BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. IV, No. 4, 1956

CHEMISTRY

On the Synthesis and Degradation of Certain Derivatives of Tetrahydro-1,3-Oxazine. II

by

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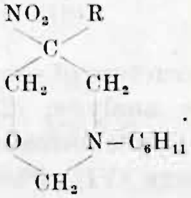
Communicated by T. URBAŃSKI at the meeting of November 28, 1955

In the previous paper [1] a number of homologous 5-nitro-5-alkyl-3-benzyltetrahydro-1,3-oxazines were prepared, their hydrolysis and degradation being studied.

In the present work, by using nitroparaffins from nitroethane to 1-nitro-*n*-butane and formaldehyde, and cyclohexylamine, a number of new compounds of the general formula (I) were obtained:



(I) (a) $R = CH_3$
(b) $R = C_2H_5$
(c) $R = C_3H_7$

all of them were 5-nitro-5-alkyl-3-cyclohexyl-tetrahydro-1,3-oxazines.

Compounds (Ia), (Ib) and (Ic) were respectively prepared from nitroethane, 1-nitropropane and 1-nitro-*n*-butane.

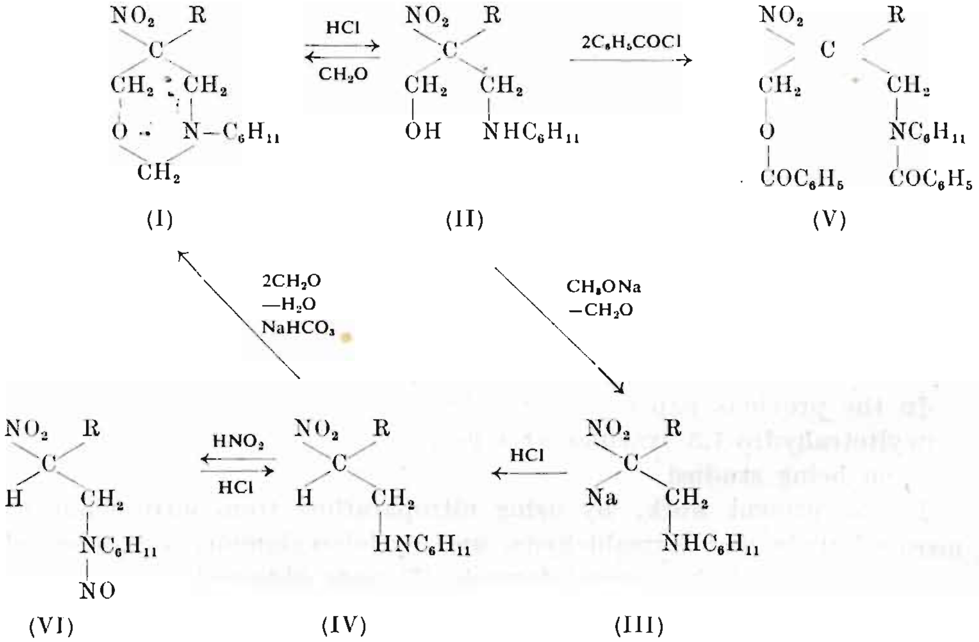
Compound (Ia) had previously been obtained and described by Senkus [2].

All compounds (Ia, b, c) were subjected to degradation in much the same way as previously described [1].

(1) By heating with hydrochloric acid diluted with alcohol to 1.5% HCl, hydrolysis occurred with the splitting off of a molecule of formaldehyde. The open chain aminoalcohols (II) were obtained in this way. Warming of compounds (II) with formaldehyde yielded the starting ring compounds (I).

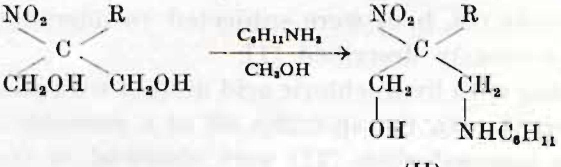
(2) By treating the aminoalcohols (II) with sodium methoxyde in methanolic solution, a mol. of formaldehyde was cloven off and sodium

salts of aminonitrocompounds (III) resulted. These, upon action of alcoholic HCl, followed by evaporation of the solvent under reduced pressure, were transformed into hydrochlorides of (IV). The hydrochlorides of (IV) yielded, when warmed with formaldehyde in the presence of sodium-hydrogen carbonate, the initial substances (I).



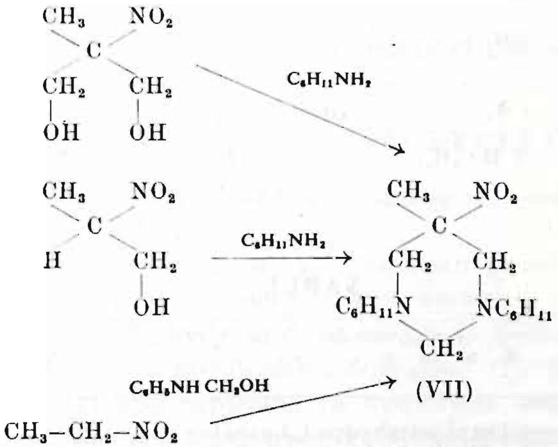
The structure of compounds (IIa, b, c) and (IVa, b, c) was established: (1) by analysis; (2) by the formation of dibenzoylderivatives (V) of (II); (3) by the formation of crystalline N-nitrozoderivatives (VI) of (IV). The products (VI), when warmed with hydrochloric acid, again yielded the amines (IV).

