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(5) The 2-azabicyclo[2.2.0]hex-5-ene ring system has been reported previously but this method is not readily applicable to the preparation of gram quantities needed in our scheme. (K. E. Wilzbach and D. J. Rausch, *J. Am. Chem. Soc.*, **92**, 2178 (1970).)

(6)(a) Carbamate **3** can be prepared in large quantities (ca. 30 g) by irradiating 5% solutions of the *N*-carbomethoxy-1,2-dihydropyridine in acetone using a Rayonet 208 photochemical reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with RUL-3000 lamps. The product is further purified by first passing it through aluminum oxide with a pentane-ether gradient followed by a bulb-to-bulb distillation; (b) F. W. Fowler, *J. Org. Chem.*, **37**, 1321 (1972).

(7) The N-substituted bicyclic amines and 1,2-dihydropyridines are easily identified because they have very characteristic spectral properties (see ref 5 and 6). We have further characterized the 1,2-dihydropyridines by reduction to the 1,2,5,6-tetrahydropyridines. These were compared to authentic samples prepared by the reaction of 1,2,5,6-tetrahydropyridine with the appropriate alkylating agent.

(8) The ring opening reaction to the dihydropyridine has been carried out in solution using an inert solvent such as benzene at 120° and in the gas phase using a sealed evacuated bulb or flow system. The 1,2-dihydropyridines can be prepared free from solvent using either the static or flow gas phase system. However, the technique we find to be most convenient is to dissolve the bicyclic amine (**5**) in an inert solvent such as benzene and to distill the mixture through a hot quartz tube (24 × 1.0 cm) at 300°. The solution phase pyrolysis is not as clean as in the gas phase and the sealed evacuated bulb (345 ml) can be used only for small quantities (50–100 mg).

(9) The disrotatory concerted ring opening reaction of the cyclobutenes **5a–c** is clearly not an allowed process according to the principles of orbital symmetry. However, the nitrogen atom introduces a considerable electronic perturbation in these ring systems. The lone pair of electrons on nitrogen can have a stablizing interaction with the transition state for a nonconcerted ring opening of these cyclobutenes. In fact, when the lone pair of electrons is more available for a bonding interaction (**3**), the activation energy for the ring opening reaction is indeed available. (The E_a values for carbamate **3** and amine **5a** are 32.0 and 30.6 kcal/mol, respectively.)

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An ^{17}O Nuclear Magnetic Resonance Chemical Shift Scale for Polyoxomolybdates

Sir:

The feasibility of observing ^{17}O NMR spectra of large group 5a and 6a polyoxoanions was demonstrated recently.[1,2] In order to determine the factors which influence chemical shifts and line widths, we have examined the spectra of a number of polyoxomolybdates under various experimental conditions.

All spectra were measured on a JEOL JMN-PS-100 spectrometer at 13.5 MHz in the Fourier mode using a Nicolet 1085 data system. Samples were pulsed at 0.33 s^{-1} utilizing 4096 data points over 15 152 Hz. An external proton lock provided frequency stabilization.

The samples studied are described in Table I and representative spectra shown in Figure 1. All of the compounds have known structures,[3,4] and chemical shift assignments given in Figure 2 are based on the previously established qualitative correlation between downfield shift and decreasing number of metals to which an oxygen atom is bonded. Compounds **1**, **3**, **4**, and **5** all have 12 symmetry equivalent terminal oxygens (O-Mo), 6 equivalent doubly bridging oxygens (O-Mo$_2$), and 6 oxygens bonded to two molybdenums and the heteroatom. Thus the resonances near −825 and −380 ppm are assigned to the terminal and doubly bridging oxygens, respectively. The very broad resonances observed for **1** and **3** at −180 and −256 ppm are assigned to the triply bridging oxygens, while the corresponding resonances in **4** and **5** are presumably too broad to observe or obscured by the solvent resonance. Compound **2** contains 12 terminal oxygens, 8 doubly bridging oxygens, 2 equivalent triply bridging oxygens, and 2 equivalent quadruply bridging oxygens. Although the terminal oxygens are not all symmetry equivalent, they have similar local environments and collectively yield a broad resonance at −814 ppm. Two of the doubly bridging oxygens, however, are distinguished from the remaining doubly bridging oxygens by unusually short bond distances to a molybdenum which has no terminal oxygens. The resonance at −757 ppm is assigned to these oxygens and the resonance at −395 ppm is assigned to the "normal" doubly bridging oxygens. Assignments for compounds **6**, **7**, and **8** have been discussed previously,[1] but the narrow line widths observed here allow the resonances

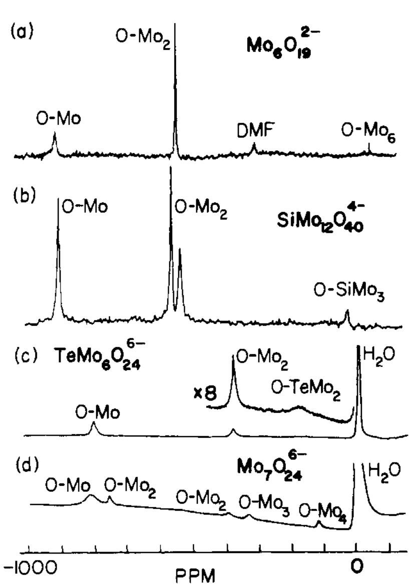

Figure 1. ^{17}O NMR spectra of (a) $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$, (b) α-$[(n\text{-}C_4H_9)_4N]_4Si_{12}O_{40}$, (c) $Na_6TeMo_6O_{24}$, and (d) $Na_6Mo_7O_{24}$, [Mo] = 2.8 M. See Table I for details regarding experimental conditions.

