Mass spectra were measured at 25 eV. Thin layer chromatography (TLC) was performed on Merk Kieselgel 60 GF_{254}.

Methyl (5*S*)-[5-$^2H_1$]-5-Deoxy-2,3-*O*-isopropylidene-5-phthalimido-β-D-ribofuranoside (2). A mixture of **1*R*** (1.1 g) and potassium phthalimide (427 mg) in HMPT (40 mL) was stirred for 1 h at 120 °C. Water (40 mL) was added to the cooled mixture, and it was then extracted three times with 40 mL of ether. The extracts were washed with water and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure to give crude crystalline product, which was recrystallized from methanol to give pure crystalline **2** (926 mg, 90%): mp 128 °C; $[\alpha]^{25}_D$ −45.2° (*c* 2.5 in $CHCl_3$); NMR (in $CDCl_3$) δ 1.27 and 1.44 (isopropylidene methyls), 3.38 (3 H, s, OCH_3), 3.8–4.9 (4 H, m, H_2, H_3, H_4, H_5), 7.8–8.0 (4 H, m, aromatic). Anal. Calcd for $C_{17}H_{18}DNO_6$: C, 61.07; H + D, 6.03; N, 4.19. Found: C, 61.00; H + D, 6.08; N, 4.15.

(*S*)-*N*-Phthaloyl[2-$^2H_1$]glycine (4). To a solution of **2** (668 mg) in acetic acid (50 mL) was added 5 N H_2SO_4 (50 mL), and the mixture was kept for 1 h at 50 °C and then cooled to room temperature. TLC indicated the complete hydrolysis of **2** to the free sugar **3** [$CHCl_3$–CH_3OH (3:1), R_f 0.58]. $KMnO_4$ (1.5 g) was added to the solution (5 min), and the solution was stirred at room temperature for 3 h. The excess reagent was decomposed by addition of aqueous 10% sodium thiosulfate. The mixture was extracted three times with 50 mL of CH_2Cl_2, and the combined CH_2Cl_2 extracts were dried over $MgSO_4$. Evaporation of the solvent gave crude crystalline **4**, which was recrystallized from 10% ethanol to give 350 mg (85%) of **4**: mp 192 °C; ORD $[\alpha]^{25}_{405}$ +2.90°, $[\alpha]^{25}_{435}$ +2.34°, $[\alpha]^{25}_{546}$ +1.430° and $[\alpha]^{25}_{77}$ +1.22° (*c* 10.5 in CH_3OH); (lit.[9] $[\alpha]^{25}_{405}$ +2.70°; $[\alpha]^{25}_{436}$ +2.18°, $[\alpha]^{25}_{546}$ +1.22°, $[\alpha]^{25}_{578}$ +0.94°); I ^{r}, 1780 and 1740 (CO and COOH) and 3000 cm^{-1} (OH); MS, *m/e* (relative intensity) M^+ = 206 (100), M^+−1 = 205 (7.5). Anal. Calcd for $C_{10}H_6DNO_4$: C, 58.25; H + D, 3.90; N, 7.00. Found: C, 58.54; H + D, 4.00; N, 6.90.

Methyl (5*S*)-[5-$^2H_1$]-5-Azido-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (5). A mixture of **1*R*** (810 mg) and sodium azide (222 mg) in DMF (50 mL) was stirred for 1.5 h at 100 °C. Water (50 mL) was added to the cooled mixture, and it was then extracted three times with 50 mL of ether. The extracts were washed with water and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure gave syrup **5** (496 mg, 95%): $[\alpha]^{25}_D$ −39.0° (*c* 1 in $CHCl_3$); NMR ($CDCl_3$) δ 1.26 and 1.46 (isopropylidene methyls), 3.38 (3 H, s, OCH_3), 3.40 (1 H, d, $J_{4,5}$ = 7.8 Hz, H-5), 5.00 (1 H, s, H-1). Anal. Calcd for $C_9H_{14}DN_3O_4$: C, 46.95; H + D, 7.00; N, 18.25. Found: C, 47.00; H + D, 6.95; N, 18.22.

