Experimental Section

^1H NMR spectra were run on Varian Model A-60A, T-60, and FT-80 spectrometers. All chemical shifts are reported in ppm relative to internal tetramethylsilane. ^{13}C and ^{31}P NMR were run on a Varian Model FT-80 spectrometer equipped with a 10-mm, variable-temperature broad-band probe. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), $-\delta$ upfield. ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane (internal).

Preparation of 10. The procedure of Ramirez[2a] was followed. The ^{13}C NMR spectrum of **10** in hexane has a doublet at δ 134.16 (J_{POC} < 1 Hz, olefinic carbons), a doublet at δ 133.05 (J_{POCC} = 11.6 Hz, ipso carbons), a doublet at δ 42.05 (J_{PNC} = 4.3 Hz, carbons of methyl groups attached to nitrogen), two resonances at δ 128.12 and 126.50 (ortho and meta or meta and ortho), and a resonance at δ 126.91 which is due to the para carbon. In deuterated methylene chloride the resonances are found at δ 136.42 (J_{POC} < 1 Hz), 135.35 (J_{POCC} = 8.8 Hz), 40.03 (J_{PNC} = 2.0 Hz), 128.16 and 126.22 (ortho and meta or meta and ortho), and 126.46 (para).

Preparation of 16. The method of Burgada[2e] was followed and the material was purified by recrystallization from tetrahydrofuran. The ^1H, ^{13}C, and ^{31}P NMR spectral data are reported in the text. These spectra were all obtained in deuterated chloroform.

Preparation of 18. The procedure of Ramirez[2b] was followed. The ^{13}C NMR spectrum in deuterated methylene chloride has a doublet at δ 37.17 (J_{PNC} = 4.2 Hz), which is assigned to methyl group carbons bonded to nitrogen, aromatic resonances at δ 120.17, 121.36, 122.21, 124.94, and 125.56, a doublet at δ 132.81 (J_{POCC} = 1.3 Hz), and another doublet at δ 142.59 (J_{POC} = 3.6 Hz).

Preparation of 14. Under nitrogen 0.420 g (2 mmol) of benzil in 2 mL of deuterated methylene chloride was added slowly to a stirred solution of 0.398 g (2 mmol) of **13** in 2 mL of deuterated methylene chloride at 10 °C. After the addition, 5 min, the mixture was allowed to warm to room temperature. The ^1H NMR spectrum at 60 MHz has an absorption at δ 1.40–2.40, which is assigned to $PNCH_2CH_2$ hydrogens, another at δ 2.40–3.50, which is assigned to $PNCH_2CH_2$ hydrogens, and an absorption at δ 7.10–7.70 for aromatic hydrogens. The ratio of the areas was 3:6:5. The ^{31}P NMR spectrum had one absorption at δ −36.8. The ^{13}C NMR spectrum had a doublet at δ 24.77 (J_{PNCC} = 6.2 Hz); another doublet was found at δ 51.36 (J_{PNC} = 2.9 Hz). Two aromatic resonances were found at δ 126.39 and 128.27 (ortho and meta or meta and ortho) and another was found at δ 127.08 (para). The ipso carbons absorb at δ 131.56 (J_{POCC} = 10.8 Hz) and the olefinic carbons are found at δ 132.78.

Preparation of 21. To a stirred suspension of 0.416 g (2 mmol) of phenanthrenequinone in 2 mL of -benzene-d_6 was added 0.398 g (2 mmol) of **13** in 2 mL of benzene-d_6 under nitrogen at −10 °C. After the addition was completed a gray-green precipitate had formed. The reaction mixture was centrifuged and the supernatant liquid showed an absorption at δ −29.4.

Preparation of 20. The same procedure was used as for the preparation of **21** except deuterated chloroform was the solvent. The ^{31}P NMR resonance was found at δ −28.9. The ^{13}C NMR spectrum had a singlet at δ 24.92 ($PNCH_2CH_2$), a doublet at δ 39.95 (J_{PNCH_3} = 2.8 Hz), a doublet at δ 48.15 (J_{PNC} = 4.8 Hz), and a singlet at δ 50.75. The last two absorptions are assigned to carbons bonded to nitrogen. The olefinic carbons were found at δ 135.67 (J_{POC} = 0.8 Hz), and the carbons adjacent absorb at δ 122.77 (J_{POCC} = 10.7 Hz). Finally there were resonances at δ 120.20 (J = 0.6 Hz), 122.97, 123.30, and 125.60.

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Ipso Nitration. Solvolytic Behavior of 1,4-Dimethyl-4-nitrocyclohexadienyl Acetate and 1,4-Dimethyl-4-nitrocyclohexadienol

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Abstract: The solvolytic rearomatizations of the *E* and *Z* isomers of 1,4-dimethyl-4-nitrocyclohexadienyl acetate (**1**) have been examined in aqueous ethanol and in sulfuric acid solutions. Solvolysis of **1** in aqueous ethanol involves the elimination of nitrous acid and the migration of the acetoxyl group to yield 2,5-dimethylphenyl acetate. The kinetic behavior of this solvolytic reaction parallels that of the secondary adduct 4-nitro-3,4,5-trimethylcyclohexadienyl acetate (**2**). No kinetic isotope effects were detected when 1,4-dimethyl-4-nitrocyclohexadienyl-*2,3,5,6-d*$_4$ acetate (**1**-d_4) or 1,4-dimethyl-4-nitrocyclohexadienyl-*Me-d*$_6$ (**1**-d_6) were used as substrates. The collected data suggest a rate-limiting loss of nitrite ion from **1** followed by migration of the acetoxyl group and proton loss. The behavior of the *E* and *Z* isomers of 1,4-dimethyl-4-nitrocyclohexadienol (**3**) in aqueous ethanol differs from that of **1** in several ways. The major product of solvolysis is 2,4-dimethylphenol. The rates of solvolysis of the stereoisomers of **3** do not differ appreciably one from the other, and the spectral yield is only 30–40% of that anticipated. These differences are taken to reflect a rate-limiting migration in the solvolysis of **3** rather than a rate-limiting loss of nitrate ion. Solvolysis of **1** in greater than 77% sulfuric acid gives 1,4-dimethyl-2-nitrobenzene in quantitative yield. The yield of nitro aromatic falls off smoothly as the acid concentration is lowered toward 50%. Within the 70–50% acid range, the yield of side-chain substitution products appears to increase, hold roughly constant, and then decrease. Larger yields of nitro aromatic and smaller yields of side-chain substitution product are found when **1**-d_6 is used as a reactant. The solvolyses in strong acids are discussed in terms of re-formation of the ipso ion and subsequent partitioning.

