Tetrahedron Letters No. 52, pp 5267 - 5268, 1972. Pergamon Press. Printed in Great Britain.

6-ACETAMIDO-5,6-DIHYDRO-1,4,2-OXATHIAZINES
A NOVEL CLASS OF COMPOUNDS

S. Hoff* and Miss E. Zwanenburg

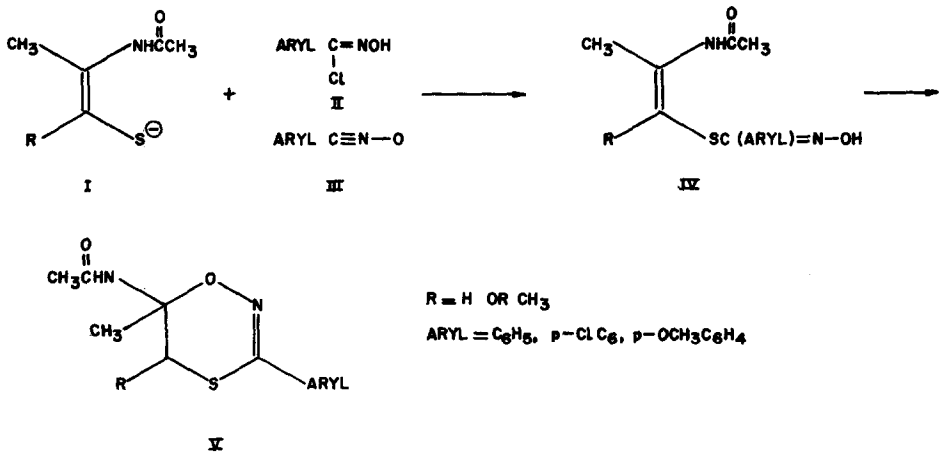
Koninklijke/Shell-Laboratorium, Amsterdam

(Shell Research N.V., Amsterdam-N., The Netherlands)

(Received in UK 1 November 1972; accepted for publication 15 November 1972)

In the previous communication[1] we have shown that sodium 2-acetamidopropenethiolates (I) can be prepared from 2,3-dihydro-4H-1,4-thiazin-3-ones by reaction with sodium in liquid ammonia. We now report one of the applications of this ionic species in the synthesis of heterocycles.

Treatment of a suspension of the sodium salt in dimethoxyethane with arylhydroximic acid chlorides (II) or arylnitrile oxides (III) led to the formation of substituted 6-acetamido-5,6-dihydro-1,4,2-oxathiazines (V), in yields of about 70 %. The first step in this reaction sequence is the formation of the corresponding thiohydroximic acid derivative IV. Its presence is revealed by the PMR spectrum showing the vinylic hydrogen (R=H) at δ = 5.20 ppm with an allylic coupling constant of 1.2 Hz[1].



The second step, the ring closure of IV, giving the oxathiazines V, is governed by the susceptibility of the double bond towards nucleophilic attack. The orientation of this intramolecular addition is directed by both the electron-donating ability of the acetamido group and the electron-withdrawing ability of sulphur[2]. The scope of this reaction is limited by the fact that only arylhydroximic acid chlorides and arylnitrile oxides can be employed. When alkyl derivatives are used the thiolate I acts as a base and generates the highly unstable alkylnitrile oxides which polymerize rather than add onto the protonated thiolate I.

The structure of the oxathiazines V is based on correct elemental analysis and IR, PMR and mass spectroscopic data. In the PMR spectra the C-5 hydrogens (R=H) appear as an AB quartet at δ = 4.15 ppm and δ = 3.15 ppm with a coupling constant of 12.8 Hz. The high-field proton shows in addition to the geminal coupling a long-range coupling (^{4}J = 1.2 Hz) with the hydrogen on the acetamido group. This coupling can be operative only when the two hydrogens involved are arranged in a so-called extended zigzag or "W" conformation. Therefore, we conclude that the acetamido group in the 1,4,2-oxathiazines occupies an axial position[3].

REFERENCES

1. S. Hoff, A.P. Blok and Miss E. Zwanenburg, previous communication.

2. H.C. Volger and J.F. Arens, Rec. Trav. Chim. 77, 1170 (1958).

3. J. Meinwald and A. Lewis, J. Am. Chem. Soc. 83, 2769 (1961).