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REACTIONS OF NITROPARAFFINS. PART XCVII *. NOVEL FEATURES OF THE REACTION OF 2,2-DINITROPROPANEDIOL-1,3 WITH PRIMARY AMINES

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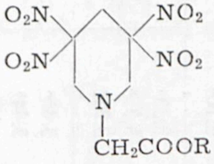
W reakcji 2,2-dwunitropropanodiolu-1,3 z chlorowodorkami amin pierwszorzędowych w obecności octanu sodu i buforu octanowego o pH 4 tworzy się mieszanina zawierająca N-alkilowe pochodne 2,2-dwunitroetyloaminy i — zależnie od rodzaju aminy — pochodne 5,5-dwunitrotetrahydro-1,3-oksazyny lub 5,5-dwunitroheksahydropirymidyny.

Реакция 2,2-динитропропандиола-1,3 с гидрохлоридами первичных аминов в присутствии ацетата натрия и ацетатного буфера (pH-4) ведет к образованию смеси, содержащей N-алкильные производные 2,2-динитроэтиламина и, в зависимости от применяемого амина, производные 5,5-динитротетрагидро-1,3-оксазина или 5,5-динитрогексагидропиримидина.

When 2,2-dinitropropanediol-1,3 reacted with primary amines (in form of their hydrochlorides) in presence of sodium acetate and the acetate buffer of pH 4, N-alkyl derivatives of 2,2-dinitroethylamine resulted. They were accompanied by derivatives of 5,5-dinitrotetrahydro-1,3--oxazine and or 5,5-dinitrohexahydropyrimidine, depending on the amine used.

Feuer, Bachman and May¹⁾ have shown that 2,2-dinitropropanediol (**1**) reacted with aminoacetic acid or hydrochloride of its ethyl ester in aqueous solution at 70°C to yield 3,3,5,5-tetranitropiperidine derivatives (**2**). The highest yield (70%) was obtained at pH 4.



2

R = H, C_2H_5

In our present work we have examined the reaction of 2,2-dinitropropanediol-1,3 (**1**) with hydrochlorides of primary amines: methyl-, ethyl-, isopropyl- and *tert*-butylamine. When using hydrochloride of the latter, we found that the reaction did not occur and unreacted **1** was recovered. We found, eventually, that the diol **1** (1 mole) reacted at room temperature with hydrochlorides of the amines (2 mole) in presence

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* Part XCVI: Piotrowska H., Urbański T., Wołochowicz I., *Bull. Acad. Polon. Sci., sér. sci. chim.*, **19**, 591 (1971).

Table 1

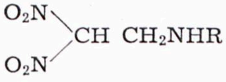
Chemical shifts (δ) of compounds **4** and **5**

R	Method	**5**		**4**			
		$N-CH_2-N$	$N-CH_2-C\begin{smallmatrix}NO_2\\NO_2\end{smallmatrix}-$	$O-CH_2-N$	$N-CH_2-C\begin{smallmatrix}NO_2\\NO_2\end{smallmatrix}-$	$O-CH_2-C\begin{smallmatrix}NO_2\\NO_2\end{smallmatrix}-$	
CH_3	A*	3.18^{s}	3.44^{s}	—	—	—	2.35^{s}
	B*	3.16^{s}	3.44^{s}	—	—	—	2.35^{s}
	C	3.16^{s}	3.46^{s}	—	—	—	2.35^{s}
C_2H_5	A	3.33^{s}	3.58^{s}	4.00^{s}	4.39^{s}	4.59^{s}	1.09^{t} 2.57^{q}
	B	3.35^{s}	3.57^{s}	3.99^{s}	4.39^{s}	4.58^{s}	1.08^{t} 2.57^{q}
	C	3.35^{s}	3.55^{s}	4.00^{s}	4.39^{s}	4.59^{s}	1.07^{t} 2.55^{q}
i-C_3H_7	A	3.46^{s}	3.59^{s}	3.90^{s}	4.41^{s}	4.58^{s}	1.09^{d} 2.98^{f}
	B	3.44^{s}	3.57^{s}	3.90^{s}	4.41^{s}	4.56^{s}	1.08^{d} 2.98^{f}
	C	3.40^{s}	3.54^{s}	3.85^{s}	4.35^{s}	4.52^{s}	1.08^{d} 2.94^{f}
t-C_4H_9	A*	—	—	3.72^{s}	4.28^{s}	4.35^{s}	1.14^{s}
	B*	3.48^{s}	3.52^{s}	3.75^{s}	4.29^{s}	4.35^{s}	1.12^{s}
	C	3.53^{s}	3.63^{s}	3.87^{s}	4.43^{s}	4.53^{s}	1.09^{s}
CH_2COOCH_3	A	3.85^{s}	3.99^{s}	—	—	—	3.52^{s} 3.74^{s}
$CH_2COOC_2H_5$	A**	3.80^{s}	3.94^{s}	—	—	—	3.46^{s} 1.31^{t} 4.15^{q}