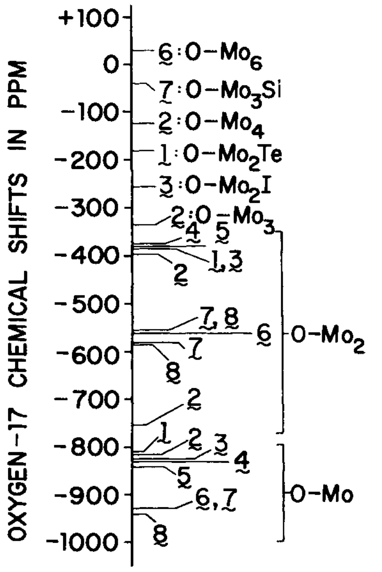

Figure 2. Assignments of ^{17}O NMR shifts given in Table I.

Table I. ^{17}O Spectral Data for Polyoxomolybdates

Compound[a]	Solvent, Temp, °C	[Mo],[b] M	No. of pulses	Chemical shifts (line widths)[c]
1 $Na_6TeMo_6O_{24}\cdot 2H_2O$	H_2O (pH 5.8), 82	8.6	4 465	−807 (15), −383 (15), −180 (40)
2 $Na_6Mo_7O_{24}\cdot 4H_2O$	H_2O (pH 5.5), 25	5.8	9 061	−821 (60), −758 (18), −400 (25), −338 (20), −123 (15)
	H_2O (pH 5.5), 25	2.8	12 844	−814 (40), −757 (14), −395 (18), −335 (15), −123 (11)
3 $Na_5IMo_6O_{24}\cdot 3H_2O$	H_2O (pH 5), 95	4.7	11 021	−825 (6), −385 (8), −256 (50)
4 $Na_3H_6AlMo_6O_{24}\cdot 4H_2O$	H_2O (pH 4.1), 25	1.9	16 384	−831 (20), −376 (20)
5 $Na_3H_6CoMo_6O_{24}\cdot 8H_2O$	H_2O (pH 2.6), 93	1.2	10 320	−838 (6), −382 (8)
6 $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$	$(CH_3)_2NCHO$, 25	1.4	5 729	−927 (10), −559 (4), +32 (<2)
7 $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4SiMo_{12}O_{40}$	CH_3CN, 75	0.2	131 072	−928 (8), −579 (6), −553 (12), −42 (10)
8 $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_3PMo_{12}O_{40}$	CH_3CN, 79	0.3	18 701	−939 (4), −586 (5), −554 (7)
	CH_3CN, 25	0.1	131 072	−939 (6), −584 (8), −553 (15)

[a] All oxygen nuclei were ^{17}O enriched to about 2 atom % except for the four oxygens bonded to phosphorus in **8**. [b] Total molybdenum concentration in moles per liter. [c] Positive chemical shift is in parts per million upfield from pure H_2O at 25 °C, externally referenced. Approximate line width is in parts per million at 13.5 MHz.

for nonequivalent doubly bridging oxygens in **7** and **8** to be resolved. The quadruply bridging oxygen resonance for **8** was not observed due to lack of enrichment at this site.

Examination of Figure 2 in its entirety confirms the correlation between upfield shift and increasing degree of bridging noted earlier. Moreover, the clustering of chemical shifts within the O-Mo and $O\text{-}Mo_2$ regions allow more detailed interpretation of ^{17}O chemical shifts to be made: (1) resonances from about −900 to −1000 ppm are all assigned to terminal oxygens bonded to molybdenums which have only one terminal oxygen, i.e., monoxo terminal oxygens; (2) resonances from about −800 to −900 ppm are all assigned to terminal oxygens bonded to molybdenums having two terminal oxygens, i.e., dioxo terminal oxygens; (3) the resonance at −757 ppm is assigned to oxygens bridging a molybdenum which has no terminal oxygen and a molybdenum which has two terminal oxygens; (4) resonances between about −500 and −650 ppm are all assigned to oxygens which bridge two molybdenums, each of which has only one terminal oxygen; (5) resonances between about −350 and −500 ppm are all assigned to oxygens which bridge two molybdenums, each of which has two terminal oxygens. We choose at this point to base this relationship between oxygen environment and chemical shift purely on empirical data. It should be mentioned, however, that this interpretation is entirely consistent with the postulate that lower electron density on an oxygen atom leads to a greater downfield shift.

The value of a chemical shift scale depends strongly on the absence of marked solvent and temperature effects on chemical shifts and the ability to obtain narrow line widths and hence resolve nearly degenerate resonances. Fortunately, solvent and temperature effects have thus far been insignificant. Quadrupole broadening of ^{17}O resonances poses a more serious problem. Significant line narrowing can in general be obtained, however, by lowering solution concentrations and hence lowering viscosity, using solvents having low viscosities, and raising solution temperatures (see Table I).

Having established a quantitative chemical shift scale, we are now in a position to utilize ^{17}O NMR for the structural elucidation of polyoxomolybdates having unknown structures. The results of such studies will be reported in the near future.

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Quaternary Ammonium Enolates as Synthetic Intermediates. Trimethylsilylacetate: A New Class of Silylating Reagent for Ketones and Alcohols

Sir:

Among various silylating reagents,[1] e.g., base-chlorosilane, silylamide, silylamine, etc., the combination of base and chlorosilane has been used as a standard method for the silylation of ketones.[2] Nevertheless, product yields in such a silylation method are not always very high, and a large amount of inorganic salt or HCl-amine salt accompanies the reaction. Further, aqueous workup usually needed has often made the preparation of moisture-sensitive silyl ethers difficult. We report here a new type of silylation reagent, ethyl trimethylsilylacetate-tetra-*n*-butylammonium fluoride (ETSA-TBAF), which circumvents these difficulties.