increases to 40% at 80 K; the change is reversible. The intensity of this O(1s) feature due to the peroxide species increases progressively with decreasing temperature. This analysis shows that the O^{2-} and O^{1-} species are progressively converted into O_2^{2-} species as the temperature is lowered. We have also observed a progressive increase in the Cu^{1+} content with decrease in temperature as measured by the Cu(LVV) Auger line intensity. We believe that the formation of "resonating" O–O bonds due to hole–hole coupling may play a crucial role in the mechanism of superconductivity of this oxide.

Preliminary XPS measurements on the superconductor $La_{1.8}Sr_{0.2}CuO_4$ have shown that this oxide also exhibits the feature due to O_2^{2-} in the O(1s) region at 300 K which intensifies on cooling. This commonality between $YBa_2Cu_3O_7$ and $La_{1.8}Sr_{0.2}CuO_4$ is noteworthy.

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Chain-Carbonyl Transposition, an Alternative Strategy for the Synthesis of the 6,8-Dioxabicyclo[3.2.1]octanes: A Synthesis of the (±)-Brevicomins and Their Oxidative Cleavage to Tetrahydrofurans

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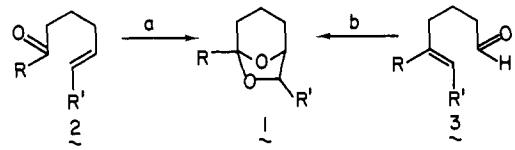
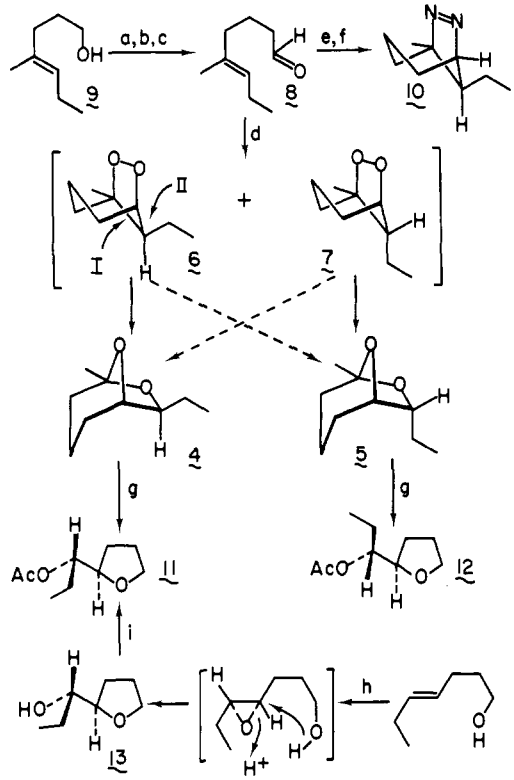
The 6,8-dioxabicyclo[3.2.1]octane system (**1** in Scheme I) has been perhaps the most widely synthesized unit in organic chemistry due to its widespread occurrence in nature[1] and the relative simplicity of many of the natural products that contain this unit. All of these syntheses have been based in actual fact or at least formally upon the corresponding acyclic olefinic unit **2** as outlined in strategy a of Scheme I.[2] In this work, we have developed an alternative strategy (b in Scheme I) which starts from a complementary acyclic olefinic carbonyl compound **3** and in which the carbonyl group and the olefinic terminal chain fragment become transposed during the course of the transformation.

This approach has been applied to the synthesis of *exo*- and *endo*-brevicomin, **4** and **5**, respectively, via the pivotal unsymmetrical endoperoxides **6** and **7** (Scheme II). The starting enal **8** is readily prepared from the alcohol **9**.[3] When enal **8** was subjected to conditions which previously had been used to produce the stable, symmetrical endoperoxide, 1,5-dimethyl-6,7-dioxabicyclo[3.2.1]octane,[4] the expected endoperoxides **6** and **7** could not be detected even when the reaction was conducted at −78 °C.

Scheme I



Scheme II[a]



[a] (a) Br_2, Ph_3P, Et_2O, 92%; (b) NaCN, DMSO, 88%; (c) DIBAL-H, Et_2O, 68%; (d) 70% H_2O_2, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −78 to 0 °C, 14 h, 53%; (e) $TsNHNH_2$, Et_2O, 6 h; (f) $BF_3{\cdot}Et_2O$, room temperature, 2 h, 53% from **8**; (g) 70% H_2O_2, $BF_3{\cdot}Et_2O$, CH_2Cl_2, room temperature, 24 h, 83% for the formation of **11**; (h) *m*-CPBA, CH_2Cl_2, 70%; (i) Ac_2O, DMAP, Et_3N, CH_2Cl_2, 81%.

