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SYNTHESIS OF HETEROCYCLES-1. ONE STEP SYNTHESIS OF ACETYLTHIADIAZOLINES.

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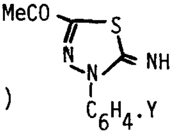
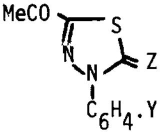
The 5-imino-Δ^2-1,3,4-thiadiazolines reported sofar[1] were prepared from hydrazidic halides and thiourea or KSCN. The preparation of the hydrazidic halides is limited to either the reaction of a hydrazide with PCl_5 or the halogenation of an aldehydic hydrazone[2]. In this communication we wish to report an efficient one step synthesis of 2-acetyl-4-aryl-5-imino-Δ^2-1,3,4-thiadiazolines (1 a-e) from (2) and aryldiazonium chlorides. No syntheses of (1) have been reported. Besides, the use of the thiocyanato group to activate the carbon-hydrogen bond of aliphatic methylene compounds in their coupling with diazotized arylamines has not been utilised in organic synthesis.



(1)

MeCOCH(SCN)COMe

(2)



$MeCOC(Cl){:}NNHC_6H_4.Y$

(8)

Y = a, H; b, p-Me; c, p-Cl; d, p-OMe; e, $p\text{-}NO_2$

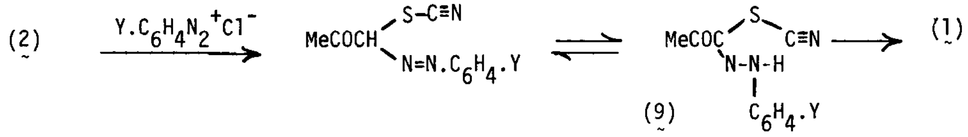
Z = (3), NNO; (4), O; (5), NHHCl; (6), NCOMe; (7), NCOPh

In an ethanolic sodium acetate buffered solution, (2)[3] was coupled with benzenediazonium chloride to give (1 a), mp. 75° (86% yield). Similarly, other diazotized arylamines coupled with (2) to give the products: (1 b), mp. 116°; (1 c), mp. 127°; (1 d), mp. 154°; and (1 e), 194-195°, in a 79% average yield. The structures of compounds (1 a-e) were inferred from their elemental and spectral analyses[4], besides a study of their chemical reactions. Thus, the ir spectrum of (1 a) revealed the presence of an imino NH (3310 cm^{-1}), unsaturated acetyl CO (1690 cm^{-1}), and C = N (1610 cm^{-1}) bands. No bands were observed in the regions 2200-2100 and 740-720 cm^{-1} due to a free SCN group. Furthermore, when a solution of (1 a) in glacial acetic acid was treated with aqueous sodium nitrite solution, the red nitroso derivative (3 a), mp. 114° (decomp.) was obtained. When heated in dry xylene, (3 a) afforded the thiadiazoline-5-one (4 a), mp. 57°. The ir spectrum of (4 a) showed two CO bands at 1690 cm^{-1}

($CH_3COC=$) and 1710 cm^{-1} (5-keto group). Boiling of either (1 a) or (3 a) with HCl gave the hydrochloride salt (5 a), mp. 217°. In addition, (1 a) or (5 a) with acetic anhydride, and with benzoyl chloride in pyridine, forms the N-acetyl derivative (6 a), mp. 119°, and the N-benzoyl derivative (7 a), mp. 241°, respectively. While the ir spectra of both (6 a) and (7 a) showed a band at 1690 cm^{-1} ($CH_3COC=$), that of (6 a) showed an extra band at 1630 cm^{-1} ($CH_3CON=$) and of (7a) a band at 1610 cm^{-1} ($C_6H_5CON=$). Further confirmation of the structure of (1) was obtained by its alternate synthesis from (8). For example, the reaction of (8 a)[5] and KSCN in ethanol at elevated temperatures afforded a product that analyzed correctly for $C_{10}H_9N_3OS$, mp. 75°, and found to be identical in every respect with (1 a) prepared earlier.

We believe that the present reaction proceeds as shown in Scheme 1 where the intermediate hydrazone (9), formed through a Japp-Klingemann reaction[6], cyclizes to give (1). Extension of this reaction to other active

Scheme 1.



methylene thiocyanates, its detailed synthetic utility, and mechansim are in progress.

References and Notes.

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4. Beside the ir spectra presented in the body of the communication, ^{1}H-N.M.R. spectra were obtained for all the compounds prepared and were in agreement with the structures assigned.
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