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REDUCTIVE ELIMINATION OF TERTIARY NITRO GROUP IN 5-NITRO-1,3-DIOXANES. PART II *. ESR SPECTRA **

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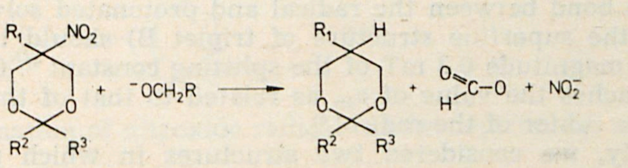
Badano przebieg redukcyjnej eliminacji grupy nitrowej 2,2,5-trimetylo-5-nitro-1,3-dioksanu działaniem benzylanu potasu, stosując technikę ESR. Stwierdzono, że reakcja ma charakter anionorodnikowy. Zarejestrowano widmo anionorodnika 2,2,5-trimetylo-5-nitro-1,3-dioksanu oraz widmo niesymetrycznie podstawionego rodnika nitrozylowego, który tworzy się w reakcji ubocznej.

Reductive elimination has been examined of the nitro group in 2,2,5-trimethyl-5-nitro-1,3-dioxane under action of potassium benzyloxide. By registering ESR signals in the course of the reaction a conclusion was made on formation of an anion-radical of 2,2,5-trimethyl-5-nitro-1,3-dioxane and a nitroxide radical. The latter is the result of a side reaction.

The authors have found that reductive agents, such as potassium ethyleneglycolate and benzyloxide, while acting on 2,2,5-trialkyl- or 2,5-dialkyl-5-nitro-1,3-dioxanes, replace the nitro group by hydrogen [1]. This can be depicted by a redox mechanism:



(1)

1 2

R = CH_2OH, C_6H_5; R^1, R^3 = alkyls; R^2 = H, alkyl.

ESR examination of reacting systems furnished the evidence of anion-radical character of the reaction.

We have now examined the reaction of 2,2,5-trimethyl-5-nitro-1,3-dioxane with benzyl alcohol and potassium hydroxide and registered ESR signals every two minutes. Two triplets A and B were present in the spectrum. They showed different splitting constants (the Figure). We

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* Part I: Łytko-Krasuska A., Piotrowska H., Urbański T., *Tetrahedron Letters*, **1979**, 1243.

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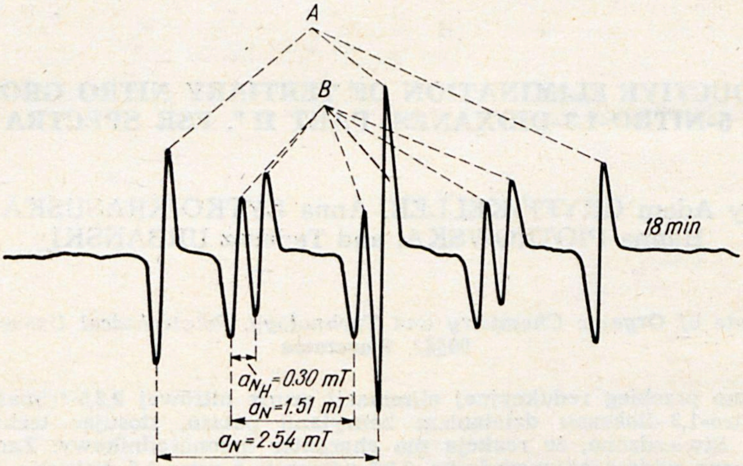
assigned the triplet A with a splitting constant $a_N = 2.54$ mT to the anion-radical of the nitro group of 2,2,5-trimethyl-5-nitro-1,3-dioxane (**1**, $R^1 = R^2 = R^3 = CH_3$). The identification was done on the basis of the splitting constant ²⁾.



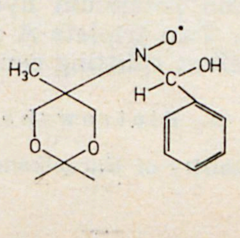
ESR spectrum of the reacting mixture: 2,2,5-trimethyl-5-nitro-1,3-dioxane, benzyl alcohol and potassium hydroxide at 110°C, after 18 min

Triplet B showed a lower splitting constant $a_N = 1.51$ mT. This was in agreement with existing data referred to aliphatic nitroxide radicals [2,3]. The presence of a nitroxide radical indicates the existence of a side reaction. The structure of the radical should be regarded as unsymmetrical, contrary to Hoffmann's observation referred to the reaction of *t*-nitrobutane with sodium [3]. This is based mainly on a superfine structure of triplet B manifested by a splitting constant 0.3 mT (one of the signals is fused with one signal belonging to A). The symmetrical structure of a radical containing two dioxane units should not produce any superfine structure with that pattern.

