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Reactions with Hydrazonoyl Halides. Part XXV.[1] Synthesis of Some New 2,3-Dihydro-1,3,4-thiadiazoles and 5-Arylazothiazoles

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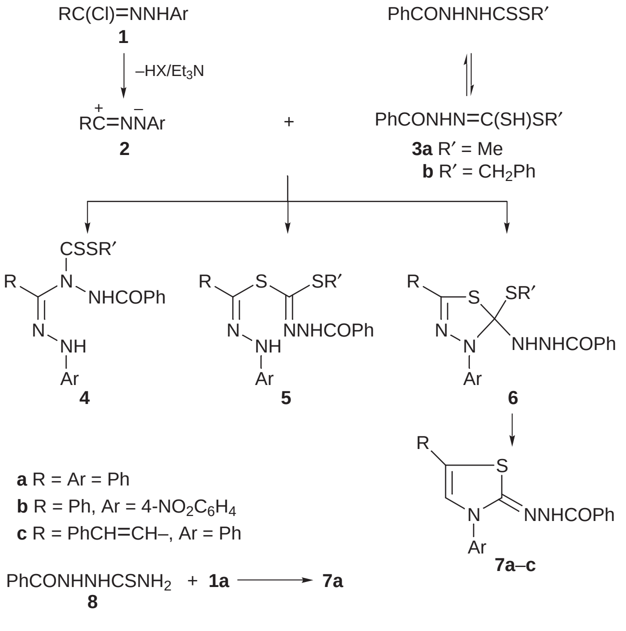
2,3-Dihydro-1,3,4-thiadiazoles are synthesized by the reaction of hydrazonoyl halides with alkyl benzoylhydrazinecarbodithioates in ethanolic triethylamine whereas α-keto hydrazonoyl halides react with benzoylthiosemicarbazides to afford 5-arylazothiazoles.

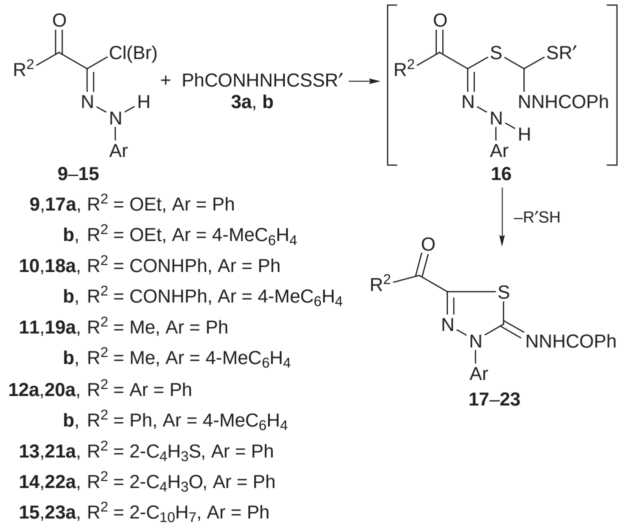
The reaction of nitrile imides **2** with alkyl benzoylhydrazinecarbodithioates **3** was carried out in ethanol at room temperature in the presence of triethylamine. TLC indicated that only one product was formed in each case. The isolation products proved to be 2,3-dihydro-1,3,4-thiadiazoles **7** on the basis of elemental analysis, spectral data and alternative synthesis[6] (Scheme 1).



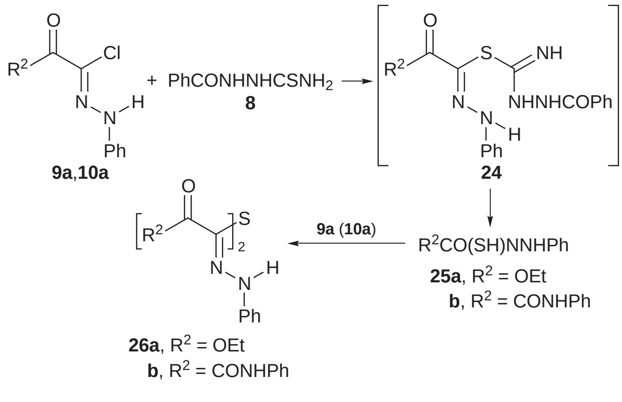
Scheme 1

Two possible pathways can account for the formation of **7**. 1,3-Addition of **2** to the thiol tautomer of **3** can give the thiohydrazonate ester **5**, which undergoes nucleophilic cyclization to yield **6**. Alternatively, 1,3-cycloaddition of nitrile imide **2** to C=S tautomer **3** can give **6** directly. The elimination of MeSH (or $PhCH_2SH$) from intermediate **6** leads the end product **7**. α-Keto hydrazonoyl halides **9**–**15** reacted with alkyl benzoylhydrazinecarbodithioates **3a**,**b** in ethanolic triethylamine to afford a single product in each case (TLC). The structures of the products were confirmed on the basis of elemental analyses, spectral data and formulated as 3-aroyl-2-benzoylhydrazono-5-substituted 2,3-dihydro-1,3,4-thiadiazoles **17**–**23** (Scheme 2).

On the other hand, hydrazonoyl chlorides **9a** and **10a** reacted with benzoylthiosemicarbazide **8** in ethanolic triethylamine gave two products in each case (Scheme 3). The first product was assigned as a C-substituted *N*-phenylhydrazonoyl sulfide **26** and the second products as a C-substituted-*N*-phenylhydrazonoyl bisulfide **25** (Scheme 3).



