

Reactions with Hydrazonoyl Halides. Part 21. Reinvestigation of the Reactions of Hydrazonoyl Bromides with 1,1-Dicyanothioacetanilide

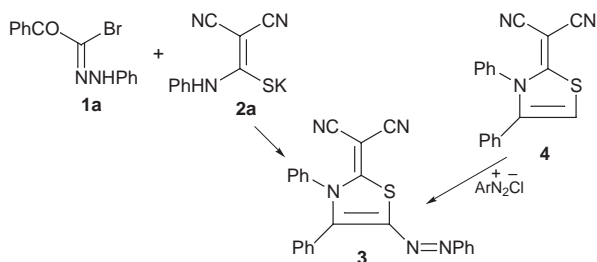
Abdou O. Abdelhamid,* Hussein F. Zohdi and Nora M. Rateb

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

J. Chem. Research (S),
1999, 184–185
J. Chem. Research (M),
1999, 0920–0932

The reaction of *C*-(benzoyl)-*N*-(phenyl)formohydrazonoyl bromide with 1,1-dicyanothioacetanilide was reinvestigated. The product was elucidated on the basis of elemental analysis, spectral data and alternative synthesis. Also, reaction of hydrazonoyl halides with different thioanilides were investigated.

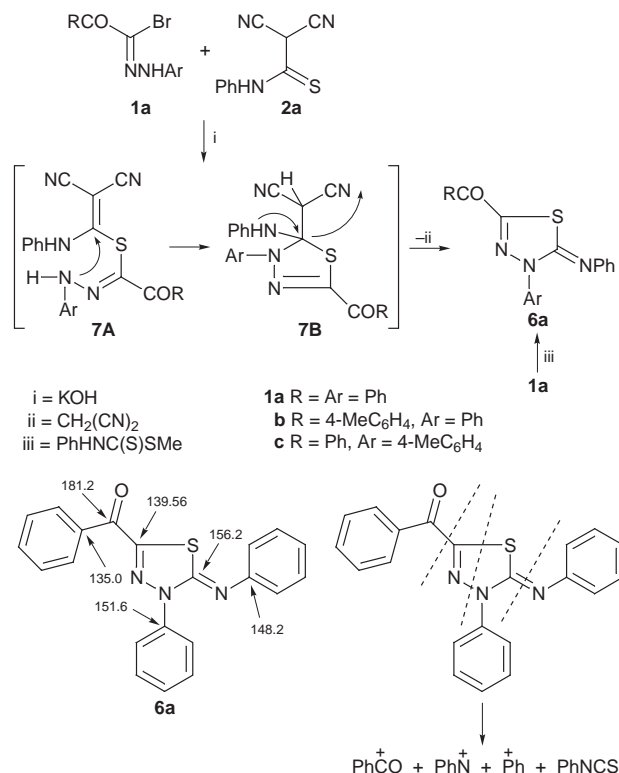
Recently an ambiguous product, namely, 2-(dicyanomethylene)-3,4-diphenyl-5-phenylazo- Δ^4 -1,3-thiazoline (**3**) was claimed² to be obtained by two different methods. One by the reaction of *C*-(benzoyl)-*N*-(phenyl)formohydrazonoyl bromide (**1a**) with the potassium salt of 1,1-dicyanothioacetanilide (**2a**) in dimethylformamide and the other by coupling of benzenediazonium chloride with 2-dicyanomethylene-3,4-diphenyl- Δ^4 -1,3-thiazoline (**4**) in ethanolic sodium acetate solution (Scheme 1). As reactions of hydrazonoyl halides with ketothioamides and substituted cyanothioanilides are expected to give 2,3-dihydro-1,3,4-thiadiazoles and thiazolinones depending on the reaction condition,^{3–5} the identity of the products from these reactions has been reinvestigated.