A hydrogen bond between the radical and protonated solvent (which could explain the superfine structure of triplet B) should be excluded because of the magnitude 0.3 mT of the splitting constant [4]. On the contrary, it approaches the value of a_H, as related to that of the proton in position β to the center of the radical [5].

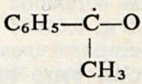
Subsequently, we considered two structures in which proton was bonded with oxygen or with carbon [6,7]. We rejected eventually the former, as being less probable in an alkaline medium, and by experiments with isotopic proton exchange: by shaking the reacting mixture with 10, 20, 30 and 60% of D_2O no fading out was recorded of the super subtle structure of the ESR spectra of the nitroxide radical.

Thus we suggest now unsymmetrical structure **3** containing a dioxane and a benzyl alcohol moieties:



(3)

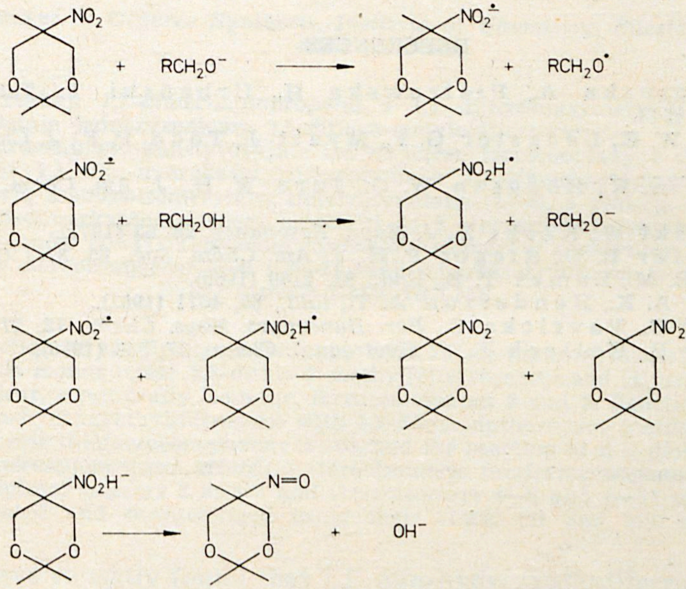
This structure was confirmed by experiment consisting in registration of ESR spectrum of a reacting mixture containing a secondary (α-phenylethyl) instead of the primary alcohol (benzyl alcohol) as in the above described experiment. If the suggested mechanism is correct the anion-radical thus formed should have an intermediate structure **4**:



$$C_6H_5\text{—}\underset{CH_3}{\underset{|}{\dot{C}}}\text{—}O^- \qquad \mathbf{4}$$

The ESR spectrum registered for the reacting mixture containing α-phenylethyl alcohol has not shown superfine structure of the nitroxide radical, thus confirming structure **3**.

We can conclude that 2,2,5-trimethyl-5-nitroso-1,3-dioxane should be formed prior to formation of **3**. While taking into consideration the papers by Kastening[8,9] we rationalize that the mechanism, as below, referred to 5-nitro-1,3-dioxanes is more probable than that of Hoffmann[3]:



(2)

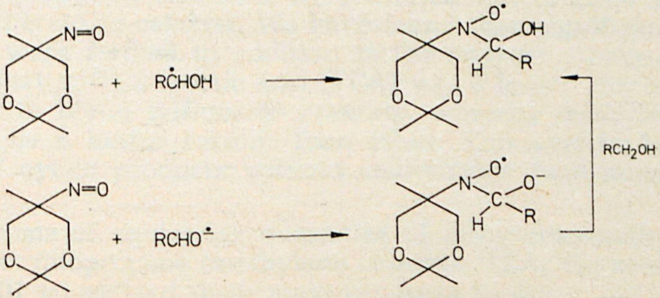
(3)

(4)

(5)

The formation of nitroxide radical can be depicted by reactions (6), (7) and (8):

$$RCHO^{\dot-} + RCH_2OH \rightleftharpoons R\dot{C}HOH + RCH_2O^- \qquad (6)$$



(7)

(8)

EXPERIMENTAL

Reductive elimination of the nitro group in 2,2,5-trimethyl-5-nitro-1,3-dioxane

2,2,5-Trimethyl-5-nitro-1,3-dioxane (0.017 g, 0.0001 mole) was dissolved in benzyl or α-phenylethyl alcohols (0.5 ccm). The solutions were introduced into a standard ESR tube, and potassium hydroxide (0.02 g, 0.00036 mole) was added. The tubes were kept in ESR spectrometer at different temperatures from ambient to 150—160°C (±2). The tubes were heated by air. The spectra were taken every 2 min.

Spectrometer ESR of Jeol was of JES 3 MEX type.

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