Formation of Adducts in the Nitration of *p*-Xylene. Exchange and Rearomatization Reactions of *p*-Xylene Adducts

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Nitration of *p*-xylene in acetic anhydride gives as the major product *cis* and *trans* isomers of the adduct 1,4-dimethyl-4-nitro-1,4-dihydrophenyl acetate (**1**) as well as 2-nitro-*p*-xylene. The acetoxynitro adducts **1***a* and **1***b* are stereospecifically cleaved to the hydroxynitro adducts **2***a* and **2***b*, respectively, by sodium methoxide. Acid-catalyzed exchange of OAc in **1** for OCH_3, OCHO, $OCH_2C_6H_4CH_3$-*p* occurs and is nonstereospecific. Rearomatization of **1** gives 2-nitro-*p*-xylene, side-chain (benzylic) derivatives, and 2,5-xylyl acetate. The relevance of these reactions to side-chain substitution of arenes under electrophilic conditions is discussed.

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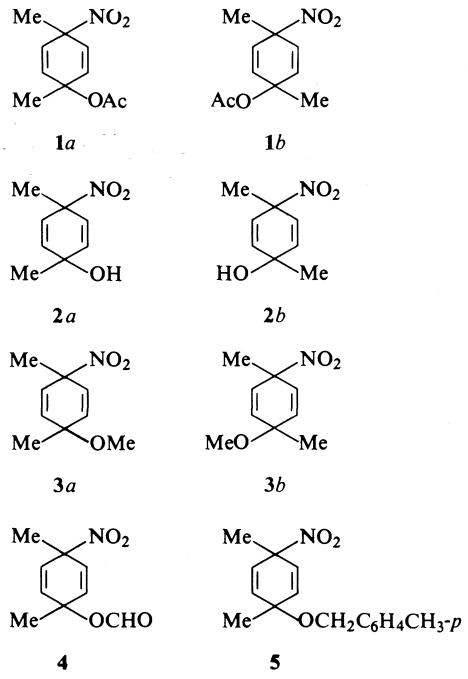
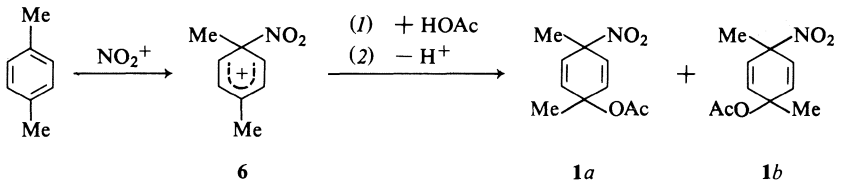
La nitration du *p*-xylène dans l'anhydride acétique conduit comme produits majeurs aux isomères *cis* et *trans* de l'adduit acétate de diméthyl-1,4 nitro-4 dihydro-1,4 phényle (**1**), de même qu'au nitro-2 *p*-xylène. Le méthylate de sodium coupe les adduits acétoxynitro **1***a* et **1***b* d'une manière stéréospécifique et conduit aux adduits hydroxynitro **2***a* et **2***b*. L'échange, catalysé par les acides, du groupe OAc dans **1** pour OCH_3, OCHO, $OCH_2C_6H_4CH_3$-*p* se produit d'une manière non-stéréospécifique. La réaromatisation de **1** conduit au nitro-2 *p*-xylène, à des dérivés benzylique et à l'acétate de xylyl-2,5. On discute du rapport qui existe entre ces réactions et les réactions de substitution sur la chaine latérale qui se produisent sur des arènes dans des conditions électrophiles. [Traduit par le journal]

Introduction

Electrophilic attack at a substituted position (*ipso* attack (1)) is well established. *Ipso* nitration of methylbenzenes in acetic anhydride affords nitronium acetate (acetyl nitrate) adducts which contain the 4-nitro-1,4-dihydro-*p*-tolyl acetate moiety (2). The diastereoisomeric adducts[1] **1** were among the first examples of such compounds to be isolated (2*b*). The present paper reports the conversion of the acetoxydienes **1** to the corresponding hydroxy **2**, methoxy **3**, and formyloxy **4** compounds, and delineates the rearomatization reactions of tertiary acetate adducts. It is because of the concomitant gain in resonance energy that the adducts readily undergo such rearomatization reactions. Indeed, the challenge in working with these compounds is to prevent inadvertent rearomatization. Secondary acetate adducts afford aryl acetates by elimination of nitrous acid (2*a–c*, 3) and nitroarenes by elimination of acetic acid accompanied by the migration of the nitro group. Both 1,2- and 1,3-shifts of nitro groups have been observed (4, 5, 3*b*, *c*). Tertiary acetate adducts, in which the simple 1,4-elimination of nitrous acid cannot occur, exhibit a greater variety of rearomatization reactions. One of these reactions is the



[1]Individual members of a pair of diastereoisomeric adducts are designated as *a* and *b*.



6 1*a* 1*b*

SCHEME 1

formation of side-chain (benzylic) derivatives (2*d*, 6). Side-chain substitution of arenes under electrophilic conditions is a well-established reaction and has been actively investigated by Baciocchi and co-workers (7) and by Suzuki and co-workers (8). Both groups have proposed a number of speculative mechanisms for side-chain substitution but no structural evidence which demonstrates the existence of any proposed intermediate has been adduced. However they have established through reactivity studies that the initial step in side-chain substitution is similar to that for nuclear substitution *viz.* attack by the electrophile at an aromatic ring position (9, 10). The present work on the *p*-xylene adducts and the preliminary report on the pseudocumene adducts (2*d*) establish that such adducts, or the *ipso* cyclohexadienyl cations from which the adducts are formed reversibly and which are obtained by *ipso* attack of nitronium ion on the arene (Scheme 1), are key intermediates in the formation of the side-chain derivatives. Furthermore, our work establishes the orientation of the side-chain substitution with respect to the initial step of *ipso* attack and delineates a common mechanistic pathway for the formation of a variety of side-chain products. Finally, we are able to relate the side-chain reactions to other rearomatization reactions leading to nitroarene and to aryl acetate.