Instead, **4** and **5** were formed directly in a ratio of 85:15.[5]

In an effort to prepare **6** and **7** by an independent route, the azoalkane **10** was prepared from enal **8** (Scheme II), and its sensitized photodecomposition studied in an effort to generate and trap the triplet 1,3-biradical with molecular oxygen.[4,6] While this approach did not lead to isolable quantities of peroxides,[7] the bicyclization of **8** to **10** proved most interesting in that only a single azoalkane isomer was formed. The absence of coupling[8] between the bridgehead proton and a syn proton on the one-carbon bridge in the ^1H NMR spectrum of **10** indicates that the ethyl substituent occupies this syn position. If the bicyclization of **8** with hydrogen peroxide displays a similar stereoselectivity,[9] then one might expect

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(2) Some representative examples of this approach to the pine beetle aggregation pheromones may be found in the following references: Wasserman, H. H.; Barber, E. H. *J. Am. Chem. Soc.* **1969**, *91*, 3674. Johnston, B. D.; Oehlschlager, A. C. *J. Org. Chem.* **1982**, *47*, 5384 and references therein. Sherk, A. E.; Fraser-Reid, B. *J. Org. Chem.* **1982**, *47*, 932. Mikami, K.; Nakai, T. *Chem. Lett.* **1982**, 1349. Matteson, D. S.; Sadhu, K. M. *J. Am. Chem. Soc.* **1983**, *105*, 2077. A number of other interesting routes have been developed, but these too are based upon the elaboration of a carbon skeleton related to **1** and **2**, for example, Mundy et al. (Mundy, B. P.; Otzenberger, R. D.; DeBernardis, A. R. *J. Org. Chem.* **1971**, *36*, 2390.) and Chaquin et al. (Chaquin, P.; Morizur, J.-P.; Kossanyi, J. *J. Am. Chem. Soc.* **1977**, *99*, 903.). See also ref 1a and 5.

(3) Depezay, J. C.; Le Merrer, Y. *Tetrahedron Lett.* **1975**, 3469. Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 553.

(4) Wilson, R. M.; Rekers, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 206.

(5) The structures of **4** and **5** were confirmed by synthesis with use of the method of Cohen and Bhupathy (Cohen, T.; Bhupathy, M. *Tetrahedron Lett.* **1983**, *24*, 4163.).

(6) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, Chapter 5, and references therein. Wilson, R. M.; Schnapp, K. A.; Merwin, R. K.; Ranganathan, R.; Moats, D. L.; Conrad, T. T. *J. Org. Chem.* **1986**, *51*, 4028.

(7) Mechanistic studies of 1,3-biradical trapping with oxygen indicate that cyclic 1,3-biradicals which are substituted in the 2-position are extremely difficult to trap with molecular oxygen. Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *106*, 929. Adam, W.; Günther, E.; Hössel, P.; Platsch, H.; Wilson, R. M., unpublished results.

(8) (a) Wilson, R. M.; Rekers, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 4005. (b) Wilson, R. M.; Rekers, J. W.; Packard, A. B.; Elder, R. C. *Ibid.* **1980**, *102*, 1633. (c) Padwa, A.; Ku, H. *J. Org. Chem.* **1980**, *45*, 3756.

(9) Bicyclizations to form azoalkanes and peroxides are thought to proceed through closely related carbocation mechanisms: see ref 8b.

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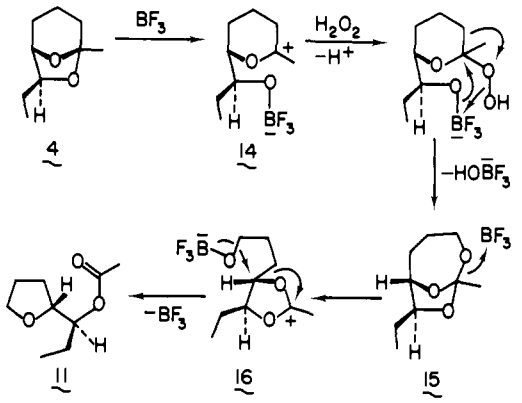
Scheme III



the formation of endoperoxide **6** to be favored over **7**. This stereochemical bias seems quite reasonable, since in both **6** and **10** the ethyl substituent is situated in the less hindered "equatorial" configuration, while in **7**, it is "axially" configured. If **6** is indeed the preferred isomer resulting from bicyclization, then concerted rearrangements of the endoperoxides **6** and **7** should lead to **4** and **5**, respectively, with **4** being the major isomer. However, since the rearrangements of the endoperoxides **6** and **7** could not be studied separately, one cannot be certain that some stereochemical scrambling does not take place as indicated by the dashed arrows in Scheme II. Nevertheless, these results not only confirm the previous observation of exclusive one-carbon rather than three-carbon bridge migration to oxygen[4,10] but also demonstrate the exclusive migration of the more highly substituted one-carbon bridge bond (I rather than II in **6** of Scheme II).

