

AN ABERRANT ACETYLATION OF 9-THIABICYCLO[3.3.1]NONAN-2,6-DIONE

Peter H. McCabe and William Routledge

Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, Scotland

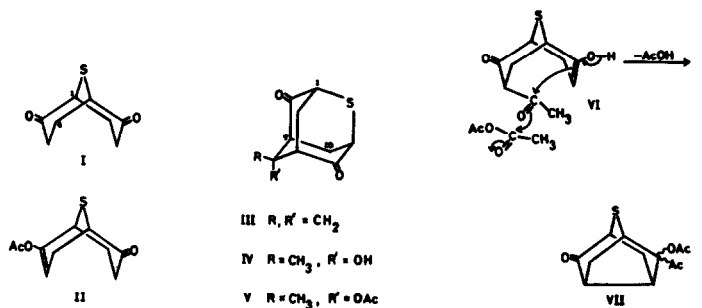
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Reaction¹ of 9-thiabicyclo[3.3.1]nonan-2,6-dione (I) with acetic anhydride-sulphuric acid at 145° yields a mono-enol acetate (II) and, on prolonged reaction, a bis-enol acetate.¹ However, acetylation of I under conditions of increased acidity or higher temperature produces two further compounds, (A), C₁₂H₁₄O₄S², m.p. 172-173°, and (B), C₁₀H₁₀O₂S, m.p. 169-170°.

(A) and (B) are structurally similar, as shown by the following chemical interconversion. (A) possesses an acetoxy group ($\nu_{\max}^{\text{CCl}_4}$ 1752 cm⁻¹; δ 2.00, 3H, s), a tertiary methyl (δ 1.65, 3H, s), and two carbonyl functions (1724 cm⁻¹, ϵ^a 840, complex³). This diketoacetate hydrolyses in aqueous base to a tertiary alcohol, C₁₀H₁₂O₃S, decomp. ca. 267°, $\nu_{\max}^{\text{CCl}_4}$ 3606 cm⁻¹. Dehydration (POCl₃/pyridine) of the alcohol furnishes an exomethylene diketone, ($\nu_{\max}^{\text{CCl}_4}$ 1723, ϵ^a 740; 905 cm⁻¹; δ 4.28, 2H, s), which is identical with product (B).

The NMR spectrum of the exomethylene diketone (B) discloses four hydrogen atoms α to carbonyl, two of which (δ 3.42, m) are allylic and two (δ 3.27, m) situated on carbon bearing sulphur. From the above evidence we assign product (B) the thiaadamantane^{3,4} structure (III). In corroboration, the NMR spectrum of III, recorded in the presence of Eu(fod)₃,⁵ show the bridgehead and saturated methylene (C-9, C-10) proton signals resolved into two coincident four-spin systems with observed major coupling constants of 13, 4 and 3 Hz.

From the close spectroscopic similarity of the tertiary alcohol and the diketoacetate to (III) it follows that the former is the diketothiaadamantanol (IV) and the latter the corresponding ester (V). Significantly, the europium-shifted NMR spectrum of IV shows two non-coincident four-spin systems, inferring the absence of a C₂ axis (cf III).



The conversion of I to V under acetylating conditions formally represents a transannular insertion of acetic anhydride with loss of water. We suggest that this is accomplished by acetylation at C-3⁶ of dione (I) yielding VI followed by an intramolecular aldol condensation. Exomethylene compound (III) is most likely formed during the acetylation reaction by pyrolytic elimination of acetic acid from V. Structure VII is a mechanistically feasible alternative for the diketetoacetate but is, however, incompatible with the NMR and chemical evidence presented

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