J = 8 Hz), 6.82 (t, 1 H, J = 8 Hz), 6.60 (d, 1 H, J = 8 Hz), 4.26 (dd, 1 H, J = 12, 2 Hz), 3.84 (dd, 1 H, J = 14, 6 Hz), 3.44 (m, 1 H),m 3.22 (dd, 1 H, J = 14, 4 Hz), 2.3–2.6 (m, 4 H), 2.42 (s, 6 H); mass spectrum, measd 278.1785 (calcd for $C_{19}H_{22}N_2$, 278.1778).

***N*-(5,6,7,12-Tetrahydro-7,12-ethanodibenzo[*b*,*g*][1,4]diazocin-14-yl)dimethylamine (26).** To a solution of **22** (89 mg, 0.26 mmol) in 5 mL of dry THF was added lithium aluminum hydride (100 mg, 2.6 mmol). The mixture was stirred at 25 °C for 20 h. After adding 0.5 mL of concentrated NH_4OH and stirring 15 min, the slurry was filtered thrugh Celite and evaporated. Column chromatography on activity III neutral alumina (33% ethyl acetate/hexanes) gave 57 mg (77%) of **26** as a white solid: mp 135–137 °C; IR (KBr) 3330, 3050, 3020, 2980, 2960, 2930, 2900, 2870, 2770, 1590, 1490, 760, 750 cm^{-1}; NMR ($CDCl_3$, 360 MHz) 7.35 (d, 1 H, J = 8 Hz), 7.17 (t, 1 H, J = 8 Hz), 7.03–7.12 (m, 3 H), 6.91 (t, 1 H, J = 8 Hz), 6.81 (t, 1 H, J = 8 Hz), 6.57 (d, 1 H, J = 8 Hz), 3.84 (dd, 1 H, J = 14, 4 Hz), 3.77 (dd, 1 H, J = 13, 8.5 Hz), 3.46 (dd, 1 H, J = 13, 8 Hz), 3.37 (m, 1 H), 3.23 (dd, 1 H, J = 14, 4 Hz), 2.52 (m, 1 H), 2.28 (s, 6 H); mass spectrum, m/e 279.1726 (calcd for $C_{18}H_{21}N_3$, 279.1735).

***N*-(5,6,7,12-Tetrahydro-5-oxo-7,12-methanodibenz[*c*,*f*]azocin-13-yl)dimethylamine (27).** To a solution of 400 mg (1.24 mmol) of **16** in 10 mL of anhydrous THF was added 190 mg (5.0 mmol) of lithium aluminum hydride. The slurry was stirred under argon for 1 h. After adding 0.2 mL of concentrated NH_4OH and stirring for 0.5 h, the slurry was filtered through Celite. Evaporation of the filtrate gave 0.32 g (93%) of a white solid. Recrystallization from ethyl acetate/hexanes gave pure **27**: mp 232–235 °C; IR (KBr) 3270, 1640, 1460, 1445, cm^{-1}; NMR ($CDCl_3$, 90 MHz) 8.38 (m, 1 H), 7.05–7.4 (m, 7 H), 6.96 (br, 1 H), 4.51 (dd, 1 H, J = 6.0, 6.5 Hz), 4.35 (d, 1 H, J = 6.0 Hz), 2.90 (t, 1 H, J = 6.0 Hz), 2.22 (s, 6 H); mass spectrum, m/e 278.1393 (calcd for $C_{18}H_{18}N_2O$, 278.1419).

***N*-(5,6,7,12-Tetrahydro-5-oxo-7,12-ethanodibenzo[*b*,*g*][1,5]diazocin-14-yl)dimethylamine (25) and *N*-(5,6,7,12-Tetrahydro-7,12-ethanodibenzo[*b*,*g*][1,5]diazocin-14-yl)dimethylamine (30).** Compound **24** (1.50 g, 4.45 mmol) was reduced in the same manner as lactam **16** by using lithium aluminum hydride (1.35 g, 35.6 mmol) in 45 mL of THF. After stirring 18 h and adding 5 mL of concentrated NH_4OH, the slurry was filtered through Celite. Evaporation of the solvent left an amorphous solid. Column chromatography on activity III alumina using 25% ethyl acetate/hexanes gave two compounds. The first compound off was diazocine **30** (0.43 g, 35%): clear oil; NMR ($CDCl_3$, 360 MHz) 6.8–7.3 (m, 8 H), 4.37 (d, 1 H, J = 17 Hz), 4.25 (d, 1 H, J = 8.2 Hz), 4.10 (d, 1 H, J = 17 Hz), 2.77 (dd, 1 H, J = 12, 4.3 Hz), 2.63 (t, J = 12 Hz), 2.5–3 (m, 1 H), 2.43 (s, 6 H), 2.01 (br, 1 H); mass spectrum, m/e 279.1722 (calcd for $C_{18}H_{21}N_3$, 279.1735). The next compound off was lactam **28** (0.36 g, 28%). Recrystallization from ethyl acetate/hexanes gave pure **25**: mp 191–192 °C; IR (KBr) 3430, 3380, 1670, 1595 cm^{-1}; NMR ($CDCl_3$, 90 MHz) 8.08 (m, 1 H), 6.7–7.5 (m, 8 H), 4.93 (d, 1 H, J = 10 Hz), 2.5–3.0 (m, 3 H), 2.37 (s, 6 H); mass spectrum, m/e 293.1531 (calcd for $C_{18}H_{19}N_3O$, 293.1528).

Direct conversion of **24** to **30** was accomplished as follows: To a solution of **24** (1.00 g, 2.97 mmol) in 30 mL of dry THF was added lithium aluminum hydride (1.14 g, 30 mmol). The mixture was refluxed for 18 h. Concentrated NH_4OH (3 mL) was added and the solution stirred until white, filtered through Celite, and dried over Na_2SO_4. Evaporation gave 0.81 g of a yellow foam. Column chromatography on activity III neutral alumina using 25% ethyl acetate/hexanes provided 0.66 g (80%) of pure **30**.

***N*-(5,6,7,12-Tetrahydro-7,12-methanodibenz[*c*,*f*]azocin-13-yl)dimethylamine (29).** A mixture of 200 mg (0.72 mmol) of **27** and 0.27 g (7.2 mmol) lithium aluminum hydride in 7 mL of THF was refluxed for 7 h. To the slurry was added 10 drops of concentrated NH_4OH, and the mixture was stirred for 0.25 h. Filtration through Celite and evaporation gave a solid. This material was passed through a small column of activity III alumina using 33% ethyl acetate/hexanes as eluent. A total of 85 mg (45%) of pure **29** was obtained as an amorphous solid: NMR ($CDCl_3$, 90 MHz) 6.85–7.55 (m, 8 H), 4.50 (d, 1 H, J = 4.5 Hz), 4.22 (d, 1 H, J = 6.0 Hz), 3.55 (d, 1 H, J = 16 Hz), 3.13 (d, 1 H, J = 16 Hz), 2.77 (br, 1 H), 2.53 (dd, 1 H, J = 6.0, 4.5 Hz), 2.21 (s, 6 H); mass spectrum, m/e 264.1617 (calcd for $C_{18}H_{20}N_2$, 264.1626).

Acknowledgment. We thank Dr. Joseph C. Calabrese for the determination of the X-ray structure, Mr. Dennis Chidester for technical assistance, and Ms. Theresa A. Bonnes for help in the prepartion of this manuscript.

Supplementary Material Available: Detailed X-ray crystal data (atomic coordinates, bond lengths, bond angles, etc.) (7 pages). Ordering information is given on any current masthead page.

Synthesis of Cyclobutanated Butyrolactones via Copper(I)-Catalyzed Intermolecular Photocycloadditions of Homoallyl Vinyl or Diallyl Ethers[1]

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

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-2699

Received July 28, 1986

Intramolecular copper(I)-catalyzed $2\pi + 2\pi$ photocycloaddition provides an effective route for the synthesis of 2-oxa- and 3-oxabicyclo[3.2.0]heptanes from homoallyl vinyl or diallyl ethers, respectively. Ruthenium-catalyzed oxidation of these multicyclic tetrahydrofuran products provides a novel annulation of cyclobutanated butyrolactones. For intermediates incorporating both methine and methylene groups next to the tetrahydrofuran oxygen, a remarkable selectivity was found for oxidation at the methylene position. Highly stereoselective generation of *exo*-2-alkylsubstituted 3-oxabicyclo[3.2.0]heptanes occurred upon photobicyclization of diallyl ethers bearing an α-alkyl substituent.

