

Trapping of Thiaziridinimines with Thiocarbonyl Compounds

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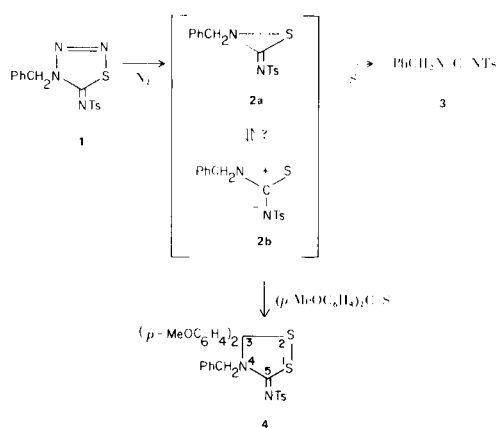
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Thermolysis of 4-benzyl-5-tosylimino-1,2,3,4-thiaziazoline at 60-70° in the presence of representative C=S unsaturated compounds furnished 1,2,4-dithiazolidin-5-imines in moderate yields. The reaction is assumed to proceed *via* the intermediacy of an unstable thiaziridinimine which is trapped by the C=S compound in a regiospecific manner. Among the thiocarbonyl compounds used are *p,p'*-dimethoxythiobenzophenone, xanthates and 3-benzylrhodanine, the latter giving rise to a spiro adduct.

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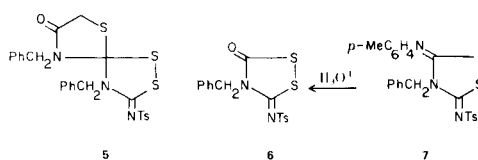
4-Alkyl-5-sulfonyl-1,2,3,4-thiaziazolines (*e.g.*, **1**) were conveniently prepared by 1,3-dipolar cycloaddition reactions of alkyl azides with sulfonyl isothiocyanates (1). Upon thermolysis, they were converted to sulfonylcarbo-diimides (*e.g.*, **3**) by loss of nitrogen and sulfur. A thiaziridinimine (**2a**) or its ring-opened 1,3-dipolar species (**2b**) was postulated as intermediate in this reaction, since it has been trapped with olefins, acetylenes and heterocumulenes (1,2).



We now want to report that the presumed thiaziridinimines are also intercepted with thiocarbonyl compounds, leading to 5-sulfonylimino-1,2,4-dithiazolidines. Thus, thermolysis of **1** at 60-70° for 4 hours in the presence of *p,p'*-dimethoxythiobenzophenone resulted in the formation of **4** in 56% yield. This compound showed a typical C=N stretching vibration at 1510 cm^{-1} in the ir spectrum (3),

and further ^1H and ^{13}C nmr absorptions consistent with its structure. The presence of an important fragment ion peak at m/e 331 (30%) for $[(\text{MeOC}_6\text{H}_4)_2\text{C}=\text{NCH}_2\text{Ph}]^+$ in the mass spectrum provides evidence for the assigned regiochemistry of the reaction.

Other thiocarbonyl compounds were also used successfully in this work. For instance, 3-benzylrhodanine furnished adduct **5** (50%) and xanthates yielded 4-benzyl-5-tosylimino-1,2,4-dithiazolidin-3-one (**6**, 21-27%) when heated with **1** in an inert solvent. In the latter case sulfide was eliminated from the initial adduct under the reaction conditions. Structure elucidation of **6** was based on spectral analysis and further confirmed by acid hydrolysis of 3-tosylimino-4-benzyl-5-tosylimino-1,2,4-dithiazolidine (**7**) (2). Since **6** is formally the COS adduct of **2**, trapping experiments were also carried out with carbon disulfide, however without success.



EXPERIMENTAL

Reaction of **1** with *p,p'*-Dimethoxythiobenzophenone.

Equimolar amounts (0.01 mole) of **1** (m.p. 101-103° dec.) (1) and the thioketone were heated in dry benzene (40 ml.) at 60° for two hours, then at 70° for another two hours. After removal of the solvent, the residue was triturated with ether (40 ml.) to

give 2.7 g. of adduct **4**. Further cooling of the solution yielded another 0.5 g., overall yield, 56%, m.p. 192-193° (methanol); ir (potassium bromide): 1510 cm^{-1} (C=NTs); ^1H nmr (deuteriochloroform): δ 2.42 (s, 3 H, *p*-Me), 3.72 (s, 6 H, *p*-MeO), 4.56 (s, 2 H, benzyl CH_2) and 6.4-7.8 (m, 17 H); ^{13}C nmr (deuteriochloroform): δ 52.5 (Ph CH_2), 87 (ring carbon at position 3), 167.9 (ring carbon at position 5); mass spectrum; *m/e* (%) 576 (0.5, M^+), 331 (30), 91 (100).

Anal. Calcd. for M^+ (determined by high-resolution exact-mass measurements): 576.121110. Found: 576.118992.

Reaction of **1** with 3-Benzylrhodanine.

Compound **1** (3.46 g., 0.01 mole) and 0.015 mole (3.35 g.) of 3-benzylrhodanine (**4**) were dissolved in dry benzene (30 ml.) and the solution was then heated at 65° for two hours. After removal of the solvent *in vacuo*, the residue was crystallized from dry carbon tetrachloride (30 ml.) at -15° to give adduct **5** in 50% yield, m.p. 166-167° (chloroform-carbon tetrachloride); ir (potassium bromide): 1700, 1510 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.38 (s, 3 H, *p*-Me), 3.86 (s, 2 H, ring CH_2), 3.78 and 4.08 (AB quartet, 2 H, *J* = 16 Hz), 4.29 and 4.97 (AB quartet, 2 H, *J* = 14 Hz) and 6.8-7.6 (m); ^{13}C nmr (deuteriochloroform): δ 33.4 (ring CH_2), 97 (ring carbon at position 3), 164.3 (ring carbon at position 5), 168.2 (C=O).

Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_3\text{S}_4$ (541): C, 55.45; H, 4.25; N, 7.77. Found: C, 55.27; H, 4.40; N, 7.43.

Reactions of **1** with Xanthates.

Compound **1** (0.01 mole) was thermolyzed at 65° in the presence of a tenfold excess of dimethyl xanthate or diethyl xanthate. After a reaction time of 5 hours, the excess of xanthate was distilled off *in vacuo* (at 22°/0.8 Torr for dimethyl xanthate

and at 65°/0.5 Torr for diethyl xanthate). Crystallization of the residue from dry ether (15 ml.) furnished **6** in 21-27% yield, m.p. 166-167° (methanol); ir (potassium bromide): 1700, 1510 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.36 (s, 3 H, *p*-Me), 4.9 (s, 2 H, benzyl CH_2) and 7.0-7.8 (m, 9 H); ^{13}C nmr (deuteriochloroform): δ 51.5 (Ph CH_2), 164.5 (ring carbon at position 5), 169.3 (ring carbon at position 3); Mass spectrum; M^+ at *m/e* 378.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3\text{S}_3$ (378): C, 50.79; H, 3.70; N, 7.41. Found: C, 50.77; H, 3.80; N, 7.38.

For the independent synthesis of **6**, 1 g. of compound **7** and 10 ml. of sulfuric acid were heated in ethanol (40 ml.) at reflux temperature for 2 hours. The solution was then cooled to room temperature and diluted with water (200 ml.). The precipitate (**6**) was filtered off, washed with water and dried, yield 92.5%. This compound was identical in all respects with that obtained from **1** and the xanthates.

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