s — singlet, d — doublet, t — triplet, q — quartet, f — multiplet. Spectra marked *were taken in carbon disulphide, marked ** — in carbon tetrachloride, others in $CHCl_3$. Tetramethylsilan was used as internal standard. Method A: reaction of **1** with hydrochlorides of amines in presence of sodium acetate in the acetate buffer solution. Method B: reaction of **3** with formaldehyde in aqueous acetate buffer of pH 4. Method C: reaction of **3** with formaldehyde in water.

of sodium acetate (2 mole) when dissolved in an acetate buffer of pH 4 (0.2 mole) to keep pH within the limits 4—5.

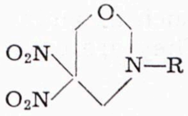
We did not obtain derivatives of piperidine of the type **2**, but three N-derivatives of: 2,2-dinitroethylamine (**3**), 5,5-dinitrotetrahydro-1,3-oxazine (**4**), and 5,5-dinitrohexahydropyrimidine (**5**).



$$(O_2N)_2CH\,CH_2NHR$$

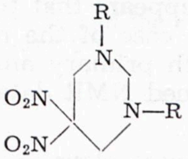
3

$R = CH_3$, C_2H_5
i-C_3H_7, t-C_4H_9



4

$R = C_2H_5$,
i-C_3H_7, t-C_4H_9



5

$R = CH_3$, C_2H_5
i-C_3H_7

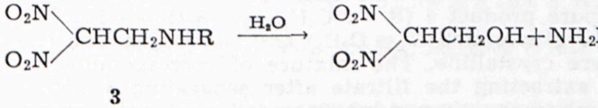
The yield of different products depended on different amines used. Thus all amines gave **3**. Methylamine hydrochloride produced **5** but did not furnish **4**. Ethyl- and *iso*-propylamine gave both: **4** and **5**. *tert*-Butylamine yielded **4** but did not yield **5**. All three compounds: **3**, **4**, and **5** have already been prepared and described in our former papers [2,3].

Products **4** and **5** were identified from the NMR spectra (Table 1).

We also examined the products when R = H, by reacting **1** with ammonium chloride. The only product was **3** (R = H) — i.e. 2,2-dinitroethylamine previously described by Kamlet and Dacons [4], and obtained in a different way.

We previously established [2] that amines **3** were intermediates in the formation of hexahydropyrimidines (**5**). We thought that they could also be suitable starting substances to obtain tetrahydro-1,3-oxazines (**4**). Subsequently we reacted **3** with excess of formaldehyde in an aqueous solution and acetate buffer of pH 4. The products were practically identical with those described above. Thus when $R = CH_3$, only **5** was formed, when $R = C_2H_5$ or i-C_3H_7, both products — **4** and **5** — were obtained. With $R = t$-C_4H_9 the main product was **4** and only a small amount of **5** was produced. As previously the identification of the products was done by means of an analysis of NMR spectra (Table 1).

Formation of **5** from amines **3** can be explained by hydrolysis of **3** yielding one mole of amine NH_2R required to form **5**, i.e.:



$$(O_2N)_2CHCH_2NHR \xrightarrow{H_2O} (O_2N)_2CHCH_2OH + NH_2R$$

3

$$3 + NH_2R + CH_2O \longrightarrow 5 + H_2O$$

The reaction was particularly favoured when R was methyl and this was probably the consequence of the high solubility of **3** ($R = CH_3$).

