.6g Reactions of Diene I with Boron Fluoride Etherate and Trifluoromethane Sulphonic Acid

The reaction of the acetoxy-nitro adduct under highly acidic conditions has been studied using trifluoromethane sulphonic acid (Sec. 2.8b), boron trifluoride etherate (Sec. 2.8a), trifluoroacetic acid in trifluoroacetic anhydride (2.8c), and 50% sulphuric acid in acetic acid (2.6g (iv)). Each of these reagents gave 2,5-diethylnitrobenzene as the major product of the reaction, but in most cases some side-chain derivatives and *p*-ethylacetophenone were also obtained. The Lewis acid, boron trifluoride, gave the same results as the protic acids. Under certain conditions with trifluoroacetic acid the formation of side-chain products could be suppressed but the other strong acids gave *p*-ethylacetophenone or the side-chain acetate in all trials. Presumably, under strongly acidic conditions, the nitrocyclohexadienyl intermediate, IV, should undergo a 1,2-nitro shift before the *para*-ethyl group can be deprontonated to give the triene, XLVI (cf. equations (3) and (4), Scheme 8), as there is no base

available to abstract the benzylic proton. However, it is not possible to ensure that the reaction does not take place until the reaction mixture is made homogeneous through mixing. The side-chain products probably arise from reactions in which the local concentration of acid in some regions of the mixture is low. The acetophenone is presumably not a primary side-chain reaction product, but is most likely formed from a side-chain nitrite or other derivative. Benzaldehydes have been observed under similar conditions in reactions of cyclohexadienyl adducts formed from *p*-xylene and related compounds. They are known to be formed from many of the benzylic products obtained on rearomatisation of diene adducts containing methyl groups.

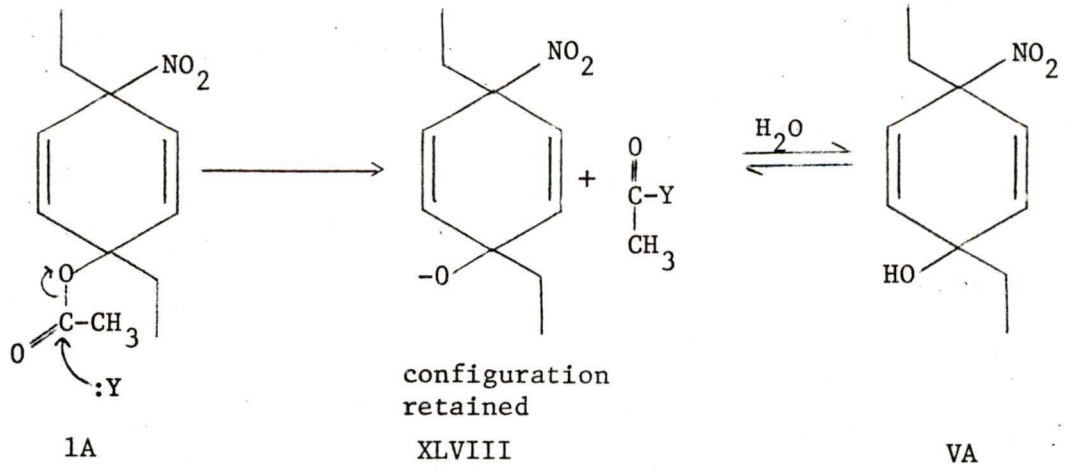
3.6h Reaction of *p*-Xylene *trans*-Diene with HCl

The S_N1 displacement of acetate by chloride from 1,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate under anhydrous conditions is catalysed by acid and gives the isomeric pair of chloronitro adducts. This reaction follows the same pathway as the previously-discussed acid-catalysed reactions, viz. protonation and loss of acetic acid to form the nitrocyclohexadienyl cation, followed by combination with chloride, and demonstrates the effect of the presence of a good nucleophile (chloride) in trapping the intermediate, in contrast to the situation where a poor nucleophile (trifluoromethanesulphonate) allows the cation to rearrange

and rearomatise. The chloro-nitro adducts can be also produced through the action of thionyl chloride on the hydroxy dienes (33). Chloro-adducts may be useful intermediates in the synthesis of other adducts or chlorinated aromatic compounds.

3.7 Base Catalysed Reactions of Dienes

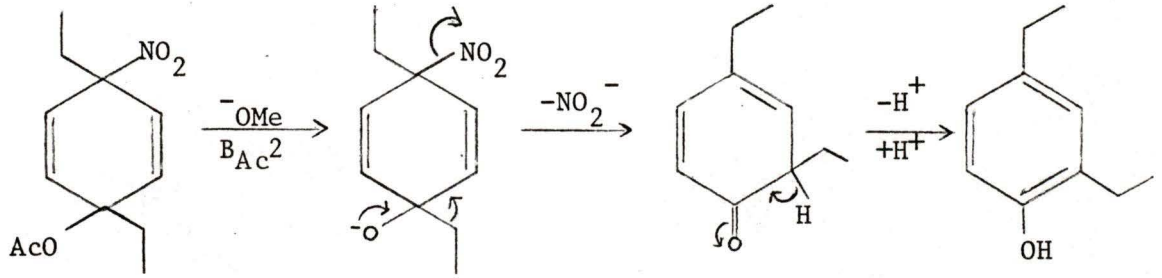
Three base-catalysed reactions of the dienes were studied. The acetoxy dienes from *p*-xylene were hydrolysed to the corresponding hydroxy dienes by sodium methoxide at 0°C. The hydroxy dienes from *p*-diethylbenzene were prepared by aluminum hydride cleavage of the acetate group, while the reaction of the acetoxynitro adducts with sodium methoxide at 35°C gave 2,4-diethylphenol. The unifying mechanism of these three reactions is the $B_{Ac}2$ hydrolysis of the acetate by methoxide or (conceptually) hydride ion.



1A XLVIII VA

configuration retained

The isolation of hydroxy dienes at 0°C allows the mechanism of the reaction of the acetoxy diene to give 2,4-diethylphenol to be deduced. The alkyl group does not migrate in the presence of an acetoxy group in any reaction of the *p*-diethylbenzene adducts: reactions in which the acetoxy cyclohexadienyl cation, VIII, is formed give products with the 1,4-orientation of the ethyl groups. The high basicity and the high ionising strength of the methoxide solutions at 35°C cause the anion XLVIII to rearrange through a 1,2-alkyl (ethyl) migration to give the dienone XLIX, which is the keto form of the phenol. The



I XLVIII XLIX XI

driving force for the reaction must be the greater stability of the nitrite anion with respect to the alkoxide anion, and the gain in resonance energy on going from the 1,4-diene to the conjugated 2,4-cyclohexadienone. Methoxy-nitro adducts of *p*-cymene, which cannot undergo cleavage to give an isomer of XLVIII, may be recovered unchanged from solutions of sodium methoxide (21). Thus the base catalysed rearomatisation of I has been shown to require intermediate

XLVIII, by analogy with the reaction of the *p*-xylene adducts, and the rearrangement of XLVIII is straightforward. This reaction may be of some utility in the synthesis of 2,4-dialkylphenols.

