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SYNTHESIS AND REACTIONS OF 2-NITRO-1-PROPEN-3-OL

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The synthesis of allyl alcohol containing a nitro group in the  $\gamma$ -position and isomerization of 1-nitro-2-propenyl oxide to 1-nitro-1-propen-3-ol were described previously [1].

The present paper is devoted to the synthesis and investigation of the properties of 2-nitro-1-propen-3-ol (I). We found that (I) is formed in the reaction of  $HNO_3$  with the 2-nitro-1,3-propanediol salt (II)

 $(HOCH_2)_2C=NO_2^{-Na^+} \xrightarrow{HNO_3} [(HOCH_2)_2C=NOOH]$   $(II) \xrightarrow{-H_2O} [(III)$   $HOCH_2C(NO_2)=CH_2 (HOCH_2)_2CHNO_2$  (I) (IV)

Apparently, the formation of (I) is the result of dehydration of nitronic acid (III), which occurs under the reaction conditions (-20 to  $-30^{\circ}$ C; ether or  $CH_2Cl_2$ ) together with isomerization to true nitro compound (IV). In our assumption, this reaction occurs via a step of intramolecular interaction of the mobile proton of the nitronic acid with the hydroxyl oxygen, forming unstable hydrate (IIIa), which decomposes with the recovery of (I)



To prevent O-nitration and oxidation [2], we decreased the reaction temperature and  $HNO_3$  concentration and showed that the formation of (I) in 50% yield occurs in the reaction of 40-45%  $HNO_3$  with (II) at -20 to -30°C.

The structure of (I) was confirmed by the IR and proton NMR spectra (see the experimental part) and also by chemical reactions. Halogenation of (I) at the double bond led to the formation of the corresponding dichloro and dibromo derivatives, and the hydroxyl group was then esterified by acetyl chloride and  $HNO_3$ .

The hydroxyl group in (I) can also be esterified by  $HNO_3$  with preservation of the double bond using an  $HNO_3$ -H<sub>2</sub>SO<sub>4</sub> nitrating mixture.

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TABLE 1

Compound	Bp, °C (p, torr), mp, °C	n <sup>20</sup> nD	Found/Calculated, %			Empirical
			С	н	N	formula
	· · ·		34.6	4.0	120	l
(I)	55-56(1)	1,481	34,95	4.66	$\frac{13.9}{13.59}$	C3H5NO3
(V)	66-67(2)	1,482	$\frac{24,1}{24,22}$	2.6	18,7	C+H/N+O+
			24,35	2.12	18,92	
(VIa)	63-64(1)	1,492	20,71	2,89	8,05	C3H5NO3Cl2
(VIb)	45-46		$\frac{13,9}{13,71}$	1.7	5,6	C3H3NO3Br2
			28.1	3.5	5,55 6,6	
(VIIa)	70-71(2)	1.463	27,80	3,27	6,48	$C_5H_7NO_4Cl_2$
(VIIb)	89-90(2)	1,516	<u>19,9</u> <u>19,69</u>	$\frac{2,5}{2,31}$	4,8	C5H7NO4Br3
(VIIIa)	61-62(1)	1,486	<u>16,8</u> 16,46	$\frac{1.7}{1.834}$	$\frac{13.1}{12.79}$	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub> Cl <sub>2</sub>
(VIIIb)	75-76(1)	1,531	$\frac{12.0}{11.70}$	1,6	9,3	C3H4N2O5Br2
(IX)	103-104	-	15.4	1.5	25,6	CsH5N7O14
(X)	48~49	-	<u>18,3</u> <u>18,03</u>	<u>1.50</u> <u>1.7</u> <u>1,51</u>	$\frac{25,35}{21.0}$	C5H5N5O10F2



Under the conditions of the Michael reaction, with excess primary polynitroalkane, (I) reacts similarly to 2-nitro-3-acetoxy-1-propene [3] with 2 moles of the polynitroalkane

 $\begin{aligned} \text{(I)} &+ 2\text{HC}(\text{NO}_2)_2\text{A} \rightarrow \text{AC}(\text{NO}_2)_2\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_2\text{A} \\ & (\text{IX}), \quad (\text{X}) \\ \text{A} &= \text{NO}_2(\text{IX}), \quad \text{F}(\text{X}). \end{aligned}$ 

The characteristics of the obtained substances are given in Table 1.

