lene chloride) afforded 0.8 g (1.5 mmol) of **5** and **6** as a clear, light yellow oil. Precipitation from chloroform–hexane gave 0.6 g (1.1 mmol, 58%) of **5** and **6** as an amorphous yellow solid: ir (film) 570, 663, 754, 863, 980, 1030, 1115, 1157, 1207, 1220, 1258, 1383, 1428, 1608, 1677, 1692, 1710, 2830, 2885, 2935, 2995 cm^{-1}; nmr ($CDCl_3$) δ 1.7–2.8 (10 H, m), 3.50 (6 H, s); mass spectrum *m/e* 536 (parent, pentuplet of spacing 2 mass units).

1,5-Dimethoxy-6,12-dibromotetracyclo[9.1.0^{3,9}.0^{5,7}]dodec-3(9)-ene (7 and 8). A. Electrochemical Reduction. A three-compartment electrolysis cell was constructed from a vigorously stirred mercury pool cathode, a platinum gauze anode, a catholyte consisting of 30 ml of 1.0 *N* LiCl in 96% DMF–4% water, and anolyte consisting of 4 ml of 1.0 *N* LiCl in 86% DMF–4% water–10% hydrazine, and a Ag–AgCl standard reference electrode. The cathode and anode chambers were separated by a fine-porosity fritted disk, and the standard electrode was isolated by a cracked-glass tube filled with the catholyte solution. All solutions were deoxygenated using argon, and argon was bubbled through the cell continuously during the electrolysis. The cell was positioned in an ice bath and operated for 15 min at a cathode potential of −2.00 V with respect to the reference electrode. A solution of 265 mg (0.5 mmol) of **5** and **6** in 4 ml of DMF was then added, and electrolysis was allowed to proceed (*ca.* 0.75 hr) until the cell current approached the previously determined background current of *ca.* 10 mA. The catholyte was poured into a mixture of 100 ml each of water and pentane, and the pentane layer was washed with water and evaporated to give 190 mg (0.5 mol, 100%) of **7** and **8**.

B. *Via* **Halogen–Metal Exchange.** A solution of 265 mg (0.5 mmol) of tetrabromides **5** and **6** in 2 ml of THF was cooled to −80° and treated with 0.7 ml (1.1 mmol) of *n*-butyllithium (Foote, 1.6 *N*). The mixture was stirred at −80° for 15 min and then quenched by the addition of 0.5 ml of methanol. Approximately 10 ml each of ether and water were added, and the ether layer was washed, dried over $MgSO_4$, and evaporated to yield crude dibromide. Preparative-layer chromatography (silica gel, eluted with $CHCl_3$) yielded 160 mg (0.42 mmol, 85%) of **7** and **8**: ir ($CDCl_3$) 605, 870, 1032, 1044, 1147, 1197, 1230, 1326, 1357, 1397, 1430, 1720, 2833, 2905, 2950, 3005, 3050, 3070 cm^{-1}; nmr ($CDCl_3$) δ 1.60 (2, H, d, J = 9 Hz), 1.65 (2 H, d, J = 9 Hz), 1.92 (2 H, s), 2.44 (6 H, broad s), 3.42 (6 H, s); mass spectrum *m/e* 377 (parent, triplet of spacing 2 mass units). This material was identical in all respects with the two dibromides prepared by method A above.

2,9-Dimethoxy-1,8-dihyroheptalene (9). A solution of 2.62 g (6.93 mmol) of **7** and **8** in 50 ml of anhydrous pyridine was stirred for 1 hr at 100°. The mixture was evaporated *in vacuo*, and the residue was taken up into ether, washed with 1 *N* $CuSO_4$ solution, dried over $MgSO_4$, and evaporated to yield 0.9 g of crude pyrolysate. Column chromatography (silica gel, eluted with $CHCl_3$) gave 0.53 g (2.46 mmol, 28%) of pure **9**: ir 1020, 1170, 1204, 1225, 1268, 1423, 1544, 1620, 2840, 2963, 3010 cm^{-1}; nmr ($CDCl_3$) δ 2.50 (2 H, d, J = 7 Hz), 2.67 (2 H, s), 3.55 (3 H, s), 3.71 (3 H, s), 5.1–6.5 (6 H, m); uv (EtOH) λ_{max} 342 nm (ϵ 6000); mass spectrum *m/e* 216.114 (parent, calcd for $C_{14}H_{16}O_2$ 216.115).