The migration of ethyl and isopropyl groups in the base-catalysed reaction is in contrast to the behaviour of the *t*-butyl adducts which eliminate the elements of *t*-butyl nitrite to give phenols (e.g., *p*-cresol from the adduct from 4-*t*-butyltoluene).

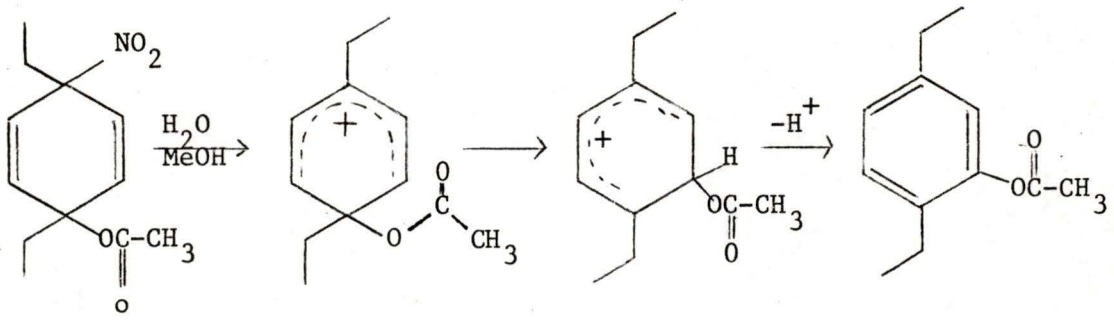
3.8 Pyrolysis and Neutral Solvolysis of Dienes

The pyrolytic decomposition of cyclohexadienyl adducts upon injection into the gas chromatograph is a general reaction of these compounds, and prevents analysis by gas chromatography of the reaction mixtures from the nitration in acetic anhydride of hydrocarbons which give rise to this class of adducts. There is a much higher proportion of pyrolysis product derived from loss of the nitro-group than from initial loss of acetate from diene I, or hydroxyl from dienol V.

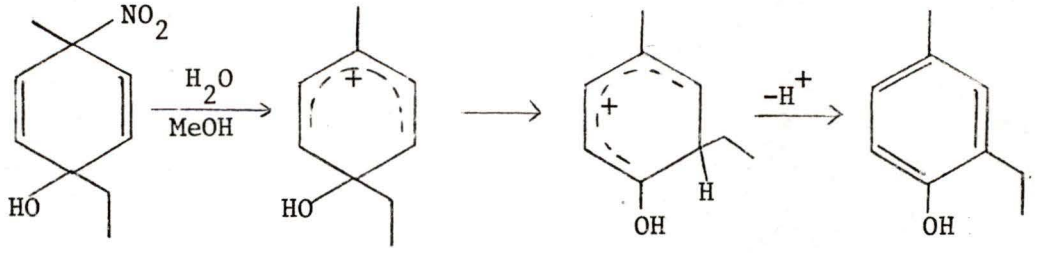
The lack of reaction of the acetoxy dienes at room temperature demonstrates the range of stability of these adducts under non-acidic and non-ionising conditions. The failure of Wright and co-workers (20) to isolate *cis*-adduct IB when their nitration was carried out at 0°C is readily understood in terms of the unfavourable conditions for

survival of the adduct: the dienes were exposed to an acid medium at an excessively high temperature.

The reaction of the diene I to give 2,5-diethylphenyl acetate in 50% aqueous methanol proceeds through ionisation of the nitro-group as nitrite, followed by the facile 1,2-shift of the acetoxy group.



Kinetic data are not available to determine whether this is an E1 loss of nitrite as shown, or whether the migration of the acetate is concerted with loss of the nitro group. In a similar reaction of *trans*-1-ethyl-4-methyl-4-nitrocyclohexa-2,5-dienol with 20% aqueous methanol, the product was 2-ethyl-4-methylphenol (59). The fate of the cation derived



from loss of nitrite is thus seen to depend not only on the solvent and temperature, but also on the relative migratory aptitudes of the substituent and its geminal alkyl group.

3.9 Conclusion

This thesis describes the preparation, isolation, and reactions of the pair of isomeric acetoxynitro diene adducts formed in the nitration of *p*-diethylbenzene by acetyl nitrate. The formation of adducts of this type is well known and has caused an extension in recent years of theories concerning the initial steps of the mechanism of electrophilic aromatic substitution to include attack of an aromatic system at a substituted position. The reactions of the adducts give rise to products which are, in many cases, similar to products of side reactions in the nitration of aromatic compounds. Study of the reactions of the adducts allows many of the side products to be attributed to the initial occurrence of *ipso*-attack.

The reactions of the adducts of *p*-diethylbenzene, which are tertiary acetates, follow the patterns established in other systems. These include exchange and solvolysis of the acetate group under suitable mild conditions to give adducts, and rearomatisation reactions from loss of the nitro group as nitrite or the acetoxy group as acetic acid, under highly ionising and highly acidic conditions, respectively. The exchange reactions of the adducts are S_N1 reactions and in each instance result in formation of a pair of diastereoisomeric dienes. The base-catalysed solvolyses, on the other hand, are $B_{AC}2$ hydrolyses and give cyclohexadienols which retain the stereochemistry of the starting

materials. Under strongly acidic conditions the acetoxy group is protonated and lost as acetic acid by an El process. The resulting nitrocyclohexadienyl cation may undergo a 1,2-nitro shift to give a Wheland intermediate, which is deprotonated to give the conventional nitration product, or the cation may proceed through a proposed cyclohexatrienyl intermediate to trap a nucleophile (or an electrophile) at the exocyclic ethylene position to give side-chain substituted products (or their styrene or acetophenone derivatives) through S_N2' (S_E2') elimination of nitrite (nitronium).

Aromatic acetates formed after ionisation of nitrite from the adduct are formed via a 1,2-shift of acetate. In the strongly basic sodium methoxide solution, the dienol formed from the solvolysis is deprotonated and the hydroxyl group does not migrate, but is converted through a cyclohexadienone to the phenol with the ethyl groups in a 2,4-orientation.

