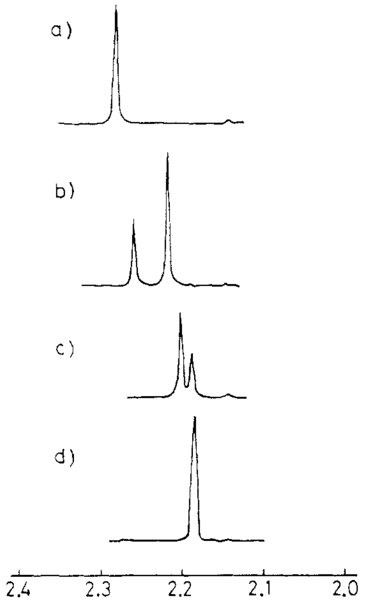

Figure 1. ^1H NMR spectra, 400 MHz, in aqueous solution of the bromide salt of (a) $[W_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$, (b) $[MoW_2O_2(CH_3COO)_6(H_2O)_3]^{2+}$, (c) $[Mo_2WO_2(CH_3COO)_6(H_2O)_3]^{2+}$, and (d) $[Mo_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$.

allowed to stand for 2 days. A mixture of the trinuclear clusters was separated into each component by SP-Sephadex C-25 cation exchange column chromatography (successive three columns of 4 cm in diameter and 140 cm in length). It took nearly a month for complete separation. Three components, orange red, orange, and yellow in elution order, were obtained with 0.1 M HBr as eluent (elution rate was ca. 1 dm^3 per day). These were eventually found to be Mo_2W, MoW_2, and W_3 clusters, respectively. Slow evaporation under reduced pressure at room temperature gave crystals of ca. 1 g of the bromide of each component, $[M_2M'(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$. Analysis of C, H, Br, Mo, and W were consistent with the formula indicated. The Mo and W contents were determined by an ICP method.

The 400-MHz ^1H NMR spectra in D_2O (Figure 1) provide the most convincing evidence that the orange red and the orange crystals are mixed-metal clusters and not a mixture of the two homonuclear trimers. One sharp methyl singlet is observed at 2.188 and at 2.285 ppm (vs. $((CH_3)_3Si)_2O$ internal standard) for the Mo_3 and the W_3 cluster, respectively. On the other hand, each of two mixed-metal complexes shows two methyl singlets with integrated intensity ratio of 2:1. The Mo_2W complex gives signals at 2.189 and 2.204 ppm (1:2 ratio) and the MoW_2 complex at 2.218 and 2.260 ppm (2:1 ratio). Electronic absorption spectra (Figure 2) of these complexes in aqueous solution show two peaks in the visible region except for the Mo_2W complex which exhibits one broad band with a distinct shoulder at lower energy side. There is a systematic trend among the W_3, MoW_2, and Mo_3 complexes that corresponding transitions shift to shorter wavelengths with an increase in intensity as molybdenum is replaced by tungsten.

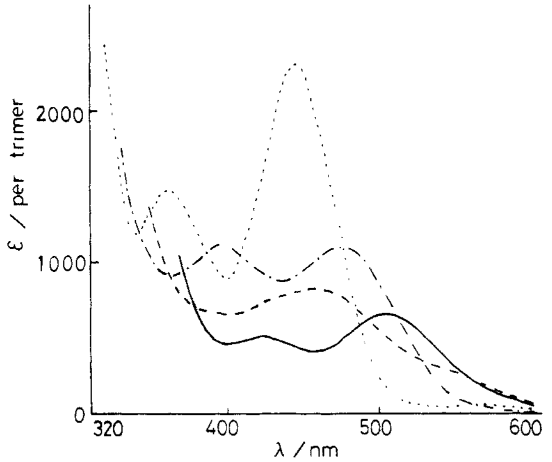

Figure 2. Electronic absorption spectra in 1 M $HClO_4$ of $[Mo_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$ (—), $[Mo_2WO_2(CH_3COO)_6(H_2O)_3]^{2+}$ (- - -), $[MoW_2O_2(CH_3COO)_6(H_2O)_3]^{2+}$ (-·-), and $[W_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$ (···).