Results and Discussion

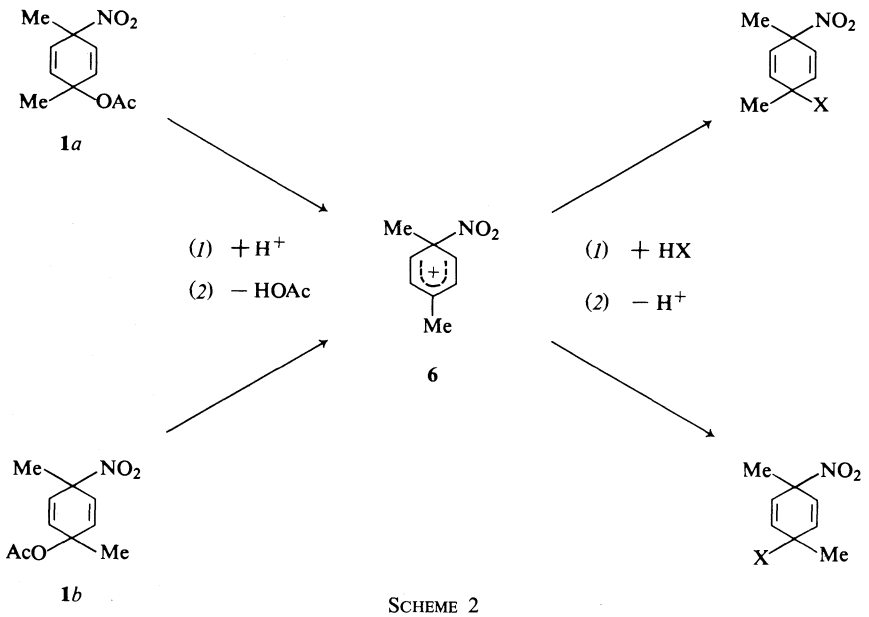
Formation and Interconversion (Exchange) Reactions of Adducts

Reaction of *p*-xylene with nitric acid in acetic anhydride gave a mixture consisting of 80% diene adducts and 2-nitro-*p*-xylene. The acetoxynitrodienes **1***a* and **1***b* and the hydroxynitrodienes **2***a* and **2***b* were isolated from the crude product by low temperature chromatography. A small amount of an adduct identified as the *p*-methylbenzyloxynitrodiene **5** was also obtained. The acetoxynitrodienes are formed by attack of nitronium ion at an *ipso* position of *p*-xylene to form the cyclohexadienyl cation **6** which subsequently adds acetate (as acetic acid or acetic anhydride followed by deprotonation or deacetylation, respectively) to generate the pair of diastereoisomeric adducts[2] (Scheme 1). The *ipso* position in *p*-xylene is more activated than the unsubstituted position (12). The origin of the hydroxynitrodienes was not established. Cation **6** could be trapped by other nucleophiles as well as acetate, such as water. It is unlikely that water would be present in the acetic anhydride solution but it is known that nitronium nitrate (**6***a*) or nitrite[3] adducts can be formed in these reaction mixtures and it is likely that the hydroxynitrodiene is formed by solvolysis of one or the other of these on work-up. A similar origin is proposed for the *p*-methylbenzyloxynitrodiene **5**. *p*-Methylbenzyl derivatives are formed as rearomatization products of the adducts. Reaction of cation **6** with such a derivative, or its solvolytic product *p*-methylbenzyl alcohol, assumed to be formed during work-up, would give **5**. The identity of **5** was confirmed through its synthesis by reaction of the acetoxydiene **1** with *p*-methylbenzyl alcohol in chloroform containing catalytic sulfuric acid. Presumably this reaction involves the intermediate formation of cation **6** which reacts with the *p*-methylbenzyl alcohol to give **5** after deprotonation (see below).

Reaction of acetoxydiene **1***a* with sodium methoxide in methanol resulted in stereospecific conversion into **2***a*; similarly **1***b* gave **2***b* stereospecifically. The methoxide must have cleaved the ester by attack at the acyl rather than the alkyl group, otherwise methoxydiene **3** would have been formed. It follows that the stereo-

[2]Only 1,4-adducts have been obtained in all of the addition reactions studied. Two reasons can be advanced for the absence of 1,2-adducts. First, the *para* position in the cyclohexadienyl cation has a greater positive charge than the *ortho* position (11) and therefore should be more reactive towards nucleophiles. Second, there would be severe eclipsing interactions in the 1,2-adduct between the nitro or methyl group and adjacent acetate group.

[3]Unpublished work with D. R. A. Leonard.



SCHEME 2

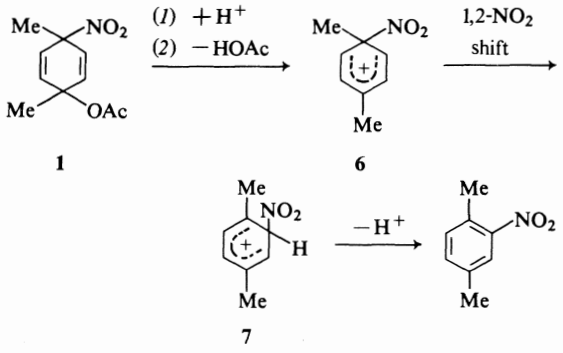
chemistry of **1***a* and **2***a* must be the same and likewise **1***b* and **2***b* must have the same stereochemistry. Base-catalyzed cleavage of a tertiary alkyl ester should conform to the $B_{AC}2$ mechanism (13) which is consistent with the above results. In contrast the acid-catalyzed methanolysis of **1***a* gave a mixture of the diastereoisomeric methoxynitrodienes **3** and likewise acid-catalyzed methanolysis of **1***b* gave the same mixture of diastereoisomers. Thus, acid-catalyzed methanolysis must involve alkyl–oxygen fission; formation of the diastereoisomeric mixture is consistent with the operation of the $A_{AL}1$ mechanism involving the intermediate cyclohexadienyl cation **6** (Scheme 2; X = OMe). The $A_{AL}1$ mechanism would be expected for the acid catalyzed solvolysis of a tertiary acetate (13) and it is especially favored here since the intermediate cation is not merely tertiary but is also stabilized by the cyclohexadienyl resonance. Even in chloroform containing only 1% methanol the exchange proceeded readily. The other exchange reactions such as the formation of the formyloxy adduct **4** on treatment of **1** with formic acid and, as mentioned above, the formation of the benzoyloxy compound **5**, and the epimerization of both **1***a* and **1***b* to form the diastereoisomeric mixture in anhydrous acetic acid, all follow the same pathway (Scheme 2: X = OCHO, $OCH_2C_6H_4CH_3$-*p*, OAc, respectively). It is likely that in solvents of low dielectric content (such as anhydrous acetic acid) the ionic species are associated. Such association, if it occurs, is without apparent effect on the reaction products and it is unnecessary to take formal account of it in the mechanism. The exchange reactions were complicated by competing or subsequent rearomatization reactions which are discussed next.

Rearomatization Reactions of Adducts

Three types of rearomatization product were obtained: (*i*) 2-nitro-*p*-xylene; (*ii*) side-chain (benzylic) derivatives; (*iii*) 2,5-xylyl acetate. The reactions leading to these products will be discussed in turn.

