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On Reaction of 1-Nitromethylcyclohexanol and Its Halogen Derivatives with Formaldehyde and Acetaldehyde

by

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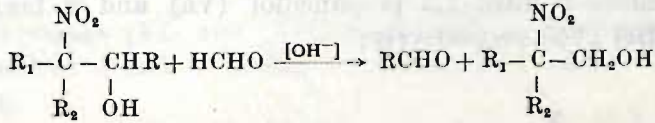
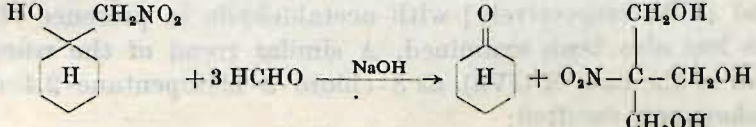
It is a well known fact, that certain secondary nitroalcohols, formed from nitroparaffins and homologues of formaldehyde can readily be subjected to a cleavage under action of formaldehyde in alkaline medium. As a result, the aliphatic aldehyde (homologue of formaldehyde) and a primary nitroalcohol, deriving from nitroparaffin and formaldehyde are formed [1], [2]:



In the case of R_1 and/or $R_2=H$, i. e. in the case of the presence of at least one active hydrogen atom, the mechanism of the reaction is probably such that formaldehyde is added in the first stage, as a result of a kind of aldolisation. Then, the molecule of aldehyde RCHO is split off, and formaldehyde is added in its place.

In the present paper the action of formaldehyde on 1-nitromethylcyclohexanol (I), the known tertiary alcohol, formed from cyclohexanon and nitromethane (according to the literature) in presence of sodium hydroxide in aqueous methanol [3] has been studied. It has now been found, that the compound (I) when reacting with an excess of formaldehyde (3 molecules to 1 molecule or (I)), in the presence of sodium hydroxide at room-temperature yielded tri-(hydroxymethyl)-nitromethane (III), and cyclohexanon (II) was split off:

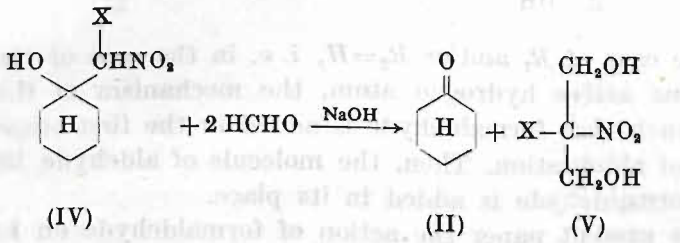


(I) (II) (III)

The products were separated by fractional extraction with ether. In the first instance cyclohexanon was extracted and identified as 2,4-dinitrophenylhydrazone. Next tri-(hydroxymethyl)-nitromethane (III) (the yield c. 79.5% of theoretical) was extracted with ether. The product (III) (m. p. 153-155°) was transformed into 5-nitro-5-hydroxymethyl-2-phenyl-1,3-dioxane, which was found to be identical with the product described in one of the former papers [4].

Two new derivatives of (I) have also been prepared: 1-chloronitromethylcyclohexanol (IVa) and 1-bromonitromethylcyclohexanol (IVb) by acting with chlorine or bromine on the sodium salt of 1-nitromethylcyclohexanol (a method analogous to that used by Schmidt and Wilkendorf [5]). We expected the halogen derivatives of (I) to be more stable than the mother substance (I). This assumption was based on the fact described in one of our earlier papers [2], where the presence of a halogen atom attached to carbon bonded with a nitrogroup was found to increase the stability of the nitroparaffin. It was possible to obtain mixed nitrodiols by reacting with formaldehyde.

It has now been found that in the case of the halogen derivatives of the tertiary alcohol (I), (i. e. of compounds (IV)) no change of reactivity occurred and both halogenetad products reacted with formaldehyde in presence of sodium hydroxide to yield cyclohexanone (II) as well as 2-chloro-2-nitro-1,3-propanediol (Va) and 2-bromo-2-nitro-1,3-propanediol (Vb) respectively:



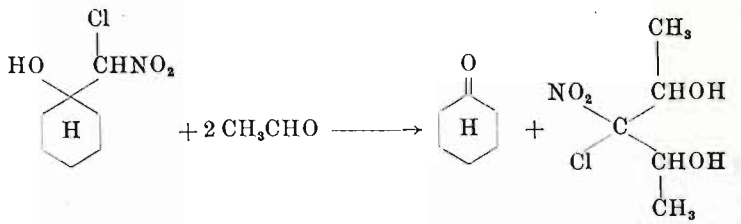
(IV) (II) (V)

(IVa) X=Cl (Va) X=Cl

(IVb) X=Br (Vb) X=Br

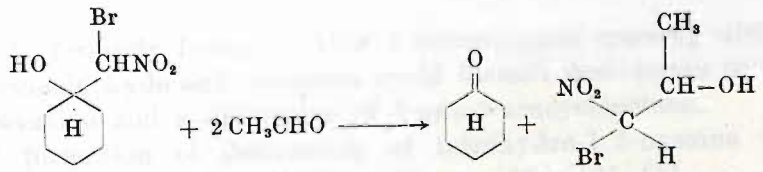
The compounds (Va) and (Vb) are identical with the compounds obtained formerly in another way [6], [7].

The reaction of 1-chloro- and 1-bromonitromethylcyclohexanol [(IVa) and (IVb) respectively] with acetaldehyde in presence of sodium hydroxide has also been examined. A similar trend of the reaction has been found in the case of (IVa), as 3-chloro-3-nitropentane-2,4-diol (VI) and cyclohexanon resulted:



(IVa) (II) (VI)

On the contrary, when 3-bromo-3-nitropentane-2,4-diol (IVb) was used, only a monohydric alcohol, 1-bromo-1-nitro-2-propanol (VII), and cyclohexanone were formed:



(IVb) (II) (VII)

The compounds (VI) and (VII) are known in literature [1], [8].

Experimental details referring to the present paper will be given elsewhere [9].

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On the contrary, when [illegible] (IX) [illegible] were formed

Compounds [illegible] (XI) and (XII) [illegible]

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[1] Z. Eckstein, T. Urbański, Roczniki Chem. [illegible]
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