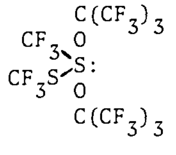
Two Stable Thiosulfuranes, $CF_3(CF_3S)S[OC(CF_3)_3]_2$ and $C_6F_5(C_6F_5S)S[OC(CF_3)_3]_2$

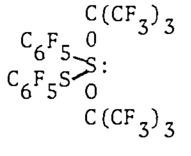
Sir:

Recently, Gombler[1] reported the synthesis of the first stable perfluoroalkyl-containing compound in which three-coordinate sulfur(IV) is bonded to sulfur(II), $CF_3S(O)SCF_3$. The considerable interest in syntheses of this type of compound is indicated by the number of unsuccessful attempts noted in the literature.[2-5]

In our continuing study of fluorinated sulfuranes, we now have been able to prepare two stable thiosulfuranes in which four-coordinate sulfur(IV) is bonded to sulfur(II).



A



B

Bis(trifluoromethyl)disulfane (1 mmol) and perfluoro-*tert*-butyl hypochlorite (2.3 mmol) were condensed into a Pyrex vessel at −196 °C and allowed to remain at 0 °C for 72 h. After all of the volatile materials were removed under dynamic vacuum at 0 °C, a colorless involatile liquid, trifluoromethyl(trifluoromethylthio)bis(nonafluoro-*tert*-butoxy)sulfurane (A), remained. It is stable indefinitely when stored under anhydrous conditions in Pyrex glass at 25 °C. However, in the presence of water at 25 °C, hydrolysis occurs:

$$A + H_2O \rightarrow CF_3SO_2SCF_3 + CF_3SSCF_3 + (CF_3)_3COH.$$

The hydrolysis products were separated by using trap-to-trap techniques and identified from their infrared spectra.

Spectroscopic data further support the existence of this new sulfurane (A). The ^{19}F nuclear magnetic resonance spectrum shows resonances at ϕ 59.2 (nonadectet; J = 1.5 Hz) assigned to $CF_3S(IV)$, 71.4 (q, $OC(CF_3)_3$), and 74.9 (s, $CF_3S(II)$). The peak area ratio is 1:6:1. The infrared spectrum has absorption bands at 1250 (s, br), 1235 (w), 1225 (w), 1191 (m-s), 1153 (s), 1100 (s), 978 (s), 965 (s), 767 (m), 758 (m), 734–732 (s), 692 cm^{-1} (w). A molecular ion is not observed. However, appropriate fragment peaks, such as *m/e* 546 ($(M - CF_3 - 3F)^+$), 364 ($[(CF_3)_2COSOC(CF_3)_2]^+$), 352 ($[(CF_3)_3COS(CF_3)O]^+$), 283 ($[(CF_3)_3COSO]^+$), and 218 ($[CF_3S(SCF_3)O]^+$). Anal. Calcd for $C_{10}O_2S_2F_{24}$: C, 17.86. Found: C, 17.70.

Two millimoles of perfluoro-*tert*-butyl hypochlorite was condensed onto 0.0358 g (~0.9 mmol) of $C_6F_5SSC_6F_5$ and allowed to warm to 0 °C. After a 24 h at 0 °C, the volatile components were removed under dynamic vacuum. The involatile yellow liquid which remained was exposed to extended pumping. The slightly yellow pentafluorophenyl(pentafluorophenylthio)bis(nonafluoro-*tert*-butoxy)sulfurane (B), although stable in Pyrex glass, is sensitive to hydrolysis. When it is allowed to stand at 25 °C for 4 h with an excess of water, $(CF_3)_3COH$ is recovered quantitatively. The involatile yellow residue formed was identified by mass spectra as $C_6F_5SSC_6F_5$ (*m/e* 398) and $C_6F_5SO_2SC_6F_5$ (*m/e* 430; $C_6F_5SO_2S$, *m/e* 263).

