Experimental Section

The compounds were prepared and purified by methods which have been described.[6] The nitrosobenzenes used in the present investigation had the following physical properties: 2,6-dibromo-, mp 134–135° (lit.[6] mp 135–136°), ϵ_0 40.54 (763 mμ); 2,6-dibromo-4-methyl-, mp 136–138° (lit.[6] mp 136.5–138°), ϵ_0 42.57 (758 mμ); 2,6-di-bromo-4-chloro-, mp 110–111° (lit.[6] mp 110–111°), ϵ_0 42.75 (773 mμ); 2,4,6-tribromo-, mp 122–124° (lit.[6] mp 122–123°), ϵ_0 43.48 (772 mμ) [lit.[4] ϵ_0 43.5 (775 mμ)].

Infrared spectra of the crystalline dimers were run as Nujol mulls and KBr or KI pellets. The spectrometer was a grating instrument with resolution of about 1–2 cm^{-1} (Perkin-Elmer 337 G). Peak positions were reproducible to within ± 1 cm^{-1} and were the same in Nujol mull or pressed disk.

Spectrophotometric measurements were carried out and temperatures were controlled to within $\pm 0.05°$ of 25° as described previously.[1] Stock solutions were made up at 25° and dilutions were made (also at 25°) by means of calibrated pipets and volumetric flasks. Practice runs on nitrosobenzene itself (which does not dimerize in dilute solution) showed that Beer's law was obeyed closely on diluting stock solutions in this way, so that solvent losses due to evaporation and other dilution errors were not serious.

Using experimental optical densities and concentrations, plots of D/CL *vs.* D^2/CL^2 were constructed and "best" straight lines were determined by least squares. The intercepts on the D/CL axes gave ϵ_0, and, from this, individual values of α, the fraction of nitroso compound actually present in solution as monomer, could be calculated from experimental optical densities. Knowing α, equilibrium constants were computed from the following relationship where C is the concentration of total nitroso compound, all figured as monomer.

$$K_c = 2C(\alpha^2/1 - \alpha)$$

Registry No.—2,6-Dibromonitrosobenzene dimer, 13084-82-7; 2,6-dichloronitrosobenzene dimer, 31084-83-8; 2,6-dibromo-4-methylnitrosobenzene dimer, 13084-84-9; 2,6-dichloro-4-methylnitrosobenzene dimer, 13084-85-0; 2,6-dibromo-4-chloronitrosobenzene dimer, 13115-02-1; 2,4,6-trichloronitrosobenzene dimer, 13084-86-1; 2,4,6-tribromonitrosobenzene dimer, 13084-87-2; 2,6-dichloro-4-bromonitrosobenzene dimer, 13084-88-3.

Decomposition of Nitrate Esters to Alcohols

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In connection with the synthesis of 3-nitraza-1,5-pentanediol from the corresponding dinitrate, we have developed a simple, high-yield procedure for the conversion of primary nitrates to alcohols. This transformation can be effected first in the presence of secondary nitramines and second without the formation of the undesirable side-reaction products which accompany hydrolytic decomposition.

Baker and co-worker[1] have carried out a systematic study of the hydrolytic decomposition of organic nitrates. The results of their investigation clearly demonstrated that the hydrolytic decomposition of organic nitrates involves the simultaneous occurrence of reactions 1–3. The formation of aldehydes and olefins under neutral, acidic, or basic conditions makes the hydrolytic decomposition of nitrate esters to alcohols of little preparative value. Other methods have been reported for the decomposition of nitrate esters to alcohols. Hydrazine hydrate is an excellent reagent for reducing sugar nitrates[2] but gives only fair yields with primary aliphatic nitrates.[3] Alkaline hydrosulfides have been reported[4] to decompose nitrates to alcohols in excellent yields if the nitrate ester does not contain functional groups such as secondary nitramines that are unstable under basic conditions.

$$\mathrm{Y + CH_2(CH_2R)ONO_2 \longrightarrow CH_2RCH_2Y + NO_3^-} \quad (1)$$

$$\mathrm{Y + HCHRCH_2ONO_2 \longrightarrow YH + CHR{=}CH_2 + NO_3^-} \quad (2)$$

$$\mathrm{Y + HCH(CH_2R)ONO_2 \longrightarrow YH + CH_2RCHO + NO_2^-} \quad (3)$$

