

A facile one step synthesis of 3-[2-(3,5-dimethyl-1H-pyrazol-1-yl)-4-thiazolyl]-2H-1-benzopyran-2-ones under solvent free conditions

V. Rajeswar Rao* and K. Srimanth

Department of Chemistry, Regional Engineering College, Warangal – 506 004, India

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Reaction of 3-(2-bromoacetyl)coumarins with thiosemicarbazide and acetylacetone gave 3-[2-(3,5-dimethyl-1H-pyrazol-1-yl)-4-thiazolyl]-coumarins in good yields.

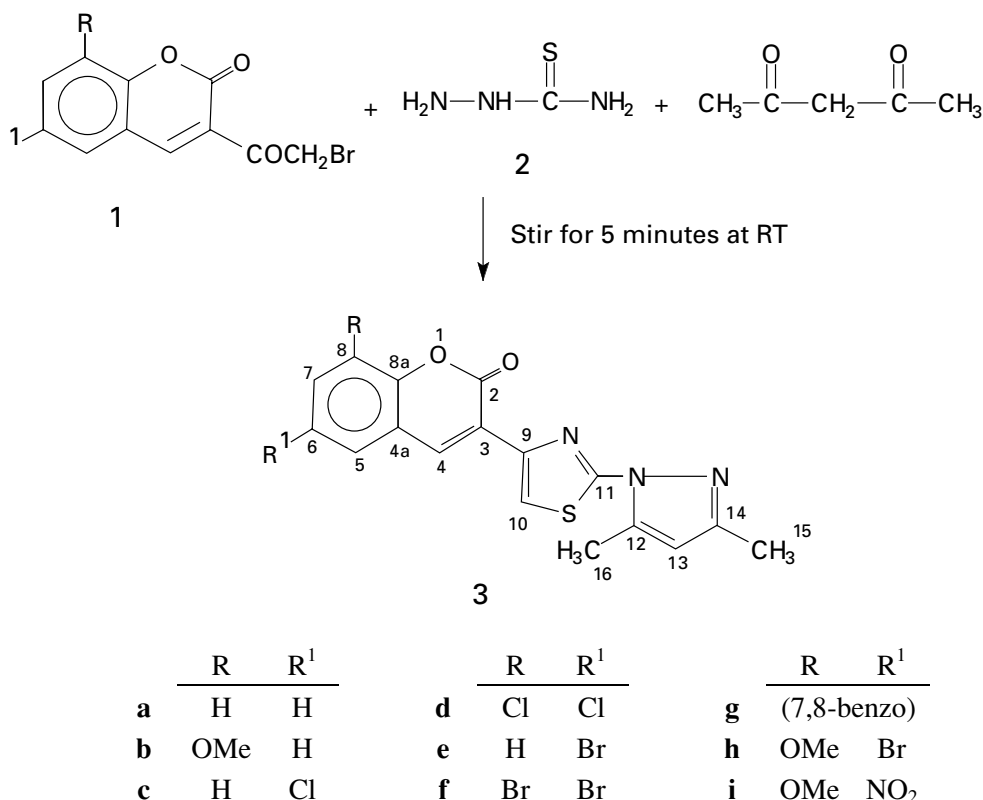
Keywords: thiazoles, pyrazoles, coumarins, solvent-free reactions

In recent years organic reactions in the absence of solvent have been attracting the synthetic organic chemists because of their simplicity and synthetic value.^{1–3} A literature survey revealed that thiazoles are generally synthesised by Hantzsch thiazole synthesis from α -halogenoketones and thioureas and thioamides.⁴ Later King *et al.*^{5,6} and other workers⁷ synthesised aminothiazoles by replacing α -halogenoketones with ketone and halogen. Despite this modification the method still remains cumbersome and time-consuming^{8a,b} (24–25hr reflux). In continuation of our earlier work on the synthesis of heterocyclic systems derived from coumarin, we report herein the facile one pot synthesis of 3-[2-(3,5-dimethyl-1H-pyrazol-1-yl)-4-thiazolyl]-2H-1-benzopyran-2-one (**3**) in a single step from easily available starting materials 3-(2-bromoacetyl) coumarin, thiosemicarbazide and acetylacetone.

We report herein for the first time the Hantzsch thiazole synthesis and simultaneous formation of pyrazole in the absence of solvent at room temperature. The procedure involves shaking of an equimolar mixture of 3-(2-bromoacetyl)coumarin and thiosemicarbazide in acetylacetone for 5 minutes at ambient temperature (Scheme 1). The yields of the products are good (80–90%).

