vestigating this methodology for the synthesis of other natural products.

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Supplementary Material Available: Spectral data for **5**–**7** (1 page). Ordering information is given on any current masthead page.

Mechanistic Studies of Unimolecular Ionic Decompositions by Deuterium and Heavy-Atom Isotope Effects. Concerted Elimination of Acetaldehyde from the Benzyl Ethyl Ether Radical Cation

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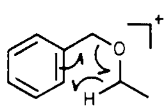
The question of whether mechanisms of the McLafferty[1,2] and related rearrangements[2] are stepwise or concerted has long been a matter of debate. Of late, the balance of opinion has swung toward the former—the prevailing view being that low-energy barriers arising as a consequence of concerted making and breaking of bonds do not occur.[2,3] The evidence in favor of stepwise mechanisms, however, is not extensive. A theoretical analysis has favored a stepwise mechanism,[4] and for one specific reaction there are experimental results clearly supporting a stepwise mechanism.[5] We present evidence that the loss of acetaldehyde from the benzyl ethyl ether radical cation proceeds *via* the six-centered γ-hydrogen rearrangement as shown in I in a concerted fashion.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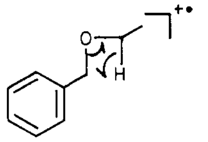
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It has been reported[6] that the loss of acetaldehyde from the benzyl ethyl ether radical cation proceeds in either a concerted or stepwise fashion via a six-membered transition state and that the deuterium isotope effect on the ion abundances in the electron impact mass spectrum is about 2. In principle, the elimination may be either six-centered (I) or four-centered (II). The product ions formed initially through I and II would be the methylenecyclohexadiene and toluene radical cations respectively. We have measured[7] the collisional activation spectra of the toluene molecular ion and the m/z 92 product ion from benzyl ethyl ether and observed significant differences in the m/z 75–78 region of the two spectra.[8] Either the m/z 92 ion formed is not the toluene radical cation or the toluene radical cation is formed initially and rearranges at least partially prior to collision.

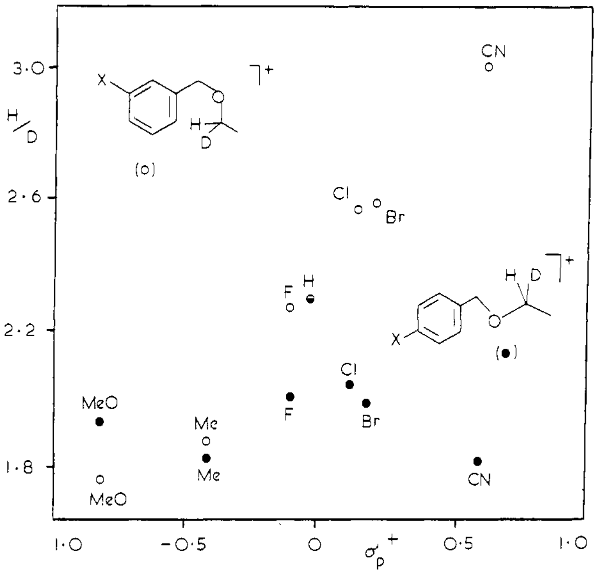

Figure 1. Plots of H/D isotope effects on metastable ion abundances for losses of CH_3CHO and CH_3CDO from the molecular ions of 3(5)-substituted benzyl ethyl-*1*-$^2H_1$ ethers and of 4-substituted benzyl ethyl-*1*-$^2H_1$ ethers vs. the σ^+ value of the substituent.