Both the compounds, Mo_2W and MoW_2, crystallize in well-formed hexagonal columns. The single crystals of Mo_2W and MoW_2 consist of the rhombohedral lattice with very similar lattice constants: for Mo_2W, $a = b = c = 11.809$ (5) Å, $\alpha = \beta = \gamma = 106.37$ (4)°, and $V = 1394.5$ (12) Å^3 and for MoW_2, $a = b = c = 11.812$ (4) Å, $\alpha = \beta = \gamma = 106.34$ (3)°, and $V = 1396.5$ (10) Å^3. These lattice parameters are again similar to those reported for Mo_3.[9] Crystal densities of Mo_2W and MoW_2 were found to be 2.33 and 2.54 g cm^{-3}, respectively, by a floatation method (acetic anhydride/$CHBr_3$), which are consistent with calculated values (2.35 for Mo_2W and 2.57 g cm^{-3} for MoW_2 based on $Z = 2$).

The results of the X-ray study indicate that, in the crystal lattice of Mo_2W or MoW_2, molybdenum and tungsten are statistically disordered, giving apparently the same crystal symmetry to Mo_2W and MoW_2 as that of Mo_3. This is not surprising, since reported bond lengths and angles about Mo in $[Mo_3O_2(CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$[9] are very similar to corresponding values about W in $[W_3O_2(CH_3COO)_6(H_2O)_3](CF_3SO_3)_2$.[10]

Acknowledgment. We are grateful to M. Ebihara for the measurement of ^1H NMR spectra, Professor F. Takei (Research Institute for Iron, Steel and Other Metals, Tohoku University) for the ICP analysis, and to Takeda Science Foundation for partial financial support. Useful discussions and constant encouragement by Professor K. Saito (Coordination Chemistry Laboratories, Institute for Molecular Science) are gratefully acknowledged.

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(9) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912-1917. Parameters for $[Mo_3O_2(CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$: $a = b = c = 11.784$ (5) Å, $\alpha = \beta = \gamma = 106.34$ (5)°, $V = 1386.6$ Å^3, $Z = 2$, density 2.18 g cm^{-3}.

(10) Bino, A.; Hesse, K.-F.; Kuppers, H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 723-725.

Intramolecular Generation and [2,3]-Sigmatropic Rearrangement of Oxonium Ylides

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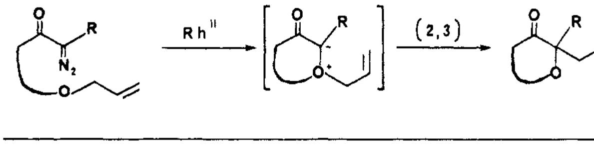
The controlled generation and utilization of reactive intermediates in the construction of organic compounds is a cornerstone of organic synthesis. However, the development of methodology utilizing oxygen-based reactive intermediates[1] has lagged far behind those based on carbon, nitrogen, phosphorous, and sulfur. We report here our preliminary results on the intramolecular generation of allylic oxonium ylides and their subsequent [2,3]-sigmatropic rearrangement to give five-, six-, and eight-membered oxygen heterocycles.



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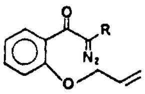
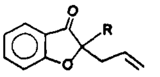
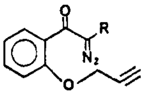
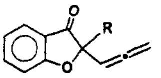
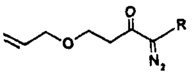
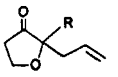
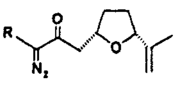
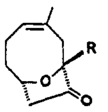
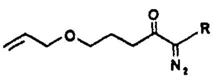
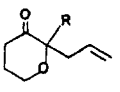
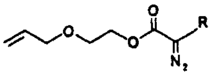
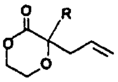
(1) For a recent example, see: Overman, L. E.; Castañeda, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 1303-1304.

