accounts of the reactions and applications of these highly reactive yet relatively stable organocopper species will be reported in due course.

Acknowledgment. Financial assistance from the National Institutes of Health (GM 28128), the American Cancer Society (JFRA No. 37 to B.H.L.), and the Committee on Research (UCSB) is gratefully acknowledged. We also thank Professors Bruce Rickborn and Ralph Pearson and Dr. David M. Floyd (FMC Corp.) for helpful discussions.

Registry No. 1 (R = *n*-Bu), 80473-69-4; **1** (R = $CH{=}CH_2$), 80473-65-0; **1** (R = Ph), 80473-66-1; **1** (R = *n*-Pr), 80473-72-9; **1** (R = Et), 80473-71-8; *erythro*-3-methylheptan-2-ol, 81120-76-5; 1-phenylhexan-1-ol, 4471-05-0; 2-phenylhexan-1-ol, 25755-73-1; 1-phenyl-3-buten-1-ol, 936-58-3; 2-phenyl-3-buten-1-ol, 6052-63-7; 2-phenylheptan-2-ol, 4436-90-2; (*E*)-2-methyl-4-phenyl-2-buten-1-ol, 52497-56-0; (*Z*)-2-methyl-4-phenyl-2-buten-1-ol, 58732-17-5; *trans*-1,2-dipropylcyclopentanol, 38338-76-0; 4-*tert*-butyl-2-ethyl-1-methylcyclohexanol, 81120-77-6; *trans*-2-phenylcyclopentanol, 42086-64-6; *cis*-2-butene oxide, 1758-33-4; styrene oxide, 96-09-3; 2-methylstyrene oxide, 2085-88-3; 2-methyl-2-vinyloxirane, 1838-94-4; 1-propylcyclopentene oxide, 30762-73-3; 4-*tert*-butyl-1-methylcyclohexene oxide, 81176-58-1; cyclopentene oxide, 285-67-6.

(15) CuCN was purchased from both MCB (tan powder) and Fluka (green crystals). Both were used directly out of the bottle as received without any purification whatsoever.

Ion-Molecule Complexes in Decompositions of Gaseous Cations: 130-nm Photolysis of 4-Pyridyl Ethers

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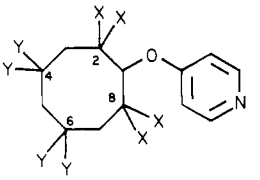
The intermediacy of ion-molecule complexes in unimolecular[1-4] and bimolecular[5,6] gas-phase reactions has been a subject of substantial recent interest. We have lately demonstrated the importance of reaction 1 in unimolecular fragmentations of mo-

$$ROAr^{+\cdot} \rightarrow \underset{\text{ion-molecule complex}}{[R^+ \quad ArO\cdot]} \rightarrow \text{decomposition products} \quad (1)$$

lecular ions derived from aryl alkyl ethers.[2,3] The species shown in brackets represents an ion-molecule complex that results from breaking the weakest covalent bond of the parent ion. The charged and the neutral fragments formed have insufficient kinetic energy to overcome their mutual charge-dipole attraction and must stay within several angstroms of each other until they react with one another via an exothermic ion-molecule reaction.

In previously reported cases,[1-6] ion-molecule complexes decompose via proton-transfer reactions (sometimes reversible) from the charged to the neutral moiety. In the case of reaction 1 where Ar = phenyl, the decomposition products are phenol molecular ions and neutral olefins, whose structures reveal rearrangements of R^+ within the complex.

We have previously described reaction 1 as a gas-phase analogue of solvolytic elimination.[2,3] This communication describes chemical consequences of the radical nature of the leaving group, ArO·. In the case of Ar = 4-pyridyl we find that first a proton and then a hydrogen atom are transferred from the alkyl to the aryloxy moiety. This reaction was anticipated on thermodynamic grounds. The 4-pyridyloxy radical was expected to be an excellent gas-phase base.[7] Its conjugate acid ought to have a hydrogen atom affinity ≥ 90 kcal/mol[8] and should therefore be able to abstract allylic hydrogens. We observe this reaction sequence from low-energy ionization of a variety of alkyl 4-pyridyl ethers and describe here our results from 130-nm photolysis of cyclooctyl 4-pyridyl ether, **1**.[9] The cyclooctyl ether was chosen for scrutiny because the