## EXPERIMENTAL

The sodium salt of 2-nitro-1,3-propanediol (II) was prepared by the method of [3].

The proton NMR spectra were recorded on a spectrometer developed in the Branch of the Institute of Chemical Physics of the Academy of Sciences of the USSR with an operating frequency of 294 MHz with a superconducting solenoid with respect to a TMS internal standard; the IR spectra were recorded on a UR-20 instrument.

<u>2-Nitro-1-propen-3-ol (1)</u>. To a suspension of 14.3 g (0.1 mole) of (II) in 150 ml of ether, 25 ml (0.2 mole) of 40% HNO<sub>3</sub> was added at -20 to -30°C with vigorous stirring for 10 min, and the whole was stirred for 30 min more at -25°C. The aqueous solution was extracted with ether (5 × 30 ml) and dried over MgSO<sub>4</sub> at 0-5°C, the ether was driven off, and after distillation 5.4 g (52%) of (I) was obtained. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1080 (-CO-), 1361, 1536 (C-NO<sub>2</sub>), 1660 (C=C), 3620-3125 (OH). Proton NMR spectrum ( $\delta$ , ppm): 4.60 singlet (2H, CH<sub>2</sub>), 5.0 broadened singlet (1H, OH), 6.08 singlet (1H, =CH<sub>2</sub>), 6.60 singlet (1H, =CH<sub>2</sub>).

<u>2-Nitro-3-nitroxy-1-propene (V)</u>. To a nitrating mixture of 10 ml of 100%  $HNO_3$  and 100 ml of 96%  $H_2SO_4$ , 4.1 g (0.04 mole) of (I) was added at -20 to -15°C with stirring. The mixture was stirred for 30 min at -10°C and poured into ice water, and the organic layer was separated, dissolved in  $CH_2Cl_2$ , washed with ice water, and dried over  $MgSO_4$ . The solvent was removed in vacuo. We obtained 4.6 g (78%) of (V), which was distilled in vacuo. IR

spectrum (v, cm<sup>-1</sup>): 1295, 1668 (ONO<sub>2</sub>), 1361, 1538 (CNO<sub>2</sub>). Proton NMR spectrum ( $\delta$ , ppm): 5.55 singlet (2H, CH<sub>2</sub>), 6.40 singlet (1H, =CH), 6.93 singlet (1H, =CH).

<u>2,3-Dichloro-2-nitro-1-propanol (VIa)</u>. Into a solution of 4.1 g (0.04 mole) of (I) in 30 ml of  $CH_2Cl_2$ , 3.5 g (0.05 mole) of  $Cl_2$  was passed at -15°C for 1.5 h. The reaction mixture was kept at 0-5°C for 12 h, the solvent was removed at decreased pressure, and the residue was distilled. We obtained 5.6 g (81%) of (VIa). Found: Cl 40.5%.  $C_{3}H_5NO_3Cl_2$ . Calculated: Cl 40.75%. IR spectrum (v, cm<sup>-1</sup>): 1097 (-CO), 1351, 1587 (CNO<sub>2</sub>), 3630-3240 (OH). Proton NMR spectrum ( $\delta$ , ppm): 4.304 (2H, CH<sub>2</sub>, spectrum of type AB,  $v_{AB} = 24.2$  Hz, J<sub>AB</sub> = 13 Hz), 4.302 (2H, CH<sub>2</sub>, spectrum of type AB,  $v_{AB} = 27.0$  Hz, J<sub>AB</sub> = 13 Hz), 4.30 singlet (1H, OH).

<u>2,3-Dibromo-2-nitro-1-propanol (VIb)</u>. To a solution of 4.1 g (0.04 mole) of (I) in 50 ml of water at 0-2°C was added 9.0 g (0.05 mole) of  $Br_2$ . The mixture was kept at 0-5°C for 12 h and extracted with ether (2 × 20 ml). After drying of the extract over MgSO<sub>4</sub>, the ether was driven off, and the crystalline residue was bicrystallized from CCl<sub>4</sub>. We obtained 9.1 g (86%) of (VIb). Found: Br 60.6%.  $C_3H_5NO_3Br_2$ . Calculated: Br 60.79%. IR spectrum (v, cm<sup>-1</sup>): 1098 (-CO-), 1348, 1567 (CNO<sub>2</sub>), 3600-3200 (OH).

