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Reactions with Hydrazonoyl Halides. Part 20.[1] Synthesis of New Unsymmetrical Azines, Dihydro-1,3,4-thiadiazoles and 5-Arylazothiazoles

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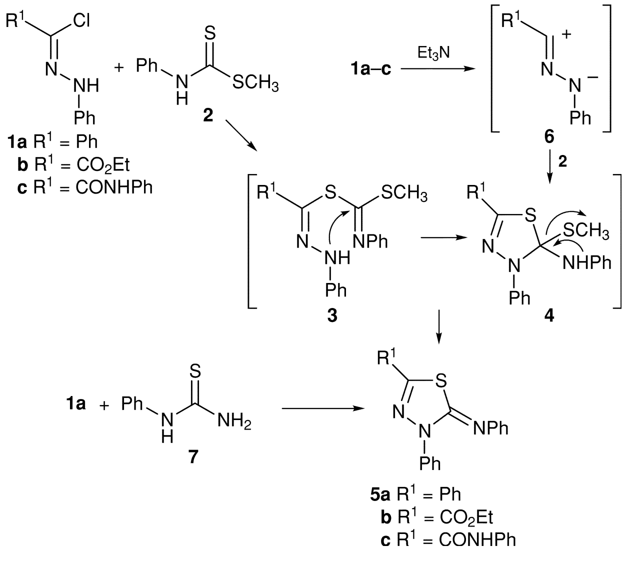
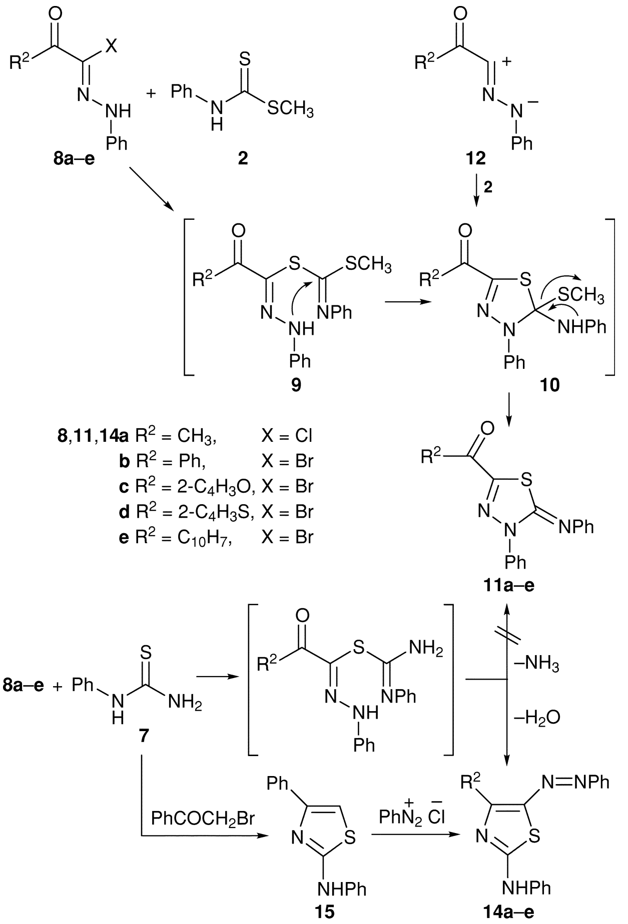
Unsymmetrical azines were obtained *via* the reaction of hydrazonoyl halides with methyl dithioate. Hydrazonoyl halides reacted with phenyldithiocarbamate and phenylthiourea to give 2-anilino-2,3-dihydro-1,3,4-thiadiazoles and 2-anilino-5-phenylazothiazoles depending on the hydrazonoyl halides used.

Hydrazonoyl halides have received considerable attention in the synthesis of heterocyclic compounds.[2] Unsymmetrical azines containing the thiadiazole ring have not been synthesized utilizing hydrazonoyl halides.[3,4]