This paper deals with the solvolytic rearomatization of 1,4-dimethyl-4-nitrocyclohexadienyl acetate (**1**).[1] Earlier we reported some studies of the solvolytic behavior of 4-nitro-3,4,5-trimethylcyclohexadienyl acetate (**2**), the ipso adduct formed by formal 1,4-addition of nitronium acetate to 1,2,3-trimethylbenzene.[2] We found that this secondary nitrocyclohexadienyl acetate lost the elements of nitrous acid in aqueous ethanol to give 5-acetoxy-1,2,3-trimethylbenzene and lost the elements of acetic acid in strong sulfuric acid solutions to give 4-nitro-1,2,3-trimethylbenzene. It seemed useful to compare the solvolytic be-

(1) Presented in part at the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977, ORGN 156.

(2) Banwell, T.; Morse, C. S.; Myhre, P. C.; Vollmar, A. *J. Am. Chem. Soc.* **1977**, *99*, 3042.

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havior of this secondary system with a tertiary system, and we selected the ipso adduct of *p*-xylene, 1,4-dimethyl-4-nitrocyclohexadienyl acetate (**1**), for study. During the course of this work, two other groups have reported on this particular system.[3,4] The studies reported here supplement published information by providing kinetic data on the solvolysis of **1** in aqueous systems and by providing additional product data and new isotope effect data for the acid solvolysis of **1** that aids delineation of mechanistic steps. In addition, the behavior of 1,4-dimethyl-4-nitrocyclohexadienol (**3**) in aqueous ethanol is compared with that of **1** and other secondary nitrocyclohexadienols.[5]

Results

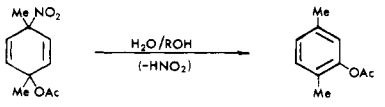
Conventional nitration of *p*-xylene with acetyl nitrate in acetic anhydride at low temperature gave a product mixture composed of 1,4-dimethyl-2-nitrobenzene, the configurational isomers of 1,4-dimethyl-4-nitrocyclohexadienyl acetate (**1**), side-chain substitution products, and 1,4-dimethyl-2,5-dinitrobenzene.[3] The nitrocyclohexadienyl acetates were separated from the other products by low-temperature chromatography over deactivated alumina with elution by pentane–ether, and they were purified by repeated fractional crystallization from pentane or pentane–ether. The predominant configurational isomer (**1a**) eluted from the column first and crystallized from pentane as well-formed needles, mp 51–52 °C. The second isomer (**1b**) crystallized from pentane–ether, mp 59–60 °C.

The configurational isomers of 1,4-dimethyl-4-nitrocyclohexadienol (**3**) were prepared by addition of methyllithium to 4-methyl-4-nitrocyclohexadienone followed by low-temperature chromatography and recrystallization. The dominant configurational isomer of **3** eluted first, mp 51–53 °C, with the minor isomer found in later fractions, mp 113–114 °C. The configuration of **1a** was correlated to the isomer of **3** with mp 113–114 °C (hereinafter referred to as **3a**) by acylation of **3a** with acetyl chloride in pyridine, and a similar correlation between **1b** and the isomer of **3** with mp 51–53 °C (hereinafter referred to as **3b**) was obtained. Isomer **3a** was also isolated from tailing fractions (ether elution) of the column used to separate the configurational isomers of **1**.

p-Xylene-*2,3,5,6-d*$_4$ was prepared by repeated exchange of *p*-xylene with trifluoroacetic acid-*d*. *p*-Xylene-*Me-d*$_6$ was prepared by repeated exchange of *p*-xylene with deuterium oxide in the presence of Raney nickel followed by subsequent back-exchange of the aromatic protons with sulfuric acid. These labeled compounds were converted to 1,4-dimethyl-4-nitrocyclohexadienyl-*2,3,5,6-d*$_4$ acetate (**1**-d_4) and 1,4-dimethyl-4-nitrocyclohexadienyl-*Me-d*$_6$ acetate (**1**-d_6) by nitration in acetic anhydride, subsequent isolation by chromatography, and recrystallization.

The crystalline adducts **1a** and **1b** were moderately stable. They could be left at room temperature for day-long periods without noticeable decomposition. Pyrolysis of **1a** and **1b** in the inlet (210 °C) of a gas chromatograph gave *p*-xylene as the major product (71% from **1a** and 89% from **1b**) plus 2,5-dimethylphenyl acetate and a number of minor products.

Adducts **1a** and **1b** underwent solvolytic elimination in aqueous ethanol to yield 2,5-dimethylphenyl acetate in greater than 99.5% yield, of products, eq 1. Analytical conditions were such that



(1)

less than 0.5% of 2,4-dimethylphenyl acetate would have been detected. None of this material was found. Rates of formation of 2,5-dimethylphenyl acetate from **1a** and **1b** could be followed by monitoring the UV absorption maxima of the product at 263 nm. Clean first-order rate plots were obtained from the purified adducts. Isomer **1a** was found to be more reactive under all conditions used. The kinetic data are collected in Table I.