(i) Formation of Nitroarene

The first reported formation of a nitroarene from an acetyl nitrate adduct was that of 3-nitro-*o*-xylene from the *o*-xylene adduct on treatment with 70% sulfuric acid (4). Subsequently there have been other examples reported of the formation of aromatic nitro compounds from adducts (2*d*, 3*b*, *c*, 5). Myhre's (4) mechanism, applied to the *p*-xylene adduct **1** is shown in Scheme 3. A 1,2-nitro shift in the *ipso* cyclohexadienyl cation **6** converts it into the cyclohexadienyl cation intermediate for substitution **7**. Such a nitro shift in the cyclohexadienyl cation from hexamethylbenzene has been shown to occur readily by Olah and co-workers (14). In the case of the *p*-xylene adduct it is not possible to distinguish between a 1,2- and a 1,3-

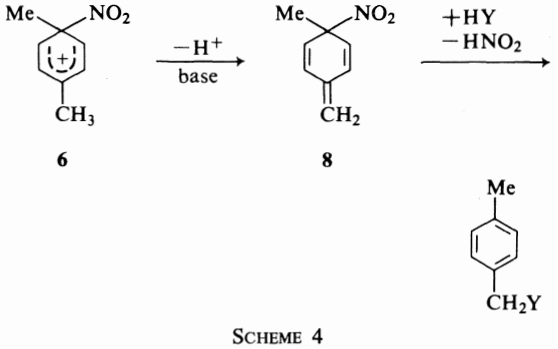


SCHEME 3

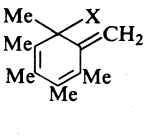
nitro shift, since both lead to 2-nitro-*p*-xylene. As mentioned in the introduction, 1,3-nitro shifts have been observed, but in those cases the 1,2-shift would give a substantially less stable cyclohexadienyl cation than either the *ipso* cation or that obtained by a 1,3-shift. Since, in the case of **6**, the cations resulting from 1,2- and 1,3-shifts are the same we suggest that the 1,2-shift is more likely. 2-Nitro-*p*-xylene was obtained when adduct **1***a* was treated with trifluoroacetic acid. It was also obtained as a significant product when adducts **1***a* and **1***b* were treated with a catalytic amount of sulfuric acid in deuteriochloroform (40–50% yield) and again when **1***a* was treated with nitric acid in chloroform (23% yield); in each case the other products were side-chain derivatives. It is to be noted that the 2-nitro-*p*-xylene is formed under conditions involving the presence of strong acid (which would catalyze the unimolecular loss of acetic acid to generate cation **6**) and the absence of nucleophiles and basic species more reactive than the acetic acid liberated in the reaction. Thus the shift of the nitro group in cation **6** is able to compete with deprotonation of **6**, a key step in the formation of the benzylic products (see below), and also with the combination of **6** with a nucleophile to form exchanged adduct (Scheme 2).

(ii) Formation of Side-chain Derivatives

Side-chain substitution products, *p*-$CH_3C_6H_4CH_2Y$, were formed in significant amounts in several reactions. Thus, *p*-methylbenzyl nitrate (77%) was obtained from reaction of **1***a* with nitric acid in chloroform, as well as 2-nitro-*p*-xylene. *p*-Methylphenylnitromethane (35%), *p*-methylbenzyl acetate (15%), and *p*-tolualdehyde (5%) were obtained from treatment of both **1***a* and **1***b* with a catalytic amount of sulfuric acid in deuteriochloroform, and again 2-nitro-*p*-xylene was the other product. *p*-Methylbenzyl acetate (29%) and *p*-methylphenylnitromethane (17%) were formed in the rearomatization accompanying the epimerization of both **1***a* and **1***b* in anhydrous acetic acid containing acetic anhydride, and 2,5-xylyl acetate was the other aromatic product. Methyl *p*-methylbenzyl ether (15%) was formed when the methoxynitrodiene **3***a* was heated under reflux in methanol containing sulfuric acid and methyl 2,5-xylyl ether was the nuclear substituted aromatic product. Finally *p*-methylbenzyl acetate, *p*-tolualdehyde, and (probably) *p*-methylphenylnitromethane were formed on pyrolysis of **1***a*, in addition to several other products. These results suggest that in the side-chain substitution product *p*-$CH_3C_6H_4CH_2Y$ the group Y originates from the nucleophilic species HY. Furthermore, these side-chain derivatives are formed in competition with the 2-nitro-*p*-xylene with larger amounts of 2-nitro-*p*-xylene being formed when only weak nucleophiles are present (*e.g.* sulfuric acid and nitric acid) and little or none being formed in the presence of substantial amounts of stronger nucleophiles (*e.g.* acetic acid and methanol). These conclusions are supported by similar results obtained with the pseudocumene adducts. We account for these results in terms of competitive processes occurring in the cyclohexadienyl cation **6**, a key intermediate in the formation of the 2-nitro-*p*-xylene. The 1,2-nitro shift in **6**, a unimolecular process, is in competition with a bimolecular process involving the abstraction of a proton from the *para*-methyl group in **6** to give the methylenecyclohexadiene intermediate **8** leading to side-chain product (Scheme 4). Clearly, the outcome of this competition will be determined by the bases present: the stronger the base and the higher its concentration the more likely that



SCHEME 4



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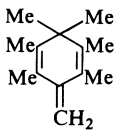

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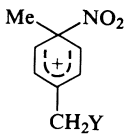

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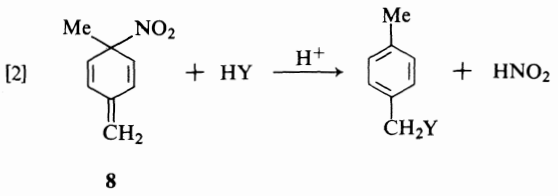
deprotonation of **6** will occur before rearrangement to **7**. Thus in the presence of sulfuric acid, or nitric acid, where the liberated acetic and nitrous acids present in only small amount are the most basic species available, the 1,2-nitro shift is an important reaction and substantial amounts of 2-nitro-*p*-xylene are formed. In contrast, in methanol as solvent, the more basic species methanol present at high concentration is able to deprotonate **6** before the nitro shift occurs and no 2-nitro-*p*-xylene is formed. Good nucleophiles present at high concentration reduce the concentration of **6** because they combine with **6** to form adducts (Scheme 2). However the effect of this should be to reduce the rate of the rearrangement and deprotonation reactions to the same extent and thus not to affect the competition between them.

Methylenecyclohexadienes have been proposed as intermediates in the formation of side-chain derivatives from arenes on treatment with electrophilic reagents by Baciocchi *et al.* (9, 15) for side-chain bromination and chlorination of hexamethylbenzene, by Andrews and Keefer (16) for side-chain chlorination of hexamethylbenzene with iodine monochloride, by Suzuki *et al.* (17) for side-chain nitrate formation from pentamethylbenzene, by Robinson (18) for side-chain nitration of 1,4-dimethylnaphthalene, and in subsequent papers by these and other authors for other side-chain substitution reactions. The earlier proposals were for a methylene-1,3-cyclohexadiene intermediate such as **9**. More recently it has been recognized that a 1,4-diene intermediate, with the methylene group and the tetrahedral carbon atom in a 1,4 relationship, is possible (10, 19) and in fact probable (7). Work with Wright and co-workers on side-chain substitution of methylbenzenes accompanying nitration (20) and our studies on the rearomatization of diene adducts (2, 3) conclusively establish that only the cross-conjugated triene such as **8** and not the conjugated triene such as **9** can be an intermediate in the formation of side-chain products. Specifically: (*i*) only those methylbenzenes which have methyl groups *para* to each other form side-chain derivatives, thus *p*-xylene does but *o*-xylene does not, pseudocumene (1,2,4-trimethylbenzene) does but hemimellitene (1,2,3-trimethylbenzene) and mesitylene do not, all of the tetramethylbenzenes do as does pentamethylbenzene (20) and hexamethylbenzene (19); (*ii*) the side-chain derivatives formed are those in which the methyl group substituted is that *para* to the most activated *ipso* position (20); (*iii*) only those adducts which have a methyl group *ipso* to the acetate give side-chain products on rearomatization, the adducts which are secondary acetates do not; (*iv*) the methyl group substituted is that *ipso* to the acetate and *para* to site of attack by the nitronium ion, not that which is *ortho* or *ipso* to the site of initial electrophilic attack. The isolation (21) of the cross-conjugated triene **10** from the methylation of hexamethylbenzene gives credence to the proposed intermediate **8**. Baciocchi *et al.* (9) and Nakamura (10) have also suggested the possibility of the simultaneous deprotonation and introduction of the group Y, thus obviating the formation of the discrete triene intermediate. These mechanisms were proposed at the time that both groups thought that the methyl group substituted was that *ortho* to the site of electrophilic attack and were associated with a cyclic intramolecular transfer of the electrophile from ring to side-chain. It is unlikely that concerted removal of the proton and shift of the electrophile to the methyl group in the *para* position could occur as has been explicitly recognised by Astolfi *et al.* (19). We therefore favor the mechanism outlined in Scheme 4 which proposes the cross conjugated triene as a discrete intermediate.