Continuing our line of research we also examined the reaction of diol **1** with hydrochlorides of methyl and ethyl esters of aminoacetic acid under the same experimental conditions, i.e. in the acetate buffer in presence of sodium acetate. We found that the reaction did not differ essentially from that described above.

When methyl ester of aminoacetic acid was used we isolated **5** ($R = CH_2COOCH_3$), but did not succeed in isolating **3** ($R = CH_2COOCH_3$)

probably due to its good solubility in the reaction solution. When ethyl ester of aminoacetic acid was used, we isolated both: **5** ($R = CH_2COOC_2H_5$) and **3** ($R = CH_2COOC_2H_5$). The products were identified by examining their NMR spectra (Table 1). Compound **3** ($R = CH_2COOC_2H_5$) has previously been described in the literature [1)].

It appears that the formation of derivatives of piperidine (**2**) is a particular case of the reaction of condensation of 2,2-dinitropropanediol-1,3 (**1**) with primary amines — such as aminoacids and their esters. We also examined NMR data of **2**. They are collected in Table 2.

Table 2

Chemical shifts (δ) of compounds *2*

R	$N{-}CH_2{-}CO$	$N{-}CH_2{-}C(NO_2)_2{-}$	$-C(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}$	
H*	3.79^s	4.19^s	4.33^s	
CH_3*	3.82^s	4.17^s	4.32^s	3.69^s
CH_3	3.63^s	3.93^s	3.97^s	3.70^s
C_2H_5	3.60^s	3.93^s	3.97^s	1.25^t 4.11^q

s — singlet, t — triplet, q — quartet.
Spectra marked * were taken in $(CD_3)_2CO$, others in $CDCl_3$. Tetramethylsilan was used as internal standard.

EXPERIMENTAL

Reaction of 2,2-dinitropropanediol-1,3 (1) with hydrochlorides of amines

Sodium acetate (10.5 g, 0.128 mole), **1** (10.5 g, 0.063 mole) and amine hydrochloride (0.128 mole) were dissolved in the acetate buffer of pH 4 (35 cm³, 0.2 mole). The solution was left at room temperature for 24 hours. The crystalline precipitate of **3** accompanied by **5** when $R = CH_3$ or by **4** when $R = t\text{-}C_4H_9$ was filtered off and washed with water. By subsequent washing with ethanol and ether products **4** ($R = t\text{-}C_4H_9$) and **5** ($R = CH_3$) were removed from **3**. Evaporation of ethanol and ether furnished pure product **4** ($R = t\text{-}C_4H_9$) and **5** ($R = CH_3$).

In the case of ethylamine ($R = C_2H_5$) and isopropylamine ($R = i\text{-}C_3H_7$) only the compounds **3** were crystalline. The mixture of corresponding compounds **4** and **5** was isolated by extracting the filtrate after separating **3** with ether. The extract was dried over anh. magnesium sulphate and the solvent evaporated. The resulting liquid mixture of **4** and **5** ($R = C_2H_5$ and $i\text{-}C_3H_7$) was identified by means of NMR spectra. The yields of **3** were: $R = CH_3$ 37%, $R = C_2H_5$ 46%, $R = i\text{-}C_3H_7$ 39%, $R = t\text{-}C_4H_9$ 33%. The yields of **4** and **5** were: compound **4**: $R = t\text{-}C_4H_9$ 25%, compound **5**: $R = CH_3$ 35%.

Reaction of 2,2-dinitropropanediol-1,3 (1) with ammonium chloride

Sodium acetate (6.0 g, 0.073 mole), **1** (6.0 g, 0.036 mole), ammonium chloride (3.9 g, 0.073 mole) were dissolved in the acetate buffer of pH 4 (20 cm³, 0.2 mole) and left at room temperature for 18 hours. Product **3** ($R = H$) was precipitated, washed with water, ethanol and acetone. 2,2-Dinitroethylamine (**3**, $R = H$), m.p. 120°C decomp., was obtained in the yield 1.1 g (0.0081 mole, 22%).