Table I. Rates of Solvolysis of 1 and 3 in Aqueous Ethanol

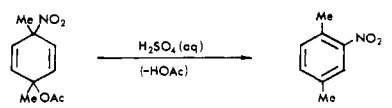
% EtOH	temp, °C	10^4k, s^{-1}	10^4k, s^{-1}
		1a	**3a**
38	15.0	9.88 ± 0.5	
38	30.0	56.9 ± 0.5	
38	45.0	224 ± 4	
47.5	15.0	3.87 ± 0.1	0.754 ± 0.09
47.5	30.0	23.2 ± 0.5	6.13 ± 0.11
47.5	45.0	109 ± 3	36.4 ± 0.9
66.5	15.0	0.69 ± 0.01	
66.5	30.0	4.73 ± 1.0	
66.5	45.0	26.6 ± 1.0	
76	45.0	11.4 ± 0.2	
		1a-d_4	
47.5	30.0	23.0 ± 0.2	
		1a-d_6	
47.5	25.0	12.0 ± 0.4	
		1b	**3b**
38	15.0	3.89 ± 0.05	
38	30.0	18.7 ± 0.2	
38	45.0	78 ± 1	
47.5	15.0	1.53 ± 0.05	0.92 ± 0.01
47.5	30.0	7.56 ± 0.2	8.36 ± 0.12
47.5	45.0	36.0 ± 2.0	46.5 ± 0.5
66.5	15.0	0.36 ± 0.02	
66.5	30.0	1.53 ± 0.03	
66.5	45.0	7.34 ± 0.10	
76	30.0	0.65 ± 0.02	
76	45.0	2.89 ± 0.05	

More limited kinetic studies of the solvolysis of **3a** and **3b** were conducted by following the growth of absorbance of 2,4-dimethylphenol and 2,5-dimethylphenol at 275 nm. It was necessary to work at very low substrate concentrations (ca. 5×10^{-4} M) and add urea (0.02 M) to obtain stable infinity values. Even under these conditions, however, the spectral yields of phenolic product were in the 30–40% range. It was found that acidification (pH 2) of the reaction mixture, after the initial reaction had ceased, resulted in a new and more rapid increase in absorbance at 275 nm. After this second burst, nearly the theoretical absorbance was reached. Kinetic data for the initial reaction, which are presumed to measure the rate of disappearance of **3**, are also collected in Table I.

The phenolic products of solvolysis of **3** appeared to consist of mainly 2,4-dimethylphenol, based on ^{1}H NMR examination. GLC analysis of silylated products of solvolysis also showed 2,4-dimethylphenol to be the major phenolic product.

The reactions of **1** in sulfuric acid solutions are too rapid to measure by conventional techniques. The yields of some of these products of reaction, particularly 1,4-dimethyl-2-nitrobenzene, were measured as a function of acidity. Stock solutions of **1a** together with an internal standard were prepared in chloroform or cyclohexane, and small portions were injected into vigorously stirred sulfuric acid solutions. Products were then extracted from the acid solutions after dilution with water, and the extracts were analyzed by GLC.

Solvolysis of **1a** in greater than 77% sulfuric acid gave 1,4-dimethyl-4-nitrobenzene in essentially quantitative yield, eq 2.



(2)

The yield of nitro aromatic decreases with decreasing acid concentration. Down to about 64% sulfuric acid, the falloff in yield of nitro aromatic is nearly balanced by the increase in yield of the side-chain substitution product, *p*-tolualdehyde. With continued decrease in the sulfuric acid concentration toward 50%, the yield of nitro aromatic continues to falloff, while the yield of *p*-tolualdehyde stabilized at about 22% over the 64–56% sulfuric

(3) Fischer, A.; Ramsay, J. N. *Can. J. Chem.* **1974**, *52*, 3960.
(4) Gibbs, H. W.; Moodie, R. B.; Schofield, K. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1145.
(5) Feldman, K. S.; McDermott, A.; Myhre, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 505.

Table II. Yields of 1,4-Dimethyl-2-nitrobenzene and *p*-Tolualdehyde from Reaction of **1a** and **1a**-d_6 in Sulfuric Acid Solutions at 25 °C

wt % of H_2SO_4	% from **1a**		% from **1a**-d_6		estd $(k_H/k_D)_{prod}$[b]
	ArCHO	$ArNO_2$	ArCDO	$ArNO_2$	
87		99		99	
77		100		100	
68	12	90	5	92	2.4
66	18	80	8	89	2.5
64	26	72	9	85	3.4
62[a]	22	60	8	76	3.5
60	22	48	9	63	3.2
58	21	38	10	49	2.7
56	21	28	11	37	2.5
54	14	13	6	17	3.0
				av $(k_H/k_D)_{obsd}$ = 3.0 ± 0.5[c]	

[a] A run containing a mixture of **1a** and **1a**-d_6 gave a 65% yield of $ArNO_2$ with a D:H ratio of 1.26. Compare with D:H of 1.27 from individual runs. [b] $(k_H/k_D)_{prod} = (ArCHO/ArNO_2)_{1a}/(ArCDO/ArNO_2)_{1a\text{-}d_6}$. [c] Not corrected for residual protium in sample.

acid range. A number of other products appear in the lower acidity region, but these could not be quantified. Among these products were dimethylphenols, *p*-methylbenzyl alcohol, and *p*-methylbenzyl acetate. Control experiments showed that these products were not extracted quantitatively by the procedures used.

Studies of the products of reaction of **1a**-d_6 in sulfuric acid solutions revealed that the same products formed but in differing distributions, particularly in the 54–66% acid range. In this region, the yields of nitro aromatic were higher, and the yields of *p*-tolualdehyde were lower for **1a**-d_6, implying an isotope effect on partitioning. Table II lists yield data collected from studies of the solvolysis of **1a** and **1a**-d_6 in sulfuric acid solutions, together with observed values for partitioning isotope effects.

