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Received July 9, 1979

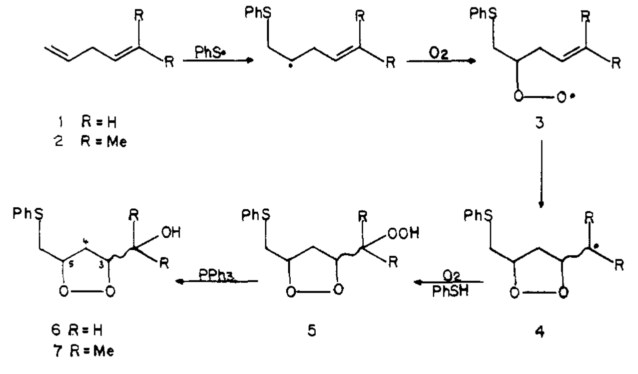
Formation of Cyclic Peroxides by Oxygenation of Thiophenol–Diene Mixtures

Sir:

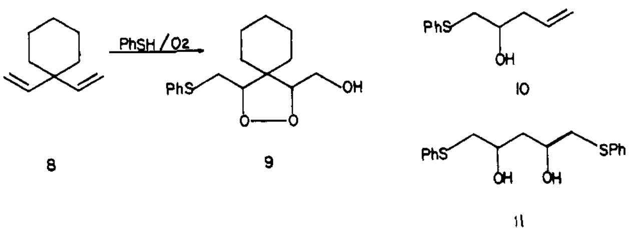
Since the biosynthetic pathway to prostanoids is believed to involve the intermediacy of 1,2-dioxolanes formed by cyclization of appropriately constituted alkylperoxy radicals,[1] there is considerable interest in accomplishing mechanistically similar transformation in vitro.[2] We now report that oxygenation of mixtures of thiophenol with suitable dienes[3] affords moderate yields of disubstituted cyclic peroxides, mainly with cis orientation, by a mechanism involving alkenylperoxy radical cyclization.

When 5-methylhexa-1,4-diene, **2** (8.8 mmol), thiophenol (8.8 mmol), and di-*tert*-butyl peroxyoxalate (0.88 mmol) in ethyl acetate–hexane (600 mL, 1:5) were stirred under oxygen at ambient temperature for 45 h, and the cooled (5 °C) solution was then treated with triphenylphosphine (8.8 mmol), the products isolated by LC were *cis*-**7** (20%) and *trans*-**7** (5%) (Scheme I). *cis*-**7**: *m/e* 254.09766 (M^+, $C_{13}H_{18}O_3S$, 254.09773); IR (CCl_4) 3600 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (5 H, m, ArH), 4.3 (1 H, m, H-5), 4.07 (1 H, t, H-3), 3.47–2.83 (2 H, m, SCH_2), 2.83–2.23 (2 H, m, H-4), 2.1 (1 H, s, OH), 1.23 (3 H, s, CH_3), 1.13 (3 H, s, CH_3). *trans*-**7**: *m/e* 254.09773 (M^+, $C_{13}H_{18}O_3S$, 254.09773); IR (CCl_4) 3600 cm^{-1}; NMR δ 7.23 (5 H, m, ArH), 4.3 (1 H, q, H-3), 4.1 (1 H, dd, J = 5, 8 Hz, H-5), 3.47–2.87 (2 H, m, SCH_2), 2.87–2.23 (2 H, m, H-4), 2.0 (1 H, s, OH), 1.23 (3 H, s, CH_3), 1.12 (3 H, s, CH_3).

Scheme I



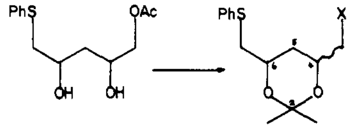
Similar treatment of **8** afforded *cis*-**9** (38%) and its trans isomer (4%), while **1** gave the alcohol **10** (23%), the diol **11** (12%), and the cis and trans isomers of the cyclic peroxide **6** (32 and 8%, respectively). 1,5-Hexadiene gave a mixture of four compounds, two of which have been tentatively identified as 1,2-dioxanes.



8 **9** **10** **11**

Having considered the previously known features of the thiol–oxygen co-oxidation reaction[3] and the catalysis of our reactions by free-radical initiators, we believe that the cyclic peroxides are formed from dienes by the mechanisms shown in Scheme I. The observed exclusive exo mode of ring closure of **3** and similar peroxy radicals is consistent with the behavior of related oxygen- and carbon-centered radicals,[4] while the nature of the products from **2** indicates that initial attack of PhS· occurs regiospecifically at the terminus of the least substituted double bond.