The synthetic utility of copper(I)-catalyzed olefin photoreactions[2] depends on their stereoselectivity and their compatibility with functional groups that may be required in the synthetic target molecule or that may facilitate subsequent transformations of synthetic intermediates. We now report that intramolecular copper(I)-catalyzed $2\pi + 2\pi$ photocycloaddition provides an effective route for the synthesis of a variety of multicyclic tetrahydrofurans from either diallyl ethers[3] or homoallyl vinyl ethers. These photoreactions tolerate hydroxyl, acetoxy, allyl, and vinyl

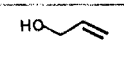
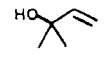
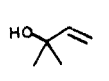
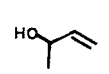
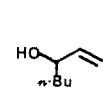
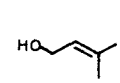
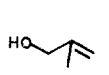
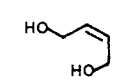
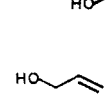
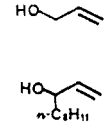
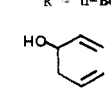
(1) Copper(I) Catalysis of Olefin Photoreactions. 15. For paper 14 in this series, see: Avasthi, K.; Salomon, R. G. *J. Org. Chem.* **1986**, *51*, 2556.

(2) For a review of homogeneous metal catalysis in organic photochemistry, see: Salomon, R. G. *Tetrahedron* **1983**, *39*, 485.

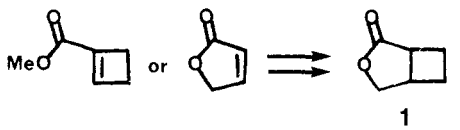
(3) The seminal discovery that copper(I) trifluoromethanesulfonate catalyzes photobicyclization of diallyl ether to produce *cis*-3-oxabicyclo-[3.2.0]heptane was reported by Evers and Mackor (Evers, J. Th. M.; Mackor, A. *Tetrahedron Lett.* **1978**, 821). An analogous reaction, photobicyclization of 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. (b) Srinivasan, R.; Carlough, K. H. *Ibid.* **1967**, *89*, 4932.

0022-3263/87/1952-0083$01.50/0

Table I. Synthesis and Copper-Catalyzed Photobicyclization of Acyclic Diallyl Ethers

Entry	Allylic Alcohol 2	Allylic Electrophile	Diallyl Ether 3	Oxabicyclo-heptane 4	Yield
a					52%
b					56%
c					54%
d					54%
e					83%
f					39%
g					41%
h					41%
i					35%
j					21%
k	R = H				71%
l	R = CH_3				80%
m	R = n-Bu				87%
n					70%

substituents. Furthermore, in conjunction with remarkably selective ruthenium-catalyzed oxidation of the tetrahydrofuran products, these photoreactions provide a novel annulation of stereoselectively cis-fused cyclobutanated butyrolactones. Previously, lactones **1** from 2-hydroxyalkylcyclobutanecarboxylic acids have been prepared by annulation of γ-butyrolactones onto cyclobutenecarboxylic esters[4] or by cyclobutanation of butenolides.[5] We now report a topologically different strategy



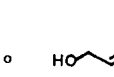
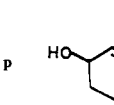
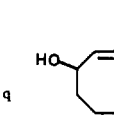
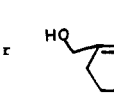
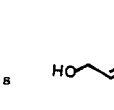
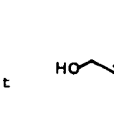
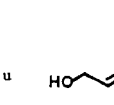
1

for construction of 3-oxabicyclo[3.2.0]heptan-2-ones **1** from readily available starting materials, allylic alcohols **2**. The new synthetic method is based on copper(I)-catalyzed intramolecular $2\pi + 2\pi$ photocycloaddition of diallyl ethers

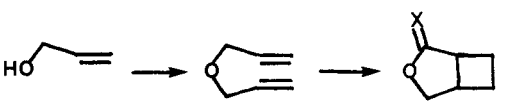
(4) (a) Clark, R. D. *Synth. Commun.* **1979**, *9*, 325. (b) Ohtsuka, Y.; Niitsuma, S.; Tadokoro, H.; Hayashi, T.; Oishi, T. *J. Org. Chem.* **1984**, *49*, 2326.

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

Table II. Synthesis and Copper-Catalyzed Photobicyclization of Monocyclic Diallyl Ethers

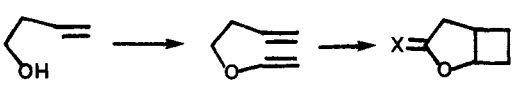
Entry	Allylic Alcohol 2	Electrophile	Diallyl Ether 3	Tetrahydrofuran 4	Yield
o					47%
p					36%
q					56%
r					35%
s		+ NBS			28%
t		+ NBS			35%
u					94%

3 and regioselective ruthenium-catalyzed oxidation of the resulting tetrahydrofuran intermediates **4**. Thus, while



2 **3** **4**, X = H_2; **1**, X = O

the ether linkage is compatible with photocyclization, it provides sufficient activation to allow selective oxidative conversion of the photoproducts into lactones. A similar strategy provides a synthesis of 2-oxabicyclo[3.2.0]heptan-3-ones **8** from homoallyl alcohols **5** via multicyclic tetrahydrofuran intermediates **7**.



5 **6** **7**, X = H_2; **8**, X = O

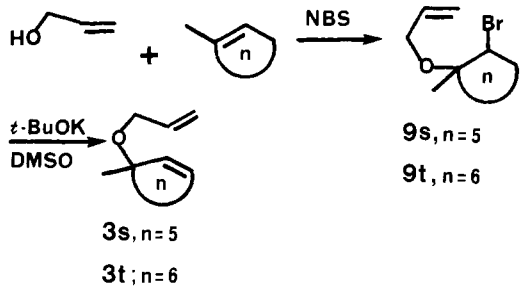
Results and Discussion

Synthesis of Diallyl and Homoallyl Vinyl Ethers. Diallyl ethers **3** are readily available in high yields from allyl alcohols **2** by O-allylation. For most of the examples presented in Tables I and II, the alcohols were first converted into sodium alkoxides by reaction with sodium hydride, and O-allylation was achieved by subsequent reaction with allylic halides.[6] Allyl Δ^2-cyclopentyl ether

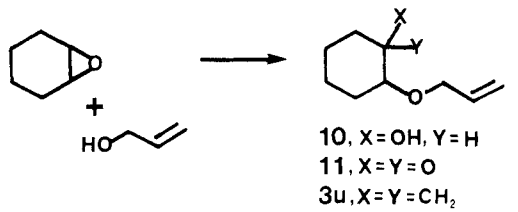
(6) Reuter, J. M.; Salomon, R. G. *J. Org. Chem.* **1977**, *42*, 3360.

(**3o**) was prepared by adding Δ^2-cyclopentenyl chloride to a suspension of sodium bicarbonate in excess allyl alcohol.[6] The 4-acetoxy-*cis*-2-buten-1-yl ethers **3i** and **3j** were prepared similarly by treating a suspension of sodium bicarbonate in the appropriate alcohol with *cis*-2-butene-1,4-diol monoacetate monomethanesulfonate.[7]

Since tertiary allylic halides would undergo β-elimination rather than nucleophilic substitution, alcohols cannot be O-allylated with tertiary allylic halides. A new synthetic method was developed to circumvent this difficulty. Thus, allyl ethers of bromohydrins were produced by reaction of allyl alcohol with alkenes and *N*-bromosuccinimide. The trisubstituted 1-methylcycloalkenes reacted regioselectively producing β-bromo tertiary ethers **9**, which afforded tertiary allylic ethers upon dehydrobromination with potassium *tert*-butoxide in Me_2SO.



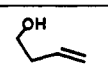
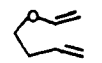
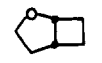
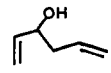
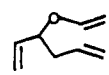
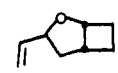
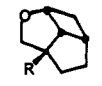
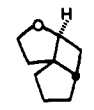
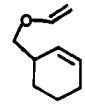
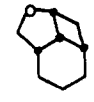
The allylic isomer **3u** of the unsymmetrical diallyl ether **3r** was prepared from allyl alcohol by a process designed to achieve net regioselective O-allylation. Thus, allyl alcohol was first alkylated with cyclohexene oxide to provide 2-(allyloxy)cyclohexanol (**10**), which delivered (allyloxy)-cyclohexanone (**11**) by oxidation. Wittig olefination of **11** then afforded the unsymmetrical diallyl ether **3u**.



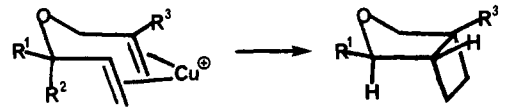
Homoallyl vinyl ethers **6** were prepared from the corresponding homoallyl alcohols **5** by mercury(II)-catalyzed transvinylation with ethyl vinyl ether. Yields reported in Table III are for products isolated by fractional distillation and are *not* corrected for unreacted alcohol. The transvinylation reaction was especially slow for the secondary alcohol **5b**.