Control experiments established that *p*-methylbenzyl alcohol is very rapidly oxidized to *p*-tolualdehyde by nitrogen (III) species in sulfuric acid solutions in the 60% range. Thus, an 8×10^{-3} *M* solution of *p*-methylbenzyl alcohol in 60% sulfuric acid was quantitatively transformed to *p*-tolualdehyde in less than 5 min by sodium nitrite (8×10^{-3} *M*).

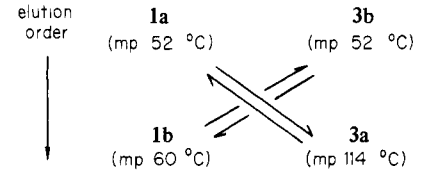
Discussion

Simple secondary ipso adducts such as **2** yield a rather limited set of solvolytic products: phenyl acetates, phenols, and nitro aromatics, the latter formed by a sequence of 1,2-shifts of the nitro group.[2] The products obtained upon solvolysis of **1** are more varied, particularly in the intermediate acidity region. This work focuses on the two regions of the solvent spectrum where the chemistry, as judged by the product complexity, is relatively simple. We shall consider the chemistry of **1** in aqueous ethanol, where kinetics can be followed, and in strong sulfuric acid solutions, where product distribution data are available. These results can be compared with those found in related studies of secondary systems such as **2**, and we shall interpolate from these end regions toward the more complex middle ground. It will also be useful to consider some of the differences in solvolytic behavior that arise when one changes from the nitrodienyl acetate **1** to the corresponding nitrodienol **3**.

Configurational Assignments. Fischer and Ramsey showed that partial transesterification of the isomeric 1,4-dimethyl-4-nitrocyclohexadienyl acetates with sodium methoxide in methanol gave specific 1,4-dimethyl-4-nitrocyclohexadienols.[3] We have been able to convert the configurational isomers of **3** to those of **1** by acylation with acetyl chloride in pyridine at reduced temperature and thereby verify the interrelationships deduced by Fischer and Ramsey. These combined results are summarized in Chart I.

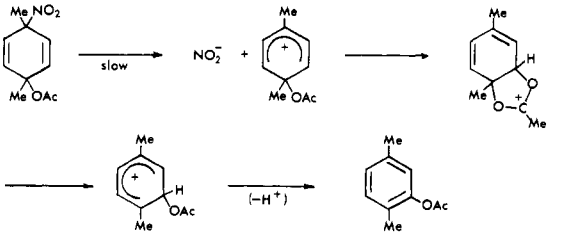
Attempts to assign configurations to the isomers of **1** and **3** with the use of shift reagents were not conclusive.[3] However, a number of pieces of circumstantial evidence led us to assign the *E* configuration to **1a**. Most of this evidence was anchored to the

Chart I



[a] NaOH/MeOH. [b] AcCl/pyridine.

Chart II



previous assignments of configuration to the isomers of 4-nitro-3,4,5-trimethylcyclohexadienyl acetate (**2**).[2] The relative yields of the isomers of **1** upon nitration of the parent hydrocarbon, the elution order of these isomers upon column chromatography, the relative melting points, and the relative rates of solvolysis in aqueous alcohol were all consistent with such an assignment. Confirmation of this assignment could also be derived from considerations of the expected stereoselectivity in the preparation of **3** from 4-methyl-4-nitrocyclohexadienone by reaction with methyllithium. The isomer **3b** was the major product of this reaction and **3b** should be the *Z* isomer, if the delivery of the methyl group to the carbonyl center occurs in such a way so as to minimize the interaction of the organometallic and the nitro group.

Definitive evidence that **1a** and **3a** are *E* isomers and that **1b** and **3b** are *Z* isomers is now available from X-ray diffraction studies of **3a** and **1b**.[6]

Solvolysis in Aqueous Ethanol. In aqueous ethanol, both configurational isomers of **1** give 2,5-dimethylphenyl acetate in greater than 99% yield, eq 1. The rates of this solvolytic elimination of the elements of nitrous acid and rearrangement of the acetoxyl group are dependent on the "ionizing power" of the solvent. Grunwald–Winstein *m* values that average 0.70 ± 0.04 for **1a** and **1b** at 15, 30, and 45 °C have been obtained from the data listed in Table I. Extrapolation of these kinetic data to pure water indicates a half-life of 18 s for **1a** and a half-life of 57 s for **1b** at 30 °C. No primary isotope effect was detected when rates of solvolysis of **1a**-d_4 were measured in 47.5% ethanol, nor were any isotope effects noted upon solvolysis of **1a**-d_6.

The solvolytic behavior of **1** in aqueous ethanol parallels that of **2**. The latter reaction was assigned an E1 pathway with rate-limiting loss of nitrite anion followed by rapid proton loss.[2] There is, however, a clear difference in the chemistry of **1** and that of **2** in these solvents, since formation of 2,5-dimethylphenyl acetate from the intermediate 1-acetoxy-1,4-dimethylcyclohexadienyl cation involves more than a simple proton loss. An additional step, the migration of the acetoxyl group, must also occur. The intramolecular character of this migration has been demonstrated,[3] and Fischer's results from study of the products of solvolysis of ipso adducts of *p*-ethyltoluene in aqueous methanol imply that the migration of the acetoxyl group involves a formal 1,2-shift.[7]

(6) In a private communication, Professor A. Fischer reported that Professor F. Einstein (Simon Fraser University) has verified the *E* configurations assigned to the nitrodienol (**3a**, mp 114 °C) by an X-ray structure determination. More recently, Professor W. Sly (Harvey Mudd College) has confirmed the *Z* configurational assignment to the nitrodienyl acetate (**1b**, mp 60 °C) by low-temperature X-ray methods.

(7) Fischer, A.; Henderson, G. N.; Thompson, R. J. *Aust. J. Chem.* **1978**, *31*, 1241.