Deuterium isotope effects on metastable ion abundances for losses of CH_3CHO and CH_3CDO from the molecular ions of 3(5)-substituted benzyl ethyl-*1*-$^2H_1$ ethers ($XC_6H_4CH_2$–O–$CHDCH_3$) have been determined[9,10] and are plotted in Figure 1 against the σ^+ value of X.[11] The corresponding plot of the 4-substituted isomers is also shown. On the basis of mechanism I, the substituent X at 3(5) is conjugated to the hydrogen acceptor site, in which case the isotope effect would be expected to increase with an increase in the electron-withdrawing capacity of X. This is what has been observed (Figure 1). On the basis of mechanism II, the conjugative effect of a 4-substituent on the electron density of the acceptor site (C-1 in the side chain) might be expected to be manifested in a trend in the isotope effects. No such trend is detected (Figure 1). These results (Figure 1) are consistent with a concerted mechanism I. The magnitude of the isotope effects rules out the possibility of a stepwise mechanism in which the second step (C–O bond cleavage) is rate determining.[12,13]

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(2) S. Meyersen and J. D. McCollum, *Adv. Anal. Chem. Instrum.*, **2**, 179 (1963); D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Chem. Rev.*, **2**, 215 (1974); J. L. Holmes, in "Isotopes in Organic Chemistry", Vol. 1, E. Buncel and C. C. Lee Eds., Elsevier, Amsterdam, 1975, p 61.

(3) J. S. Splitter and M. Calvin, *J. Am. Chem. Soc.*, **101**, 7329 (1979).

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(6) J. K. MacLeod and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 5182 (1967).

(7) Measurements were made on a reversed-sector instrument at the University of New South Wales. See P. G. Cullis, G. M. Neumann, D. E. Rogers, and P. J. Derrick, *Adv. Mass Spectrom.*, **8**, 1729 (1980).

(8) Our results are in agreement with those reported for $[C_7H_8]^{+\cdot}$ isomers by F. W. McLafferty, R. Kornfield, W. F. Haddon, K. Levsen, I. Sakai, P. E. Bente, S.-C. Tsai, and H. D. R. Schuddemage, *J. Am. Chem. Soc.*, **95**, 3886 (1973). Loss of $CH_3\cdot$ is more pronounced from the toluene molecular ion than from the methylenecyclohexadiene radical cation. See also P. C. Burgers, J. K. Terlouw, and K. Levsen, *Org. Mass Spectrom.*, **17**, 295 (1982).

(9) All new compounds prepared for this investigation gave correct analytical results. Incorporation of deuterium: $^2H_1$ = 100% for all compounds shown in Figure 1; $^2H_2$ = 100% for compound **2**. Deuterium isotope effects were measured for decompositions in the first field-free region of an Hitachi Perkin-Elmer RMU 7D instrument. Precision of measurements were ±0.1.

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(11) The H transfer in the system is site specific as evidenced by the losses of CH_3CDO and CH_3CHO from the molecular ions of $C_6H_5CH_2OCD_2CH_3$ and $C_6D_5CD_2OCH_2CH_3$, respectively. No H/D equilibration occurs for decompositions in field-free regions.

(12) Quasi-equilibrium theory calculations have been performed. For the method employed see P. J. Derrick and K. F. Donchi in "Comprehensive Chemical Kinetics", Suppl. Vol. 1, C. H. Bamford and C. F. H. Tipper, Eds. Elsevier, Amsterdam, 1983.

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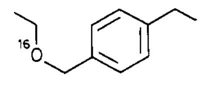
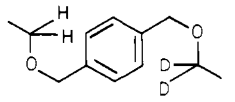
Calculations[12] indicate that a $^{16}O/^{18}O$ isotope effect would be significant if the decomposition were concerted (or stepwise with the second-step rate determining). The intramolecular isotope effect on loss of $CH_3CH^{16}O$ and $CH_3CH^{18}O$ from the molecular ion of **1** has been measured as 1.15 ± 0.04.[13] Metastable ions



1



2

were measured;[7,13] the mass difference allowed the peaks for loss of $CH_3CH^{16}O$ and $CH_3CH^{18}O$ to be resolved clearly. The deuterium isotope effect measured for **2** was 3.2.

