formic acid and the solution refluxed overnight. The formic acid was removed under vacuum and the crude diformate dissolved in 250 ml of methanol and refluxed for 49 hr. The reactions were followed by the disappearance or appearance of the hydroxyl, formate, and nitrate ester bands in the infrared spectrum. After removal of the methanol under vacuum, the crude diol was dissolved in 100 ml of methylene chloride and filtered through 100 g of silica gel. Evaporation of the methylene chloride gave 7.2 g of pure diol (89% of theory) as a viscous, colorless liquid. The nmr spectrum, which was determined in water with external tetramethylsilane as a reference, showed an A_2B_2 multiplet centered at τ 5.58 ($CH_2CH_2^-$) and a signal at 4.86 (OH) with relative areas of 4:1. *Anal.* Calcd for $C_4H_{10}N_2O_4$: C, 32.01; H, 6.67; N, 18.66. Found: C, 31.63; H, 6.50; N, 18.27.

Pentaerythritol.—The conversion of pentaerythritol trinitrate[9] to pentaerythritol was carried out as described for dinitroxydiethylnitramine with the exception that the methanolysis required 96 hr. After removal of the methanol under vacuum and recrystallization from water–ethanol, the yield of pentaerythritol, mp 254–259°, was 72% of theory. The nmr and infrared spectra of the purified product were identical with those of an authentic sample.

Registry No.—3-Nitraza-1,5-pentanediol, 13084-48-5.

Acknowledgment.—This research was supported by the Army Missile Command under Contract DA-01-021-AMC-11735(Z).

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(9) Pentaerythritol trinitrate was generously supplied by E. I. du Pont de Nemours and Co.

The Hydrolysis of α,α'-Dimethoxydihydromenthofuran

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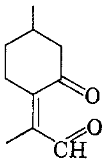
Schenck and Foote[1] have reported the synthesis of the γ-ketoaldehyde **1** by the hydrolysis of α,α'-dimethoxydihydromenthofuran (**2**). However, they[1] did not conclusively identify their $C_{10}H_{14}O_2$ product and merely considered it to have the ketoaldehyde structure **1** in analogy to the formation of β-acetylacrolein (**3**)[2] in the hydrolysis of 2,5-dimethoxy-2,5-dihydrosylvan (**4**).[2-5]



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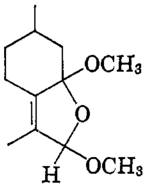

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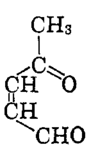

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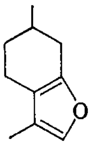

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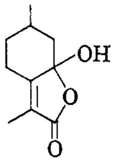
On repeating the hydrolysis of α,α'-dimethoxydihydromenthofuran (**2**), prepared from menthofuran (**5**) by electrolytic methoxylation according to the method of Clauson-Kaas,[3] a procedure analogous to that leading to β-acetylacrolein (**3**)[2] was adopted. Infrared spectroscopy of the crude hydrolysate indicated[7,8] the presence of lactonic materials. The hemiketal lactone **6** was isolated from the hydrolysate and identified by comparison with an authentic sample.[9,10] The formation of this product indicated that either the starting material or a hydrolysis product had undergone air oxidation.

Repetition of the hydrolysis of **2** on a 2.2-g (10-mmole) scale under a nitrogen atmosphere produced, after steam distillation, vapor phase chromatography, and vacuum distillation, 0.1 g of the α,β-unsaturated γ-lactone **7**, which was identified by comparison with material previously prepared by a different route.[10] Upon repetition of the hydrolysis on twice this scale, steam distillation left a residue of 2.3 g of darkly colored, apparently polymeric, material. The steam distillate was collected in ether and, after removal of solvent, was vacuum distilled in a bulb to bulb apparatus to produce 1.2 g (34.2% yield) of a colorless liquid. This product was found to be a 3:1 mixture of the β,γ-unsaturated γ-lactone **8** and the α,β-unsaturated γ-lactone **7** by spectral analysis (ultraviolet, infrared, and proton magnetic resonance). When the hydrolysis reaction was carried out in the presence of dilute mineral acid, the rate of the reaction was significantly enhanced; however, no change in product ratio was noted.



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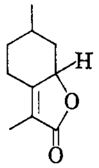

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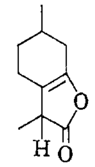

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The mixture of unsaturated lactones could be converted to the α,β-unsaturated lactone **7** in quantitative yield by heating the mixture in a sealed tube at 155°, an isomerization process well documented for lactones of this type.[7,11-15] Air oxidation of the enol lactone isomer **8** to the hemiketal lactone **6** was found to be very facile,[16] while the conjugated lactone **7** appeared to be stable to air oxidation.

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(1) G. O. Schenck and C. S. Foote, *Angew. Chem.*, **70**, 505 (1958).

(2) L. Birkofer and R. Dutz, *Ann.*, **657**, 94 (1962).

(3) N. Clauson-Kaas, F. Limborg, and P. Dietrich, *Acta Chem. Scand.*, **6**, 545 (1952); N. Clauson-Kaas, F. Limborg, and K. Glens, *ibid.*, **6**, 531 (1952); and previous papers.