Bicyclo[5.5.0]dodeca-1,9,11-triene-4,7-dione (12). A solution of 100 mg of **9** in 3 ml of acetone, 0.6 ml of water, and 0.3 ml of concentrated hydrochloric acid was stirred for 25 min at room temperature. The reaction mixture was poured into saturated $NaHCO_3$ solution, which was extracted three times with ether. The ether layers were combined, washed with water, dried over $MgSO_4$, and evaporated to yield 86 mg (0.46 mmol, 100%) of nearly pure **12**. Recrystallization from EtOH–water gave 81 mg (0.43 mmol, 93%) of **12**, mp 107–109°: ir 790, 972, 1143, 1188, 1240, 1405, 1574, 1707, 2920, 3015, 3400 cm^{-1}; nmr ($CDCl_3$) δ 3.06 (4 H, d, J = 6 Hz), 3.26 (4 H, s), 5.89 (2 H, d of t, J = 5.5, 6 Hz), 6.33 (2 H, d, J = 11 Hz); uv (EtOH) showed end absorption only; mass spectrum *m/e* 188.085 (parent, calcd for $C_{12}H_{12}O_2$ 188.084).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.21; H, 6.37.

Bicyclo[5.5.0]dodeca-1,9,11-triene-4,7-diol (13). A solution of 130 mg (0.69 mmol) of **12** and 50 mg (1.3 mmol) of sodium borohydride in 10 ml of anhydrous EtOH was stirred for 1 hr at 0°. The reaction mixture was poured into water and extracted three times with ether. The combined ether layers were washed with water, dried over $MgSO_4$, and evaporated to yield 125 mg of crude diol. Preparative-layer chromatography gave 110 mg (0.58 mmol, 84%) of pure **13**: ir ($CDCl_3$) 910, 1018, 1082, 1262, 1444, 2910, 2950, 3005, 3440, 3608 cm^{-1}; nmr ($CDCl_3$) δ 2.01 (2 H, broad s), 2.2–2.5 (2 H, m), 2.51 (4 H, d, J = 6 Hz), 4.39 (2 H, quintet, J = 6 Hz), 5.89 (4 H, s); mass spectrum *m/e* 192.118 (parent, calcd for $C_{12}H_{16}O_2$ 192.115).

Bicyclo[5.5.0]dodeca-1,9,11-triene-4,7-diacetate (14). A solution of 20 mg (0.104 mmol) of **13**, 75 mg of acetic anhydride, and 135 mg of 4-(*N*,*N*-dimethylamino)pyridine in 2 ml of CH_2Cl_2 was stirred for 15 min at room temperature. The reaction mixture was cooled to 0°, 0.5 ml of methanol was added, and all volatiles were evaporated. The residue was taken up into ether, which was washed with 2 *N* HCl and then with saturated $NaHCO_3$ solution. The ethereal solution was dried over $MgSO_4$ and evaporated to give 27 mg (0.98 mmol, 94%) of pure **14**: ir ($CHCl_3$) 1022, 1100, 1260, 1378, 1443, 1734, 2962 cm^{-1}; nmr ($CDCl_3$) δ 2.04 (6 H, s), 2.1–2.4 (4 H, m), 2.49 (4 H, d, J = 6 Hz), 5.28 (2 H, m), 5.89 (4 H, d, J = 2 Hz); mass spectrum *m/e* 276 (parent), 216 (loss of HOAc), 156 (base peak, loss of 2 HOAc).

Acknowledgment. We are grateful to Professor David Dolphin for assistance with electrochemical aspects of this work and to Professor Weston Borden for helpful discussions.

Registry No.—**4**, 1614-82-0; **5**, 53165-97-2; **6**, 53187-74-9; **7**, 53165-98-3; **8**, 53187-75-0; **9**, 53165-99-4; **12**, 53166-00-0; **13**, 53166-01-1; **14**, 53166-02-2; 2,7-dimethoxynaphthalene, 3469-26-9.