Photocyclization of Diallyl and Homoallyl Vinyl Ethers. Ultraviolet irradiation of the acyclic diallyl ethers **3a–n** in the presence of copper(I) trifluoromethanesulfonate[8] (CuOTf) produced 3-oxabicyclo[3.2.0]heptanes **4a–n** (Table I). The ^1H NMR spectrum of **4d** shows that this product is a single isomer since only one doublet is apparent for the methyl substituent. That this methyl substituent occupies the exo position was confirmed by conversion into the corresponding lactone **1d** (vida infra), which has been thoroughly characterized previously.[5] Since CuOTf-catalyzed $2\pi + 2\pi$ photocycloaddition requires coordination of both reacting C=C bonds with the copper(I) catalyst,[9] the stereoselectivity observed must arise from a preference for formation of the less sterically

Table III. Synthesis and Copper-Catalyzed Photobicyclization of Homoallyl Vinyl Ethers

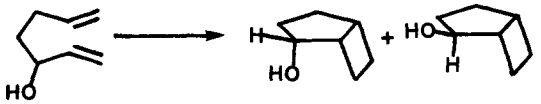
Entry	Homoallyl Alcohol 5	Homoallyl Vinyl Ether 6	Yield (%)	Tetrahydrofuran 7	Yield (%)
a			26		60
b			64		58
c	 R = H		24		92
d	R = CH_3		63		50
e			32		40
f			17		48

crowded copper(I)–diene complex **12x** over the more sterically congested complex **12n**. For similar reasons, an



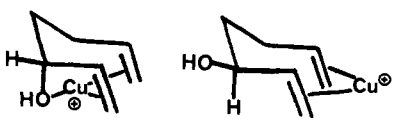
12x, $R^1=CH_3$, $R^2=H$ **4d**, $R^1=CH_3$, $R^3=H$
12n, $R^1=H$, $R^2=CH_3$ **4e**, $R^1=n$-Bu, $R^3=CH_3$

exo-4-butyl structure is presumed for **4e** that is also a single isomer as evidenced by only one sharp singlet for the bridgehead methyl group in the ^1H NMR spectrum of the photoproduct from **3e**. The present observations provide a dramatic contrast with the opposite stereoselectivity that we discovered for copper(I)-catalyzed photobicyclizations of 1,6-heptadien-3-ols. Thus, irradiation of **13** in the presence of CuOTf generates a 9:1 mixture of endo and exo epimers **14n** and **14x**, respectively.[10] Here stereose-



13 **14n** (9:1) **14x**

lection is presumed to arise from a coordinative interaction of the hydroxyl substituent with the copper(I) catalyst. A preference for tridentate coordination as in **15n** over bidentate coordination as in **15x** overcomes the thermodynamic preference for a pseudoequatorial disposition of the allylic substituent. Thus, copper(I)-catalyzed photobicyclizations provide an excellent means for stereoselective construction of cyclobutyl carbinyl stereocenters.

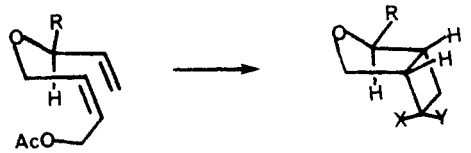


15n **15x**

On the other hand, these reactions do not occur with stereospecific translation of geometric configuration about

(7) Karger, M. H.; Mazur, Y. *J. Org. Chem.* **1971**, *36*, 532.
(8) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889.
(9) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1137.
(10) Salomon, R. G.; Coughlin, D. J.; Ghosh, S.; Zagorski, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 998.

the C=C bonds into that about the cyclobutane ring. Rather, the *cis*-alkenes **3i** and **3j** react nonstereospecifically. Two singlets corresponding to two epimeric acetate methyl groups appear in the ^1H NMR spectra of both photoproducts **4i** and **4j**. Thus, both *exo*- and *endo*-6-acetoxymethyl epimers are produced upon UV irradiation of the stereochemically pure *cis*-alkenes.



3i, R = H
3j, R = *n*-C_8H_{11}

exo, X = H, Y = CH_2OAc
endo, X = CH_2OAc, Y = H

The compatibility of copper(I)-catalyzed photobicyclizations with hydroxyl, acetoxy, allyl, and vinyl substituents is demonstrated by entries **h–n** in Table I. The high yields obtained from photobicyclization of the conjugated dienes **3k–m** are especially noteworthy. These cyclizations provide an alternative synthetic route to other derivatives. For example, propenyl compound **4k** provides acetoxymethyl derivative **4i** in good overall yield upon ozonolysis with reductive workup followed by acetylation.

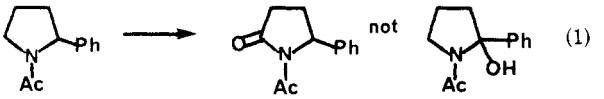
Ultraviolet irradiation of the monocyclic diallyl ethers **3o–u** in the presence of CuOTf generated the tricyclic ethers **4o–u** (Table II). Similarly, copper(I)-catalyzed photobicyclization of homoallyl vinyl ethers **6a–f** produced bi- or tricyclic cyclobutanated tetrahydrofurans **7a–f** (Table III). The structure of **7a** was confirmed by ^1H NMR spectral comparison with an authentic sample prepared by catalytic hydrogenation of 2-oxabicyclo[3.2.0]-hept-6-ene.[11] The structures of **7b–f** are presumed also to be derivatives of 2-oxabicyclo[3.2.0]heptane in analogy with the **6a** to **7a** 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.[12] The new photoreaction provides a general and topologically unique route to a variety of polycyclic ethers. Previous routes to 2-oxabicyclo[3.2.0]-heptanes include photoelectrocyclization of 2,3-dihydrooxepins followed by catalytic hydrogenation,[11] intermolecular photocycloaddition of alkenes with 4,5-dihydrofurans,[13] or intermolecular photocycloaddition of alkynes with 4,5-dihydrofurans followed by catalytic hydrogenation.[13,14]

Oxidation of Tetrahydrofurans with Ruthenium Tetraoxide. Moderate selectivity for oxidation of the methylene group in 1-methyltetrahydrofuran was noted previously with ruthenium tetraoxide.[15] We now find that the fused multicyclic tetrahydrofuran photoproducts **4** or **7** undergo highly selective oxidation of the methylene group to afford butyrolactones **1** or **8**, respectively, with sodium periodate and a catalytic amount of ruthenium tetraoxide (Table IV). With one exception, i.e., **4p**, only products arising from oxidation at the methylene position were isolated from reactions of substrates incorporating both methine and methylene groups next to the tetrahydrofuran oxygen, i.e., **4d**, **4e**, **4o**, **4q**, **4u**, **8c**, **8e**, and **8f**.

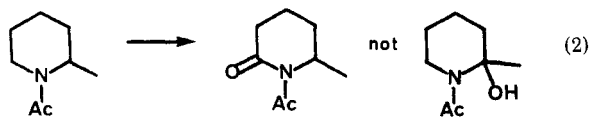
Table IV. Ruthenium Catalyzed Oxidation of Tetrahydrofurans

tetrahydrofuran							butyrolactone (yield, %)	
	R^1	R^2	R^3	R^4	R^5	R^6		
4a	H	H	H	H	H	H	1a (91)	
4b	Me	Me	H	H	H	H	1b (94)	
4c	Me	Me	H	H	H	Me	1c (44)	
4d	Me	H	H	H	H	H	1d (56)	
4e	n-Bu	H	H	H	H	Me	1e (83)	
4f	H	H	H	Me	Me	H	1fy (28)	1fx (19)
4g	H	H	Me	H	H	H	1gy (46)	1gx (20)
4o	R=H, n=5						1o (73)	
4p	R=H, n=6						1p (4)	20 (20)
4q	R=H, n=8						1q (56)	
4s	R=Me, n=5						1s (87)	
4t	R=Me, n=6						1t (82)	
4r							1rx (44)	1ry (34)
4u							1u (65)	
7c	R=H, n=5						8c (78)	
7d	R=Me, n=5						8d (71)	
7f	R=H, n=6						8f (85)	
7e							8e (70)	

The oxidations of **4e** and **7f** demonstrate an *at least* 5 to 1 preference for oxidation at a methylene position in competition with a methine (N.B. no other oxidation products were isolated). While the mechanistic basis of this selectivity remains unknown, its synthetic utility is evident. These remarkably selective ruthenium-catalyzed oxidations are reminiscent of the preferential oxidation of methylene groups rather than methine groups next to the nitrogen atom in *N*-acetylpyrrolidines, e.g., eq 1, and *N*-acetylpiperidines, e.g., eq 2.[16]



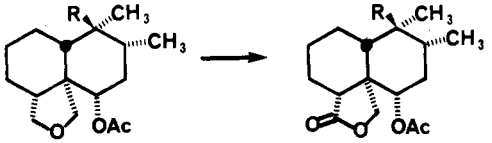
(1)



(2)

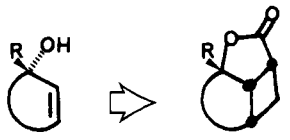
(11) Paquette, L. A.; Barrett, J. H.; Spitz, R. P.; Pitcher, R. *J. Am. Chem. Soc.* **1965**, *87*, 3417.
(12) Salomon, R. G.; Ghosh, S.; Zagorski, M. G.; Reitz, M. *J. Org. Chem.* **1982**, *47*, 829.
(13) Rosenberg, H. M.; Serve, M. P. *J. Org. Chem.* **1971**, *36*, 3015.
(14) Serve, M. P.; Rosenberg, H. M. *J. Org. Chem.* **1970**, *35*, 1237.
(15) Smith, A. B., III; Scarborough, R. M., Jr. *Synth. Commun.* **1980**, *10*, 205. Also see: Wolff, M. E.; Kerwin, J. F.; Owings, F. F.; Lewis, B. B.; Blank, B. *J. Org. Chem.* **1963**, *28*, 2729.
(16) Tangari, N.; Tortorella, V. *J. Chem. Soc., Chem. Commun.* **1975**, *71*.

