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THE AZO COUPLING OF ACTIVE METHYLENE THIOCYANATE COMPOUNDS. A CONVENIENT SYNTHESIS OF 5-IMINO-4-ARYL-2-BENZOYL- Δ^2-1,3,4-THIADIAZOLINES

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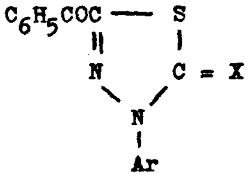
Aliphatic compounds containing an activated methylene group are known to react with aromatic diazonium salts to form azo compounds or their hydrazone tautomers.[3] An examination of the many active methylene compounds that have been subjected to this reaction reveals that compounds of type I in which the methylene group is activated by a thiocyanato and some other activating group have not yet been investigated. We wish to report a convenient one step synthesis of the title compounds (II) from I and diazotized arylamines. No syntheses of II have been reported.

$ArCOCH_2SCN$

I



$C_6H_5COC(Br){:}NNHAr$

VII

II, X = NH
III, X = NH.HCl
IV, X = NCOMe
V, X = NNO
VI, X = O

a, Ar = C_6H_5; b, Ar = p-MeC_6H_4 ; c, Ar = p-ClC_6H_4 ; d, Ar = p-$O_2NC_6H_4$

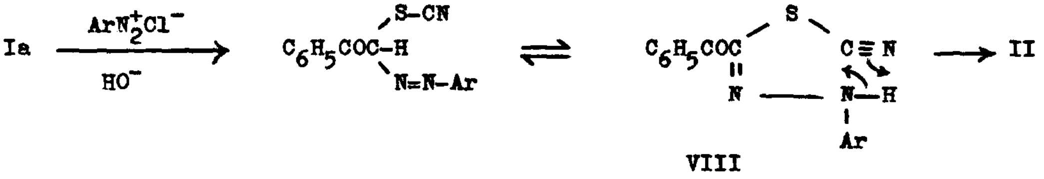
In NaOAc buffered solution of EtOH, Ia coupled with benzenediazonium chloride to yield 5-imino-4-phenyl-2-benzoyl- Δ^2-1,3,4-thidiazoline (IIa), mp. 89-90° (75% yield). In a similar manner, other diazotized arylamines coupled with Ia and gave the products: IIb, mp. 112°; IIc, mp. 127°; and IId, mp. 191°. The structures of these products IIa-d were inferred from the results of their elemental and spectral analyses and from a study of their chemical reactions. For example, the IR spectrum of IIa revealed the presence of imino NH (3320 cm^{-1}) , α,β-unsaturated benzoyl CO (1650 cm^{-1}), and C=N (1620 cm^{-1}) bands. No bands were observed in the 2200-2100 cm^{-1} region due to a free SCN group. With HCl, IIa gave the hydrochloride salt, IIIa, mp. 247°. IIa (or IIIa) with acetyl chloride in pyridine forms the acetyl derivative (IVa),mp. 165°. The IR spectrum of IVa showed two bands at 1640 cm^{-1} (MeCON=) and at 1650 cm^{-1} (PhCON=). Furthermore, IIa in glacial acetic acid gave with concentrated aqueous sodium nitrite solution the nitroso derivative

Va, mp. 136°. When heated in dry xylene, Va afforded 4-phenyl-2-benzoyl-1,3,4-thiadiazolin-5-one (VIa), mp. 113°. The IR spectrum of VIa showed two CO bands at 1650 cm^{-1} (PhCOC=) and at 1705 cm^{-1} (5-keto group). Boiling of Va with HCl gave the hydrochloride salt IIIa.

The structure of II was further confirmed by its alternate synthesis from VII. Thus, treatment of VIIa[4] with two equivalents of KSCN in ethanol at room temperature gave a product that analyzed correctly for $C_{15}H_{11}N_3OS$, mp. 90°, and proved to be identical in all respects (mp., m.mp., IR) with that of IIa prepared above. All 5-imino-Δ^2-1,3,4-thiadiazolines reported[5] were prepared from the hydrazidic chlorides (or bromides), PhC(Cl):NNHAr, and KSCN or thioure. As hydrazidic halides are limited by their general methods of preparation, namely halogenation of an aldehydic hydrazone or reaction of a hydrazide with phosphorus pentachloride[6], the reaction of diazonium salts with active methylene thiocyanates appears to be an efficient and rapid experimental procedure for synthesis of II.

A plausible reaction sequence is illustrated in scheme 1. Presumably, the reaction proceeds through the intermediary of the hydrazone VIII, which subsequently cyclizes to give II. The details of this reaction and its extension to other active methylene thiocyanates will be the subject of a future communication.

Scheme 1.



References:

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2. Taken in part from the Ph.D. Thesis of Mr. A.O. Abdelhamid, University of Cairo, 1974.
3. M. Parmerter, "Organic Reactions", (Ed. R. Adams), Vol. 10; chapter 1., p.4, Wiley & Sons, New York, N.Y., 1959.
4. F. Krollpfeiffer and H. Hartmann, Chem. Ber., 83, 90 (1950).
5. R. Fusco et al, Gazz. Chim. ital., 63, 3 (1937); ibid., 68, 59, 147, 665 (1938).
6. F. L. Scott, J. A. Cronin and J. Donovan, Tetrahedron Letters, 4615 (1969).