Reactions of the 1-hydroxy-1,4-dimethylcyclohexadienyl cation,[1] an intermediate in the solvolysis of 1,4-dimethyl-4-nitrocyclohexa-2,5-dien-1-ol

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This paper is dedicated to Professor Arthur N. Bourns

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Solvolysis of 1,4-dimethyl-4-nitrocyclohexa-2,5-dien-1-ol in mixed aqueous organic solvents gives the diastereomers of 1,4-dimethylcyclohexa-2,5-diene-1,4-diol, 1,4-dimethylcyclohexa-3,5-diene-1,2-diol, 2-nitro-*p*-xylene, 2,4-dimethylphenol (all derived from the title cation, itself formed by ionization of the nitro group as nitrite), and 2,5-dimethylphenol. In aqueous methanol the diastereomers of 4-methoxy-1,4-dimethylcyclohexa-2,5-dienol are also obtained. Significant yields of 2,5-dimethylphenol are only obtained on the acid-catalysed further reaction of the dienediol (or the methoxydienol) and involve the intermediate formation of 1,4-dimethylcyclohexa-3,5-diene-1,2-diol. In the absence of added base the acid released in the solvolysis catalyses this reaction and leads to the aromatization of the dienes.

ALFRED FISCHER, GEORGE N. HENDERSON et TREVOR A. SMYTH. Can. J. Chem. **64**, 1093 (1986).

La solvolyse du diméthyl-1,4 nitro-4 cyclohexadiène-2,5 ol-1 dans des mélanges de solvants organiques aqueux conduit aux diastéréoisomères du diméthyl-1,4 cyclohexadiène-2,5 diol-1,4 et du diméthyl-1,4 cyclohexadiène-3,5 diol-1,2 ainsi qu'au nitro-2 *p*-xylène et au diméthyl-2,4 phénol (tous dérivés du cation mentionné dans le titre qui est lui-même formé par ionisation du groupement nitro sous forme de nitrite) et au diméthyl-2,5 phénol. Dans le méthanol aqueux, on obtient aussi les diastéréoisomères du méthoxy-4 diméthyl-1,4 cyclohexadiène-2,5 ol-1. On n'obtient des rendements importants de diméthyl-2,5 phénol que lors d'une réaction subséquente, catalysée par les acides, du diènediol (ou du méthoxydiènol) et celle-ci implique la formation du diméthyl-1,4 cyclohexadiène-3,5 diol-1,2. Lorsqu'on n'ajoute pas de base, l'acide qui est formée lors de la solvolyse catalyse cette réaction qui conduit à l'aromatisation des diènes.

[Traduit par la revue]

Introduction

The adducts obtained on nitration of arenes in acetic anhydride, typically derivatives of 4-methyl-4-nitrocyclohexa-2,5-dienyl acetate, are labile and readily undergo rearomatization reactions in solution (1–6). A variety of rearomatization products have been obtained but the pathways to many of these appear to have one or other of two competitive initial steps, each of which involves the formation of a cyclohexadienyl cation (6, 7). For these routes rearomatization is initiated by unimolecular ionization of the nitro group as nitrite, forming a 1-acetoxy-4-methylcyclohexadienyl cation, or by acid-catalysed loss of the acetate function as acetic acid ($A_{Al}1$), forming a 4-methyl-4-nitrocyclohexadienyl cation. Formation of various substituted 4-methyl-4-nitrocyclohexadienyl cations and, more generally, substituted 4-alkyl-4-nitrocyclohexadienyl cations has been demonstrated by trapping experiments, e.g. both diastereomers of 4-ethyl-1-methyl-4-nitrocyclohexa-2,5-dienol were obtained when (*Z*)-4-ethyl-1-methyl-4-nitrocyclohexa-2,5-dienyl acetate was hydrolysed in acidified aqueous acetone (2). In the present paper we are concerned with the fate of the cyclohexadienyl cation obtained on solvolysis of the nitro group. We have investigated the solvolysis of 1,4-dimethyl-4-nitrocyclohexadienyl acetate (**1***a*), the corresponding dienol **1***b*, and the methyl ether **1***c*, and thus the formation and reactions of the 1-acetoxy-1,4-dimethylcyclohexadienyl cation (**2***a*) and its 1-hydroxy and 1-methoxy analogues **2***b* and **2***c*, respectively. Studies of the 1,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate system have been reported by Moodie, Schofield, *et al.* (6), by Myhre and co-workers (7), and by Fischer and Ramsay (8). The 1-hydroxy-1,4-dimethylcyclohexadienyl cation and its 2-hydroxy isomer are simultaneously-formed intermediates in the acid-catalysed ring opening of 1,4-dimethylbenzene oxide (9, 10). In the present work the individual chemistries of the two cations can be distinguished since they are not formed simultaneously, and the 1-hydroxy cation can be studied in the absence of its isomer.

Results and discussion

Configurations of 1,4-substituted cyclohexadienes

The configuration of (*E*)-1,4-dimethyl-4-nitrocyclohexa-2,5-dienol has been established by X-ray crystallography and those of the corresponding nitrodienyl acetates and methyl ethers by stereospecific interconversion reactions (11). Addition of methyllithium to 4-methyl-4-nitrocyclohexa-2,5-dienone gives preferentially the (*Z*)-dienol (12). Applying a similar argument, the major product isomer of the dienediol **3***bn* obtained on addition of methyllithium to 4-hydroxy-4-methylcyclohexa-2,5-dienone has been assigned the (*Z*) configuration (13). As would be expected, the (*E*)-dienediol has the higher melting point. The assignment is also supported by our shift reagent studies. There is only a small difference in the gradients of the shifts of the 4-CH_3 protons of the diastereomers produced on the addition of *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)$_3$). However, in accord with expectation, the (*E*) isomer, with the 4-CH_3 *cis* to the europium complexed at 1-OH, has the larger slope, 0.34 versus 0.31.

In the methylation reactions the stereochemistry at the asymmetric centres is not disturbed. Thus the configurations of the methoxydienols and the dimethoxydienes follow from the partial methylation of (*Z*)-**3***bn* to a mixture of (*Z*)-**3***bo* and (*Z*)-**3***co*, the methylation of (*Z*)-**3***bo* to (*Z*)-**3***co*, the partial methylation of (*E*)-**3***bn* to (*E*)-**3***bo*, and the methylation of (*E*)-**3***bo* to (*E*)-**3***co*.

Solvolysis reactions

Strongly ionizing solvents and low acidity are the conditions that favour the ionization of the nitro group over the competing

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[1] In this paper enumeration of the cyclohexadienyl cations follows that of the parent cyclohexadienes.

TABLE 1. Solvolysis of (*E*)-1,4-dimethyl-4-nitrocyclohexa-1,4-dien-1-ol ((*E*)-1*b*) in 50% (v/v) methanol–water[a]

Expt. no.	*T* (°C)	*t* (h)	Base	[Base] [(*E*)-1*b*]	3*bo*	3*bn*	6*p*	7*b*+6*n*	Other
101	20	1	[b]	—	40	8	5	14	[c]
102	24	2	[d]	—	52	9	4	29[e]	[e,f]
103	25	3	Urea	2.2	43	19[g]	0	38[e]	[e,g]
104	40	4	—	—	9	0	0	62[e]	[e,h,i]
105	40	6	—	—	0	0	0	[j]	[j]
106	40	18	—	—	0	0	0	[j]	[j]
107	40	18	DPE[k]	1.1	28	20	0	52	
108	40	18	DPE	1.1	37	9	9	45	
109	40	1	DPE	1.1	26	29	4	42	
110	40	1	DPE	1.1	26	27	7	41	
111	40	1	DPE	2.2	22	14	7	58	
112	40	1	NBA[l]	0.5	49	12	12	27	
113	40	1	NBA	1.1	42	25	9	24	
114	40	1	NBA	2.2	36	14	11	39	
115	40	1	26LU[m]	1.6	59	13	12	17	
116	40	1	26LU	3.0	47	16	20	18	
117	40	1	KOAc	1.1	50	23	14	14	
118	40	1	KOAc	2.2	45	20	15	20	