The $^{16}O/^{18}O$ isotope effect rules out the possibility of a stepwise mechanism in which the first step is rate determining.[12] The $^{16}O/^{18}O$ and H/D isotope effects taken together, considering also the substituent effects, leave only one possibility, namely, that the elimination of acetaldehyde from the benzyl ethyl ether molecular ion is concerted and that the reaction occurs through the six-centered transition-state I.[14] The benzyl ethyl ether molecular ion provides a clear example of the concerted rupture and formation of a number of bonds under conditions of low energy, since metastable ions were studied. We conclude that the concerted reaction possesses a low critical energy relative to that of a stepwise reaction, i.e., syncopated movement of the atoms is the lowest energy pathway for this decomposition.

Acknowledgment. The support of the Australian Research Grants Committee is acknowledged.

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[13] The electric sector was swept under computer control, and the peaks were signal averaged. Abundances were determined from both peak heights and peak areas, giving isotope effects $^{16}O/^{18}O$ of 1.19 ± 0.005 and 1.12 ± 0.005, respectively. The figure 1.15 ± 0.04 represents the maximum uncertainty. A small correction was necessary for loss of $C_2H_5{}^{16}OH$—a process observed with **1** but not with benzyl ethyl ether.

[14] A referee has suggested that the intervention of an ion-molecule complex $C_6H_5\dot{C}H_2\text{--}{}^{+}OCH_2CH_3$ might provide an alternative explanation of the results. See T. H. Morton, *J. Am. Chem. Soc.*, **102**, 1596 (1982) and references therein. The crucial objection to this mechanism is that if the rearrangement of the complex to give the products is rate determining as suggested by the referee, the $^{16}O/^{18}O$ isotope effect is unexplained.

Highly Reduced Organometallics. 13.[1] Synthesis and Chemistry of the Tricarbonylnitrosylmanganate(2–) Ion, $Mn(CO)_3NO^{2-}$

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Reductions of compounds of the general formula $M(CO)_xL_y$, where L is a better acceptor group than CO, should result in the preferential loss of coordinated CO or a reduced form thereof and the formation of the substituted dianions $M(CO)_{x-1}L_y{}^{2-}$, provided coordinated L is not reduced.[2] In this paper we report on the first successful reaction of this type, which provides the initial example of a previously unknown class of substituted carbonylmetallate dianions of the general formula $M(CO)_{x-1}(NO)_y{}^{2-}$.[3]

Ten equivalents of potassium tri-*sec*-butylborohydride (1.0 M solution in THF) react at reflux with $Mn(CO)_4NO$[4] or at room temperature with $Mn(CO)_3(NO)(PPh_3)$[5] to provide, after about 3 h, 60% or 80% yields, respectively, of the same nearly insoluble microcrystalline yellow solid. This material gives satisfactory analyses for the composition $K_2[Mn(CO)_3NO]$.[6] Formally analogous reductions of $Fe(CO)_4L$ (L = CO[7] or PPh_3[8]) by $K[HBR_3]$ have been shown previously to provide high yields of the isoelectronic species $K_2[Fe(CO)_4]$.

Sodium amalgam reductions of $Mn(CO)_4(NO)$ and $Mn(CO)_3(NO)(PPh_3)$ were also examined and provide remarkable contrasts. Reduction of $Mn(CO)_4NO$ by Na–Hg proceeds slowly (>12 h) at room temperature to provide $Mn(CO)_5{}^-$ as the only carbonyl-containing product in low yields (10–15%), a result similar to those reported previously for reductions of $Fe(CO)_2(NO)_2$[9] and $Co(CO)_3NO$.[10] However, Na–Hg or Na–Ph_2CO reductions of $Mn(CO)_3(NO)(PPh_3)$ in THF at room temperature (eq 1) provide within 2 h essentially quantitative yields of a soluble orange-yellow substance that is formulated as $Na_2[Mn(CO)_3NO]$ on the basis of its spectral and chemical properties (vide infra).