Even oxidations involving competition between two nonequivalent methylene groups, i.e., tetrahydrofurans **4f**, **4g**, and **4r**, showed a small preference for oxidation at the sterically less congested methylene. Characterization of the major product from oxidation of **4f** as the lactone **1fy** was firmly established by ^{1}H NMR comparison with an authentic sample prepared by an unambiguous synthesis from methyl 3,3-dimethylcyclobutenecarboxylate.[4b] A considerably more impressive example of such sterically directed selective oxidation with ruthenium(VIII) was noted previously for the conversion of **16a** or **16b** into **17a** or **17b**, respectively, both in 95% yield.[17]

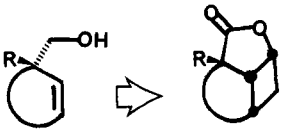


16a, R = $(CH_2)_3OAc$ **17a**, R = $(CH_2)_3OAc$
16b, R = CH_3 **17b**, R = CH_3

The cyclobutyl ring in the products **1o–t** (eq 3) and **8c–f** (eq 4) is necessarily incorporated cis to the original allylic

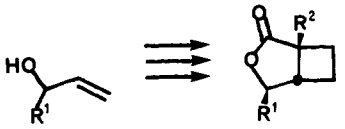


(3)

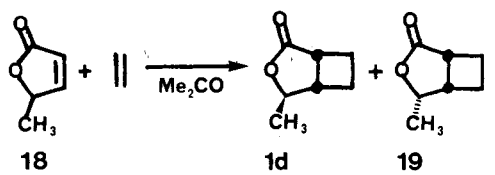


(4)

or homoallylic alcohol substituent. Even more remarkable are the highly stereoselective syntheses of **1d** and **1e** from allylic alcohols **2d** and **2e**, respectively. This synthetically valuable stereoselectivity is in sharp contrast with a topologically different previous synthesis of **1d** by intramolecular photocycloaddition of ethylene with **18**, which affords an equal yield of the endo epimer **19**.[5]



2d, $R^1 = CH_3$ **1d**, $R^1 = Me$, $R^2 = H$
2e, $R^1 = n$-Bu **1e**, $R^1 = n$-Bu, $R^2 = Me$



18 **1d** **19**

Experimental Section

General. Small-scale irradiations (15–50 mL) were conducted in cylindrical quartz vessels that were cooled with an internal water-cooled cold finger. The reaction mixtures were stirred magnetically and irradiated externally with a Rayonet photochemical reactor (Southern New England Ultraviolet Co. Model RPR-100) with 254-nm lamps. Large-scale irradiations (0.1–1.0 L) were conducted under dry nitrogen in cylindrical Pyrex vessels with a quartz water-cooled double-walled immersion well. The reaction mixtures were stirred magnetically and irradiated internally with a Hanovia medium-pressure 450-W mercury vapor lamp. Preparative gas–liquid-phase chromatography was performed with a Varian Model 3700 instrument. Proton magnetic resonance spectra were recorded with a Varian A60A spectrometer in $CDCl_3$ solutions with tetramethylsilane as internal standard. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

Materials. Diethyl ether solvent for photolyses was freshly distilled from lithium aluminum hydride under dry nitrogen immediately before use. Tetrahydrofuran (THF) was distilled under dry nitrogen from potassium benzophenone ketyl. *cis*-2-Butene-1,4-diol monoacetate monomethanesulfonate[7] and copper(I) triflate–benzene complex $[(CuOTf)_2 \cdot C_6H_6]$[8] were prepared by reported procedures. Homoallylic alcohols **5c**, **5d**, and **5f** were prepared as described for **5d**[18] by reduction of the corresponding carboxylic methyl esters with lithium aluminum hydride. The requisite esters, methyl 2-cyclopentenecarboxylate, methyl 1-methylcyclopent-2-enecarboxylate, and methyl 2-cyclohexenecarboxylate, were prepared by the method of Bunnell and Fuchs.[19]

Synthesis of Diallyl Ethers. Allyl 4-Hydroxy-*cis*-2-buten-1-yl Ether (3h). In a 500-mL, three-necked round-bottomed flask fitted with a mechanical stirrer, a droping funnel, and condenser, under nitrogen, was placed NaH (4 g, 92 mmol, 57% oil dispersion). The oil was removed by washing with dry pentane (2 × 10 mL), and distilled THF (150 mL) was added with mechanical stirring. *cis*-2-Butene-1,4-diol (7.40 mL, 90 mmol) was added dropwise. After complete addition, the reaction mixture was refluxed for 2 h. HMPA (30 mL) followed by allyl bromide (8.22 mL, 95 mmol) was added to the warm reaction mixture at a rate that maintained a gentle reflux. Refluxing was continued for another 2 h. After cooling to 20 °C, 10% HCl (50 mL) was added, and the resulting mixture was extracted with pentane (3 × 50 mL). The pentane extract was washed successively with 10% HCl (2 × 15 mL), water (2 × 15 mL), saturated aqueous $NaHCO_3$ (2 × 15 mL), and brine (15 mL) and dried ($MgSO_4$). Removal of solvent followed by distillation of the residual oil afforded a colorless liquid (8.71 g): bp 94–105 °C (12 mmHg). Chromatography of this oil through SiO_2 (60–200 mesh) led to isolation of three fractions: Fraction 1, eluted with 20% ethyl acetate in hexane, was distilled to afford **1,4-bis(allyloxy)-*cis*-2-butene** (800 mg, 5%): ^{1}H NMR δ 4.56–4.92 (m, 8 H), 5.05–6.25 (m, 8 H). Fraction 2, eluted later with 20% ethyl acetate in hexane was distilled to afford 2.61 g of a liquid that was not characterized further. Fraction 3, eluted with 50% ethyl acetate in hexane, was distilled to afford the title ether **3h** (2.15 g, 19%): ^{1}H NMR δ 2.40 (br s, H), 3.9–4.3 (6 H), 5.0–5.5 (2 H), 5.5–6.3 (3 H). Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.47; H, 9.37.

4-Acetoxy-*cis*-2-buten-1-yl Allyl Ether (3i). A mixture of *cis*-2-butene-1,4-diol monoacetate monomethanesulfonate[7] (10.4 g, 50 mmol), an excess of allyl alcohol (20 mL), and powdered $NaHCO_3$ was stirred vigorously and heated in an oil bath at 80–85 °C for 14 h. After being cooled to 20 °C, the reaction mixture was poured into cold water (100 mL) and extracted with pentane (3 × 50 mL). The pentane extract was washed with saturated aqueous $NaHCO_3$ (25 mL) and brine (2 × 25 mL) and dried ($MgSO_4$). Removal of solvent followed by distillation of the residual liquid afforded **3i** (5.49 g, 65%); bp 114 °C (20 mmHg); ^{1}H NMR δ 2.05 (s, 3 H), 3.9–4.2 (4 H), 4.5–4.7 (2 H), 5.0–5.5 (2 H), 5.5–6.3 (3 H). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.55; H, 8.25.

