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The Action of Polyphosphoric Acid on 2-Nitro-1,3-Propanediols and Some of Their Carbonate, Sulfite, and 1,3-Dioxane Derivatives[1]

L. W. Kissinger, T. M. Benziger, and R. K. Rohwer

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The dehydration of simple alcohols by polyphosphoric acid (PPA) to olefins and low molecular weight polymers has been described by Snyder[2] and Jean.[3] More recently the esterification of 2,2-dinitropropanol with several aliphatic acids was accomplished in PPA.[4] Identification of acetal by-products in the latter process and related work on the preparation of oxetanes prompted the study on 2-nitro-1,3-propanediols described in this note.

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. R. Snyder and F. X. Werber, J. Am. Chem. Soc., 72, 2966 (1950).

(3) J. W. Jean, U. S. Pat. 2,373,475; Chem. Abstr., 39, 3652 (1945).

(4) L. W. Kissinger, M. Schwartz, and W. E. McQuistion, J. Org. Chem., 26, 5203 (1961).

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2-Nitro-1,3-propanediol and its 2-methyl-,2-ethyl-, and 2-chloromethyl-derivatives react smoothly with PPA at 70-90° to give the corresponding 1,3-dioxanes (see Table I) which sublime from the reaction mixture under reduced pressure. Better yields of the dioxanes are obtained by including an equivalent of paraformaldehyde in the reaction mixture. At higher temperatures, particularly in the presence of small amounts of copper powder, the elements of nitrous acid and water are eliminated and acrolein or the α-alkyl acroleins may be distilled from the reaction mixture under reduced pressure. In the case of 2-chloromethyl-2-nitro-1,3-propanediol, however, a mixture of substituted acroleins seems to be formed, characterized by two carbonyl b hands in the infrared. The mixture tentatively is believed to contain the isomeric α-chloromethylacrolein and α-methyl-β-chloroacrolein. A similar reaction occurs between PPA and the 5-nitro-1,3-dioxanes at elevated temperatures to give the acroleins in approximately the same yields. The elimination of the nitro group observed by Rondesvedt and Mantell[5] when 2-isopropyl-5-methyl-5-nitro-1,3-dioxane was pyrolyzed over pumice and an undisclosed yield of α-methacrolein was produced is probably an analogous reaction.

When the 2-nitropropanediols contain certain other negative groups

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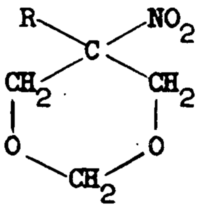
(5) C. S. Rondesvedt, Jr., and G. J. Mantell, *J. Am. Chem. Soc.*, 84, 3307 (1962).

TABLE I

DIOXANES



R	Yield (%)	mp	Molecular Formula	C	H	N
H	92	37.5-38°	$C_4H_7NO_4$	Calcd. 36.09	5.30	10.52
				Found 36.06	5.77	10.13
Methyl	79	71°^{a}		---	----	-----
				---	----	-----
Ethyl	71	53.2°^{a}		---	----	-----
				---	----	-----
Chloro	84	61-62°	$C_4H_6ClNO_4$	Calcd.^{b} 28.67	3.61	8.36
				Found^b 29.03	3.68	8.09
Fluoro	72	66-67°	$C_4H_6FNO_4$	Calcd^c 31.79	4.00	9.27
				Found^c 31.90	4.11	8.93
Nitro	64	53-53.5°^{a}		---	----	-----
				---	----	-----
Chloromethyl	92	40.5-41°	$C_5H_8ClNO_4$	Calcd^d 33.07	4.44	7.71
				Found^d 32.88	4.45	7.48

(a) M. Senkus, *J. Am. Chem. Soc.*, *63*, 2635 (1941).
(b) Anal. Calc'd. for $C_4H_6ClNO_4$: Cl, 21.16 . Found: Cl, 20,75.
(c) Anal. Calc'd. for $C_4H_6FNO_4$: F, 12.57 . Found: F, 12.49.
(d) Anal. Calc'd. for $C_5H_8ClNO_4$: Cl, 19.53 . Found: Cl, 19.40.