Table III. Activation Parameters for Solvolysis of 1 and 3 in Aqueous Ethanol

% ethanol	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
	1a		1b	
38	18.2	−8.9	17.5	−13.5
47.5	19.5 ± 0.5	−6.6 ± 1.6	18.4 ± 0.6	−12.1 ± 2
66.5	21.5 ± 0.7	−3.2 ± 2.5	18.9 ± 1.7	−18 ± 6
	3a		3b	
47.5	22.8 ± 0.2	1.7 ± 1	23.0 ± 0.4	4.5 ± 1.4
	2a		2b	
47.5[a]	20.1 ± 0.5	−3.1 ± 1.8	18.8 ± 0.5	−10.3 ± 1.8

[a] Reference 2.

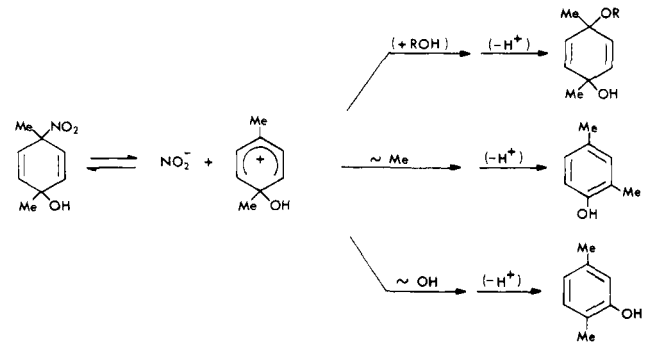
The accumulated data on the solvolysis of **1** in aqueous ethanol seem consistent with the path shown in Chart II, where the rate-limiting step is the heterolytic cleavage of the carbon–nitrogen bond and the subsequent steps involving migration of the acetoxyl group and proton loss are fast. The very close parallelism between the activation parameters for the configurational isomers of **1** and the configurational isomers of **2** (see Table III) prompted us to tentatively assign the *Z* configuration to **1a** and the *E* configuration to **1b**. It is to be noted that both **1a** and **2a** have lower free energies of activation at 25 °C than the corresponding isomers, but in both cases this is due to the counterbalancing of slightly greater enthalpies of activation by less negative entropies of activation.

Two important points implicit in the scheme shown in Chart II are not addressed by the data. The first concerns verification that solvolysis of **1** involves a 1,2-shift of the acetoxyl group. The data of Fischer on the solvolysis of adducts of *p*-ethyltoluene seem to be strong confirmation for this view, but the data of Moodie and Schofield on solvolysis of the adducts of pseudocumene indicate that some 1,3-migration of the acetoxyl group occurs in dilute aqueous acid.[4,7] We note that **1** may be prepared with either the 1-methyl or the 4-methyl group specifically labeled by a sequence involving nitration of *p*-tolyl acetate, addition to methyllithium to the resulting 4-methyl-4-nitrocyclohexadienone, and acylation of the nitrodienol. Work on the preparation of suitably labeled derivatives of **1** is in progress, and they will be used for the purpose outlined. The second point concerns the bridged intermediate in the pathway shown in Chart I that involves the bonding of the carbonyl oxygen of the acetoxyl group to the adjacent ring carbon atom. There is abundant evidence for this type of bridged intermediate, but this crucial feature should be verified by suitable oxygen-18 studies.

The low spectral yields in the solvolytic rearomatization of the configurational isomers of the nitrodienol **3** are taken as an indication of trapping of the intermediate as nonaromatic products. Clear verification has been provided by recent work in Fischer's laboratory where the solvolysis of **3a** in 50% methanol was found to yield about 30% 2,4-dimethylphenol, 50% 1,4-dimethylcyclohexadiene-1,4-diol (**4**), the monomethyl ether of **4**, plus smaller amounts of 2,5-dimethylphenol, dimethylanisole, and 1,4-dimethyl-2-nitrobenzene.[8] This result demonstrates capture of the intermediate 1,4-dimethyl-1-hydroxycyclohexadienyl cation by solvent as well as other nucleophiles in the system. Further, this result is consistent with the report of Bruice that solvolytic ring opening of 1,4-dimethylbenzene oxide under weakly acidic conditins gives appreciable quantities of dienediol **4**.[9] We found that acidification of kinetic solutions of **3** that had reached a stable infinite-time absorbance causes a renewed growth of the band attributed to 2,4-dimethylphenol. This can be explained as the consequence of the acid-catalyzed aromatization of the solvolysis product **4** or the monomethyl ether of **4**, a reaction previously noted and studied by Bruice.[9]

(8) Fischer, A. Henderson, G. N.; Smyth, T. A., in press.
(9) Kaspereck, G. J.; Bruice, T. C.; Yagi, H.; Kaubisch, N.; Jerina, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 7876.

Chart III



It is also important to note that the observed rates of rearomatization of **3** under uncatalyzed conditions are slower by a factor of about 20 than one might predict on the basis of solvolysis data for 4-methyl-4-nitrocyclohexadienol, a secondary nitrodienol that yields a structurally similar cyclohexadienyl cation intermediate.[5] Further, there appears to be little difference between the observed rates of aromatization of **3a** and **3b**. Both **3a** and **3b** show small positive entropies of activation while all other nitrodienols and nitrodienyl acetates that have been studied show negative entropies of activation of approximately −10 cal deg^{-1} mol^{-1}.[2,5]

The combined data suggest a possible scheme. This scheme, outlined in Chart III, is an elaboration of the scheme shown in Chart II in which one now requires return from an ion pair intermediate to be more rapid than capture or rearrangement. Additionally, one must require capture to be somewhat faster than rearrangement. Finally, the results suggest that, while the acetoxyl group migrates in preference to a methyl group, the methyl group migrates in preference to a hydroxyl group.