Two different general mechanisms for the conversion of the triene intermediate **8** into side-chain product can be envisaged: (*i*) electrophilic attack at the methylene group with prior, simultaneous, or subsequent loss of the nitro group as a nitronium ion, eq. 1, and (*ii*) nucleophilic attack at the methylene group with prior (S_N1'), simultaneous (S_N2'), or (unlikely) subsequent (acid-catalyzed) loss of the nitro group as nitrite, eq. 2. Reaction by pathway *i* has been proposed by Astolfi *et al.* (19) for the side-chain nitration of hexamethylbenzene and by Illuminati *et al.* (7) for the side-chain chlorination of isodurene. Robinson (18) and Suzuki and Nakamura



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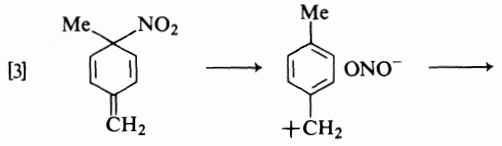
(22) have both proposed an addition–elimination sequence which is a variant of *i* for the side-chain nitration of 1,4-dimethylnaphthalene. It is evident that while the formation of side-chain nitro and halo derivatives could conceivably occur via *i*, involving the nitronium and (incipient) halonium ions as the active electrophiles, the side-chain ester compounds could not be formed directly by this pathway. Reaction by pathway *ii* has been suggested (7) to account for the formation of side-chain chloride in the chlorination of isodurene in acetic acid and a special variant of the S_N1' mechanism involving a cage rearrangement via an ion-pair intermediate has been proposed (10) to account for the formation of side-chain nitrate via nitrite, eq. 3. A similar ion-pair mechanism has been recognised as a possible mechanism for side-chain chlorination (7).

We suggest that *all* of the side-chain products are formed via pathway *ii*, eq. 2, and thus the derivatives p-$CH_3C_6H_4CH_2Y$: Y = NO_2, OAc, ONO_2, OMe are obtained by nucleophilic attack of HONO (nucleophilic nitrogen), HOAc, $HONO_2$ (nucleophilic oxygen), HOMe, respectively on **8**. Nitrous acid and acetic acid are liberated from the adducts in the course of the rearomatization reaction and thus these are available to compete as nucleophiles with introduced nucleophiles (if any). Thus when a catalytic amount of sulfuric acid in chloroform is used only the acetate and the nitromethane are formed but when nitric acid or methanol is present these are able to compete effectively and the nitrate and methyl ether are obtained, respectively. We reject pathway *i* for formation of the side-chain nitro derivative on two counts. First, pathway *i* requires the nitronium ion to be a leaving group from carbon. The nitronium ion would be most disposed to act as a leaving group if it were leaving from a positively charged species, *i.e.* if the electrophile Y^+ was added prior to the departure of NO_2^+ so that the intermediate cyclohexadienyl cation **11** was formed. Loss of NO_2^+ from a cyclohexadienyl cation has been observed but only in the case where the cation contains the strongly electron-withdrawing cyano substituent attached to the ring (3*c*). Such loss has not been observed in other cations which contain less strongly electron-withdrawing substituents and would not be expected in the case of **11** (2, 3). Attempts to detect the release of nitronium ion from the cyclohexadienyl cation formed from hexamethylbenzene, by intercepting it with benzene and mesitylene, were unsuccessful (14). Second, the side-chain nitro derivative is often formed in competition with side-chain esters which can only be formed directly by pathway *ii* (eq. 2). It seems unlikely that these products would be formed at comparable rates under quite different conditions, as observed, if they were formed by entirely different mechanisms.



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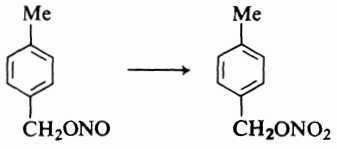


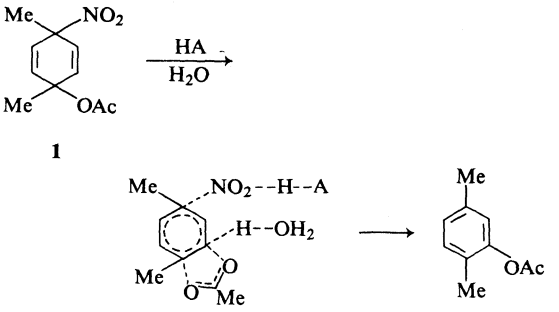
Our results which support pathway *ii*, eq. 2, for the conversion of the triene **8** to side-chain derivatives do not distinguish between the unimolecular (S_N1') and bimolecular (S_N2') variations of this pathway. A variant of the S_N1' pathway is that involving formation of a benzyl cation nitrite anion ion-pair with recombination in the solvent cage to form *p*-methylbenzyl nitrite (10) and (we would suggest) *p*-tolylnitromethane. Suzuki and Nakamura have suggested that the benzylnitrite formed in this way is subsequently converted into the nitrate and acetate. Formation of the acetate in this indirect manner is unlikely since the conversion of benzyl nitrate to benzyl acetate is slow, even in refluxing acetic acid (23), and nitrate would be expected to be

more readily displaced than nitrite. It seems similarly unlikely that nucleophilic displacement of nitrite by nitrate could be sufficiently fast to account for the formation of the benzyl nitrate. Pentamethylbenzyl acetate accompanies the pentamethylbenzyl chloride formed by chlorination of hexamethylbenzene in acetic acid. It has been shown that the side-chain chloride is not solvolyzed under the reaction conditions and thus the side-chain acetate cannot be formed via the pentamethylbenzyl chloride (9).

p-Tolualdehyde often accompanied the formation of other side-chain products. Benzyl nitrite gives benzaldehyde on autodecomposition (24) and benzyl nitrate undergoes acid-catalyzed oxidative cleavage to benzaldehyde (23, 25). Thus the *p*-tolualdehyde could have been formed via *p*-methylbenzyl nitrite or nitrate.

