Limiting structures for 1,2-cyclohexadiene (**1** and **2**) contain twisted or planar bent allene moieties with overall C_2 or C_s molecular symmetry. Initial MNDO calculations[9] predicted **1** to be 1.5 kcal/mol lower than **2**. Calculations at various levels of ab initio theory were then performed. Geometries were optimized at the SCF level within appropriate (C_2 or C_s) symmetry contraints for the 1^1A state of **1** and the $1^1A''$ state of **2**, by using an analytical gradient procedure and an STO-3G basis set;[10] results are shown in Figure 1. The allenic hydrogens are bent in opposite directions 30° out of the plane defined by the allenic carbons, with significant rehybridization at C_1 and C_3. Energies and resulting energy differences are given in Table I. At the STO-3G level, **2** is predicted to be 4.4 kcal/mol below **1**. This basis set has some well-known deficiencies with respect to π bonding,[11] and although we expect geometries to be reliable, absolute energies are suspect. Calculations with the more flexible 3-21G basis set[12] reversed this ordering, predicting **2** to be 3.5 kcal/mol above **1**. Although this qualitatively agrees with experiment, it seemed unlikely that single-determinant SCF calculations could accurately predict the energy difference between the closed shell **1** and open shell species **2**, the latter having one less electron pair. To assess this difference, we applied the full optimized reaction space (FORS) approach of Ruedenberg and co-workers.[13] These MCSCF calculations include configurations generated by distributing the four electrons intimately involved in the inversion, within the π MO's and the in-plane hybrid at C_2.[14] As expected, the FORS-MCSCF calculations recovered more correlation energy for **1** (1.86 eV) than for **2** (1.38 eV), increasing their difference to 13.1 kcal/mol. We thus conclude that 1,2-cyclohexadiene should have a chiral equilibrium geometry.

The origins of the energy difference between **1** and **2** are of some interest. The C_1–C_2 length in **1** is significantly shorter than that in **2**, which suggests some recovery of π bonding in **1**. Increased π bonding in **1**, relative to **2**, is due to interaction of the nonbonding allyl-like MO of **2** with the σ sp^2 hybrid on C_2, as C_1 and C_3 are rehybridized. However, this rehybridization also results in a loss of π bonding in the lowest lying allyl-like MO, due to nonplanarity. The net energy gain in **1** over **2** at the SCF level is thus rather minimal, and the ultimate barrier is due primarily to correlation energy differences, as shown through MCSCF calculation.

Calculations also were performed for the lowest C_s closed shell state ($1^1A'$, corresponding to **3**) and the C_s triplet ($1^3A''$). With an STO-3G basis, the zwitterion **3** ($1^1A'$) is predicted to be 4.46 eV higher in energy than **1** ($1^1A''$). The triplet diradical proved only slightly lower (2.06 kcal/mol) than the singlet, which implies that the triplet lies ca. 11 kcal/mol above closed-shell **1**, if electron correlation were included.

In conclusion, these calculations should resolve some important theoretical questions concerning the structure of 1,2-cyclohexadiene, including its experimentally demonstrated chirality.[3] The ground-state potential surface has a well-defined minimum corresponding to **1**, closely connected to diradical **2**, while zwitterions **3** and **4** are excited states. We speculate that **1** might be trapped and observed under matrix isolation conditions.[15]

Acknowledgment. The present work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Ames Laboratory, U.S. Department of Energy, operated by Iowa State University under Contract W-7405-Eng-82, with the research support of the Director of Energy Research, Office of Basic Energy Science, WPAS-KD-01-03-01-2.

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(7) R. P. Johnson and B. Lam, to be submitted for publication. MCSCF calculations on C_{2v} planar allene show an open-shell diradical corresponding to **2** to be the singlet ground state, with zwitterions such as **3** and **4** much higher in energy; cf. ref 8.

(8) A C_{2v} bent diradical has been predicted to correspond to the barrier to rotation in allene: Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103.

(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1976**, *99*, 4907.

(10) Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog, 1 Prog. No. QG01, GAMESS, 1980; Vol. 1.

(11) (a) Newton, M. D. In "Applications of Electronic Structure Theory"; Schaefer, H. F., III, Ed., Plenum Press: New York, 1977; Chapter 6, p 223. (b) As pointed out to us by Professor Joel Liebman, greater stabilization (45–50 kcal/mol) accrues on introduction of the extended basis set on carbons 1–3 than on carbons 4–6. This is due to the fact that the STO-3G basis underestimates the stability of π bonds more than that of σ bonds. Similar trends are observed in comparison of literature values for ethane vs. ethylene. Optimization with an extended basis set undoubtedly would improve our geometry somewhat, but we doubt that changes in total energy would be significant.