1, X = Y = H
2, X = D; Y = H
3, X = H; Y = D

cyclooctyl cation is known to have a bridged structure,[10] which leads to a characteristic interconversion of ring positions[11,12] that

Table I. Distribution of Label in Principal Fragment Ions from 130-nm Photolysis of Specifically Deuterated Cyclooctyl 4-Pyridyl Ethers at 10^{-7} torr[a]

position of substitution	% of Σ[b]			corrected isotope ratio[c]	
	m/z 96	*m/z* 97	*m/z* 98	$C_5H_5DNO^+$	$C_5H_4D_2NO^+$
d_0 (1)	44.1	2.6	0.2	0[d]	0[d]
2,2,8,8-d_4 (2)	41.0	16.6	6.0	0.354[e]	0.124[e]
4,4,6,6-d_4 (3)	36.5	12.6	4.0	0.297[e]	0.104[e]
5,5-d_2	51.6	7.6	1.0	0.082[d]	0.004[d]
1-d_1	44.5	4.3	0.3	0.037[d]	0.001[d]

[a] Relative abundances of fragment ions do not change with variation of the nominal pressure from 4×10^{-8} to 2×10^{-7} torr. Conventional mass spectra were recorded at $\leq 10^{-6}$ Torr for 1 and 2 on an MS-902 using 12- and 70-eV electron impact ionization, and the same distribution of fragment ions was observed. Contributions from ion-molecule reactions can therefore be dismissed. [b] The quadrupole mass filter of the photoionization mass spectrometer gives wide variations from day to day in intensities of molecular ions relative to these fragment ions. Values of % Σ are reported for optimized instrument settings, but the variation among them is not significant. The *m/z* 96:97:98 ratio does not change substantially even when the molecular ion intensity fluctuates by an order of magnitude. [c] Relative to $C_5H_6NO^+ = 1$; corrected for ^{13}C natural abundance, but not for incomplete deuteration of starting material. [d] Standard deviation of the mean <0.002. [e] Mean of three independent series. Standard deviation of the mean is ≤0.007.

(1) Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Chem. Commun.* **1981**, 836-838 and references contained therein.
(2) Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 1596-1602.
(3) Hall, D. G.; Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 5686-5688.
(4) Longevialle, P.; Botter, R. *J. Chem. Soc., Chem. Commun.* **1980**, 823-825.
(5) Squires, R. B.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256-4258 and references contained therein.
(6) Liehr, J. G.; Brenton, G. A.; Beynon, J. H.; McCloskey, J. A.; Blum, W.; Richter, W. J. *Helv. Chim. Acta* **1981**, *64*, 835-843.

(7) Reported proton affinities of substituted pyridines lie in the range 209-236 kcal/mol as compared to the proton affinities of simple acyclic and ≥4-member-ring cyclic alkenes, which lie below 204 kcal/mol [Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 2-51]. We estimate the proton affinity of the 4-pyridyloxy radical to be ≥220 kcal/mol, based on the reported proton affinity of 4-methoxypyridine (226.6 kcal/mol) and the fact that the proton affinity of phenoxy radical is only 3 kcal/mol less than that of anisole.[2]
(8) If we take the adiabatic IP of 4-hydroxypyridine to be no lower than 15 kcal/mol below the reported first vertical ionization potential [Cook, M. J.; El Abbady, S.; Katritsky, A. R.; Guimon, C.; Pfister-Guillouzo, G. *J. Chem. Soc., Perkin Trans. II* **1977**, 1652-1656] and estimate its proton affinity to be at least 220 kcal/mol, the hydrogen atom affinity of the corresponding molecular ion is >105 kcal/mol. Other tautomers may have lower hydrogen atom affinities, but we surmise that a lower bound is given by the hydrogen atom affinity of the molecular ion of *N*-methyl-4-pyridone, which is >90 kcal/mol. This value is based on the experimental gas-phase basicity of the neutral molecule, 222.3 kcal/mol [Aue, D. H., personal communication], from which we infer a proton affinity of 229.6 kcal/mol, and the assumption that the adiabatic IP is no lower than 15 kcal/mol below the reported first vertical IP [Cook, et al.].
(9) Schmid, G. H.; Wolkoff, A. W. *Can. J. Chem.* **1972**, *50*, 1181-1187.
(10) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1979**, *101*, 3240-3243.
(11) Cope, A. C.; Gale, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 3747-3752.
(12) Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans II* **1975**, 1647-1651.