(iii) Formation of Aryl Acetate

2,5-Xylyl acetate formed by elimination of nitrous acid with rearrangement of the acetate was obtained in several reactions, most notably on treatment of adduct **1** with wet acetic acid and with aqueous acidic tetrahydrofuran. The rearrangement is intramolecular. Propionate was not incorporated when the decomposition was carried out in propionic acid (2*b*), in acetic acid-d_4 only minor incorporation of the deuterated acetate was observed, and in aqueous tetrahydrofuran the acetate rather than the phenol was the major product. It is likely that the acetate shift is 1,2, as in the case of the pseudocumene adducts (2*d*) rather than 1,3. Water has a striking catalytic effect on the reaction. In anhydrous acetic acid adduct **1** was epimerized. Decomposition to the xylyl acetate occurred to the extent of 35% over 18 h and 20% of the *p*-methylbenzyl acetate and 13% of 2-nitro-*p*-xylene were also formed. However in wet acetic acid adduct **1** decomposed completely in less than 30 min to the xylyl acetate, the only product. We suggest that there is concerted acid-catalyzed loss of the nitro group (to form nitrous acid) accompanied by migration of the acetate (Scheme 5). A possible reason for the dramatic catalytic effect of the water is that it acts as base accepting the proton in a fully concerted transition state **12**. It is plausible that when the more weakly basic acetic acid has to accept the proton then the energy of the transition state is raised sufficiently for reactions via the cyclohexadienyl cation (epimerization, formation of 2-nitro-*p*-xylene and side-chain derivative) to be able to compete.



SCHEME 5

Rearomatization of the methoxynitro adduct **3** gave methyl 2,5-xylyl ether as the major product and some methyl *p*-methylbenzyl ether. Formation of the side-chain derivative presumably occurs via the cyclohexadienyl cation **6** and the triene **8**. Insufficient information is available to delineate the mechanism of formation of the nuclear substitution product.

Attempted Assignment of the Stereochemistry of Diastereoisomeric Adducts

Two methods were used to assign the stereochemistry of the acetoxynitrodienes **1***a* and *b* and hydroxynitrodienes **2***a* and *b*. Addition of the shift reagent *tris*-(1,1,1,2,2,3,3-heptafluoro-7,7-[$^2H_6$]dimethyl-4,6-[$^2H_3$]octanedionato)europium(III) {Eu([$^2H_9$]fod)$_3$} which complexes at the acetate and hydroxyl functions respectively of **1** and **2** should shift the 4-methyl protons of the *trans* isomers, with europium *cis* to 4-methyl, more rapidly downfield than in the *cis* isomers (2*c*). The relative gradients of the slopes of plots of the chemical shift against amount of reagent added, normalized to a gradient of the 1-CH_3 protons = 1.0, are shown in Table 1. The normalized gradients for corresponding protons of the members of each diastereoisomeric pair are the same, even in the case of the 4-methyl protons. Thus this method of assignment failed.

The second method of stereochemical assignment used dipole moment measurements. For the acetoxynitrodienes **1** the *cis* isomer is calculated to have a lower dipole moment than the *trans* (6*a*). Similar calculations for the hydroxynitrodienes **2**, using 1.60 D and 63° as values for the group moment of the OH group and its angle to the C—O bond, respectively (26), indi-

TABLE 1. Relative gradients (gradient 1-CH_3 = 1.00) of proton chemical shifts for diene adducts resulting from the addition of Eu([$^2H_9$]fod)$_3$

Compound	2-H	3-H	4-CH_3	1-OCH_3	1-$OCOCH_3$
1*a*	1.24	0.36	0.25	—	1.53
1*b*	1.21	0.40	0.24	—	1.45
2*a*	1.05	0.39	0.24	—	—
2*b*	1.06	0.43	0.26	—	—
3*a*	0.82	0.68	0.39	1.06	—
3*b*	0.74	0.62	0.48	1.00	—

cate that the *trans* isomer of **2** should have the lower dipole moment (*cis* = 3.68 D, *trans* = 2.77 D). Thus **1***a* should be the *cis* isomer and **1***b* the *trans* and likewise **2***a* the *trans* isomer and **2***b* the *cis*, although it should be noted that the measured dipole moments of **2***a* and *b* differ by less than 0.2 D. This assignment of stereochemistry is in conflict with the established stereochemical relationship between **1***a* and **2***a* and between **1***b* and **2***b* (see above) and thus the dipole moment method of assignment failed.

The effect of Eu([$^2H_9$]fod)$_3$ on the methoxynitrodienes **3***a* and *b* was also investigated and the normalized gradients are also shown in Table 1. In this case the normalized gradient of the 4-CH_3 protons of adduct **3***b* is 23% larger that that of the corresponding protons of **3***a*, whereas for all of the other protons the normalized gradients in **3***b* are slightly less than in **3***a*. These results suggest that **3***b* is the *trans* adduct with OCH_3 *cis* to 4-CH_3. However since the method failed in the cases of the acetoxynitro- and hydroxynitrodienes, which are each more sensitive to the addition of the shift reagent than the methoxynitrodienes, this conclusion must be regarded as tentative.

Experimental

Ultraviolet spectra were determined on Cary 17 or Unicam SP 700 spectrometers. Infrared spectra were determined on a Perkin–Elmer 337 spectrometer calibrated with polystyrene. Nuclear magnetic resonance spectra at 60 MHz were obtained on Perkin–Elmer R12A and Varian HA-60-IL spectrometers and, at 220 MHz, on the Varian HR 200 spectrometer at the Ontario Research Foundation, Sheridan Park, Ontario. Tetramethylsilane was used as an internal standard. Mass spectra were obtained on an Hitachi Perkin–Elmer RMU-7 spectrometer. Molecular weights were determined in methylene dibromide using an Hitachi Perkin–Elmer Model 115 molecular weight apparatus (vapor pressure osmometer). Dipole moments (**p**) were derived by use of Higasi's equation (27) from dielectric constant measurements (3*a*) of benzene solutions of the adducts. The dielectric constants were measured with a Sargent Chemical Oscillometer Model V with inductive cell compensator. Microanalyses were by Dr. D. McGillivray. Gas–liquid chromatography analyses were performed on a Micro Tek MT 220 gas chromatograph using as stationary phases QF1 (5%), PEGA (2½%), and DEGS (10%) on Chromosorb G acid-washed and silanized. Nitric acid was purified by distilling the fuming acid (300 cm^3) at 100 Pa from urea (10 g) and sulfuric acid (500 cm^3). Alumina was deactivated with 4% of 10% acetic acid. Ether and pentane were dried by distillation from sodium and phosphorus pentoxide, respectively. *p*-Methylbenzyl alcohol (Aldrich), *p*-xylene (Eastman), 2,5-dimethylphenol (Aldrich), and *p*-tolualdehyde (Baker) were commercial products. 2,5-Dimethylphenyl acetate (i.r. (CCl_4) 1775 and 1230 cm^{-1} ($OCOCH_3$), n.m.r. (CCl_4) τ 3.15 (m, Ar*H*), 7.70 (s, 5-CH_3), 7.80 (s, $OCOCH_3$), and 7.91 (s, 2-CH_3)) was obtained by acetylation of 2,5-dimethylphenol with acetic anhydride (28*a*). Methyl 2,5-xylenyl ether (n.m.r. (CCl_4) τ 3.4 (m, Ar*H*), 6.30 (s, OCH_3), 7.72 and 7.90 (ArCH_3)) was prepared from 2,5-dimethylphenol (2,5-xylenol) by heating under reflux with sodium and methyl iodide (28*b*). *p*-Methylbenzyl acetate (i.r. (CCl_4) 1750 and 1230 cm^{-1} ($OCOCH_3$); n.m.r. (CCl_4) τ 2.96 (m, Ar*H*), 5.12 (s, CH_2), 7.75 (s, ArCH_3), and 8.10 (s, $OCOCH_3$)) was obtained by acetylation (28*c*) of *p*-methylbenzyl alcohol. *p*-Methylbenzyl bromide (n.m.r. (CCl_4) τ 2.82 (m, Ar*H*), 5.60 (s, CH_2), 7.65 (s, CH_3)) was formed by reaction of the alcohol with phosphorus tribromide (29). *p*-Methylbenzyl nitrate (i.r. 1650 and 1270 cm^{-1} (ONO_2); n.m.r. (CCl_4) τ 2.90 (Ar*H*), 4.75 (CH_2), 7.70 (CH_3)) was prepared from the bromide by heating under reflux with silver nitrate in acetonitrile (30). Methyl *p*-methylbenzyl ether (n.m.r. (CCl_4) τ 3.00 (Ar*H*), 5.75 (CH_2), 6.80 (OCH_3), 7.72 (CH_3)) was obtained by heating the bromide under reflux with sodium methoxide in methanol (31). The appropriate parent ion and fragment peaks were observed in the mass spectra of the compounds described.