The isolation of adducts formed from electrophilic attack *ipso-* to ethyl groups had not been reported at the inception of this study. The isolation of adducts of *p*-diethylbenzene with both the *cis-* and *trans-* orientations of the nitro and acetoxy groups is reported for the first time in this thesis.

REFERENCES

1. (a) Hoggett, J. G., Moodie, R. B., Penton, J. R., and Schofield, K., *Nitration and Aromatic Reactivity*, University Press, Cambridge, 1971, Chapter 1;

   (b) *Ibid.*, pp. 103-105;

   (c) *Ibid.*, pp. 124-5;

   (d) *Ibid.*, pp. 57-60.

2. Tobe, K. A., and Doumani, T. F., in *Organic Synthesis, Collective Volume 3*, John Wiley and Sons, New York, 1955, p. 653.

3. (a) Olah, G. A., Kuhn, S. J., and Flood, S., J. Amer. Chem. Soc., 83, 4571 (1961);

   (b) *Ibid.*, 83, 4581 (1961);

   (c) Kuhn, S. J., and Olah, G. A., J. Amer. Chem. Soc., 83, 4564 (1961).

4. Ingold, C. K., *Structure and Mechanism in Organic Chemistry, 2nd Ed.*, Bell, London, 1969.

5. Marziano, N. C., Passerini, R., Rees, J. H., and Ridd, J. H., J. Chem. Soc., Perkin II, 1977, 1361.

6. (a) Norman, R. O. C., and Taylor, R., *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, Amsterdam, 1965, p. 69;

   (b) *Ibid.*, p. 34;

   (c) *Ibid.*, p. 76.

7. Hartshorn, S. R., Chem. Soc. Reviews, 3, 167 (1974).

8. Wheland, G. W., J. Amer. Chem. Soc., 64, 900 (1942).

9. Moodie, R. B., Schofield, K., and Weston, J. B., J. Chem. Soc., Chem. Comm., 1974, 382.

10. Olah, G. A., Lin, H. C., Olah, J. A., and Navang, S. C., Proc. Nat. Acad. Sci. U.S.A., 75, 545, 1978.

11. Perrin, C. L., and Skinner, G. A., J. Amer. Chem. Soc., 93, 3389 (1971).

12. Fischer, A., and Ramsay, J. N., J. Chem. Soc., Perkin II, 1973, 237.

13. Seyan, S. S., M.Sc. Thesis, University of Victoria, 1978.

14. Barnes, C. E., and Myhre, P. C., J. Amer. Chem. Soc., 100, 975 (1978).

15. Fischer, A., and Röderer, R., J. Chem. Soc., Chem. Comm., 1975, 798.

16. Olah, G. A., Lin, H. C., and Mo, Y. K., J. Amer. Chem. Soc., 94, 3367 (1972).

17. Janzen, E. G., Accounts Chem. Res., 4, 31 (1971).

18. (a) Blackstock, D. J., Fischer, A., Richards, K. E., Vaughan, J., and Wright, G. J., J. Chem. Soc., Chem. Comm., 1970, 641;

    (b) Blackstock, D. J., Cretney, J. R., Fischer, A., Hartshorn, M. P., Richards, K. E., Vaughan, J., and Wright, G. J., Tetrahedron Lett., 1970, 2793.

19. Fischer, A., Henderson, G. N., and Thompson, R. J., Aust. J. Chem., 31, 1241 (1978).

20. Clemens, A. H., Hartshorn, M. P., Richards, K. E., and Wright, G. J., Aust. J. Chem., 30, 103 (1977).

21. Fischer, A., and Röderer, R., Can. J. Chem., 54, 423 (1976).

22. (a) Fischer, A., and Röderer, R., Can. J. Chem., 54, 3978 (1976);

    (b) ref. 15, this work.

23. Ramsay, J. N., Ph.D. Dissertation, University of Victoria, Victoria, 1973.

24. Fischer, A., and Teo, K. C., Can. J. Chem., 56, 258 (1978).

25. Fischer, A., and Leonard, D. R. A., Can. J. Chem., 54, 1795 (1976).

26. Fischer, A., and Leonard, D. R. A., unpublished results.

27. Fischer, A., and Fowler, B. R., unpublished results.

28. Fischer, A., and Greig, C. C., unpublished results.

29. Fischer, A., and Greig, C. C., J. Chem. Soc., Chem. Comm., 1974, 50.

30. Blackstock, D. J., Ph.D. Dissertation, University of Canterbury, 1970 (quoted in ref. 13).

31. Fischer, A., and Greig, C. C., Can. J. Chem., 52, 1231 (1974).

32. Fischer, A., Greig, C. C., and Röderer, R., Can. J. Chem., 53, 1570 (1975).

33. Iyer, L. M., personal communication.

34. Fischer, A., and Leonard, D. R. A., J. Chem. Soc., Chem. Comm., 1973, 300.

35. Fischer, A., and Wilkinson, A. L., Can. J. Chem., 50, 3988 (1972).

36. Fischer, A., and Leonard, D. R. A., Can. J. Chem., 50, 3367 (1972).

37. Fischer, A., Greig, C. C., Wilkinson, A. L., and Leonard, D. R. A., Can. J. Chem., 50, 2211 (1972).

38. Hahn, R. C., and Galley, M. W., J. Amer. Chem. Soc., 96, 4337 (1974).

39. Hahn, R. C., and Groen, M. B., J. Amer. Chem. Soc., 95, 6128 (1973).

40. Fischer, A., and Teo, K. C., Can. J. Chem., 56, 1758 (1978).

41. Myhre, P. C., J. Amer. Chem. Soc., 94, 7921 (1972).

42. Banwell, T., Morse, C. S., Myhre, P. C., and Vollmar, A., J. Amer. Chem. Soc., 99, 3092 (1977).

43. Barnett, J. W., Moodie, R. B., Schofield, K., and Weston, J. B., J. Chem. Soc., Perkin II, 1975, 648.

44. Hahn, R. C., and Strack, D., J. Amer. Chem. Soc., 96, 4335 (1974).

45. Perrin, C. L., J. Org. Chem., 36, 420 (1971).

46. Fischer, P. B., and Zollinger, H., Helv. Chim. Acta., 55, 2139 (1972).

47. Fischer, A., and Seyan, S. S., Can. J. Chem., 56, 1348 (1978).

48. Nightingale, D. V., Chem. Rev., 40, 117 (1947).

49. (a) Olah, G. A., and Kuhn, S. J., Amer. Chem. Soc., 86, 1067 (1964);

(b) *Ibid.*, and ref. 15 this work.