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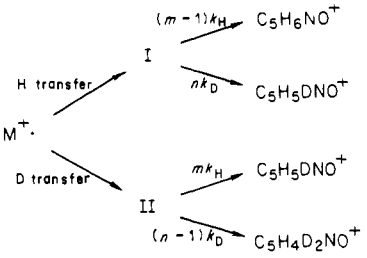
Scheme I

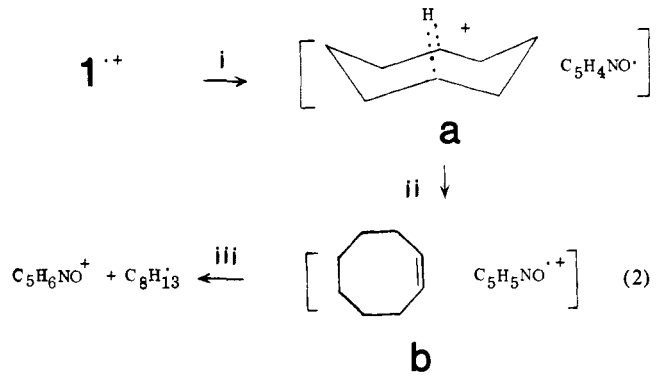


serves, therefore, as a diagnostic for reaction 1. Intervention of the cation renders positions 2 and 8 equivalent to positions 4 and 6.

The photoionization mass spectrometer has been previously described,[13] and it has the advantage that intensity ratios of adjacent peaks in the mass spectrum can be measured precisely. Low-energy ionization gives rise to fragmentation patterns in which simple bond fissions contribute only a small fraction of the total ionization.[14] At 130 nm (9.5 eV),[15] protonated hydroxypyridine ($C_5H_6NO^+$) constitutes nearly half of the total ionization (Σ), and the other prominent fragments (the M - 1, C_8H_{15}, and C_8H_{14} ions) constitute only 7%, 6%, and 3% of Σ, respectively. At this low ionizing energy, further fragmentation of the base peak is not observed.

The pathway by which protonated hydroxypyridine arises from photoionization of **1** is revealed by examination of the deuterated analogues **2** and **3**.[16] From the data summarized in Table I, it can be seen that simple vicinal elimination cannot be a major step in transferring two hydrogens to the aromatic moiety, since the perprotio daughter ion still predominates even when all of the β positions are deuterated (**2**). The isomeric deuterated ether **3** gives very nearly the same peak ratios as does **2**,[17] and the $C_5H_5DNO^+/C_5H_4D_2NO^+$ ratio is the same (2.85) for both d_4 analogues. Can this be explained by hydrogen scrambling? If n deuterium atoms become completely scrambled with m protons in the molecular ion prior to its decomposition, then the pertinent kinetic expressions can be derived from Scheme I.[18] A kinetic analysis based on the relative abundance in Table I reveals that there is no kinetic isotope effect k_H/k_D that can account for the data. Therefore, Scheme I can be ruled out as representing the major pathway.

A mechanism based on reaction 1 provides an explanation for the experimental results. The specific pathway is proposed in reaction 2 and is corroborated by examination of the d_1 and d_2 analogues listed in Table I. Ion-molecule complex a is formed by a simple bond cleavage (step i). Proton transfer (step ii) yields



(2)

ion-molecule complex b, and the nitrogen-containing radical cation subsequently abstracts a hydrogen atom (step iii). In step iii, abstraction of an allylic hydrogen is preferred but not exclusive. Thus, a negligible proportion of $C_5H_4D_2NO^+$ results from the 5,5-d_2 analogue, and levels of $C_5H_5DNO^+$ from the 1-d_1 and 5,5-d_2 analogues are low.

The experiments illustrate the utility of photoionization measurements above threshold in probing fragmentation mechanisms of gaseous ions. The scope of reaction 1 has been widened to include a new class of double hydrogen transfers. A more detailed kinetic analysis of these data will be presented in a full paper.

Acknowledgment. We are grateful to Professor J. N. Pitts and Dr. G. W. Harris, in whose laboratory the photoionization experiments were conducted. This work was supported by the NIH (Grant NS 17109), the donors of the Petroleum Research Fund, administered by the Americal Chemical Society (Grant 10840-AC4), and the NSF (Grant CHE 81 27133).