4-Acetoxy-*cis*-2-buten-1-yl Undec-1-en-3-yl Ether (3j). A mixture of *cis*-2-butene-1,4-diol monoacetate monomethanesulfonate[7] (6.24 g, 30 mmol), undec-1-en-3-ol (5.1 g, 30 mmol), and powdered $NaHCO_3$ (7.56 g, 90 mmol) was stirred vigorously and heated at 90–95 °C for 38 h. After being cooled to room temperature, the reaction mixture was diluted with water (50 mL). The product was extracted into pentane (3 × 50 mL). The

(17) Luteijn, J. M.; de Groot, A. *Tetrahedron Lett.* **1971**, *22*, 789.
(18) Nakamura, N.; Sakai, K. *Tetrahedron Lett.* **1976**, *2049*.
(19) Bunnell, C. A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 5184.

pentane extract was washed with water (2 × 20 mL) and dried ($MgSO_4$). Removal of solvent followed by distillation of the residual oil afforded the starting allyl alcohol (3.13 g), bp 65–75 °C (0.5 mm), and the desired ether **3j** (3.11 g, 95% based on alcohol consumed: bp 130 °C (0.5 mmHg); ^1H NMR δ 0.88 (br t, 3 H, J = 5 Hz), 1.1–1.8 (br s, 14 H), 2.05 (s, 3 H), 3.4–3.9 (3 H), 3.9–4.1 (2 H), 4.6–4.7 (2 H), 4.9–6.0 (5 H). Anal. Calcd for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71. Found: C, 72.23; H, 10.70.

Method A. O-Allylation via Sodium Allyloxides. NaH (57% dispersion in oil, 0.070–0.084 mol) was washed twice with dry pentane and THF (100–120 mL) was then added. To this stirred suspension was added the allylic alcohol (0.070–0.084 mol) dropwise at room temperature under dry nitrogen. After the addition was over, the reaction mixture was stirred at room temperature for $^1/_2$ h followed by gentle reflux for 2 h. It was cooled to room temperature, HMPA (20–24 mL) and allyl bromide (0.08–0.096 mol) were successively added to it, and the solution was refluxed for 2 h. The reaction mixture was cooled to room temperature, diluted with water, acidified with 10% aqueous hydrochloric acid (25 mL), and extracted with pentane (4 × 50 mL). The combined organic extract was washed thoroughly with water and dried over $MgSO_4$, and finally solvent was removed by rotary evaporation to furnish a clear oil that was finally distilled under reduced pressure.

2,4-Hexadienyl allyl ether (3k) was obtained from 2,4-hexadien-1-ol and allyl bromide by method A in 84% yield: bp 86–90 °C (25 mm); ^1H NMR δ 1.63–1.9 (3 H, d, J = 6 Hz), 3.88–4.13 (4 H, m), 5.03–6.48 (7 H, m). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.42; H, 10.27.

2-(Allyloxy)-3,5-heptadiene (3l) was obtained from 3,5-heptadien-2-ol and allyl bromide by method A in 85% yield: bp 38–40 °C (0.4 mm); ^1H NMR δ 1.25 (3 H, d, J = 6 Hz), 1.75 (3 H, d, J = 5.5 Hz), 3.65–4.25 (3 H, m), 4.98–6.65 (7 H, m). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.97; H, 10.55.

5-(Allyloxy)-6,8-decadiene (3m) was obtained from 6,8-decadien-5-ol and allyl bromide by method A in 88% yield: bp 68–70 °C (0.5 mm); ^1H NMR δ 0.73–1.65 (9 H, m), 1.75 (3 H, d, J = 5 Hz), 3.5–4.27 (3 H, m), 4.97–6.37 (7 H, m). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.33; H, 11.46.

1,5-Hexadien-3-yl allyl ether (3n) was obtained from 1,5-hexadien-3-ol and allyl bromide by method A in 71% yield: bp 57–60 °C (15 mm); ^1H NMR δ 2.17–2.5 (2 H, m), 3.57–4.08 (3 H, m), 4.87–6.27 (9 H, m). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.21; H, 10.13.

Allyl Δ^2-Cyclohexenyl Ether (3p). Sodium hydride (2.0 g, 46 mmol, 57% oil dispersion) in a 100-mL, three-necked flask equipped with reflux condenser, mechanical stirrer, and addition funnel was washed with pentane (two 10-mL portions). THF (50 mL) was then added followed by 2-cyclohexen-1-ol (2.4 g, 24 mmol), and the resulting mixture was stirred under reflux for 2 h. Then while the mixture was still warm, HMPA (12 mL) was added followed by allyl bromide (3.2 mL, 36 mmol) at such a rate as to maintain a gentle reflux. Then the mixture was again boiled under reflux for 2 h. After being cooled to room temperature, the mixture was quenched with 10% aqueous HCl (25 mL) and extracted with pentane (2 × 50 mL). The combined extracts were washed with 10% aqueous HCl, saturated $NaHCO_3$, water, and saturated NaCl and dried ($MgSO_4$). Solvent was removed by rotary evaporation and the residual oil distilled under reduced pressure to afford **3p**, 2.3 g (69%): bp 81–85 °C (12 mm); ^1H NMR δ 1.4–2.2 (6 H), 3.7–4.1 (3 H), 5.0–5.4 (2 H), 5.5–6.3 (3 H). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.27; H, 10.16.

Allyl Δ^2-cyclooctenyl ether (3q) was prepared from 2-cycloocten-1-ol (3.8 g, 30 mmol), NaH (2 g, 46 mmol), and allyl bromide (3.9 mL, 45 mmol) as described above for **3p**. The ether **3q** (71%) showed the following: bp 92–93 °C (15 mm); ^1H NMR δ 1.2–2.3 (10 H), 3.9–4.1 (2 H), 4.1–4.5 (H), 5.0–5.47 (2 H), 5.47–6.3 (3 H). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.52; H, 11.02.

3-(Allyloxy)-3-methylcyclopentene (3s). To a well-stirred and ice-cold suspension of NBS (8.9 g, 50 mmol) in excess allyl alcohol (12 mL) was added dropwise methylcyclopentene (4.09 g, 50 mmol). The mixture was stirred for 30 min at 0 °C and 1.5 h at 20 °C. The reaction mixture was poured into cold water (40 mL) and extracted with pentane (3 × 30 mL). The pentane extract was washed with water (2 × 10 mL) and dried ($MgSO_4$). Removal of solvent followed by distillation of the residual liquid afforded **1-(allyloxy)-2-bromo-1-methylcyclopentane (9s)**, 7.47 g (67%): bp 75–80 °C (12 mmHg); ^1H NMR δ 1.45 (s, 3 H), 1.6–2.7 (6 H), 3.7–4.15 (2 H), 4.27 (m, H), 5.0–5.5 (2 H), 5.5–6.2 (m, H). Anal. Calcd for $C_9H_{15}BrO$: C, 49.33; H, 6.90. Found: C, 49.65; H, 6.97.

A solution of the bromide (1.10 g, 5 mmol) in dry Me_2SO (5 mL) was heated at 90–95 °C in the presence of potassium *tert*-butoxide (1.12 g, 10 mmol) for 3 h. The reaction mixture was cooled to 20 °C, then poured into cold water (20 mL), and extracted with hexane (3 × 20 mL). The hexane extract was washed with water (2 × 20 mL) and dried ($MgSO_4$). Removal of solvent followed by distillation of the residual liquid afforded **3s**, 489 mg (78%): bp 85–90 °C (50 mmHg); ^1H NMR δ 1.36 (s, 3 H), 1.7–2.1 (2 H), 2.2–2.6 (2 H), 3.83 (d m, 2 H, J = 5 Hz), 4.9–5.5 (2 H), 5.5–6.3 (3 H). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.21; H, 10.13.

3-(Allyloxy)-3-methylcyclohexene (3t). Following the procedure described above for preparation of **9s**, **1-(allyloxy)-2-bromo-1-methylcyclohexane (9t)** was prepared from 1-methylcyclohexene in 81% yield: bp 53–56 °C (0.2 mmHg); ^1H NMR δ 1.29 (s, 3 H), 1.35–2.45 (8 H), 3.84–4.30 (3 H), 4.94–5.39 (3 H). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.52; H, 7.35. Found: C, 51.39; H, 7.30.

By the procedure described above for **3s**, the diene **3t** was obtained in 85% yield from bromide **9t** as a colorless liquid: bp 58–60 °C (15 mmHg); ^1H NMR δ 1.25 (s, 3 H), 1.53–2.13 (6 H), 3.81–3.98 (2 H), 4.90–6.25 (5 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.82; H, 10.57.