0002-7863/86/1508-6060$01.50/0

Table I.[a] [2,3]-Sigmatropic Rearrangement of Oxonium Ylides

entry	diazo compounds[18]	heterocyclic products	R = H yield[b]	R = H time[c]	$R = CO_2R'$ yield[b]	$R = CO_2R'$ time[c]	R′
1			71	0.2	95	8.0	Et
2			0[d]	1.0	92	8.0	Me
3			70[e]	2.0	91	2.0	Me
4			81	0.2	67	1.5	Me
5			33[f]	3.0	53[g]	1.0	Me
6			0[h]	0.5	51	4.0	Et

[a] Reaction conditions: 2 mol % rhodium(II) acetate (Aldrich), 0.01 M in CH_2Cl_2,[14] 25 °C. [b] Yield of isolated products (flash chromatography). [c] Reaction time in hours. [d] None isolated; product unstable. [e] TLC and GC analysis (15-m SE54 J&W fused silica capillary column) indicate this is the only product formed; low yield is due to volatility of product. [f] 23% of C–H insertion product isolated. [g] 37% 2-(methoxycarbonyl)-2-cyclopentenone isolated (C–H insertion followed by elimination). [h] 39% of dimerization products and 24% of C–H insertion products isolated.

Although no spectroscopic or crystallographic data are available to establish the existence of oxonium ylides, they have been postulated as intermediates to explain the products observed upon decomposition of diazocompounds (either thermally, photochemically, or catalytically) in the presence of 2-phenyl-1,3-dioxolane,[2] styrene oxide,[3] allylic ethers,[4] aliphatic ethers,[5,6] allylic acetals,[7] and oxetanes.[8] Oxonium ylides have also been generated by desilylation[9] and deprotonation[9] of oxonium ions and are currently believed to play an important role in the zeolite-catalyzed conversion of methanol to ethylene.[10]

The oxonium ylides in the present investigation are generated under mild conditions via the transition-metal-catalyzed decomposition of α-diazo carbonyl compounds.[7,11] The use of carbenoid methodology for ylide generation has the inherent disadvantage of having alternative reaction pathways available to the carbenoid (e.g., C–H insertion, cyclopropanation, and dimerization). Earlier studies[4,7] of the [2,3]-sigmatropic rearrangement of oxonium ylides in which *the substrate was used as the solvent* observed ylide-derived products in yields of <60% as a result of these side reactions.

From the data available on intramolecular reactions[11a,12,13] of carbenoids derived from transition-metal-catalyzed decompositions of α-diazo carbonyl compounds, we expected these alternative reaction pathways to be minimized by the kinetic preference for five-membered ring formation and by the high "effective-concentration" of allylic ether present. To further minimize intermolecular reactions all reactions were carried out in methylene chloride under high-dilution conditions (0.01 M).[14]

Entries[15] 1–4 in Table I demonstrate that 3-furanones are prepared in good to excellent yields. Extension of the chain length to give a six-membered oxonium ylide significantly increases the importance of the C–H insertion pathway as seen in entries 5 and 6. Rapoport and co-workers[11a] recently observed that yields of six-membered heterocycles formed by the intramolecular X–H insertion reaction are dependent upon the reaction conditions (solvent, temperature, and catalyst concentration) and studies are currently under way in our laboratories to determine if similar factors are important in the formation and [2,3]-sigmatropic rearrangement of oxonium ylides.

The preference of the ylide to undergo the symmetry-allowed [2,3]-sigmatropic rearrangement over the symmetry-forbidden [1,2]-process is illustrated by entries 2 and 4. This is in agreement with earlier results obtained by Ando[4] and Doyle.[7]

Finally, the efficient formation of the eight-membered oxygen heterocycle via a three-carbon ring expansion in entry 4 is noteworthy. Ring expansion by the [2,3]-sigmatropic rearrangement has recently received considerable attention in the formation of eight-membered nitrogen and sulfur heterocycles[16]

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(2) Gutsche, C. D.; Hillman, M. *J. Am. Chem. Soc.* **1954**, *76*, 2236–2240.

(3) Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1965**, 2563–2567.

(4) Ando, W.; Yagihara, T.; Kondo, S.; Nakayama, K.; Yamato, H.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1971**, *36*, 1732–1736. Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, *94*, 3870–3876.