in the 2-position, the reaction proceeds to the 1,3-dioxanes which, in these cases, are much more stable in PPA than the corresponding alkyl derivatives described above. 2-Chloro-2-nitro-1,3-propanediol reacts in PPA to form the corresponding 1,3-dioxane which is stable in the reaction medium up to about 130°, after which it slowly reacts to produce α-chloroacrolein. 2-Fluoro-2-nitro-1,3-propanediol behaves similarly giving a very low yield of α-fluoroacrolein and a good yield of the stable 5-fluoro-5-nitro-1,3-dioxane. 2,2-Dinitro-1,3-propanediol forms 5,5-dinitro-1,3-dioxane under these conditions which reacts further to produce oxides of nitrogen, water, and other water soluble decomposition products at elevated temperatures. 2-Nitro-2-phenyl-1,3-propanediol, on the other hand, reacts in PPA even under mild conditions to give oxides of nitrogen and a mixture of products which appeared, from its infrared absorption, to contain aromatic nitro compounds.

2-Methyl-2-nitrotrimethylene carbonate reacted smoothly with PPA to form α-methylacrolein in yields comparable to those from the diol, but the linear polycarbonate, from which the cyclic monomer had been removed by sublimation, decomposed in PPA at elevated temperatures and gave only a trace of acrolein. Several other carbonates were treated with PPA, but considering the extra step involved in their preparation, they do not offer any advantage over the direct use of the diol.

2-Methyl-2-nitromethylene sulfite is stable in warm PPA from which it distills unchanged under reduced pressure.

Experimental[6]

2-Nitro-1,3-propanediol[7], 2-ethyl-2-nitro-1,3-propanediol[8], 2-nitro-2-phenyl-1,3-propanediol[9], 2-chloro-2-nitro-1,3-propanediol[7], and 2,2-dinitro-1,3-propanediol[10] were prepared essentially as described in the literature. 2-Methyl-2-nitro-1,3-propanediol was obtained from Commercial Solvents Corporation.

2-Chloromethyl-2-nitro-1,3-propanediol - A suspension of 9.55 g. (0.05 mole) of 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane[11], and 3.95 g. (0.05 mole) of pyridine in 25 ml. of ethylene chloride was warmed until solution was complete. Liquid sulfuryl chloride, 2.1 ml. (0.025 mole),

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(6) Microanalyses were performed by M. J. Naranjo

(7) E. Schmidt and R. Wilkendorf, *Ber.*, *52*, 393 (1919).

(8) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, *32*, 34 (1940).

(9) L. F. Fieser and M. Gates, *J. Am. Chem. Soc.*, *68*, 2250 (1946).

(10) M. H. Gold, E. E. Hamel, and K. Klager, *J. Org. Chem.*, *22*, 1665 (1957).

(11) M. Senkus, *U. S. Pat. 2,368,071*, *Chem. Abs.*, *39*, 4098 (1945).

was then added dropwise to the stirred solution at room temperature. After several hours at room temperature, the reaction mixture was heated briefly to reflux, cooled, and washed with dilute sodium bicarbonate solution. The solution was dried with magnesium sulfate and the solvent removed under reduced pressure giving 7.36 g. (71% yield) of white crystalline 5-chloromethyl-2,2-dimethyl-5-nitro-1,3-dioxane, m.p. 52-55°.[12]

Recrystallization from 50% methanol raised the m.p. to 56-57°.

<u>Anal</u>. Calcd. for $C_7H_{12}ClNO_4$: C, 40.10; H, 5.77; N, 6.68. Found: C, 40.31; H, 5.85; N, 6.64.

A suspension of 34 g. (0.16 moles) of this dioxane derivative in 60 ml. water containing 3 ml. of conc. hydrochloric acid was heated under reflux for 1-2 hr., chilled and filtered to remove the first crop of crystalline 2-chloromethyl-2-nitro-1,3-propanediol (14.5 g.). An additional 7.6 g. of crude product was obtained by ether extraction of the filtrate. The combined product was crystallized from an ethylene chloride-petroleum ether mixture giving 20.5 g. (80% yield) of 2-chloromethyl-2-nitro-1,3-propanediol, m.p. 109-110° (sublimes).