50. Gaudion, W. J., Hook, W. H., and Plant, S. J., J. Chem. Soc., 1947, 1631.

51. Augustine, R. L., *Catalytic Hydrogenation*, Marcel Dekker, New York, 1965, pp. 36, 152.

52. Vogel, A. I., *A Text-Book of Practical Organic Chemistry*, Longmans, Green and Co., New York, 1951, p. 613.

53. Adams, R., and Noller, C., in *Organic Syntheses, Collective Volume 1, 2nd Ed.*, John Wiley and Sons, New York, 1941, p. 109.

54. Roberts, R. M., Gibert, J. C., Rodewald, L. B., and Wingrove, A. S., *An Introduction to Modern Experimental Organic Chemistry*, Holt, Rinehart and Winston, Inc., New York, 1969, Chapter 17.

55. (a) Buehler, C. A., and Pearson, D. E., *Survey of Organic Syntheses*, Wiley-Interscience, New York, 1970, p. 1007.

(b) Emmons, W. D., and Pagano, A. S., J. Amer. Chem. Soc., 77, 4557 (1955).

56. Beilstein, Hauptwerke, Vol. VI, p. 608.

57. Bhacca, N. S., Hollis, D. P., Johnson, L. F., Pier, E. A., and Shoolery, J. N., *Varian High Resolution N.M.R. Spectra Catalog*, Varian Associates, Palo Alto, #498.

58. Teo, K. C., Personal Communication.

59. Henderson, G. N., unpublished results.

60. Olah, G. A., Kuhn, S. J., Flood, S., and Evans, J. C., J. Amer. Chem. Soc., 84, 3687 (1962).

61. (a) Hirsch, J. A., *Concepts in Theoretical Organic Chemistry*, Allyn and Bacon, Inc., Boston, 1974, p. 133;

(b) *Ibid.*, pp. 118-119;

(c) *Ibid.*, p. 104.

62. Hinkley, C. C., J. Amer. Chem. Soc., 91, 5160 (1969).

63. Sanders, J. K. M., and Williams, D. H., J. Amer. Chem. Soc., 93, 641 (1971).

64. Fischer, A., and Wright, G. J., Aust. J. Chem., 27, 217 (1974).

65. Norman, R. O. C., and Radda, G. K., J. Chem. Soc., 1961, 3610.

66. Illuminati, G., Mandolini, L., Arnett, E. M., and Smoyer, R., J. Chem. Soc. (B), 1971, 2206.

Reactions of Dienes

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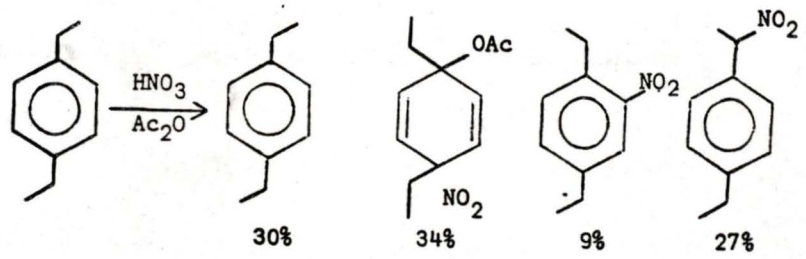
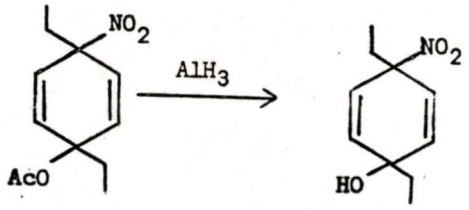
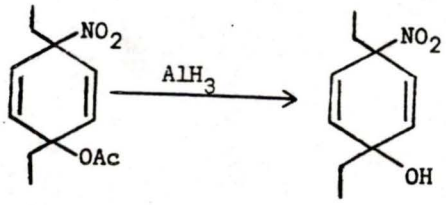
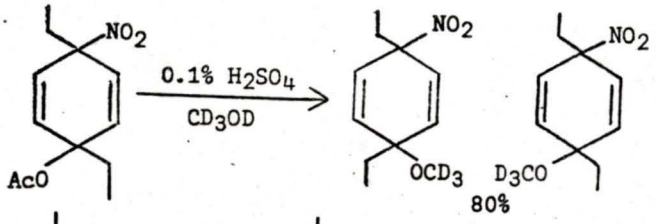
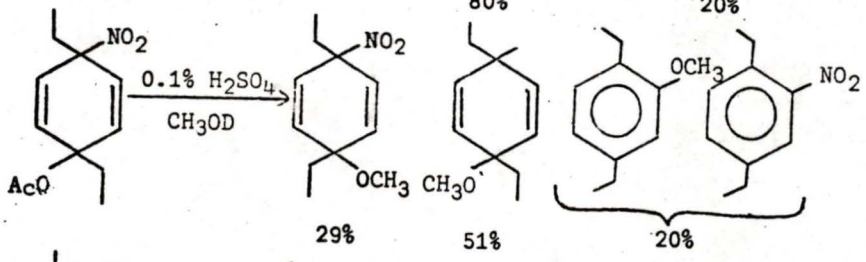
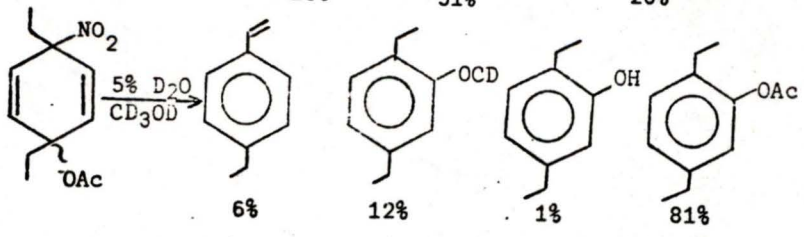
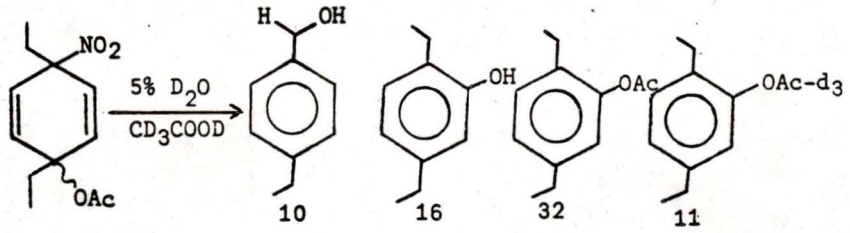
	2.2. a	1
	2.6. a	2a
	2.6. b	2b
	2.6. c	3a
	2.6. c	3b
	2.6. d	4