(5) Iwamura, H.; Imahashi, Y.; Kushida, K. *Tetrahedron Lett.* **1975**, 1401–1404. Iwamura, H.; Imahashi, Y.; Kushida, K.; Aoki, K.; Satoh, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1690–1696.

(6) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* **1984**, *49*, 2116–2120.

(7) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; van Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917–1925.

(8) Friedrich, K.; Jansen, U.; Kirmse, W. *Tetrahedron Lett.* **1985**, *26*, 193–196. Kirmse, W.; Chiem, P. V. *Tetrahedron Lett.* **1985**, *26*, 197–200.

(9) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* **1984**, *49*, 2112–2116. Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S. *J. Org. Chem.* **1985**, *50*, 4847–4851.

(10) For leading references, see: Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S.; Grdina, M. J.; Karpeles, R.; Keumi, T.; Inaba, S.; Ip, W. M.; Lammertsma, K.; Salem, G.; Tabor, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 2143–2149. Mole, T. *J. Catal.* **1983**, *84*, 423–434.

(11) (a) Moyer, M. P.; Feldman, P. L.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 5223–5230. (b) See also ref 3–6 therein.

(12) For a general review of intramolecular diazo carbonyl reactions, see: Burke, S. D.; Grieco, P. A. *Org. React.* (*N. Y.*) **1979**, *26*, 361–475.

(13) Taber, D. F.; Petty, E. H. *J. Org. Chem.* **1982**, *47*, 4808–4809.

(14) High-dilution conditions are employed to allow comparison of substrate reactivity and are not required for all substrates. For example: Entry 1 (R = H) gives 69% and 65% yields of 3-furanone at concentrations of 0.1 M (20 mg/mL) and 0.5 M (100 mg/mL), respectively.

(15) Methyl 2-diazo-3-oxo-4-(2-propenyloxy)butanoate and 1-diazo-3-(2-propenyloxy)-2-propanone afforded no oxonium ylide derived products.

(16) Vedejs, E.; Hagen, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6878–6880. Vedejs, E.; Hagen, J. P.; Roach, B. L.; Spear, K. L. *J. Org. Chem.* **1978**, *43*, 1185–1190. Schmid, R.; Schmid, H. *Helv. Chim. Acta* **1977**, *60*, 1361–1366. Cerè, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1981**, *46*, 3315–3321.

yet the corresponding oxygen analogue has received little attention.[7] Entry 4 illustrates the synthetic potential of utilizing a similar approach to medium-ring oxygen heterocycles. This is of particular interest as the oxocane skeleton is found in several marine natural products.[17]

In summary, the intramolecular generation and [2,3]-sigmatropic rearrangement of oxonium ylides represents the first example of a synthetically viable method utilizing an oxonium ylide and provides a novel entry into five-, six-, and eight-membered oxygen heterocycles.

Acknowledgment. We thank W. R. Grace for a Grace Foundation Fellowship (J.A.W.) and the NSF (CHE 8215712) for financial support. NMR spectra were obtained on instruments provided by NSF equipment Grants CHE 8414329 and CHE 8109064. M.C.P. is a Presidential Young Investigator (NSF CHE 8451324).

Supplementary Material Available: Brief experimental details for synthesis of substrates (2 pages). Ordering information is given on any current masthead page.

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[17] Several examples can be found in: Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 251-280.

[18] See information regarding supplementary material.

Generation and Rearrangements of Oxonium Ylides

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Ylides of phosphorus, sulfur, and nitrogen are ubiquitous in organic chemistry as key intermediates in a variety of simple and complex transformations. The chemistry of oxonium ylides has been noticeably scant, although they have been suggested as intermediates. Most recently their presence has been invoked in the deprotonation of oxonium salts,[1] in the intermolecular trapping reaction of carbenes with ethers,[2] and in the production of ethylene from methanol using zeolites.[3] In this paper, several oxonium ylide derived rearrangements will be recounted and the mechanisms we believe to be involved will be outlined.