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A New Fragmentation Reaction and Its Application to the Synthesis of (±)-Grandisol

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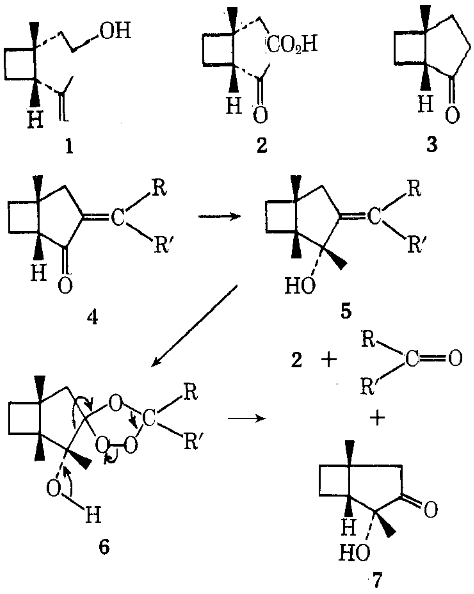
Received July 1, 1974

Grandisol (**1**), a component of the pheromone released by the male boll weevil, *Anthonomus grandis* Boehman,[1] has been synthesized by a variety of routes.[2] We report here a convenient synthesis of racemic **1** that involves a novel fragmentation of an ozonide.

Condensation of **3** with benzaldehyde, furfural, or acetone provided an alkylidine derivative **4**. Reaction of **4** with methyllithium yielded the corresponding tertiary alcohol **5**. Ozonolysis of **5** at −70° in methylene chloride followed by decomposition of the presumed ozonide **6** in aqueous sodium bicarbonate gave keto acid **2** in an overall yield of 40–50% from **3**. Conversion of **2** into **1** has been reported.[2]

Although all three alkylidine derivatives **5a–c** gave **2** in acceptable yields, **5c** is the preferred intermediate. Ozonol-



a, R = Ph; R′ = H
b, R = Fu; R′ = H
c, R = R′ = CH$_3$

ysis decomposition of **5a** always gave some benzoic acid whose separation from **2** was difficult. Neither of the furfurylidine compounds **4b** or **5b** was obtained sufficiently pure for complete characterization, but **5b** was converted cleanly into **2**. In one case, when decomposition of ozonide **6c** was carried out at *ca.* 25°, keto acid **2** was obtained in only 34% yield, and it was accompanied by the "normal" ozonolysis product **7**.

Decomposition of the ozonide **6** presumably occurs *via* the electronic change indicated. This fragmentation[3] provides a convenient method for the cleavage of ketones (as the derived alcohols) between the carbonyl carbon and an adjacent methylene group.[4]

Experimental Section[5]

5-Methylbicyclo[3.2.0]heptan-2-one (3). A solution of 9.96 g (104 mmol) of 3-methylcyclopentenone in 250 ml of reagent grade methylene chloride was irradiated (Pyrex) with a 450-W mercury arc at −70° with a continuous flow of ethylene (Matheson CP) through the solution. The Pyrex probe was cooled by circulating ethanol (cooled to −70°) through it, and the vessel was suspended in a Dewar flask containing a −70° bath. Reaction progress was followed by vpc (10% Carbowax 1000, 8 ft × 0.25 in., 135°). The addition was complete in 29 hr. The vessel was allowed to warm to room temperature in a hood so that the excess ethylene could escape. Removal of solvent yielded 10.16 g (85%) of **3**: bp 88–90° (36 Torr); ir (CCl$_4$) 1735 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.25 ppm (s, 3, CH$_3$).

Anal. Calcd for C$_8$H$_{12}$O: C, 77.37; H, 9.74, Found: C, 77.19; H, 9.76.

