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.

Scheme I

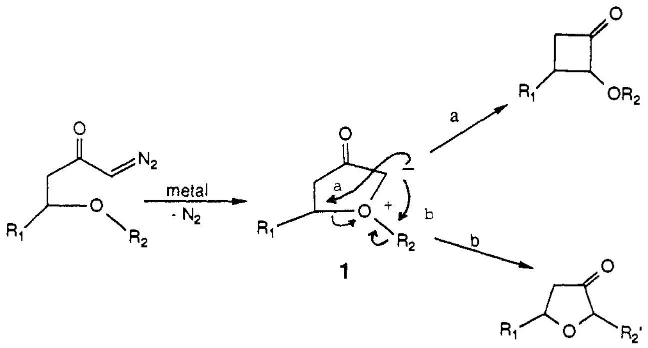
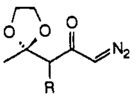
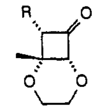
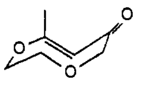
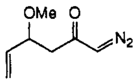
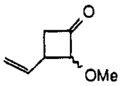
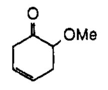
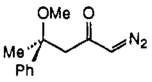
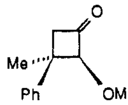
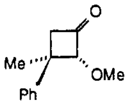
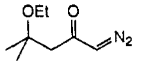
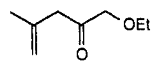


Table I. Reaction of Alkoxy-Substituted Diazoketones Catalyzed by Rhodium(II) Acetate[a]

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 ^{1}H 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.

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

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[1] Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* **1984**, *49*, 2116; **1984**, *49*, 2116.

[2] Friedrich, K.; Jansen, K.; Kirmse, W. *Tetrahedron Lett.* **1985**, *26* (2), 193. Kirmse, W.; Chiem, P. V. *Ibid.* **1985**, *26* (2), 197. Gutsche, D. C.; Hillman, M. *J. Am. Chem. Soc.* **1954**, *76*, 2236. Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1966**, *22*, 3393. Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917.

[3] 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.

[4] Johnson, C. R.; Barbachyn, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 2459. Johnson, C. R.; Penning, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 5655.

[5] Trost, B. M.; Melvin Jr., L. S. *Sulfur Ylides*; Academic Press: New York, 1975.

[6] Paulissen, R.; Reimlinger, H.; Hayez, E.; Hubert, A. J.; Teyssie, P. *Tetrahedron Lett.* **1973**, *24*, 2233.

[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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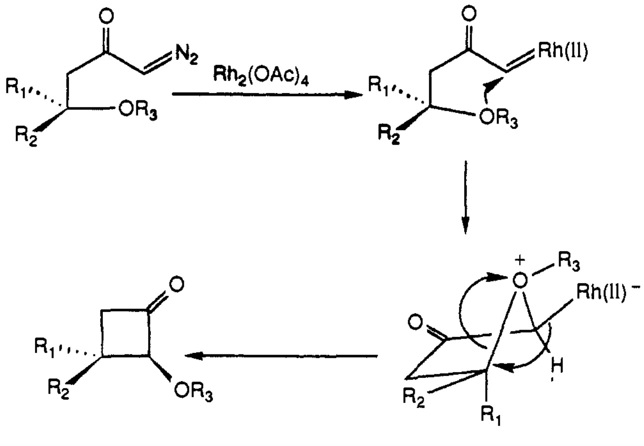
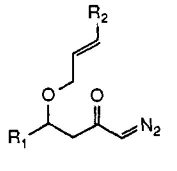
Scheme II



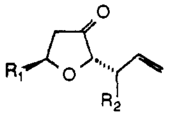
21

suitable candidates for the [2,3]-sigmatropic process. When **13** was treated with rhodium acetate it was found to undergo a rearrangement to yield furanones **14** and **15** (93:7) (65%). The preference for [2,3]-sigmatropic rearrangements over 1,2 migrations is additionally demonstrated by the results of reactions of **16** and **18** which provided **17** and **19**, respectively. Such rearrangements could be also extended to provide pyrans, e.g., **20**.



