

THE THERMAL DECOMPOSITION OF α -NITRO KETONES

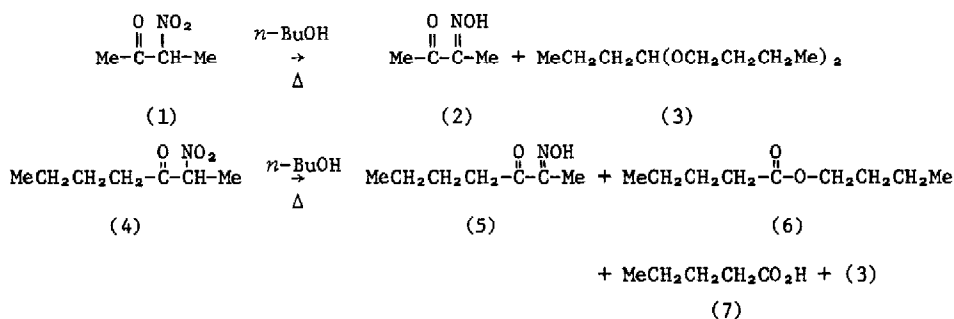
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α -Nitro ketones are known to undergo a variety of reactions in solution; treatment of acyclic and cyclic α -nitro ketones with mineral acids leads to carbon-carbon bond cleavage and the formation of a hydroxylamine salt and a carboxylic acid.¹ Cleavage is also observed in α -nitrocyclohexanone in addition to ketal formation on refluxing in methanol/HCl.² 3-Nitrocampbor³ and certain steroidal α -nitro ketones,⁴ however, undergo rearrangement to the corresponding *N*-hydroxyimide in the presence of acid. Carbon-carbon bond cleavage is also the major pathway observed on treatment with base.^{5,6} In this paper, the results of the thermal decomposition of some acyclic and cyclic α -nitro ketones in solution are reported.

Decomposition of 3-nitrobutan-2-one⁷ (1) in refluxing butan-1-ol for 20 hours led to the formation of two products, 3-hydroxyiminobutan-2-one (2) in 20% yield and the solvent derived product, the dibutylacetal of butanal (3). The acetal was synthesised unambiguously from butanal.⁸ Other acyclic α -nitro ketones were shown to undergo analogous conversions; 2-nitroheptan-3-one (4), prepared by oxidation of the known nitro-alcohol,⁹ gave the corresponding oxime (5) in 25% yield, together with *n*-butyl valerate (6), valeric acid (7), and the dibutylacetal of butanal (3). Products were identified by comparison with authentic samples.



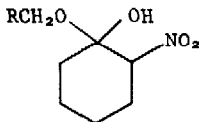
The influence of the solvent on the decomposition of 3-nitrobutan-2-one was also investigated. A slower reaction occurred in refluxing propan-1-ol leading to the formation of a complex mixture of products; 3-hydroxyiminobutan-2-one and the di-*n*-propylacetal of propanal were

cleavages are well known in the gas phase,¹¹ but unknown in solution. Nitrogen dioxide undergoes a fast reaction with both alcohols and ethers; with alcohols, the products are nitric acid and the corresponding nitrites,^{12,13} whereas with ethers, nitrogen dioxide is reported to react vigorously and sometimes explosively.¹⁴ The first step in both these reactions is probably hydrogen abstraction from the solvent giving nitrous acid (eq. 2). Nitrous acid is unstable and readily decomposes to nitric oxide and nitric acid (eq. 3). Recombination of radical (11) and nitric oxide leads to the formation of a nitroso compound, which under the conditions of the reaction, can be expected to isomerise to the more stable oxime (eq. 4). Evidence supporting this part of the postulated pathway comes from a separate experiment in which 3-nitrobutan-2-one was heated under reflux in butan-1-ol whilst a stream of nitrogen was passed through the solution. After 15 hours, with 93% of the nitro ketone undergoing decomposition, only 3% of the keto oxime (2) was obtained. Comparison with the data presented above shows that the amount of oxime formed is considerably reduced. This is clearly the result of removal of nitric oxide in the nitrogen gas flow before reaction with the radical (11) can occur.

The presence of nitric acid in the reaction mixture accounts for the formation of the other products. Nitric acid is known to cleave α -nitro ketones to the corresponding carboxylic acids,¹ and under the conditions of the reaction, esterification would be expected to occur with nitric acid acting as the acid catalyst (eqs. 5 and 6). In support of this viewpoint, it was found that a solution of valeric acid in butan-1-ol in the presence of nitric acid gave, after refluxing for 20 hours, a good yield of *n*-butyl valerate and the dibutyl acetal of butan-1-al (3), whereas in the absence of nitric acid, esterification was very slow and no acetal (3) was detected. The formation of this acetal (3) can readily be accounted for if one assumes that butanal is formed in the reaction by the oxidation of butan-1-ol with nitric acid (eq. 7). The possible conversion of butan-1-ol to the acetal (3) was confirmed by refluxing the alcohol with nitric acid for 20 hours, a procedure which resulted in the formation of the acetal. A much higher yield of the acetal was obtained, however, on refluxing a solution of butanal in butan-1-ol for 20 hours in the presence of a trace of nitric acid.

The results of earlier studies of the reaction of nitrogen dioxide with alcohols suggest that *n*-butyl nitrite should also be a reaction product.^{12,13} The formation of nitrites was not observed in our studies, but it was found that on refluxing a solution of *n*-butyl nitrite in butan-1-ol for 20 hours, the acetal (3) was obtained as the major product. *n*-Butyl nitrate may also be an intermediate, and this too was found to give the acetal (3) on refluxing in butan-1-ol.

In the decomposition of the cyclic α -nitro ketone, 2-nitrocyclohexanone (8), a different mechanism is probably implicated. The products can be envisaged as arising from the hemiketal intermediate (12), previously described by Feuer,² but the possibility of this reaction requiring acid catalysis, presumably with nitric acid resulting from carbon-nitrogen bond cleavage, cannot be ignored.



(12) R = MeCH₂CH₂, MeCH₂

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