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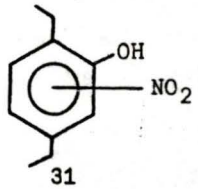

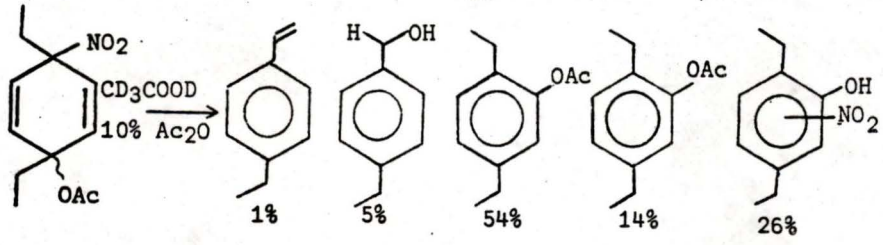

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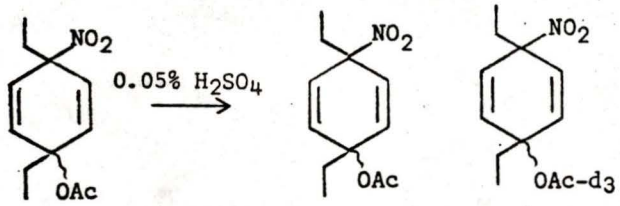

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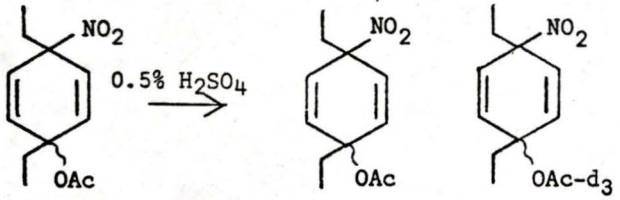

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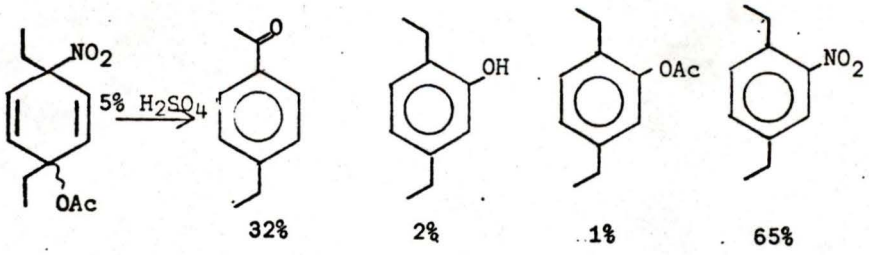

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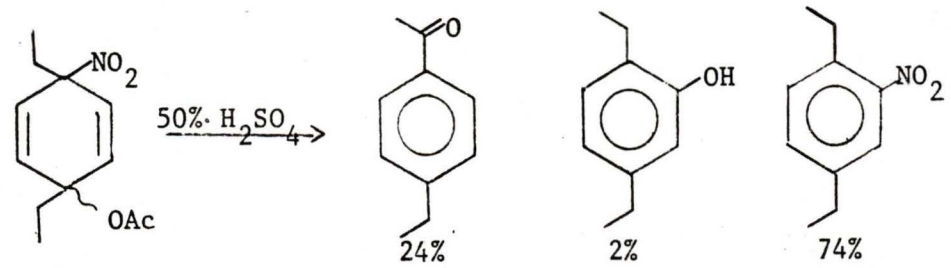

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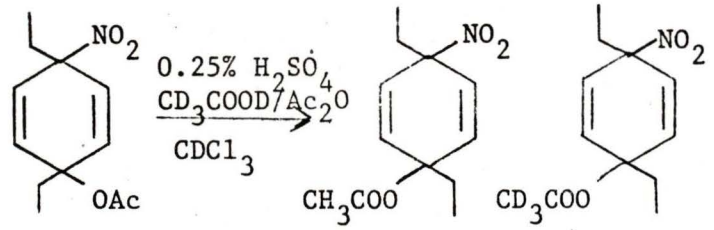

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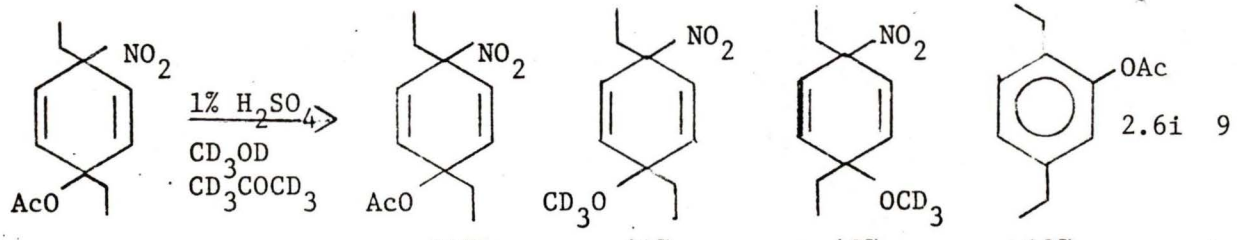

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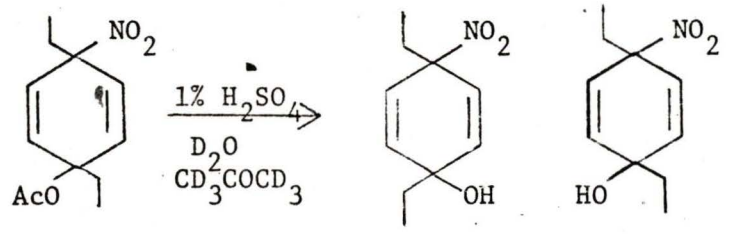

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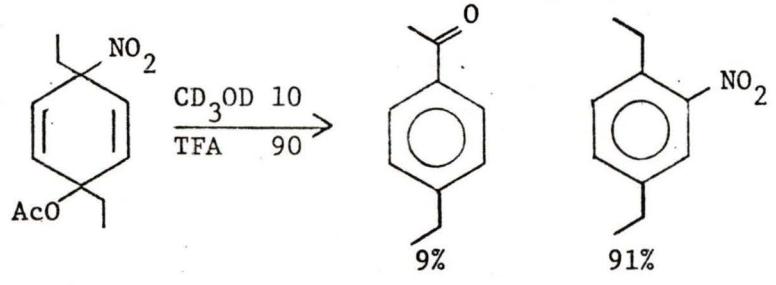

