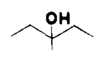
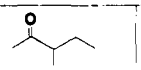
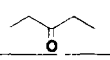
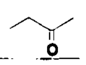
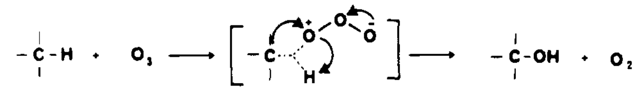
Table II. Product Distribution[a] from Ozonation of 3-Methylpentane at Various Temperatures

Temp. (°C)				
-45	32	15	20	33
-23	30	15	20	35
0	22	13	20	44
30	8	10	23	60

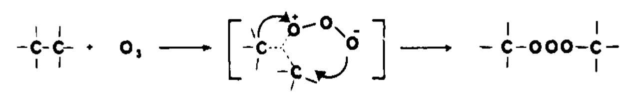
[a] In molar yield (percent), and based on detected products by VPC analysis.

Scheme I



A

Scheme II



B

However, when the ozonation temperature is raised above −20 °C, the respective amounts of the ketones originating from the cleavage of the more highly substituted alkyl groups increases mainly at the expense of the tertiary alcohols as shown by the products distribution in 3-methylpentane at various temperatures (Table II). This temperature dependence is even more pronounced in 2,3-dimethylbutane which at 25 °C gives 70% acetone and 1.5% 2,3-dimethylbutan-2-ol compared with 27% and 31% respectively at −45 °C (Table I, entry 1).

Thus it may be assumed that at higher temperatures the fragmentation of alkanes into ketones occurs mainly via tertiary alkoxy radicals generated in the initial cleavage of the tertiary C-H bonds by ozone.[8]

On the other hand, the product distribution at low temperatures indicates that the fragmentation of the C-C bonds cannot result solely from the attack of ozone on the tertiary C-H bonds.[9] Neither is the formation of the cleavage products by an attack on the primary or the secondary C-H bonds probable. Ozonation of the secondary C-H bonds leads to ketones which are stable under these experimental conditions. The reactivity toward ozone of the primary C-H bonds is comparatively low (the relative activity toward ozone of primary to secondary and tertiary hydrogens was estimated to be ~0.01:0.1:1[10]) and, if products are formed, they will be mainly the corresponding carboxylic acids and to a lesser degree the primary alcohols, but not C-C fragmentation products.

We therefore assume that an alternative mechanism involving a direct insertion of ozone into C-C bonds operates. This insertion leads to the highly reactive dialkyl trioxides which decompose to give the cleavage products.[11] The formation of acetone as a product of ozonation of 2,2,3-trimethylpentane (Table I, entry 8) may be explained by this mechanism. To gain additional evidence for the direct attack of ozone on the C-C bond, we have chosen to ozonize neopentane and have isolated 8% acetone as the only product.[12]

We have previously proposed that the mechanism of C-H bond ozonation involves the formation of an ozone-alkane complex[13] which decomposes electrophilically inserting an oxygen atom into the C-H bond. The transition state for this reaction may be represented by a dipolar structure A (Scheme I) containing a pentacoordinated carbon atom analogous to that proposed by Olah for ozonations of alkanes in superacids,[14] decomposing with the evolution of a molecule of oxygen. We assume that the reaction of the neutral ozone with the C-C bonds proceeds also by a mechanism similar to that considered by Olah for the analogous reaction of protonated ozone,[15] namely through a dipolar intermediate B (Scheme II), which collapses forming dialkyl trioxide.

References and Notes

(1) (a) Y. Mazur, *Pure Appl. Chem.*, **41**, 145 (1975); (b) Z. Cohen, E. Keinan, Y. Mazur, and T. H. Varkony, *J. Org. Chem.*, **40**, 2141 (1975); (c) E. Keinan and Y. Mazur, *Synthesis*, **8**, 523 (1976); (d) Z. Cohen, E. Keinan, Y. Mazur, and A. Ulman, *J. Org. Chem.*, **41**, 2651 (1976); (e) Z. Cohen, E. Keinan, Y. Mazur, and T. H. Varkony, *Org. Synth.*, in press.

(2) (a) E. Trifilieff, L. Bang, and G. Ourisson, *Tetrahedron Lett.*, 2991 (1977); (b) E. Trifilieff, L. Bang, A. S. Narula, and G. Ourisson, *J. Chem. Res. (M)*, 601 (1978).

(3) (a) A. L. J. Beckwith, C. L. Bodkin, and T. Duong, *Aust. J. Chem.*, **30**, 2177 (1977); *Chem. Lett.*, 425 (1977). (b) A. L. J. Beckwith and T. Duong, *J. Chem. Soc., Chem. Commun.*, 413 (1978).