<u>Anal</u>. Calcd. for $C_4H_8ClNO_4$: C, 28.33; H, 4.76; Cl, 20.91; N, 8.26. Found: C, 28.40; H, 5.02; Cl, 21.01; N, 8.29.

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(12) The application of this chlorination technique to several mono and polynitro alcohols is the subject of a note soon to appear from this Laboratory.

2-Fluoro-2-nitro-1,3-propanediol. A solution of 19.1 g. (0.10 mole) of 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane[11] in 100 ml. of methanol was treated with a solution of 13.5 g. (0.25 mole) of sodium methoxide in 75 ml. of methanol with stirring and cooling. The precipitated salt was filtered and, while still moist with methanol, was suspended in 200 ml. of dichloromethane. (Use a protective shield!) The suspension was stirred and treated with fluorine gas (diluted 8-10 times its volume with nitrogen) during about 3 hr. at 0°. Steam distillation and extraction of the distillate with dichloromethane gave, after removal of the solvent, 7.7 g. of crude 2,2-dimethyl-5-fluoro-5-nitro-1,3-dioxane, n_D^{25} 1.4318. Distillation through a 5" Vigreaux column gave, after a small fore-run, 6.2 g. of product, b.p. 56-58°/2 mm., n_D^{25} 1.4310; λ NO_2 6.34 and 7.22μ.

Anal. Calcd. for $C_6H_{10}FNO_4$: C, 40.22; H, 5.63; N, 7.82. Found: C, 40.20; H, 5.87; N, 7.37.

A solution of 9 g. (0.05 mole) of this dioxane derivative in 30 ml. of 65% methanol containing 0.5 ml. of concentrated hydrochloric acid was heated under reflux for 20 hr., decolorized with Norit, and the solvent removed under reduced pressure giving 6.8 g. of crude 2-fluoro-2-nitro-1,3-propanediol, m.p. 77-79°. Sublimation at 60°/0.01 mm. gave an analytical sample, m.p. 87-88°.

Anal. Calcd. for $C_3H_6FNO_4$: C, 25.90; H, 4.35; F, 13.66; N, 10.07. Found: C, 26.32; H, 4.61; F, 13.42; N, 9.98.

2-Methyl-2-nitrotrimethylene carbonate. A solution of 4 g. (0.03 moles) of 2-methyl-2-nitro-1,3-propanediol and 4.8 g. (0.06 moles) of pyridine in 100 ml. of dichloromethane was stirred at 0° while 2.2 ml. (0.03 moles) of liquid phosgene was allowed to evaporate in a stream of nitrogen and bubble into the solution during 1/2 hr. after which the reaction mixture was warmed to reflux temperature for 3 hr. The crude carbonate was isolated by washing the solution with water, drying over magnesium sulfate, and removing the solvent under reduced pressure to give 3.7 g. (78%), m.p. 138-145°. Sublimation of 2.8 g. at 90-115°/0.05 mm. gave 1.23 g. of cyclic carbonate as sublimate, m.p. 112-114°; $\lambda C = O$ 5.60, λNO_2 6.39, 7.40, $\lambda C - O - C$ 8.93µ in a KBr pressing.

Anal. Calcd. for $C_5H_7NO_5$: C, 37.27; H, 4.38; N, 8.69. Found: C, 37.16; H, 4.97; N, 8.73.

The residue, m.p. 142-145°, weighed 1.60 g. and showed λOH 2.90 (weak), $\lambda C = O$ 5.67 (strong), λNO_2 6.43 (strong), and a strong, broad band at 7.8-8.1µ in the infrared in a KBr pressing and is believed to be a polycarbonate.

Anal. Found: C, 36.67; H, 5.23; N, 9.09.

2-Ethyl-2-nitrotrimethylene carbonate. Similar treatment of 2-ethyl-2-nitro-1,3-propanediol[8] gave an 89% yield of crude cyclic carbonate, m.p. 67-69°. Recrystallization from a mixture of dichloromethane and petroleum ether gave a mat of fine white needles, m.p. 72-72.5°, $\lambda C = O$ 5.69, λNO_2 6.43, 7.36, $\lambda C{-}O$ 8.47 - 8.54.