(4) B. L. Van Duuren and F. L. Schmitt, *J. Org. Chem.*, **25**, 1761 (1960).

(5) The hydrolysis to form β-acetylacrolein (**3**)[2] was repeated. After preparative vapor phase chromatography, the product was found to be an approximately 1:1 mixture of the *cis*- and *trans*-enediones (**3**)[6] by 60- and 100-Mc proton magnetic resonance studies.

(6) After completion of this work, the formation of *trans*-enediones of this type was reported by D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Am. Chem. Soc.*, **88**, 515 (1966).

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(10) J. W. Wheeler, Jr., Ph.D. Dissertation, Stanford University, 1961.

(11) R. H. Leonard, *Ind. Eng. Chem.*, **48**, 1331 (1956).

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(14) W. Herz and L. A. Glick, *J. Org. Chem.*, **28**, 2970 (1963); **29**, 613 (1964).

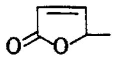
(15) N. Cohen, Ph.D. Dissertation, Northwestern University, 1965.

(16) F. A. Kuehl, R. P. Linstead, and B. A. Orkin, *J. Chem. Soc.*, 2213 (1950).

The isomerization of the supposed γ-ketoaldehyde intermediate **1** to the lactonic structures **7** and **8** is analogous to the conversion of β-acetylacrolein (**3**) to levulinic acid (**9**) and the angelica lactones **10** and **11**. Our attempts to isolate the presumed intermediate **1** were unsuccessful.

$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH$

9



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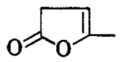

11

Experimental Section

General.—Proton magnetic resonance spectra were recorded in deuteriochloroform solutions with tetramethylsilane as an internal standard using a Varian A-60 spectrophotometer. Infrared spectra were obtained on liquid films using Perkin-Elmer Model 421 or Model 237B spectrophotometers. Only major absorptions are listed herein. Ultraviolet spectra were obtained on 95% ethanol solutions (unless otherwise stated) using a Cary Model 14 recording spectrophotometer or a Bausch and Lomb Spectronic 505 spectrophotometer. All combustion analyses were performed in the microanalytical laboratory at Stanford University. Mass spectra were obtained in the mass spectroscopy laboratory at Stanford University.

Menthofuran (5).—Menthofuran was prepared essentially by the procedure of Wither[9,17] as modified by Wheeler,[10] from Oil of Pennyroyal (*Mentha pulegium L.*) *via* the intermediate sultone. The crude methofuran from the pyrolysis of the sultone was steam distilled from a sodium carbonate solution and then, after appropriate separation and drying, was distilled from sodium; the pure product, bp 90–94° (22 mm), was identical with previous samples.[9,10,17,18]

α,α′-Dimethoxydihydromenthofuran (2).—Electrolysis[18] of 9.77 g (66 mmoles) of menthofuran (**5**) in 100 ml of absolute methanol containing 1.1 g of ammonium bromide using platinum electrodes (one annular cylindrical electrode, height 5 cm, diameter 2.6 cm; one strip electrode, 1.4 cm × 5 cm) at temperatures below 0° with magnetic stirring at 0.4–0.5 amp for 9.5 hr produced a yellow solution. This solution was poured into 20 ml of a methanolic solution of sodium methoxide which contained base equivalent to the ammonium bromide used. The product was concentrated on a steam bath with periodic filtration to remove the solid material which separated. After all solvent and solids had been removed, the dark, liquid residue was fractionally distilled to obtain 11.37 g (82.4% yield) of the isomers of **2**, bp 76–90° (7 mm).[18]

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.09; H, 9.36.

The spectra were as follows: infrared, 1095 cm^{-1}; ultraviolet, λ_{max}^{MeOH} 287 mμ (ε 12), 281 (12), 277 (12), 255 (33, sh), 246 (38, sh), end absorption; proton magnetic resonance, broad singlets at δ 5.60 and 5.14 (hydrogen on carbon bearing two oxygen atoms), singlets at 3.47, 3.37, 3.09, and 3.00 (two types of methoxy methyl groups), singlet at 1.67 (methyl group on double bond), doublet centered at 0.89 (J = 6.5 cps, methyl group adjacent to methine carbon atom), methylene absorptions; mass spectrum, molecular ion m/e 212, base peak m/e 148.

In approximately half of the runs of this reaction, yields were reduced to 30–45% and a dark blue color was apparent throughout the electrolysis. No explanation for these phenomena was found.

Hydrolysis of α,α′-Dimethoxydihydromenthofuran (2).—Hydrolysis by heating under reflux 3.55 g (17 mmoles) of **2** dissolved in 30 ml of ether with 30 ml of distilled water for 1 week using magnetic stirring produced, after steam distillation and removal of solvent from the distillate, an oily residue which contained a minimum of three components on the basis of thin layer chromatography on silica. After standing at room temperature for 1 week, solid material began to separate from the oily material. Filtration, washing with pentane, and crystallization from benzene produced material identical in every respect with a sample of hemiketal lactone **6**,[9,10] mp 189–191°.

