A Molecular Rearrangement of 4β-Acetoxy-1,2-dihydrosantonene

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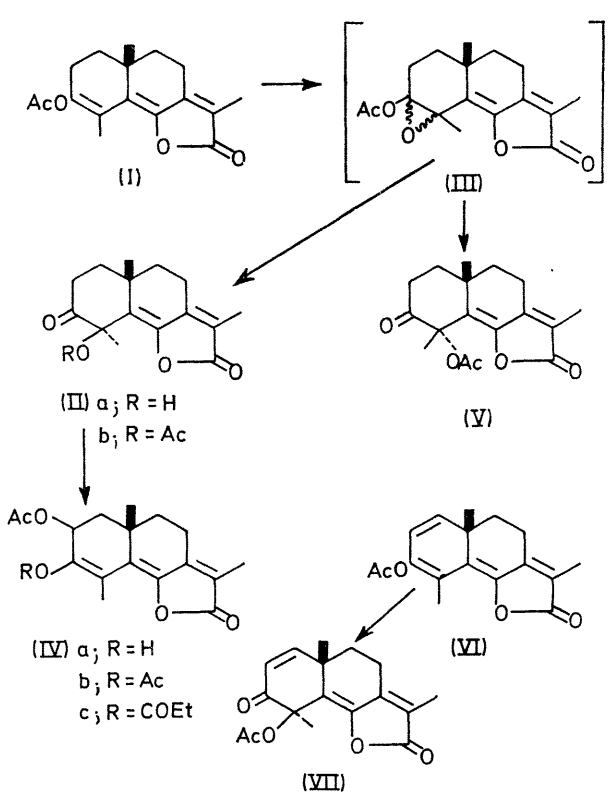
Summary 4β-Acetoxy-1,2-dihydrosantonene (IIb), which can be prepared by oxidation of 1,2-dihydrosantonene 3-acetate (I), rearranges with acetic anhydride–pyridine to afford 2β-acetoxy-1,2-dihydrosantonene 3-acetate (IVb) by a mechanism involving intramolecular transfer of the 4β-acetate to the 2-position of the enolic form of (IIb).

RECENTLY we showed that 1,2-dihydro-4β-hydroxysantonene (IIa) on acetylation afforded the 2β,3-diacetate (IVb),[1] but we were unable to isolate the presumed intermediate acetate (IIb). We have now found that oxidation of the enol acetate (I) with chromium trioxide in t-butyl alcohol[2] affords the 4β-acetate (IIb), m.p. 168—170°, $[\alpha]^{20}$ + 149°, ν_{max} 1768, 1750, 1727, and 1655 cm^{-1}, and traces of the known 4α-acetate (V).[1] Probable intermediates in the reaction[3] are epoxyacetates of the type (III) which then undergo rearrangement. Similar oxidation of santonene enol acetate (VI)[4] affords 4β-acetoxysantonene (VII).

Treatment of the 4β-acetate (IIb) with acetic anhydride–pyridine affords the diacetate (IVb). Substitution of propionic for acetic anhydride affords a monoacetate monopropionate (IVc), m.p. 126—128°, $[\alpha]_D$ − 608°, M^+, 316, ν_{max} 1770, 1760, 1735, and 1640 cm^{-1}. This suggests that of the two alternative mechanisms considered,[1,5] that involving an intramolecular transfer of the 4-acetate in the enol form of (IIb) is correct. The chromophoric system can also be formed on treatment of the 4β-acetate (IIb) with an excess of triethylamine in tetrahydrofuran. We were unable to isolate the resulting enol (IVa) in a pure state, but characterised it as the diacetate (IVb) and monoacetate monopropionate (IVc). This experiment showed that the rearrangement did not require the prior formation of a 2-enol ester. Further, little enolisation occurred in (IVa) towards the 2-position, as might be expected to occur in the keto-form corresponding to (IVa). There is no ester exchange between the 2- and 3-oxygen substituents under the influence of base.



Satoh *et al.*[6] have recently suggested that 4β-bromo-5β-cholestanone is converted into 2α-acetoxy-5β-cholestanone by the alternative S_N2' mechanism which we considered as a possibility, and which involves an unusual *trans*-arrangement of attacking and leaving groups.[7]

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[1] T. B. H. McMurry and R. C. Mollan, *J. Chem. Soc. (C)*, 1969, 1619.
[2] K. Heusler and A. Wettstein, *Helv. Chim. Acta*, 1952, **35**, 284.
[3] *Cf.* A. H. Soloway, W. J. Considine, D. K. Fukushima, and T. F. Gallagher, *J. Amer. Chem. Soc.*, 1954, **76**, 2941; N. S. Leeds, D. K. Fukushima, and T. F. Gallagher, *ibid.*, p. 2943.
[4] T. B. H. McMurry and R. C. Mollan, *J. Chem. Soc. (C)*, 1967, 1813.
[5] *Cf.* J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.*, 1967, **89**, 3457.
[6] J. Y. Satoh and T. T. Takahashi, *Chem. Comm.*, 1970, 1714.
[7] *Cf.* N. T. Ahn, *Chem. Comm.*, 1968, 1089.