Allyl 2-Methylenecyclohexyl Ether (3u). To pyridinium chlorochromate (9.7 g, 44 mmol) in CH_2Cl_2 (30 mL) was added *trans*-2-hydroxycyclohexyl allyl ether (3.1 g, 20 mmol) in CH_2Cl_2 (10 mL), and the resulting mixture was stirred at 20 °C for 30 h. The mixture was diluted with ether (250 mL), and the ether solution decanted from a black residue which was washed with ether (4 × 25 mL). The combined ether extracts were filtered through Florisil. Rotary evaporation of solvent followed by distillation under reduced pressure provided 2-(allyloxy)cyclohexanone: bp 103–105 °C (12 mm) (65%); ^1H NMR δ 1.3–2.6 (8 H), 3.7–4.4 (3 H), 5.0–5.5 (2 H), 5.6–6.7 (H, m). This ketone (2.1 g, 13.6 mmol) was added to a solution of methylenetriphenylphosphorane prepared from methyltriphenylphosphonium bromide (7.2 g, 20 mmol) in THF (50 mL) and MeLi in Et_2O (13.6 mL of 1.4 M, 19 mmol). After being stirred overnight at 20 °C, the mixture was poured into water and extracted into pentane (3 × 50 mL). The pentane extract was washed with water (3 × 30 mL) and dried ($MgSO_4$). Solvents were removed by rotary evaporation and the residual oil was distilled under reduced pressure to afford **3u** (2.0 g, 97%): bp 125–130 °C (12 mm); ^1H NMR δ 1.3–1.65 (6 H), 1.95–2.4 (2 H), 3.6–4.0 (3 H), 4.81 (2 H), 4.9–5.5 (2 H), 5.6–6.3 (H, m). A sample for analysis was purified by GC on a $^1/_4$ in. × 6 ft column filled with 15% FFAP on 60/80 Chrom W. Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.84; H, 10.51.

Synthesis of Homoallyl Vinyl Ethers. Method B. O-Vinylation of Homoallyl Alcohols. To a solution of the alcohol (2.3 to 8.5 g) in freshly distilled ethyl vinyl ether (225 to 750 mL) was added mercuric trifluoroacetate (0.15 to 0.6 g), and the homogeneous reaction mixture was boiled under reflux with stirring under nitrogen for 6 h for primary alcohols or 15 days for the secondary alcohol. The mixture was then cooled to room temperature and anhydrous K_2CO_3 (5 g) was added. Excess ethyl vinyl ether was removed by distillation under atmospheric pressure. The residue was distilled under reduced pressure.

3-Buten-1-yl vinyl ether (6a) was obtained from 3-buten-1-ol by method B in 26% yield: bp 90 °C; ^1H NMR δ 2.43 (2 H, apparent q, J = 6.5 Hz), 3.75 2 H, t, J = 7 Hz), 3.9–4.38 (2 H), 4.9–5.4 (2 H), 5.5–6.2 (H, m), 6.46 (H, dd, J = 7, 14 Hz). Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.47; H, 10.22.

Hexa-1,5-dien-3-yl vinyl ether (6b) was obtained from 1,5-hexadien-3-ol by method B in 64% yield: bp 80–90 °C (90 mmHg); ^1H NMR δ 2.1–2.6 (2 H), 3.9–4.5 (3 H), 4.8–5.4 (4 H), 5.5–6.0 (2 H), 6.33 (H, dd, J = 6.5, 14 Hz). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.36; H, 9.70.

Cyclopent-1-en-3-ylmethyl vinyl ether (6c) was obtained from cyclopent-2-enemethanol by method B in 24% yield: bp 50–53 °C (12 mmHg); ^1H NMR δ 1.3–2.6 (4 H), 2.8–3.4 (H, m),

3.60 (2 H, d, J = 7 Hz), 3.9–4.4 (2 H), 5.6–6.0 (2 H, m), 6.49 (H, dd, J = 14 Hz). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.25; H, 9.73.

3-Methylcyclopent-1-en-3-ylmethyl vinyl ether (6d) was obtained from (1-methylcyclopent-2-ene)methanol by method B in 63% yield: bp 50–58 °C (12 mmHg); ^{1}H NMR δ 1.10 (3 H, s), 1.48–1.93 (2 H), 2.2–2.6 (2 H), 3.47 (2 H, s), 3.8–4.3 (2 H), 5.4–5.9 (2 H), 6.49 (H, dd, J = 7, 14 Hz). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.17; H, 10.11.

2-(Cyclopenten-1-yl)ethyl vinyl ether (6e) was obtained from 2-cyclopent-1-enylethanol by method B in 32% yield: bp 72–76 °C (15 mmHg); ^{1}H NMR δ 1.6–2.6 (8 H), 3.6–4.4 (4 H), 5.43 (H, br s), 6.47 (H, dd, J = 7, 14 Hz). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.20; H, 10.25.

Cyclohex-1-en-3-ylmethyl vinyl ether (6f) was obtained from cyclohex-2-enemethanol by method B in 17% yield: bp 68–73 °C (12 mmHg); ^{1}H NMR δ 1.2–2.2 (6 H), 2.7–2.6 (H), 3.57 (2 H, d, J = 6 Hz), 3.8–4.4 (2 H), 5.4–6.0 (2 H), 6.49 (H, dd, J = 7, 14 Hz). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.13; H, 10.20.

Photocyclization of Diallyl Ethers. General Procedure for Cu-Catalyzed Photocyclization. To a solution of the diene (1–2 g) in anhydrous ether (140 mL) was added copper trifluoromethanesulfonate (1–2 mol %). This homogeneous solution was irradiated under an atmosphere of nitrogen with a medium-pressure mercury vapor Hanovia lamp through a water-cooled quartz immersion well, until disappearence of the starting diene (usually 15–40 h) monitoring by GC. After completion of the reaction, the ether solution was poured into a mixture of crushed ice and 30% NH_4OH (100 mL) and shaken well. The two layers were separated and the deep blue aqueous layer was extracted with ether (2 × 50 mL). The combined ether extracts were washed with brine and dried ($MgSO_4$). Ether was removed by rotary evaporation and the residual oil was distilled to afford the cyclized product.

3-Oxabicyclo[3.2.0]heptane (4a) was obtained from diallyl ether (**3a**) in 52% yield: bp 115–118 °C; ^{1}H NMR δ 1.45–2.45 (4 H), 2.75–3.15 (2 H), 3.48 (d m, 2 H, J = 9 Hz), 3.85 (d, 2 H, J = 9 Hz). Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.49; H, 10.26.

2,2-Dimethyl-3-oxabicyclo[3.2.0]heptane (4b) was obtained from allyl α,α-dimethylallyl ether (**3b**)[6] in 56% yield: bp 45–48 °C (12 mmHg); ^{1}H NMR δ 1.03 (s, 3 H), 1.25 (s, 3 H), 1.4–3.2 (6 H), 3.71 (d, H, J = 7.5 Hz), 3.89 (dd, H, J = 3.4, 7.8 Hz). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.15; H, 11.07.

2,2,5-Trimethyl-3-oxabicyclo[3.2.0]heptane (4c) was prepared from α,α-dimethylallyl β-methylallyl ether (**3c**) in 54% yield: bp 45–47 °C (12 mmHg); ^{1}H NMR δ 0.73 (s, 3 H), 1.23 (s, 3 H), 1.25 (s, 3 H), 1.6–2.3 (5 H), 3.48 (d, H, J = 9 Hz), 3.74 (d, H, J = 9 Hz), 3.87 (q, H, J = 6 Hz). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.97, H, 11.59.

***exo*-2-Methyl-3-oxabicyclo[3.2.0]heptane (4d)** was prepared from allyl α-methylallyl ether (**3d**)[6] in 54% yield: bp 70–72 °C (50 mmHg); ^{1}H NMR δ 1.02 (d, 3 H, J = 7 Hz), 1.47–3.11 (6 H), 3.46 (d, H, J = 7 Hz), 3.67 (dd, H, J = 3.2, 9 Hz), 3.97 (br q, H, J = 6.7 Hz). Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.02; H, 10.80.

***exo*-4-Butyl-1-methyl-3-oxabicyclo[3.2.0]heptane (4e)** was prepared from **3e** in 83% yield: bp 80–83 °C (12 mmHg); ^{1}H NMR δ 0.89 (t, 3 H, J = 5.5 Hz), 1.25 (s, 3 H), 1.08–1.55 (6 H), 1.60–2.27 (5 H), 3.42 (d, H, J = 9 Hz), 3.69 (d, H, J = 9 Hz), 3.84 (br t, H, J = 5.5 Hz). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.48; H, 12.09.

6,6-Dimethyl-3-oxabicyclo[3.2.0]heptane (4f) was prepared from **3f**[6] in 39% yield: bp 47–50 °C (12 mmHg); ^{1}H NMR δ 0.93 (s, 3 H), 1.15 (s, 3 H), 1.05–3.08 (4 H), 3.2–3.6 (2 H), 3.73 (d, H, J = 8.5 Hz), 4.07 (d, H, J = 10 Hz). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.96; H, 11.25.

1-Methyl-3-oxabicyclo[3.2.0]heptane (4g) was prepared from **3g**[6] in 41% yield: bp 72–75 °C (80 mmHg); ^{1}H NMR δ 1.25 (s, 3 H), 1.4–2.6 (5 H), 3.15 (d, H, J = 9 Hz), 3.4–4.1 (3 H). Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.90; H, 10.65.