(4) (a) This method is less favorable for the oxidation of secondary C-H bonds, except in special cases, such as in case of bonds in vicinal position to a cyclopropyl group.[4b] (b) E. Proksh and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **15**, 761 (1976); *Tetrahedron Lett.*, 4851 (1976).

(5) Reference 1b and unpublished results.

(6) When the ozonation was performed either in neat or in CCl_2F_2 solution, the conversions were much lower, but the products distribution was similar to that of dry silica. Thus, after 2-h ozonation of a solution of 3-methylpentane at −45 °C, the total yield was 6% products which consisted of methyl ethyl ketone, diethyl ketone, 3-methylpentan-2-one, and 3-hydroxy-3-methylpentane in a 2:1:2:5 ratio.

(7) As compared to the ozonation of olefins or amines which are very fast reacting under similar conditions.

(8) A free-radical mechanism was postulated for ozonation of hydrocarbons at temperatures of 10–40 °C: L. V. Ruban, S. K. Rakovski, and A. A. Popov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **9**, 1950 (1976).

(9) Ozonation of tertiary alcohols at −45 °C results in low conversion to a mixture of ketones, with a preponderance of the ones originating from the cleavage of the more substituted C-C bonds. This is exemplified by the formation of acetone and methyl propyl ketone in 9:1 ratio and 3% total yield from ozonation of 2-hydroxy-2-methylpentane.

(10) G. R. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.*, **No. 77**, 15 (1968).

(11) The formation of a trioxide was postulated previously by T. Preuss, E. Proksch, and A. de Meijere, *Tetrahedron Lett.*, 833 (1978), to explain the cleavage of the C-C bond in bicyclo[*n*.1.0]alkanes as well as by Beckwith et al.[3a] for the formation of ketones from 3,7-dimethyloctyl acetate and saturated derivative of cyclopentadiene trimer.

(12) The formation of acetone by a mechanism involving oxidation of the methyl group is unlikely. The ozonation of the corresponding primary alcohol, the neopentyl alcohol, under similar conditions gave as a major product pivalic acid and undetectable amounts of acetone.

(13) T. H. Varkony, S. Pass, and Y. Mazur, *J. Chem. Soc., Chem. Commun.*, 437 (1974).

(14) G. A. Olah, Y. Yoneda, and D. Parker, *J. Am. Chem. Soc.*, **98**, 5261 (1976).

(15) N. Yoneda and G. A. Olah, *J. Am. Chem. Soc.*, **99**, 3113 (1977).

Daniel Tal, Ehud Keinan, Yehuda Mazur*
Department of Organic Chemistry
The Weizmann Institute of Science, Rehovot, Israel

Received July 25, 1978

Organometallic Models for Possible Fischer-Tropsch Intermediates. Synthesis, Structure, and Reactions of a Formaldehyde Complex of Osmium

Sir:

The interrelationship between organometallic chemistry, surface chemistry, and heterogeneous catalysis has been discussed by several authors.[1] A recognized role for organometallic chemistry is to provide stable models for postulated surface species thus allowing structural studies to define precisely the geometrical features of the interaction between ligand (postulated as intermediate) and transition metal atom. For the Fischer-Tropsch reaction, various mechanisms have been considered[2] and in a recent review Henrici-Olivé and Olivé put forward[3] a plausible scheme which involves successive formation of formyl, formaldehyde, hydroxymethyl, carbene, and alkyl surface intermediates. Now that several transition metal formyl derivatives have been characterized,[4] each of these bound intermediates is firmly grounded upon

0002-7863/79/1501-0503$01.00/0

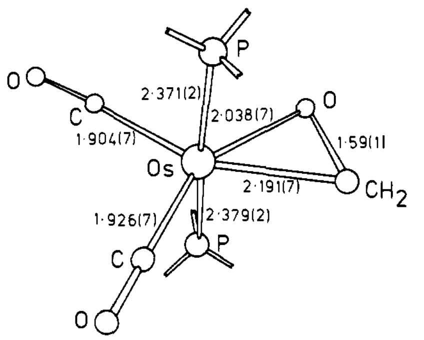


Figure 1. The inner coordination sphere of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$.

Table I. IR Data[a] for Osmium Complexes[b]

compd	$\nu(CO)$
$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$	1977, 1902
$Os(CHO)H(CO)_2(PPh_3)_2$	2023, 1972
$[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]CF_3SO_3$	2045,1967
$Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$	2028, 2018, 1952, 1935
$Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$	2042, 2032, 2020, 1972, 1959 1943[c]

[a] In reciprocal centimeters. Measured as Nujol mulls. [b] All compounds have satisfactory elemental analyses. [c] Solid-state splitting. A solution spectrum (CH_2Cl_2) has ν(CO) 2035 and 1960 cm^{-1}.

established organometallic precedents—with the notable exception of coordinated formaldehyde.[5] In this paper we describe a crystalline osmium complex in which formaldehyde functions as a dihapto ligand.