<u>2,3-Dichloro- and 2,3-Dibromo-2-nitropropyl Acetates (VIIa and VIIb) (General Method)</u>. A solution of 0.05 mole of (VIa) or (VIb) in 15 ml of AcCl was heated with a reflux condenser at 75-80°C for 4 h and cooled, and the volatile components were removed at decreased pressure. The residue was distilled. We obtained 8.9 g (83%) of (VIIa). Found: Cl 32.5%.  $C_{5}H_{7}NO_{4}Cl_{2}$ . Calculated: Cl 32.83%. IR spectrum (v, cm<sup>-1</sup>): 1075 (-CO-), 1390, 1579 (CNO<sub>2</sub>), 1752 (C=0).

From (VIb), we obtained 12.4 g (81%) of (VIIb). Found: Br 52.3%. C<sub>5</sub>H<sub>7</sub>NO<sub>4</sub>Br<sub>2</sub>. Calculated: Br 52.41%. IR spectrum (v, cm<sup>-1</sup>): 1079 (-CO-), 1389, 1572 (CNO<sub>2</sub>), 1752 (C=O).

<u>2,3-Dichloro- and 2,3-Dibromo-2-nitropropyl Nitrates (VIIIa) and (VIIIb) (General</u> <u>Method)</u>. To a nitrating mixture of 10 ml of 96%  $H_2SO_4$  and 10 ml of 100%  $HNO_3$ , 0.03 mole of (VIIa) or (VIIb) was added in small portions at -5°C with vigorous stirring. After 15 min, the reaction mixture was poured into ice water, the organic layer was dissolved in 10 ml of  $CH_2Cl_2$ , and the extract was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed, and the residue was distilled in vacuo. We obtained 5.7 g (87%) of (VIIIa). Found: Cl 32.1%.  $C_3H_4N_2O_5Cl_2$ . Calculated: Cl 32.38%. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1088 (-CO-), 1298, 1670 (ONO<sub>2</sub>), 1349, 1580 (CNO<sub>2</sub>).

From (VIIb), we obtained 8.2 g (89%) of (VIIIb). Found: Br 51.6%.  $C_{3}H_{4}N_{2}O_{5}Br_{2}$ . Calculated: Br 51.90%. IR spectrum (v, cm<sup>-1</sup>): 1040 (-CO-), 1295, 1667 (ONO<sub>2</sub>), 1344, 1576 (CNO<sub>2</sub>).

Into a solution of 5.2 g (0.03 mole) of (V) in 25 ml of  $CH_2Cl_2$ , 0.9 liter (0.04 mole) of  $Cl_2$  was passed at 0°C for 1 h. The reaction mixture was kept at 0°C for 12 h, the solvent was removed, and the residue was distilled. We obtained 5.4 g (82%) of (VIIIa).

Under similar conditions, when  $Cl_2$  was replaced by 6.4 g (0.04 mole) of  $Br_2$ , 4.7 g (83%) of (VIIIb) was obtained.

<u>1,1,1,3,5,5,5-Heptanitropentane (IX)</u>. To an aqueous solution containing 3.1 g (0.03 mole) of (I), 10.6 g (0.07 mole) of trinitromethane was added at 0-5°C with stirring. The reaction mixture was heated to ~20°C, and the crystals were filtered. After bicrystallization from CCl<sub>4</sub>, 10.0 g (86%) of (IX) was obtained.

<u>1,5-Difluoro-1,1,3,5,5-pentanitropentane (X)</u>. A solution of 30.8 g (0.25 mole) of fluorodinitromethane in 20 ml of MeOH was added at 0-5°C with stirring to a solution of 10.3 g (0.1 mole) of (I) in 30 ml of MeOH. The reaction mixture was kept at  $\leq 10$ °C for 72 h, the highly volatile components were removed, and the residue was recrystallized from CHCl<sub>3</sub>. We obtained 18.7 g (56%) of (X). Found: F 11.6%.  $C_5H_5N_5O_{10}F_2$ . Calculated: F 11.39%.