[a] Procedures as described in the experimental section. Analysis by ^{1}H nmr in $CDCl_3$ in which (*E*)-3*bn* is only partially soluble. Yields were reproducible to ±5 mol%.
[b] 2,6-Lutidine (1.1 mol proportion) added immediately prior to work-up.
[c] (*E*)-1*b* (34%) unreacted.
[d] Diisopropylethylamine (1.1 mol proportion) added immediately prior to work-up.
[e] Anisoles present and included in the phenol fraction.
[f] (*E*)-1*b* (6%) unreacted.
[g] Dimethoxycyclohexadienes (3*co*) present and included in the 3*bn* fraction.
[h] 3*co* (9%).
[i] Unidentified aromatic component (20%).
[j] Essentially complete rearomatization occurred. No attempt was made to identify the aromatic products, presumably dimethylphenols and dimethylanisoles.
[k] Diisopropyethylamine.
[l] *N*-Butylamine.
[m] 2,6-Lutidine.

loss of the hydroxyl, acetate, or methoxyl group in the solvolysis of the nitrocyclohexadienols, their acetates, or methyl ethers (2, 5, 6). Accordingly, we studied initially the solvolysis of *E*-1*b* in 50% aqueous methanol (Tables 1 and 2). Experiments 101–106, 201, 202, and 206 were carried out either in the absence of base or in the presence of the very weak base urea. For reaction times of up to ten solvolysis half-lives (i.e. up to 1 h at 40°C), dienes, including the methoxydienol 3*bo* and the diol 3*bn*, were obtained, as well as aromatic products, which were mainly phenols (expts. 102, 103, 201, 202, 206). However, after a longer reaction time (expt. 104) the diene components decreased and the aromatic components increased, and at very long reaction times only aromatic products were obtained as the initially formed dienes were aromatized (expts. 105 and 106). Except in the case of the shortest reaction time (expt. 101) the dienes obtained also included the dimethoxy compound 3*co* and the aromatic component also included dimethylanisoles, suggesting that these are secondary reaction products. In these reactions in the absence of base only minor amounts of 2-nitro-*p*-xylene (6*p*) were formed and the amount did not increase with extended reaction times, which otherwise resulted in an increase in the total amount of aromatic product. Solvolysis in acidified aqueous methanol (pH 3.2) gave 3*co* (12%) and a complex mixture of aromatic products (88%) that included dimethylanisole(s).

When the solvolysis of (*E*)-1*b* was carried out in the presence of base, formation of the dimethoxydienes and anisoles was suppressed and the methoxydienol 3*bo* and dienediol 3*bn* were either not subject to rearomatization or the rate of rearomatization was greatly reduced (compare expts. 104–106 with 107 and 108). The product distribution then was 3*bo* (44%), 3*bn* (22%), 6*p* (20%), 2,4-dimethylphenol (7*b*, 11%), and 2,5-dimethylphenol (6*n*, 2%) (expts. 209–211, 214, 215), both diastereomers of 3*bo* and 3*bn* being formed from the single diastereomer of the substrate. In the presence of potassium nitrite (in addition to potassium acetate) the yield of 2-nitro-*p*-xylene was greatly enhanced and that of the diene and phenol components correspondingly reduced (compare expts. 216 and 217). Solvolysis in methanol containing *N*,*N*-diisopropylethylamine gave 3*bo* (47%), 6*p* (36%), and 7*b* and 6*n* (17%). Solvolysis in the presence of base in aqueous acetone, aqueous tetrahydrofuran, and in ether–water mixtures gave both diastereomers of dienol 3*bn*, 2-nitro-*p*-xylene, and the 2,4- and 2,5-dimethylphenols (Table 3). Solvolysis in aqueous dioxan at pH 3.2 gave a complex mixture of aromatic products including nitrodimethylphenol(s).

Solvolysis of (*E*)-1*c* in aqueous methanol containing *N*,*N*-diisopropylethylamine gave 3*co* (21%), 3*cn* (≡ 3*bo*, 34%), 6*p* (4%), and dimethylanisoles plus dimethylphenols (41%).

Solvolysis of (*E*)-1*a* in aqueous methanol gave 2,5-dimethylphenyl acetate (8*a*) as the sole product. In the presence of base, 8*a* was the very dominant (initial) product but partial solvolysis of 8*a* to 8*b* ensued. Solvolysis of 4-methyl-4-nitrocyclohexa-2,5-dien-1-ol in the presence of base gave *p*-cresol (90%) and unidentified diene (10%).

Reaction of (*E*)-3*bn* with trifluoroacetic acid gave 7*b* (98%) and 6*n* (2%). In aqueous methanol at pH 3.2 7*b* (68%) and 6*n* (32%) were obtained, although in a reaction carried out at a lower temperature, and which was therefore incomplete, some methoxydienes (12%) and dimethylanisoles (10%) were

TABLE 2. Solvolysis of (*E*)-1,4-dimethyl-4-nitrocyclohexa-1,4-dien-1-ol ((*E*)-**1***b*) in 50% methanol–water at 40°C[a]

Expt. no.	Base[b]	**3***bo*	**3***bn*	**6***p*	**7***b*	**6***n*	Other
201	—	22	2	0	33	7	^{c}
202	Urea^{d}	36	21^{e}	0	25^{f}	^{g}	^{h}
203	DPE	30	21	7	38	5	
204	26LU^{k}	49	21	16	13	1	
205	KOAc	51	14	13	15	6	^{j}
206	—	43	7	5	21	5	^{k}
207	HPO_4^{l}	0	0	20	50	^{g}	^{m}
208	DPE	39	14	11	32	5	
209	Tris^{n}	43	23	23	12	1	
210	Tris	45	20	25	10	1	
211	$NaHCO_3$	47	25	18	11	1	
212	$NaHCO_3$	42	29	16	13	1	
213	C_5D_5N	36	28	13	12	^{g}	^{o}
214	C_5D_5N	43	28	17	9	4	
215	KOAc	42	17	16	17	6	^{p}
216	KOAc	44	15	16	18	7	
217	KOAc^{q}	16	18	56	11	^{g}	

[a] Procedures as described in the experimental section. For experiments 201–205, substrate concentration = 0.075 mol dm^{-3}, reaction time = 1 h, precision ±5 mol%. For experiments 206–217, substrate concentration = 0.3 mol dm^{-3}, reaction time = 20 min, and precision ±3 mol%.

[b] [Base] = 0.33 mol dm^{-3}.

[c] Dimethoxydienes **3***co* (16%), dimethylanisoles (10%), unidentified aromatic compound (11%).

[d] [Urea] = 0.66 mol dm^{-3}.

[e] Includes dimethoxydiene **3***co*.

[f] **7***b* + **6***n*; hplc analysis was prevented by an interfering peak.

[g] **7***b*:**6***n* ratio not determined and the amount tabulated for **7***b* includes that of **6***n*.

[h] Dimethylanisoles (19%).

[i] 2,6-Lutidine, removed after work-up by extensive pumping at reduced presure before ^{1}H nmr analysis.

[j] Dimethylanisoles (2%).

[k] Dimethoxydiene **3***co* (7%), dimethylanisoles (7%), unidentified aromatic compound (5%).

[l] Na_2HPO_4, only partially soluble.

[m] Diene **3***co* (15%), dimethylanisoles (16%). The presence of the anisoles prevented the determination of the ratio of **7***b*:**6***n* by nmr.

[n] Tris(hydroxymethyl)aminomethane.

[o] Diene (*E*)-**1***b* (11%); reaction incomplete because the use of a thick-walled reaction vessel reduced the period for which the reaction was at 40°C.

[p] Dimethylanisoles (3%).

[q] KNO_2 (3 mol dm^{-3}) also added.

