= 128 Hz, CH_3), 38.1 (q, *J* = 132 Hz, C(O)*C*H_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.

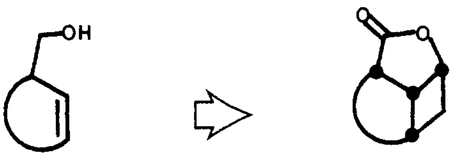
Copper(I) Catalysis of Olefin Photoreactions. 11. Synthesis of Multicyclic Furans and Butyrolactones via Photobicyclization of Homoallyl Vinyl and Diallyl Ethers[1]

Swadesh R. Raychaudhuri, Subrata Ghosh, and
Robert G. Salomon*

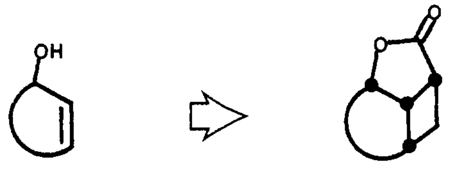
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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 the 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.

0002-7863/82/1504-6841$01.25/0

Table I. Copper(I)-Catalyzed Photobicyclization of Homoallyl Vinyl Ethers[8]

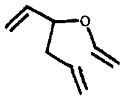
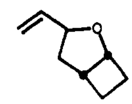
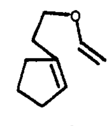
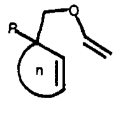
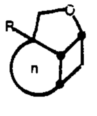
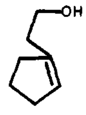
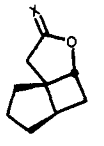
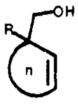
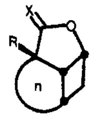
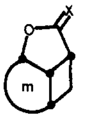
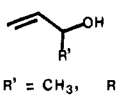
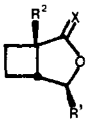
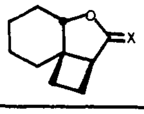
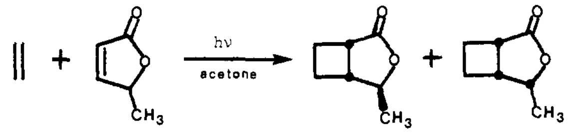
Entry	Vinyl Ether **1**	Irradiation Time (h)	Photocyclization Product **2**	Yield (%)
a		16		60
b		40		58
c		58		40
				
d	R = H, n = 5	24		92
e	R = CH$_3$, n = 5	24		50
f	R = H, n = 6	18		48

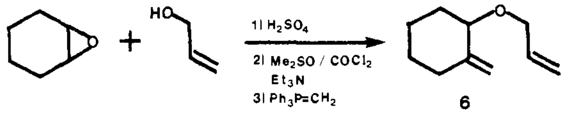
Table II. Synthesis of Multicyclic Butyrolactones by Selective Oxidation of Tetrahydrofuran Derivatives with Ruthenium Tetraoxide

Entry	Hydroxyolefin Precursor	Ether **2** (X = H$_2$) Lactone **3** (X = O)	Oxidation Time (h)	Yield (%)
c			10	70
				
d	R = H, n = 5		80	78
e	R = CH$_3$, n = 5		8	71
f	R = H, n = 6		14	85
				
g	m = 5		4	73
h	m = 8		170	56
				
i	R' = CH$_3$, R^2 = H		1	56
j	R' = n-C$_4$H$_9$, R^2 = CH$_3$		120	83
k	see text		16	65

of the methylene group to afford butyrolactones **3c-k** with sodium periodate and a catalytic amount of ruthenium tetraoxide (Table II).[9,15] Table II entries c–f demonstrate novel annulations of multicyclic butyrolactones from homoallyl alcohols. The cyclobutyl ring in the products **3d-f** is necessarily incorporated cis to the original alcohol substituent. Similar annulations from allylic alcohols via unsymmetrical diallyl ethers are demonstrated by Table II entries g–j. The requisite diallyl ethers for photoannulation of **2g-j** are readily available by Williamson synthesis from the hydroxy olefin precursors indicated. It is noteworthy that the stereochemistry of the substituent R^1 in **3i** and **3j** is exclusively exo.[16] This synthetically valuable stereoselectivity is in sharp contrast with a topologically different previous synthesis of **3i** by intermolecular photocycloaddition of ethylene with **4**, which affords an equal yield of the endo-epimer **5** (eq 3).[17] The requisite diallyl ether **6** for photoannulation of **2k** was prepared from cyclohexene oxide and allyl alcohol according to eq 4. Other synthetically useful transformations of the photoproducts **2** as well as copper(I)-catalyzed photocyclizations of unsaturated ethers incorporating additional functionality are under investigation and will be described in a full account.



4 **3i** (18%) **5** (18%) (3)



6 (4)

Acknowledgement 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. We thank Professors L. A. Paquette and H. Uda for copies of ^{1}H NMR spectra of **2a** and of **3i** and **5**, respectively.

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(16) A discussion of the mechanistic basis of this stereoselectivity is deferred to a future full paper.

(17) Kosugi, H.; Sekiguchi, S.; Sekita, R.; Uda, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 520–28.

Conrotatory Ring Opening of Cis-Fused 3-Aminocyclobutenes. X-ray Analysis of a *cis,trans*-2*H*-Thiocin

G. W. Visser, W. Verboom, and D. N. Reinhoudt*

Laboratory of Organic Chemistry
Twente University of Technology
Enschede, The Netherlands

S. Harkema and G. J. van Hummel

Laboratory of Chemical Physics
Twente University of Technology
Enschede, The Netherlands

Received April 28, 1982

The thermal valence isomerization of (hetero) cyclobutenes to (hetero) 1,3-butadienes is a classic example of a stereospecific reaction, the conrotatory mode of which is in agreement with the principle of conservation of orbital symmetry in electrocyclic reactions.[1,2] A large amount of work has been carried out on the thermal isomerization of compounds in which the cyclobutene moiety is cis annulated to another ring system. It is generally accepted that when the annulated ring possesses less than eight atoms, ring opening *must* occur by way of the symmetry-forbidden disrotatory mode[3] or by homolytic[4] or heterolytic[5] pathways, all

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(1) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1971.

(2) Pennings, M. L. M.; Reinhoudt, D. N.; Harkema, S.; van Hummel, G. J. *J. Am. Chem. Soc.* **1980**, *102*, 7570–7571.