By taking advantage of the high reactivity of transition-metal-generated carbenes and the kinetics of intramolecular reactions, we reasoned that oxonium ylides (**1**) should be generated from appropriate substrates. A variety of synthetically intriguing pathways (simplistically shown in Scheme I) appeared viable from such ylides. One pathway of special concern to us because of an interest in oxygenated cycloalkanones[4] was predicted to result in cyclobutanones. Another which has much precedent in the chemistry of other heteroatom ylides involves [2,3]-sigmatropic arrangements.[5]

When diazodetone **2** was treated with rhodium(II) acetate[6] in benzene at room temperature a reaction ensured to yield after ~1 h a major product **3** (68%) and a minor product **4** (16%) (Table I). These products are consistent with carbenoid generation followed by capture of an oxygen of the ethylene ketal to generate an intermediate ylide which rearranges to yield **3** and **4**. When substitution was introduced (e.g., **5**), excellent diastereoselectivity was observed; cyclobutanone **6**, with the methyl group syn to the dioxetane ring, predominanted in a ratio >97:3.[7] We have also observed that allyl and benzyl ethers (e.g., **7**, **10**) can yield cyclobutanones (**8**, **11**, **12**). The key to cyclobutanone formation appears to be stabilization of electron deficienty at the α′ carbon (see **1**) by oxygen, vinyl, or aryl substituents. Simple tertiary center stabilization does not appear to be effective.

A [2,3]-sigmatropic rearrangement appeared to account for minor product **9** (Table I). Substrates such as **13** seemed more

Scheme I

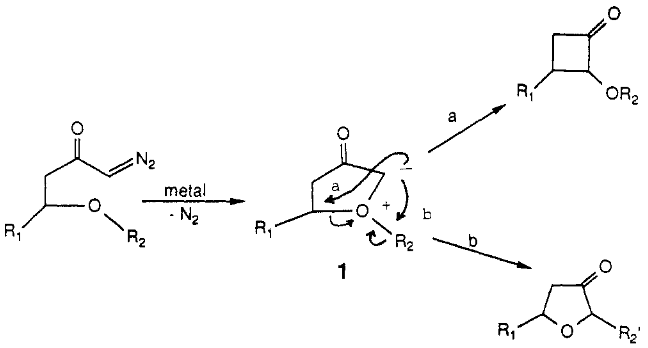
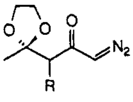
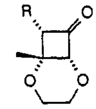
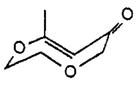
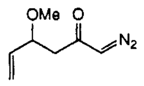
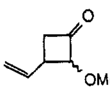
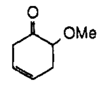
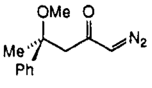
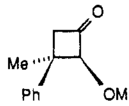
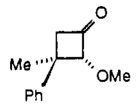
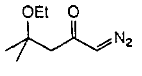
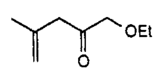


Table I. Reaction of Alkoxy-Substituted Diazoketones Catalyzed by Rhodium(II) Acetate[a]

substrates	products (yields)	
		
2 R = H **5** R = CH_3	**3** (68%) **6** (54%)[b]	**4** (16%)
		
7	**8** (45%)[c]	**9** (10%)
		
10	**11** (57%)	**12** (17%)
		
	(70%)	

[a] The α-diazo ketones were prepared from the corresponding acid chlorides by treatment with an excess of diazomethane in diethyl ether at 0 °C for 1 h. After evaporation of the excess diazomethane in the hood, the crude diazo ketone was chromatographed on silica gel (hexane/EtOAc). Rhodium(II) acetate (1 mol %, powdered) was added to a stirred solution of diazo ketone (1 mmol) in benzene (10 mL) at room temperature. The reaction was followed by TLC until the diazoketone was consumed (30 min-6 h). The benzene was removed under vacuo and the remaining oil was chromatographed on silica gel (hexane/EtOAc) to yield the product. All new products were characterized by elemental analysis or HRMS, as well as high-field ^1H and ^{13}C NMR and IR. [b] The major isomer **6** predominated in a ratio of 97:3. [c] The ratio of cyclobutanones **8** was 3:1. [d] A single diastereomer was formed in 65% yield.

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[7] The relative stereochemistry was determined by the long-range *W* coupling constants (J = 2.3 Hz) for the syn cyclobutyl protons.

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