TABLE 3. Solvolysis of (*E*)-1,4-dimethyl-4-nitrocyclohexa-1,4-dien-1-ol ((*E*)-**1***b*) in aqueous mixtures[a]

Expt. no.	Solvent[b]	*T* (°C)	*t* (h)	Base[c]	**3***bn*	**6***p*	**7***b* + **6***n*	Other
301	50% acetone	25	4.5	KOAc	23	24	39	^{d}
302	33% acetone	40	1	DPE	38	11	43	^{e}
303	9% acetone	40	0.5	DPE	39	8	37	^{f}
304	9% acetone	20	2	KOAc	35	11	30	^{g}
305	50% THF^{h}	40	0.3	Tris^{i}	14	7	7	^{j}
306	33% THF	40	1	DPE	42	15	44	
307	50% ether	40	0.3	Tris	20	11	11	^{k}
308	50% ether	40	2	Tris	22	15	13	^{l}

[a] Analyses by ^{1}H nmr. The conjugated dienol **5***bn* was probably present in all of the reactions.

[b] Organic component and its percentage specified; the other component was water. The diethyl ether mixtures were heterogeneous.

[c] The mole ratio of base to (*E*)-**1***b* was 1.1 except for expts. 301 (2.2) and 304 (1.3).

[d] (*E*)-**1***b* (14%).

[e] **5***bn* (8%).

[f] **5***bn* (6%), unidentified components with ^{1}H nmr peaks at 1.95 ppm (6%) and 2.25 ppm (4%).

[g] The 1.95-ppm (15%) and 2.25-ppm (9%) components.

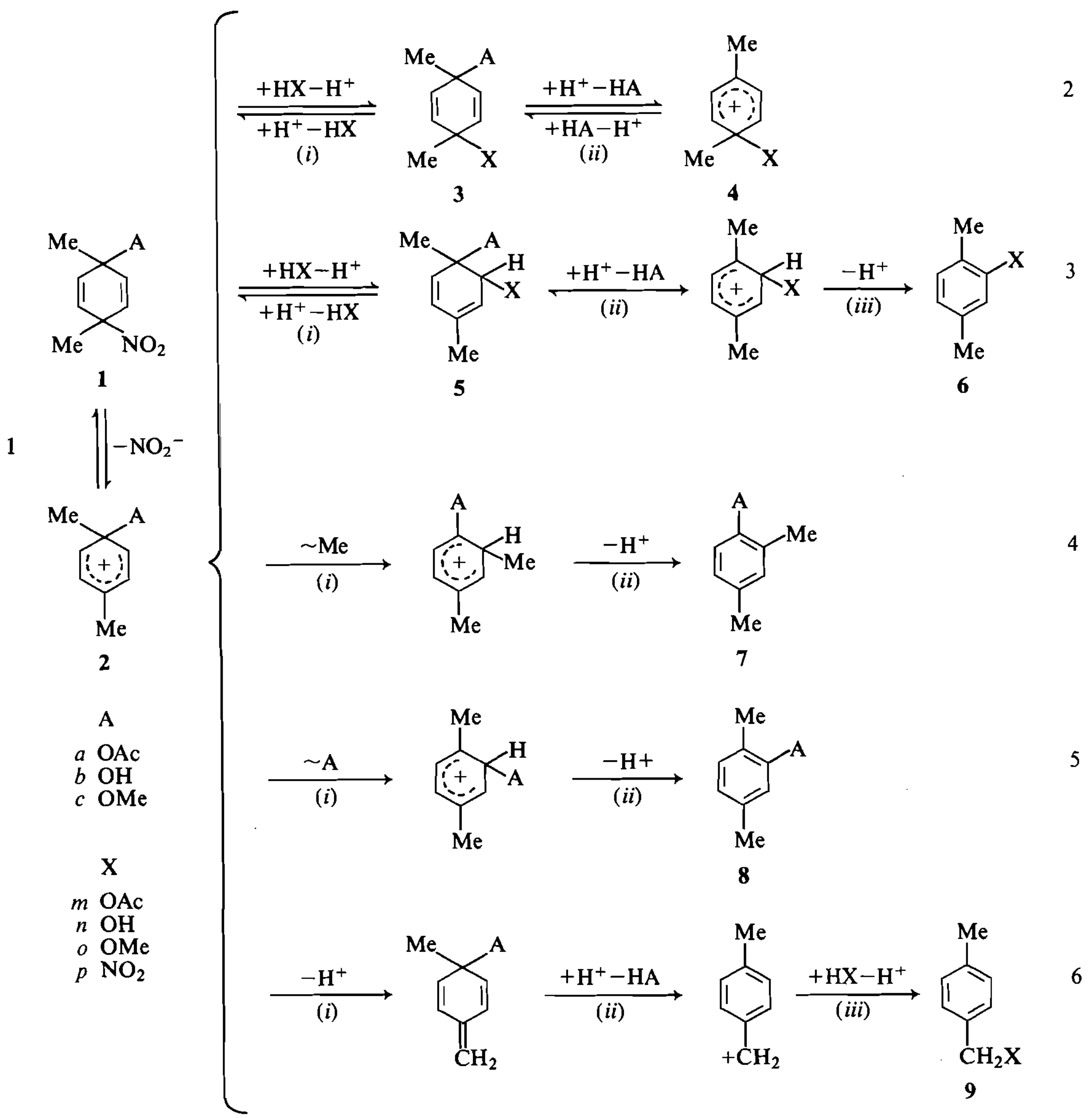
[h] Tetrahydrofuran.

[i] Tris(hydroxymethyl)aminomethane.

[j] (*E*)-**1***b* (72%).

[k] (*E*)-**1***b* (59%).

[l] (*E*)-**1***b* (51%).

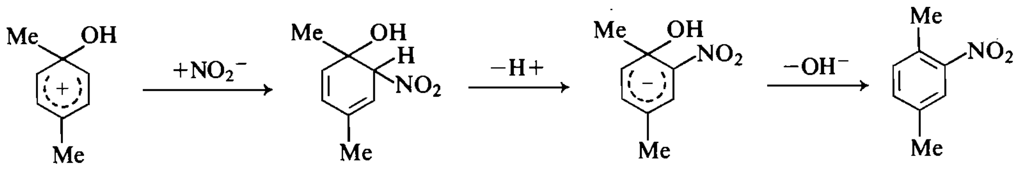


SCHEME 1

present in addition to the xylenols. In aqueous dioxan at pH 3.2 **7***b* and **6***n* were obtained in the 2:1 ratio. Reaction of (*Z*)-**3***co* with trifluoroacetic acid gave **7***c*.

We account for the solvolysis reaction products in terms of the formation and further reactions of a 1-A-1,4-dimethylcyclohexadienyl cation (**2**), as illustrated in Scheme 1, an elaboration of earlier schemes (2, 6, 7). Reactions 2(*i*) and 3(*i*) represent additions of a nucleophile to the electrophilic centre that is in a 1,4 or 1,2 relationship to the tetrahedral centre of the cation, respectively. As shown, these reactions may be followed by further reactions of the new cyclohexadienes. Reactions 4 and 5 in their initial steps (*i*) involve competing 1,2 migrations of the methyl and substituent A groups at the tetrahedral centre of the cation. Reaction 6 involves deprotonation of the cation to a triene followed by S_N1' substitution to form a benzylic derivative.

