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Mendeleev Commun., 1993, **3(1)**, 15–16
Mendeleev Communications

Synthesis of 4-Arylsulfonyl-1,2,4-triazolidine-3-thiones

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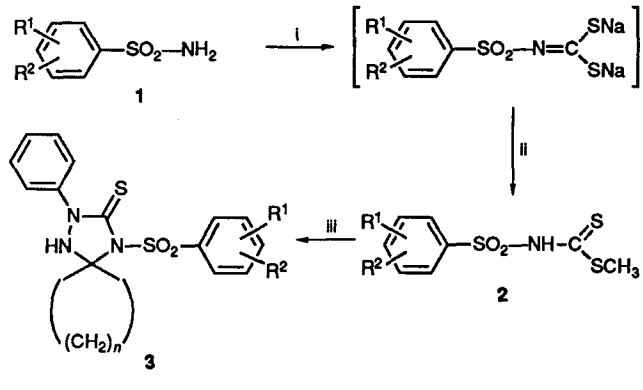
A convenient method is described for the synthesis of the title compounds from phenylhydrazones and arylsulfonyldithiocarbamic acid esters in a one-pot reaction.

The synthesis of 1,2,4-triazolidine-3-thiones by addition of isothiocyanates to hydrazones is well known. N-4 Unsubstituted triazolidinethiones are obtained by the reaction of hydrazones with isothiocyanic acid.[1–6] Alkyl-, aryl- and heteroaryl-isothiocyanates add to phenylhydrazine to give the corresponding 4-substituted triazolidine-3-thiones.[7–10] Little is known regarding the synthesis of 4-acyltriazolidinethiones.[11]

We were able to synthesize 4-arylsulfonyl-1,2,4-triazolidine-3-thiones **3** from phenylhydrazones and arylsulfonyldithiocarbamic acid esters **2**† in a one-pot reaction with arylsulfonylisothiocyanates as intermediates.



R^1 = H, 4-CH_3, 5-CH_3; R^2 = H, 2-CH_3, 2-OCH_3; n = 3,4

Scheme 1 *Reagents and conditions:* i, NaH, CS_2, room temp., in DMF, -2 H_2; ii, 1. CH_3I, in DMF, 2. H_2O, conc. HCl; iii, 1. $C_6H_5NHNH_2$, cycloalkanone, 1 h, 78 °C, in ethanol 2. +**2**, 3 h, 110 °C, in toluene

† *Selected physical data:* **2** ($R^1 = R^2 = H$) m.p. 94–95 °C; ($R^1 = 2$-CH_3, $R^2 = 5$-CH_3) m.p. 80 °C; ($R^1 = 4$-CH_3, $R^2 = H$) m.p. 114–115 °C; ($R^1 = 2$-OCH_3, $R^2 = 5$-CH_3) m.p. 146–148 °C. **3** ($R^1 = 4$-CH_3, $R^2 = H$) m.p. 199 °C; δ_H ($CDCl_3$) ppm = 1.6–2.0 (m, 10H, —CH_2—), 2.38 (s, 3H, —CH_3), 5.1 (s, 1H, NH) and 7.2–7.8 (m, 9H, aryl); δ_C ($CDCl_3$) ppm = 21.53; 23.44; 25.09; 36.08 (—CH_2—); 122.95; 126.96; 128.66; 129.20; 138.88; 139.75; 142.81 (aryl); and 167.66 (CS); m/z = 481 (15, M^+), 188(100), 171(50), 154(28) and 143(65).

The carbamic acid esters **2** can be easily obtained from the sulfonamides **1** with the dithiocarbamates as unisolated intermediates.[12] The esters **2** were refluxed with a mixture of cyclohexanone and phenylhydrazine in toluene until the evolution of methanethiol had ceased.

The triazolidinethiones **3** crystallise as colourless solids from ethanol. Their structures were determined by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy† including elemental analysis.‡ In the ^{1}H NMR spectra of the triazolidinethiones **3** the N—H group appears as a singlet at $\delta = 4.5$–5.1 ppm, and this shows that compounds **3** can not be the cyclohexanone thiosemicarbazones (N—H at 7–8 ppm). In addition, the band at $\delta = 167$ ppm for the thiocarbonyl carbon in the ^{13}C NMR spectrum rules out the isomeric 1,3,4-thiadiazolidine imine.

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‡ Satisfactory elemental analyses were obtained for all new compounds.

Received: Cambridge, 27th July 1992
Moscow, 21st September 1992; Com. 2/03992C