The literature reveals two potential methods for the preparation of 3-nitraza-1,5-pentanediol from the corresponding dinitrate. Acetolysis of the dinitrate followed by acid hydrolysis of the diacetate with methanolic hydrochloric acid as described by Feuer and Swarts[5] gave only a trace of the desired diol. Apparently, the diol forms and then cyclizes under the acidic conditions of the hydrolysis to a morpholine derivative.[6] The alternative procedure involves the room-temperature decomposition of nitrate esters by trifluoroacetic acid to a mixture of the corresponding trifluoroacetate, carboxylic acid, and nitric oxide.[7] We speculated that under refluxing conditions, evolution of the nitric oxide would occur, facilitating formation of high yields of the trifluoroacetate, which, on subsequent methanolysis, would result in the attainment of the desired diol. Decomposition of the dinitrate of 3-nitraza-1,5-pentanediol in refluxing trifluoroacetic acid does, indeed, eliminate oxidation to the carboxylic acid by the nitric oxide; however, the trifluoroacetolysis is exceedingly slow, requiring a reaction time of 1 week. Substitution of formic acid for trifluoroacetic acid gives the diformate after refluxing overnight. Subsequent methanolysis yields the desired diol in almost quantitative yield.

The generality of the formolysis reaction is further demonstrated by the conversion of pentaerythritol trinitrate to pentaerythritol. The absence of any molecular rearrangement in this neopentyl system is obtained from the H^1 nmr spectrum of the methanolysis product. The spectrum is identical with that obtained for pentaerythritol. The decomposition of nitrate esters to alcohols *via* an intermediate formate ester enjoys several advantages over previously described procedures. The yields are high, the reaction can be carried out in the presence of a nitramine, and product isolation is simplified.

Experimental Section

CAUTION! Nitrate esters should be handled with care.

3-Nitraza-1,5-pentanediol.—The dinitrate of 3-nitraza-1,5-pentanediol,[8] 13 g (0.054 mole), was dissolved in 150 ml of 97%

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[1] J. W. Baker and T. G. Heggs, *J. Chem. Soc.*, 616 (1955), and preceding papers.

[2] K. S. Ennor and J. Honeyman, *ibid.*, 2586 (1958).

[3] R. T. Merrow and R. W. Van Dolah, *J. Am. Chem. Soc.*, **76**, 4522 (1954).

[4] R. T. Merrow, S. J. Cristol, and R. W. Van Dolah, *ibid.*, **75**, 4259 (1953).

[5] H. Feuer and W. A. Swarts, *J. Org. Chem.*, **27**, 1455 (1962).

[6] M. J. Astle, "Industrial Organic Nitrogen Compounds," Reinhold Publishing Corp., New York, N. Y., Chapter 3, p 159.

[7] R. T. Merrow and G. C. Whitnack, *J. Org. Chem.*, **23**, 1224 (1958).

[8] W. J. Chute, K. G. Herring, L. E. Toombs, and G. F. Wright, *Can. J. Research*, **B26**, 89 (1948).

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.

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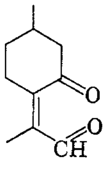
Schenck and Foote[1] have reported the synthesis of the γ-ketoaldehyde **1** by the hydrolysis of α,α'-dimethoxydihydromenthofuran (**2**). However, they[1] did not conclusively identify their $C_{10}H_{14}O_2$ product and merely considered it to have the ketoaldehyde structure **1** in analogy to the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



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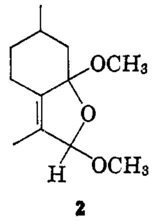

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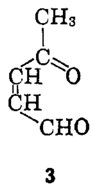

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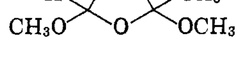

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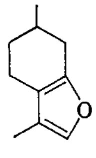

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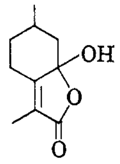
On repeating the hydrolysis of α,α'-dimethoxydihydromenthofuran (**2**), prepared from menthofuran (**5**) by electrolytic methoxylation according to the method of Clauson-Kaas,[3] a procedure analogous to that leading to β-acetylacrolein (**3**)[2] was adopted. Infrared spectroscopy of the crude hydrolysate 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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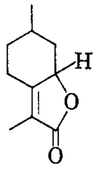

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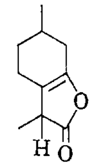

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The mixture of unsaturated lactones could be converted to the α,β-unsaturated lactone **7** in quantitative yield by heating the mixture in a sealed tube at 155°, an isomerization process well documented for lactones of this type.[7,11–15] Air oxidation 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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(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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