Spectroscopic data support this new sulfurane (B). The high resolution ^{19}F nuclear magnetic resonance spectrum is complex. It is apparent that both C_6F_5 groups and both $(CF_3)_3CO$ groups are nonequivalent. The fact that all four substituents on the sulfur are chemically nonequivalent arises from the oxidative addition of two $(CF_3)_3CO$ to only one of the sulfur atoms which immediately causes the C_6F_5 groups to exist in unlike chemical environments. Free rotation of three such massive substituents on the sulfur is hindered which causes the $(CF_3)_3CO$ groups to become nonidentical. Integration of the low resolution spectrum shows $(C_6F_5)_1:(C_6F_5)_2:[(CF_3)_3CO]_1:[(CF_3)_3CO]_1$ = 5:5:9:9. The infrared spectrum has bands at 1649 (ms), 1511 (s), 1491 (vw), 1410 (w), 1278 (vs), 1180 (w), 1160 (w), 1106 (w), 1000 (vs), 870 (w), 820 (m), 782 (m), 745–739 cm^{-1} (s). A molecular ion (*m/e* 868, M^+) is observed in the mass spectrum as well as appropriate fragment peaks, such as *m/e* 849 ($(M - F)^+$), 669 ($(M - C_6F_5S)^+$), 649 ($[M - C(CF_3)_3]^+$), 663 ($[M - OC(CF_3)_3]^+$), 450 ($[M - C(CF_3)_3 - C_6F_5S]^+$), 434 ($[M - OC(CF_3)_3 - SC_6F_5]^+$), 398 ($[M - 2OC(CF_3)_3]^+$). Anal. Calcd for $C_{20}O_2S_2F_{28}$: C, 27.65; F, 61.3. Found: C, 26.17; F, 59.7.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

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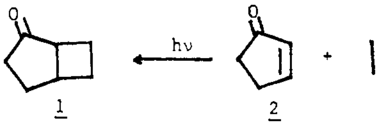
Copper(I) Catalysis of Olefin Photoreactions. 8. A Stepwise Olefin Metathesis Synthesis of Cyclopent-2-en-1-ones via Photobicyclization of 3-Hydroxyhepta-1,6-dienes[1]

Sir:

The most useful conventional approach for synthesis of bicyclo[3.2.0]heptan-2-ones **1** involves photocycloaddition of cyclopent-2-en-1-ones **2** with alkenes.[2] We report here an effective new method for the preparation of **1** involving photobicyclization of 3-hydroxy-1,6-heptadienes. This development also provides a useful new synthesis of cyclopentenones since thermal fragmentation of **1** proceeds cleanly to afford **2**.



Photocycloadditions of allylic alcohols and ketones are of synthetic interest since the products bear activating functionality which can facilitate useful transformations involving cleavage of the cyclobutane ring. Although direct irradiation of 1,5-hexadien-3-one gives bicyclo[2.1.1]hexan-2-one in fair yield,[3] direct irradiation of the homologous 1,6-heptadien-3-one does not result in photobicyclization, only polymer being

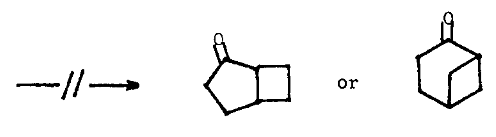


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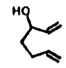
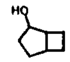
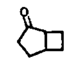
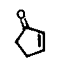
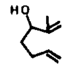
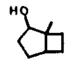
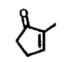
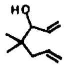
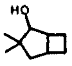
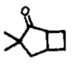
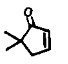
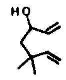
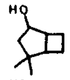
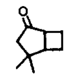
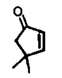
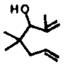
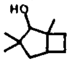
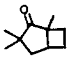
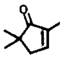
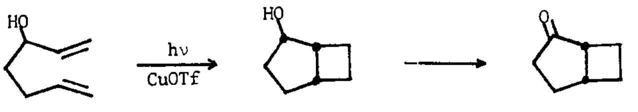
Table I. Synthesis of Cyclopentenones via 3-Hydroxy-1,6-heptadienes

ENTRY	HYDROXYDIENE 3 (% yield)*	BICYCLOHEPTANOL 4 (% yield)*	BICYCLOHEPTANONE 5 (% yield)*	CYCLOPENTANONE 6 (% yield)
a	 (73)	 (86)	 (78)	 (70)
b	 (82)	 (81)	 (67)	 (72)
c	 (86)	 (91)	 (92)	 (78)
d	 (67)	 (84)	 (92)	 (87)
e	 (86)	 (83)	 (93)	 (54)

* Yields are of pure products isolated by distillation.

