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The new compound 3-(*tert*-butyl)perhydro-1,5,3-dithiazepine has been synthesised from 5-(*tert*-butyl)perhydro-1,3,5-triazin-2-one in 45% yield. In the reaction, urea acts as the leaving group being exchanged for the S-CH₂-CH₂-S fragment of the product.

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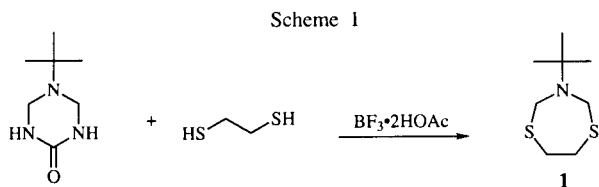
Introduction.

In our search for new energetic materials we have recently focused our attention towards possible modifications of hexahydro-1,3,5-trinitro-1,3,5-triazine (cyclonite). One example of such a cyclonite analogue is 2-oxohexahydro-1,3,5-trinitro-1,3,5-triazine (keto-cyclonite) prepared from 5-(*tert*-butyl)-2-oxohexahydro-1,3,5-triazine [1].

One of our approaches towards other cyclonite based compounds consists in modifying 5-(*tert*-butyl)-2-oxohexahydro-1,3,5-triazine, the starting material for hexahydro-2-oxo-1,3,5-trinitro-1,3,5-triazine. Nitration of these modified starting materials is then a possible route towards new desired energetic compounds.

Results.

When 5-(*tert*-butyl)hexahydro-2-oxo-1,3,5-triazine was treated with 1,2-ethanedithiol and boron trifluorideacetic acid complex, according to Sondej and Katzenellenbogen [2], 3-(*tert*-butyl)perhydro-1,5,3-dithiazepine (**1**) was obtained in 45% yield (Scheme 1).



Perhydrodithiazepines have previously been prepared from Mannich-type condensations using 1,2-ethanedithiol, formaldehyde and hydroxylamine hydrochloride [3] and from cyclocondensations of isocyanates with 1,2-ethanedithiol [4]. These types of compounds have been used to prevent fading of organic coloured materials [5].

The advantage of the new synthesis presented in this paper is that the sulphur containing part can be introduced at a late stage in a multistep synthesis of substituted perhydrodithiazepines by using the urea moiety in perhydro-1,3,5-triazin-2-ones as a leaving group. This late introduction of sulphur is advantageous if previous steps require reagents or catalysts that otherwise would be poisoned by sulphur.

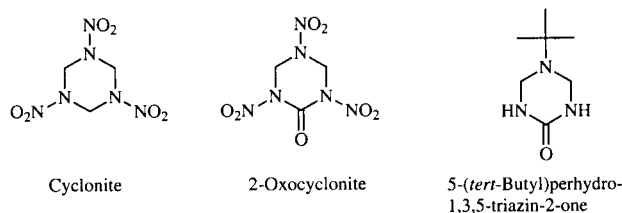


Figure 1.

EXPERIMENTAL

Melting point was recorded on a Mettler DSC 30, ¹H- and ¹³C-NMR spectra were recorded on a Varian 200 MHz spectrometer, mass spectrum was recorded on a Jeol D300 spectrometer, elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

3-(*tert*-Butyl)perhydro-1,5,3-dithiazepine (**1**).

5-(*tert*-Butyl)-2-oxohexahydro-1,3,5-triazine [1] (5.00 g, 31.8 mmol) was mixed with 1,2-ethanedithiol (10.8 ml, 127 mmol) under nitrogen. Boron trifluoride-acetic acid complex (4.4 ml, 32 mmol) was added during vigorous stirring. The reaction mixture was kept at room temperature for two hours and was then diluted with 100 ml of diethyl ether. The organic phase was washed twice with 100 ml of each of the following aqueous solutions: saturated sodium bicarbonate, 15% sodium hydroxide and saturated sodium chloride. The organic phase was dried over magnesium sulphate, filtered and evaporated to yield 4.7 g of crude product. This was purified by flash chromatography on silica 60 using heptane/ethyl acetate 9/1 as eluent, yield 2.75 g (45%), mp: 22–24°, ¹H-nmr (deuteriochloroform): 1.13 (s, 9H, *t*-Bu), 2.91 (s, 4H, S-CH₂-CH₂-S), 4.41 (s, 4H, N-CH₂-S); ¹³C-nmr (deuteriochloroform): 28.1, 37.4, 53.9, 55.6; ms: (EI, 70 eV) Calcd. for C₈H₁₇NS₂: 191.3. Found: 191.

Anal. Calcd. for C₈H₁₇NS₂: C, 50.22; H, 8.95; N, 7.32; S, 33.51. Found: C, 49.82; H, 8.69; N, 7.65; S, 33.84.

REFERENCES AND NOTES

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