It is this last consideration that is crucial. Assume for simplcity that the rates of return, external capture, and methyl migration are the same in solvolysis of the tertiary nitrodienyl acetate **1** and the tertiary nitrodienol **3**. A very facile migration of the acetoxyl group in the intermediate formed from **1** would prevent significant formation of capture products and would render return a process of minimal importance. However, the barrier to migration of the methyl group in the intermediate formed from **3** must be at least 3 kcal mol^{-1}.[10] Such a barrier to migration should be sufficient to render the competitive return and capture processes effective. A scheme such as that shown in Chart III is subject to considerably more detailed scrutiny, but further discussion will be postponed until more data are available.

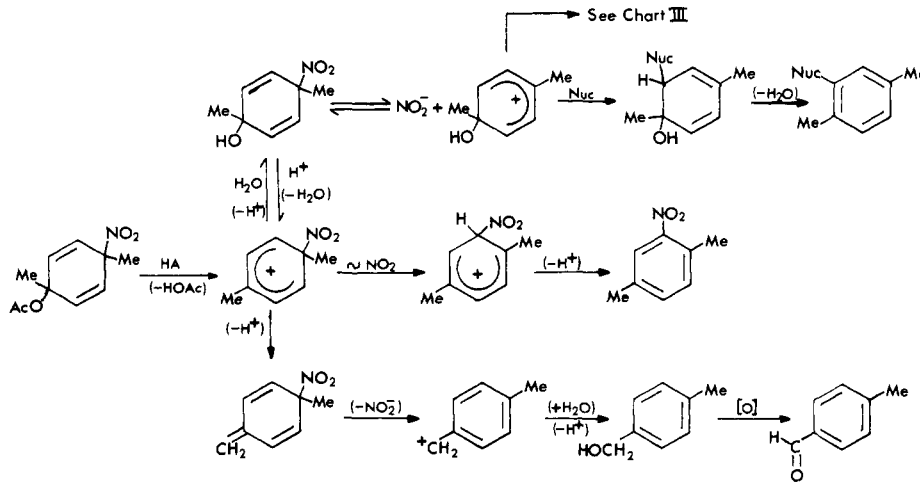
The seemingly subtle change from a tertiary nitrodienyl acetate to a nitrodienol results in rather remarkable changes in the solvolytic behavior in neutral aqueous systems. These changes can be traced to the migratory aptitudes of the acetoxyl, methyl, and hydroxyl groups.

Solvolysis of 1 in Sulfuric Acid. As in the case with other nitrodienyl acetates, the solvolytic rearomatization of **1** in strong acid takes a different course. The acetoxyl group leaves, presumably as acetic acid, to yield the 1,4-dimethyl-1-nitrocyclohexadienyl cation **5**. This ipso ion **5** can react by several paths including a 1,2-shift of the nitro group, leading to 1,4-dimethyl-2-nitrobenzene, a reaction with water in the solvent to yield the nitrodienol **3**, and loss of a proton from the methyl group to form a methylenecyclohexadiene derivative **6**.[2-4] The intermediate **6** can be envisioned as the precursor of a benzyl cation which would give side-chain substitution products by reaction with nucleophiles in the solvent.[11] These pathways are summarized in Chart IV.

The yield data for formation of 1,4-dimethyl-2-nitrobenzene as a function of acidity, Table II, are in accord with those reported by Moodie and Schofield.[4] *p*-Tolualdehyde proved to be the major

(10) This estimate is a minimum value based on our failure to detect any 2,4-dimethylphenyl acetate (with detection limits at <0.5 mol %) in the solvolysis of either **1a** or **1b**.
(11) Suzuki, H.; Mishina, T.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 191.

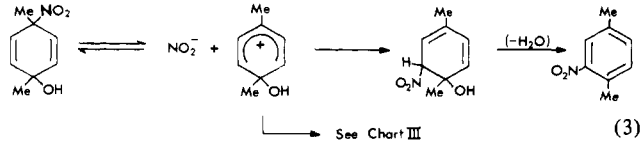
Chart IV



isolable side-chain substitution product under our reaction conditions. It is noteworthy that upon use of **1**-d_6 in place of **1**, the yield of nitro aromatic increased and the yield of *p*-tolualdehyde decreased, but the sum of nitro aromatic and *p*-tolualdehyde remained essentially constant for both **1** and **1**-d_6. Further, mass spectral examination of the 1,4-dimethyl-2-nitrobenzene derived from **1**-d_6 in 62% sulfuric acid showed no loss of deuterium from the methyl groups. Finally, the dimethylphenol product (detected as the nitrophenol derivative) formed from solvolysis of **1** or **1**-d_6 in 40% sulfuric acid was identified as 2,4-dimethylphenol.

The results, which include the constancy of the sum of nitro aromatic and aldehyde products from solvolysis of **1** and **1**-d_6, the existence of a partition isotope effect, and the absence of hydrogen exchange at methyl carbon, provide rather clear evidence for the irreversible partitioning of the ipso ion **5** along two of its several reaction paths (see Chart IV). One of these paths leads to the nitro aromatic. The other of these paths involves irreversible proton loss from the methyl carbon and leads eventually to side-chain substitution products. The dominance of *p*-tolualdehyde rather than more simple side-chain substitution products such as *p*-methylbenzyl alcohol is explicable in terms of the very rapid oxidation of benzyl alcohols by nitrogen(III) species at the concentration levels used in our experiments. The rate and efficiency of this oxidation has been verified by control experiments and more recently by detailed studies of Ross.[12]

At sulfuric acid strengths below about 50%, the product situation becomes quite complex. As indicated in Chart IV, the region of moderate acidity is one in which both **1** and **3** would be expected to function as reactants, and the products should reflect the mixed chemistry of the nitrodienyl acetate and the nitrodienol. A detailed discussion of this region has been provided by Moodie and Schofield based on their studies of the solvolysis of **1a** in a wide range of sulfuric acid solutions.[4] We note that the 1,4-dimethyl-2-nitrobenzene product that persists in about 4% yield for 40–10% sulfuric acid may be formed in this low-acid region by nucleophilic capture as shown in eq 3 and not by a nitro group



(3)

migration involving **5**. The evidence provided by Fischer for such capture is strong. This additional route to nitro aromatics via cyclohexadienyl cations invites synthetic exploitation.

