# Synthesis of Novel Cage Oxaheterocycles

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*m*-CPBA-promoted Baeyer−Villiger oxidation of pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-4-one (**1**) afforded the corresponding lactone **2** in 93% yield. Lithium aluminum hydride promoted reduction of lactones **2**, **6**, and **9**, performed in the presence of $BF_3$·$OEt_2$ reagent, afforded the corresponding cage ethers, i.e., **4**, **7**, and **10**, respectively. Two methods that can be used to replace a cage C═O group by ether oxygen without concomitant rearrangement are delineated. A key step in the first of these methods employs *m*-CPBA promoted "double Criegee rearrangement", which was used to convert pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-4-one diethyl acetal (**11**) into 7,9-dioxapentacyclo-[8.3.0.$0^{2,6}$.$0^{3,12}$.$0^{5,11}$]tridecan-8-one (**12**). Subsequently, **12** was converted into 4-oxapentacyclo-[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**14**) via a two-step reduction−dehydration reaction sequence. The second method utilized PhI$(OAc)_2$−$I_2$ reagent to convert cage lactols **15** and **17** into the corresponding cage ethers, i.e., **14** and 2-oxaadamantane (**18**), respectively.

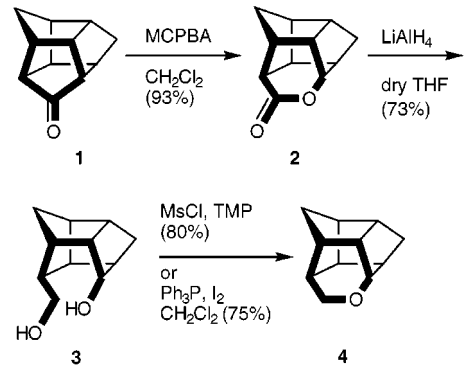
## Introduction

There is considerable current interest in the development of new methods for preparing cyclic and acyclic ethers.[1] An example in this regard is provided by a recently reported two-step procedure for synthesizing ethers that involves DIBAL-H-promoted reductive acetylation of acyclic esters with subsequent reduction of the resulting α-acetoxy ethers under acidic conditions.[2] However, relatively few methods exist that can be used generally to prepare *cage-annulated* ethers.[3] We now report potentially general procedures that can be used to synthesize cage ethers by replacing a carbonyl group in a cage ketone (i) by ring oxygen or (ii) by $CH_2O$ (i.e., replacement of ring C═O by ring O with concomitant homologation).

## Results and Discussion

**Replacement of a Carbonyl Group in Cage Ketones by an Ether Oxygen Atom with Ring Homologation.** In 1961, Doorenbos and Wu[4] reported a procedure by which 4-oxa-5α-cholestan-3-one could be converted successfully into 4-oxa-5α-cholestane. In the present study, we have adopted a similar regimen to convert pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-4-one (i.e., "trishomocubanone", **1**[5]) into 7-oxapentacyclo[7.3.0.$0^{2,6}$.-$0^{3,11}$.$0^{5,10}$]dodecane (**4**; see Scheme 1). Thus, Baeyer−Villiger oxidation of **1**[5] followed by $LiAlH_4$-promoted reduction of the resulting lactone, **2**, afforded the corresponding diol **3**. Subsequent dehydration of **3** afforded **4** in 75−80% yield.

**Scheme 1**




A simple and potentially general method was utilized to obtain several cage ethers. Lithium aluminum hydride reduction of esters and lactones, when performed in the presence of $F_3B$·$OEt_2$, has been reported to afford ethers[6] and cyclic ethers, respectively.[6,7] Thus, cage-annulated lactone **6**,[8] prepared via *m*-CPBA-promoted oxidation of pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one (i.e., **5**,[9] Scheme 2), when allowed to react with $LiAlH_4$ in the presence of $BF_3$·$OEt_2$, produced the corresponding cage annulated

(1) See: Elliott, M. C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1291 and references therein.

(2) (a) Dahanukar, V. H.; Rychnovsky, S. D. *J. Org. Chem.* **1996**, *61*, 8317. (b) Kopecky, D. J.; Rychnovsky, S. D. *J. Org. Chem.* **2000**, *65*, 191.

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(4) Doorenbos, N. J.; Wu, M. T. *J. Org. Chem.*, **1961**, *26*, 4550.

(5) Eaton, P. E.; Hudson, R. A.; Georadano, C. *J. Chem. Soc., Chem. Commun.* **1974**, 978.

(6) (a) Pettit, G. R.; Kasturi, T. R. *J. Org. Chem.*. **1960**, *25*, 875. (b) Pettit, G. R.; Ghatak, U. R.; Green, B.; Kasturi, T. R.; Piatak, D. M. *J. Org. Chem.* **1961**, *26*, 1685. (c) Pettit, G. R.; Kasturi, T. R. *J. Org. Chem.* **1961**, *26*, 4553. (d) Pettit, G. R.; Piatak, D. M. *J. Org. Chem.* **1962**, *27*, 2127. (d) Ager, D. J.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1982**, 248.

(7) Goff, D. L.; Murray, R. K., Jr. *J. Org. Chem.* **1978**, *43*, 3179.

(8) It should be noted that unlike cage ketones **1** or **8**, Baeyer−Villiger oxidation of **5** potentially might proceed via migration of either (or both) of two nonequivalent carbon-to-carbonyl bonds, thereby leading to either (or both) of two cage lactones. In our hands, only one lactone was obtained from this reaction. Structure **6** has been assigned to this lactone by analogy to the previously reported course of the corresponding Baeyer−Villiger oxidation of a closely related substrate, i.e., pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione; see: Surapaneni, C. R.; Gilardi, R. *J. Org. Chem.* **1986**, *51*, 2380.

(9) (a) Lerman, B. M.; Galin, F. Z.; Umanskaya, L. A.; Tolstikov, G. A. *J. Org. Chem. USSR* **1978**, *14*, 2336. (b) Dekker: T. G.; Oliver, D. W. *S. Afr. J. Chem.* **1979**, *32*, 45. (c) Marchand, A. P.; Kaya, R. *J. Org. Chem.* **1983**, *48*, 5392.