Treatment of hydrazonoyl chlorides **1a**–**c** with methyl phenyldithiocarbamate (**2**) gave one isolable product in each case. The reaction of **1a** with phenylthiourea in boiling ethanol gave an identical product,[12] in all respects (mp, mixed mp and spectra), to that obtained before. Consequently, the product was identified as 3,5-diphenyl-2-*N*-phenylimino-2,3-dihydro-1,3,4-thiadiazole (**5a**). The product **5a** may result *via* elimination of methanethiol from the corresponding cycloadduct **4**, which is formed from the acyclic hydrazone **3** or may also be formed *via* 1,3-dipolar cycloaddition of the nitrile imide **6** to C=S of methyl dithiocarbamate **2** (Scheme 1). Similarly, the reaction of **1b**,**c** with **2** afforded **5b**,**c**, respectively. Also, the hydrazonoyl halides **8a**–**e** reacted with methyl phenyldithiocarbamate (**2**), in ethanolic triethylamine solution, to afford products which were formulated as 2,3-dihydro-1,3,4-thiadiazoles **11a**–**e** (Scheme 2). In contrast, the reaction of hydrazonoyl halides **8a**–**e** with phenylthiourea (**7**) in ethanolic triethylamine solution, at room temperature, afforded 5-phenylazothiazoles **14a**–**e**. Structure **14** was elucidated on the basis of elemental analyses, spectral data and by coupling benzenediazonium chloride with 2-anilinothiazoles (**15**).



Scheme 1



Scheme 2

Treatment of the appropriate hydrazonoyl chlorides **1a**,**c** and **8a**–**e** with methyl phenylhydrazinedithioate[16] **16** in ethanolic triethylamine solution afforded one isolable product in each case. On the basis of elemental analyses and spectral data, the product seemed to be formulated as 2,3-dihydro-2-phenylhydrazono-1,3,4-thiadiazoles **19a**,**c** and **20a**–**e**, respectively (Scheme 3). The formation of compounds **20a**–**e** is assumed to proceed *via* elimination of methanethiol from cycloadduct **18**, formed from 1,3-dipolar cycloaddition of nitrile imide intermediate **12** to C=S of **16**, or it can also be explained by a stepwise path involving substitution to afford the acyclic hydrazone **17** which readily cyclizes to give intermediate **18**, which subsequently eliminates methanethiol to give the final products (Scheme 3).

Treatment of **1a**–**c** with the appropriate methyl carbodithioate derivatives **22a**–**j** gave 2,3-dihydro-1,3,4-thiadiazole derivatives **25a**–**j**–**27a**–**j** (Scheme 4). The structure of compounds **25**–**27** was established on the basis of their elemental analyses, spectral data and independent synthesis. Also, the

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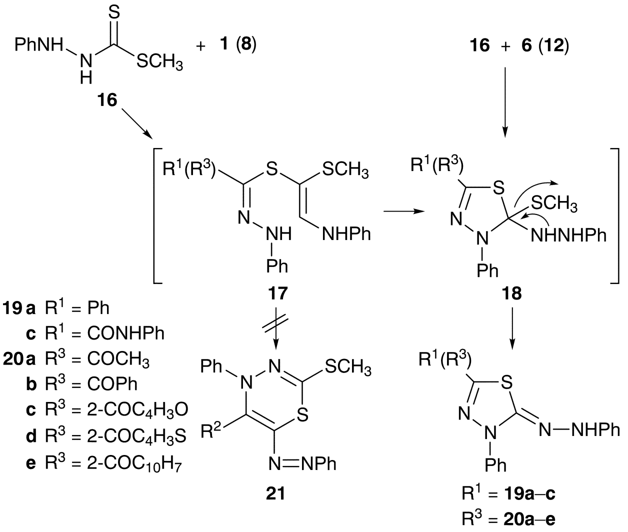


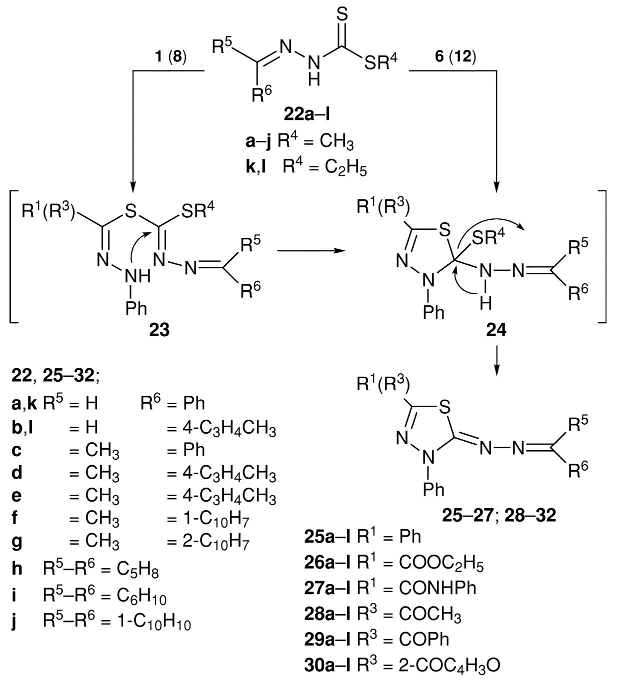
Scheme 3

hydrazonoyl halides **8a**–**e** reacted with the appropriate alkyl carbodithioate derivatives **22a**–**j** to produce 2,3-dihydro-1,3,4-thiadiazoles **28a**–**j**–**32a**–**j**, respectively.