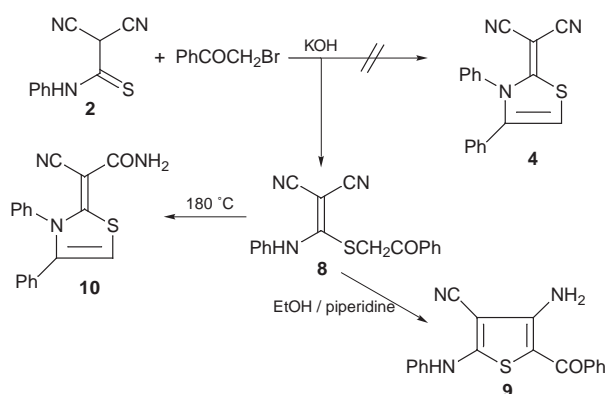
Scheme 1

Treatment of *C*-(benzoyl)-*N*-(phenyl)formohydrazonoyl bromide (**1a**) with the potassium salt of 1,1-dicyanothioacetanilide (**2a**) gave a product, which analytically, and in accord with data was 5-benzoyl-3-phenyl-2-phenylimino-2,3-dihydrothiadiazole (**6a**). The structure of **6a** was elucidated on the basis of spectral data (IR, ¹H NMR and ¹³C NMR) and authenticated *via* the reaction of hydrazonoyl bromide **1a** with methyl phenylthiocarbamate⁶ in ethanolic triethylamine (Scheme 2).

Also, thioamide **2a** reacted with ω -bromoacetophenone in dimethylformamide containing potassium hydroxide to give the acyclic product **8**, completely different from the reported² thiazoline **4** (Scheme 3).



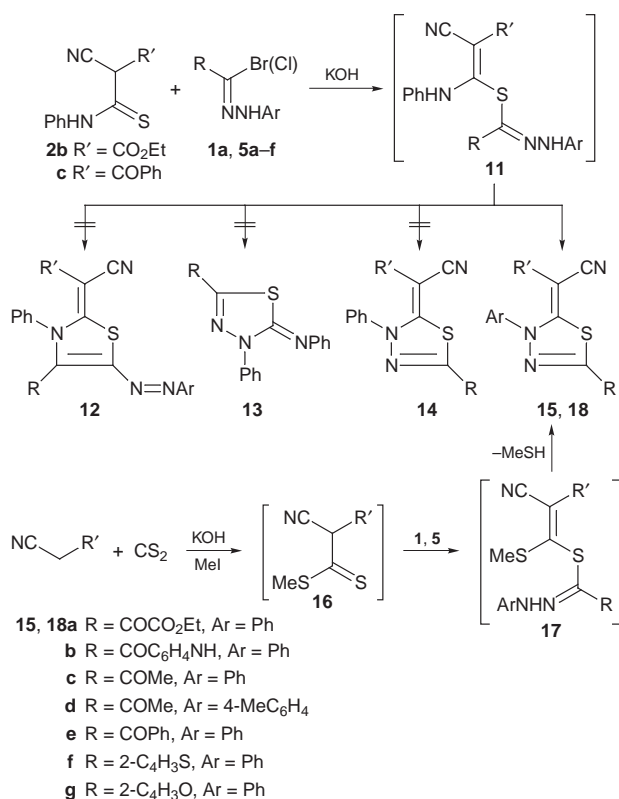
Scheme 2



Scheme 3

*To receive any correspondence.

In contrast, the thiomides **2b,c** reacted with hydrazonoyl halides **1** and **5a–g** to give products **15** and **18** (Scheme 4).