Assignments of structure and stereochemistry to the various cyclic peroxides rest on chemical and spectral evidence. Thus the mixture of *cis*-**6** and *trans*-**6** obtained from the thiol co-oxidation of **1** readily formed a mixture of monoacetates, which, when treated with cobalt chloride and $NaBH_4$, gave a mixture of the stereoisomers of the acetoxy diol **12**. Treatment of **12** with dimethoxypropane in acetone afforded a mixture of 1,3-dioxanes which were separated by TLC. The minor fraction was identified as *trans*-**13**: NMR (CCl_4) δ 7.17 (5 H, m, ArH), 4.9–4.3 and 4.1–3.7 (2 H, 2 m, H-4 and H-6), 3.7–3.4 (2 H, m, OCH_2), 3.1–2.8 (2 H, m, SCH_2), 1.9 (3 H, s, $COCH_3$), 2.4–1.9 and 1.8–1.2 (2 H, 2 m, H-5), 1.2 (6 H, s, 2 CH_3). The major fraction was *cis*-**13**: NMR (CCl_4) δ 7.16 (5 H, m, ArH) 4.2–3.7 (2 H, m, H-4 and H-6), 3.9 (2 H, d, OCH_2), 3.2–2.6 (2 H, m, SCH_2), 2.0 (3 H, s, $COCH_3$), 2.0–1.5 (2 H, 2 overlapping m, H-5), 1.43 and 1.40 (6 H, 2 s, 2 CH_3). The assignment of stereochemistry, which accords with the observation that the NMR spectrum of the trans isomer shows the two acetonide methyls as coincident whereas those in the cis isomer are not, was confirmed by conversion of the major product into *cis*-**15**.



12

13 X = OAc
14 X = OH
15 X = SPh

Reduction of *cis*-**13** with $LiAlH_4$ and conversion of the resultant alcohol, *cis*-**14**, into the phenylthio ether by treatment of the mesylate with lithium thiophenoxide afforded *cis*-**15**: NMR (CCl_4) δ 7.3 (10 H, m, ArH), 4.2–3.6 (2 H, m, H-4 and H-6), 3.3–2.7 (4 H, m, SCH_2), 2.1–1.8 and 1.6–1.2 (2 H, 2 m, H-5 and H-5′), 1.38 and 1.35 (6 H, 2 s, 2 CH_3). When the sample was irradiated at the H-4 frequency, the signal attributed to the protons at C-5 collapsed to a doublet pair (J = 12.2 Hz), while on irradiation at the H-5′ frequency the signal for H-4 and H-6 became a simple triplet. When the SCH_2 protons were irradiated, H-4 and H-6 were seen as a doublet pair (J = 9.8 and 1.4 Hz). The ^{13}C NMR spectrum of *cis*-**15** shows two methyl resonances at 30.18 and 19.98 ppm, whereas the spectrum for *trans*-**15** contains only one such signal at 25.08 ppm. This spectral evidence confirms the structure of the compound as *cis*-**15**, which, since it possesses a plane of

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symmetry, has two nonequivalent protons at C-5 and two nonequivalent methyl substituents at C-1. Since *cis*-**15** is formed from the major component of the oxidation reaction of **1**, the assignment of stereochemistry to *cis*-**6** is thereby confirmed. Close spectral similarity between *cis*-**6** and the major products from the other co-oxidation reactions strongly suggests that they also possess cis stereochemistry.

The conclusion that alkylperoxy radicals of type **3** preferentially afford cis-disubstituted cyclic products is fully consistent with the behavior of closely related carbon-centered radicals,[5] and has important implications for prostanoid synthesis and biosynthesis since it is only through intermediates of cis orientation that prostaglandin endoperoxides can be constructed.

Acknowledgment. We thank the Commonwealth of Australia for a Commonwealth Postgraduate Research Award (to R.W.) and the Australian Research Grants Committee for financial support.