3-Benzylidene-5-methylbicyclo[3.2.0]heptan-2-one (4a). To a solution of 6.19 g (50 mmol) of **3** in 75 ml of 95% ethanol was added 8 ml of freshly distilled benzaldehyde, then 2 ml of 15% NaOH solution. The flask was stoppered and the mixture was stirred overnight. The solvent was removed *in vacuo* the residue dissolved in ether, and the resulting solution was washed with saturated sodium *m*- bisulfite solution. After the ethereal solution was dried (MgSO$_4$) and filtered, the solvent was removed leaving a yellow solid. Recrystallization from hexane yielded 8.06 g (76%) of **4a**: mp 72–73°; ir (CCl$_4$) 1695 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.36 (s, 3, CH$_3$), 7.5–7.0 ppm (m, 6, vinyl and aromatic).

Anal. Calcd for C$_{15}$H$_{16}$O: C, 84.87; H, 7.60. Found: C, 84.74; H, 7.61.

3-Furfurylidene-5-methylbicyclo[3.2.0]heptan-2-one (4b) was prepared from **3** as described for the preparation of **4a** except that freshly distilled furfural was substituted for benzaldehyde. The yield of **4b**, a yellow oil, was 72%: ir (CCl$_4$) 1700 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.38 (s, 3, CH$_3$), 6.42 (d of d, 1, $J_{4'5'}$ = 2 Hz, $J_{3'4'}$ = 3 Hz, 4′-H), 6.57 (d, 1, $J_{3'4'}$ = 3 Hz, 3′-H), 7.08 (t, 1, J = 3 Hz, vinyl), and 7.47 ppm (d, 1, $J_{4'5'}$ = 2 Hz, 5′-H); mass spectrum (70 eV) *m/e* 202 (M$^+$).

3-Isopropylidene-5-methylbicyclo[3.2.0]heptan-2-one (4c). A dry 250-ml round-bottomed flask, flushed with nitrogen, and equipped with a reflux condenser and a magnetic stirrer was charged with 50 ml of dry methanol (commercial absolute methanol distilled from magnesium). To the methanol was added 2 g (87 mg-atoms) of sodium. When the solution had cooled, the mixture was further cooled to −10°. To the stirred solution was added 2.35 g (18.9 mmol) of **3** in 25 ml of reagent grade acetone. The mixture was stirred at −10° for 48 hr, and then stirred at room temperature for 12 hr. The dark brown solution was poured into 75 ml of water and acidified with concentrated HCl. The resulting solution was extracted four times with 50-ml portions of ether. The ether extracts were combined, dried (MgSO$_4$), and concentrated. Fractional distillation at aspirator pressure (removal of acetone and mesityl oxide) and then at vacuum pump pressure yielded 2.39 g (77%) of **4c**: bp 80–85° (1.25 Torr); ir (CCl$_4$) 1700 (C=O), 1625 cm^{-1} (C=C); nmr (CCl$_4$) δ 1.30 (s, 3, CH$_3$), 1.83 (m, 3, CH$_3$C=C), 2.20 ppm (m, 3, CH$_3$C=C).

Anal. Calcd for C$_{11}$H$_{16}$O: C, 80.44, H, 9.83. Found: C, 80.59; H, 9.86.

2,5-Dimethyl-3-benzylidenebicyclo[3,2.0]heptan-2-ol (5a). A solution of 7.21 g (34 mmol) of **4a** in 50 ml of dry ether was prepared in a 250-ml round-bottomed flask equipped with a magnetic stirrer. A few milligrams of *o*-phenanthroline was added to act as an indicator for excess alkyllithium. A solution of 2.0 *M* methyllithium in ether was added to the above solution until an excess of methyllithium was indicated by the dark brown color of the solution. The flask was stoppered and the solution was stirred for 2 hr. Water was added dropwise to the dark brown solution until the dark color faded and then a further 50-ml portion of water was added. The layers were separated, the aqueous phase extracted with 25 ml of ether, and the ether layers were combined. The ethereal solution was dried (MgSO$_4$) and concentrated and the crude product was chromatographed on 150 g of Alcoa F-20 alumina (hexane) yielding 7.99 g (100%) of **5a** as a yellow oil: nmr (CCl$_4$) δ 1.25 (s, 3, CH$_3$) 1.32 (s, 3, CH_3-COH), 6.56 (m, 1, vinyl), and 7.25 ppm (m, 5, aromatic).