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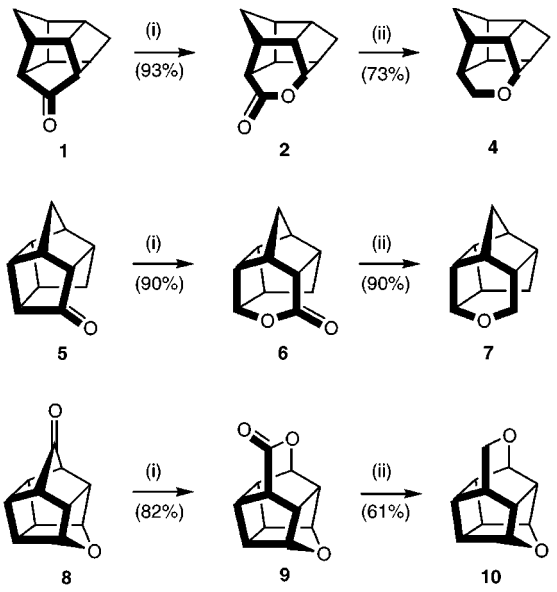
**Scheme 2**[a]




[a] Key: (i) *m*-CPBA, $CH_2Cl_2$; (ii) $LiAlH_4$, $F_3B{\cdot}OEt_2$, dry $Et_2O$.

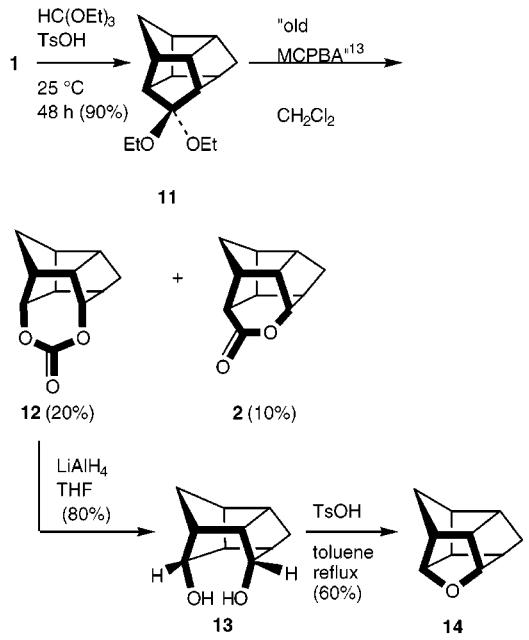
ether, **7**, in 92% yield. Similarly, lactones **2** and **9** (prepared via *m*-CPBA-promoted oxidation of **1** and **8,** respectively) could be reduced by $LiAlH_4$ in the presence of $BF_3{\cdot}OEt_2$ to afford the corresponding cage-annulated ethers, i.e., **4** (90%) and **10** (61%), respectively (Scheme 2). The foregoing examples serve to illustrate the utility of the two-step procedure shown in Scheme 2 for replacement of a C═O group in cage ketones by an ether linkage with concomitant homologation.

**Replacement of a Carbonyl Group in Cage Ketones by an Ether Oxygen Atom.** Several investigators[10] have reported that cyclic acetals can be converted into lactones via their reaction with peracids under acidic conditions. Bailey and Shih[11] have reported examples whereby *m*-CPBA-promoted oxidation of acyclic and cyclic acetals produces the corresponding orthocarbonates in low to moderate yields.

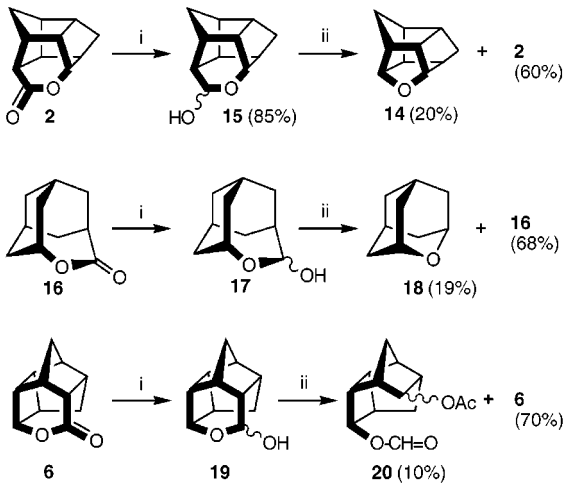
Recently, trifluoroperacetic acid promoted oxidation of 2-methyl-2-hydroxyadamantane has been reported[12] to result in "double Criegee rearrangement", thereby affording the corresponding cyclic carbonate ester. However, to our knowledge, this reaction has not been applied previously to cage acetals. In our hands, reaction of pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-4-one diethyl acetal (**11**, Scheme 3) with excess *m*-CPBA resulted in "double Criegee rearrangement", thereby affording the corresponding cage-annulated carbonate ester, **12**, in low yield. Interestingly, the course of *m*-CPBA-promoted oxidation of **11** proved to be highly sensitive to the purity of the *m*-CPBA employed as oxidant.[13,14]

Subsequent $LiAlH_4$-promoted reduction of **12** produced the corresponding tetracyclic *endo,endo*-diol, i.e., tetracyclo-[5.2.1.$0^{2,6}$.$0^{4,8}$]decane-*endo,endo*-3,9-diol (**13**), in 80% yield. Finally, acid-catalyzed dehydration of **13** afforded the

**Scheme 3**




**Scheme 4**[a]




[a] Key: (i) DIBAL-H, $CH_2Cl_2$ −78 °C; (ii) $PhI(OAc)_2$, $I_2$, *hν*, $CH_2Cl_2$ 25 °C.

desired cage ether, 4-oxapentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-undecane (**14**), in 60% yield.

An alternative synthesis of **14** from cage lactone **2** is shown in Scheme 4. (Diacetoxyiodo)benezene has been used to generate alkoxy radicals from alcohols[15] and carbon radicals from carboxylic acids.[16] DIBAL-H-promoted reduction of **2** afforded a mixture of diastereoiso-

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(11) (a) Bailey, W. F.; Shih, M.-J. *J. Am. Chem. Soc.* **1982**, *104*, 1769. (b) Bailey, W. F.; Bischoff, J. J. *J. Org. Chem.* **1985**, *50*, 3009.