Unimolecular ionization of the nitro group in (*E*)-**1***b* leads to the hydroxycyclohexadienyl cation **2***b* (Scheme 1, reaction 1, A = OH). The methoxydienol **3***bo* and the dienediol **3***bn* are formed by solvent methanol or water, respectively, trapping **2***b* (reaction 2(*i*), A = OH and HX = HOMe or HOH). Reaction 2(*i*) is the dominant reaction of **2***b* since some 65% of the product consisted of **3***bn* and **3***bo*. The fact that both diastereomers of **3***bo* and **3***bn* are formed from a single diastereomer of **1***b* confirms the S_N1 substitution mechanism. 2-Nitro-*p*-xylene (**6***p*) was obtained in 19% yield. Addition of the nitrite ion, released in the ionization step, to the *ortho* position of **2***b* would give the nitrodiene **5***bp*, which, on elimination of water, would give the nitroarene. The addition–elimination would more likely follow the base-catalysed sequence depicted in Scheme 2 than the acid-catalysed sequence of reaction 3, Scheme 1. This is shown by the fact that only small amounts of **6***p* were formed in the reactions carried out in the absence of base, when the liberated nitrite would be present as the less nucleophilic nitrous acid. Our previous study of the methanolysis of 1-ethyl-4-methyl-4-nitrocyclohexadienol, which gave 4-ethyl-3-nitrotoluene in addition to 2-ethyl-4-methylphenol and the diastereomers of 1-ethyl-4-methoxy-4-methylcyclohexadien-1-ol, confirms that the nitro group is added at the position *meta* to its original position (2). The nitrite anion might also be expected to add to the *para* position of **2***b*. This reaction (2(*i*), X = NO_2) is just the reverse of the ionization reaction (reaction 1) and Myhre and



SCHEME 2

co-workers have argued that such return from the ion-pair is facile (7). The fact that in the presence of external nitrite the yield of 2-nitro-*p*-xylene from *E*-**1***b* increased to over 50% indicates that nitrite is a very effective competitor for cation **2***b* and establishes the intermolecular pathway of the formation of **6***p*. A 36% yield of **6***p* was obtained when the solvolysis reaction was carried out in methanol (containing diisopropylethylamine). This increased yield is presumably attributable to the effect of the lower dielectric constant solvent increasing the rate of the reaction between carbonium ion and nitrite anion, involving charge annihilation, relative to the rates of the other reactions of the carbonium ion, in which charge is preserved.

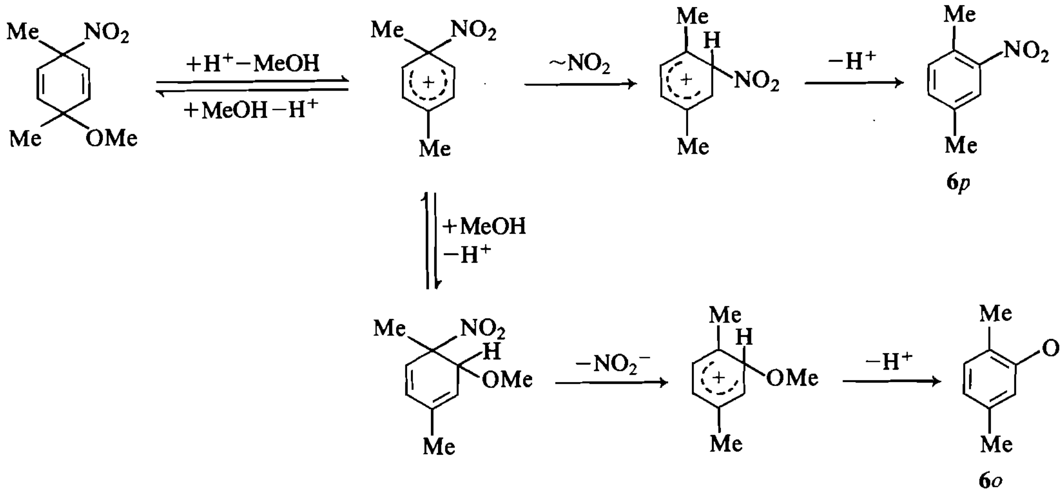
The 2,4-dimethylphenol (**7***b*), formed in 13% yield in the aqueous methanol solvolysis, arises via reaction 4. Since 2,5-dimethylphenol was formed in much lower yield (3%), it is evident that in cation **2***b* the methyl is much more prone to migrate (reaction 4(*i*)) than the hydroxyl (reaction 5(*i*)). This preference is even more marked than it appears since 2,5-dimethylphenol is also formed (and likely only formed) via reaction 3. The reaction of diol **3***bn* with trifluoroacetic acid, which gave 98% of 2,4-dimethylphenol, indicates that the relative migratory aptitude of methyl to hydroxyl in **2***b* is at least 50:1. The preference for methyl migration over migration of hydroxyl (or methoxyl) in cyclohexadienyl cations is well established in dienone–phenol rearrangement studies (14–16). Reaction of solvent at the position adjacent to the tetrahedral centre of **2***b* (reaction 3(*i*): S_N1') is slower than reaction at the *para* position (reaction 2(*i*): S_N1). On separation of the product of a large-scale reaction we obtained a small amount of the 1,2-diol (**5***bn*). It was difficult to establish the presence of **5***bn* and (or) **5***bo* in the solvolysis reaction mixtures because of the overlap of the methyl peaks with those of (*E*)-**1***b* (at 1.77 ppm) and of the products **3***bn* and **3***bo* (at 1.29 ppm). However, in a few reactions carried out in aqueous acetone and in aqueous tetrahydrofuran it was possible to establish from the absence of the quartet centred at 6.0 ppm that all of the reactant was consumed. The peak at 1.77 ppm could then be attributed to **5***bn*. In these reactions **5***bn* was present to the extent of 20% of the amount of **3***bn*, about 7% of the total reaction product. A further indication of the formation of **5***bn* was provided by the observation that in weakly acid solution (pH 3.2) the dienediol **3***bn* gave ca. 33% of **6***n*, presumably by the sequence **3***bn* → **2***b* → **5***bn* → → **6***n*. We conclude that the conjugated dienediol **5***bn* is a necessary intermediate between **2***b* and **6***n*. In dilute acid conditions the conversion of **5***bn* to **6***n* must be relatively efficient, since the extent of formation of **6***n* is half that of **7***b* although **5***bn* is only 20% of **3***bn*.

The formation of dienediol and (or) methoxydienol as intermediates in the solvolysis of the nitrocyclohexadienol has been inferred from kinetics studies (7). Our study of the products of solvolysis of 1-ethyl-4-methyl-4-nitrocyclohexa-2,5-dienol (2) and the present investigation provide the first reports of the positive identification of the dienediols and the methoxydienols as nitrocyclohexadienol solvolysis products and, in the case of the 1,2-diol, the first direct evidence of its formation in any reaction. The intermediate formation of **3***bn* in the second of two acid-catalysed mechanisms of ring opening of 1,4-dimethylbenzene oxide and its aromatization to **7***b* and **6***n* has been conclusively demonstrated by Bruice, Jerina, and co-workers (9). They proposed alternative pathways for the conversion of the diol to **7***b* and **6***n*, one being that depicted in Scheme 1 (**3***bn* → **2***b* → **5***bn* → → **6***n* and **3***bn* → **2***b* → → **7***b*), and the other, re-formation of the protonated oxide and its direct conversion to **7***b* and **6***n*. They preferred the second path. Our results, which demonstrate the intermediate formation of the 1,2-diol **5***bn* and the fact that **6***n* is not formed when **2***b* cannot be trapped by water (e.g. in trifluoroacetic acid), are in accord with the first. Our results also show that reversible formation of protonated oxide from cation **2***b* cannot occur since this would lead to a ratio **7***b*:**6***n* from the nitrodienol solvolysis reaction in the acid region (2:1), and from the reaction of the dienediol with acid, identical to that observed in reaction of the oxide with acid. However, the oxide reaction gives more **6***n* than **7***b* at pH 3.5 and **6***n* is even more favoured in stronger acid (9, 17).

No benzylic compounds were obtained in the solvolysis of (*E*)-**1***b* and thus the deprotonation of **2***b* (reaction 6(*i*)) must be slower than reactions 2(*i*), 3(*i*), or 4(*i*). Examples of reaction type 6 are known for nitrocyclohexadienyl cations, e.g. the nitrodimethylcyclohexadienyl cation formed by protonation of **1** at A and loss of HA (7, 8). However, there have been no reports of benzylic products being formed via cations such as **2***a*, **2***b*, or **2***c*.