Experimental Section

Instrumentation. All melting points were observed in capillary tubes on a Mel-Temp apparatus and are corrected. Routine ^{1}H NMR spectra were recorded on a Varian A-60 or a Varian 360L spectrometer. Infrared spectra were recorded on a Perkin-Elmer Infracord. Kinetic studies were conducted with the use of a Varian-Cary 16K spectrometer. GLC analyses were performed on a Varian 1200 instrument equipped with a flame ionization detector, disc integrator, and printer. Mass spectral data were obtained with the use of a Hitachi Perkin-Elmer RMU-6D instrument and a Finnigan 3200 gas chromatograph/mass spectrometer.

Reference Substances. 2,5-Dimethylphenol, 2,4-dimethylphenol, and *p*-tolualdehyde were obtained from Aldrich Chemical Co. 1,4-Dimethyl-2-nitrobenzene (bp 93–94 °C (3 torr)) was prepared by the method of Brand and Mahr.[13] *p*-Methylbenzyl bromide (bp 92 °C (12 torr)) was prepared from *p*-xylene by reaction with *N*-bromosuccinimide in carbon tetrachloride and treated with sodium acetate in acetic acid to yield *p*-methylbenzyl acetate (bp 102–103 °C (10 torr)). Saponification of the acetate gave *p*-methylbenzyl alcohol (mp 58–59 °C). 2,5-Dimethylphenyl acetate (bp 97 °C (10 torr)) and 2,4-dimethylphenyl acetate (bp 98 °C (10 torr)) were prepared from the corresponding phenols by reaction with acetic anhydride in pyridine. Structures of reference substances were verified by ^{1}H NMR and infrared analysis, and purities were determined by GLC on several columns.

1,4-Dimethyl-4-nitrocyclohexadienyl Acetates (1). The acetyl nitrate adducts of *p*-xylene were prepared by following methods described by Fischer.[3] The crude product which contained adducts, side-chain substitution products, aromatic nitration products, and unconverted hydrocarbon was separated by column chromatography at 0 °C over Bio-Rad AG-7 alumina that had been deactivated by addition of 33 g of 10 wt % aqueous acetic acid to 1 lb of activity grade I alumina. Thus, a 5.68-g sample of crude nitration product that contained about 20 mol % dienes and 60 mol % *p*-xylene was applied to a column of 400 g of alumina. Elution was begun with 450 mL of pentane (300-mL void volume) and followed with 150-mL portions to which stepwise increments of 10% ether were added. The eluent was collected in 15-mL portions with the use of a Gilson fraction collector. Isomer **1a** was isolated from fractions 58–64, and repeated recrystallization from pentane afforded 0.349 g of well-formed colorless needles, mp 51–52 °C (lit.[3] mp 47–49), with an additional crop (0.256, mp 51–52 °C) recovered from the mother liquors: NMR ($DCCl_3$) δ 1.46 (s, 3 H, 1-Me), 1.82 (s, 3 H, 4-Me), 1.94 (s, 3 H, OAc), 6.00 (s, 4 H, vinyl); IR (KBr) 1740, 1530, 1250, 1071, 808 cm^{-1}. Isomer **1b** was isolated from fractions 68–76 and purified by repeated crystallization from pentane–ether to yield 438 mg of colorless needles: mp 59–60 °C (lit.[3] mp 58–59 °C); NMR ($DCCl_3$) δ 1.46 (s, 3 H, 1-Me), 1.67 (s, 3 H, 4-Me), 1.93 (s, 3 H, OAc), 6.18 (s, 4 H, vinyl); IR (KBr) 1725, 1550, 1225, 815 cm^{-1}.

Acetyl Nitrate Adducts of *p*-Xylene-2,3,5,6-d_4 (1-d_4) and *p*-Xylene-Me-d_6 (1-d_6). The aromatic hydrogens of *p*-xylene were replaced with deuterium by repeated exchange in refluxing trifluoroacetic acid-*d*. Approximately 24 h was required for each equilibration. Four exchanges gave product with greater than 95% deuteration at aromatic carbon. The hydrogen at the methyl carbons of another sample of *p*-xylene was replaced with deuterium by repeated exchange in the presence of deuterium oxide and Raney nickel that had been prepared from the alloy by reaction with sodium deuterioxide in deuterium oxide.[14] The final product from these equilibrations was then repeatedly exchanged in 73% sulfuric acid

(12) Ross, D. S.; Hum, G. P. 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, ORGN 168.

(13) Brand, K.; Mahr, J. *J. Prakt. Chem.* **1935**, *142*, 153.

(14) Hirota, K.; Neda, T. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 228.

to remove deuterium from the aromatic carbons. The resulting product analyzed for 96% deuterium at the methyl carbons (78% d_6, 20% d_5, 2% d_4). These labeled samples of *p*-xylene were converted to the acetyl nitrate adducts **1**-d_4 and **1**-d_6 by the method described, and configurational isomers were separated by column chromatography.

1,4-Dimethyl-4-nitrocyclohexadienol (3). The preparation and chromatographic separation of the configurational isomers of **3** by reaction of 4-methyl-4-nitrocyclohexadienone with methyllithium and subsequent column chromatography has been described.[15] The first eluting isomer of **3**, mp 52 °C, was converted to **1b** by treatment of a stirred pyridine solution of the nitrodienol with a methylene chloride solution of acetyl chloride at −40 °C and a 2-day reaction period at −10 °C. The second eluting isomer of **3**, mp 114 °C, was converted to **1a** by the same procedure.