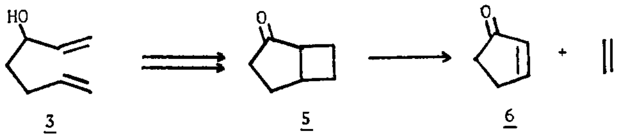
formed.[4] In contrast, although 1,5-hexadien-3-ol is inactive,[5] we now find that photobicyclization of 1,6-heptadien-3-ols **3** in the presence of copper(I) trifluoromethane sulfonate[1a,6] (CuOTf) is a clean, high yield (81–91%) new method for synthesis of bicyclo[3.2.0]heptan-2-ols **4** (Table I).[7,8] This development has fundamental significance for synthetic applications of these compounds and their derivatives which were not so readily available previously. No reaction occurs in the absence of Cu(I), but <1 mole % of catalyst is required. The photobicyclization products **4** are readily oxidized to afford bicyclic ketones **5**.



3a 4a 5a

Previous methodology for synthesis of bicyclo[*m*.2.0]alkan-2-ones relies on a structurally different dissection of the carbon skeleton. Thus, photocycloaddition of cycloalkenones with olefins provides bicyclic ketones in fair yields.[2,9] For example, bicyclo[3.2.0]heptan-2-one (**5a**) is obtained, after a difficult distillation, by photolysis of a dichloromethane solution of cyclopent-2-en-1-one while ethylene is bubbled through the reaction mixture.[10] Of course, this approach is limited by the availability of the requisite cycloalkenone and has no value for synthesis of cycloalkenones *via* stepwise metathesis (vide infra).

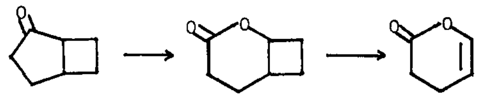
Bicyclo[3.2.0]heptanones are generally recognized as versatile synthons.[11] Our new copper-catalyzed photobicyclization approach is often the method of choice for synthesis of these compounds. Thus, photobicyclization followed by oxidation affords bicyclo[3.2.0]heptan-2-one (**5a**) in 67% overall yield (see Table I) compared with 30% from cyclopentenone. Furthermore, the carbonyl group in **5** should facilitate homolysis of the 1,5 or 1,7 C–C bonds.[12] In fact, thermal fragmentation of bicyclo[3.2.0]heptan-2-ones **5** proceeds cleanly to afford cyclopent-2-en-1-ones **6** upon passage through a quartz tube packed with quartz chips which is heated to 580 °C. The overall process, **3** → **6**, provides the first examples of a novel stepwise olefin metathesis approach to cycloalkene synthesis.



3 5 6

One particularly effective synthesis of the requisite dienols **3** involves reaction of vinyl organometallics with 4-pentenals which are readily available via Claisen rearrangement of allyl vinyl ethers.[13]

Baeyer–Villager oxidation of **5a** with *m*-chloroperbenzoic acid in 1,2-dichloroethane affords **7** (93%, bp 135 °C (15 mm)). The importance of a neighboring carbonyl group for facile fragmentation of the cyclobutyl ring is underscored by the refractoriness of **7**. Only traces of fragmentation occurs at 580 °C, but **7** undergoes 59% conversion at 620 °C to afford **8** (50%).



5a 7 8

The procedure for a stepwise metathesis is illustrated by the preparation of 5,5-dimethylcyclopent-2-en-1-one (**6c**), an important synthon for the antitumor sesquiterpene, illudin M.[14] Hydroxydiene **3c** (0.17 mol) in ether (200 mL) with (CuOTf)$_2$·C$_6$H$_6$ (0.4 g) is irradiated for 21 h in a cylindrical Pyrex vessel with an internal 450-W Hannovia mercury vapor lamp in a water-cooled quartz well. The resulting solution is poured into a mixture of ice (100 g) and concentrated NH$_4$OH (100 mL). The aqueous phase is extracted with ether (100 mL) and the combined organic extracts are washed with saturated aqueous NaCl (100 mL) and dried (Na$_2$SO$_4$). Distillation provides **4c** (18.5 g, bp 85–89 °C (12 mm)). Oxidation of **4c** in acetone with Jones reagent affords ketone **5c** (92%, bp 73–75 °C (12 mm)).

