

Reaction of an Enaminone with 1-Nitrocyclopentene: Synthesis of a Triquinane

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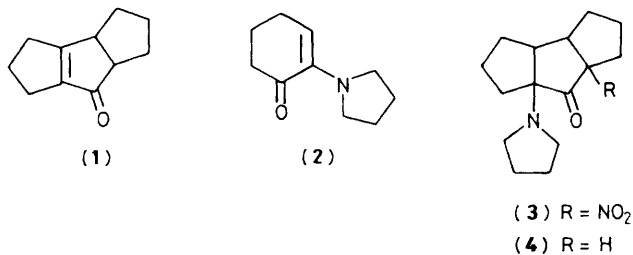
A convergent synthesis of a functionalized triquinane is reported which proceeds in three steps and 72% yield from 2-(1-pyrrolidino)cyclohex-2-en-1-one and 1-nitrocyclopentene.

The synthesis of various naturally occurring tricyclo-[6.3.0.0^{2,6}]undecanes (linear triquinanes) has attracted a great deal of recent attention.¹ Although a number of very elegant approaches to these compounds have been devised, many of these syntheses employ either iterative cyclopentannulations or thermal rearrangements to generate the triquinane nucleus.

We now describe a short, convergent synthesis of a functionalized triquinane (**1**) which proceeds in good overall

yield from readily available starting materials. This synthetic approach is based on the recently described reaction of various 2-aminocyclohex-2-en-1-ones with 1-phenyl-2-nitropropene which proceeds with ring contraction to afford hydro-pent-1-enes.² Extension of this reaction to alicyclic nitroalkenes appeared to be a promising approach to the synthesis of fused polycyclic systems, in particular linear triquinanes.

Accordingly, reaction of 2-(1-pyrrolidino)cyclohex-2-en-1-



one (2)³ with 1 equiv. of 1-nitrocyclopentene⁴ (neat, 25 °C) gave a quantitative yield of the desired aminonitrotriquinane (3) as a low melting solid which decomposed on attempted purification, $\nu_{\text{C=O}}$ 1760 cm⁻¹, ν_{NO_2} 1550, 1360 cm⁻¹, m/z 278(M^+). The ¹H n.m.r. spectrum showed no peaks below δ 3.5.† Reductive removal of the nitro group⁵ [Bu₃SnH, azoisobutyronitrile (AIBN), toluene, reflux, 80%] gave the aminoketone (4) as an unstable oil, $\nu_{\text{C=O}}$ 1760 cm⁻¹, m/z 233(M^+). The ¹H n.m.r. spectrum again showed the absence of any low field protons. The conversion of (4) into the

† The piperidine enamine apparently reacted similarly; however, the product decomposed on isolation.

triquinane target (1) was effected by a modified Cope elimination⁶ (*m*-chloroperbenzoic acid, CH₂Cl₂, NaHCO₃, reflux, 1 week, 90%). Enone (1), $\nu_{\text{C=O}}$ 1720 cm⁻¹, exact mass 162.1044, (calc. 162.1045), was obtained as a somewhat air sensitive oil.

This procedure leads to a functionalized triquinane in three steps and an overall yield of 72% from readily available precursors. Extension of this approach to appropriately substituted nitroalkenes and enaminoketones will provide substrates suitable for elaboration to naturally occurring triquinanes.

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References

- 1 See e.g. L. A. Paquette, *Top. Curr. Chem.*, 1984, 119; M. Ranaiah, *Synthesis*, 1984, 529, and references therein.
- 2 G. Barbarella, S. Bruckner, G. Pitacco, and E. Valentin, *Tetrahedron*, 1984, **40**, 2441.
- 3 M. A. Tobias, J. G. Strong, and R. P. Napier, *J. Org. Chem.*, 1970, **35**, 1709.
- 4 E. J. Corey and H. Estreicher, *J. Am. Chem. Soc.*, 1978, **100**, 6294.
- 5 N. Ono, H. Miyake, and A. Kaji, *J. Org. Chem.*, 1984, **49**, 4997.
- 6 R. L. Funk and G. L. Bolton, *J. Org. Chem.*, 1984, **49**, 5021.