The solvolysis reaction generates nitrous acid. In the absence of added base the solution becomes acidic and the initially formed dienes **3***bo* and **3***bn* can reform the cation **2***b* by acid-catalysed loss of methoxy or hydroxyl, respectively (reverse of reaction 2(*i*)), as discussed above. However, **3***bo* can also undergo acid-catalysed loss of hydroxyl (reaction 2) to generate the methoxycyclohexadienyl cation **4***o*. This, on reaction with methanol, would generate the dimethoxydiene **3***co*. Prolonged exposure to the acid conditions would lead to complete formation of aromatic products (phenols and anisoles) via reactions 3 and 4, and this was demonstrated by the results of solvolysis reactions carried out at pH 3.2 in which (*i*) little or no diene was obtained; (*ii*) in the case of the reaction in aqueous methanol, the small amount of diene obtained was largely **3***co*, reflecting the (acid-catalysed) exchange of the original hydroxyl group, and the aromatic compounds included anisoles, also indicative of this exchange; (*iii*) the phenols were nitrated under the acid conditions. We can thus understand why, in the aqueous methanol solvolyses of (*E*)-**1***b*, anisoles were significant components of the aromatic products and dimethoxydienes were formed only in the absence of added base and why these products were not obtained, even in the absence of added base, when the reaction time was very short.

Solvolysis of (*E*)-**1***c* in aqueous methanol follows analogous pathways to those described for (*E*)-**1***b* and does not require additional comment. Reaction of (*E*)-**1***c* with 50% trifluoroacetic acid in methanol gave **6***p*, **7***c*, and **6***o*. At such acidity this reaction presumably involves, at least in part, the nitrocyclohexa-



SCHEME 3

dienyl cation as shown in Scheme 3. However, the formation of **7***c* under these conditions must involve the methoxycyclohexadienyl cation **2***c*. Thus in this solvent mixture ionization of nitrite and the acid-catalysed loss of methanol are competitive. The reaction of (*Z*)-**3***co* with trifluoroacetic acid, which gave **7***c*, demonstrates the preferential migration of methyl rather than methoxyl in cation **2***c*.

Solvolysis of (*E*)-**1***a* differed from solvolysis of (*E*)-**1***b* and (*E*)-**1***c* in that essentially a single product (**8***a*) was obtained. The 1,2 shift of the acetate group in ion **2***a* should be facilitated by the formation of a bond to the carbonyl oxygen so that rearrangement (reaction 5) can occur via a cyclic transition state. We investigated the possibility that rearrangement of the acetate was concerted with the ionization of the nitro group by measuring the rates of solvolysis of (*E*)-**1***a* and (*E*)-**1***b*. Although (*E*)-**1***a* reacts faster than (*E*)-**1***b*, the rate ratio was only 2:1. The enhancement seems too small to require a concerted transition state, although it should be noted that formation of **2***a* should be slower than **2***b* since the acetoxy group is more electron withdrawing than the hydroxy group. Thus the true rate enhancement must be greater than is apparent. In any event, since cation **2***a* was not effectively trapped by nucleophiles, in contrast to **2***b* and **2***c*, the rearrangement of the acetate must occur very soon after **2***a* is formed if it is not synchronous with the ionization step.

Experimental

Infrared spectra were obtained on a Perkin–Elmer 283 spectrometer. The ^{1}H nmr spectra, at 90 MHz, were determined using a Perkin–Elmer R32 spectrometer. The ^{13}C nmr spectra, at 15.1 MHz, were obtained with a Nicolet TT-14 spectrometer. Mass spectra were determined on a Hitachi Perkin–Elmer RMU7 spectrometer. High pressure liquid chromatography (hplc) was carried out with a Waters system 500 (preparative) and on a Varian model 5000 (analytical) chromatograph. The gas–liquid chromatograph used was a Varian Aerograph model 2400.

2,4-Dimethylphenol, 2,4-dimethylanisole, 2,5-dimethylanisole, *N*,*N*-diisopropylethylamine, chlorotrimethylsilane, iodotrimethylsilane, bis(trimethylsilyl)acetamide, and 2,6-lutidine were from Aldrich. 2,5-Dimethylphenol, from Eastman, was recrystallized twice from *n*-heptane. Methyl iodide was from Mallinckrodt, trifluoroacetic acid was from Matheson, Coleman and Bell, and the Eu([^{2}H$_9$]fod)$_3$ shift reagent was from Merck, Sharp and Dohme. 2,5-Dimethylphenyl acetate was prepared by acetylation of the phenol with acetic anhydride (18).

1,4-Disubstituted cyclohexa-2,5-dienes

(*E*)-1,4-Dimethyl-4-nitrocyclohexa-2,5-dienyl acetate ((*E*)-**1***a*) was obtained by nitration of *p*-xylene (8, 11). Reaction of (*E*)-**1***a* with aluminum hydride gave (*E*)-1,4-dimethyl-4-nitrocyclohexa-2,5-dienol (*E*))-**1***b*) (11). Methylation of (*E*)-**1***b* gave (*E*)-**1***c* (11). Reduction of 4-methyl-4-nitrocyclohexa-2,5-dienone with sodium borohydride gave 4-methyl-4-nitrocyclohexa-2,5-dien-1-ol (12). Both diastereomers of 1,4-dimethylcyclohexa-2,5-diene-1,4-diol (**3***bn*) were obtained by addition of methyllithium to *p*-benzoquinone (13). Addition of methyllithium to 4-methoxy-4-methylcyclohexa-2,5-dienone (itself prepared from the chlorodienone by reaction with silver nitrate in methanol, cf. ref. 19) gave both isomers of 4-methoxy-1,4-dimethylcyclohexa-2,5-dienol (**3***bo*) in a 1:3 ratio. The isomers were separated by hplc. The minor isomer (*E*)-**3***bo* had mp 95–96°C (lit. (9) mp 94–95°C); ir (Nujol): 3415 (OH), 2820 (OCH$_3$), 1120, 1065 (C—O), 800 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ: 1.30 (s, 3), 1.33 (s, 3), 1.80 (s, 1, O*H*), 3.02 (s, 3, OC*H*$_3$), 5.57 (d, 2, *J* = 10 Hz, 3-*H* and 5-*H*), 6.02 (d, 2, *J* = 10 Hz, 2-*H* and 6-*H*) ppm; ^{13}C nmr (CDCl$_3$) δ$_C$: 27.9 (1-CH$_3$ and 4-CH$_3$), 51.5 (OCH$_3$), 65.4 (*C*-1), 71.0 (*C*-4), 130.4 (*C*-3 and *C*-5), 136.4 (*C*-2 and *C*-6) ppm. The major isomer (*Z*)-**3***bo* was obtained as oil; ir (film): 3410 (OH), 2830 (OCH$_3$), 1135, 1085 (C—O), 780 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ: 1.22 (s, 3), 1.28 (s, 3), 2.35 (s, 1, O*H*), 3.10 (s, 3, OC*H*$_3$), 5.59 (d, 2, *J* = 10 Hz, 3-*H* and 5-*H*), 5.95 (d, 2, *J* = 10 Hz, 2-*H* and 6-*H*) ppm; ^{13}C nmr δ$_C$: 28.0 and 29.0 (1-*C*H$_3$ and 4-*C*H$_3$), 51.9 (O*C*H$_3$), 65.4 (*C*-1), 71.0 (*C*-4), 130.3 (*C*-3 and *C*-5), 135.7 (*C*-2 and *C*-6) ppm.