A stream of nitrogen (25–30 mL min^{-1}) is passed through a vertical quartz column (30 cm) packed with quartz chips and heated at 600 °C. The ketone **5c** is added dropwise (0.1 mL min^{-1}) with a Sage syringe pump at the top of the column. The product which is trapped in a receiver cooled to −78 °C is distilled to give analytically pure **6c** (78%, bp 155–160 °C) and recovered **5c** (11%). The overall yield (65%) compares favorably with the best previous synthesis which gives **6c** (40%) from 2,2-dimethylpent-4-enoic acid.[15]

Acknowledgment. We thank the National Science Foundation for generous support of our investigations on homogeneous catalysis in organic synthesis. Also acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of our research on homogeneous transition metal catalysis of organic photochemical reactions.

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(7) The stereochemical course of this reaction, which yields almost exclusively the cis-fused cis alcohol **4a** from **3a**, will be discussed in the full paper.

(8) Satisfactory elemental analyses were obtained for all new compounds which were characterized structurally by ^{1}H NMR spectra and conversion into the known cyclopentenones **6**.

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Received February 26, 1979

Sodium Tetramolybdenum Hexoxide ($NaMo_4O_6$). A Metallic Infinite-Chain Polymer Derived by Condensation of Octahedral Clusters

Sir:

Recently there has been intense activity in the study of metal-metal bonded compounds of molybdenum, which cover the range from discrete dimers with $\mathrm{Mo}\overset{n}{—}\mathrm{Mo}$ bonds of order 1 to 4,[1] to the larger cluster units containing three,[2] four,[3-5] five,[6] and six metal atoms. A particularly important family of compounds, known generally as Chevrel phases,[7] incorporate the discrete Mo_6X_8 cluster unit with X = S, Se, and Te. Representative of this family are Mo_6Se_8, $PbMo_6S_8$, and $Mo_6S_6I_2$, all having the same basic solid-state structure and interesting properties as superconductors with high critical temperature and magnetic field values.[7] We report here the synthesis and structure of the compound $NaMo_4O_6$ which contains octahedral cluster units welded on opposite edges to form linear chains.

This new compound represents the result of condensation of cluster units, a consequence of progressive lowering of nonmetal/metal ratio. One way to achieve lower nonmetal/metal ratios is by substitution of divalent nonmetal atoms for monovalent atoms in the structure. For example, by substitution of chalcide atoms for halogens in the molybdenum(II) halides $(Mo_6X_8)X_2X_{4/2}$, the ligand/metal ratio is decreased and the Mo_6X_8 cluster units become more closely coupled together through filling the "exo" coordination sites of one cluster unit by the nonmetal atoms of neighboring cluster units, as represented by the formulation[8] $(Mo_6S_2{}^{i}S_{6/2}{}^{i-o})S_{6/2}{}^{o-i}$ for the compound Mo_6S_8. This close coupling of the Mo_6S_8 cluster units combined with electron delocalization leads to the interesting solid-state properties observed (vide supra). Continued lowering of the nonmetal/metal ratio for Mo_6X_8 clusters can be viewed conceptually as causing condensation of the cluster units via sharing of both nonmetal and metal atoms, thereby resulting in fusion of adjacent clusters to form chain and sheet structures. In halide compounds, examples of such condensed cluster systems have been reported recently by Corbett and Simon, e.g., in the structures of Gd_2Cl_3,[9] ZrCl,[10] GdCl,[11] TbCl,[11] Sc_5Cl_8,[12] and Sc_7Cl_{10}.[13] The structure of Gd_2Cl_3 contains extended chains of condensed octahedral clusters derived from the M_6X_8 unit,[14] as represented by the formulation $Gd_2Gd_{4/2}Cl_4Cl_{4/2}$, whereas in the structure of Sc_5Cl_8 the extended chains are formed by condensation of M_6X_{12} units,[12] as represented in the anion of the formula $[ScCl_2{}^+][Sc_2Sc_{4/2}Cl_2Cl_{8/2}{}^-]$, the first example of this mode of condensation. The structure of $NaMo_4O_6$, described below as a second example of M_6X_{12} cluster condensation, provides evidence that the range of compounds with such structures may extend over numerous metal-nonmetal combinations.