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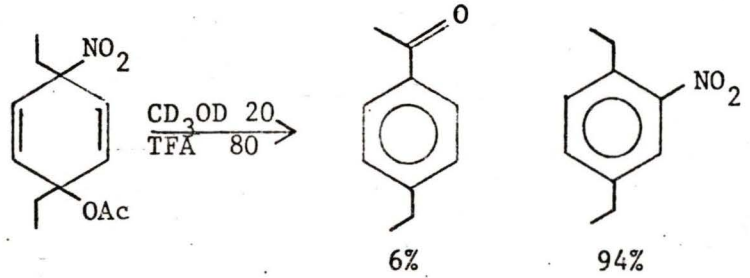

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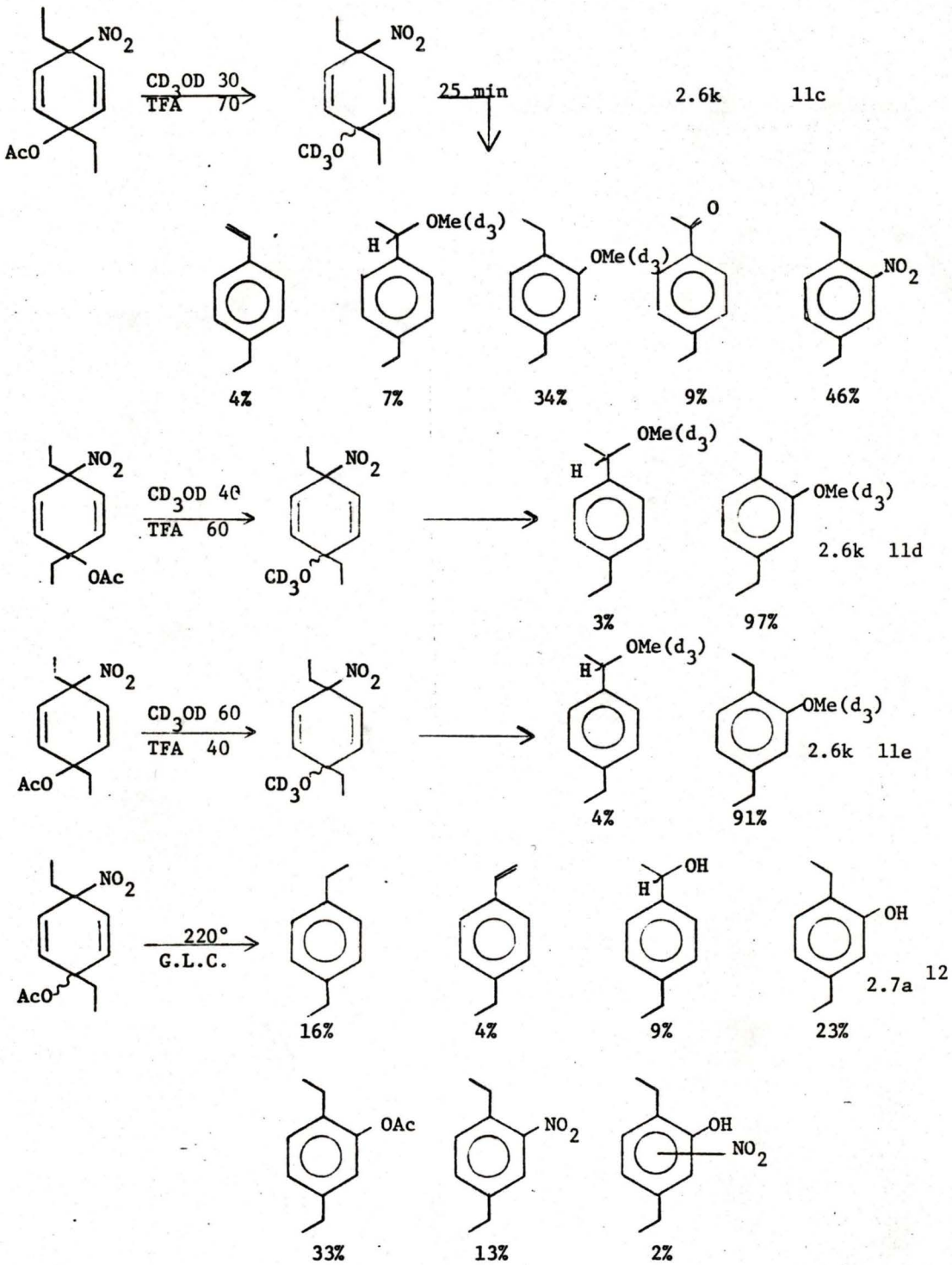
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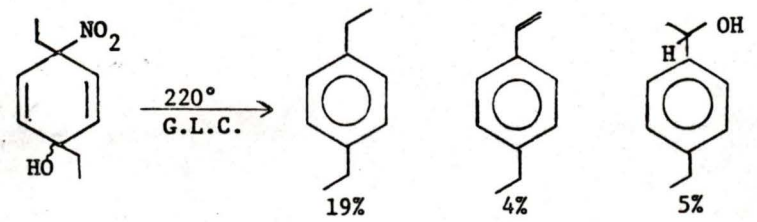
CD3OD 30
TFA 70
AcO
CD3O
25 min
2.6k 11c
OMe(d3)
H
O
4%
7%
34%
9%
46%
OAc
3%
97%
2.6k 11d
2.6k 11e
4%
91%
220°
G.L.C.
OH
16%
23%
2.7a 12
33%
13%
2%



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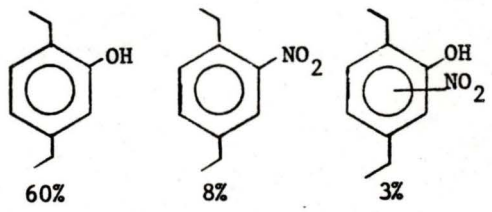

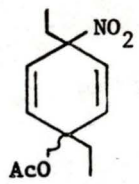

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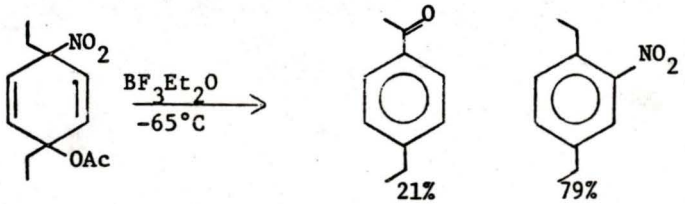