(*E*)-3,6-Dimethoxy-3,6-dimethylcyclohexa-1,4-diene ((*E*)-**3***co*) was obtained by methylation of the methoxydienol (*E*)-**3***bo*. A mixture of freshly precipitated silver oxide (1.2 g), methyl iodide (4.5 cm^3), potassium hydroxide (0.03 g), and (*E*)-**3***bo* (0.30 g) was stirred at ambient temperature. The disappearance of the dienol (*E*)-**3***bo* was monitored by ^{1}H nmr and after 18 h, when none remained, the reaction mixture was filtered and the residue washed with ether (3 × 10 cm^3). The combined filtrate and washings were dried (MgSO$_4$) and the solvent evaporated at 30°C; ^{1}H nmr indicated that the solid residue (0.22 g) was essentially pure (*E*)-**3***co*. Crystals were obtained from pentane and a sample was sublimed at 40–60°C and had ir (KBr): 2820 (OCH$_3$), 1080 (C—O), 780 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ: 1.29 (s, 6, 3-C*H*$_3$ and 6-C*H*$_3$), 3.03 (s, 6, 3-OC*H*$_3$ and 6-OC*H*$_3$), 5.75 (s, 4, 1-*H*, 2-*H*, 4-*H*, 5-*H*) ppm; ^{13}C nmr (CDCl$_3$, −10°C) δ$_C$: 27.6 (3-*C*H$_3$ and 6-*C*H$_3$), 51.6 (3-O*C*H$_3$ and 6-O*C*H$_3$), 71.0 (*C*-3 and *C*-6), 134.1 (*C*-1, *C*-2, *C*-4, *C*-5) ppm; ms (70 eV) *m*/*e* (relative intensity): 168 (0.5, *M*), 153.085 (100, M_r ^{12}C$_9$^{1}H$_{13}$^{16}O$_2$: 153.092, *M* − CH$_3$), 137 (94), 122 (62), 121 (13), 105 (19), 91 (46), 79 (22), 78 (12), 77 (39), 65 (16), 53 (13), 51 (20), 43 (38). *Anal.* calcd. for C$_{10}$H$_{16}$O$_2$: C 71.39, H 9.59; found: C 71.20, H 9.61.

Similar methylation of the dienol (*Z*)-**3***bo* for 34 h gave (*Z*)-3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene ((*Z*)-**3***co*) in essentially quantitative yield. The dimethoxydiene was also prepared by methylation of the dienediol (*Z*)-**3***bn* (0.8 g) by stirring with a mixture of methyl iodide (27 cm^3), potassium hydroxide (0.165 g), and silver oxide (14 g added in 1–3 g portions over the reaction period) for 8 days. After work-up, ^{1}H nmr showed that the residue consisted of (*Z*)-**3***co* (92%) and (*Z*)-**3***bo* (8%). Sublimation at 60–70°C gave colourless plates of (*Z*)-**3***co*, mp 56°C (with sublimation); ir (KBr): 2820 (OCH_3), 1090 (C—O), 800 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ: 1.23 (s, 6, 3-CH_3 and 6-CH_3), 3.15 (s, 6, 3-OCH_3 and 6-OCH_3), 5.82 (s, 4, 1-*H*, 2-*H*, 4-*H*, 5-*H*) ppm; ^{13}C nmr ($CDCl_3$, −10°C) δ_C: 28.4 (3-*C*H_3 and 6-*C*H_3), 52.3 (3-O*C*H_3 and 6-O*C*H_3), 70.9 (*C*-3 and *C*-6), 134.0 (*C*-1, *C*-2, *C*-4 and *C*-5) ppm; ms (70 eV) *m*/*e* (relative intensity): 168 (0.3), 153.091 (100, M_r $^{12}C_9{}^1H_{13}{}^{16}O_2$: 153.092, $M - CH_3$), 138 (31), 137 (97), 123 (13), 122 (51), 121 (13), 107 (10), 106 (16), 105 (17), 91 (41), 79 (26), 78 (14), 77 (43), 65 (19), 53 (19), 52 (13), 51 (25), 43 (63), 41 (25). *Anal.* calcd. for $C_{10}H_{16}O_2$: C 71.39, H 9.59; found: C 70.93, H 9.47.

*Shift reagent studies on the diastereomers of 4-methoxy-1,4-dimethylcyclohexa-2,5-dienol (3*bo*)*

A solution of Eu([$^2H_9$]fod)$_3$ (150 mg) in [^{2}H]chloroform (450 mm^3) was prepared and measured volumes were added, at 0°C, to solutions of the methoxydienols (*E*)-**3***bo* and (*Z*)-**3***bo* (30 mg) in [^{2}H]chloroform (300 mm^3) containing tetramethylsilane (20 mm^3). The ^{1}H nmr of each solution was measured at 0°C after addition of the shift reagent. Plots of the chemical shifts of the other protons against that of the 1-CH_3 protons gave relative shift gradients (gradient 1-CH_3 = 1.00) as follows: (*E*)-**3***bo*: 0.34 (4-CH_3), 0.35 (4-OCH_3), 0.45 (3-*H* and 5-*H*), 1.06 (2-*H* and 6-*H*); (*Z*)-**3***bo*: 0.31 (4-CH_3), 0.35 (4-OCH_3), 0.43 (3-*H* and 5-*H*), 1.02 (2-*H* and 6-*H*).

*Solvolysis of (*E*)-1,4-dimethyl-4-nitrocyclohexadienol ((*E*)-1*b*) in aqueous methanol*

Initial experiments (101–118) were carried out using (*E*)-**1***b* (100 mg, 0.6 mmol) in aqueous methanol (1:1 v/v, 8 cm^3), in both the presence and absence of a weak base, and at both ambient temperature and 40°C. These reactions were not stirred, as the nitrodienol appeared to dissolve completely. The products were worked up by first saturating the reaction mixture with sodium chloride, extracting with ether (3 × 20 cm^3), and washing the combined ether layers with saturated brine (3 × 10 cm^3). The ethereal solution was dried ($MgSO_4$) and the ether evaporated; ^{1}H nmr analysis ($CDCl_3$; 0°C) gave the results listed in Table 1.

Generally, integration of characteristic methyl peaks was the preferred means of determining the product ratios. The methyl peaks of 2-nitro-*p*-xylene were clearly separated from those of the dimethylphenols and the product dienes **3***bn* and **3***bo*. The C-CH_3 peaks of **3***bn* and **3***bo* overlapped but the total integral could be subdivided using the O-CH_3 peak to measure the amount of **3***bo*. In some cases, e.g. when *N*,*N*-diisopropylethylamine was used, the methyl region was partially obscured and the ratio of (**3***bn* + **3***bo*):**6***p*:(**7***b* + **6***n*) was determined from the integral of the vinyl and aromatic regions of the ^{1}H nmr spectrum. In subsequent experiments (below) the ratio of **7***b* to **6***n* was determined by analytical hplc. Careful examination of the aromatic phenol region of the ^{1}H nmr of mixtures of known phenol composition showed that it was possible to determine the ratio of **7***b*:**6***n* by ^{1}H nmr using solutions of known composition for standardization. The (*E*) isomer of the dienediol **3***bn* was not completely soluble in $CDCl_3$ and in later experiments [$^2H_6$]dimethylsulfoxide was the preferred solvent for ^{1}H nmr.

In the second set of experiments (201–205) a solution of (*E*)-**1***b* (1.0 g, 5.9 mmol) in aqueous methanol (1:1 v/v, 80 cm^3) was stirred at 40°C for 1 h. In most reactions a weak base was added. Each reaction mixture was worked up by cooling to 0°C, saturating the solution with sodium chloride, and extracting with cold ether (3 × 100 cm^3). The combined ethereal extracts were washed with brine (3 × 50 cm^3) and dried ($MgSO_4$). The ether was evaporated at 30°C and final traces of ether were removed under reduced pressure. Analysis was carried out by ^{1}H nmr using $(CD_3)_2CO$, $(CD_3)_2SO$, or $CDCl_3$ as solvent. The ratio of 2,4- to 2,5-dimethylphenol was determined by hplc. The peaks of the phenols overlapped and the amounts of each were determined by cutting and weighing the peaks, having first calibrated the system using solutions of known phenol ratios prepared from pure phenols. Results are listed in Table 2 (expts. 201–205).

