

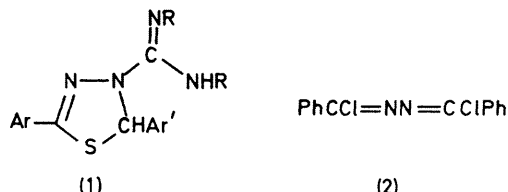
Synthesis of Annelated 1,3,4,6-Thiatriazepines from Dichlorodiazabutadienes and Cyclic Thioureas

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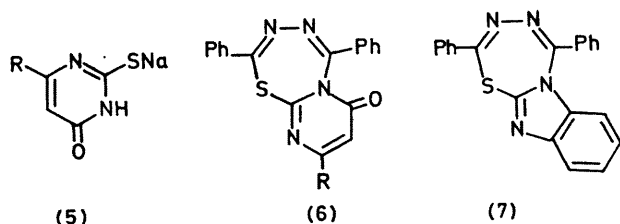
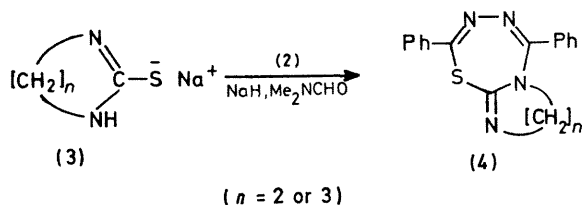
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Summary Treatment of 1,4-dichlorodiphenyl-2,3-diazabutadiene (2) with the sodium salts of cyclic thioureas has yielded the first examples of a new type of seven-membered heterocycle, annelated 1,3,4,6-thiatriazepines.

As previously reported,¹ chloro-2,3-diazabutadienes ($\text{Ar-ClC}=\text{NN}=\text{CHAr}'$) 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



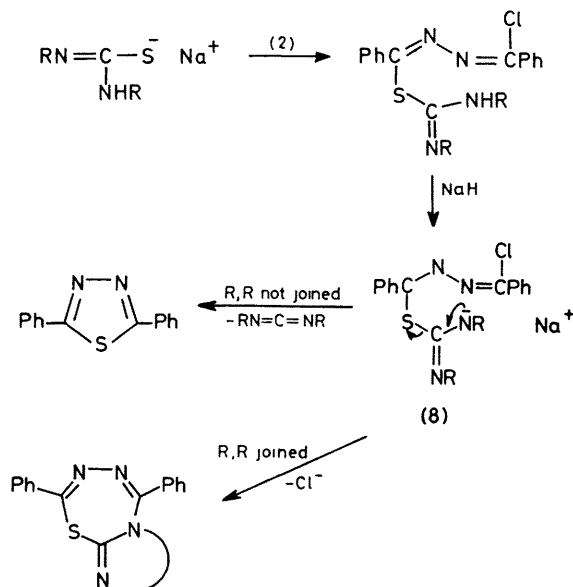
When 1,4-dichloro-1,4-diphenyl-2,3-diazabutadiene (2) is treated with thiourea alone,³ or in the presence of triethylamine, only 2,5-diphenyl-1,3,4-thiadiazole is obtained. However, during further study of this type of reaction we treated (2) with the sodium salt of ethylenethiourea (3, $n = 2$), and 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 (^1H 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 $\text{C}=\text{N}$ bonds; (iii) mass spectrometric and elemental analyses; and *X*-ray crystallographic analysis, details of which will be published separately.⁴

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, $\text{R} = \text{H}$ or Me) yield (6, $\text{R} = \text{H}$) (36%), m.p. 234–236 °C (decomp.) and (6, $\text{R} = \text{Me}$) (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



SCHEME

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.