Finally, treatment of **8** with $H_2O_2 \cdot BF_3$ leads to the formation of two additional products which become the major reaction products at higher temperatures and prolonged reaction times (Scheme II). These products were shown to be the diastereomeric furanyl acetates **11** and **12** on the basis of their spectroscopic properties[11] and an independent synthesis of **11** (vide infra). Furthermore, treatment of pure **4** and **5** with $H_2O_2 \cdot BF_3$ under slightly more vigorous conditions then used in their formation led to the exclusive formation of **11** and **12**, respectively. The alcohol **13**[12] was prepared and correlated with the acetate **11** derived from **4** as shown in Scheme II. This correlation not only confirms the relative stereochemistries of **11** and **12** but also demonstrates that the oxidative cleavage of the bicyclic ketals to **11** and **12** occurs with inversion at one of the two ether carbon atoms of **4** and **5**.

A mechanism for this oxidative cleavage which is consistent with the aforementioned observations is outlined in Scheme III. In the very few instances where these normally robust bicyclic ketals are known to undergo acid-catalyzed cleavage,[13] the two-atom bridge undergoes cleavage at the ketal carbon. Thus, the carbocation **14** is probably the initial intermediate in this oxidative cleavage. Reaction of **14** with H_2O_2, followed by a ketal analogue of the Baeyer-Villiger rearrangement[14] might form the bicyclic ortho ester **15** or some closely allied species. Acid-catalyzed cleavage of **15** followed by collapse of the carbocation **16** with inversion during the formation of the new carbon-oxygen bond would afford the furanyl acetate **11**.

In summary, this work not only provides the first expression of this new strategy for the synthesis of bicyclic ketals but also further defines the stereoelectronic factors involved in this bicyclization approach to endoperoxides and their subsequent rearrangement to bicyclic ketals. In addition, a new and unexpected correlation has been observed between the ubiquitous, naturally occurring 6,8-dioxabicyclo[3.2.1]octane and 2-(1′-hydroxyalkyl)furanyl[15] structural units. Finally, the high degree of stereoselectivity available from acyclic precursors through these transformations should make them of considerable utility in the synthesis of polyether natural products.

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Registry No. (±)-**4**, 60018-04-4; (±)-**5**, 62532-53-0; **8**, 110243-75-9; **10**, 110243-76-0; (±)-**11**, 110243-77-1; (±)-**12**, 110243-78-2; (±)-**13**, 110243-79-3; (*E*)-$CH_3CH_2CH{=}CH(CH_2)_3OH$, 24469-79-2.

Supplementary Material Available: Spectroscopic data are available for compounds **10-13** (1 page). Ordering information is given on any current masthead page.

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(11) All new compounds obtained in this work have spectroscopic properties in accord with the proposed structures. See Supplementary Material.
(12) The erythro alcohol **13** and its threo isomer have been synthesized previously (Lebouc, A. *Bull. Soc. Chem. Fr.* **1971**, 3037.), but without high field NMR data, it was impossible to correlate the data from these alcohols with that obtained from the alcohols derived from the brevicomin oxidation products **11** and **12**. See Supplementary Material.
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Synthesis and Characterization of Symmetrical and Unsymmetrical Low-Valent Rhenium-Oxo Dimers, $Re_2O_2(RC{\equiv}CR)_4$

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The preference for terminal or bridging ligation of an oxo group is of fundamental importance to the chemistry of inorganic reagents (permanganate vs MnO_2),[2] catalysts (different crystal faces of MoO_3),[3] metalloenzymes (cytochrome P450 vs hemerythrin),[4] and materials (osmium tetroxide vs zirconia).[5] Terminal oxo ligands, with metal-oxygen multiple bonds, are normally favored only in high oxidation state species.[6] In the course of our studies of novel rhenium(III) oxo-acetylene compounds.[6,7] we have prepared two very different forms of rhenium-oxo dimers $Re_2O_2(RC{\equiv}CR)_4$. The symmetric form is a rhenium(II) dimer, the first example of an isolated terminal oxo complex with a metal formal oxidation state as low as +2 or with an electron count as high as d^5.[8] Remarkably this rhenium(II) terminal oxo complex is more stable than an asymmetric isomer with both bridging and terminal oxo groups.

(1) (a) University of Washington. (b) University of Delaware. (c) Danforth-Compton Fellow.
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(3) Farneth, W. E.; Staley, R. H.; Sleight, A. W. *J. Am. Chem. Soc.* **1986**, *108*, 2327-2332, and references therein.
(4) *Cytochrome P-450*; Sato, R., Omura, T., Eds.; Kodansha Ltd: Tokyo, 1987. *Cytochrome P-450: Structure, Mechanism, and Biochemistry*, Ortiz de Montellano, P., Ed.; Plenum Press: New York, 1986, especially J. T. Groves, Chapter 1. Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618-622, and references therein.
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