6-(Hydroxymethyl)-3-oxabicyclo[3.2.0]heptane (4h) was prepared from **3h** in 41% yield: bp 118–120 °C (12 mmHg); ^{1}H NMR δ 1.0–2.5 (5 H), 1.5–3.2 (2 H), 3.2–4.2 (5 H). Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.64; H, 9.48.

6-(Acetoxymethyl)-3-oxabicyclo[3.2.0]heptane (4i) was prepared from **3i** in 35% yield as an epimeric mixture: bp 60–65 °C (0.28 mmHg); ^{1}H NMR δ 1.0–2.5 (3 H), 2.00 and 2.05 (2s, 3 H), 2.51–3.1 (2 H), 3.1–4.2 (4 H). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.50; H, 8.34.

6-(Acetoxymethyl)-*exo*-2-octyl-3-oxabicyclo[3.2.0]heptane (4j) was obtained from **3j** in 21% yield after column chromatography through SiO_2 (60–200 mesh) with ethyl acetate/hexane as eluent: ^{1}H NMR δ 0.88 (t, 3 H, J = 5 Hz), 1.0–1.7 (17 H), 1.7–2.9 (8 H), 2.01 (s, 3 H) and 2.05 (2s, 3 H), 3.4–4.0 (3 H), 4.05, 4.15 (2s, 55% and 45%, respectively, 2 H). Anal. Calcd for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71. Found: C, 72.05; H, 10.49.

6-(1-Propenyl)-3-oxabicyclo[3.2.0]heptane (4k) was obtained from **3k** in 71% yield: bp 83–85 °C (15 mm); ^{1}H NMR δ 1.35–2.18 (5 H, m), 2.35–3.17 (3 H, m), 3.17–4.28 (4 H, m), 5.02–5.93 (2 H, m). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.28; H, 10.19.

6-(1-Propenyl)-4-methyl-3-oxabicyclo[3.2.0]heptane (4l) was obtained from **3l** in 80% yield: bp 44 °C (0.45 mm); ^{1}H NMR δ 1.00 (3 H, d, J = 7 Hz, C_4-Me), 1.37–3.13 (8 H, m), 3.47–4.37 (3 H, m), 4.97–5.9 (2 H, m, vinylic H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.75; H, 10.62.

4-*n*-Butyl-6-(1-propenyl)-3-oxabicyclo[3.2.0]heptane (4m) was obtained from **3m** in 87% yield: bp 68–70 °C (0.5 mm); ^{1}H NMR δ 0.62–2.13 (14 H, m), 2.22–3.18 (3 H, m), 3.52–4.35 (3 H, m), 5.15–5.85 (2 H, m). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.45. Found: C, 80.31; H, 11.45.

4-Allyl-3-oxabicyclo[3.2.0]heptane (4n) was obtained from **3n** in 70% yield: bp 76–80 °C (12 mm); ^{1}H NMR δ 1.57–2.52 (6 H, m), 2.52–3.2 (2 H, m), 3.68–4.22 (3 H, m), 4.73–5.33 (2 H, m), 5.4–6.2 (H, m). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.28; H, 9.98.

2-Oxatricyclo[4.2.1.0^{4,9}]nonane (4o) was prepared from **3o**[6] in 47% yield: bp 50–52 °C (12 mmHg); ^{1}H NMR δ 1.0–3.3 (9 H), 3.59 (dd, H, J = 3, 9 Hz), 3.79 (d, H, J = 9 Hz), 4.43 (dd, H, J = 3, 5 Hz). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.44; H, 9.70.

2-Oxatricyclo[4.3.1.0^{4,10}]decane (4p) was prepared from **3p** in 36% yield: bp 60–65 °C (12 mmHg); ^{1}H NMR δ 1.0–3.0 (11 H), 3.47 (dd, H, J = 3.5, 9 Hz), 3.78 (d, H, J = 9 Hz), 3.92 (H). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.28; H, 10.22.

8-Oxatricyclo[5.4.1.0^{10,12}]dodecane (4q) was prepared from **3q** in 56% yield: bp 115 °C (12 mmHg); ^{1}H NMR δ 1.1–3.1 (15 H), 3.44 (dd, H, J = 3.5, 8.7 Hz), 3.6–4.2 (H), 4.03 (dd, H, J = 7.2, 8.7 Hz). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.30; H, 10.89.

3-Oxatricyclo[5.4.0.0^{1,5}]undecane (4r) was prepared from **3r**[6] in 35% yield: bp 92–95 °C (15 mmHg); ^{1}H NMR δ 1.0–2.3 (11 H), 2.4–2.8 (H), 3.21 (d, H, J = 9 Hz), 3.59 (dd, H, J = 4, 9 Hz), 3.75–3.95 (2 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.83; H, 10.63.

1-Methyl-2-oxatricyclo[4.2.1.0^{4,9}]nonane (4s) was prepared from **3s** in 28% yield: bp 48–50 °C (12 mmHg); ^{1}H NMR δ 1.25 (s, 3 H), 1.2–3.0 (9 H), 3.76 (2 H). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.26.

1-Methyl-2-oxatricyclo[4.3.1.0^{4,10}]decane (4t) was prepared from **3t** in 35% yield: bp 76 °C (10 mmHg); ^{1}H NMR δ 0.96 (s, 3 H), 1.08–2.91 (11 H), 3.55 (d, 2 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.76; H, 10.53.

2-Oxatricyclo[5.4.0.0^{4,7}]undecane (4u) was prepared from **3u** in 94% yield: bp 94–95 °C (18 mmHg); ^{1}H NMR δ 1.0–2.5 (13 H), 3.5–4.1 (3 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.97, H, 10.48.

Photocyclization of Homoallyl Vinyl Ethers. General Procedure. To a solution of the homoallyl vinyl ether **6** (0.4 g to 1.8 g) in anhydrous ether (140 to 200 mL) was added copper(I) trifluoromethanesulfonate (0.08 g to 0.21 g) under nitrogen with stirring. The homogeneous solution was irradiated for 16 to 58 h with a 450-H Hanovia lamp. After completion of the irradiation, the reaction mixture was poured into a mixture of crushed ice and aqueous 30% NH_4OH (50 mL) and shaken well. The deep blue aqueous layer was separated and extracted with ether (2 × 100 mL). The combined ether extract was washed with saturated NaCl solution (100 mL) and dried over $MgSO_4$. Solvent was removed by distillation under atmospheric or reduced pressure,

and the residual oil was distilled under reduced pressure to afford the cyclized product **7**.

2-Oxabicyclo[3.2.0]heptane (7a) was obtained in 60% yield: bp 100–110 °C; ^{1}H NMR δ 1.5–2.5 (6 H, m), 2.7–3.3 (H, m), 3.9–4.3 (2 H), 4.4–4.8 (H, m). Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.40; H, 10.33.

3-Vinyl-2-oxabicyclo[3.2.0]heptane (7b) was obtained in 58% yield: bp 80–85 °C (30 mmHg); ^{1}H NMR δ 1.4–2.6 (6 H), 2.6–3.2 (H), 4.2–4.8 (2 H), 4.9–5.5 (2 H), 5.6–6.4 (H, m). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.40; H, 9.77.

3-Oxatricyclo[4.2.1.0^{4,9}]nonane (7c) was obtained in 92% yield: bp 70–72 °C (12 mmHg); ^{1}H NMR δ 1.0–2.1 (5 H), 2.1–3.0 (3 H), 3.0–3.4 (H, m), 3.73–3.88 (2 H, m), 4.2–4.6 (H, m). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.31; H, 9.65.

1-Methyl-3-oxatricyclo[4.3.1.0^{4,9}]nonane (7d) was obtained in 50% yield: bp 76–78 °C (12 mmHg); ^{1}H NMR δ 1.13 (3 H, s), 1.3–2.9 (8 H), 3.47 (H, d, J = 8 Hz), 3.77 (H, d, J = 8 Hz), 4.2–4.6 (H, m). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.18; H, 10.20.

3-Oxatricyclo[5.3.0.0^{4,7}]decane (7e) was obtained in 40% yield. The product was purified by gas chromatography using a 3 ft × $^1/_4$ in. 10% DC 710 column at 100 °C: ^{1}H NMR δ 1.3–2.4 (11 H), 3.7–4.3 (3 H). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.25; H, 10.21.

3-Oxatricyclo[5.3.1.0^{4,10}]decane (7f) was obtained in 48% yield: bp 36–40 °C (0.25 mmHg); ^{1}H NMR δ 1.3–1.7 (6 H), 1.7–2.9 (5 H), 3.6–4.3 (2 H), 4.4–4.7 (H, m). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.29; H, 10.15.