The products (IIb) and (IIc) were also prepared in a direct way on acting with cyclohexylamine on the corresponding diols: 2-ethyl-2-nitropropane-1,3-diol (i. e. $R=C_2H_5$) and 2-propyl-2-nitropropane-1,3-diol (i. e. $R=C_3H_7$), respectively, at room temperature.



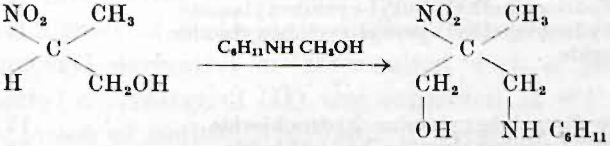
(II)

When $R=CH_3$, i. e. the derivative of nitroethane, was used, the reaction was very vigorous, a partial decomposition occurred, and a derivative of hexahydropyrimidine (VII) was formed. The dilution of reagents with ether or alcohol did not alter the trend of the reaction. When the temperature was kept near 0°, the same product (VII) was obtained. The same product (VII) resulted, when the monohydric alcohol deriving from nitroethane (i. e. 2-nitro-propan-1-ol) reacted with cyclohexylamine at room temperature, or nitroethane reacted with N-hydroxymethylcyclohexylamine in the same conditions:



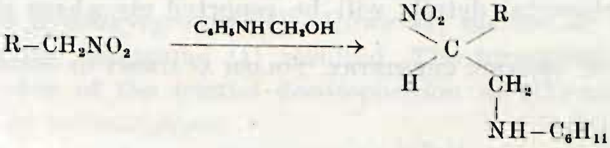
(VII)

It was, however, found that (IIa), i. e. $R = CH_3$, could be obtained by acting on 2-nitropropan-1-ol with N-hydroxymethylcyclohexylamine:



(IIa)

The action of N-hydroxymethylcyclohexylamine on 1-nitropropane and 1-nitrobutane led to the formation, respectively, of the compounds (IVb, $R = C_2H_5$) and (IVc, $R = C_3H_7$):

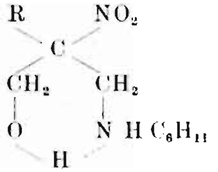


(IV)

Thus, the behaviour of nitroethane and its hydroxymethylderivatives differs from that of 1-nitropropane and 1-nitrobutane.

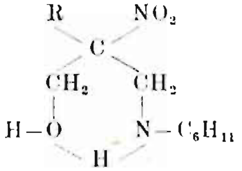
Appended is a list of the new compounds described in the present paper and the known compound (Ia), together with their melting points.

Attention is directed to the fact that the melting points of the oxazine derivatives (I) are lower than the m. pts. of the open chain aminoalcohols (II). This we ascribe to the existence of intramolecular hydrogen bonds, as previously suggested by one of us [3], [4]. In addition to the hydrogen bonds between the nitrogroup and hydrogen atoms of hydroxylic or aminogroups, hydrogen bonds between OH and NH C_6H_{11} groups can also be postulated, i. e. the structures (A) and (B):



(A)

or



(B)

TABLE

Name	Number	m. p.
5-nitro-5-methyl-3-cyclohexyl-tetrahydro-1,3-oxazine	I a	50-51°
5-nitro-5-ethyl-3-cyclohexyl-tetrahydro-1,3-oxazine	I b	59-60°
5-nitro-5-propyl-3-cyclohexyl-tetrahydro-1,3-oxazine	I c	69-70°
I a hydrochloride		182° (d)
I b „		187° (d)
I c „		179° (d)
N-(-2-nitro-2-hydroxymethyl)-propyl-cyclohexylamine	II a	68-70°
N-(-2-nitro-2-hydroxymethyl)-butyl-cyclohexylamine	II b	77-79°
N-(-2-nitro-2-hydroxymethyl)-pentyl-cyclohexylamine	II c	79-81°
II a hydrochloride		169° (d)
II b „		170° (d)
II c „		167° (d)
N-(2-nitro-propyl)-cyclohexylamine hydrochloride	IV a	148° (d)
N-(2-nitro-butyl)-cyclohexylamine hydrochloride	IV b	160° (d)
N-(2-nitro-pentyl)-cyclohexylamine hydrochloride	IV c	162° (d)
N-nitrosocompound derivatives of IV a	VI a	61° (d)
„ „ „ „ IV b	VI b	95° (d)
„ „ „ „ IV c	VI c	97° (d)
N, O-dibenzoyl derivatives of II a	V a	106-107°
„ „ „ „ II b	V b	101-102°
„ „ „ „ II c	V c	140-142°

The experimental details will be reported elsewhere [5].

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[1] D. Gürne, T. Urbański, *On the synthesis and degradation of some derivatives of tetrahydro-1,3-oxazine*, Bull. Acad. Polon. Sci., Cl. III, **3** (1955), 175.

[2] M. Senkus, J. Am. Chem. Soc. **72** (1950), 2967.

[3] T. Urbański, *On the structure of some aliphatic nitrocompounds*, Bull. Acad. Polon. Sci., Cl. III, **1** (1953), 239.

[4] T. Urbański, D. Ciecierska, Roczniki Chem. **29** (1955), 11.

[5] D. Gürne, T. Urbański, Roczniki Chem. (in the press).