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# REDUCTIVE ELIMINATION OF A TERTIARY NITRO GROUP IN 5-NITRO--1,3-DIOXANES[1]

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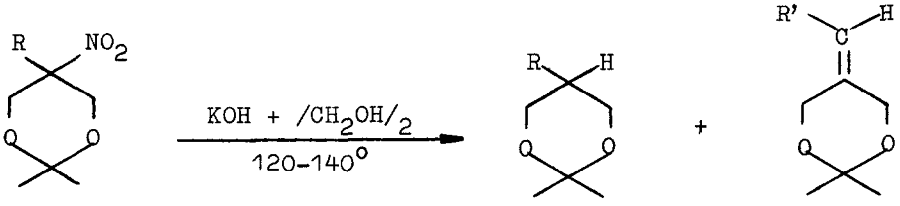
The recent paper by N. Kornblum and associates[2] prompts us to report our own work on breaking the C-N bond in 5-nitro-1,3-dioxanes /1/[3] and replacing the tertiary nitro group by hydrogen atom to yield 1,3-dioxanes /2/.

Ethylene glycol solution of potassium hydroxide was used as the reducing agent, viz.:



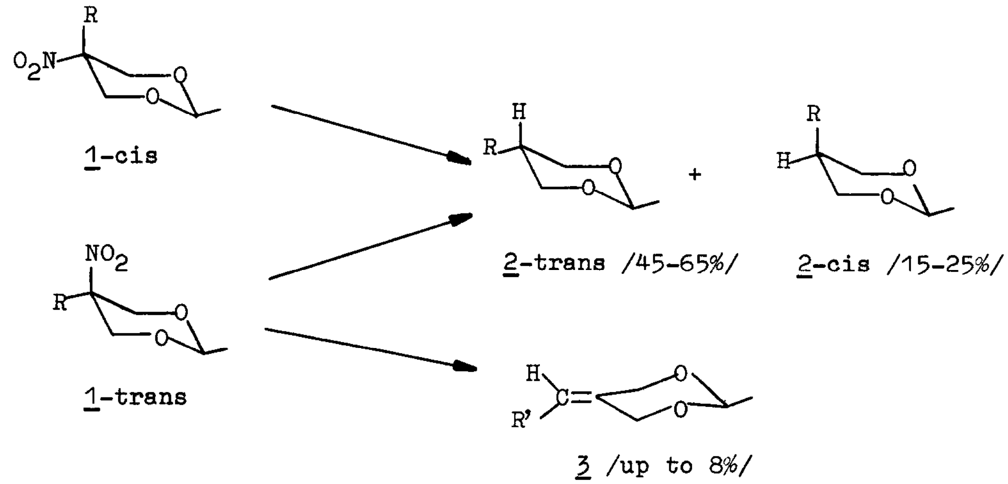
1 2 3

$R=CH_3$, $C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$     /50-55%/     /up to 8%/

$R'=H$, $CH_3$, $C_2H_5$, $n\text{-}C_3H_7$

A certain amount of 1,3-dioxanes /3/ with an exo-alkenyl group in position 5 were formed through the elimination of nitrous acid. /Ethylene glycol in alkaline medium as reducing agent has been described by Tadros et al.[4] and Kleinfelter[5]. Toivonen et al.[6] using diethylene glycol or glycerol and KOH reduced the secondary nitro group of 2- and 3-nitrobornanes to bornane/.

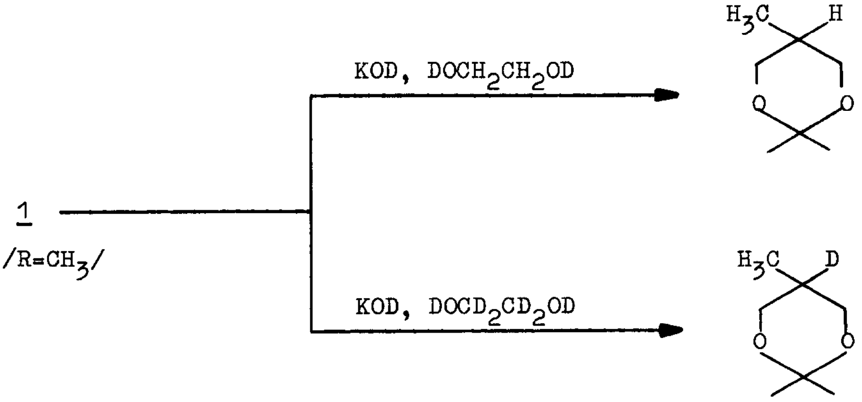
We examined the influence of stereochemistry of /1/ on the result of the reaction and to that respect we subjected cis- and trans-dioxanes /1/[3] to the reaction of reductive elimination:



The ratio $\frac{\text{2-trans}}{\text{2-cis}}$ was 2-3.5.