In the third set of experiments (206–217) a solution of (*E*)-**1***b* (100 mg, 0.6 mmol) in aqueous methanol (1:1 v/v, 2 cm^3), also containing added reagent, was maintained at 40°C in an ultrasonic bath for 20 min. Ether (50 cm^3) was added and the solution dried, first over sodium sulfate and then over magnesium sulfate. The drying agents were washed with ether and the combined ether solution evaporated at 30°C. Analysis was carried out by ^{1}H nmr. The ratio of 2,4- to 2,5-dimethylphenol was determined by analytical hplc, or by nmr using the nmr of reaction mixtures in which the phenol ratio had previously been determined by analytical hplc as standards. Results are given in Table 2. Experiments 206–216 were carried out under the most carefully controlled conditions and using refined methods of product analysis. Of the reactions carried out in the presence of base, expts. 209–211, 214, and 215 were without complication and the results may be regarded as particularly reliable. Experiments 208, 212, and 216 are of less, but acceptable, reliability. Reaction 207 was complicated by the insolubility of the base disodium hydrogen phosphate and reaction 213 did not go to completion. The mean product distribution from the particularly reliable set of experiments is **3***bo* (44%), **3***bn* (22%), **6***p* (20%), **7***b* (11%), and **6***n* (2%) and from the particularly reliable plus reliable sets is **3***bo* (43%), **3***bn* (21%), **6***p* (18%), **7***b* (15%), and **6***n* (3%).[2]

A solvolysis reaction was also carried out under acid conditions. (*E*)-**1***b* (0.07 g, 0.4 mmol) was added to aqueous methanol (1:1 v/v, 10 cm^3) containing potassium chloride (7.5 mg, 1 mmol) after the pH of the solution had been adjusted to 3.2 by the addition of hydrochloric acid. The solution was stirred at ambient temperature for 22 h. The product, obtained after work-up as described above for expts. 101–118, contained (^{1}H nmr) dimethoxydienes (12%) and a mixture of aromatic compounds (88%) including dimethylanisoles, dimethylphenols, and, tentatively, dimethylnitrophenol(s).

In a larger-scale reaction (*E*)-**1***b* (3 g, 0.018 mol) was dissolved in aqueous methanol (1:1 v/v, 240 cm^3) and potassium acetate (1.9 g, 0.02 mol) was added. The solution was stirred at 40°C and then chilled. A sample (8 cm^3) was worked up to confirm completion of the solvolysis. The main reaction mixture was then saturated with salt, stirred for 5 min, and extracted with ether (3 × 200 cm^3). The combined ether layers were washed with brine (3 × 100 cm^3) and dried, first over sodium sulfate and then over magnesium sulfate. Evaporation of the ether at 30°C and removal of the final traces under reduced pressure gave an oil (2.4 g) that contained (by nmr) the methoxydienols **3***bo* (60%), dienediols **3***bn* (12%), dimethylphenols plus dimethylanisoles (16%), and 2-nitro-*p*-xylene (12%). Preparative hplc on silica and elution with ether gave four fractions, the first containing the aromatic compounds, the second was methoxydienol (*E*)-**3***bo*, the third its isomer (*Z*)-**3***bo* containing some (*E*)-**3***bo* (7%), and the fourth a mixture of (*Z*)-**3***bo* and the dienediols **3***bn*. Recrystallization of the second fraction from ether–pentane gave colourless crystals, mp 95–97°C (lit. (9) mp 94–95°C) with ^{1}H nmr identical to that of an authentic sample of (*E*)-**3***bo*. The ^{1}H nmr of the major component of the third fraction was identical to that of an authentic sample of (*Z*)-**3***bo*. Some crystals separated from the fourth fraction on standing. They were washed free of the oil with ether, dissolved in [$^2H_6$]acetone, and then had ^{1}H nmr identical to that of authentic (*E*)-**3***bn*.

*Solvolysis of (*E*)-1*b* in methanol*

A solution of (*E*)-**1***b* (70 mg, 0.41 mmol) and *N*,*N*-diisopropylethylamine (82 mm^3, 0.45 mmol) in CD_3OD (0.6 cm^3) was observed by nmr. Little or no reaction occurred over 1 h at 40°C. After 6 min at

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[2] We have ignored the fact that the product distribution may be a function of the particular base used. The product distributions for reactions in which the same base was used are more closely similar than the product distributions for experiments involving different bases. However, such differences are small compared to those between reactions carried out with and without base. We have also ignored the likely presence of a small amount of **5***bn* and (or) **5***bo*.

60°C, formation of the two diastereomers of the methoxydienol **3***bo* was apparent. The reaction half-life at 60°C was 75 min and after 5.3 h the reaction mixture was worked up to give (^{1}H nmr) a mixture of **3***bo* (47%), dimethylphenols (17%), and 2-nitro-*p*-xylene (36%). A small amount of the dimethoxydiene **3***co* or dienediol **3***bn* was observed in the reaction mixture prior to work-up.

Solvolysis of (E)*-1*b *in aqueous tetrahydrofuran, aqueous ether, aqueous acetone, and aqueous dioxan*

The nitrodienol (100 mg, 0.59 mmol) was dissolved in the organic solvent, the requisite amount of water and the base were then added, and the solution stirred at the chosen temperature for the specified time. Work-up and ^{1}H nmr analysis gave the results summarized in Table 3.

Solvolysis was also carried out under acidic conditions in aqueous dioxan. The pH of the dioxan solution (1:1 v/v) containing potassium chloride was adjusted to 3.2 by the addition of hydrochloric acid. (*E*)-**1***b* was added and the mixture was stirred for 22 h at ambient temperature. After work-up, ^{1}H nmr indicated that aromatization was essentially complete and ^{1}H nmr and gc–ms indicated that the two major products were 2-nitro-*p*-xylene and dimethylnitrophenol.

In a larger-scale reaction a solution of (*E*)-**1***b* (10 g, 0.059 mol) in acetone (200 cm^3) and water (400 cm^3) containing *N*,*N*-diisopropylethylamine (11.7 cm^3, 0.065 mol) was stirred at 40°C for 1 h. The reaction mixture was saturated with salt, extracted with ether, and the combined ethereal extracts washed with brine, dried ($MgSO_4$), and the ether evaporated. The ^{1}H nmr analysis indicated that the mixture consisted of dienediol **3***bn* (35%), dimethylphenols (56%), and 2-nitro-*p*-xylene (10%). Addition of carbon tetrachloride gave colourless crystals of (*E*)-**3***bn* (0.7 g), which after recrystallization from acetone had mp 158–159°C; ir (KBr): 3370, 3330, 1125, and 1070 (OH), 1410 (C—CH_3), 780 (*cis* vinyl) cm^{-1}; ^{1}H nmr ($(CD_3)_2CO$, 0°C) δ: 1.18 (s, 6, 1-C*H*$_3$ and 4-C*H*$_3$), 3.02 (s, 2, 1-O*H* and 4-O*H*), 5.67 (s, 4, 2-*H*, 3-*H*, 5-*H*, and 6-*H*) ppm; ^{13}C nmr ($(CD_3)_2CO$) δ_C: 29.3 (1-*C*H$_3$ and 4-*C*H$_3$), 65.4 (*C*-1 and *C*-4), 133.9 (*C*-2, *C*-3, *C*-5, and *C*-6) ppm; ms (70 eV) *m*/*e* (relative intensity): 140 (1), 126 (17), 125.059 (100, M_r $^{12}C_7{}^1H_9{}^{16}O_2$: 125.060, $M - CH_3$), 124 (8), 122 (7), 111 (8), 110 (30), 108 (6), 107 (20), 106 (13), 105 (7), 97 (12), 91 (20), 79 (14), 77 (15). *Anal.* calcd. for $C_8H_{12}O_2$: C 68.55, H 8.63; found: C 68.62, H 8.61.