Registry No. 1, 37054-59-4; **2**, 80906-63-4; **3**, 80906-64-5; [5,5-$^2H_2$]-cyclooctyl 4-pyridyl ether, 80906-65-6; [1-^{2}H]-cyclooctyl 4-pyridyl ether, 80906-66-7; 5-oxocyclooctyl tetrahydropyranyl ether, 2616-83-3.

Supplementary Material Available: 130-nm photoionization mass spectra of compounds **1-3** (1 page). Ordering information is given on any current masthead page.

(13) Biermann, H. W.; Harris, G. W.; Pitts, J. N., Jr. *J Phys. Chem.*, in press.

(14) Morton, T. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 2355-2362; **1977**, *99*, 1288.

(15) The light source used for these studies was an oxygen resonance lamp, with a microwave discharge through 1% oxygen in helium [Davis, D.; Braun, W. *Appl. Opt.* **1968**, *7*, 2071-2074] and a calcium fluoride window.

(16) Compound **2** was prepared from the corresponding ketone-d_4,[11] while the alcohol corresponding to compound **3** was prepared from the monotetrahydropyranyl ether of *cis*-cyclooctane-1,5-diol[12] as follows: Oxidation with pyridinium chlorochromate to 5-oxocyclooctyl tetrahydropyranyl ether [bp 108-119 °C/(0.3 torr)] was followed by repetitive exchange with basic D_2O, and the labeled ketone was reduced with lithium aluminum hydride and then converted to the labeled cyclooctanol by a procedure analogous to that described in ref 12. The 5,5-d_2 compound was prepared by a similar procedure. The 4-pyridyl ethers were purified by distillation at 0.2 torr, followed by extraction from a CCl_4 solution with 10% aqueous HCl, basification, and reextraction of the aqueous layer with CCl_4. Approximate isotopic purities, as estimated from corrected molecular ion intensities, are as follows: **2**, 96 atom % D; **3**, 92 atom % D; the 5,5-d_2 ether, 75-80 atom % D; the 1-d_1 ether, 94 atom % D.

(17) The proportions of $C_5H_6NO^+$ differ by a slight amount, which we attribute to the lower level of deuteration of compound **3**.

(18) The steady-state approximation gives the following expressions, where $a = [I]/[II]$ and $b = k_H/k_D$: $[C_5H_5DNO^+]/[C_5H_6NO^+] = (na + mb)/(m - 1)ab$; $[C_5H_4D_2NO^+]/[C_5H_6NO^+] = (n - 1)/(m - 1)ab$. Solution of these formulas for b gives a quadratic equation for which there are no real roots when experimental values for the isotopic ratios are substituted. An exact solution for Scheme I gives an identical result.

Natural Product Synthesis via Allylsilanes. 1. Synthesis and Reactions of (1*E*,3*E*)-4-Acetoxy-1-(trimethylsilyl)-1,3-butadiene and Its Use in the Total Synthesis of (±)-Shikimic Acid

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The structural moiety **2** and its epoxidized derivatives are frequently found in biologically active natural products such as the antitumor agent crotepoxide and its congeners[1] and in most of the active metabolites of carcinogenic polycyclic aromatic hydrocarbons.[2] In addition, the extreme lability associated with the presence of this moiety renders synthetic endeavors highly challenging. Here, we describe the synthesis and Diels-Alder reactions of the novel diene (1*E*,3*E*)-4-acetoxy-1-(trimethylsilyl)-1,3-butadiene (**1**) and its application to the efficient total synthesis of (±)-shikimic acid (**11**).

The *trans*-enediol **2** could be envisaged as being derived from **3** through a stereospecific oxidative allylic desilylation (Scheme I).[3] The allylsilane **3** in turn may be obtained via the Diels-Alder

(1) (a) Holbert, G. W.; Ganem, B. *J. Am. Chem. Soc.* **1978**, *100*, 352 and references cited therein. (b) Ganem, B. *Tetrahedron* **1978**, *34*, 3353.

(2) (a) Gelboin, H. V., Ts'o, P. O. P., Eds. "Polycyclic Hydrocarbons and Cancer"; Academic Press: New York, 1978; Vols. 1 and 2. (b) Harvey, R. G. *Acc. Chem. Res.* **1981**, *14*, 218.

0002-7863/82/1504-2308$01.25/0