Anal. Calcd for C$_{16}$H$_{20}$O: C, 84.16; H, 8.83. Found: C, 84.34; H, 8.69.

2,5-Dimethyl-3-furfurylidenebicyclo[3.2.0]heptan-2-ol (5b) was prepared as described above for the preparation of **5a**. The yield of **5b**, a yellow oil, was 90%: nmr (CDCl$_3$) δ 1.22 (s, 3, CH$_3$), 1.28 (s, 3, CH_3COH), 2.10 (b, s, 1, OH), 6.15 (d, 1, $J_{3'4'}$ = 3 Hz, 3′-H), 6.40 (m, 2,4′-H and vinyl), and 7.30 ppm (d, 1, $J_{4'5'}$ = 2 Hz, 5′-H); mass spectrum (70 eV) *m/e* 218 (M$^+$).

2,5-Dimethyl-3-isopropylidenebicyclo[3.2.0]heptan-2-ol (5c) was prepared from **4c** as described above for the preparation of **5a**. The yield of **5c**, mp 64–65° (recrystallized from pentane), was 85%: nmr (CCl$_4$) δ 1.18 (s, 3, CH$_3$), 1.24 (s, 3, CH_3COH), 1.65 (s, 3, CH_3C=C), 1.91 ppm (s, 3, CH_3C=C).

Anal. Calcd for C$_{12}$H$_{20}$O: C, 79.94; H, 11.18. Found: C, 79.71; H, 10.94.

General Procedure for Ozonolysis of the Alcohols 5a–c. The alcohol was dissolved in ethyl acetate (50 ml for each 5 g of alcohol) and cooled to −70°. Ozone (about 2% in oxygen) was bubbled through the cold solution until the solution turned a bright blue color, indicating that an excess of ozone was present. The solution was allowed to warm to near room temperature and the solvent was removed by use of a rotary evaporator. (The flask containing the solution was not heated in any way as the solvent was removed.) Then, 25 ml of saturated aqueous NaHCO$_3$ was added for each 5 g of alcohol used. The mixture was stirred overnight, washed with ether, acidified, saturated with salt, and extracted with ether. The ether extract of the acidic solution was dried (MgSO$_4$) and filtered, and the ether was removed leaving the crude keto acid **2**: ir (CDCl$_3$) 1730 (acid C=O), 1710 cm^{-1} (ketone C=O); nmr (CDCl$_3$) δ 1.40 (s, 3, CH$_3$), 2.09 (s, 3, CH_3C=O), 2.47 (s, 2, CH_2COOH), and 8.6 ppm (COOH).

(A) ozonolysis following the above procedure of 4.91 g (22 mmol) of **5a** in 50 ml of ethyl acetate yielded 3.06 g of a yellow oil. Nmr analysis of this oil showed it to be a mixture of 13 mol % benzoic acid and 87 mol % **2** (78% yield).

(B) Ozonolysis as above of 5.15 g (23.5 mmol) of **5b** in 50 ml of ethyl acetate yielded the desired keto acid **2** in 72% yield.

(C) Ozonolysis of 1.06 g (6 mmol) of **5c** in 25 ml of ethyl acetate as above gave keto acid **2** in 71% yield. In this case it is imperative that the temperature of the ozonide be kept below 10–20°. In an experiment using 2.56 g (14.2 mmol) of **5c** in which the ozonide was allowed to warm to *ca.* 25° the yield of **2** was reduced to 0.87 g (34%). Examination of the ether wash of the basic aqueous solution yielded 0.75 g of a keto alcohol identified as **7**: mp 53–54°; ir (CCl_4) 1745 cm^{-1} (C═O); nmr (CCl_4) δ 1.16 (s, 3, $\mathbf{CH_3}$), 1.33 (s, 3, CH_3COH), and 2.85 ppm (s, 1, OH); mass spectrum (70 eV) *m/e* 154 (M^+).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.31; H, 9.23.