Hydrolysis of 2.2 g (10 mmoles) of **2** dissolved in 30 ml of ether with 30 ml of distilled water as above under a nitrogen atmosphere produced an oily residue. Preparative vapor phase chromatography (1/2 in. × 6 ft column, 20% SE-30 on Wilkens 60/80 mesh firebrick column, 200°, 150 ml of helium per minute) followed by bulb to bulb distillation at 5 mm and bath temperatures of up to 165° produced 0.1 g of liquid assigned the α,β-unsaturated γ-lactone structure **7** on the basis of its spectra.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.15; H, 8.47.

The spectra were as follows: infrared, 1752 and 1681 cm^{-1} (α,β-unsaturated γ-lactone absorptions[7,8,10]); ultraviolet, λ_{max} 218 mμ (ε 15,900); proton magnetic resonance, triplet centered at δ 1.80 (three protons, J = 2 cps, methyl group on a double bond and adjacent to a carbonyl group), doublet centered at 1.00 (three protons, J = 6 cps, methyl group adjacent to a methine carbon atom), split quartet centered at 4.63 (one proton, J = 12, 8, and 1.5 cps, allylic proton on carbon adjacent to oxygen, probably axial from the magnitude of the coupling constants[19]), methylene absorptions; mass spectrum, molecular ion m/e 166, base peak m/e 41.

Treatment of 4.5 g (21 mmoles) of **2** in 30 ml of ether with 30 ml of 0.1 M aqueous sulfuric acid at reflux under a nitrogen atmosphere for 3 days produced, after steam distillation, 2.2 g of dark material as residue and 2.27 g of a pale yellow, crude liquid product in the distillate. After removal of solvent, this yellow material was distilled at 5 mm and 90–110° bath temperatures in a bulb to bulb apparatus to give 1.2 g of a colorless liquid deduced to be a 3:1 mixture of the β,γ-unsaturated γ-lactone **8** and the α,β-unsaturated γ-lactone **7** from its spectral properties.

The spectra were as follows: infrared, 1797 and 1710 (β,γ-unsaturated γ-lactone absorptions[7,8]), 1755 and 1685 cm^{-1} (α,β-unsaturated γ-lactone absorptions[7,8,10]); ultraviolet, λ_{max} 218 mμ (ε 3760), based on ε 15,900 for the pure conjugated lactone (see above (which, corresponds to the presence of 23.6% of the conjugated lactone in the mixture; proton magnetic resonance, doublet centered at δ 1.05 (three protons, J = 5.5 cps, methyl group adjacent to methine carbon atom), doublet centered at 1.27 (three protons, J = 8 cps, methyl group adjacent to methine carbon atom, the methine carbon atom being adjacent to a carbonyl group and allylic), quartet centered at 3.08 (one proton, J = 8 and 2 cps, methine hydrogen adjacent to methyl group, carbonyl group, and tetrasubstituted vinyl position), methylene absorptions, and those signals previously found in the spectrum of the conjugated lactone (see above). The integrals assigned to the enol lactone **8** were approximately three times those integrals assigned to the conjugated lactone **7**.

Thermal Equilibration of the Unsaturated Lactones.—A portion of the lactone mixture (**7** and **8**) was sealed under nitrogen in a thick-walled tube and heated in a Wood's metal bath at 155° for 48 hr. The reaction mixture turned green on being cooled to room temperature, but the proton magnetic resonance spectrum of the product, either before or after bulb to bulb distillation at 5–6 mm, was consistent with the presence of only the α,β-unsaturated γ-lactone **7**.

Air Oxidation of the Unsaturated Lactones.—Samples of the mixture of unsaturated lactones **7** and **8** and of the pure conjugated lactone **7** were exposed to the air for varying periods of time. The conjugated lactone was unchanged after 4 months. The mixture of lactones showed evidence of crystal formation within 24 hr and was extensively solidified within 2 weeks. Proton magnetic resonance studies of this 2-week-old material showed the disappearance of those signals assigned to the β,γ-unsaturated γ lactone **8**, the retention of weak signals assigned to the α,β-unsaturated γ-lactone **7**, and the appearance of strong absorptions due to the hemiketal lactone **6**.[10] The solid material was separated by filtration and found to be impure hemiketal lactone **6**, mp 170–179° (lit.[9] 188–189°). The solid was dissolved in aqueous sodium hydroxide, and the solution was acidified with dilute aqueous hydrochloric acid to produce a white solid which, after crystallization from benzene, melted at 187–189° alone or when mixed with an authentic sample[10] of the hemiketal lactone **6**.

Registry No.—**2**, 13341-70-3; **6**, 514-93-2; **7**, 13341-72-5.

Acknowledgments.—We are indebted to Dr. John M. Erikson for preliminary hydrolysis experiments and to Dr. Lois L. Durham for assistance with the proton magnetic resonance spectra.

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[17] R. P. Wither, Ph.D. Dissertation, Stanford University, 1955.

[18] J. M. Erikson, Ph.D. Dissertation, Stanford University, 1965.

[19] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry—Illustrations from the Steroid Field," Holden-Day, Inc., San Francisco, Calif., 1965, pp 50–51.