## CONCLUSIONS

1. The reaction of the sodium salt of 2-nitro-1,3-propanediol with an aqueous nitric acid solution gave 2-nitro-1-propen-3-ol. Chlorination and bromination of this compound gave 2,3-dichloro- and 2,3-dibromo-2-nitropropanols.

2. The addition of trinitromethane and fluorodinitromethane to 2-nitro-1-propen-3-ol gave 1,1,1,3,5,5,5-heptanitro- and 1,5-difluoro-1,1,3,5,5-pentanitropentanes.

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N-(β-HYDROXYALKYL)DIAZENE-N'-OXIDES AND SOME OF THEIR

## TRANSFORMATIONS

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- The majority of known N-hydroxyalkyldiazene-N'-oxides (HADO's) are isolated from natural sources (see for example [1-3]), which is explained by the absence of general methods for their synthesis.

In this paper we have proposed two general methods for synthesis of HADO's. The first method consists of reaction of aromatic or aliphatic nitroso compounds (Ia, b) with N-( $\beta$ -hydroxyalkyl) hydroxylamine (II) [4]

 $\begin{array}{c} \text{RNO} + \text{HNCH}_2\text{CHCH}_2\text{OPh} \rightarrow \text{R-N} = \text{NCH}_2\text{CHCH}_2\text{OPh};\\ \textbf{(Ia, b)} \quad \begin{matrix} | & | & | & | & | \\ \text{OH} & \text{OH} & \text{OH} \\ \text{(II)} & \textbf{(IIIa, b)} \end{array}$   $\begin{array}{c} \text{PhOCH}_2\text{CHCH}_2\text{N} = \text{NCH}_2\text{CHCH}_2\text{OPh} \\ \hline \text{OH} & \text{OH} \\ \text{OH} & \text{OH} \\ \text{(IV)} \end{array}$   $R = \text{Ph} (a), Me_2\text{C}(\text{NO}_2) (b). \end{array}$ 

Contrary to literature data on the reaction of nitroso compounds with N-alkylhydroxysilamines, which usually gives mixtures of regioisomeric diazene oxides [5, 6], the reactions of (Ia, b) with (II) proceed regioselectively and lead to isomers with the hydroxyl group in the distant position relative to the "oxidized" nitrogen atom.

Upon reaction of (Ib) with (II), together with (IIIb) a compound is formed in comparable amounts which, according to elemental analysis and spectral characteristics may be a mixture of either cis-trans- or diasteroisomers of N,N'-bis(2-hydroxy-3-phenoxypropyl)diazene oxide (IV).

The IR spectrum of (IV) (Table 1) has absorption bands of the azoxy group at 1300 and 1510 cm<sup>-1</sup> and the mass spectrum of (IV) contains the molecular ion. Probably due to the long relaxation times of nitrogen atoms no signals were detected in the <sup>15</sup>N NMR spectrum and the <sup>14</sup>N NMR spectrum has one signal with a half-height width  $(\Delta v_{\frac{1}{2}})$  of  $\sim$ 1400 Hz centered at -45.5 ppm (from MeNO<sub>2</sub>), i.e., in the region of chemical shifts characteristic of the oxidized nitrogen atom of diazene oxides. The <sup>13</sup>C NMR spectrum (IV) contains four signals which belong to OCH, CHOH, and NCH<sub>2</sub> groups and pairs of Cipso and Cpara signals. This spectrum does not contradict the assumption of a mixture of either cis-trans- or diastereoisomers. The PMR spectrum of (IV) contains a great number of multiplets the most intense of which change gradually in ratio upon boiling of (IV) in toluene (without decomposition), achieving an equilibrium state.

Formation of (IV) can be explained by oxidation of some of (II) by pseudonitrol (Ib) to 2-hydroxy-l-phenoxy-3-nitrosopropane and condensation of the latter with starting (II)

 $\begin{array}{c} \text{HNCH}_{2}\text{CHCH}_{2}\text{OPh} \xrightarrow{\text{(Ib)}} \begin{bmatrix} \text{O}=\text{NCH}_{2}\text{CHCH}_{2}\text{OPh} \\ \downarrow \\ \text{OH} & \text{OH} \end{bmatrix} \xrightarrow{\text{(II)}} (\text{IV}) \end{array}$ 

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