The carbon tetrachloride soluble extract contained 21% of dienes. After evaporation of the solvent a sample (5.5 g) of the residue was subjected to hplc on silica using ether eluant. The initial fraction (4.9 g) was a mixture of 2-nitro-*p*-xylene and dimethylphenols. The next fraction (0.19 g) was (*Z*)-**3***bn* containing a small amount of its (*E*) isomer and the final fraction (0.35 g) was a mixture containing **5***bn*. Purification by short-path distillation below 50°C at 50 Pa in a sublimator gave **5***bn* as an oil; ^{1}H nmr ($CDCl_3$, 270 MHz) δ: 1.29 (s, 3, 1-C*H*$_3$), 1.77 (t, 3, 4-C*H*$_3$), 2.81 (b, O*H*), 3.85 (bd, 1, 2-*H*), 5.61 (bd, 1, 3-*H*), 5.70 (dd, 1, $J = 2, 10$ Hz, 5-*H*), 5.75 (d, 1, $J = 10$ Hz, 6-*H*) ppm. In the 90-MHz spectrum, irradiation at 1.77 ppm collapsed the peaks at 3.85 and 5.61 to the doublets of an AB quartet ($J = 4$ Hz); irradiation at 3.85 collapsed the peak at 1.77 ppm to a doublet ($J = 1.8$ Hz) and sharpened the peak at 5.61 to an incompletely resolved quartet; irradiation at 5.61 collapsed the peak at 1.77 to an uneven doublet ($J = 1.6$ Hz) and sharpened the peak at 3.85 ppm to an incompletely resolved quartet.

Solvolysis of (E)*-3-methoxy-3,6-dimethyl-6-nitrocyclohexa-1,4-diene ((*E*)-1*c*)*

Solvolysis of (*E*)-**1***c* (100 mg, 0.55 mmol) was carried out for 5 h at 56°C in aqueous methanol (1:1 v/v, 8 cm^3) containing diisopropylethylamine (108 mm^3, 0.61 mmol). The substrate was not completely soluble. After work-up as described for expts. 101–118, the products obtained were (*E*)- and (*Z*)-**3***co* (21%), (*E*)- and (*Z*)-**3***cn* (34%), dimethylanisoles and dimethylphenols (41%), and 2-nitro-*p*-xylene (4%). The reaction was repeated at 40°C and at 25°C in the absence of added base. The reaction did not go to completion but a similar product distribution was obtained.

Reaction of (E)*-1*c *with methanol – trifluoroacetic acid*

Diene (*E*)-**1***c* (100 mg, 0.55 mmol) was dissolved in a mixture of methanol (250 mm^3) and trifluoroacetic acid (250 mm^3) at 0°C. After 16 h at 35°C aromatization was complete (^{1}H nmr). The solvent was evaporated and the residue was dissolved in ether (20 cm^3) and washed with aqueous sodium bicarbonate (3 × 10 cm^3) and water (10 cm^3). After drying ($MgSO_4$) the ether was evaporated to give an oil (55 mg) containing 2,4-dimethylanisole (16%), 2,5-dimethylanisole (34%), and 2-nitro-*p*-xylene (50%). Analysis by glc (10% FFAP) confirmed the presence of dimethylanisoles (single peak) and the 2-nitro-*p*-xylene. Similar results were obtained when the reaction was repeated at ambient temperature for 100 h.

Solvolysis of (E)*-1,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate ((*E*-1*a*)*

Acetate (*E*)-**1***a* (100 mg, 0.47 mmol) was dissolved in aqueous methanol (1:1 v/v, 8 cm^3) and the mixture stirred at ambient temperature for 2 h. The reaction was worked up as described for expts. 101–118. 2,5-Dimethylphenyl acetate (47 mg) was the sole product (^{1}H nmr). The same result was obtained when the reaction was carried out for 1 h at 40°C. The reaction was also carried out in the presence of added base (diisopropylethylamine, potassium acetate) when partial solvolysis of the 2,5-dimethylphenyl acetate to 2,5-dimethylphenol occurred. A control experiment showed that 2,5-dimethylphenyl acetate was solvolysed to the phenol under these conditions. Any acetoxydienol formation could not have exceeded 3% of the product.

Solvolysis of 4-methyl-4-nitrocyclohexa-2,5-dien-1-ol

The nitrodienol (100 mg, 0.65 mmol) was weighed into a chilled flask and aqueous methanol (1:1 v/v, 2 cm^3), at −10°C, and sodium bicarbonate (57 mg, 0.68 mmol) were added. The mixture was heated in an ultrasonic bath at 40°C for 20 min. Ether (50 cm^3) was added, the solution dried over Na_2SO_4 and then over $MgSO_4$, and the solvent evaporated to give an oil (51 mg) consisting of *p*-cresol (90%) and unidentified dienes (δ: 1.57 and 5.95 ppm, 10%). Solvolysis was also carried out on a 0.16-mmol scale in D_2O–CD_3OD (1:1) containing C_5D_5N (0.18 mmol) and the reaction monitored by ^{1}H nmr. Again *p*-cresol (90%) and unidentified dienes (10%) were obtained. The half-life of **10** was 50 min at −10°C and 10 min at 0°C. When the solvolysis was carried out in acetone–water (1:2 v/v) containing sodium bicarbonate, *p*-cresol (90%) and unidentified diene (10%) were formed.

Rates of solvolysis of (E)*-1*a *and* (E)*-1*b

The diene (0.3 mmol) was dissolved in CD_3OD (1 cm^3) at 0°C, and cold D_2O (1 cm^3) and C_5D_5N (27 mm^3, 0.33 mmol) were added. A sample of the solution was quickly transferred to a nmr tube and the FT ^{1}H nmr spectrum observed (50 scans per spectrum) at the desired temperature. The time taken for the integral of the aliphatic methyl region to decrease to half of the original intensity was determined from a first-order plot. For (*E*)-**1***a*, $t_{1/2} = 2.5$ min at 40°C and 75 min at 27°C. For (*E*)-**1***b*, $t_{1/2} = 5.5$ min at 40°C and 210 min at 27°C.

Reaction of (E)*-1,4-dimethylcyclohexa-2,5-diene-1,4-diol ((*E*)-3*bn*) with trifluoroacetic acid*

The dienediol (*E*)-**3***bn* (40 mg) was dissolved in trifluoroacetic acid (0.5 cm^3) at 0°C in an nmr tube. After 15 min at 0°C and 10 min at 38°C, ^{1}H nmr indicated that aromatization was complete and that the product was largely 2,4-dimethylphenol. The same result was obtained when the experiment was repeated using (*E*)-**3***bn* (50 mg) in trifluoroacetic acid (1 cm^3) and allowing the solution to stand at ambient temperature for 1.5 h. The product phenol was isolated by neutralization of the trifluoroacetic acid with sodium bicarbonate solution and extraction with ether. The ^{1}H nmr of the isolated products from the two reactions confirmed that 2,4-dimethylphenol was the predominant product. Each reaction product was treated with bistrimethylsilylacetamide and the resulting mixtures of trimethylsilyloxydimethylbenzenes analysed by glc: the product from each reaction was determined to be trimethylsilyloxy-2,4-dimethylbenzene (98%) and trimethylsilyloxy-2,5-dimethylbenzene (2%).

Reaction of (E)*-3*bn *with dilute acid*

(*E*)-**3***bn* was solvolysed at 50°C for 5 h and at ambient temperature for 72 h, in aqueous methanol at pH 3.2, as described for (*E*)-**1***b*. After work-up and ^{1}H nmr measurement, the ratio of dimethylphenols was determined by addition of bistrimethylsilylacetamide and analysis by glc: 2,4- (68%) and 2,5-dimethylphenol (32%) were the only products. In a second experiment, in which the mixture was heated for 21 h at 40°C, aromatization was not complete; ^{1}H nmr and glc–ms confirmed the presence of (*E*)-**3***co* (4%), (*Z*)-**3***co* (4%), (*E*)- and (*Z*)-**3***bo* (4%), **7***b* (55%), **6***n* (22.5%), and **6***o* plus **7***o* (10.5%). Solvolysis of (*E*)-**3***bn*, at ambient temperature for 26 h, was also carried out in aqueous dioxane at pH 3.2. Silylation and glc analysis gave the product distributions **7***b* (68.5%), **6***n* (31.5%) and **7***b* (64.4%), **6***n* (35.6%) in duplicate experiments.

Reaction of (Z)-3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene ((Z)-3co) with trifluoroacetic acid

The ether (*Z*)-**3***co* (31 mg) was dissolved in trifluoroacetic acid (0.5 cm^3) and the reaction was monitored by ^{1}H nmr over 1 h, after which time rearomatization was complete. The nmr spectrum showed that 2,4-dimethylanisole was formed.

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