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2-ARYLIMINO-3-THIAZOLINES - FORMATION OF UNUSUAL TAUTOMERS OF 2-ARYLAMINO-THIAZOLINES - A REVISION

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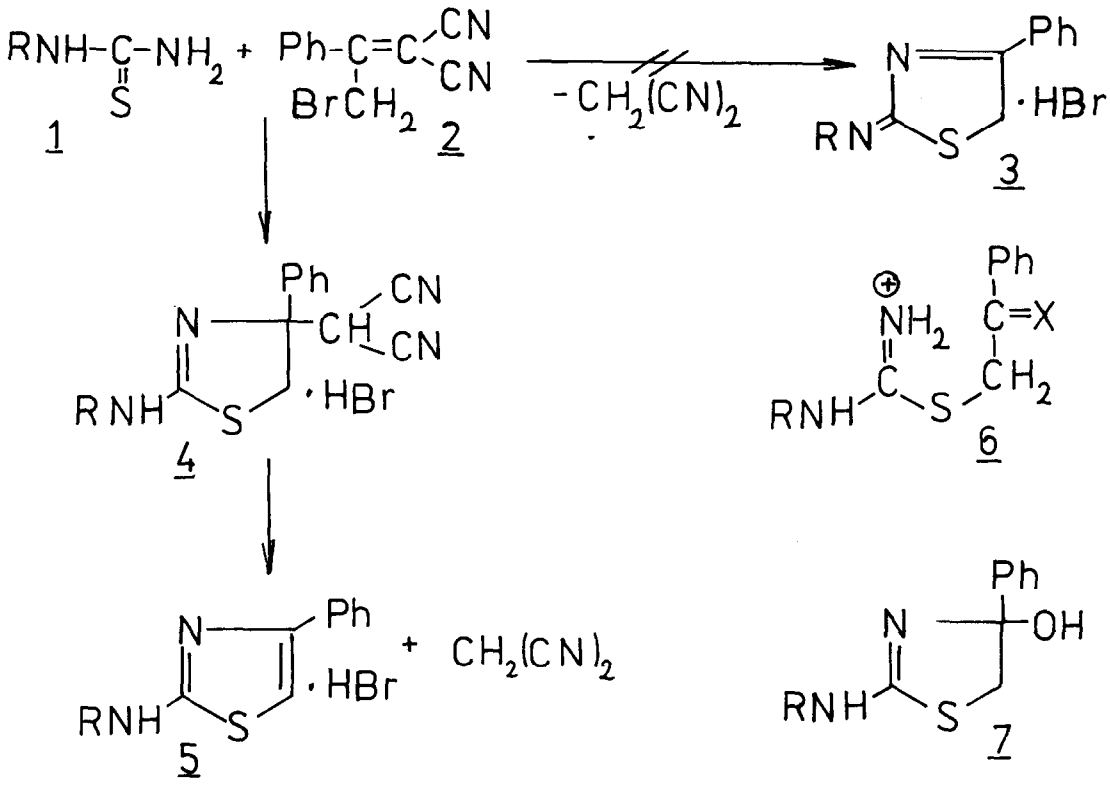
ABSTRACT: In contrast to previously reported results the products formed in the reaction of arylthioureas with 3-bromomethyl-2-cyanocinnamonitrile are not 2-arylimino-3-thiazolines but 2-arylamino-4-dicyanomethyl-2-thiazolines.

Recently /1/ we reported on the reactions of thioureas 1 with 3-bromomethyl-2-cyanocinnamonitrile 2 giving rise to the formation of the hydrobromides of either 2-aminothiazoles 5 or of the unstable 2-imino-3-thiazolines 3. Further investigations have shown that the latter result has to be revised. The structure of the compounds obtained from phenyl or 4-chlorophenylthiourea 1 (R = C_6H_5 or 4-ClC_6H_4) and 2 in acetone or chloroform is not 3 but a corresponding 2-amino-4-dicyanomethyl-2-thiazoline 4 /2/. Instead of the original compounds the ^{1}H NMR spectra reported in our previous publication /1/ turned out to represent the mixtures of the 2-aminothiazole hydrobromide 5 and malodinitrile which are formed from the corresponding 2-amino-4-dicyanomethyl-2-thiazolines 4 due to unsuitable standing of the solution for about 30 minutes before running the measurement. These ^{1}H NMR spectra (CH_2 at about 4.40 ppm as a singlet) had led us to the wrong conclusion that the isolated compounds were 2-imino-3-thiazolines 3. In contrast the ^{1}H NMR spectra of the freshly prepared solutions of 2-amino-2-thiazolines 4 /2/ show signals at 5.87 ppm (singlet) of the dicyanomethyl H-atom and at 3.80 ppm (quadruplet) of a typical AB-system which is represented by the diastereotopic CH_2-group at 5-position adjacent to the chiral carbon atom at position 4. The intensity of these signals decreases with time while the CH_2-singlet of malodinitrile at 4.40 ppm increases. The same decomposition of the 2-amino-4-dicyanomethyl-2-thiazolines 4 probably takes place in the mass spectrometer since the MS spectra obtained are a superimposition of the spectra of the corresponding 2-aminothiazole 5 and malodinitrile.

The formation of the 2-amino-4-dicyanomethyl-2-thiazolines 4 can be easily understood by first S-alkylation of the arylthioureas 1 and subsequent Michael-like addition of the aminogroup of the resulting isothioureas 6 [X = $=C(CN)_2$] to the C=C-bond of the ylidenemalodinitrile fragment. Hence the formation of the 2-aminothiazoles 5 /1,3/ starting from thioureas 1 and 3-bromomethyl-2-cyanocinnamonitrile 2 takes place in a similar fashion like



the classical Hantzsch synthesis using phenacyl bromide. In the latter case either corresponding S-phenacylthioureas 6 (X = O) or 4-hydroxy-2-thiazolines 7 comparable with the 4 were observed as intermediates /4/. It is noteworthy that 7 can not be isolated under the conditions used for the synthesis of the 2-amino-4-dicyanomethyl-2-thiazolines 4.

Further examples of the formation of 2-amino-4-dicyanomethyl-2-thiazolines as well as other pecularities of the transformation of 4 to 2-aminothiazoles are reported together with kinetic results in a further publication.

/1/ J. Liebscher, E. Mitzner, Tetrahedron Lett. 1985, 1835.

/2/ 4a (R = C_6H_5): m.p. 274-290°C (dec.); yield 96 %.
MS m/e (rel. intensity): 253(19), 252(100,M^+), 251(63), 150(23), 149 (18), 134(47), 104(27), 90(18), 77(24), 66(11), 51(21), 39(15).
4b (R = 4-ClC_6H_4): m.p. 187-197°C (dec.); yield 82 %.
^{1}H NMR (DMSO-d_6, 80 MHz) δ[ppm]: 3.80(q;2H), 5.87(s;1H), 7.20-8.18 (m;11H).

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