Registry No.—(±)-**1**, 28117-21-7; **2**, 53166-10-2; **3**, 50459-35-3; **4a**, 53166-11-3; **4b**, 53166-12-4; **4c**, 53166-13-5; **5a**, 53166-14-6; **5b**, 53166-15-7; **5c**, 53166-16-8; **7**, 53166-17-9; methyllithium, 917-54-4; 3-methylcyclopentenone, 2758-18-1; ethylene, 74-85-1; benzaldehyde, 100-52-7; furfural, 98-01-1; acetone, 67-64-1.

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(3) For a review of fragmentation reactions see (a) C. A. Grob and P. W. Schiess, *Angew. Chem., Int. Ed. Engl.,* **6,** 1 (1967); (b) J. A. Marshall and J. L. Belletire, *Tetrahedron Lett.,* 871 (1971).

(4) The conversion, **3** → **2** *via* **4** and **5,** may be viewed as being catalyzed by the carbonyl reagent (benzaldehyde, *etc.*).

(5) Microanalyses were performed by Afred Bernhardt, Microanalytisches Laboratorium, Elbach über Engelskirchen, Mülheim (Ruhr), West Germany.

Synthesis of 2,5-Dihydroxy-2,5-dihydrofurans by Anodic Oxidation of Furans

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Received August 23, 1974

During synthetic work on *Lactarius* sesquiterpenes, we needed an efficient method of converting furans into maleic acid derivatives. Hydrolysis of 2,5-dimethoxy-2,5-dihydrofurans[1] followed by Jones oxidation[2] gave only a low yield of anhydride, partly because of the formation of lactones and polymeric material in the hydrolysis step.[3] Direct oxidation of the 2,5-dimethoxy-2,5-dihydrofurans with Jones reagent[2] according to Marei and Raphael[4] gave the desired maleic acid derivative but with significant amounts of γ-methoxy-α, β-unsaturated γ-lactones (up to 35%) and polymeric material.

In order to avoid the hydrolysis step we examined the oxidation of 2,5-dihydroxy-2,5-dihydrofurans to maleic anhydrides. Remarkably, no preparative route to this type of compound has been reported other than a hydroxylation of furan with osmium tetroxide–hydrogen peroxide to 2,5-dihydroxy-2,5-dihydrofuran which was obtained only as the corresponding bis(phenylhydrazone).[5] We now wish to report a preparatively useful route to 2,5-dihydroxy-2,5-dihydrofurans by anodic oxidation of furans. Table I shows the results obtained.

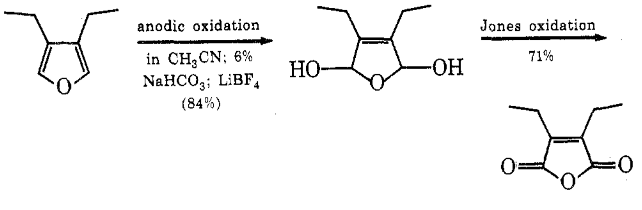
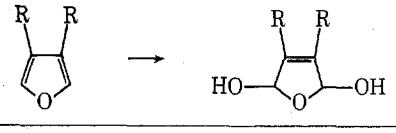
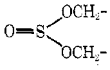
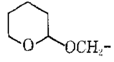


Table I
Anodic Oxidations



Starting material	R	Product	Yield, %	Current yield, %
1[a]	CH_3CH_2-	**8**	84	100
2		**9**	78	87
3[6]	CH_3COOCH_3-	**10**	86	100
4[7]		**11**	77	75
5[8]	Cl-CH_2-	**12**	*ca.* 70[b]	90
6	H-		*c*	
7[6]	CH_3CH_2OOC-		*d*	

[a] Peak potential relative to saturated calomel electrode: E_p = 1.62 V (cyclic voltammetry in MeCN). [b] **12** was unstable and decomposed on SiO_2 chromatography. EtOAc extraction gave a fairly pure crude product: nmr ($CDCl_3$) δ 6.00, 5.74 (s, 2, HO–CH), 4.30 (s, 4, Cl–CH_2). [c] Low yield of undefined material. [d] No reaction.

The electrolysis product (**8**) is conveniently oxidized further to anhydride by standard Jones oxidation.