Pyrolysis of 1,4-Dimethyl-4-nitrocyclohexadienyl Acetates. Stock solutions containing carefully weighed amounts of the nitrodienyl acetate **1a** (mp 51–52 °C) and **1b** (mp 59–60 °C) and an internal standard, 1,2-dimethyl-4-nitrobenzene, were prepared in cyclohexane at a concentration of about 30 mg mL^{-1}. Portions of these solutions were injected into the gas chromatograph with an inlet temperature of 210 ± 5 °C and a Silar 10-C column (10 ft × 0.125 in.) which was held at 50 °C for 10 min and programmed thereafter at 20 °C min^{-1} to a maximum temperature of 150 °C. Under these conditions *p*-xylene had a retention time of 6.8 min, and the internal standard had a retention time of 26.7 min. A large number of minor product peaks were detected, but only the yield of *p*-xylene was quantified. Under these pyrolytic conditions **1a** gave 71 ± 4% *p*-xylene and **1b** gave 89 ± 3% of the same hydrocarbon.

Kinetics of Solvolytic Elimination in Aqueous Ethanol. Rates of solvolytic rearomatization of the nitrodienyl acetates were followed by monitoring the UV absorption maxima of 2,5-dimethylphenyl acetate (262 nm). The typical procedure involved weighing about 3 mg of one of the adducts in a capillary tube, dissolving the sample in absolute ethanol (40 μL), and injecting 2–5 μL of the stock solution into a series of temperature-equilibrated cells containing 3–4 mL of the appropriate solvent. Plots of log ($A_\infty - A_t$) vs. time were generally linear over 80–90% of reaction. Final values of rate constants were obtained by least-squares treatment of data. Rate constant data and kinetic isotope effects are collected in Table I. Activation parameters are tabulated in Table III. Product analyses of kinetic reaction solutions conducted after more than 9 half-lives revealed only 2,5-dimethylphenyl acetate. The conditions of GLC analysis were such that less than 0.5 mol % of 2,4-dimethylphenyl acetate or *p*-methylbenzyl acetate would have been detected.

Kinetics of solvolytic rearomatization of **3** in aqueous ethanol were followed in a similar way by monitoring the growth of the absorption maxima at 275 nm. It was necessary to use quite dilute solutions (~1 × 10^{-4} M) and add 0.02 M urea to the solvent in order to obtain stable infinity values. The spectral yield of phenolic product, however, was found to be 30–40% of the calculated value. It was found, however, that acidification of the system after a stable infinity value had been reached led to a new burst of absorption at 275 nm with an absorbance that stabilized near the calculated value. Silylation of the product mixture from a kinetic run conducted without acidification of the reaction mixture and subsequent GLC analysis revealed silylated 2,4-dimethylphenol and 2,5-dimethylphenol, but the significance of this finding is doubtful since capture product, such as 1,4-dimethylcyclohexadiene-1,4-diol, would certainly aromatize under the GLC conditions. NMR spectral studies of the products of aqueous solvolysis indicated that the 2,4-isomer predominated. The kinetic data obtained from the uncatalyzed formation of dimethylphenol are listed in Table I, and activation parameters derived from these data are listed in Table III. These data are taken to represent the rate of decomposition of **3** in the reaction system.

Solvolysis of 1 and 1-d_6 in Sulfuric Acid Solutions. Stock solutions were prepared by dissolving carefully weighed samples of the adduct together with an internal standard (*p*-nitrotoluene or 4-nitro-*o*-xylene) in chloroform. The ^{1}H NMR spectrum of the stock solution was recorded and integrated as a check on the composition. Approximately 30-μL portions of the stock solution were added to 2.0-mL portions of acid solutions contained in vials fitted with screw caps and Teflon liners, and the mixture was vigorously mixed for a 1-h period with the use of a Vortex mixing apparatus. The mixtures were quenched in ice and water, and organic products were partitioned into cyclohexane by repeated extraction. The dried cyclohexane extract was analyzed by GLC with the use of a HiEff-8BP or a Silar 10-C column.

Acknowledgment. We thank the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants supporting this work.

(15) Barnes, C. E.; Feldman, K. S.; Johnson, M. W.; Lee, H. W. H.; Myhre, P. C. *J. Org. Chem.* **1979**, *44*, 3925.

Protonation of Polymethylnaphthalenes and Hexahydropyrene. Formation of Stable Naphthalenium Ions and Observation of Isomerizations Based on ^{1}H and ^{13}C Nuclear Magnetic Resonance Studies[1]

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Abstract: Some tri- and tetramethylnaphthalenes and hexahydropyrene have been protonated with FSO_3H–SbF_5 (1:1) and/or FSO_3H in SO_2ClF, and the results have been classified in terms of distinct equilibria, isomerization processes, and the formation of selected stable naphthalenium ions, as determined by ^{1}H and ^{13}C NMR spectroscopy. The formation of stable "free" α-, ipso α-, and "free" β-naphthalenium ions and a β,β-naphthalenium dication are reported and the electronic features of the ions discussed on the basis of the ^{13}C NMR data. Both 1,4,5-tri- and 1,4,5,8-tetramethylnaphthalene are subject to kinetic vs. thermodynamically controlled protonation and 1,2-methyl migration occurs in the ions upon temperature changes. For the temperature-dependent protonation of 1,4,6,7-tetramethylnaphthalene a dynamic proton exchange and isomerization cycle is proposed.

Previously the protonation of dimethylnaphthalenes was reported[2] as an extension on the large body of research on the protonated alkylbenzenes.[3] Here we wish to go into detail on some special features of some polymethylnaphthalenium ions.

Naphthalene[4,5] and its mono-[4,5] and dimethylderivatives[2,4] are known to be protonated at an unsubstituted ("free") α-position.

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(1) Carbenium Ions. 5. As previous parts in this series are regarded: Part 1, see ref 2. Part 2, see ref 17. Part 3, Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257. Part 4, Lammertsma, K.; Cerfontain, H. *Ibid.* **1980**, *102*, 4528.

(2) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1979**, *101*, 3618.

0002-7863/81/1503-2062$01.25/0