(12) Krasutsky, P. A.; Kolomitsyn, I. V.; Kiprof, P.; Carlson, R. M.; Fokin, A. A. *J. Org. Chem.* **2000**, *65*, 3926

(13) Two samples of commercial *m*-CPBA were available in our laboratory: (i) "old *m*-CPBA", obtained from Aldrich Chemical Co., catalog no. C-6,270-0, "*m*-chloroperoxybenzoic acid, tech., approximately 80−90%; mp 92−94 °C dec" and (ii) "new *m*-CPBA", obtained from Aldrich Chemical Co., catalog no. 27,303-1, "3-chloroperoxybenzoic acid, tech., 77% max., remainder 3-chlorobenzoic acid and water, mp 69−71 °C". Reaction of **11** with "old *m*-CPBA" afforded **12** in low yield along with a small amount of the corresponding lactone, **2**. However, when oxidation of **11** was performed by using "new *m*-CPBA" (either as obtained from Aldrich Chemical Co. or further purified by extraction with 5% aqueous $NaHCO_3$ to remove *m*-chlorobenzoic acid followed by recrystallization from $CH_2Cl_2$), **2** was produced as the exclusive reaction product. The alternative use of magnesium monoperoxyphthalate[14] as oxidant failed to convert **11** to **12**.

(14) Brougham, P.; Cooper, M. S.; Cummerson, D. A.; Heaney, H.; Thompson, N. *Synthesis* **1987**, 1015.

meric lactols (**15**, 85% yield). Subsequent photolytic reaction of **15** with $PhI(OAc)_2$, when performed in the presence of $I_2$, produced **14** in low yield (20%) along with recovered **2** (60%), which could be recycled. Similarly, lactone **16**[17] was converted into 2-oxaadamantane (**18**)[12,18] via cage lactol **17**.[19]

Interestingly, photolytic reaction of $PhI(OAc)_2-I_2$ with cage lactol **19** (obtained via DIBAL-H-promoted reduction of **6**) resulted in ring fragmentation with concomitant formation of diester **20** in low yield accompanied by **6** (70% yield). The reasons for the failure of this reaction to proceed in the same manner as the corresponding reactions of **15** and **17** with $PhI(OAc)_2-I_2$ reagent are not clear at present. This reaction is undergoing further scrutiny in our laboratory.

## Summary and Conclusions

Procedures are described whereby the C═O moiety in cage ketones can be replaced (i) by ring $CH_2O$, which results in homologation of the cage system (Scheme 2), and (ii) by ether oxygen (Schemes 3 and 4).[19] Both of these reaction sequences proceed without concomitant rearrangement of the carbocyclic cage skeleton.

To the best of our knowledge, with a single exception[15a] applications of reactions of $PhI(OAc)_2-I_2$ with lactols have been confined to sugars.[15a,c] Herein, we demonstrate that extended application of this reaction to cage lactols derived from cage ketones provides a simple method to convert cage ketones into the corresponding cage ethers with the same ring size.[19,20]

## Experimental Section

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M−H−W Laboratories, Phoenix, AZ. High-resolution mass spectral data reported herein were obtained at the Mass Spectrometry Facility at the Department of Chemistry and Biochemistry, University of Texas at Austin, by using a ZAB-E double sector high-resolution mass spectrometer (Micromass, Manchester, England) that was operated in the chemical ionization mode.

**General Procedure for the *m*-CPBA-Promoted Oxidation of Cage Ketones.** To a mixture of the cage ketone (12.5 mmol) and 0.5 M aqueous $NaHCO_3$ (25 mL, 12.5 mmol) in $CH_2Cl_2$ (60 mL) at ambient temperature was added portionwise with stirring *m*-CPBA (4.3 g of commercial *m*-CPBA, purity 77% max[13]). The resulting mixture was stirred at ambient temperature during 3 h. The excess peracid was quenched via addition of 15% aqueous $Na_2SO_3$ (30 mL), and the resulting mixture was stirred at ambient temperature during 1 h. The layers were separated, and the organic layer was washed sequentially with water (20 mL), 5% aqueous $NaHCO_3$ (25 mL), water (20 mL), and brine (20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue thus obtained was purified by column chromatography on silica gel by eluting with 20% EtOAc−hexane.

***m*-CPBA-Promoted Oxidation of Trishomocubanone (1).** By using the general procedure described above, trishomocubanone[5] (**1**, 2.00 g, 12.5 mmol) was oxidized to 7-oxapentacyclo[7.3.0.$0^{2,6}$.$0^{3,11}$.$0^{5,10}$]dodecan-8-one (**2**). The reaction product was further purified via fractional recrystallization from $CH_2Cl_2$−hexane. Pure **2** (2.05 g, 93%) was thereby obtained as a colorless microcrystalline solid: mp 189−190 °C; IR (KBr) 2963 (s), 2884 (m), 1761 (s), 1472 (w), 1373 (s), 1051 (s), 909 (m), 735 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.22−1.28 (*A*B, $J_{AB}$ = 11.8 Hz, 1 H), 1.28−1.32 (*A*B, $J_{AB}$ = 10.9 Hz, 1 H), 1.41 (A*B*, $J_{AB}$ = 11.8 Hz, 1 H), 1.62 (A*B*, $J_{AB}$ = 10.9 Hz, 1 H), 2.05−2.45 (m, 7 H), 4.30 (dd, $J_1$ = 6.7 Hz, $J_2$ = 1.7 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 28.9 (t), 34.4 (t), 34.9 (d), 36.9 (d), 42.6 (d), 42.9 (d), 46.6 (d), 47.9 (d), 49.1 (d), 82.5 (d), 175.2 (s). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.16; H, 6.84.

***m*-CPBA-Promoted Oxidation of 5.** By using the general procedure described above, pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one (**5**)[8] (2.00 g, 12.5 mmol) was converted into 12-oxapentacyclo[5.5.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]dodecan-11-one (**6**, 1.98 g, 90%). Pure **6** was thereby obtained as a colorless microcrystalline solid: mp 228−229 °C; IR (KBr) 2962 (s), 2871 (m), 1755 (s), 1363 (m), 1226 (m), 1109 (m), 1007 (m), 784 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.45−1.78 (m, 4 H), 2.41−2.50 (m, 1 H), 2.52−2.68 (m, 3 H), 2.74−2.92 (m, 2 H), 3.03−3.14 (m, 1 H), 4.87 (t, $J$ = 8.4 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 30.1 (t), 37.5 (t), 38.1 (d), 38.3 (d), 41.3 (d), 41.4 (d), 43.3 (d), 48.1 (d), 48.4 (d), 71.3 (d), 174.8 (s). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.83; H, 6.88.