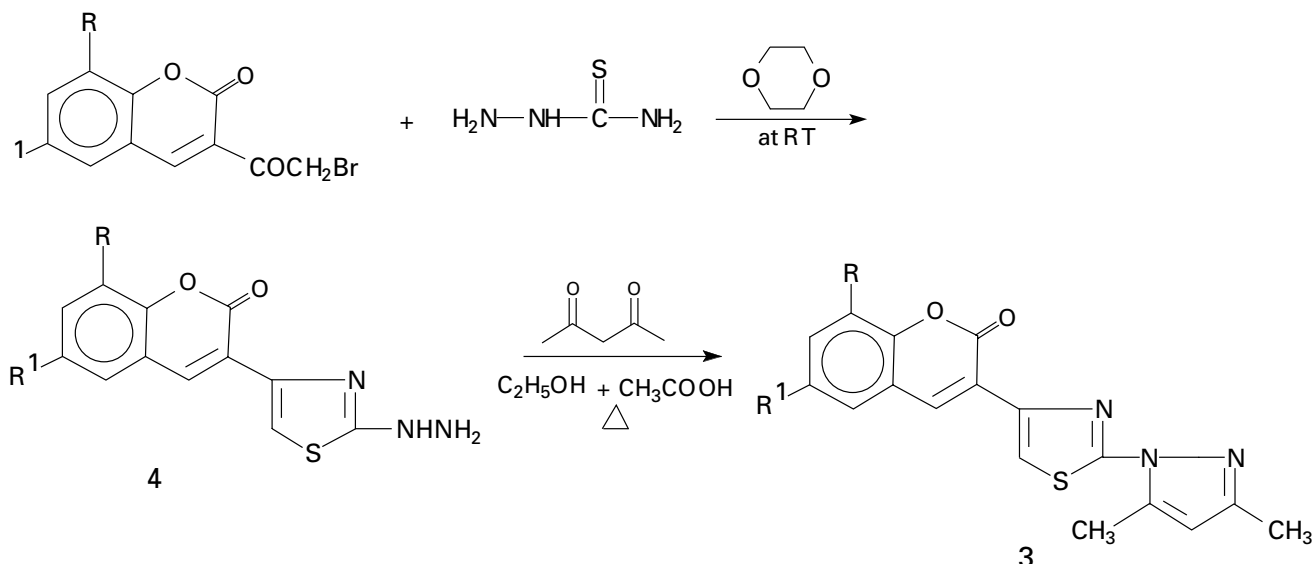
The compounds **3** can also be synthesised by alternative method involving condensation of 3-(2-bromoacetyl) coumarin^{9a,b} with thiosemicarbazide in dioxan to yield the corresponding 3-(2-hydrazino-4-thiazolyl)coumarins¹⁰ (**4**). These on reaction with acetylacetone in presence of traces of acetic acid resulted in the formation of **3** (Scheme 2).

The IR spectra of compounds **3** showed prominent peaks at 1270 cm^{-1} (C–S), 1600 cm^{-1} (C=N) and 1720 cm^{-1} (lactone carbonyl), which indicate the formation of compounds **3**. The



Scheme 1

* To receive any correspondence. E-mail: vrayw@recw.ernet.in, srimanthk@rediffmail.com



For specification of R and R¹ see Scheme 1

Scheme 2

¹H NMR (CDCl_3) spectrum of **3a** (R = R¹ = H) showed signals at δ 2.30 (s, C₃-methyl), 2.8 (s, 3H, C₅ methyl), 6.0 (s, 1H, pyrazole proton), 8.2 (s, 1H, C_{5'} of thiazole) confirms the same. The mass spectral analysis (70 eV EI) recorded the molecular ion for **3a** at 323 (100%). The molecular ion under electron impact readily loses CO and methyl cyanide to yield (M – 28)⁺ and (M – 41)⁺ peaks respectively. All the compounds were characterised by their spectral data and elemental analyses.

The IR spectra of compounds **4** showed prominent peaks at 3100 and 3315 cm^{-1} (NH-NH₂). The exchangeable (D_2O) NH and NH₂ appeared at δ 10.0 and 10.6 respectively in the NMR. The mass spectrum of **4a** gave the molecular ion at m/z 259. The structures of all the compounds were consistent with their spectral data and elemental analyses.

Techniques used: ¹³C and ¹H NMR, Mass spectrometry, IR

References: 9

Schemes: 2

Table: yields, melting points, elemental analysis of compounds **3a-i** and **4a-i**.

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