$$Mn(CO)_3(NO)(PPh_3) \xrightarrow[\text{Na-Ph}_2\text{CO, THF}]{\text{Na-Hg or}} Na_2[Mn(CO)_3NO] + PPh_3 \quad (1)$$

Fluorolube mull infrared spectra of $K_2[Mn(CO)_3NO]$ in the $\nu(CO,NO)$ region show three principal bands at 1900 (m), 1755 (vs), and 1420 (s) cm^{-1}. In the same region, THF solution spectra of $Na_2[Mn(CO)_3NO]$ show principal bands at 1918 (s), 1815 (vs, br), 1380 (m, br), and 1345 (m, br) cm^{-1}. The two very low-energy bands for the disodium salt are undoubtedly caused by significant interactions between sodium cations and nitrosyl oxygens. These interactions appear to be destroyed by adding 2 equiv of cryptand(2.2.2)[11] to a THF solution of $Na_2[Mn(CO)_3NO]$. The resulting light yellow precipitate, $[Na(crypt(2.2.2))]_2[Mn(CO)_3NO]$,[12] has a mull spectrum in the $\nu(CO,NO)$ region consisting of three relatively sharp bands: 1840 (s), 1720 (vs), and 1480 (m) cm^{-1}, where the $\nu(CO)$ values are significantly lower and the $\nu(NO)$ value is higher than corresponding bands of $K_2[Mn(CO)_3NO]$ and $Na_2[Mn(CO)_3NO]$. These $\nu(NO)$ values are among the lowest ever observed for compounds containing only terminal NO groups.[13] By comparison, infrared spectra in the $\nu(CO,NO)$ region of $Na[Fe(CO)_3NO]$ in Et_2O, where the NO group is believed to be tightly ion paired with Na^+ (2001, 1900, 1599 cm^{-1}) and $[(Ph_3P)_2N][Fe(CO)_3NO]$ in THF, where no such interaction is possible (1978, 1876, 1645 cm^{-1}), show trends similar to those observed above, but the corresponding bands are at considerably higher energies.[14]

Further confirmation of the natures of $Na_2[Mn(CO)_3NO]$ and $K_2[Mn(CO)_3NO]$ has been obtained from an examination of their chemical properties, which are essentially identical. Equimolar

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[1] Part 12: Rochfort, G. L.; Ellis, J. E. *J. Organomet. Chem.*, in press.

[2] Reductions of $M(CO)_xL_y$, where L is a poorer π-acceptor group than CO, usually result in the loss of L if it is a good leaving group. For example, $Cr(CO)_4(TMED)$ (TMED = tetramethylethylenediamine) undergoes reduction to give $Na_4Cr(CO)_4$: Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 3605.

[3] It is noteworthy that only two examples of carbonylnitrosylmetallate monoanions presently exist, $Fe(CO)_3NO^-$ and the recently prepared $Mn(CO)_2(NO)_2{}^-$: Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 4981.

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[6] Anal. Calcd for $C_3K_2MnNO_4$: C, 14.58; K, 31.64; Mn, 22.23; N, 5.66; H, 0.00. Found: C, 13.80; K, 31.79; Mn, 22.00; N, 5.50; H, 0.24. All of the above analyses were obtained for one sample. Other attempts to obtain a better carbon analysis were no more successful.

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[11] 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane or Kryptofix-222.

[12] The chemical properties of this product are identical with those of $K_2[Mn(CO)_3NO]$. The crystal structure of the related $[Na(crypt(2.2.2)]_2[Fe(CO)_4]$ shows the presence of an essentially undistorted tetrahedral $Fe(CO)_4{}^{2-}$ unit, free of ion pairing. Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1104.

[13] The related $K_3[Mn(NO)_2(CN)_2]$, presumably containing linear nitrosyls, also has very low $\nu(NO)$ values: 1455, 1425 cm^{-1}. Behrens, H.; Lindner, E.; Schindler, H. *Z. Anorg. Allg. Chem.* **1969**, *365*, 119.

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