The products were distilled from the reaction solution as azeotrops with water and ethylene glycol, the components were separated by gas chromatography. The compounds 2-cis, 2-trans and 3 were identified by comparing their spectroscopic features /especially $^1$H-NMR/ with the literature data [7,8].

By using deuterated potassium hydroxide and O-deuterated or per-deuterated ethylene glycol we were able to find that hydrogen in position 5 /replacing the nitro group/ takes its origin from $CH_2$ of the ethylene glycol:



Thus the overall reaction can be written:

$$\underline{1} + KOH + /CH_2OH/_2 \longrightarrow \underline{2} + KNO_2 + H_2O + \begin{array}{l}CHO\\|\\CH_2OH\end{array}$$

β-Hydroxyacetaldehyde could not be isolated from the products, neither as such or as derivatives /e.g. dinitrophenylhydrazone/ owing to its fast polymerization in alkaline medium at high temperature. We succeeded however establishing the oxidation of the primary alcoholic group to an aldehyde by replacing ethylene glycol with benzyl alcohol. In the reaction mixture were detected: benzaldehyde and benzoic acid, the latter being formed through the Cannizzaro reaction.

We rationalized a radical anion chain mechanism of the reaction much on the same line as suggested by Kornblum in his reaction[2]. However in addition to the main reaction we also registered the presence of a nitroxide radical formed in the course of a side reaction.

The trend of the reaction was followed in an ESR spectrometer which gave signals of unpaired electron localised at the nitro group of /$\underline{1}$/. The hyperfine coupling constant of the triplet has the value of 2.54 mT /typical for the nitro group in aliphatic compounds[9]/. During the reaction we observed that the spectrum consisted of a combination of two triplets with the hyperfine coupling constants 2.54 mT and 1.51 mT /typical for the nitroso group in aliphatic compounds[10]/. The latter was split into triplet and doublets with a hyperfine coupling constant 0.30 mT. At the end of the reaction the triplet 2.54 mT disappeared and only the 1.51 mT triplet was left.

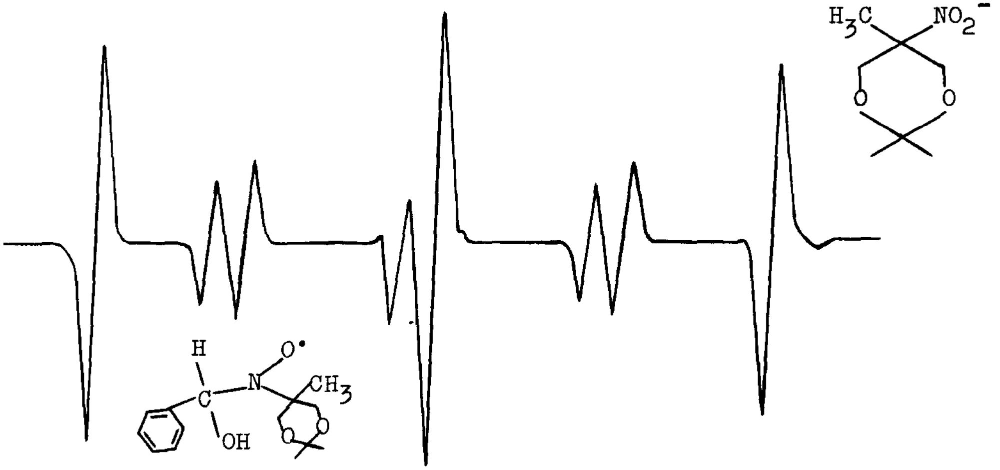


Fig. 1. ESR spectrum of the reaction mixture during reductive elimination in benzyl alcohol, temp. 110°.

The structure of the nitroxide radical and the mechanism of its formation will be a subject matter of another publication.

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