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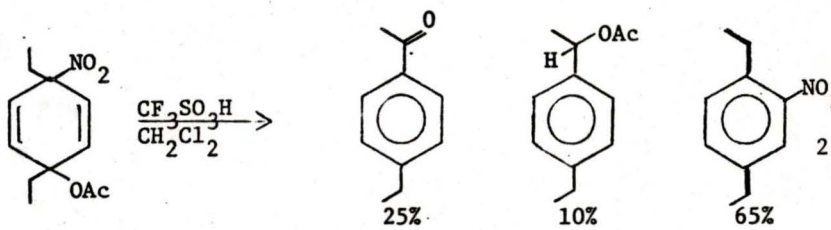

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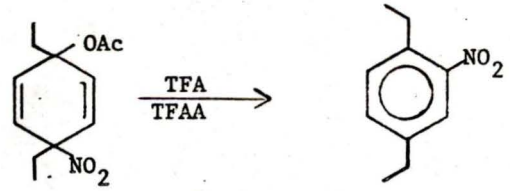

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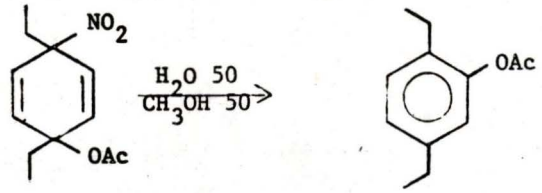

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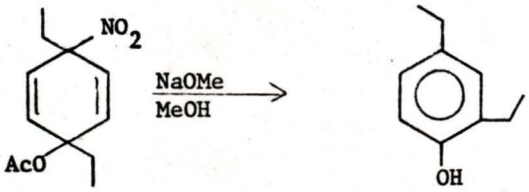

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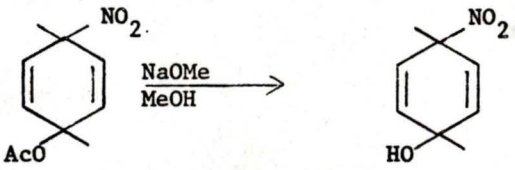

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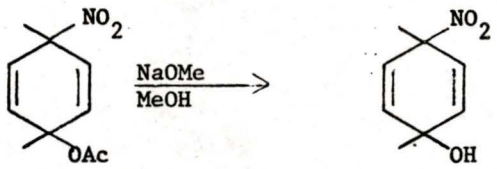

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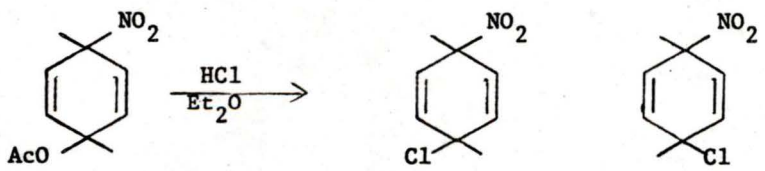
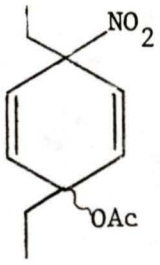


2.9c 21

APPENDIX II: KEY TO NUMBERED STRUCTURES



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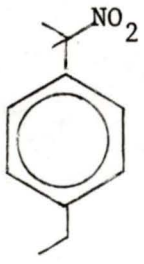

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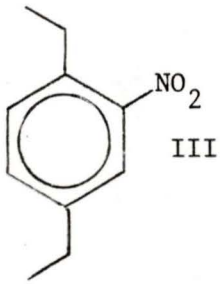

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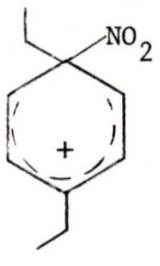

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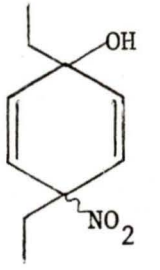

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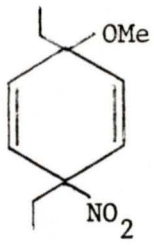

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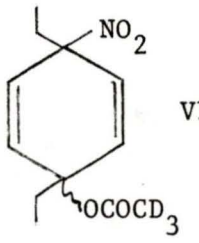

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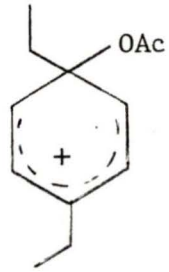

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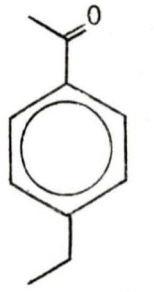

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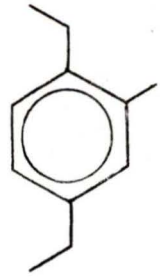

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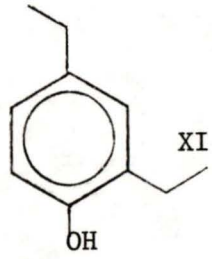

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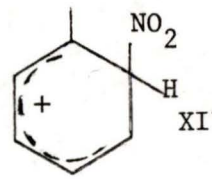

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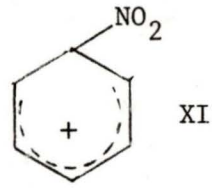

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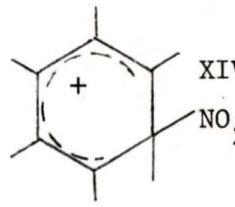

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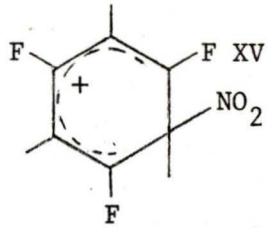

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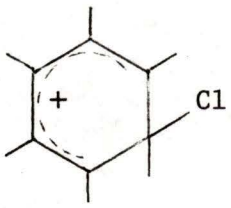

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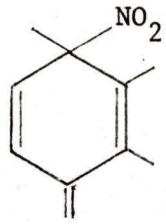

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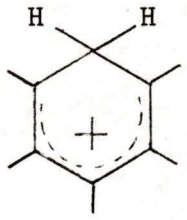

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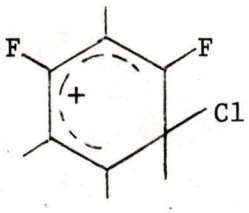

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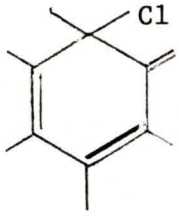

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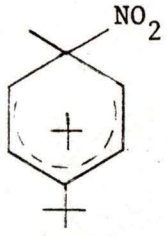

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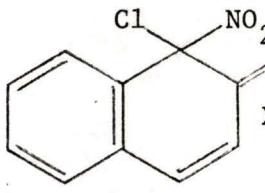

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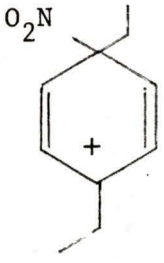