Nitration of p-Xylene in Acetic Anhydride

A cold solution of nitric acid (94 g, 1.5 mol) in acetic anhydride (250 cm^3) was added slowly with stirring to *p*-xylene (106 g, 1 mol) in acetic anhydride (250 cm^3) at −45° and the mixture was stirred for 30 min. The solution was then cooled to −70° in solid carbon dioxide–methanol, ether (2 dm^3) added, and ammonia condensed into the stirred solution. Excess ammonia was removed with an aspirator, more ether added, and the mixture poured onto ice-water. The combined ethereal layer and ether extract of the aqueous layer was washed and dried ($MgSO_4$) and the ether evaporated at 14°. Integration of

the n.m.r. spectrum of the crude reaction mixture revealed that diene adducts constituted 80% of the reaction mixture.

Chromatography at −45° on 4% deactivated alumina and elution first with pentane yielded 2-nitro-*p*-xylene; i.r. 1540 and 1350 cm^{-1} (NO_2); n.m.r. (CCl_4) τ 2.35 (s, 3-*H*), 2.88 (s, 5- and 6-*H*), 7.53 (s, 1-CH_3), 7.65 (s, 4-CH_3). Further elution with ether–pentane mixtures yielded in the 10% ether fraction 2,5-dinitro-*p*-xylene, m.p. 150° (lit. (32) 142°); i.r. (CCl_4) 1550 and 1350 cm^{-1} (NO_2); n.m.r. ($CDCl_3$) τ 2.10 (s, 2, 3-*H* and 6-*H*), 7.40 (s, 6, 1-CH_3 and 4-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 196 (15, M), 179 (35, M − OH), 133(25), 123(20), 105(35), 91(55), 77(100).

Also isolated from the 10% ether fraction, after removal of the dinitroxylene was 1,4-dimethyl-4-nitro-1,4-dihydrophenyl *p*-methylbenzyl ether (**5**); i.r. (CCl_4) 1550 and 1345 cm^{-1} (NO_2); n.m.r. (CCl_4) τ 3.00 (s, Ar*H*), 4.00 (m, 2-, 3-, 5-, and 6-*H*), 5.85 (s, ArCH_2), 5.95 (s, ArCH_2), 7.70 (s, ArCH_3), 8.27 (s, 4-CH_3), 8.35 (s, 4-CH_3), 8.65 (s, 1-CH_3), 8.72 (s, 1-CH_3). The n.m.r. spectrum indicates that both diastereomers were present with the aromatic, diene, and aromatic methyl peaks of the two isomers overlapping.

The 20% ether fraction afforded one diastereoisomer of 1,4-dimethyl-4-nitro-1,4-dihydrophenyl acetate (**1***a*) as a white solid, m.p. 47–49 °C; u.v. (CH_3OH) 198 nm (ε 840 m^2 mol^{-1}); i.r. (CCl_4) 1755 and 1240 ($OCOCH_3$), 1555 cm^{-1} (NO_2); n.m.r. (220 MHz, C_6D_6) τ 4.26 (s, 4, 2-, 3-, 5- and 6-*H*), 8.42 (s, 3, $OCOCH_3$), 8.50 (s, 3, 4-CH_3), 8.80 (s, 3, 1-CH_3); n.m.r. (220 MHz $CDCl_3$) τ 3.93 (s, 4), 8.01 (s, 3, $OCOCH_3$), 8.21 (s, 3, 4-CH_3), 8.54 (s, 3, 1-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 164 (3, M − HNO_2), 123(100), 106(50), 91(75), 43(25); μ 3.75 D (12.5 × 10^{-30} C m).

Mol. Wt. Calcd. for $C_{10}H_{13}NO_4$: 211. Found: 211.

The 40% ether fraction contained a 1:1 mixture of dienes **1***a* and *b* which on rechromatography yielded in the 15% ether fraction a second diastereoisomer of 1,4-dimethyl-4-nitro-1,4-dihydrophenyl acetate (**1***b*) as a white solid, m.p. 58–59 °C; u.v. (CH_3OH) 196 nm (ε 1400 m^2 mol^{-1}); i.r. (CCl_4) 1745 and 1230 ($OCOCH_3$), 1550 cm^{-1} (NO_2); n.m.r. (220 MHz, C_6D_6) τ 4.00 (m, 2, 3-*H* and 5-*H*), 4.10 (m, 2, 2-*H* and 6-*H*), (J_{23} 10.25, J_{26} 2.30, J_{35} 2.34 Hz), 8.40 (s, 3 $OCOCH_3$), 8.75 (s, 6, 4-CH_3 and 1-CH_3); n.m.r. (220 MHz $CDCl_3$) 3.81 (s, 4), 8.03 (s, 3, $OCOCH_3$), 8.29 (s, 3, 4-CH_3), 8.51 (s, 3, 1-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 164 (10, M − HNO_2), 123(100), 106(55), 91(62), 43(25); μ 4.18 D (13.9 × 10^{-30} C m).

Mol. Wt. Calcd. for $C_{10}H_{13}NO_4$: 211. Found: 212.