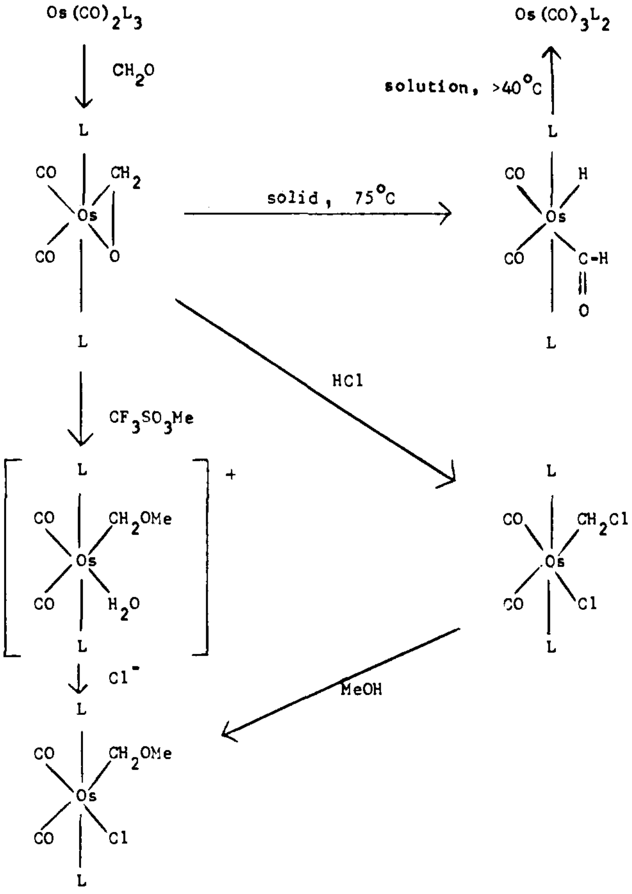
The mononuclear, zerovalent osmium entity $Os(CO)_2(PPh_3)_2$,[7] forms complexes with many unsaturated molecules including C_2H_4,[10] O_2,[10] S_2,[11] and CH_2S,[12] and as part of our study of this molecule we have examined reaction with CH_2O. When a 40% aqueous formaldehyde solution (~1.5 equiv) was added to a bright yellow benzene solution of $Os(CO)_2(PPh_3)_3$ (1 equiv), decolorization took place over several hours. Reaction time could be reduced by conducting the reaction under a tungsten-halogen sun lamp. From the colorless solution could be isolated crystals of composition $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$. The two ν(CO) bands at 1977 and 1902 cm^{-1} (see Table I for IR data for all new compounds reported) are found at positions similar to those found for other η^2 adducts of $Os(CO)_2(PPh_3)_2$.[10-12] Formaldehyde ν(C-H) is at 2910 (w) and 2820 (m) cm^{-1} (Kel-F mull) and a band of medium intensity at 1017 cm^{-1} is probably associated with formaldehyde ν(CO). In the ^1H NMR spectrum ($CDCl_3$) the formaldehyde protons appear as a triplet at τ 7.44 (^3J(H-P) = 4.0 Hz).

To confirm the mononuclear formulation rather than the possible alternative with bridging CH_2O groups, an X-ray crystal structure determination was undertaken.[13] The inner coordination sphere, confirming the mononuclear formulation, is depicted in Figure 1. Most bond distances are as expected, but the formaldehyde C-O bond at 1.59 (1) Å is long, consistent with the IR band assigned to ν(C-O) at 1017 cm^{-1}.

Heating the crystalline η^2-formaldehyde complex at ~75 °C for several hours results in a novel rearrangement with formation of the formyl-hydrido complex, $Os(CHO)H(CO)_2(PPh_3)_2$. The formyl proton in the ^1H NMR spectrum (CH_2Cl_2) now appears as a multiplet at the low-field position of τ −4.41 and the osmium hydride at τ 15.35 (^2J(H-P) = 21.5 Hz). Formyl ν(C-H) is at 2760 (w), 2680 (w), and 2540 (m) cm^{-1} and formyl ν(CO) at 1601 cm^{-1}. Solutions of this complex are unstable at temperatures above 40 °C eliminating H_2 and forming $Os(CO)_3(PPh_3)_2$:

$$Os(CHO)H(CO)_2(PPh_3)_2 \rightarrow Os(CO)_3(PPh_3)_2 + H_2\uparrow$$

Scheme I. Synthesis and Some Reactions of an Osmium Formaldehyde Complex (L = PPh_3).