(12) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(13) Feller, D. F.; Schmidt, M. W.; Ruedenberg, K. *J. Am. Chem. Soc.* **1982**, *104*, 960 and references therein.

(14) The full 3-21G basis proved too large for the MCSCF calculations, thus for these calculations, the split valence 3-21G basis was used only on the three carbons and two hydrogens of the allene moiety, while the minimal STO-3G basis was applied for the C_3H_6 skeleton. This combined basis is denoted 3-21G and STO-3G.

(15) See, for example: West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779.

Construction of Bridging Organosulfur Ligands in Hexacarbonyldiiron Complexes via Proximity-Induced Reactions of Bis(μ-mercapto)bis(tricarbonyliron) with α,β-Unsaturated Substrates

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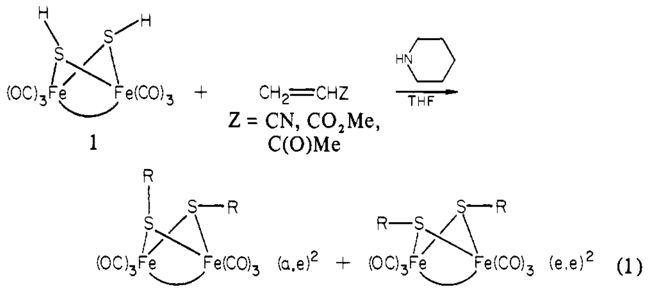
We have reported that bis(μ-mercapto)bis(tricarbonyliron), **1**, undergoes base-induced addition to terminally unsubstituted α,β-unsaturated substances such as acrylonitrile, methyl acrylate, and methyl vinyl ketone (eq 1).[1] Since this apparently general reaction has the potential of being a useful synthetic route in organosulfur chemistry,[3] we have examined base-induced reactions of **1** with other olefinic and with acetylenic α,β-unsaturated systems. We report our preliminary findings at this time since some novel and potentially useful reactions have been discovered in which cyclic bridging organosulfur ligands have been formed as a result of the proximity of the two μ-HS functions in the molecule.[4]



Like the terminally unsubstituted α,β-unsaturated systems, those with only one substituent (e.g., *trans*-3-penten-2-one, 2-cyclo-

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(1) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *218* C34.

(2) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

(3) Note the useful sulfur ligand release reactions (to give disulfides, sulfides and mercaptans) reported by Russian workers: Nametkin, N. S.; Tyurin, V. D.; Kukina, M. A. *J. Organomet. Chem.* **1978**, *149*, 355.

(4) In (μ-EtS)$_2$Fe$_2$(CO)$_6$ (a,e isomer) the S···S distance is 2.93 Å: Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 328.

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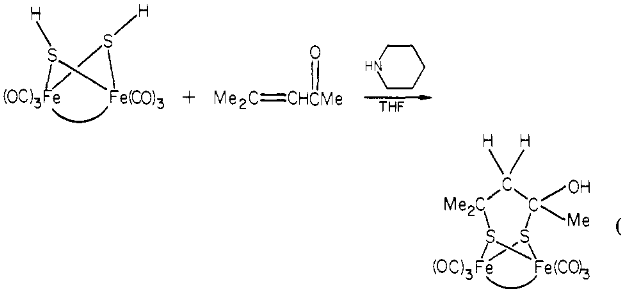
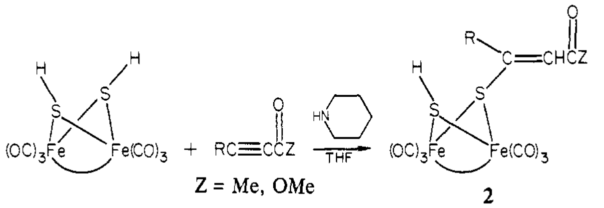
hexenone, methyl crotonate, and diethyl maleate) reacted with **1** in the presence of piperidine to form 2:1 adducts. Thus, 2-cyclohexenone and *trans*-3-penten-2-one gave 2:1 adducts in yields of 70% and 62%, respectively.[5] These compounds can exist as a,e and e,e isomers, and these were observed to be present in those cases where either ^{1}H or ^{13}C NMR spectroscopy allowed a distinction between them. In contrast, α,β-unsaturated ketones in which the terminal carbon atom is disubstituted were found to react in an unprecedented manner to give a 1:1 adduct, as shown in eq 2 for the case of mesityl oxide. In effect, not only has one SH group added to the C=C bond but the other SH group has added to the carbonyl function, and a three carbon atom bridge between the two sulfur atoms has been formed. Similar reactions were observed with EtMeC=CHC(O)Et and cyclohexylideneacetone but not with 3-methyl-2-cyclohexenone. The alcohol products proved to be difficult to purify, but conversion to the trimethylsilyl ethers (via $(Me_3Si)_2NH/Me_3SiCl$) gave easily purified red solid products. Such a reaction was not observed with $Me_2C{=}CHCO_2Me$. Apparently such HS addition to the ester C=O group does not occur.