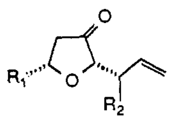
13 $R_1 = CH_3$ $R_2 = H$

16 $R_1 = H$ $R_2 = CH_3$

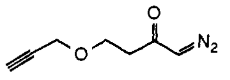


14 (60%)

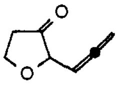
17 (63%[d])



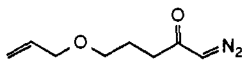
15 (5%)

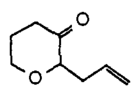


18



19 (74%)

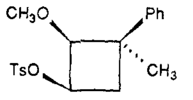




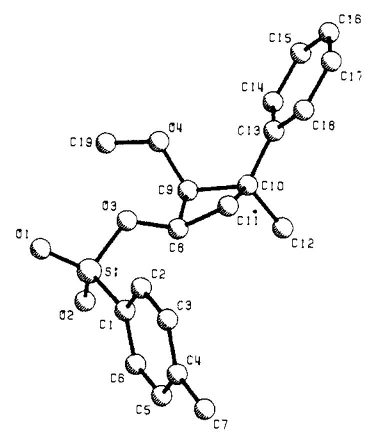
20 (61%)

Several detailed mechanisms are readily conceivable for the observed rearrangements. The most obvious, a direct C–O insertion by the carbene, can be ruled out, since it fails to account for the [2,3]-sigmatropic rearrangement products. Two other mechanisms involving metal carbenoids which react with the oxygen lone pair to form an intermediate of the type **21** must then be considered. Such an intermediate could decompose via several routes to yield the observed products: (i) loss of the metal to form an enolate, (ii) formation of a metallocycle which would then undergo a reductive elimination to regenerate the catalyst and form the carbon–carbon bond, or (iii) a direct formation of the carbon–carbon bond proceeding with inversion of configuration of the carbon–metal bond and retention of configuration of the oxonium–carbon bond. On the basis of our observation that ratios of **11** and **12** formed from **10** vary from 1:3 to 10:1 depending on the catalyst used,[8] the "free enolate" mechanism seems unlikely.

Diazoketone **10** (prepared optically pure from (*S*)-3-methoxy-3-phenylbutanoic acid) upon treatment with rhodium acetate gave cycloubutanones **11** $[\alpha]^{D}_{25}$ +62.1° (c 1.0, $CHCl_3$) and **12** $[\alpha]^{D}_{25}$ −33.8° (c 0.56, $CHCl_3$) in a ratio of 3:1 (yield 74%). The absolute configuration at the quaternary center in **11** was established by conversion to (*S*)-dimethyl-3-methyl-3-phenyl-1,4-dibutanoate.[9] The relative configuration of the methoxy group was established by X-ray crystallography of the derived tosylate **22**.



22



Cyclobutanone **11** was formed with complete retention of configuration at the quaternary center. The data currently available appear consistent with the hypothesis that the cyclobutane formation proceeds in the manner illustrated in Scheme II. The observed sigmatropic reactions could occur in a similar fashion.

The results herein described suggest that oxonium ylides should receive considerable attention in synthetic chemistry. We are continuing to explore the synthetic and mechanistic aspects of this chemistry.[10]

Acknowledgment. This work was supported by a grant from the National Science Foundation. We are grateful to Dr. Mary Jane Heeg of the Wayne State University Central Instrumentation Facility for the X-ray structure determination.

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[8] Catalyst selectivity for **11** vs. **12**: $Rh_2(OAc)_4$, 3:1; $Cu(acac)_2$, 1:6; $Rh^{I}Cl(Ph_3P)_3$, 1:10.

[9] Abbayes, H.; Dabard, R. *Tetrahedron* **1975**, *31*, 2111.

[10] This work was presented at the Third International Kyoto Conference on New Aspects of Organic Chemistry, Nov 1985; Abstr O-43, p 113.

Dioxygenyl Hexafluoroantimonate: A Useful Reagent for Preparing Cation Radical Salts in Good Yield

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Received June 9, 1986

Organic cation radicals have been prepared by using Brønsted acids, Lewis acids, halogens, and metal salts.[1] These methods suffer from a reaction stoichiometry that is either variable or unknown and often provide a cation radical in which the counteranion is ill-defined. Thus, only rarely can one use chemical oxidation procedures to prepare isolable cation radical salts. Although electrochemical oxidation procedures have also been developed for preparing cation radicals,[2] the utility of the method for preparing stable cation radical salts is quite limited.[3]

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[1] Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

[2] (a) Melchior, M. T.; Maki, A. H. *J. Chem. Phys.* **1961**, *34*, 471. (b) Piette, L. H.; Ludwig, P.; Adams, R. N. *Anal. Chem.* **1962**, *34*, 916. (c) Goldberg, I. B.; Bard, A. J. In *Magnetic Resonance in Chemistry and Biology*; Herak, J. N., Adamič, K. J., Eds.; Dekker: New York, 1975; Chapter 10.

[3] (a) Chiang, T. C.; Reddoch, A. H.; Williams, D. F. *J. Chem. Phys.* **1971**, *54*, 2051. (b) Fritz, H. P.; Gebauer, H.; Friedrich, P.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 275. (c) Kröhnke, C.; Enkelmann, V.; Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 912.

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