***m*-CPBA-Promoted Oxidation of 8.** By using the general procedure described above, 4-oxahexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$$0^{8,11}$]-dodecan-12-one (**8**)[21] (2.30 g, 13.3 mmol) was converted into the corresponding cage lactone, i.e., 4,12-dioxahexacyclo-[5.4.2.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]tridecan-13-one (**9**). The reaction product was further purified via fractional recrystallization from $CH_2Cl_2$−hexane. Pure **9** (2.06 g, 82%) was thereby obtained as a colorless microcrystalline solid: mp 263.5 °C (sealed tube); IR (KBr) 3011 (m), 2995 (m), 2962 (m), 1747 (s), 1371 (s), 1203 (m), 1039 (s), 901 (m) 860 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 2.69−3.09 (m, 7 H), 4.72−4.89 (m, 2 H), 4.95−5.06 (m, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 35.6 (d), 36.8 (d), 41.5 (d), 41.8 (d), 42.7 (d), 45.6 (d), 46.9 (d), 77.9 (d), 81.0 (d), 84.5 (d), 173.5 (s). Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.45; H, 5.3. Found: C, 69.50; H, 5.42.

***m*-CPBA-Promoted Oxidation of Adamantanone.**[17] By using the general procedure described above, adamantanone (3.0 g, 20 mmol) was oxidized with *m*-CPBA (7.15 g, 25.0 mmol) in the presence of 0.5 M aqueous $NaHCO_3$ (40 mL, 20 mmol). Workup of the reaction mixture afforded pure 4-oxatricyclo-[4.3.1.$1^{3,8}$]undecan-5-one (**16**).[17] Pure **16** (2.8 g, 85%) was thereby obtained as a colorless microcrystalline solid: mp 287−288 °C (lit.[17a] mp 288−290 °C; mp[17b] 286−289 °C; mp[17d] 286−288 °C). The IR, $^1H$ NMR, and $^{13}C$ NMR spectra of this material were essentially identical with published spectral data for authentic **16**.[17]

***endo*-3-Hydroxymethyltetracyclo[5.4.1.$0^{2,6}$.$0^{4,8}$]decan-*endo*-9-ol (3).** A suspension of $LiAlH_4$ (155 mg, 4.08 mmol) in dry THF (20 mL) was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise with stirring a solution of **2** (600 mg, 3.4 mmol) in dry THF (10 mL). After all of the lactone had been added, the external cold bath was removed, and the reaction mixture was allowed to warm gradually with stirring to ambient temperature. The reaction mixture was refluxed for 3 days and then was quenched via sequential addition of EtOAc (5 mL) and saturated aqueous $NH_4Cl$ (5 mL). The resulting aqueous

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(19) Suginome, H.; Yamada, S. *Synthesis* **1986**, 741.

(20) An analogous method that employs HgO−$I_2$ as oxidant has been reported as part of a four-step conversion of cyclic ketones into cyclic ethers. See: (a) Suginome, H.; Yamada, S. *Tetrahedron Lett.* **1984**, *25*, 3995. (b) Reference 19.

(21) Mehta, G.; Nair, M. S. *J. Am. Chem. Soc.*, **1985**, *107*, 7519.

suspension was filtered. The filtrate was diluted with water (50 mL), and the resulting aqueous suspension was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried ($Na_2SO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was triturated with $Et_2O$ (3 × 5 mL), whereupon pure **3** (443 mg, 73%) solidified as a colorless microcrystalline solid: mp 148−149 °C; IR (KBr) 3416 (s), 2944 (s), 2874 (s), 1468 (m), 1393 (w), 1042 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 0.95−1.65 (m, 5 H), 1.80−2.35 (m, 7 H), 3.35−3.90 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 29.9 (t), 34.7 (t), 35.9 (d), 37.3 (d), 38.2 (d), 39.2 (d), 39.9 (d), 47.7 (d), 48.5 (d), 62.0 (t), 75.9 (d); exact mass (CI HRMS) calcd for $C_{11}H_{16}O_2$ $[M_r + H]^+$ *m/z* 181.12286, found $[M_r + H]^+$ *m/z* 181.12255.

**7-Oxapentacyclo[7.3.0.0$^{2,6}$.0$^{3,11}$.0$^{5,10}$]dodecane (4). Method A.** A solution of **3** (90 mg, 0.5 mmol) in $CH_2Cl_2$ (10 mL) was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added with stirring 2,2,6,6-tetramethylpiperidine (TMP, 706 mg, 0.84 mL, 5 mmol) followed by dropwise addition of a solution of MsCl (69 mg, 0.6 mmol) in $CH_2Cl_2$ (2 mL). The reaction mixture was stirred at 0 °C for 3 h. Methylene chloride (20 mL) then was added, and the resulting mixture was washed successively with water (10 mL), 5% aqueous HCl (2 × 10 mL), water (10 mL), and brine (10 mL). The organic layer was dried ($Na_2SO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by eluting with 5% EtOAc−hexane. Pure **4** (65 mg, 80%) was thereby obtained as a colorless microcrystalline solid: mp 160−161 °C; IR (KBr) 2962 (s), 2887 (m), 2838 (w), 1141 (s), 1037 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.12 (*A*B, $J_{AB}$ = 10.3 Hz, 1 H), 1.21 (*A*B, $J_{AB}$ = 9.6 Hz, 1 H), 1.35 (A*B*, $J_{AB}$ = 10.3 Hz, 1 H), 1.48 (m, 2 H), 2.05 (dd, $J_1$ = 12.5 Hz, $J_2$ = 5.6 Hz, 2 H), 2.18−2.32 (m, 3 H), 2.42 (br s, 1 H), 3.53 (d, $J$ = 6.8 Hz, 1 H), 3.83 [d(*AB*) $J_{AB}$ = 9.2 Hz, $J$ = 3.3 Hz, 1 H], 3.90 (A*B*, $J_{AB}$ = 9.2 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 30.2 (t), 35.0 (t), 36.3 (d), 37.7 (d), 38.5 (d), 39.6 (d), 40.2 (d), 48.0 (d), 48.8 (d), 62.4 (t), 76.3 (d); exact mass (CI HRMS) calcd for $C_{11}H_{14}O$ $[M_r + H]^+$ *m/z* 163.11229, found: $[M_r + H]^+$ *m/z* 163.11298. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.60; H, 8.82.