This behavior contrasts with the corresponding formyl-chloro complex, $Os(CHO)Cl(CO)_2(PPh_3)_2$ which loses CO:[4d]

$$Os(CHO)Cl(CO)_2(PPh_3)_2 \rightarrow OsHCl(CO)_2(PPh_3)_2 + CO\uparrow$$

Reaction of the formaldehyde complex with HCl is fast to yield the chloromethyl complex $Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$. This reaction may proceed through the hydroxymethyl species, $Os(CH_2OH)Cl(CO)_2(PPh_3)_2$, which would be formed by initial protonation at the oxygen atom. Other alkoxymethyl complexes[14] react rapidly with HCl to form chloromethyl derivatives. With 1 equiv of CF_3CO_2H a compound with spectral properties appropriate for the hydroxymethyl species, $Os(CH_2OH)(O_2CCF_3)(CO)_2(PPh_3)_2$, is obtained, but this could not be isolated in a pure form. Methylation with methyl trifluoromethanesulfonate gives the methoxymethyl complex $[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]CF_3SO_3$. These reactions are summarized in Scheme I.[15]

References and Notes

(1) R. Ugo, *Catal. Rev.–Sci. Eng.*, **11,** 225 (1975); H. F. Schaefer III, *Acc. Chem. Res.*, **10,** 287 (1977); R. Mason, *Isr. J. Chem.*, **15,** 174 (1977).

(2) M. A. Vannice, *Catal. Rev.–Sci. Eng.*, **14,** 153 (1976).

(3) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **15,** 136 (1976).

(4) (a) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95,** 4089, (1973); (b) C. P. Casey and S. M. Neumann, *ibid.*, **98,** 5395 (1976); (c) S. R. Winter, G. W. Corbett, and E. A. Thompson, *J. Organomet. Chem.*, **133,** 339 (1977); (d) T. J. Collins and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1044 (1976); (e) B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1546 (1977); (f) J. A. Gladysz and W. Tam, *J. Am. Chem. Soc.*, **100,** 2545 (1978).

(5) A compound of reported composition $RuH_2(OCH_2)(PPh_3)_3$ has been described,[4e] but it could not be obtained in a pure state and therefore was not well characterized. The apparent oxidation state of this material and the ν(CO) value are quite different from those of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$. Also a compound with a probable bridging CH_2O ligand has been described ($(Cp_2ZrCl)_2CH_2O$).[6]

(6) G. Fachinetti, C. Floriani, A. Roselli, and S. Pucci, *J. Chem. Soc., Chem. Commun.*, 269 (1978).

(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]

(8) J. Halpern and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 629 (1973).

(9) J. Halpern and T. A. Weil, *J. Chem. Soc., Chem. Commun.*, 631 (1973).

(10) B. E. Cavit, K. R. Grundy, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 60 (1972).

(11) G. R. Clark, D. R. Russell, W. R. Roper, and A. Walker, *J. Organomet. Chem.*, **136**, C1 (1977).

(12) T. J. Collins and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 901 (1977).

(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.

(14) M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. A*, 1508 (1967).

(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 $Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$.

Kevin L. Brown
Department of Scientific and Industrial Research
Petone, New Zealand

George R. Clark, Christine E. L. Headford,
Karen Marsden, Warren R. Roper*
Department of Chemistry, University of Auckland
Auckland, New Zealand

Received August 17, 1978

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

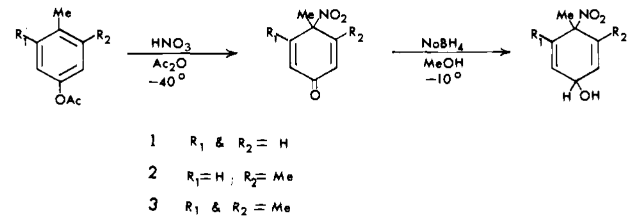
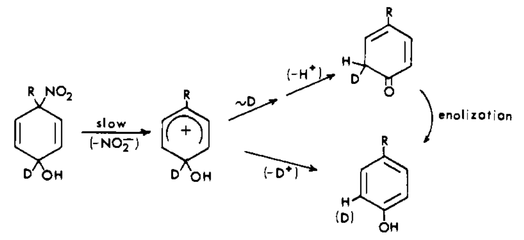


Table I. Kinetic Parameters for Solvolysis of Some *cis*-4-Methyl-4-nitrocyclohexadienols and *cis*-4-Methyl-4-nitrocyclohexadienyl Acetates in Aqueous Ethanol[a]

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

0002-7863/79/1501-0505$01.00/0