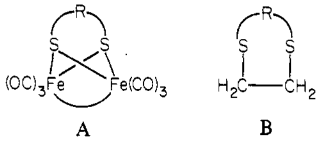
(2)

The addition of **1** to an acetylenic α,β-unsaturated carbonyl compound in the first step will result in formation of a vinyl derivative, **2**, as shown in eq 3. Intramolecular addition of the remaining HS function to the vinyl group should be very favorable because of the close proximity of the two thio bridges in the complex.[4] Addition could occur at the α- or the β-carbon atom. Which mode of addition occurs depends on the substituents on the C=C carbon atom of **2**. Reaction of **1** with a 5-fold excess of dimethyl acetylenedicarboxylate in THF in the presence of triethylamine (−78 °C to start, with warming to room temperature), gave a red solid product, mp 119–120 °C, in 68% yield. Its ^{1}H NMR spectrum (CDCl$_3$) showed two singlets at δ 3.71 (CH) and 3.77 (OCH$_3$), its ^{13}C NMR spectrum a quartet at δ 53.1 (J = 148 Hz, OCH$_3$), a doublet at δ 54.9 (J = 147 Hz, C–C), and singlets at δ 169.0 (ester C=O) and 206.9 (Fe(CO)$_3$). These data indicate structure **3**; i.e., vicinal addition has taken place to give the *trans* isomer.



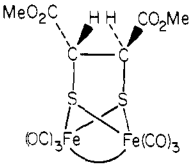
(3)

Table I. ^{1}H and ^{13}C NMR Data for Methylene- and Ethylene-Bridged Dithio Compounds of Types A and B

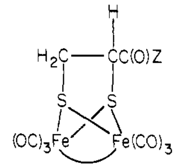


no.	bridge (R)	compd type	δ bridge protons	 bridge carbons
1	CH_2	A	4.64	62.35[a]
2	CH_2CH_2	A	2.45	36.1
3	$MeO_2CCHCHCO_2Me$	A	3.71	54.9
4	$CHCH_2CO_2Me$	A	5.07	72.6
5	$CHCH_2C(O)Me$	A	5.02	72.3
6	$MeCCH_2C(O)Me$	A		82.3
7	CH_2	B	3.81[b] (CH_2) 3.11 (CH_2CH_2)	34.5[c] (CH_2) 38.1 (CH_2CH_2)
8	MeCH	B	4.52[b] (Me*CH*) 3.15, 3.25 (CH_2CH_2)	48.1[c] (MeCH) 39.1 (CH_2CH_2)
9	PhCH	B	5.52[b] (Ph*CH*) 3.27, 3.42 (CH_2CH_2)	

[a] Data from: Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* 1979, *101*, 1313. [b] Data from: Sternson, L. A.; Coviello, D. A.; Egan, R. S. *Ibid.* 1971, *93*, 6529. [c] Data from: Hoppmann, A.; Weyerstahl, P.; Zummack, W. *Liebigs Ann. Chem.* 1977, 1547.

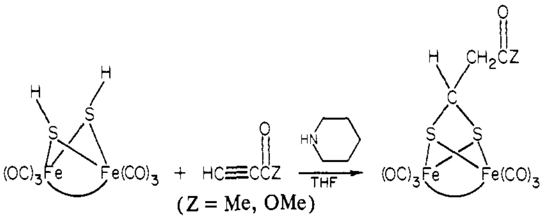


3



4

Terminal acetylenes bearing ester or acyl substituents, as well as MeC≡CC(O)Me, reacted to give products with a one carbon atom bridge (eq 4). Proton and ^{13}C NMR spectroscopy were used to establish the indicated structure. Table I gives relevant NMR chemical shifts for the bridged products prepared in this study from α,β-unsaturated acetylenes as well as for some model compounds. It is seen that chemical shifts of the bridging carbon atoms and of attached protons in the methylene-bridged compounds are downfield with respect to those in two-carbon ethylene-bridged compounds (model compound entries 1, 5, 7–9). On this basis it is likely that products whose structure is in question (entries 2 and 3) contain methylene rather than ethylene bridges. Furthermore, an ethylene-bridged structure, **4**, resulting from vicinal rather than geminal diaddition in the case of these two compounds, would contain a chiral carbon atom which would be expected to result in diastereotopic CH$_2$ protons and hence slightly more complicated and different proton NMR spectra.