**Method B.** A solution of $Ph_3P$ (525 mg, 2 mmol) and **3** (90 mg, 0.5 mmol) in $CH_2Cl_2$ (10 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise with stirring a solution of $I_2$ (508 mg, 2 mmol) in $CH_2Cl_2$ (10 mL), and the resulting mixture was stirred at 0 °C for 3 h. The external cooling bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature and then was refluxed during 3 h. The reaction mixture was allowed to cool gradually to ambient temperature. Methylene chloride (20 mL) was added, and the resulting solution was washed successively with 20% aqueous $Na_2S_2O_3$ (2 × 15 mL), water (15 mL), and brine (15 mL). The organic layer was dried ($Na_2SO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by eluting with 5% EtOAc−hexane. Pure **4** (61 mg, 75%) was thereby obtained as a colorless microcrystalline solid: mp 160−161 °C. The IR, $^1H$ NMR, and $^{13}C$ NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra obtained previously for **4** (vide supra).

**General Procedure for the $BF_3$·$OEt_2$−$LiAlH_4$-Promoted Reduction of Cage Lactones.** A suspension of $LiAlH_4$ (800 mg, 21 mmol) in anhydrous $Et_2O$ (100 mL) was cooled to 0 °C via application of an external ice−water bath. To this cooled suspension was added dropwise with stirring a solution of the lactone (2.84 mmol) and $F_3B$·$OEt_2$ (10 mL, 79 mmol) in anhydrous $Et_2O$ (40 mL). After the addition had been completed, the resulting mixture was stirred at 0 °C during 45 min, at which time the external ice−water bath was removed, and the reaction mixture was refluxed during 2 h. The reaction mixture then was allowed to cool gradually to ambient temperature while stirring, and excess $LiAlH_4$ was destroyed via careful, dropwise addition of 10% aqueous HCl (25 mL, excess) with stirring. The layers were separated and the aqueous layer was extracted with $Et_2O$ (2 × 50 mL). The combined organic layers were washed successively with 5% aqueous $NaHCO_3$ (4 × 25 mL), water (30 mL) and brine (25 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting with 20% EtOAc−hexane.

**12-Oxapentacyclo[5.5.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]dodecane (7).** By using the general procedure described above for $LiAlH_4$−$F_3B$·$OEt_2$-promoted reduction of cage lactones, **6** (500 mg, 2.84 mmol) was reduced to the corresponding cage ether, **7**. Workup of the reaction mixture as described above afforded pure **7** (423 mg, 92%) as a colorless microcrystalline solid: mp 187−188 °C (subl); IR (KBr) 2929 (s), 2838 (m), 1147 (s), 1121 (m), 1043 (m), 1004 (m), 769 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.30 (*A*B, $J_{AB}$ = 10.0 Hz, 1 H), 1.55 (A*B*, $J_{AB}$ = 10.0 Hz, 1 H), 1.56 [d(*AB*), $J_{AB}$ = 12.8 Hz, $J$ = 5.8 Hz, 1 H], 1.86 (A*B*, $J_{AB}$ = 12.8 Hz, 1 H), 1.93−2.04 (m, 1 H), 2.05−2.14 (m, 1 H), 2.26−2.43 (m, 2 H), 2.48−2.58 (m, 1 H), 2.65−2.81 (m, 1 H), 2.92 (dd, $J_1$ = 13.4 Hz, $J_2$ = 6.0 Hz, 1 H), 3.88 [d(*AB*), $J_{AB}$ = 10.3 Hz, $J$ = 3.3 Hz, 1 H], 4.11 (A*B*, $J_{AB}$ = 10.3 Hz, 1 H), 4.22 (dd, $J_1$ = 8.4 Hz, $J_2$ = 8.3 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 30.7 (t), 34.7 (d), 37.4 (t), 39.4 (d), 40.2 (d), 40.6 (d), 42.5 (d), 46.2 (d), 50.7 (d), 64.6 (t), 66.3 (d). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.22; H, 8.68.

**7-Oxapentacyclo[7.3.0.0$^{2,6}$.0$^{3,11}$.0$^{5,10}$]dodecane (4). Method C.**[12] By using the general procedure described above for $LiAlH_4$−$F_3B$·$OEt_2$-promoted reduction of cage lactones, **2** (500 mg, 2.84 mmol) was reduced to the corresponding cage ether, **4**. Workup of the reaction mixture as described above afforded pure **4** (410 mg, 90%) as a colorless microcrystalline solid: mp 161.0−161.5 °C. The IR, $^1H$ NMR, and $^{13}C$ NMR spectra of the material thereby ob-tained were essentially identical to the corresponding spectra obtained previously for **4** (vide supra).

**4,12-Dioxahexacyclo[5.4.2.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$.0$^{8,11}$]tridecane (10).** By using the general procedure described above for $LiAlH_4$−$F_3B$·$OEt_2$-promoted reduction of cage lactones, **9** (500 mg, 2.63 mmol) was reduced to the corresponding cage diether, **10**. The material thereby obtained was further purified via preparative TLC by eluting with 10% EtOAc−hexane. The eluate was concentrated in vacuo; the residue is highly volatile, and care must be taken to avoid loss of material during product workup. Final product purification was carried out via vacuum sublimation. Pure **10** (287 mg, 61%) was thereby obtained as colorless platelets: mp 205−205.5 °C (sealed tube); IR (KBr) 2995 (s), 2868 (m), 1334 (w), 1099 (s), 1010 (m), 910 (s), 870 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.79−1.92 (m, 1 H), 2.30−2.85 (m, 6 H), 3.56 (dd, $J_1$ = 9.1 Hz, $J_2$ = 2.1 Hz, 1 H), 3.71 (dd, $J_1$ = 9.0 Hz, $J_2$ = 2.0 Hz, 1 H), 3.79 (dd, $J_1$ = 5.0 Hz, $J_2$ = 4.9 Hz, 1 H), 4.59 (dd, $J_1$ = 5.0 Hz, $J_2$ = 4.4 Hz, 1 H), 4.78 (t, $J$ = 4.8 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 32.3 (d), 34.3 (d), 36.1 (d), 42.4 (d), 43.0 (d), 44.5 (d, 2 C), 60.4 (t), 69.0 (d), 80.8 (d), 84.0 (d); exact mass (CI HRMS) calcd for $C_{11}H_{12}O_2$ $[M_r + H]^+$ *m/z* 177.091555, found $[M_r + H]^+$ *m/z* 177.091878. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.81; H, 7.08.

**Pentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecan-4-one Diethyl Acetal (11).** To a solution of **1** (2.00 g, 12.5 mmol) in $HC(OEt)_3$ (6 mL, excess) was added TsOH (100 mg, catalytic amount), and the resulting mixture was stirred at ambient temperature during 48 h. The reaction mixture was concentrated in vacuo, and the residue was purified via column chromatography on silica gel by eluting with 5% EtOAc−hexane. Workup of the eluate thereby obtained afforded pure **11** (2.6 g, 90%) as a colorless oil; IR (neat) 2960 (s), 2876 (s), 1319 (s), 1122 (s), 1070 (s), 958 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.17 (t, $J$ = 7.0 Hz, 6 H), 1.26 (*A*B, $J_{AB}$= 10.1 Hz, 2 H), 1.41[d(A*B*), $J_{AB}$= 10.1 Hz, $J$ = 2.0 Hz, 2 H], 1.98 (br s, 2 H), 2.12 (br s, 4 H), 2.33 (br s, 2 H), 3.53 (dq, $J_1$ = 7.2 Hz, $J_2$ = 2.1 Hz, 2 H), 3.58 (dq, $J_1$ = 7.2 Hz, $J_2$ = 2.1 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 15.6 (q), 33.3 (t), 42.0 (d), 43.9 (d), 47.3 (d), 51.2 (d), 58.0 (t), 112.9 (s). Exact mass (CI HRMS) Calcd for $C_{15}H_{22}O_2$: $[M_r + H]^+$ *m/z* 235.16981. Found: $[M_r + H]^+$ *m/z* 235.17074.

***m*-CPBA-Promoted Oxidation of 11.** A solution of *m*-CPBA (9.83 g, 34.2 mmol, purity of commercial *m*-CPBA: 88%, "old-*m*-CPBA"[13]) in $CH_2Cl_2$ (100 mL) under argon was cooled to 15 °C via application of an external cold water bath. To this

cooled solution was added dropwise with stirring a solution of **11** (2.00 g, 8.54 mmol) in $CH_2Cl_2$ (10 mL) during 10 min. After the addition of **11** had been completed, the resulting mixture was stirred at 20 °C during 16 h. The reaction mixture then was poured with vigorous stirring into ice-cold 5 N aqueous NaOH (100 mL) to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 50 mL). The combined organic layers were washed successively with 3% aqueous $Na_2SO_3$ (30 mL) and water (50 mL), dried ($Na_2SO_4$), and filtered, and the filtrate was concentrated in vacuo. Analysis of the $^1$H and $^{13}$C NMR spectra of the residue thereby obtained revealed that the crude product consisted of a mixture of **2** and **12** (product ratio **2**: **12** = 1:2). The residue was purified via column chromatography on silica gel by eluting with 20% EtOAc−hexane. Workup of the first chromatography fraction afforded pure **2** (150 mg, 10%) as a colorless microcrystalline solid: mp 189−190 °C. The IR, $^1$H NMR, and $^{13}$C NMR spectra of this material were essentially identical with the corresponding spectra of **2** prepared previously (vide supra).

Continued elution of the chromatography fraction afforded a second fraction. Workup of this chromatography fraction afforded pure **12** (320 mg, 20%) as a colorless microcrystalline solid: mp 258−259 °C; IR (KBr) 2984 (m), 2890 (w), 1736 (vs), 1427 (m), 1230 (s), 1136 (s), 748 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$) $\delta$ 1.28 [br(*A*B), $J_{AB}$ = 11.3 Hz, 2 H], 1.42 [d(A*B*), $J_{AB}$ = 11.3 Hz, $J$ = 2.0 Hz, 2 H), 2.42 (br s, 4 H), 2.71(br s, 2 H), 4.08 (d, $J$ = 6.0 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 30.8 (t), 37.4 (d), 41.7 (d), 46.1 (d), 83.9 (d), 151.5 (s); exact mass (CI HRMS) calcd for $C_{11}H_{12}O_3$ [$M_r$ + H]$^+$ *m/z* 193.08647, found [$M_r$ + H]$^+$ *m/z* 193.08662. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.72; H, 6.30. Found: C, 68.58; H, 6.28.

**Lithium Aluminum Hydride Promoted Reduction of 12.** A solution of **12** (300 mg, 1.56 mmol) in dry THF (5 mL) was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added portionwise with stirring $LiAlH_4$ (12 mg, 3.1 mmol) under argon. After the addition of the reducing agent had been completed, the external ice−water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature while being stirred continuously during 2 h. The reaction mixture was quenched via careful dropwise addition of saturated aqueous $Na_2SO_4$ (8 mL). The resulting mixture was filtered, brine (10 mL) was added to the filtrate, and the resulting mixture was extracted with EtOAc (3 × 30 mL). The organic extracts were dried ($Na_2SO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by eluting with 50% EtOAc−hexane. Pure **13** (210 mg, 80%) was thereby obtained as a colorless microcrystalline solid: mp 246−247 °C; IR (KBr) 3148 (br, w), 2968 (s), 2897 (w), 1273 (w), 1122 (m), 1074 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$) $\delta$ 1.82 (s, 4 H), 2.01−2.13 (m, 2 H), 2.16−2.28 (m, 4 H), 3.61 (d, $J$ = 6.0 Hz, 2 H), 6.75 (br s, peak disappears when sample is shaken with a few drops of $D_2O$, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 31.5 (t), 39.0 (d), 42.6 (d), 46.8 (d), 77.6 (d). Exact mass (CI HRMS) Calcd for $C_{10}H_{14}O_2$ [$M_r$ + H]$^+$ *m/z* 167.10721, found [$M_r$ + H]$^+$ *m/z* 167.10799.

**4-Oxapentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane (14).** A solution of **13** (100 mg, 0.602 mmol) and TsOH (10 mg, catalytic amount) in $PhCH_3$ (10 mL) was placed in a boiling flask that had been fitted with a Dean−Stark apparatus, and the resulting mixture was refluxed with periodic removal of distillate during 12 h. The reaction mixture was allowed to cool gradually to ambient temperature and then was washed successively with saturated aqueous $NaHCO_3$ (5 mL), water (2 × 5 mL), and brine (5 mL). The organic extracts were dried ($Na_2SO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by eluting with 3% EtOAc−hexane. Pure **14** (53 mg, 60%) was thereby obtained as a colorless, gummy semisolid: IR ($CHCl_3$) 2929 (s), 2858 (m), 1141 (s), 1122 (w), 1104 (m), 1043 (m), 867 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$) $\delta$ 1.48 (s, 4 H), 1.96−2.09 (m, 2 H), 2.12−2.30 (m, 4 H), 4.43−4.51 (m, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 30.4 (t), 42.4 (d), 47.5 (d), 48.5 (d), 85.2 (d); exact mass (CI HRMS) calcd for $C_{10}H_{12}O$ [$M_r$ + H]$^+$ *m/z* 149.09664, found [$M_r$ + H]$^+$ *m/z* 149.09721.

