(7) $Os(CO)_2(PPh_3)_2$ has not been isolated as such, but solutions of $Os(CO)_2(PPh_3)_3$[10] must be in equilibrium with small amounts of $Os(CO)_2(PPh_3)_2$[8] just as $RhCl(PPh_3)_3$ is in equilibrium with small amounts of $RhCl(PPh_3)_2$ and $Pt(PPh_3)_3$ with $Pt(PPh_3)_2$.[9]

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(13) Crystal data and refinement results: $[Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O]$; triclinic; $a = 18.739\ (2)$, $b = 11.157\ (1)$, $c = 9.986\ (1)$ Å; $\alpha = 116.70\ (1)$, $\beta = 93.20\ (1)$, $\gamma = 107.93\ (1)°$; space group $P\bar{1}$; $Z = 2$. Intensity data were collected on a four-circle diffractometer and the structure was solved by conventional methods. Least-squares refinement, with anisotropic thermal parameters assigned to the atoms of the coordination sphere, has given $R = 0.048$ for 3508 observed reflections. The water molecules of crystallization exist as hydrogen-bonded dimers (O --- O, 2.58 Å) with a space-filling role only, the nearest contact being 3.55 Å to a carbon atom of a phenyl ring.

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(15) Experimental conditions for the reactions depicted in Scheme I are as follows: (a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ suspended in CH_2Cl_2 reacts with HCl(g) (bubbled through the solution for 20 min) to give $Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$, which is isolated using *n*-hexane; (b) $Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$ heated under reflux in CH_2Cl_2–MeOH (1:1) for 30 min yields $Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$; (c) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ suspended in dry benzene reacts with methyl trifluoromethylsulfonate (1.3 equiv) to give $[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]CF_3SO_3$ which crystallizes upon the addition of *n*-hexane; (d) $[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]^+$ reacts rapidly with lithium chloride in ethanol to produce $Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$.

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Ipso Nitration. Preparation of 4-Methyl-4-nitrocyclohexadienols and Detection of Intramolecular Hydrogen Migration (NIH Shift) upon Solvolytic Rearomatization

Sir:

4-Alkyl-4-nitrocyclohexadienols are formally the 1,4 adducts of nitric acid and the parent alkylbenzene. Evidence of formation of these ipso nitration products during nitration in aqueous systems is convincing, although none of these intermediates have been isolated from direct nitration.[1,2] In contrast, the acetate derivatives of these nitrodienols have been repeatedly isolated from nitrations in acetic anhydride.[3] We have found that several 4-methyl-4-nitrocyclohexadienols may be readily prepared by reduction of the corresponding 4-methyl-4-nitrocyclohexadienones, and we report here studies of the solvolytic behavior that illustrate some interesting differences in the reactivity of nitrodienols and their acetate derivatives.[2]

The nitrodienols (**1**, **2**, and **3**) were prepared by reduction of the corresponding nitrodienones with sodium borohydride in methanol at −10 °C (Scheme I). Reduction with sodium borodeuteride gave the nitrodienols with deuterium at C-1, and reduction of 3,4-dimethyl-4-nitrocyclohexadienone-*2,6-d*$_2$ with borohydride afforded dienol **2** with deuterium at C-2 and C-6.[4] In all cases the reduction was stereoselective with the cis isomer dominant.[5] The product nitrodienols were isolated as pale yellow oils or low-melting solids by careful low-temperature extraction. Characterization was accomplished by low temperature ^1H NMR. Undiluted preparations decompose readily at room temperature to yield the corresponding phenol and nitrophenols; the latter products are presumably formed by nitrosation and subsequent oxidation. The more stable nitrodienyl acetates were prepared from the nitrodienols by acylation with acetyl chloride and pyridine at −40 °C.[6]

Scheme I

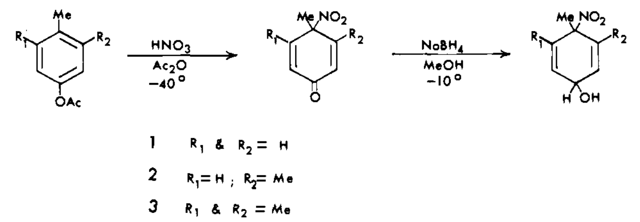
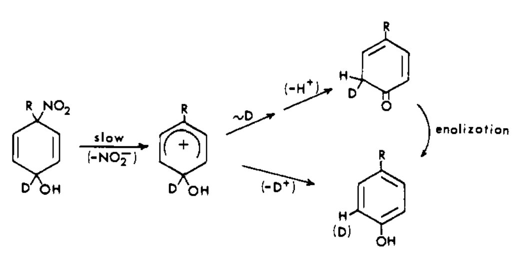


