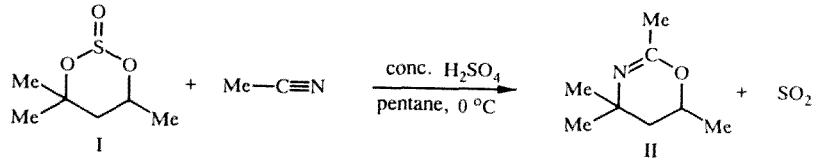
REACTION OF CYCLIC SULFITES WITH ACETONITRILE

V. V. Kuznetsov

One method for the synthesis of 5,6-dihydro-1,3-oxazines, valuable precursors of 1,3-aminoalcohols, is based on the reactions of 1,3-dioxanes with acetonitrile [1]. Using 4,4,6-trimethyl-1,3,2-dioxathiane-2-oxide (I) as an example, we have shown for the first time that reaction of cyclic sulfites with acetonitrile also leads to the corresponding 2-methyl-5,6-dihydro-1,3-oxazine (compound II).



I II

Acetonitrile (4 ml, ~0.07 mol) followed by compound I (3.5 g, 0.021 mol) were added slowly to a stirred mixture of pentane (10 ml) and conc. H_2SO_4 at 0°C. The mixture was stirred at 0°C for 2 h and then poured onto ice (100 g). The aqueous layer was washed with chloroform (2 x 25 ml), was made alkaline with solid NaOH to pH 9-10 while cooling, and was then extracted with ether (3 x 50 ml). The ether extract was dried over $MgSO_4$, the solvent was removed in vacuum and the residue was fractionated in vacuum to give 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine (II) (2.4 g, 80%), b.p. 49-50°C (18 mmHg), identical by glc with a sample obtained by different synthesis [1].

The result of the reaction is very dependent on the number of methyl substituents on the ring; the yield of the corresponding dihydrooxazine when 4-methyl-1,3,2-dioxathiane-2-oxide reacted with acetonitrile under the conditions mentioned above was only 3%.

The observed reaction broadens the range of chemical conversions of substituted cyclic sulfites and adds to the existing methods for the synthesis of 5,6-dihydro-1,3-oxazines.

The cyclic sulfite starting materials were prepared by reaction of the corresponding 1,3-diols with thionyl chloride [2].

REFERENCES

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A. V. Bogatskii Physicochemical Institute, Ukraine National Academy of Science, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, p. 275, February, 1995. Original article submitted January 15, 1995.

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