**General Procedure for DIBAL-H-Promoted Reduction of Cage Lactones.** To a solution of the lactone (11.4 mmol) in $CH_2Cl_2$ (60 mL) at −78 °C under argon was added dropwise with stirring ($i$-Bu)$_2$AlH (DIBAL-H, 12.5 mL of a 1 M solution in $CH_2Cl_2$, 12.5 mmol) during 10 min. After all of the reducing agent had been added, the reaction mixture was stirred at −78 °C during 1 h, at which time excess DIBAL-H was quenched via careful, dropwise addition of MeOH (0.5 mL, excess) with stirring at −78 °C. The external cold bath then was replaced by an ice−water bath, and the reaction mixture was allowed to warm gradually to 0 °C while stirring during 1 h. Saturated aqueous potassium sodium tartrate solution (30 mL) was added to the reaction mixture, and the resulting mixture was stirred until separation of the organic layer became clearly apparent. At that time, the organic layer was separated and then was washed sequentially with water (2 × 30 mL) and brine (30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting with 20% EtOAc−hexane to furnish the corresponding lactol.

**DIBAL-H Promoted Reduction of 2.** By using the general procedure for DIBAL-H promoted reduction of cage lactones (vide supra), lactone **2** (2.00 g, 11.4 mmol) was reduced to the corresponding lactol (**15**). Workup of the reaction mixture as described above afforded pure **15** (1.7 g, 85%) as a colorless microcrystalline solid. Compound **15** was thereby obtained as a mixture of two diastereoisomeric lactols, product ratio 7:3: IR (KBr) 3993 (br, s), 2968 (s), 2877 (m), 1272 (w), 1037 cm$^{-1}$ (s); $^1$H NMR ($CDCl_3$) $\delta$ 1.12 (*A*B, $J_{AB}$ = 10.3 Hz, 1 H), 1.25 (*A*B, $J_{AB}$ = 9.5 Hz, 1 H), 1.35 (A*B*, $J_{AB}$ = 10.3 Hz, 1 H), 1.55 (A*B*, $J_{AB}$ = 9.5 Hz, 1 H), 1.71−1.82 (m, 1 H), 1.97 (q, $J$ = 6.0 Hz, 0.7 H), 2.05−2.55 (m, 5.3 H), 3.22 (br s, 1 H), 3.10 and 3.70 (2 d, $J$ = 6.9 Hz, total area 1 H), 5.23−5.31 (m, 1 H); $^{13}$C NMR ($CDCl_3$) major product: $\delta$ 30.4 (t), 32.1 (d), 34.6 (t), 35.9 (d), 38.5 (d), 41.9 (d), 43.5 (d), 48.4 (d), 49.0 (d), 76.0 (d), 91.3 (d); minor product $\delta$ 29.9 (t), 33.5 (d), 34.3 (t), 35.6 (d), 37.0 (d), 40.2 (d), 45.7 (d), 47.9 (d), 48.0 (d), 77.6 (d), 91.6 (d); exact mass (CI HRMS) calcd for $C_{11}H_{14}O_2$ [$M_r$ + H]$^+$ *m/z* 179.10721, found: [$M_r$ + H]$^+$ *m/z* 179.10744.

**DIBAL-H-Promoted Reduction of 16.** By using the general procedure for DIBAL-H promoted reduction of cage lactones (vide supra), lactone **16**[17] (2.00 g, 11.4 mmol) was reduced to the corresponding lactol (**17**). Workup of the reaction mixture as described above afforded pure **17**[19] (1.92 g, 95%) as a colorless microcrystalline solid: mp 243−245 °C (sealed tube) (lit.[19] mp 216−217.5 °C); IR (KBr) 3383 (br, s), 2904 (s), 2847 (m), 1248 (w), 1132 (w), 1043 (s), 976 (m), 756 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$) $\delta$ 1.45−1.56 (m, 4 H), 1.58−2.05 (m, 7 H), 2.06−2.25 (m, 2 H), 3.75−4.02 (br s, peak disappears when sample is shaken with a few drops of $D_2O$, 1 H), 4.18 (br s, 1 H), 5.30 (t, $J$ = 7.2 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 26.5 (d), 26.6 (d), 29.2 (t), 32.9 (t), 35.6 (t), 35.7 (t), 37.0 (t), 38.0 (d), 38.3 (t), 72.1 (d), 99.9 (d); exact mass (CI HRMS) calcd for $C_{10}H_{16}O_2$ [$M_r$ + H]$^+$ *m/z* 169.12285, found [$M_r$ + H]$^+$ *m/z* 169.12223.

**DIBAL-H-Promoted Reduction of 6.** By using the general procedure for DIBAL-H-promoted reduction of cage lactones (vide supra), lactone **6** (2.47 g, 14.0 mmol)was reduced to the corresponding lactol (**19**). Workup of the reaction mixture as described above afforded pure **19** (2.14 g, 86%) as a colorless microcrystalline solid. Compound **19** was thereby obtained as a mixture of two diastereomeric lactols, product ratio 7:3: IR (KBr) 3400 (br, s), 2955 (s), 2865 (m), 1143 (m), 1101 (m), 1062 (s), 999 (m), 756 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$) $\delta$ 1.40 (*A*B, $J_{AB}$ = 11.0 Hz, 0.7 H), 1.45−1.72 (m, 3.3 H), 2.02−2.15 (m, 1 H), 2.30−2.57 (m, 4 H), 2.59−2.94 (m, 2 H), 3.50−3.85 (br s, peak disappears when sample is shaken with a few drops of $D_2O$, 1 H), 4.38 (t, $J$ = 8.1 Hz, 0.7 H), 4.45 (t, $J$ = 8.1 Hz, 0.3 H), 5.29 (t, $J$ = 3.2 Hz, 0.3 H), 5.53 (d, $J$ = 6.5 Hz, 0.7 H); $^{13}$C NMR ($CDCl_3$, major product): $\delta$ 29.2 (d), 30.4 (t), 36.8 (t), 39.9 (d), 40.0 (d), 40.7 (d), 44.2 (d), 45.1 (d), 49.5 (d), 67.0

(d), 92.6 (d); exact mass (CI HRMS) calcd for $C_{11}H_{14}O_2$ [$M_r$ + H]$^+$ *m/z* 179.10721, found [$M_r$ + H]$^+$ *m/z* 179.10658.