Table I. Kinetic Parameters for Solvolysis of Some *cis*-4-Methyl-4-nitrocyclohexadienols and *cis*-4-Methyl-4-nitrocyclohexadienyl Acetates in Aqueous Ethanol[a]

compd	10^4k, s^{-1} [b]	$\Delta H^{\ddagger}$, kcal mol^{-1} [c]	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1} [c]	k_H/k_D[b]	**m**[d]
1-OH	72.0	17.4 ± 0.4	−10.1 ± 1.4	1.3	0.56
1-OAc	2.60	19.3 ± 0.4	−10.3 ± 1.4	1.1	0.78
2-OH	179	16.9 ± 0.4	−10.0 ± 1.4	1.2	0.54
2-OAc	7.10	19.7 ± 0.8	−7.0 ± 2.8	1.1	0.83
3-OH	185	15.9 ± 0.4	−13.3 ± 1.4	1.2	0.63
3-OAc[e]	5.87	18.8 ± 0.5	−10.3 ± 1.8	1.2	0.64

[a] All runs were conducted at 47.5% ethanol containing 0.02 M urea except those used to determine the **m** parameter. [b] At 25.0 °C. [c] Activation parameters were determined in replicate runs that spanned a range of at least 40 °C. [d] Grunwald-Winstein **m** parameter. [e] Reference 2.

Solvolysis of the nitrodienols in aqueous ethanol containing urea gave the corresponding phenol as the only detectable product. Rates of formation of these phenols by solvolytic elimination of nitrous acid from **1**, **2**, or **3** were followed by previously described procedures.[2] Some kinetic parameters derived from the kinetic studies are summarized in Table I. Salient points include (1) an apparent 25-30-fold difference in rate between a given nitrodienol and the related nitrodienyl acetate; (2) structural effects and solvent effects that are not inconsistent with rate-limiting formation of a carbocation (eq 1); (3) modest kinetic isotope effects for all substrates that do not indicate major changes in force constants of the C–H bond in the rate-limiting step.



(1)

Product studies reveal an important difference in the paths of solvolytic elimination of nitrodienols and nitrodienyl acetates. Intramolecular hydrogen migration attends solvolytic elimination reactions of the nitrodienols but *not* the nitrodienyl acetates (Table II). The extent of hydrogen migration was measured by the retention of deuterium label in the phenolic product. As shown in Table II, the retention values for the nitrodienols were relatively insensitive to changes in pH or substrate structure. No change in deuterium retention was observed when **3**-OD was solvolyzed in EtOD/D_2O.

This type of hydrogen migration, the so-called NIH shift, has been repeatedly observed during liver microsome mediated

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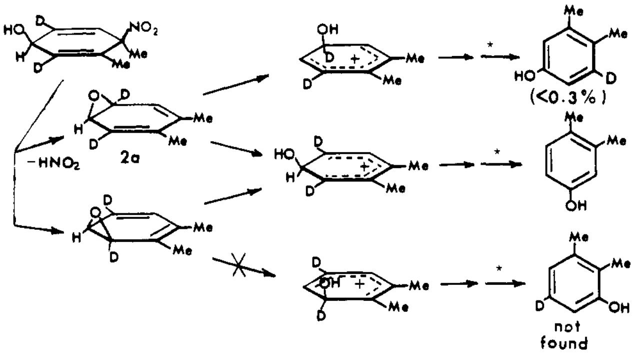
Table II. Deuterium Retention upon Solvolysis of 4-Methyl-4-nitrocyclohexadienol-*1*-*d*, 4-Methyl-4-nitrocyclohexadienyl-*1*-*d* Acetate, and Related Compounds

compd	solvent	% deuterium retention[a]
1-OH	50% EtOH, pH 2	24
	50% EtOH, pH 7	27
	50% EtOH, pH 10	28
2-OH	50% EtOH, pH 5	25
	50% EtOH, pH 7	25
	50% EtOH, pH 9	23
3-OH	50% EtOH	32
3-OD	50% EtOD	33
1-OAc	50% EtOH, pH 7	<0.2
2-OAc	50% EtOH, pH 7	<0.2
3-OAC	50% EtOH	<0.3

[a] Measured by replicate scans with use of a Finnigan 3200 GC/MS operated at an electron energy of 12 V. Measurement precision was ±1%.