(4)

The structure determination of the MeC≡CC(O)Me-derived product was unambiguous. Its proton NMR spectrum showed singlets at δ 1.89 (3 H), 2.13 (3 H), and 3.21 (2 H). Its proton-coupled ^{13}C NMR spectrum showed signals at δ 30.7 (q, J

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(5) A typical procedure: $(\mu\text{-HS})_2Fe_2(CO)_6$ was prepared at −78 °C from 2.91 mmol of $(\mu\text{-S}_2)Fe_2(CO)_6$ in 50 mL of THF.[1] Then 1.46 mL (15 mmol) of *trans*-3-penten-2-one and 0.5 mL (5.05 mmol) of piperidine were added successively. The reaction mixture was stirred at −78 °C for 30 min and overnight at room temperature. The solvent then was removed at reduced pressure, leaving a brown oil which was chromatographed (silicic acid/dichloromethane). A red band that was eluted yielded, after removal of solvent, 1.27 g of a red oil. Further column chromatography silicic acid; 3:1 (by volume) CH$_2$Cl$_2$/pentane) of this oil gave a yellow band (trace of brown solid, not identified), an orange band (0.118 g of red oil, a mixture (by NMR) of product and organic impurities), and a red band (0.928 g, 62%) of the expected product, a slighlty air-sensitive red oil. Catalytic amounts of piperidine (e.g., 0.06 mmol) suffice, but generally we have used near-stoichiometric quantities. This compound and all other new compounds prepared in this study were characterized by their combustion analyses and their IR and NMR (always ^{1}H, often also ^{13}C) spectra.

(6) Hieber, W.; Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91.

= 128 Hz, CH_3), 38.1 (q, J = 132 Hz, C(O)CH_3), 62.7 (t, J = 128 Hz, CH_2), 82.3 (s, S-C-S), 201.8 (s, ketone C=O), 208.1, and 208.2 (s, $Fe(CO)_3$). These data can be rationalized only in terms of the methylene-bridged structure shown in Table I.

It is clear from these results that the $Fe_2(CO)_6$ system is a useful template for the designed construction of cyclic organosulfur ligands. In the Michael-type addition which is the subject of the present communication, activating functional groups (CO_2R, CN, C(O)R, etc.) must be present. Whether a one-carbon, two-carbon, or a three-carbon bridge is formed between the two sulfur atoms depends upon the type and the substitution pattern of the α,β-unsaturated substrate that is used. Clearly, further variations are possible.

Further work based on this novel concept for organosulfur compound synthesis is in progress.

Acknowledgment. We are grateful to the National Science Foundation for support of this work and to R. M. Weinstein and M. K. Gallagher for assistance in obtaining NMR and mass spectra.

Copper(I) Catalysis of Olefin Photoreactions. 11. Synthesis of Multicyclic Furans and Butyrolactones via Photobicyclization of Homoallyl Vinyl and Diallyl Ethers[1]

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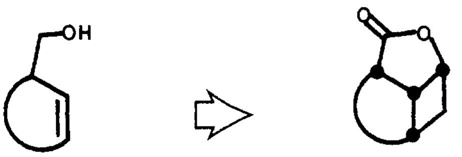
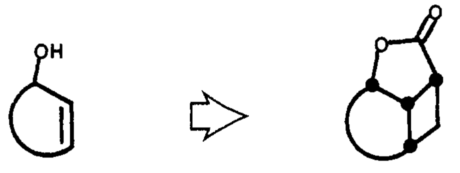
Received July 12, 1982

Since functional substituents enhance the potential synthetic utility of olefin photoreactions,[2] we are exploring photobicyclization of unsaturated ethers.[5] We now report that copper(I) trifluoromethanesulfonate (CuOTf) catalyzes intermolecular photocycloadditions of homoallyl vinyl ethers to produce 2-oxabicyclo[3.2.0]heptanes. In conjunction with remarkably selective ruthenium-catalyzed oxidation of these tetrahydrofuran derivatives, the new photoreaction provides a novel annulation of multicyclic butyrolactones that incorporate a cis-fused cyclobutane ring, e.g., eq 1. Similar annulations, e.g., eq 2, are also reported that involve 3-oxabicyclo[3.2.0]heptane intermediates generated by copper(I)-catalyzed photobicyclization of unsymmetrical diallyl ethers.



