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REDUCTION OF 2- AND 3-NITROBORNANES TO BORNANE

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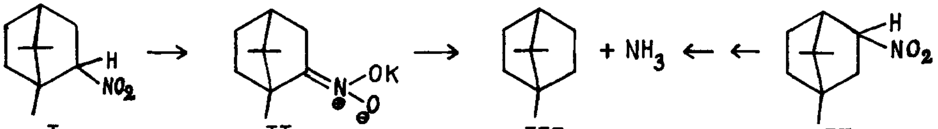
In the course of some experiments concerning the reactions of the alkali salts of 2-nitrobornane (I,II) we found that on heating in alkaline high-boiling alcohol the nitro compound is largely reduced to the parent hydrocarbon, bornane (III). Gaseous ammonia is evolved from the reaction mixture as a reduction product of the nitro group. Simultaneously, the solvent alcohol is oxidized to different carbonyl compounds. Camphor and camphor oxime are formed as byproducts in the reaction.



I II III IV

The boiling point of the solvent alcohol suitable for the reaction must be high enough, as the reduction of the nitro compound does not take place at a temperature lower than 200°C. Ethylene glycol, diethylene glycol, triethylene glycol, glycerol, monoethanol amine and benzyl alcohol were tried out as possible solvents. Of these, glycerol and diethylene glycol proved to be the most suitable.

Potassium hydroxide (10 g.) is first dissolved into diethylene glycol or glycerol (50 ml.) by warming to ca. 100°. The nitrobornane (5 g.) is dissolved into the warm alkaline solution, after which the water is removed under diminished pressure at 100°. On raising the temperature of the mixture to 200-220°, the reduction reaction of the nitro compound commences and the hydrocarbon formed distils into the condenser, together with a little water and the oxidation products of the solvent used.

The amount of bornane formed in these conditions, is ca. 60 % of the theory (according to the GLC), the practical yield, after column chromatographic purification from by-products, being ca. 40 % of the theory. Camphor and camphor oxime are formed to the extent of 10-13 and 7-9 mole-% of the nitrobornane used. The corresponding amines, bornyl or isobornyl amine cannot be detected among the products.

The amount of ammonia produced in the reduction reaction varied, according to several determinations, between 60 and 65 mole-% of the nitrobornane.

3-Nitrobornane (IV), synthetized[1] from epicamphor oxime through 3-bromo-3-nitrobornane, is also reduced to bornane in similar conditions. The yield of the hydrocarbon is the same as in the previous case. Epicamphor and epicamphor oxime are formed as by-products.

Concerning the mechanism of the reduction, the facts indicate that in the decisive step of the reaction the alcoholate anion (from the solvent alcohol) gives up a hydride ion [cf.2] to the α-carbon atom of the nitronate anion, and is in turn oxidized to a carbonyl compound (Figure 1). The bond between carbon and nitrogen possibly breaks before the reduction of the NO_2-group for no amine can be found among the products. Under similar conditions potassium nitrite is reduced nearly quantitatively to ammonia.

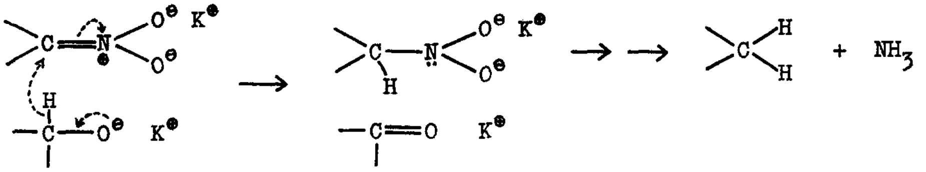


Figure 1.

The final hydrocarbon is possibly generated through a short-lived carbanion intermediate, as for example in the decarboxylation of carboxylic acids.

References

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