The 70% ether fraction of the original reaction mixture was subjected to rechromatography and gave in the 50–60% ether fraction one diastereoisomer of 1,4-dimethyl-4-nitro-1,4-dihydrophenol (**2***b*), recrystallized from ether–pentane to give colorless crystals, m p. 52°; u.v. (CH_3OH) 194 nm (ε 900 m^2 mol^{-1}); i.r. (CCl_4) 3610 (OH) 1555 cm^{-1} (NO_2); n.m.r. (220 MHz, $CDCl_3$) τ 3.88 (m, 2, 3-*H* and 5-*H*), 3.96 (m, 2, 2-*H* and 6-*H*), (J_{23} 9.97, J_{25} −0.08, J_{26} 2.32, J_{35} 2.32 Hz), 8.30 (s, 3, 4-CH_3), 8.67 (s, 3, 1-CH_3); mass spectrum (70 eV) *m/e* relative intensity) 123 (95, M − NO_2), 108(85), 91(100); μ 3.13 D (10.4 × 10^{-30} C m).

Anal Calcd. for $C_8H_{11}NO_3$: C, 56.80; H, 6.55; N, 8.30. Found: C, 56.41; H, 6.44; N, 8.40.

Elution with 100% ether gave the second diastereoisomer of 1,4-dimethyl-4-nitro-1,4-dihydrophenol (**2***a*), recrystallized to give colorless crystals, m.p. 114°; u.v. (CH_3OH) 196 nm (ε 1065 m^2 mol^{-1}); i.r. ($CDCl_3$) 3610 (OH), 1550 cm^{-1} (NO_2); n.m.r. (220 MHz, $CDCl_3$) τ 3.86 (m, 2, 3-*H* and 5-*H*), 3.99 (m, 2, 2-*H* and 6-*H*), (J_{23} 9.94, J_{25} −0.10, J_{26} 2.33, J_{35} 2.30 Hz), 8.25 (s, 3, 4-CH_3), 8.63 (s, 3, 1-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 123 (100, M − NO_2), 108(70), 91(85); μ 2.97 D (9.9 × 10^{-30} C m).

Anal. Calcd. for $C_8H_{11}NO_3$: C, 56.80; H, 6.55; N, 8.30. Found: C, 56.70; H, 6.71; N, 7.85.

Base-catalyzed Methanolysis of the Acetate Adducts **1**

Diene **1***a* (50 mg 0.24 mmol) was dissolved in methanol (10 cm^3) containing sodium hydroxide (50 μmol) at ambient temperature and stirred for 18 h. The solution was then extracted with ether, washed, dried ($MgSO_4$) and the solvent evaporated. Integration of the n.m.r. spectrum revealed that partial methanolysis (30%) of the acetate had taken place and that no other (rearomatization) products had been formed. The presence of the hydroxy diene **2***a* (τ 4.0, 8.25, 8.63) was confirmed by addition of an authentic sample which enhanced the characteristic n.m.r. peaks.

In a similar experiment with **1***b* the acetate function was cleaved to the extent of 40% to form the hydroxy diene **2***b*, n.m.r. τ 4.0, 8.30, and 8.67, whose presence was confirmed by peak enhancement on addition of authentic **2***b*.

In neither experiment were the remaining acetate adducts, the predominant constituent of each product mixture, epimerized.

Reaction of Adducts **1***a and* **1***b with Acidified Methanol*

The *p*-xylene adduct **1***a* (50 mg, 0.24 mmol) was dissolved in deuteriochloroform containing methanol (1%) and sulfuric acid (10 μmol). The n.m.r. spectrum, two superimposed quartets in the region τ 3.7–4.2 (4, vinyl *H*) and methyl signals at 7.0 and 7.1 (s, OCH_3), 8.2 and 8.3 (s, 4-CH_3), and 8.70 and 8.78 p.p.m. (s, 1-CH_3), showed that exchange of the methoxyl for the acetoxy group had taken place and that the diastereoisomers of methyl 1,4-dimethyl-4-nitro-1,4-dihydrophenyl ether (**3**) had been formed in a 1:1 ratio.

The same product mixture was obtained when the reaction was repeated using the adduct **1***b*. The reaction was also carried out in neat [$^2H_4$]methanol (0.4 cm^3) containing sulfuric acid (10 μmol). The exchange was complete in 15 min and both **1***a* and *b* gave the same 1:1 mixture of the diastereoisomeric [$^2H_3$]methyl 1,4-dimethyl-4-nitro-1,4-dihydrophenyl ethers with n.m.r. identical to that of **3** above apart from the absence of the methoxyl proton singlets at τ 7.0 and 7.1.

On a preparative scale adduct **1***a* (5 g, 0.024mol) was dissolved in methanol (200 cm^3) containing sulfuric acid (1 mmol) and stirred for 8 h at 20°. After work-up the n.m.r. spectrum of the crude reaction mixture revealed complete conversion of the acetoxynitrodiene to the methoxynitrodiene (absence of the acetoxy signal at τ 8.1) and that the *cis* and *trans* methoxynitro isomers were present in a 1:1 ratio. Chromatography at −45° on 3% deactivated alumina, and elution with pentane and ether–pentane mixtures afforded in the 4% ether fraction one

diastereoisomer of 1,4-dimethyl-4-nitro-1,4-dihydrophenyl methyl ether (**3***a*) as an oil; n.m.r. (CCl_4) 1555 and 1345 cm^{-1} (NO_2); τ (60 MHz, CCl_4), 3.87 (m, 2, 3-*H* and 5-*H*), 4.24 (m, 2, 2-*H* and 6-*H*), (J_{23} 9.98, J_{25} −0.14, J_{26} 2.27, J_{35} 2.27 Hz), 6.95 (s, 3, OCH_3), 8.32 (s, 3, 4-CH_3), 8.78 (s, 3, 1-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 137.095 (55, M − NO_2, $^{12}C_9{}^1H_{13}{}^{16}O_1$ requires 137.097), 122(80), 106(75), 91(100). Elution with 12½% ether yielded the other diastereoisomer of 1,4-dimethyl-4-nitro-1,4-dihydrophenyl methyl ether (**3***b*) as an oil; i.r. (CCl_4) 1555 and 1345 cm^{-1} (NO_2); τ (60 MHz, CCl_4) 3.90 (m, 2, 3-*H* and 5-*H*), 4.17 (m, 2, 2-*H* and 6-*H*), (J_{23} 10.1, J_{25} −0.13, J_{26} 2.5, J_{35} 2.5 Hz), 7.03 (s, 3, OCH_3), 8.26 (s, 3, 4-CH_3), 8.71 (s, 3, 1-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 137.092 (78, M − NO_2, $^{12}C_9{}^1H_{13}{}^{16}O_1$ requires 137.097), 122(78), 106(60), 91(100).

Reaction of Adduct **1***a with Benzyl Alcohol*

Diene **1***a* was reacted with benzyl alcohol in chloroform containing a catalytic amount of sulfuric acid. The product exhibited i.r. and n.m.r. absorptions of the expected 1,4-dimethyl-4-nitro-1,4-dihydrophenyl *p*-methylbenzyl ether (see above) as well as those of rearomatization products.