(1)



(2)

Ultraviolet irradiation of the homoallyl vinyl ethers[6] **1a–f** in the presence of CuOTf[7] produces cycloadducts **2a–f** (Table I).[8,9] The structure of **2a** was confirmed by ^1H NMR spectral comparison with a sample prepared by catalytic hydrogenation of 2-oxabicyclo[3.2.0]hept-6-ene.[10] The structures of **2b–f** are assumed to be derivatives of 2-oxabicyclo[3.2.0]heptane in analogy with the **1a** → **2a** conversion and the generation of multicyclic derivatives of bicyclo[3.2.0]heptane from various derivatives of 1,6-heptadiene by copper(I)-catalyzed photobicyclization.[1] The new photoreaction provides a general and topologically unique route to a variety of polycyclic ethers.[11]

Synthetically useful transformations of the photoproducts **2** are facilitated by the ether functional group. These transformations are most valuable if they can be achieved selectively at one of the two carbon centers which may be activated by the ether oxygen. Moderate selectivity for oxidation of the methylene group in 1-methyltetrahydrofuran was noted previously with ruthenium tetraoxide.[14] We now find that the fused multicyclic tetrahydrofuran photoproducts **2c–k** undergo highly selective oxidation

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[1] For previous papers in this series see: Salomon, R. G.; Ghosh, S.; Zagorski, M. G.; Reitz, M. *J. Org. Chem.* **1982**, *47*, 829–36 and references cited therein.

[2] Previously, this concept led to our discovery of intermolecular[3] and intramolecular[1,4] photocycloadditions of allylic alcohols. Copper(I)-catalyzed photocycloadditions of simple alkenes, i.e., those lacking functional substituents, are known only for *cyclic* olefins: (a) Srinivasan, R. *J. Am. Chem. Soc.* **1963**, *85*, 3048–49. (b) Srinivasan, R. *Ibid.* **1964**, *86*, 3318–21. (c) Baldwin, J. E.; Greeley, R. H. *Ibid.* **1965**, *87*, 4514–16. (d) Trecker, D. J.; Henry, J. P.; McKeon, J. E. *Ibid.* **1965**, *87*, 3261–63. (e) Haller, I.; Srinivasan, R. *Ibid.* **1966**, *88*, 5084–86. (f) Trecker, D. J.; Foote, R. S.; Henry, J. P.; McKeon, J. E. *Ibid.* **1966**, *88*, 3021–26. (g) Meinwald, J.; Kaplan, B. E. *Ibid.* **1967**, *89*, 2611–18. (h) Whitesides, G. M.; Goe, G. L.; Cope, A. C. *Ibid.* **1969**, *91*, 2608–15. (i) Angel, A. C. Ph.D. Thesis, University of Arizona, 1972. (j) Salomon, R. G.; Kochi, J. K. *Tetrahedron Lett.* **1973**, 2529–32. (k) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1137–44. (l) Salomon, R. G.; Folting, K.; Streib, W. E.; Kochi, J. K. *Ibid.* **1974**, *96*, 1145–51. (m) Schwendiam, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719–21. (n) Kutal, C.; Schwendiman, D. P.; Grutsch, P. A. *Sol. Energy* **1977**, *19*, 651–55. (o) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677–82. (p) Grutsch, P. A.; Kutal, C. *Ibid.* **1977**, *99*, 6460–63. (q) Evers, J. Th. M.; Mackor, A. *Rec. J. Roy. Neth. Chem. Soc.* **1979**, *98*, 423–24. (r) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1979**, *101*, 4228–33. (s) Evers, J. Th. M.; Mackor, A. *Tetrahedron Lett.* **1980**, *21*, 415–18. (t) Sterling, R. F.; Kutal, C. *Inorg. Chem.* **1980**, *19*, 1402–05. (u) Maruyama, K.; Terada, K.; Naruta, Y.; Yamamoto, Y. *Chem. Lett.* **1980**, 1259–62.

[3] Salomon, R. G.; Sinha, A. *Tetrahedron Lett.* **1978**, 1367–70.