**General Procedure for the Photolytic Reaction of PhI(OAc)$_2$−I$_2$ with Cage Lactols.**[15] A stirred mixture of the lactol (10.6 mmol), $PhI(OAc)_2$ (7.18 g, 22.3 mmol), and $I_2$ (50 mg, 0.2 mmol, catalytic amount) in $CH_2Cl_2$ (40 mL) at ambient temperature was irradiated by using a 100 W tungsten filament lamp during 1 h. The resulting light reddish-purple suspension was stirred at ambient temperature for 6 h. To the reaction mixture was added with stirring 15% aqueous $Na_2S_2O_3$ (25 mL), and the resulting mixture was extracted with $CH_2Cl_2$ (2 × 30 mL). The combined organic extracts were washed with water (30 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting with 3% EtOAc−hexane. The corresponding cage ether was thereby obtained in about 20% yield.

Continued elution of the chromatography column with 20% EtOAc−hexane afforded a second fraction that contained the corresponding lactone (ca. 60%, in each case).

**Photolytic Reaction of PhI(OAc)$_2$−I$_2$ with 15.** The general procedure for the photolytic reaction of $PhI(OAc)_2$−$I_2$ with cage lactols was applied to a mixture of **15** (1.89 g, 10.6 mmol), $PhI(OAc)_2$ (7.18 g, 22.3 mmol), and $I_2$ (50 mg, 0.2 mmol) in $CH_2Cl_2$ (40 mL) (vide supra). Workup of the first chromatography fraction obtained by eluting the column with 3% EtOAc−hexane afforded pure **14** (300 mg, 20%) as a gummy semisolid. The IR, $^1$H NMR, and $^{13}$C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra obtained previously for **14** (vide supra).

Continued elution of the chromatography column with 20% EtOAc−hexane afforded the corresponding cage lactone, **2** (1.5 g, 60%), which was thereby obtained as a colorless microcrystalline solid: mp 189−190 °C. The IR, $^1$H NMR, and $^{13}$C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra obtained previously for **2** (vide supra).

**Photolytic Reaction of PhI(OAc)$_2$−I$_2$ with 17.** The general procedure for the photolytic reaction of $PhI(OAc)_2$−$I_2$ with cage lactols was applied to a mixture of **17** (1.90 g, 11.3 mmol), $PhI(OAc)_2$ (7.64 g, 23.8 mmol), and $I_2$ (50 mg, 0.2 mmol) in $CH_2Cl_2$ (40 mL) (vide supra). Workup of the first chromatography fraction obtained by eluting the column with 3% EtOAc−hexane afforded pure 2-oxaadamantane (**18**,[12,18] 300 mg, 19%) as a colorless microcrystalline solid: mp 230−232 °C (sealed tube), (lit.[18a] mp 232.5 °C, mp[18b] 225−230 °C, mp[18d] 232−233 °C, mp[19] 226−229 °C); IR ($CHCl_3$) 2929 (s), 2858 (m), 1141 (s), 1122 (w), 1104 (m), 1043 (m), 867 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$) $\delta$ 1.64 (d, $J$ = 9.2 Hz, 4 H), 1.88 (s, 2 H), 2.01−2.15 (m, 6 H), 3.99 (s, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 26.5 (d), 35.9 (t), 36.2 (t), 68.0 (d).

Continued elution of the chromatography column with 20% EtOAc−hexane afforded the corresponding cage lactone, **16** (1.5 g, 60%), which was thereby obtained as a colorless microcrystalline solid: mp 287−288 °C. The IR, $^1$H NMR, and $^{13}$C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra reported previously for **16**.[17]

**Photolytic Reaction of PhI(OAc)$_2$−I$_2$ with 19.** The general procedure for the photolytic reaction of $PhI(OAc)_2$−$I_2$ with cage lactols was applied to a mixture of **19** (1.65 g, 9.26 mmol), $PhI(OAc)_2$ (6.56 g, 20.4 mmol)), and $I_2$ (2.35 g, 9.26 mmol) in $CH_2Cl_2$ (40 mL) (vide supra). Workup of the first chromatography fraction obtained by eluting the column with 10% EtOAc−hexane afforded pure **20** (210 mg, 10%) as a colorless, gummy semisolid: IR (film) 2970 (s), 2881 (w), 1730 (s), 1389 (m), 1369 (m), 1253 (s), 1176 (s), 1045 (m), 964 cm$^{-1}$ (w); $^1$H NMR ($CDCl_3$) $\delta$ 1.55−1.74 (m, 2 H), 1.85 [d(*AB*), $J_{AB}$ = 14.6 Hz, $J$ = 7.6 Hz, 1 H), 1.95−1.99 (m, 1 H), 2.10 (s, 3 H), 2.08−2.21 (m, 2 H), 2.24−2.34 (m, 1 H), 2.41−2.50 (m, 2 H), 2.73 (ddd, $J_1$ = 11.6 Hz, $J_2$ = 7.3 Hz, $J_3$ = 4.4 Hz, 1 H), 4.54 (d, $J$ = 6.5 Hz, 1 H), 4.95 (t, $J$ = 6.6 Hz, 1 H), 8.01 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.2 (q), 26.6 (t), 33.5 (t), 38.2 (d), 39.6 (d), 40.6 (d), 44.4 (d), 44.5 (d), 45.0 (d), 67.3 (d), 77.9 (d), 160.1 (d), 170.3 (s); exact mass (CI HRMS) calcd for $C_{13}H_{16}O_4$ [$M_r$ + H]$^+$ *m/z* 237.11268; found [$M_r$ + H]$^+$ *m/z* 237.11257.

Continued elution of the chromatography column with 20% EtOAc−hexane afforded a second fraction. Workup of the second chromatography fraction afforded pure **6** (1.2 g, 70%) as a colorless microcrystalline solid: mp 228−229 °C. The IR, $^1$H NMR, and $^{13}$C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra obtained previously for **6** (vide supra).

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**Supporting Information Available:** Proton and $^{13}$C NMR spectra of **2**, **4**, **6**, **7**, and **9**−**20**; table of $^1$H and $^{13}$C NMR spectral assignments for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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