Experimental Section

3,4-Diethylfuran (1). Methyllithium in ether (0.36 mol) was added to cuprous iodide (14.5 g, 0.165 mol) in ether (100 ml) at 0°. 3,4-Bis(chloromethyl)furan[8] (**5**) (6.9 g, 0.056 mol) in ether (50 ml) was added dropwise at 0° with stirring (continued for 12 hr).[9] Addition of water (300 ml), extraction with ether, drying (Na_2SO_4), and distillation gave 3,4-diethylfuran (**1**) (3.65 g, 70%): bp 39–40° (11 mm); n^{21}D 1.4500; ir (neat) 3160, 1555, 1475, 1060, 887, 805 cm^{-1}; nmr ($CDCl_3$) δ 7.13 (s, 2), 2.36 (q, 4, J = 7.5 Hz), 1.17 (t, 6, J = 7.5 Hz).

Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.4; H, 9.8.

2-Oxofuro[5,6-*c*]-1,3,2-dioxathiepane (2). 3,4-Bis(hydroxymethyl)furan[8] (25.6 g, 0.2 mol) and triethylamine (40.4 g; 0.4 mol) were dissolved in dry methylene chloride (400 ml). Thionyl chloride (47.2 g, 0.4 mol) in methylene chloride (130 ml) was added dropwise at 0° with stirring (continued for 30 min) (*cf.* ref 10). The reaction mixture was poured into cold water (300 ml) and the methylene chloride phase was separated. Drying (Na_2SO_4), evaporation, and distillation gave 3,4-bis(chloromethyl)furan (**5**)[8] (1.5 g, 5%) and 2-oxofuro[5,6-*c*]-1,3,2-dioxathiepane (**2**) (17.0 g, 49%): bp 56–57° (0.2 mm); n^{23}D 1.5210; ir (neat) 3140, 1565, 1460, 1185, 1053, 885, 813 cm^{-1}; nmr ($CDCl_3$) δ 7.35 (s, 2), 5.72, 4.56 (AB q, 4, J = 14.0 Hz).

Anal. Calcd for $C_6H_6SO_4$: C, 41.4; H, 3.5; S, 18.4. Found: C, 41.5; H, 3.5; S, 18.2.

General Hydroxylation Procedure. The anodic oxidation was performed at constant current (100 mA) in a water-jacketed beaker (100 ml) equipped with magnetic stirrer, Pt anode (120 × 40 × 0.1 mm) and Ni cathode (helical wire, 400 × 1.6 mm). The furan (*ca.* 5 mmol) was dissolved in acetonitrile (50 ml) and saturated sodium bicarbonate solution (3 ml) was added together with lithium tetrafluoroborate (*ca.* 10 mg as supporting electrolyte). After complete oxidation of the furan (tlc: SiO_2/CH_2Cl_2) the reaction mixture was evaporated and the residue chromatographed (35 g SiO_2/EtOAc) to give a mixture of *cis*- and *trans*-2,5-dihydroxy-2,5-dihydrofurans.

3,4-Diethyl-2,5-dihydroxy-2,5-dihydrofuran (8): yield, 84%; n^{21} D 1.4889; ir (neat) 3400 cm^{-1}; nmr ($CDCl_3$) δ 6.05, 5.71 (s, broad, 2, HO–**CH**), 2.20 (q, broad, 4, J = 8.0 Hz), 1.06 (t, broad, 6, J = 8.0 Hz).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found C, 60.9; H, 8.2.

2-Oxo-(2,5-dihydroxy-2,5-dihydrofuro)[5,6-*c*]-1,3,2-dioxathiepane (9): yield, 78%; n^{23}D 1.5180; ir (neat) 3400, 1200 cm^{-1}; nmr (D_2O; sodium 4,4-dimethyl-4-silapentane-1-sulfonate[11]) 6.11, 5.82 (s, 2, HO–**CH**), 4.45–5.50 (m, 4, CH_2) ppm.

Anal. Calcd for $C_6H_8SO_6$: C, 34.6; H, 3.9. Found: C, 35.0; H, 4.1.