BASE-CATALYZED DEHYDRATION OF ALDOXIMES IN DIMETHYL SULFOXIDE

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Nitriles can be obtained from aldoximes under mild conditions and in a high yield by the reaction with acids or their derivatives, diorganyl phosphites [1], chlorothionoformates [2], or phosphononitrilo chloride [3]. Some aldoximes can be almost quantitatively dehydrated into nitriles during prolonged boiling in hexametapol (220-240°) without any reagent of an acid character [4]. The dehydration of aldoximes in the presence of bases has been little studied. It is known [5] that when oximes are heated with metal oxides or hydroxides, ammonia is liberated and the carbonyl compound is partially regenerated. Sometimes it is possible to obtain nitriles by the action of KNH_2 in a liquid NH_3 on oxime O-alkyl ethers [5].

We found that oximes of both aliphatic and aromatic aldehydes are readily converted into the corresponding nitriles on moderate heating (120-140°) with KOH in DMSO in a 65-92% yield

$$RCH{=}NOH \xrightarrow[120\text{-}140^\circ,\ 3\ h]{KOH/DMSO} RCN + H_2O$$

$$R = CH_3,\ C_7H_{15},\ C_6H_5$$

At 140°, other conditions being equal, benzaldoxime is converted into benzamide (BA) in a 25% yield

$$C_6H_5CH{=}NOH \xrightarrow[140^\circ,\ 3\ h]{KOH/DMSO} C_6H_5CONH_2$$

The yield of BA is not significantly increased (30%), when the reaction is carried out in boiling DMSO. Since under these conditions the primary dehydration of aldoximes has been proved, it is clear that BA is not formed by the Beckmann rearrangement scheme, but is produced as the result of the hydration of the intermediate benzonitrile

$$C_6H_5CN + H_2O \xrightarrow[140^\circ,\ 3\ h]{KOH/DMSO} C_6H_5CONH_2$$

Because acetophenoneoxime does not form amides under these conditions, but is recovered unchanged from the reaction, the Beckmann rearrangement is not probable.

The conditions found can be used for the preparation of amides from nitriles as well as from aldoximes, especially in the presence of fragments which are unstable toward acids. In the absence of DMSO, benzaldoxime is dehydrated by the alkali at the boiling point only (200°).

EXPERIMENTAL METHOD

The aldoximes were purified by recrystallization. "Chromatographically pure" samples were used, but they were not separated into the syn- and anti-isomers.

Dehydration of Acetaldoxime. A 5-g (0.07 mole) portion of acetaldoxime and 0.5 g (0.009 mole) of KOH in 40 ml of DMSO were heated for 3 hours at 140° in a steel rotating autoclave. The reaction mixture was washed with water, extracted by ether, dried over Na_2SO_4, and distilled. The yield of acetonitrile,

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bp. 80°; n_D^{20} 1.3430, was 1.9 g (70%). According to the retention volume (GLC) and the IR and PMR spectra, the product obtained was identical with a known sample.

Dehydration of 1-Octanaldoxime. A 5-g (0.035 mole) portion of 1-octanaldoxime and 0.5 g (0.009 mole) of KOH in 40 ml of DMSO were heated for 5 hours at 140° in a steel rotating autoclave. The yield of caprylonitrile, bp 200°, n_D^{20} 1.4180, was 2.9 g (65%). According to IR and PMR spectra, the product was identical with a known sample.

Dehydration of Benzaldoxime. a) A 12.1-g (0.1 mole) portion of benzaldoxime and 1 g (0.018 mole) of KOH in 45 ml of DMSO were heated for 3 hours at 120°. By distillation in vacuo, 9.4 g (91%) of benzonitrile were obtained, bp 191°, n_D^{20} 1.5290; d_4^{20} 1.0049. According to the IR spectrum and the gas — liquid chromatogram, the product was identical with a known sample.

b) A 6-g (0.049 mole) portion of benzaldoxime and 0.5 g (0.009 mole) of KOH were boiled for 3 hours. By fractionation 4.7 g (92.5%) of benzonitrile were isolated.

Conversion of Benzaldoxime into Benzamide by the Action of KOH/DMSO. A 12.1-g (0.1 mole) portion of benzaldoxime and 1 g (0.018 mole) of KOH in 45 ml of DMSO were heated for 3 hours at 140°, and the DMSO was distilled in vacuo. From the distillation residue, 3 g (25%) of benzamide, mp 130°, were isolated by recrystallization. According to the IR spectrum, the product was identical with a known sample.

b) A 5-g (0.041 mole) portion of benzaldoxime and 1 g (0.018 mole) of KOH in 35 ml of DMSO were heated for 3 hours at 200°. By distillation in vacuo, 0.3 g (5.85%) of benzonitrile were obtained, and from the distillation residue in acetone, 1.4 g (29.3%) of benzamide were obtained.

CONCLUSIONS

A convenient method is proposed for the alkaline dehydration of aldoximes into nitriles in the presence of KOH in dimethyl sulfoxide at 140°.

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