(*S*)-[2-$^2H_1$]Glycine. To a solution of **5** (220 mg) in acetic acid (25 mL) was added 5 N H_2SO_4 (25 mL). The mixture was kept for 2 h at room temperature. TLC indicated the presence of only 5-azido-5-deoxyribose **6** [$CHCl_3$–CH_3OH (3:2), R_f 0.26]. $KMnO_4$ (500 mg) was added to the solution (5 min), and the solution was stirred at room temperature for 5 h. The excess reagent was decomposed by addition of aqueous 10% sodium thiosulfate. The mixture was extracted three times with 25 mL of CH_2Cl_2, and combined CH_2Cl_2 extracts were dried over $MgSO_4$. After evaporation of CH_2Cl_2, the acetic acid solution was vigorously shaken with 10% palladium on charcoal (200 mg) under a hydrogen atmosphere for 1 h. The catalyst was filtered off and washed with acetic acid (10 mL). The combined filtrate was evaporated under reduced pressure to give a crude crystalline product, which was recrystallized from aqueous methanol to give 47 mg (60%) of pure (*S*)-[2-$^2Hh_1$]glycine: mp 233–234 °C (dec; ORD $[\alpha^{25}_{210}$ −7.90°, $[\alpha]^{25}_{220(max)}$ −80.0°, $[\alpha]^{25}_{227}$ −68.0°, $[\alpha]^{25}_{238}$ −40.0°, $[\alpha]^{25}_{250}$ −25.0°, $[\alpha]^{25}_{275}$ −14.0° (*c* 2.0 in H_2O); MS, *m/e* (relative intensity) M^+ = 76 (100), M^+ −1 = 75 (8.6). Anal. Calcd for $C_2H_4DNO_2$: C, 31.58;% H + D, 7.95; N, 18.41. Found: C, 31.90; H + D, 8.20; N, 8.31.

Acknowledgment. We are very grateful to Yamasashoyu Co. LTD. for a gift of D-ribose and to Mrs. Chieko Suzuki for measurement of NMR spectra. This work was supported in part by a grant from the Ministry of Education, Science and Culture, Japan.

Registry No. **1R**, 97254-21-2; **2**, 97254-22-3; **3**, 97254-23-4; **4**, 62061-63-6; **5**, 97254-24-5; **6**, 97254-25-6; **7**, 97254-26-7; (*S*)-[2-$^2H_1$]glycine, 62061-52-3; potassium phthalimide, 1074-82-4; glycine, 56-40-6; D-ribose, 50-69-1.

Formation of Cyclic Ethers in the Double Baeyer–Villiger Oxidation of Ketals Derived from Cyclic Ketones[1]

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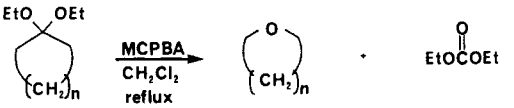
We recently reported that the formal equivalent of a double Baeyer–Villiger oxidation may be accomplished by oxidation of dialkyl ketals with *m*-chloroperoxybenzoic acid (MCPBA) in CH_2Cl_2 solution at room temperature.[2] This exothermic process, which normally converts the ketal to an orthocarbonate or its hydrolysis products, provides an efficient method for the removal of a carbonyl function from a ketone.[2] Exploration of the scope of the reaction has revealed that oxidation of diethyl ketals derived from certain five- and six-membered cyclic ketones may lead to the formation of cyclic ethers via oxidative loss of the latent carbonyl moiety *when conducted at reflux temperatures in CH_2Cl_2 solution.*



As shown in Table I, the yield of cyclic ether is strongly dependent on the structure of the ketal employed in the reaction. Thus, although tetrahydropyrans are produced in 20–63% yield in the double Baeyer–Villiger oxidation of ketals derived from cyclohexanones (Table I, entries 1–3) and THF is formed in 44% yield upon oxidation of the diethyl ketal of cyclopentanone (Table I, entry 4), ether formation is negligible in the oxidation of ketals prepared from 2-alkylcyclopentanones or cycloheptanone (Table I, entries 5–6).

