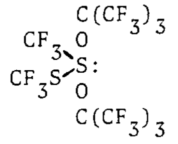
Two Stable Thiosulfuranes, $CF_3(CF_3S)S[OC(CF_3)_3]_2$ and $C_6F_5(C_6F_5S)S[OC(CF_3)_3]_2$

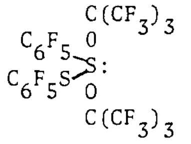
Sir:

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.

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References and Notes

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(6) On leave from Department of Chemistry, Marshall University, Huntington, W.Va.

Qui-Chee Mir, Daniel P. Babb,[6] Jean'ne M. Shreeve*
Department of Chemistry, University of Idaho
Moscow, Idaho 83843

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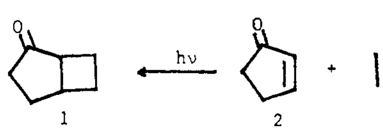
Copper(I) Catalysis of Olefin Photoreactions. 8. A Stepwise Olefin Metathesis Synthesis of Cyclopent-2-en-1-ones via Photobicyclization of 3-Hydroxyhepta-1,6-dienes[1]

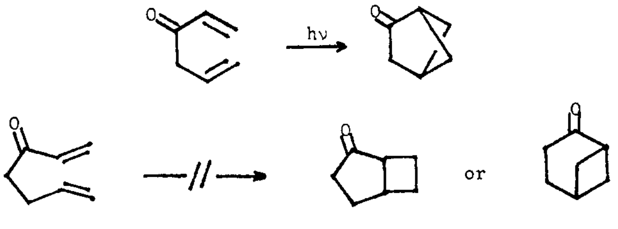
Sir:

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.**



1 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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