RuO_4 Oxidation of Tetrahydrofuran Derivatives. To a vigorously stirred two-phase mixture of CCl_4 (10.0–12.5 mL) and water (10.0–12.5 mL) containing sodium metaperiodate (0.50 g to 0.67 g) was added ruthenium dioxide (20 mg, 0.15 mmol) at room temperature. After stirring for 10 min, the black RuO_2 dissolved to produce a deep yellow solution of RuO_4 in the CCl_4 layer. To this mixture was added dropwise the tetrahydrofuran derivative (0.65 to 1.00 mmol, either neat or as a solution in CCl_4). Stirring was continued until complete consumption of the starting tetrahydrofuran was indicated by TLC analysis (30% ethyl acetate in hexane). The reaction mixture was then filtered through Celite and the residue was thoroughly washed with CH_2Cl_2. The organic layer was separated. The aqueous layer was saturated with sodium chloride and extracted several times with CH_2Cl_2. Isopropyl alcohol (200 μL) was added to the combined organic extracts, and the mixture was shaken vigorously to reduce all RuO_4 to RuO_2. The organic extracts were dried over $MgSO_4$ and filtered through Celite, and the solvent was rotary evaporated to furnish the lactone, which was quite pure by ^{1}H NMR. For analysis the lactones were purified further by GC on a 4 ft × $^1/_4$ in. column packed with 15% FFAP on Chromosorb W at 100–200 °C.

3-Oxabicyclo[3.2.0]heptan-2-one (1a) was obtained in 91% yield: ^{1}H NMR δ 1.9–2.8 (4 H), 2.9–3.4 (2 H), 4.1–4.5 (2 H). Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.08; H, 7.23.

4,4-Dimethyl-3-oxabicyclo[3.2.0]heptan-2-one (1b) was obtained in 94% yield: ^{1}H NMR δ 1.28 (s, 3 H), 1.38 (s, 3 H), 1.8–3.4 (6 H). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.49; H, 8.62.

3-Oxa-1,4,4-trimethylbicyclo[3.2.0]heptan-2-one (1c) was obtained in 44% yield: ^{1}H NMR δ 1.33 (s, 3 H), 1.36 (s, 3 H), 1.41 (s, 3 H), 1.8–2.7 (5 H). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.16; H, 9.14.

3-Oxa-*exo*-4-methylbicyclo[3.2.0]heptan-2-one (1d) was obtained in 56% yield: ^{1}H NMR δ 1.26 (d, 3 H, J = 6.5 Hz), 1.8–3.5 (6 H), 4.51 (9d, H, J = 6.5, 1.5 Hz). This spectrum is identical with that reported previously for **1d**.[5]

***exo*-4-Butyl-1-methyl-3-oxabicyclo[3.2.0]heptan-2-one (1e)** was obtained in 83% yield: ^{1}H NMR δ 0.91 (br t, 3 H, J = 5 Hz), 1.39 (s, 3 H), 1.2–1.8 (6 H), 1.9–2.7 (5 H), 4.32 (br t, H, J = 6.5 Hz). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.49; H, 10.63.

RuO_4 Oxidation of 6,6-Dimethyl-3-oxabicyclo[3.2.0]heptane (4f). Oxidation of **4f** produced a 4:6 mixture respectively of the isomeric lactones **1fx** and **1fy** (47% yield) which were separated by GC. Minor isomer, **7,7-dimethyl-3-oxabicyclo[3.2.0]heptan-2-one (1fx)**: ^{1}H NMR δ 1.14 (s, 3 H), 1.34 (s, 3 H), 1.6–2.4 (2 H), 2.76 (dd, H, J = 2.7, 8 Hz), 2.87–3.25 (m, H), 4.1–4.5 (2 H). Major isomer, **6,6-dimethyl-3-oxabicyclo[3.2.0]heptan-2-one (1fy)**: ^{1}H NMR δ 1.15 (s, 3 H), 1.20 (s, 3 H), 1.7–2.3 (2 H), 2.6–3.3 (2 H), 4.1–4.5 (2 H); agrees with the ^{1}H NMR spectrum reported[4b] for **1fy**.

RuO_4 Oxidation of 1-Methyl-3-oxabicyclo[3.2.0]heptane (4g). Oxidation of **4g** produced a 3:7 mixture respectively of two isomeric lactones **1gx** and **1gy** in 65% yield. These products were separated by GC. Minor isomer, **1-methyl-3-oxabicyclo[3.2.0]heptan-2-one (1gx)**: ^{1}H NMR δ 1.36 (s, 3 H), 1.6–3.0 (5 H), 4.0–4.5 (m, 2 H). Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.59; H, 7.92. Major isomer, **5-methyl-3-oxabicyclo[3.2.0]heptan-2-one (1gy)**: ^{1}H NMR δ 1.35 (s, 3 H), 1.6–2.8 (5 H), 3.92 (d, H, J = 9 Hz), 4.24 (d, H, J = 9 Hz). Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.69; H, 8.12.

2-Oxatricyclo[4.2.1.0^{4,9}]nonan-3-one (1o) was obtained in 73% yield: ^{1}H NMR δ 1.5–2.4 (5 H), 2.5–3.6 (4 H), 5.03 (dd, H, J = 3, 6 Hz). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.47; H, 7.32.

RuO_4 Oxidation of 2-Oxatricyclo[4.3.1.0^{4,10}]decane (4p). Oxidation of **4p** afforded a mixture of hemiketal **20** and lactone **1p** from which pure products were isolated by preparative TLC (60% ethyl acetate in hexane). **1-Hydroxy-2-oxatricyclo[4.3.1.0^{1,4}]decane (20)** (20% yield): mp 104–5 °C; ^{1}H NMR δ 1.0–2.3 (8 H), 2.4–3.1 (4 H), 3.67 (d, H, J = 8.5 Hz), 3.93 (dd, H, J = 3.5, 8.5 Hz). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.23; H, 9.20. **2-Oxatricyclo[4.3.1.0^{4,10}]decan-3-one (1p)** (4% yield): ^{1}H NMR δ 1.1–2.3 (8 H), 2.4–3.3 (3 H), 4.80 (H). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.09; H, 7.80.

8-Oxatricyclo[6.4.1.0^{11,13}]dodecan-9-one (1q) was obtained in 56% yield as a white crystalline solid: mp 70 °C; ^{1}H NMR δ 1.1–3.1 (15 H), 4.6–5.1 (H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.62.

RuO_4 Oxidation of 3-Oxatricyclo[5.4.0.0^{1,5}]undecane (4r). A 1.3:1 mixture respectively of two isomeric lactones **1rx** and **1ry** was obtained in 78% yield. Samples of each pure lactone were obtained by GC. Major product, **3-oxatricyclo[5.4.0.0^{1,5}]undecan-4-one (1rx)**: ^{1}H NMR δ 1.1–2.4 (11 H), 2.9–3.3 (H), 4.0–4.4 (2 H). Minor product, **3-oxatricyclo[5.4.0.0^{1,5}]undecan-2-one (1ry)**: ^{1}H NMR δ 1.2–2.6 (11 H), 2.6–2.9 (H), 3.95 (d, H, J = 9 Hz), 4.33 (d, H, J = 9 Hz).

1-Methyl-2-oxatricyclo[4.2.1.0^{4,9}]nonan-3-one (1s) was obtained in 87% yield: ^{1}H NMR δ 1.48 (s, 3 H), 1.6–2.4 (5 H), 2.6–3.3 (4 H). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.06; H, 8.12.

1-Methyl-2-oxatricyclo[4.3.1.0^{4,10}]decan-3-one (1t) was obtained in 82% yield as a white crystalline solid: mp 59 °C; ^{1}H NMR δ 1.32 (s, 3 H), 1.0–3.5 (11 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.34; H, 8.55.

2-Oxatricyclo[5.4.0.0^{4,7}]undecan-3-one (1u) was obtained in 65% yield as a colorless liquid: ^{1}H NMR δ 1.1–2.7 (13 H), 4.20 (m, H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.23; H, 8.37.

3-Oxatricyclo[4.2.1.0^{4,9}]nonan-2-one (8c) was obtained in 78% yield: ^{1}H NMR δ 1.4–2.5 (5 H, m), 2.5–3.7 (4 H), 4.6–5.0 (H). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: 69.68; H, 7.31.

1-Methyl-3-oxatricyclo[4.2.1.0^{4,9}]nonan-2-one (8d) was obtained in 71% yield: ^{1}H NMR δ 1.33 (3 H, s), 1.4–3.2 (8 H), 4.5–5.0 (H). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.89; H, 7.91.

4-Oxatricyclo[5.3.0.0^{1,5}]decan-3-one (8e) was obtained in 70% yield: ^{1}H NMR δ 1.4–2.6 (9 H), 2.63 (2 H, s), 4.3–4.6 (H, m). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.04; H, 8.03.

3-Oxatricyclo[4.3.1.0^{4,10}]decan-2-one (8f) was obtained in 85% yield: ^{1}H NMR δ 1.2–1.7 (4 H), 1.7–3.4 (7 H), 4.7–5.1 (H, m). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.07; H, 8.00.

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