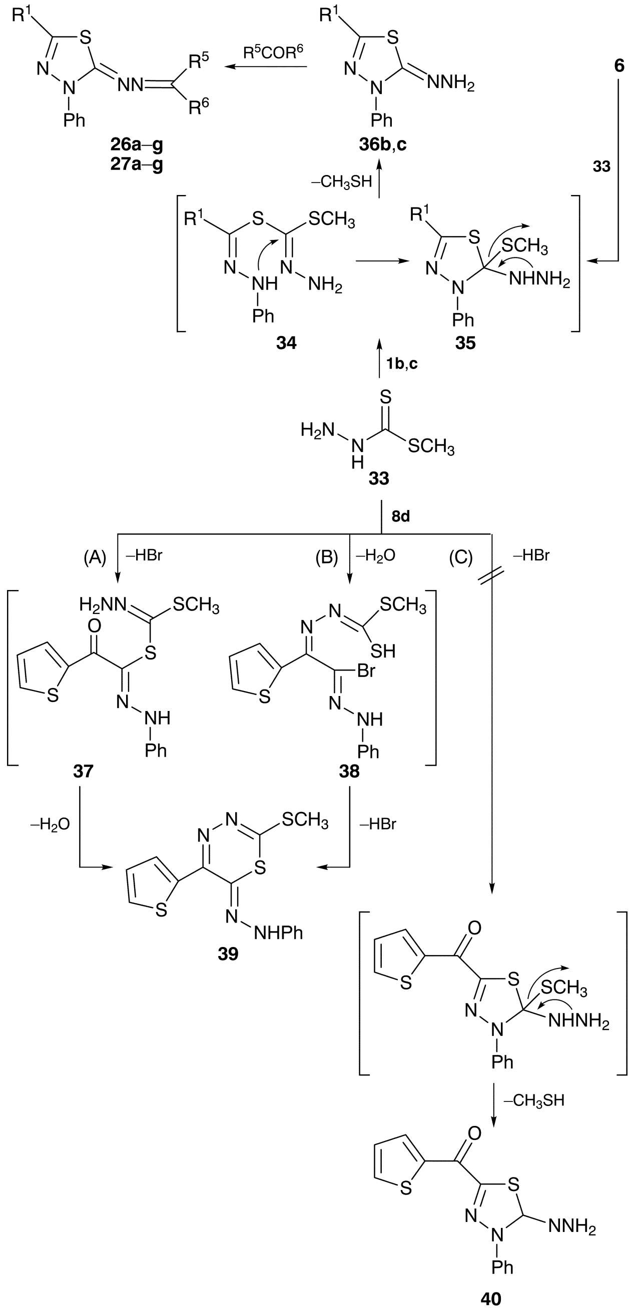
Treatment of methyl hydrazinedithioate (**33**) with hydrazonoyl chloride **1b**, in ethanolic triethylamine solution, gave one isolable product.

The product was formulated as 5-ethoxycarbonyl-2-hydrazono-2,3-dihydro-3-phenyl-1,3,4-thiadiazole (**36b**). Similarly, **1c** reacted with **33** to afford 2,3-dihydro-2-hydrazono-5-phenylcarbamoyl-3-phenyl-1,3,4-thiadiazole (**36c**). Unequivocal support for structure **27** was provided by the reaction of **36b**,**c** with the appropriate aldehyde or ketone, in ethanol, to give products identical in all respects (mp, mixed mp and spectra) with **26a**–**g** and **27a**–**g** obtained earlier (Scheme 5).

In contrast, the reaction of **8d** with methyl hydrazinedithioate (**33**) afforded 2-methylthio-6-phenylhydrazono-5-thienyl-1,3,4-thiadiazines **39** (Scheme 5).



Scheme 4



Scheme 5

Techniques used: IR, ^{1}H NMR and mass spectrometry

References: 29

Schemes: 5

Table 1: Characterization of the newly synthesized compounds

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