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Metal-to-Metal Triple Bonds—to Cluster or Not to Cluster? Structural Characterization of Octakis(*tert*-butoxy)tetrakis(μ-fluoro)-tetramolybdenum and Octakis(*tert*-butoxy)tris(μ-fluoro)-(μ-dimethylamido)-tetramolybdenum

Sir:

We note that the chemistry of molybdenum and tungsten in the +3 oxidation state is currently dominated by compounds containing the central $(M{\equiv}M)^{6+}$ unit.[1] This is in contrast to the coordination chemistry of Cr(3+) which has a marked propensity to form octahedral complexes.[2] Furthermore, tetranuclear complexes of molybdenum and tungsten in the +3 oxidation state in which there is a central tetrahedral M_4 skeleton with delocalized M—M bonding are relatively rare.[3] Thus we have been trying to establish an equilibrium of the type expressed in (eq 1) below since it seemed plausible that,

(1)

for a given ligand X, or combinations of ligands X and Y, such an equilibrium could be established.[4] We report herein the structural characterization of two novel tetranuclear complexes of molybdenum formed by the coupling of two dinuclear species, $(M{\equiv}M)^{6+}$

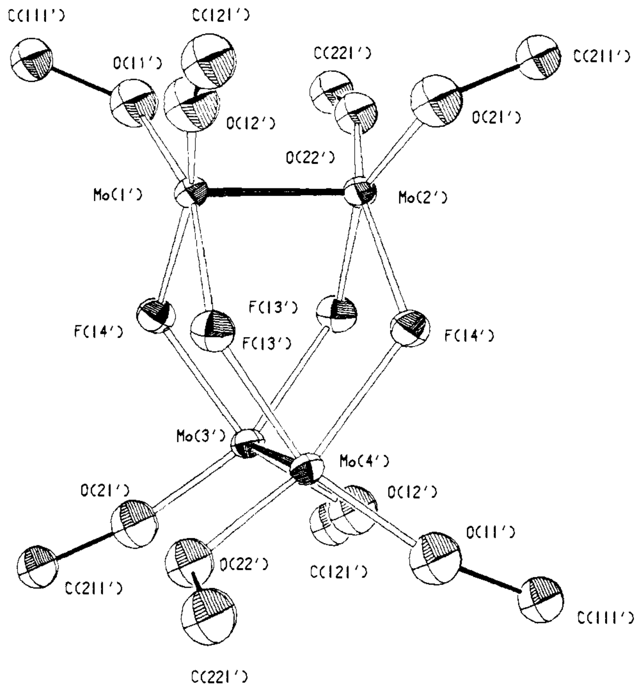

Figure 1. An ORTEP view of the central $Mo_4(\mu\text{-}F)_4(OC)_8$ skeleton of the $Mo_4(\mu\text{-}F)_4(OBu^t)_8$ molecule showing the atomic numbering scheme used in Table I. All atoms are represented by 50% thermal ellipsoids. A center of symmetry is located in the center of the molecule and the four alternate molybdenum positions have been removed for clarity.

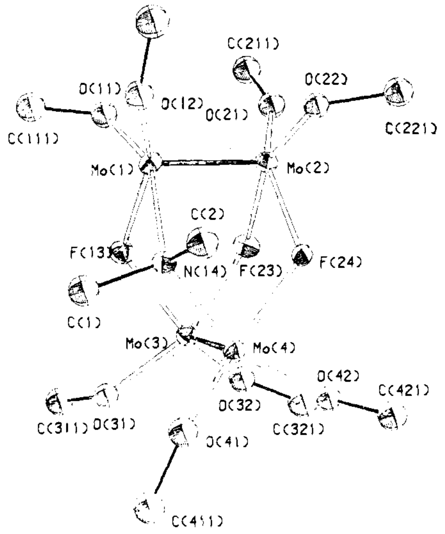

Figure 2. An ORTEP view of the central $Mo_4(\mu\text{-}F)_3(\mu\text{-}NC_2)(OC)_8$ skeleton of the $Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8$ molecule showing the atomic numbering scheme used in Table II. All atoms are represented by 50% thermal ellipsoids.

Addition of PF_3 (2 equiv) to a hydrocarbon solution of $Mo_2(OBu^t)_6$ (M≡M) leads to a F- for -OBu^t exchange reaction in a similar manner to that previously reported in the preparation of $Mo_2Cl_2(NMe_2)_4$ from $Mo_2(NMe_2)_6$ and Me_3SiCl (2 equiv).[5] The resulting black, air-sensitive, hydrocarbon-soluble solid of empirical formula $MoF(OBu^t)_2$ is, however, tetranuclear unlike $Mo_2Cl_2(NMe_2)_4$ (M≡M). In one preparation of this new molybdenum compound, crystals suitable for detailed X-ray work were grown from a hexane solution.

A preliminary solution of an X-ray data set collected at room temperature indicated that there were three Mo_4-containing molecules in the unit cell.[6] One molecule was disordered about the origin but refined well as $Mo_4(\mu\text{-}F)_4(OBu^t)_8$. See Figure

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