Scheme II



a *, exchange.

oxidations of aromatic substrates and during solvolytic studies of appropriately labeled arene oxides.[7,8] Present interpretations of the solvolytic NIH shift of arene oxides involve a rate-limiting ring opening to yield the 1-hydroxycyclohexadienyl cation followed by an intramolecular hydrogen transfer and subsequent dienone-phenol rearrangement.[8]

Our results are not inconsistent with rate-limiting formation of the 1-hydroxycyclohexadienyl cation, but they do force consideration of a subsequent partitioning of the intermediate between two reaction paths (eq 1). The change of the hydroxyl group to an acetate apparently causes a pronounced shift in the partition ratio favoring direct proton loss to the solvent.

The possible formation of an arene oxide intermediate prior to an NIH shift has been *eliminated* by the experiment outlined in Scheme II. If 3,4-dimethylphenol were formed via the symmetrical arene oxide (**2a**) shown in Scheme II, the phenol would have to be partially deuterated at C-5. Since hydrogens acid, the experimental test is straightforward. Gas chromatographic analysis of the product of solvolysis of **2**-*2,6*-d_2 in aqueous ethanol revealed only 3,4-dimethylphenol, and mass spectral analysis of the phenol indicated <0.3% deuterium after acid-catalyzed exchange. Hence we must reject the path indicated in Scheme II.[10]

The data collected demonstrate the short lifetimes of nitrodienols that are formed by ipso nitration in aqueous acid. Even if re-formation of the ipso ion could be suppressed, the alternative path of aromatization (loss of the elements of nitrous acid) would make isolation impracticable.[2] Support for the view that 1-hydroxycyclohexadienyl cations are key intermediates in the NIH shift is provided. Consideration of $\sigma_p{}^+$ constants for the methyl (−0.31), hydroxyl (−0.92), and acetoxyl (−0.08)[9] suggests an explanation for the failure of the 1-acetoxycyclohexadienyl cation to aromatize via a NIH shift.

Reasonable extrapolations from the substituent constant data indicate that a 1,2 shift of hydrogen would be energetically "downhill" for the 1-hydroxycyclohexadienyl cation and "uphill" for the 1-acetoxycyclohexadienyl cation. The absence of a change in deuterium retention when **3**-OD is solvolyzed in EtOD/D_2O indicates that the proton transfer from oxygen occurs after the partition stage. With a flexible, convenient synthesis of substrates in hand, more detailed studies of these intramolecular migrations may now be projected.

Acknowledgment. We are pleased to acknowledge the helpful comments of Professors A. Fischer and K. Schofield, and we thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants supporting this work

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(10) Following a similar line, the results from **2**-OAc-*1-d* rule out bridging of the acetoxyl group during solvolytic eliminations.

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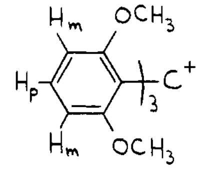
Electrophilic Aromatic Protonation of Stable π Carbocations

Sir:

We noted with interest the recent report[1] of a new type of electrophilic aromatic substitution: the reaction of H^+ and D^+ with an aromatic cyclopropenyl cation. This highly unusual reaction involves bringing together two positively charged species. We report here that the protonation of aromatic carbocations may be common and much more facile than anyone has imagined.

The NMR spectrum of the familiar trityl cation (**1**) in trifluoroacetic acid is identical with that reported by Martin[2] and is unexceptional. Quite remarkably, the spectrum in the much stronger triflic acid (CF_3SO_3H)[3] is dramatically different. The doublet at δ 6.75 observed in trifluoroacetic acid and assigned to H_m has completely disappeared and the triplet at 7.79, assigned to H_p, has collapsed to a singlet.[4] Clearly all six H_m sites are exchanging more rapidly than the spectrometer can detect. Because of the nature of the medium (low nucleophilicity and high acidity[3]) and the high pK_{R^+} associated with **1** (>6.5)[2] it follows that it is **1** which is reacting with H^+.



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Planar carbocations also undergo a similar exchange. In the lower ¹H NMR spectrum of Figure 1 is shown the aromatic region of carbocation **2a** in triflic acid.[5] No exchange phe-

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