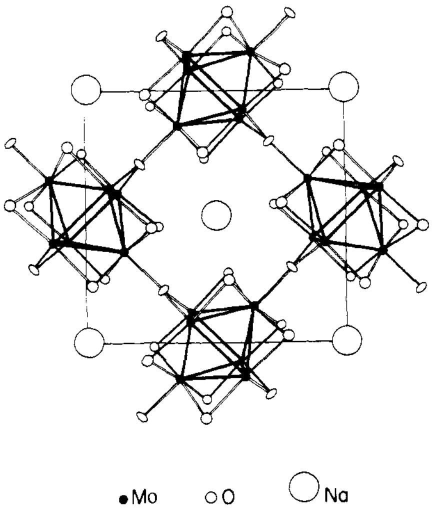

Figure 1. The structure of $NaMo_4O_6$ as viewed down the *c* axis of the tetragonal crystal. All atoms occupy positions in mirror planes at $z = 0$ or $z = \frac{1}{2}$.

This new ternary oxide was first detected as one product resulting from reaction of Na_2MoO_4, MoO_2, and ZnO (in 1:5:2 mole ratio, respectively) in a sealed molybdenum tube at 1100 °C; the other identified product was the well-known compound $Zn_2Mo_3O_8$.[15] The new compound grew from the surface of the pressed reaction mixture and container walls as thin whiskers with metallic luster. Electron microprobe analysis of the whiskers established that Na and Mo were the only metallic elements present. By viewing crystals on a hot-stage microscope, it was determined that the compound is stable in air up to at least 300 °C. A rough two-probe measurement showed that the crystals were moderately good electrical conductors.

A single crystal selected from this reaction provided excellent X-ray diffraction data from which both the composition and structure were established.[16,17] Once again nature has provided a structure remarkable in its complexity, yet beautiful in its ultimate simplicity and symmetry. The 22 atoms in the tetragonal unit cell all are located in mirror planes at $z = 0$ or $z = \frac{1}{2}$ with the repeat distance along the *c* axis of only 2.860 (1) Å. A view of the structure along the *c* axis is given in Figure 1, from which it can be discerned that the Na^+ ions occupy sites in channels formed by four metal oxide cluster chains cross-linked by metal-oxygen bonds. A view of one of the chains which are extended parallel to the *c* axis is provided in Figure 2. The architecture of the chains is comprised of clusters of the type Mo_6O_{12} fused at opposite edges by removal of two edge-bridging O atoms and sharing of the metal atoms on those edges between cluster units, as indicated by the formulation $Na^+[Mo_2Mo_{4/2}O_2O_{8/2}{}^-]$. Thus the structure of these chains is exactly the same as that in the anion component of $[ScCl_2{}^+][Sc_4Cl_6{}^-]$. However, because of the greater number of valence electrons available per repeat unit for metal-metal bonding in the Mo chains, viz., 13 in $[Mo_4O_6{}^-]$ vs. 7 in $[Sc_4Cl_6{}^-]$, the metal-metal bonds are stronger and closer to being equivalent over the various edges of the octahedral units. The individual Mo-Mo bond distances, 2.751 (3) (1x), 2.860 (1) (4x), and 2.778 (2) (8x)Å within the repeat unit, result in an average distance of 2.801 Å, which is only 0.076 Å longer than the distance between nearest neighbors in bcc molybdenum metal. Each O atom is strongly bonded to three Mo atoms at distances of 2.014 (8) to 2.067 (8) Å, with the shortest of these involving the O atoms bridging between chains.

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