[4] (a) Salomon, R. G.; Coughlin, D. J.; Easler, E. M. *J. Am. Chem. Soc.* **1979**, *101*, 3961–2. (b) Salomon, R. G.; Coughlin, D. J.; Ghosh, S.; Zagorski, M. G. *Ibid.* **1982**, *104*, 998–1007. (c) Shih, C.; Fritzen, E. L.; Swenteon, J. S. *J. Org. Chem.* **1980**, *45*, 4462–71. (d) McMurry, J. E.; Choy, W. *Tetrahedron Lett.* **1980**, *21*, 2477–80.

[5] The seminal discovery that copper(I) trifluoromethanesulfonate catalyzes photobicyclization of diallyl ether to produce *cis*-3-oxabicyclo[3.2.0]heptane was reported by Evers and Mackor (Evers, J. Th. M.; Mackor, A. *Tetrahedron Lett.* **1978**, 821–4). An analogous reaction, photobicyclization of 1,6-heptadiene to produce *cis*-bicyclo[3.2.0]heptane, is sensitized by mercury: (a) Srinivasan, R.; Hill, K. A. *J. Am. Chem. Soc.* **1965**, *87*, 4988–92. (b) Srinivasan, R.; Carlough, K. H. *Ibid.* **1967**, *89*, 4932–6.

[6] These were prepared by mercury(II)-catalyzed transvinylation of homoallyl alcohols with ethyl vinyl ether. Details will be reported in a full account of this work.

[7] Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1900.

[8] Representative procedure: To 2-cyclopentenylmethyl vinyl ether (**1d**) (1.16 g, 9.3 mmol) in ether (200 mL, freshly distilled from $LiAlH_4$) was added $(CuOTf)_2C_6H_6$ (0.21 g, 0.4 mmol). The homogeneous solution is irradiated for 24 h in a cylindrical Pyrex vessel with an internal 450-W Hanovia mercury vapor lamp in a water-cooled quartz well. After completion of the irradiation, the mixture is poured into a slurry of crushed ice (25 g) in concentrated aqueous NH_4OH (25 mL) and shaken well. The deep blue aqueous phase is separated and extracted with ether (2 × 50 mL). The combined ether solutions are washed with saturated aqueous NaCl (50 mL) and dried ($MgSO_4$). Distillation provides **2d** (92%, bp 70–72 °C (12 mmHg)).

[9] Satisfactory elemental analyses were obtained for all new compounds, which also exhibited ^1H NMR spectra consistent with the structures assigned.

[10] Paquette, L. A.; Barrett, J. H.; Spitz, R. P.; Pitcher, R. *J. Am. Chem. Soc.* **1965**, *87*, 3417–22.

[11] Previous routes to 2-oxabicyclo[3.2.0]heptanes include photoelectrocyclization of 2,3-dihydrooxepins followed by catalytic hydrogenation,[10] intermolecular photocycloaddition of alkenes with 4,5-dihydrofurans,[12] or intermolecular photocycloaddition of alkynes with 4,5-dihydrofurans followed by catalytic hydrogenation.[12,13]

[12] Rosenberg, H. M.; Servê, M. P. *J. Org. Chem.* **1971**, *36*, 3015–18.

[13] Servê, M. P.; Rosenber, H. M. *J. Org. Chem.* **1970**, *35*, 1237.

[14] Smith, A. B., III; Scarborough, R. M., Jr. *Synth. Commun.* **1980**, *10*, 205–11.

[15] General procedure: To a vigorously stirred two-phase mixture of CCl_4 (10 mL) and water (10 mL) containing $NaIO_4$ (0.50 g) is added RuO_2 (20 mg). The black dioxide dissolves after stirring about 10 min at 22 °C to produce a yellow solution of RuO_4 in the CCl_4 layer. To this is added ihe tetrahydrofuran derivative (0.65 mmol). The mixture is stirred at 22 °C until complete consumption of the starting material is observed by thin-layer chromatography on silica gel. The mixture is then filtered through Celite, which is then washed thoroughly with CH_2Cl_2. The aqueous layer is saturated with NaCl and extracted with CH_2Cl_2 (3 × 5 mL). Isopropanol (0.20 mL) is added to the combined organic extracts, which are shaken vigorously to reduce RuO_4 to RuO_2, dried ($MgSO_4$), filtered, and stripped of solvent to afford the lactone, which is usually quite pure by ^1H NMR. Analytical samples were prepared by gas–liquid-phase chromatography on a 4 ft × $^1/_4$ in. column filled with 15% FFAP on 60/80 Chromosorb P.