The formation of cyclic ethers is most likely a consequence of the facile loss of diethyl carbonate from the orthocarbonate produced in the oxidation[2] (Scheme I). Indeed, an intermolecular variant of this novel transformation has long been known in the acid-catalyzed conversion of tetraethyl orthocarbonate to diethyl ether and diethyl carbonate.[3]

The modest yields of tetrahydrofurans and tetrahydropyrans produced upon oxidation of the appropriate ketals at reflux temperatures compares favorably with the overall yields of a recently reported, four-step transformation of cyclic ketones to cyclic ethers.[4] The relative ease with which ethers may be isolated from the bulk of the carbonates, benzoates, and diols produced in the double Baeyer–Villiger reaction[2] suggests that this facile oxidative replacement of a carbonyl group with an oxygen atom may be of some synthetic utility.

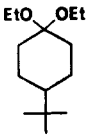
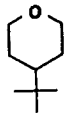
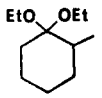
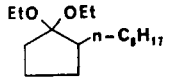
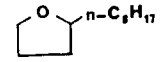
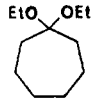
Experimental Section

Proton magnetic resonance spectra were recorded on Varian EM-360 or Bruker WH-90 instruments and shifts are referenced with respect to internal Me_4Si. Carbon-13 magnetic resonance spectra were obtained at 22.6 MHz on a Bruker WH-90 spectrometer using $CDCl_3$ solutions; shifts are referenced with respect

(1) "Abstracts of Papers", 14th Northeast Regional Meeting of the American Chemical Society, Fairfield, CT, June 11, 1984; American Chemical Society: Washington, DC, 1984; ORGN 121.
(2) Bailey, W. F.; Shih, M.-J. *J. Am. Chem. Soc.* **1982**, *104*, 1769.
(3) (a) Ladenberg, A.; Wichelhaus, H. *Justus Liebigs Ann. Chem.* **1869**, *152*, 163. (b) McKenna, J. M.; Sowa, F. *J. Am. Chem. Soc.* **1938**, *60*, 124.
(4) Suginome, H.; Yamada, S. *Tetrahedron Lett.* **1984**, 3995.

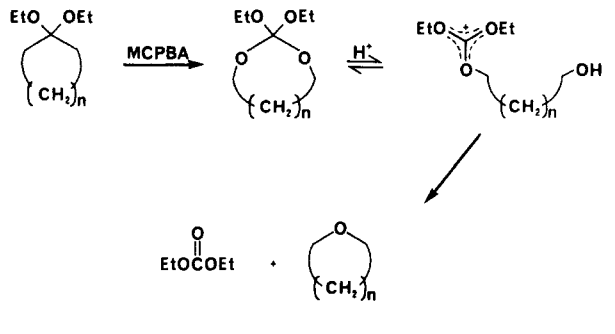
0022-3263/85/1950-3009$01.50/0

Table I. Oxidation of Ketals Derived from Five- and Six-Membered Ring Ketones[a]

entry	ketal	ether	yield,[b,c] %
1			28
2			63 (40)
3			20
4			44
5			6.4 (5.2)
6			0

[a] Oxidations were conducted as described in ref 2 (3–4 molar equiv MCPBA in CH_2Cl_2). Following complete consumption of the ketal, the product mixture was stirred for several hours at reflux in the presence of the *m*-chlorobenzoic acid generated from MCPBA. [b] Absolute yields determined either by GLC or ^1H NMR analysis using internal standards. [c] Isolated yield of purified material in parentheses.

