CHEMISTRY OF NITROSOIMINES. V.[1]

REACTION OF 3-SUBSTITUTED 2-NITROSOIMINO-2,3-DIHYDROBENZOTHIAZOLES WITH LITHIUM ALUMINUM HYDRIDE

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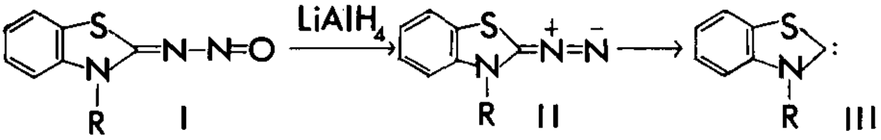
Reaction of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles with lithium aluminum hydride gave corresponding thiazolone azines and bis [o-(N-substituted N-formylamino)phenyl] disulfides as major products.

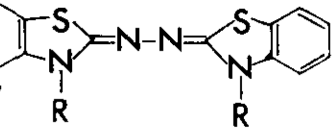
Nitrosoimines are usually unstable, but a number of nitrosoimines contained in five membered heterocycles are known to be stable.[2] As a series of investigation on nitrosoimines, we reduced 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (I) with $LiAlH_4$ in order to obtain the hitherto unknown diazo compounds (II), based on the finding by Zimmerman and Paskovich that N-nitrosodimesitylmethyleneimine was reduced with $LiAlH_4$ to give corresponding diazo compound.[3]

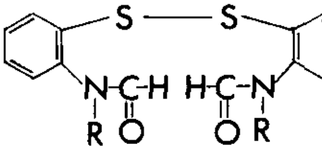


a) R=Ph b) R=Me c) R=Et

To a stirred solution of Ia (10g) in tetrahydrofuran (700 ml), $LiAlH_4$ (2.234g) was added portionwise at -70∼-40 °C under nitrogen atmosphere. Vigorous evolution of gas (N_2) took place immediately. Stirring was continued for further 10 h at room temperature after the addition. Residual $LiAlH_4$ was decomposed with methanol (150 ml) and products were separated by column chromatography on silica gel after usual work-up.

3-Phenyl-2,3-dihydrobenzothiazoloneazine (IVa; 16%, mp 274.0-275.0°C) and bis [o-(N-formyl-N-phenylamino)phenyl] disulfide (Va; 30%, mp 161.5-162.0°C) were eluted as major products with benzene and chloroform-ether (1:1), respectively.


IV

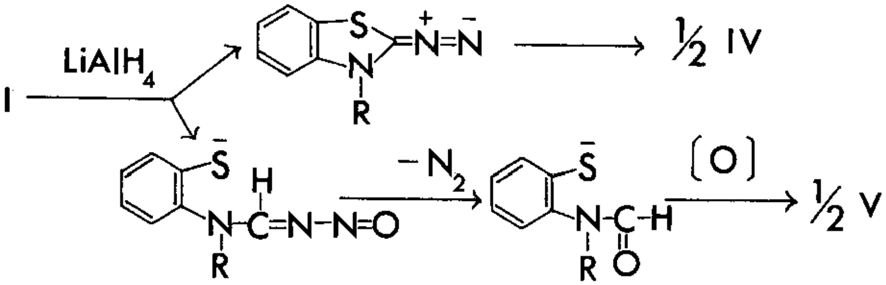

V

a) R=Ph b) R=Me c) R=Et

Similar reaction of Ib and Ic with $LiAlH_4$ gave IVb (27%, mp 259.0-260.0°C)[4] and Vb (22%, mp 107.0-108.5°C),[5] and IVc (30%, mp 189.5-190.0°C)[6] and Vc (28%, mp 113.0-113.5°C), respectively.

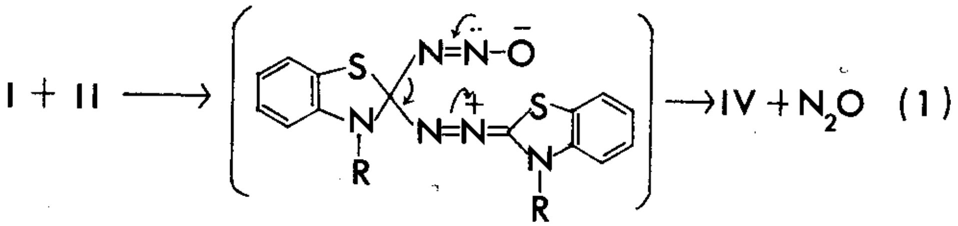
A couple of minor products were separated by column chromatography, but some of them were not fully characterized.

Formation of IV and V can be rationalized as follows:



Although attempt to trap II or III with styrene or β-naphthol was unsuccessful, the existence of II and/or III as precursor(s) of IV is still to be believed.

The reaction was also carried out under argon atmosphere and evolved gas was analyzed by mass-spectrometry. The gas was shown to be pure nitrogen and nitrous oxide was not detected at all. This fact rules out the possibility of reaction (1) to produce IV.



It is noteworthy here to mention that 2-hydrazono-3-phenyl-2,3-dihydrobenzothiazole was oxidized with mercuric oxide very slowly at 0°C to yield corresponding thiazolone azine as a major product, which is one of typical methods to prepare diazo compounds.

REFERENCES

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Received, 2nd July, 1973