Reaction of Adducts **1***a and* **1***b with Acetic Acid*

Diene **1***a* (50 mg, 0.24 mmol) was added to [$^2H_4$]acetic acid (0.4 cm^3) and the reaction was followed by n.m.r. The reaction was complete after 30 min. The major product was 2,5-dimethylphenyl acetate; i.r. 1775 and 1230 cm^{-1}; n.m.r. τ 3.15, 7.70, 7.80, and 7.91 p.p.m., addition of the shift reagent Eu([$^2H_9$]fod)$_3$ to a solution of the isolated product moved the acetate peak downfield from the aromatic methyl peaks and integration of the resulting spectrum revealed that the ratio of these was 0.75:2 and thus not more than 25% of the acetate had exchanged with the [$^2H_3$]acetate from the solvent. The retention time of the product was identical with that of an authentic sample of 2-acetoxy-*p*-xylene on coinjection into the gas chromatograph. When one reaction was worked up after 15 min a small amount of the diastereoisomeric hydroxy dienes **2** was detected; i.r. 3400 (OH); n.m.r. τ 8.64 and 8.68 (1-CH_3 of each isomer).

The same results were obtained with diene **1***b* except that even less of the acetate exchanged with the solvent.

The experiment was repeated using acetic anhydride made anhydrous by heating under reflux with 10% acetic anhydride for 18 h. The solution of adduct **1***a* was allowed to stand at 20 °C for 18 h and then worked up and examined by n.m.r. The product consisted of 24% **1***a*, 8% **1***b*, 35% 2,5-dimethylphenyl acetate, 20% *p*-methylbenzyl acetate, and 13% *p*-methylphenylnitromethane (n.m.r. τ 4.70). The i.r. confirmed the presence of both aryl acetate (1780 cm^{-1}) and alkyl acetate (1750 cm^{-1}). From **1***b* there was obtained 30% **1***a*, 20% **1***b*, 28% 2,5-dimethylphenyl acetate, 14% *p*-methylbenzyl acetate, and 7% *p*-methylphenylnitromethane.

When water was added to a solution of **1***a* in anhydrous acetic acid decomposition proceeded rapidly (< 30 min) and only 2,5-dimethylphenyl acetate was obtained.

Reaction of Adduct **1** *with Formic Acid*

The diene **1***a* (50 mg, 0.24 mmol) was added with stirring to formic acid at 8° until the first appearance of color (30 s). The mixture was immediately cooled to −70 °C, ether was added and the resulting solution poured onto ice-water and worked up. Rearomatization had occurred to the extent of 25% but the predominant product was 1,4-dimethyl-4-nitro-1,4-dihydrophenyl formate; i.r. 1745 (OCOH) and 1550 cm^{-1} (NO_2); n.m.r. τ 2.2 (s, 1, OCO*H*), 4.0 (m, 4, vinyl *H*), 8.2 (s, 3, CH_3), 8.3 (s, 3, CH_3).

Pyrolysis of Adduct **1***a*

A solution of diene **1***a* in carbon tetrachloride was injected into the inlet of a gas chromatograph, at 225 °C. Decomposition proceeded smoothly giving rise to sharp, well-resolved peaks. Seven products were observed, six of which were identified by coinjection of authentic samples and comparison of their retention times with those in the decomposed mixture. The compounds were in order of decreasing peak area: *p*-xylene, 2-nitro-*p*-xylene, 2,5-dimethylphenyl acetate, unidentified compound, *p*-methylbenzyl acetate, tolualdehyde, and 2,5-dimethylphenol. It is likely that the unidentified compound was *p*-methylphenylnitromethane.

Reaction of Adduct **1***a in Acidified Aqueous Tetrahydrofuran*

Diene **1***a* (50 mg, 0.24 mmol) was dissolved in 50% aqueous tetrahydrofuran (10 cm^3) containing sulfuric acid (10 μmol). The reaction mixture was stirred for 18 h after which time the solution was worked up in the usual manner. Infrared and n.m.r. spectra revealed the presence of 2,5-dimethylphenyl acetate (86%), and 2,5-dimethylphenol (14%; i.r. 3400 cm^{-1} (OH); τ 3.55 (ArH)). The identities of the nuclear acetate and the phenol were confirmed by the correspondence of retention times with those of authentic samples on gas chromatography (PEGA). A second reaction was worked up after 15 min and the n.m.r. spectrum revealed the presence of small amounts of hydroxy dienes **2** (i.r. 3620 cm^{-1} (OH); τ 8.64 and 8.68 (1-CH_3)).

Reaction to Adduct **1***a with Nitric Acid in Chloroform*

Diene **1***a* (50 mg, 0.24 mmol) was dissolved in chloroform (3 cm^3), cooled to −60°, and nitric acid (70 μmol) added. The solution was then warmed to 0°, quenched immediately in water, and worked up. Infrared and n.m.r. established that the products were *p*-methylbenzyl nitrate (77%; i.r. 1650 and 1280 cm^{-1} (ONO_2); τ 2.90, 4.75, and 7.70 p.p.m.; and 2-nitro-*p*-xylene (23%; i.r. 1545 cm^{-1} (NO_2); τ 2.35, 2.90, 7.50 and 7.70 p.p.m.).

Reaction of Adducts **1***a and* **1***b with Sulfuric Acid in Deuteriochloroform*

Diene **1***a* (50 mg, 0.24 mmol) was dissolved in deuteriochloroform (0.4 cm^3) containing sulfuric acid (10 μmol) and the reaction followed by n.m.r. The four products observed were *p*-tolylnitromethane (40%; i.r. 1560 cm^{-1} (NO_2); τ 2.80, 4.80, and 7.75 p.p.m.), 2-nitro-*p*-xylene (40%; i.r. 1535 cm^{-1} ($ArNO_2$); τ 2.35, 2.90, 7.50, 7.70 p.p.m.), *p*-methylbenzyl acetate (15%; i.r. 1750 cm^{-1} ($OCOCH_3$); τ 2.95, 5.05, 7.75 p.p.m.), and tolualdehyde (5%; i.r. 1700 cm^{-1} (CHO); τ 0.15). The presence of 2-nitro-*p*-xylene, *p*-methylbenzyl acetate and tolualdehyde was confirmed by the identity of retention times with those of authentic samples on g.l.c.

Similar results were obtained when the reaction was carried out on **1***b*.

Reaction of 1a with Trifluoroacetic Acid

Diene **1***a* (50 mg, 0.24 mmol) was added to trifluoroacetic acid (5 cm^3) at $-60°$. The solution was allowed to warm to $-30°$ then quenched in ice-water and worked up. Infrared and n.m.r. spectra revealed one major product, 2-nitro-*p*-xylene (i.r. 1545 cm^{-1} (NO_2); τ 2.35, 2.90, 7.50, and 7.65), confirmed by g.l.c.

Rearomatization of the Methoxynitro Diene 3a

Diene **3***a* (50 mg) was refluxed in methanol (10 cm^3) containing sulfuric acid (200 μmol) for 18 h. After work-up the n.m.r. spectrum revealed the presence of methyl 2,5-xylenyl ether (85%; τ 3.35, 6.30, 7.70, and 7.90 p.p.m.), and methyl-*p*-methylbenzyl ether (15%; τ 3.00, 5.75, 6.80, and 7.70 p.p.m.), which could not be separated on g.l.c.

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