Scheme I



to internal Me_4Si and peak multiplicities are reported for off-resonance, proton-decoupled spectra. Analytical gas–liquid chromatography (GLC) was effected with a Perkin-Elmer Model 3920-B instrument fitted with a 10-ft, 10% FFAP on Chromosorb W (60/80 mesh) column. Area ratios were determined with a Linear Instrument Model 282 recording integrator, and all yields determined by GLC (Table I) have been corrected for detector response under the conditions of the analysis by using weighed samples of pure product and hydrocarbon standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Methylene chloride was distilled from P_2O_5 prior to use, and commercial (80–85%) *m*-chloroperoxybenzoic acid (Aldrich) was employed in the oxidations. Commerical samples of cyclopentanone, cyclohexanone, cycloheptanone, 2-methylcyclohexanone, and 4-*tert*-butylcyclohexanone were purified before use, and 2-*n*-octylcyclopentanone was prepared as previously described.[5] Diethyl ketals were prepared by a standard method[6] from equimolar amounts of ketone and triethyl orthoformate dissolved in excess anhydrous ethanol containing a catalytic quantity of anhydrous HCl generated by addition of acetyl chloride to the dry ethanol. With the exception of 4-*tert*-butyltetrahydropyran, the cyclic ethers generated in the oxidations (Table I) are known compounds and structures were established by comparison of the physical and spectroscopic properties of isolated material with those reported for 2-*n*-octyltetrahydrofuran[7] or available from authentic samples of tetrahydrofuran, tetrahydropyran, and 2-methyltetrahydropyran.

Oxidations were conducted using 3–4 molar equiv of *m*-chloroperoxybenzoic acid as previously described,[2] and, following complete consumption of the ketal, the product mixture was stirred for several hours at reflux in the presence of the *m*-chlorobenzoic acid generated from the peroxy acid. The following preparation is illustrative of the general procedure.

4-*tert*-Butyltetrahydropyran. A flame-dried, three-necked, round-bottomed flask fitted with a reflux condenser, addition funnel, efficient stirrer, and argon inlet was charged with 40.6 g of 80–85% *m*-chloroperoxybenzoic acid (180–220 mmol) in 480 mL of dry CH_2Cl_2. The suspension was rapidly stirred under argon, and 11.40 g (50 mmol) of 1,1-diethoxy-4-*tert*-butylcyclohexanone was added over a 10-min period. The stirred mixture was heated at gentle reflux for 8.5 h and then rapidly poured into 500 mL of vigorously stirred, ice-cold 2.5% aqueous NaOH solution. The organic phase was separated and the aqueous phase was extracted with two 250-mL portions of diethyl ether. The combined organic extracts were washed successively with two 150-mL portions of 15% aqueous Na_2SO_3 and 150 mL of brine, dried (K_2CO_3), and concentrated by rotary evaporation. Distillation of the residue through a short, vacuum-jacketed Vigreux column afforded 2.81 g (40%) of product: bp 70–72 °C (24 mm); ^1H NMR ($CDCl_3$) δ 0.88 (s, 9 H), 0.97–1.75 (m, 5 H), 2.92–3.52 (m, 2 H), 3.65–4.12 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.00 (q, CH_3), 27.72 (t, C(3,5)), 32.15 (s, $C(CH_3)_3$), 45.79 (d, C(4)), 68.67 (t, C(2,6)). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 76.13; H, 13.14.

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Registry No. 1 (ketal), 1670-47-9; 1 (ether), 142-68-7; 2 (ketal), 1900-58-9; 2 (ether), 96964-38-4; 3 (ketal), 1528-18-3; 3 (ether), 10141-72-7; 4 (ketal), 23786-93-8; 4 (ether), 109-99-9; 5 (ketal), 96964-37-3; 5 (ether), 5921-92-6; 6 (ketal), 1130-34-3; 6 (ether), 592-90-5; methylene chloride, 75-09-2; *m*-chloroperoxybenzoic acid, 937-14-4; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; 2-methoxycyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; 2-*n*-octylcyclopentanone, 40566-23-2; triethyl orthoformate, 122-51-0; ethanol, 64-17-5; acetyl chloride, 75-36-5.

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(6) Carswell, J. E.; Adkins, J. *J. Am. Chem. Soc.* **1928**, *50*, 235.
(7) Elad, D.; Youssefyeh, R. D. *J. Org. Chem.* **1964**, *29*, 2031.

Electroreduction of Cyclobutadienopleiadiene. Cathodic Hydrogenation of a Fused Cyclobutene Ring

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With the availability of numerous chemical reducing agents, the electrochemical reduction of unsaturated hydrocarbons to their corresponding dihydro derivatives has traditionally played only a minor role as a synthetic tool. One exception to this, however, is the Birch reduction of appropriately substituted aromatic compounds to 1,4-cyclohexadienes, which can be accomplished in high yield at a mercury electrode in aqueous electrolyte[1,2] and thereby

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