One-step Synthesis of Oxazolidine-2-thiones in Dimethyl Sulphoxide

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Summary The Knorr reaction when conducted in an aprotic polar solvent provides a new route to oxazolidine-2-thiones.

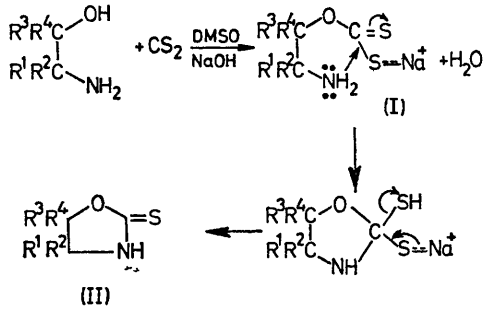
REACTION of α-amino-alcohols with carbon disulphide in basic aqueous or alcoholic media is known[1] to give either an oxazolidine-2-thione or a thiazolidine-2-thione depending on the structure of the amino-alcohol.[2] The route taken by the reaction in aqueous KOH in refluxing CS_2 is constrained by the steric requirements of the carbon bearing the hydroxy-group. Thus primary alcohols react to give thiazolidine-2-thiones, whereas amino-alcohols with a sterically hindered hydroxy-group give oxazolidine-2-thione.

Amino-alcohol	R^1	R^2	R^3	R^4	M.p.	Yield
$CH_2OH{\cdot}CH_2NH_2$ ..	H	H	H	H	99°	82%
$MeCH(OH){\cdot}CH_2NH_2$ ..	H	H	H	Me	74°	93%
$Me_2C(OH){\cdot}CH_2NH_2$ ..	H	H	Me	Me	109°	94%
$CH_2OH{\cdot}CH(NH_2)Me$ ..	H	Me	H	H	76°	72%
$CH_2OH{\cdot}C(NH_2)_2Me$ ..	Me	Me	H	H	123°	74%

We report that by conducting the reaction in an aprotic polar solvent a very extensive acceleration of the xanthate (I) formation is observed (Scheme).†

A representative procedure for the preparation of an oxazolidine-2-thione is given as follows.

To 150 ml of anhydrous DMSO, containing a small amount of KOH powder (or $NaNH_2$), 0·05 mol of ethanolamine was added with stirring, temperature <11°, followed by addition of the stoicheiometric amount of carbon disulphide.



SCHEME

The reaction mixture was then heated (50°, 2 h). The disappearance of (I) (λ_{max} 292 nm) and the appearance of (II) (λ_{max} 245, 345 nm) were followed by u.v. spectra and t.l.c. The solvent was then removed and the oxazolidine-2-thione was recrystallised from cyclohexane–benzene. Other amino-alcohols used are shown in the Table.

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† An alternative one-step synthesis has been described but the yields are lower (N. Somerville and C. Anderson, *J. Org. Chem.*, 1960, **25**, 656.)

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[2] M. G. Ettlinger, *J. Amer. Chem. Soc.*, 1950, **72**, 4792; J. C. Crawhall and D. F. Elliot, *J. Chem. Soc.*, 1952, 3094.