Reaction of 2,2-dinitropropanediol-1,3 (1) with hydrochlorides of esters of aminoacetic acid

Sodium acetate (6.0 g, 0.073 mole), **1** (6.0 g, 0.036 mole) and hydrochloride of methyl or ethyl aminoacetate (0.073 mole) were dissolved in acetate buffer of pH 4 (20.0 cm^3, 0.2 mole) and left for 18 hours at room temperature. When methyl ester of aminoacetic acid was used product **5** ($R = CH_2COOCH_3$) was extracted with ether, the solution dried over magnesium sulphate, ether was evaporated and the crystalline product resulted 2.6 g (0.0081 mole, 22% yield), m.p. 63.5—65.5°C.

Analysis:

For $C_{10}H_{16}N_4O_8$ — Calcd.: 37.5% C, 5.0% H, 17.5% N;
found: 37.7% C, 5.2% H, 17.6% N.

When ethyl ester of aminoacetic acid was used, the precipitate composed of **3** and **5** ($R = CH_2COOC_2H_5$) was washed with ether to remove oily product **5**. The residue from washing was crystalline **3** ($R = CH_2COOC_2H_5$) with the yield 1.2 g (0.0054 mole, 15%), m.p. 107—108°C.

Analysis:

For $C_6H_{11}N_3O_6$ — Calcd.: 32.6% C, 5.0% H, 19.0% N;
found: 32.7% C, 5.2% H, 19.2% N.

The solution of **5** ($R = CH_2COOC_2H_5$) in ether was evaporated and the oily product **5** was identified on the basis of its NMR spectrum.

Reaction of N-alkyl derivatives of 2,2-dinitroethylamine (3) with formaldehyde

Compound **3** (0.0225 mole) was suspended in water (35 cm^3) or acetate buffer of pH 4 (0.2 mole), aqueous 36% formaldehyde solution (18.8 cm^3, 0.225 mole) was added and left for 3 days. The product **5** ($R = CH_3$) or **4** (t-C_4H_9) contaminated with ca. 15% of **5** ($R = t$-C_4H_9) was collected, washed with water and dried in a desiccator over phosphorous pentoxide. A particularly high yield (31%) and purity of the substance was obtained when $R = CH_3$. When R was C_2H_5, i-C_3H_7 the liquid mixture of the products **4** and **5** was extracted with ether, the solution was dried over magnesium sulphate, the solvent evaporated and the components of the liquid mixture of the products were identified with NMR spectroscopy.

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REAKCJE NITROPARAFIN. XCVII. NOWE SPOSTRZEŻENIA W REAKCJI 2,2-DWUNITROPROPANODIOLU-1,3 Z AMINAMI PIERWSZORZĘDOWYMI

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Kontynuując prace nad reakcją 2,2-dwunitropropanediolu-1,3 (**1**) z aminami zbadaliśmy reakcję **1** z chlorowodorkami amin pierwszorzędowych w obecności równomolowej ilości octanu sodu i buforu octanowego o pH 4. Stwierdziliśmy, że pow-

stały wówczas trzy rodzaje produktów: N-alkilowe pochodne 2,2-dwunitroetyloaminy (**3**), 5,5-dwunitrotetrahydro-1,3-oksazyny (**4**) i 5,5-dwunitroheksahydropirymidyny (**5**). Związki **3** powstawały we wszystkich przypadkach. Po użyciu metyloaminy powstawał związek **5** ($R = CH_3$), a po użyciu *t*-butyloaminy — związek **4** ($R = t\text{-}C_4H_9$). Gdy do reakcji stosowano etyloaminę i izopropyloaminę powstawała obok **3** mieszanina odpowiednich pochodnych **4** i **5**. Wszystkie te związki opisaliśmy poprzednio [2,3].

Wychodząc z chlorowodorków aminooctanu metylu i etylu otrzymaliśmy w opisanych wyżej warunkach pochodne **5** ($R = CH_2COOCH_3$ lub $CH_2COOC_2H_5$). Gdy zamiast chlorowodorku aminy użyliśmy chlorku amonu produktem reakcji był związek **3** ($R = H$).

Takie same produkty otrzymaliśmy działając na **3** nadmiarem formaldehydu w obecności buforu octanowego o pH 4. Powstawanie w tym przypadku pochodnych **5** jako jednego z produktów reakcji można wytłumaczyć częściową hydrolizą związków **3** w środowisku reakcji z uwolnieniem odpowiedniej aminy, potrzebnej do zamknięcia pierścienia heksahydropirymidynowego.