Synthesis of Annelated 1,3,4,6-Thiatriazepines from Dichlorodiazabutadienes and Cyclic Thioureas

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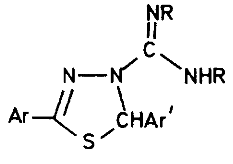
Summary Treatment of 1,4-dichlorodiphenyl-2,3-diazabutadiene (**2**) with the sodium salts of cyclic thioureas has yielded the first examples of a new type of seven-membered heterocycle, annelated 1,3,4,6-thiatriazepines.

As previously reported,[1] chloro-2,3-diazabutadienes ($\mathrm{ArCCl{=}NN{=}CHAr'}$) react with acyclic thioureas to form the hydrochlorides of 4-amidino-Δ^2-1,3,4-thiadiazolines (**1**), a conversion which has since been extended to cyclic thioureas without unexpected results.[2]

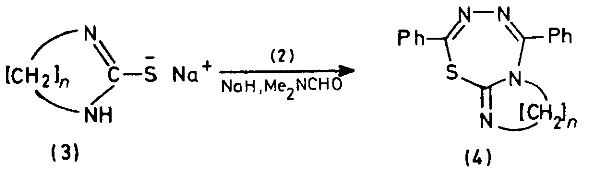


(1)

$\mathrm{PhCCl{=}NN{=}CClPh}$

(2)

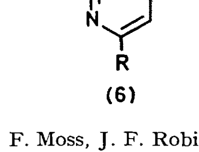
When 1,4-dichloro-1,4-diphenyl-2,3-diazabutadiene (**2**) is treated with thiourea alone,[3] or in the presence of triethylamine, only 2,5-diphenyl-1,3,4-thiadiazole is obtained. However, during further study of this type of reaction we treated (**2**) with the sodium salt of ethylenethiourea (**3**, n = 2), and observed the formation of a pale yellow product, the yield of which was maximised at 35% by ensuring that a one-molar excess of sodium hydride was initially present. The solid, m.p. 177—179 °C (decomp.) has been identified as 7,8-dihydro-2,5-diphenylimidazo[1,2-*f*]-1,3,4,6-thiatriazepine (**4**, n = 2) on the basis of (i) n.m.r. resonances (^{1}H δ 3·78, ^{13}C δ 47·9 and 53·0 p.p.m., the latter two appearing as triplets in the off-resonance spectrum) characteristic of an *S,N*-disubstituted ethyleneisothiourea; (ii) three ^{13}C n.m.r. resonances (at δ 143·9, 147·2, and 159·0 p.p.m., singlets in the off-resonance spectrum) due to sp^2-hybridised carbons in C=N bonds; (iii) mass spectrometric and elemental analyses; and *X*-ray crystallographic analysis, details of which will be published separately.[4]



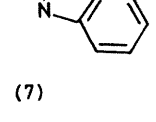
(3) (4)

(n = 2 or 3)

(5)



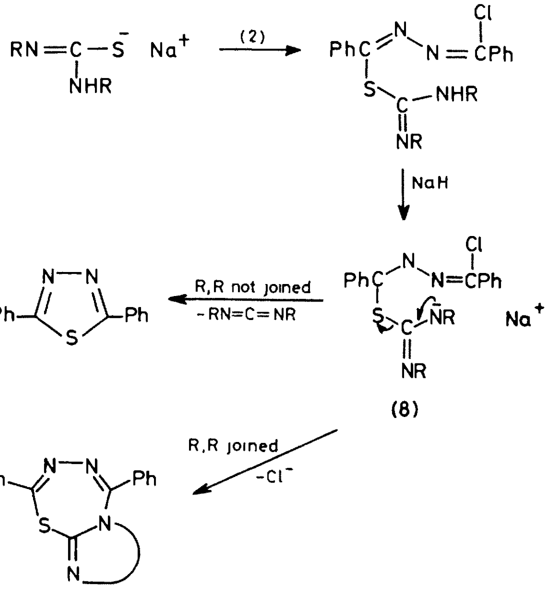
(6)



(7)

This reaction appears to be a general one for cyclic thioureas. Thus, the sodium salt of the dihydropyrimidine-2-thione (**3**, n = 3) yields (**4**, n = 3) (63%), m.p. 180—182 °C (decomp.), the sodium salts of the 4-oxo-pyrimidine-2-thiones (**5**, R = H or Me) yield (**6**, R = H) (36%), m.p. 234—236 °C (decomp.) and (**6**, R = Me) (26%), m.p. 226 °C) (decomp.), respectively, and the sodium salt of benzimidazole-2-thiol affords (**7**) (49%), m.p. 203—204 °C. All these new thiatriazepines analysed correctly and had spectroscopic data consistent with the proposed structures.

Attempts to include acyclic thioureas (*e.g.*, thiourea, *N*-methyl- and *NN'*-dimethyl-thioureas) in this series of conversions met with no success, and only 2,5-diphenyl-1,3,4-thiadiazole was obtained. We believe that the different behaviour of acyclic thioureas stems from an alternative reaction path (Scheme) in which a carbodi-imide is eliminated from the intermediate anion (**8**). Such an option would not be energetically favourable for a cyclic thiourea, for which ring closure of (**8**) is therefore more likely.



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[1] W. T. Flowers, S. F. Moss, J. F. Robinson, D. R. Taylor, A. E. Tipping, and M. J. Haley, *J.C.S. Chem. Comm.*, 1979, 149.

[2] S. F. Moss and D. R. Taylor, unpublished results.

[3] W. T. Flowers, J. F. Robinson, D. R. Taylor, and A. E. Tipping, *J.C.S. Perkin I*, submitted for publication.

[4] B. Beagley, S. F. Moss, R. J. Pritchard, and D. R. Taylor, unpublished results.