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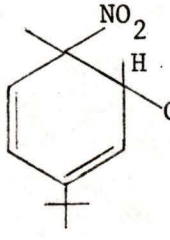

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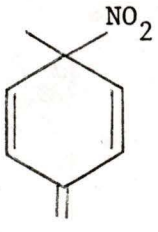

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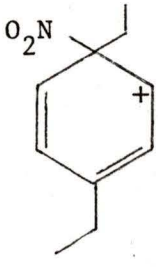

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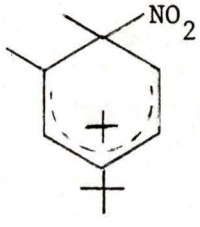

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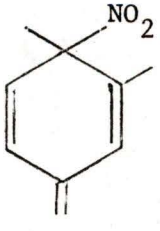

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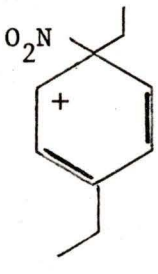

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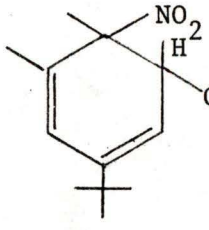

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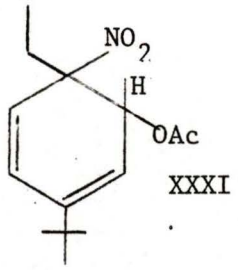

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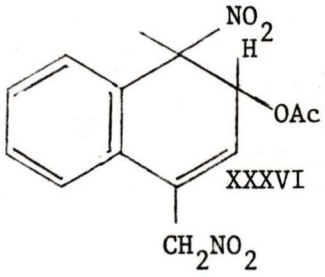

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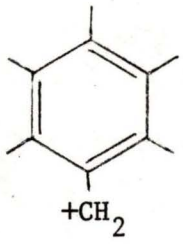

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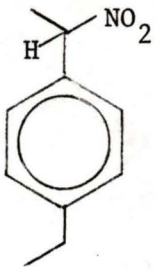

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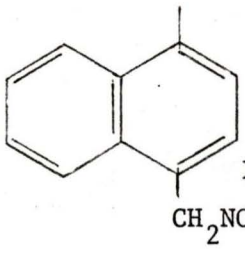

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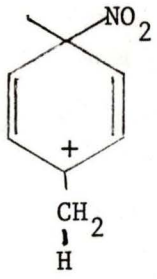

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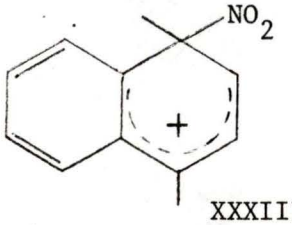

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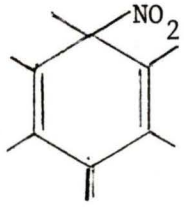

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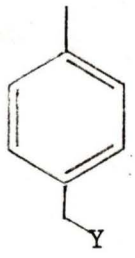

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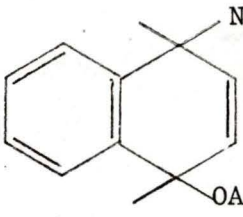

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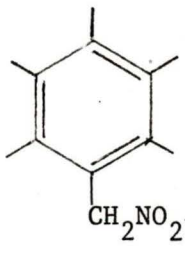

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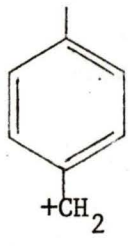

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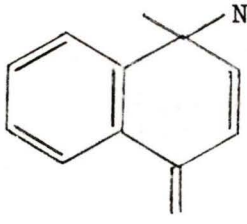

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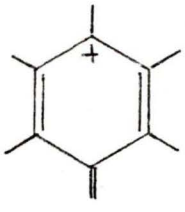

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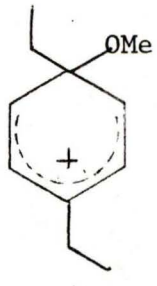

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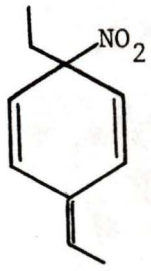

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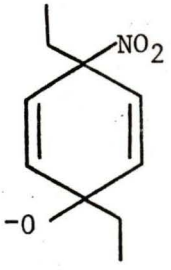

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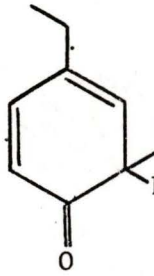

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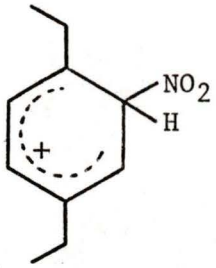

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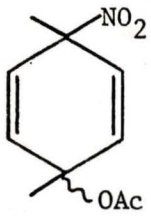

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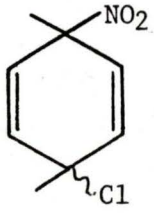

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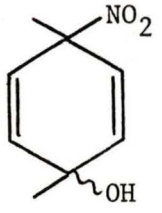

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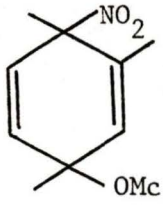

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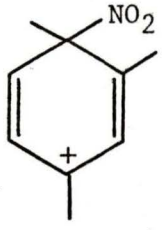

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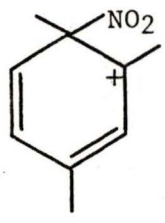

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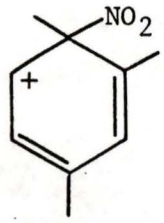

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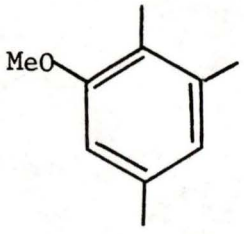

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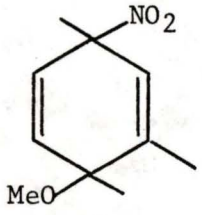

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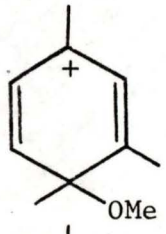

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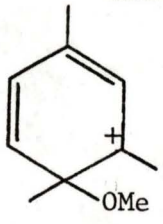

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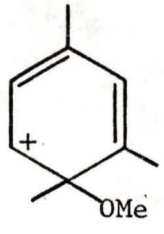

LXII

VITA

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UNIVERSITY OF VICTORIA, VICTORIA, B.C.	1973 to 1976
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Author [redacted]

Signature

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Name

OCTOBER 30, 1978

Date