Anal. Calcd. for $C_6H_9NO_5$: C, 41.14; H, 5.18; N, 8.00. Found: C, 41.08; H, 5.57; N, 7.83.

2-Chloro-2-nitrotrimethylene carbonate. In the same way, 2-chloro-2-nitro-1,3-propanediol[7] was converted to the cyclic carbonate, m.p. 133.5-134° after recrystallization from dichloromethane-petroleum ether, in 69% yield; λ CO 5.66, λNO_2 6.34 and 7.47, λ other 8.45, 8.76, 10.04, 11.79, 13.18, and 14.63.

Anal. Calcd. for $C_4H_4ClNO_5$: C, 26.46; H, 2.22; Cl, 19.53; N, 7.72. Found: C, 26.25; H, 2.67; Cl, 19.79; N, 7.59.

2-Chloromethyl-2-nitrotrimethylene carbonate. Treatment of 2-chloromethyl-2-nitro-1,3-propanediol with phosgene under the same conditions gave the crude carbonate. Sublimation at 100-110° @ 0.01 mm. gave the cyclic carbonate, m.p. 108-9°, in 63% yield; λ C = O 5.70, λNO_2 6.39 and 7.42, λ other 8.44, 8.68, 11.80, and 13.25 in a KBr pressing.

Anal. Calcd. for $C_5H_6ClNO_5$: C, 30.71; H, 3.09; Cl, 18.13; N, 7.16. Found: C, 30.64; H, 3.20; Cl, 18.45; N, 7.22.

The residue from the sublimation, m.p. 164-166°, had approximately the same infrared spectrum and is believed to be a linear polycarbonate.

Anal. Found: C, 30.93; H, 3.43; Cl, 18.30; N, 6.88.

2-Methyl-2-nitrotrimethylene sulfite. A solution of 5.4 g. (0.04 mole) of 2-methyl-2-nitro-1,3-propanediol and 6.3 g. (0.08 mole) of pyridine in 50 cc. of dichloromethane was treated with 4.7 g. (0.04 mole) of thionyl chloride at room temperature. After 1 hr. the mixture was heated to refluxing, cooled, and washed with water. Removal of the dried solvent under reduced pressure gave 6.1 g. (83%) of product m.p. 106-8°. Recrystallization from 50% ethanol gave white needles, m.p. 109-10°, b.p. 234° (575 mm.); λNO_2 6.41 and 7.41, λ S = O 8.48, λ other 9.72, 10.11, and 11.83 in a KBr pellet.

Anal. Calcd. for $C_4H_7NO_5S$: C, 26.52; H, 3.89; N, 7.73. Found: C, 26.83; H, 4.12; N, 7.57.

Reactions with PPA

(a) Preparation of 1,3-dioxanes. A suspension of 0.02 mole of 1,3-diol and 0.60 g. (0.0066 mole) of trioxane in 15-20 g. PPA was heated to 70-95° in a small sublimation apparatus at 0.1 mm. The pure 5-substituted 1,3-dioxane derivatives with the properties given in Table I were obtained directly from the cold finger. (The yields were reduced to 35-45% when the trioxane was omitted.)

Alternatively, the reaction mixture was warmed on a steam bath for 1-3 hrs. in a round bottomed flask, extracted with three volumes of dichloromethane to which approx. an equal weight of crushed ice had been added, and the product isolated from the dried dichloromethane by evaporation. Crystallization from dichloromethane-petroleum ether or sublimation under reduced pressure gave samples identical to those described in Table I.

(b) Preparation of acroleins. A suspension of 0.05 mole of the 1,3-diol in 20-25 g. of PPA[13] containing about 0.2 g. of copper powder was stirred and warmed to 160° (oil bath temp.) during 1 hr. (When the temperature reached 100°, the pressure was reduced to 3-6 mm. sufficiently slowly to prevent excessive foaming.) At 3-6 mm. pressure, the temperature was maintained between 160-180° for another 2 hrs. while the crude product was collected in an acetone-Dry-Ice bath. The acrolein distillate also contained oxides of nitrogen, water, and gave infrared evidence for the presence of a carboxylic acid. The α-substituted acroleins were purified by drying with magnesium sulfate and distilling, in the presence of a little hydroquinone, through a 4" Vigreaux column. Semicarbazones were prepared by the addition of a hot solution of a 10-20% excess of semicarbazide hydrochloride in 25% ethanol to the crude product obtained directly from the reaction mixture.

