1,3,4-Thiadiazolinethiones

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Yields of 1,3,4-thiadiazolinethiones are trebled by recrystallizing the crude products from solvent containing mercaptoethanol.

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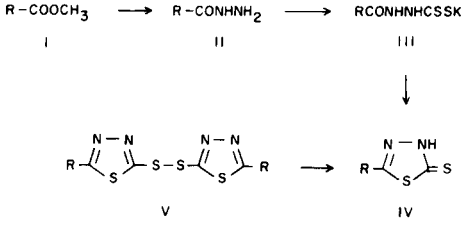
A convenient synthesis of 1,3,4-thiadiazoline-2-thiones IV comprises conversion of an ester I *via* the acid hydrazide II into the carbazate salt III [1] which cyclises in cold concentrated sulfuric acid [2] to produce the desired heterocycle. Yields in the first two steps are excellent, but the approach is marred by poor yields in the third step, typically about 30% at best and much less if the carbazate is not freshly prepared or if the temperature is allowed to rise during the cyclization [2]. The rest of the product is the disulfide V of the tautomeric 2-mercapto-1,3,4-thiadiazole, and we find that isolated yields of the pure title compounds may be raised to 85-90% simply by recrystallizing the crude product mixture from solvent containing mercaptoethanol.



EXPERIMENTAL

The preparation of 2-*p*-chlorophenyl-1,3,4-thiadiazoline-5-thione is typical. Finely powdered potassium *p*-chlorophenyldithiocarbazate (III, R = *p*-chlorophenyl, 60 g, 0.21 mole, prepared as described by Hoggarth [1b] but not recrystallized) was added portion-wise to well-stirred ice-cooled concentrated sulfuric acid (250 ml) as described by Baron and Wilson [2] the temperature being kept below 10°.

The solution obtained was poured into crushed ice (2 liters), stirred 1 hour, and the granular precipitate filtered, washed thoroughly with water and allowed to dry in air overnight. The crude product mixture [3] was taken up in boiling 95% ethanol (500 ml) containing mercaptoethanol (40 ml), the solution cooled somewhat (~60°), filtered from a little insoluble material, reheated to boiling, diluted with hot water (150 ml) and allowed to cool. The product which crystallized (38.0 g, 79%) had mp 209-211° (lit [2] 210-212°). A further crop (2.9 g, 6%), mp also 209-211°, was obtained by diluting the mother liquor with hot water (200 ml) and chilling in ice.

Acknowledgement.

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REFERENCES AND NOTES

[1a] M. Busch and M. Stark, *J. Prakt. Chem.*, **93**, 49 (1916); [b] E. Hoggarth, *J. Chem. Soc.*, 4811 (1952).

[2] M. Baron and C. V. Wilson, *J. Org. Chem.*, **23**, 1021 (1958).

[3] Still slightly damp, the crude product is a 1:2 mixture of thione IV and disulfide V. Both substances dissolve in hot 50% ethanol and they crystallize together on cooling, but the former is freely soluble in warm 95% or absolute ethanol whereas the latter is practically insoluble even at the boiling point.