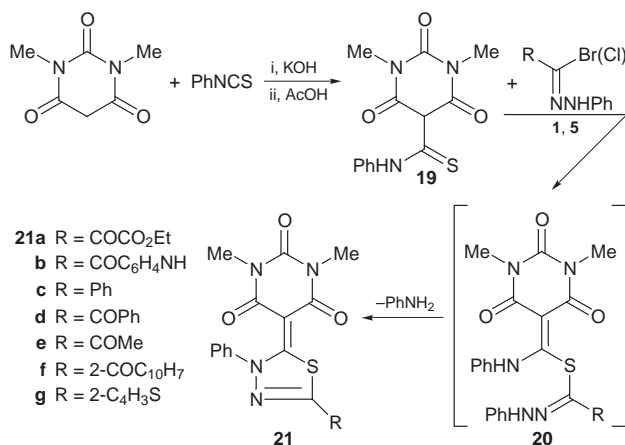


Scheme 4

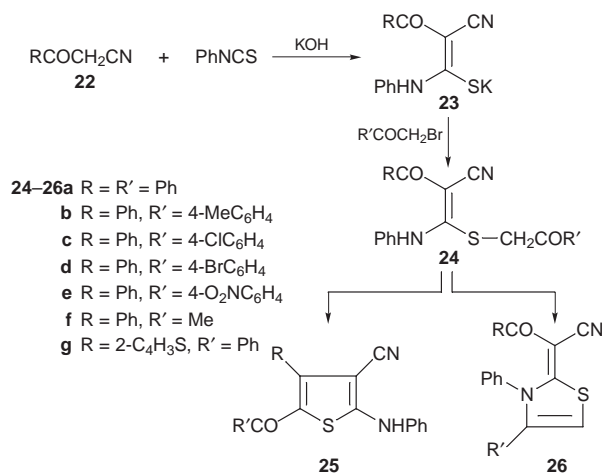
For example, compound **2b** reacted with *C*-(benzoyl)-*N*-(phenyl)formohydrazonoyl bromide (**1a**) in dimethylformamide to give the same product (mp, mixed mp, spectra) as that obtained by the reaction of (**1a**) with methyl (1-ethoxycarbonyl-1-cyano)ethanedithioate (**16**) in ethanolic triethylamine. On the basis of spectral data and elemental analyses, this product was formulated as 2-benzyl-5-(cyanoethoxycarbonylmethylene)-4-phenyl-2,3-dihydro-1,3,4-thiadiazole (**15a**). The formation of products **15a,b** is assumed to proceed through the reaction of **2b,c** with the hydrazonoyl halides **1**, **5a–g** to form acyclic intermediate **11** from which **15** is obtained *via* loss of aniline. An authentic sample **15** is obtained through the reaction of hydrazonoyl halides with methyl carbodithioate **16** (Scheme 4).

Furthermore, hydrazonoyl halides **1** and **5a–g** reacted with thioamide **19** in dimethylformamide containing potassium hydroxide to give 2,3-dihydrothiadiazoles **21a–g**, in good yield. The structure of the products was confirmed on the basis of elemental analyses and spectral data (Scheme 5).

It is noteworthy that Augusti *et al.* reported⁷ that aroylacetonitrile (**22**) reacted with phenyl isothiocyanate in dimethylformamide in the presence of sodium hydride to form an intermediate (not isolated) which reacted with α -haloketones to give 2-anilino-4-phenyl-5-substituted-3-thiophenecarbonitrile (**25**). When the reaction was repeated in the presence of potassium hydroxide instead of sodium hydride the acyclic compound (**24**) was isolated (Scheme 6). Compounds **24** were converted to thiophenes **25** (by boiling in ethanolic triethylamine) and thiazoles **26** (by conc. sulfuric acid at room temperature) (Scheme 6).



Scheme 5



Scheme 6

Techniques used: IR, ¹H NMR, ¹³C NMR and MS

Schemes: 6

Table 1: Physical constants and elemental analyses of new compounds

Table 2: Spectral data

References: 15

Received, 29th September 1998; Accepted, 2nd December 1998
 Paper E/8/07566B

References cited in this synopsis

- Part 20: H. F. Zohdi, N. A. Rateb, M. M. M. Sallam and A. O. Abdelhamid, *J. Chem. Res.*, 1998, (S) xxx; (M) xxx (E/8/02941E).
- R. M. Mohareb and S. M. Sherif, *Arch. Pharm. (Weinheim)*, 1991, **324**, 469.
- D. Pocar, L. M. Rossi and P. Trimaro, *J. Heterocycl. Chem.*, 1975, **12**, 401.
- H. M. Hassaneen, A. S. Shawali and T. A. Abdallah, *Sulfur Lett.*, 1992, **15**, 103.
- H. M. Hassaneen, A. E. Harhash, N. M. Abounada, T. A. Abdallah and M. S. Algharib, *J. Chem. Res. (S)*, 1993, 194.
- G. C. S. Pak, I. Youn and Y. S. Lee, *Synthesis*, 1982, 969.
- M. Augustin, W. D. Rudolf and U. Schmidt, *Tetrahedron*, 1976, **32**, 3055