In the cases noted below in which the substituted 1,3-dioxanes and trimethylene carbonates undergo a similar decomposition reaction, the experimental procedure was unchanged except to substitute an equivalent of the appropriate derivative for the 1,3-diol.

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(13) In several experiments, 10-15 g. of dry potassium acid sulfate was also included in the reaction medium. Less foaming occurred, less water accompanied the crude product, and the yields were approximately the same.

Acrolein was obtained in 33% yield from 2-nitro-1,3-propanediol; b.p. 45-47°/580 mm.; λ C = O 5.82, λ C = C 6.27μ in chloroform; semicarbazone, m.p. 168-170° (lit. m.p. 171°).[14]

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(14) J. U. Nef, Ann., 335, 211 (1904).

α-Methylacrolein was obtained in 52% yield from 2-methyl-2-nitro-1,3-propanediol, in 39% yield from 5-methyl-5-nitro-1,3-dioxane, and in 43% yield from 2-methyl-2-nitrotrimethylene carbonate; b.p. 60-62°/580 mm; n_D^{20} 1.4186; semicarbazone, m.p. 196-198° (lit. m.p. 197.5-198°).[15]

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(15) L. Shriner and A. G. Sharp, J. Am. Chem. Soc., 62, 2245 (1940).

α-Ethylacrolein was obtained in 34% yield from 2-ethyl-2-nitro-1,3-propanediol, 31% yield from 5-ethyl-5-nitro-1,3-dioxane, and in 35% yield from 2-ethyl-2-nitrotrimethylene carbonate; b.p. 71-74°/580 mm; λ C = O, 5.90; λ C = C 6.02μ in dichloromethane; semicarbazone, m.p. 189-192° (lit. m.p. 183-184°).[16]

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(16) F. G. Fischer, L. Ertel, and K. Lowenberg, Ber., 64B, 30 (1931).

Anal. Calcd. for $C_6H_{11}N_3O$: C, 51.04; H, 7.85; N, 29.77. Found: C, 51.03; H, 8.18; N, 29.30.

α-Chloroacrolein[17] was obtained in 12% yield from 2-chloro-2-nitro-1,3-propanediol, in 14% yield from 2-chloro-2-nitrotrimethylene carbonate and in 2-3% yield from 5-chloro-5-nitro-1,3-dioxane (over 75% of the dioxane derivative sublimed unchanged from the reaction mixture during a typical run); b.p. 35-40°/30 mm; λ C = O, 5.82, λ C = C 6.21μ in dichloromethane; slowly turns to a brown viscous oil.

Anal. Calcd. for C_3H_3ClO: C, 39.81; H, 3.34; Cl, 39.17. Found: C, 40.03; H, 3.44; Cl, 39.34.

Semicarbazone, m.p. 172-175° (dec.).

Anal. Calcd. for $C_4H_6ClN_3O$: C, 32.55; H, 4.10; Cl, 24.03; N, 28.48. Found:[18] C, 32.77; H, 4.18; Cl, 23.19; N, 28.98.

Attempted α-fluoroacrolein. The primary product from the treatment of 2-fluoro-2-nitro-1,3-propanediol with PPA was the stable 1,3-dioxane derivative. A carbonyl containing compound λ C = O 5.79, λ C = C 6.01 in dichloromethane, believed to be the fluoroacrolein was obtained in an estimated yield of 3-5%, but a solid derivative could not be obtained.

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[17] C. Moureu and P. Robin, Ann. Ch., [9] 15, 211 (1921).

[18] Crude sample. Recrystallization from 25% ethanol gave samples with variable and lower chlorine and higher nitrogen content.

Attempted α-chloromethylacrolein. The product from the treatment of 2-chloromethyl-2-nitro-1,3-propanediol with PPA showed absorptions in the carbonyl region of the infrared of nearly equal intensity at 5.81 and 5.89μ in dichloromethane and appeared free of carboxylic acid absorption in the 3μ region. Pure components could not be separated from this mixture by distillation.

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