Scheme 2



Scheme 3

By contrast, α-ketohydrazonoyl halides **11a**–**15a** reacted with **8** in ethanolic triethylamine to give, in each case, one product (TLC) which was assigned as a 5-phenylazothiazole **28**. The reaction is believed to take place *via* formation of an intermediate **27**(**A**,**B**), which readily loses one molecule of water to afford **28**. Further proof for thiazole structure **28** was provided by independent synthesis (*via* treatment of benzenediazonium chloride with the thiazoles[9] **29a**,**b** in ethanolic sodium acetate solution)

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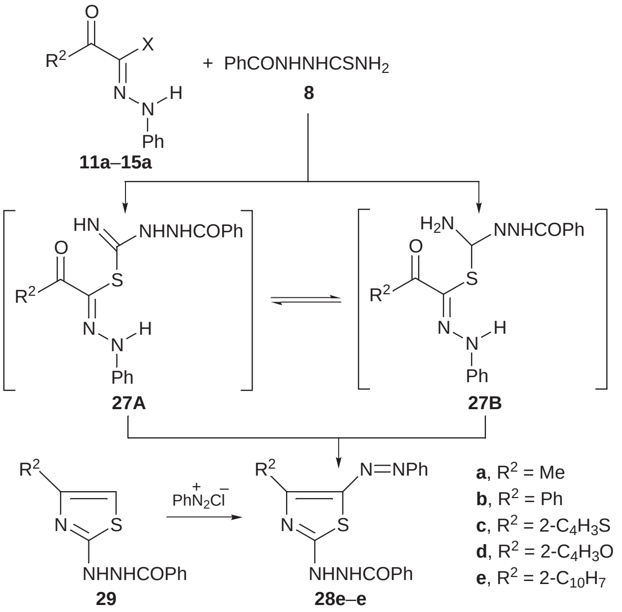
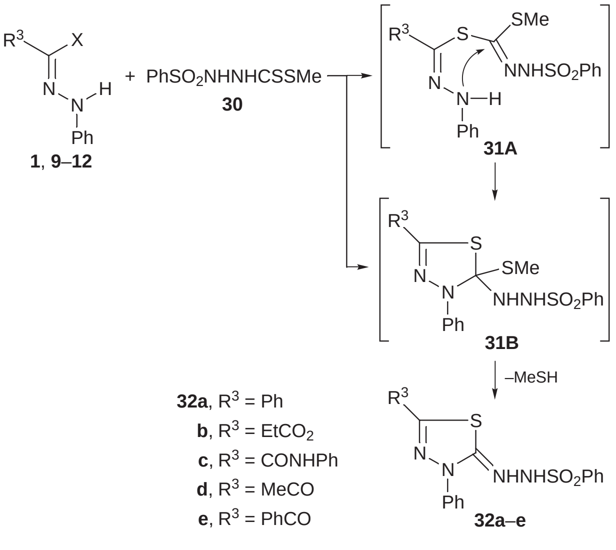
which afforded compounds **28a** and **28b**, respectively (Scheme 4).



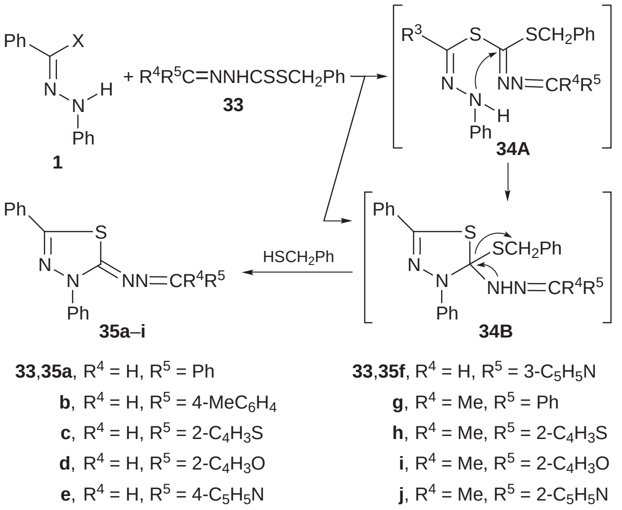
Scheme 4

Hydrazonyl halides **1** and **9**–**15** reacted with methyl benzenesulfonylhydrazinecarbodithioate **30** in ethanolic triethylamine at room temperature to afford 2,3-dihydro-1,3,4-thiadiazole derivatives **32a**–**h** respectively.The formation of **32** can be explained *via* elimination of MeSH from the corresponding cycloadduct **31B**, which is assumed to be formed from the 1,3-dipolar cycloaddition of nitrile imides to the C=S double bond in **30**. Alternatively, the formation of **32** can also explained by a stepwise pathway involving substitution to give acyclic hydrazone **31A**. The intermediate is readily converted to **32** *via* elimination of MeSH from **31B** (Scheme 5).



Scheme 5

It should be noted that hydrazonoyl chloride **1** reacted with benzyl carbodithioate derivatives **33a-j** in ethanolic triethylamine to afford 2,3-dihydro-1,3,4-thiadiazoles **35a**,**j**, respectively (Scheme 6). The products obtained are identical in all respects (mp, mixed mp and spectra) with corresponding authentic samples.[10–12] The reaction is believed to take place *via* the intermediate formation of **34A** or **34B**, that readily loses one molecule of $PhCH_2SH$.



Scheme 6

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

References: 23

Tables: 2

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