Pummerer Rearrangement of 1,3-Oxathiolan-5-one *S*-Oxides

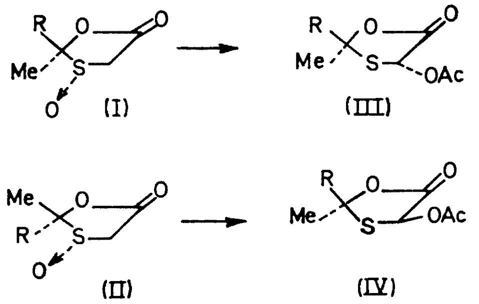
By S. GLUE, I. T. KAY,* and M. R. KIPPS

(*Imperial Chemical Industries Limited, Plant Protection Ltd., Jealott's Hill Research Station, Bracknell, Berkshire* RG12 6EY)

Summary In their reaction with acetic anhydride, 2,2-dialkyl-1,3-oxathiolan-5-one *S*-oxides give by a highly stereoselective process the corresponding 4-acetoxy-2,2-dialkyl-1,3-oxathiolan-5-ones, in which the acetoxy-group is introduced on the side of the ring formerly occupied by the *S*-oxide bond.

DURING the last ten years the Pummerer rearrangement[1] has been the subject of several mechanistic studies, and these have formed part of the subject matter of a recent review[2] of the chemistry of sulphoxides. The outstanding question concerning the rearrangement is whether it occurs by an intra- or inter-molecular process,[3] and in this communication we present evidence that 1,3-oxathiolan-5-one *S*-oxides in their reaction with acetic anhydride rearrange by an intramolecular process.

The acid-catalysed removal of water from a mixture of an aliphatic ketone and thioglycollic acid gives 2,2-dialkyl-1,3-oxathiolan-5-ones as stable oils,[4] and we have now found that these undergo smooth oxidation (hydrogen peroxide in glacial acetic acid, 25°) to their crystalline *S*-oxides, which may be separated into their isomeric forms (I and II).

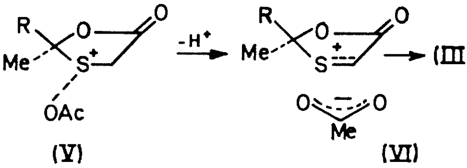


(I) (III) (II) (IV)

The assignment of their configurations by the use of n.m.r. data alone was inconclusive, and awaits a definitive model for the screening environment of sulphoxides.[5] However, since sulphoxidation under these conditions is known to be subject to steric approach control,[6] the configurations of the racemates (*e.g.* I and II; R = Pr^i) were inferred from the preferred (7 : 3) formation of (I; R = Pr^i), m.p. 114°. [Isomer (II; R = Pr^i) had m.p. 94—95°.] Furthermore, oxidation of 2-methyl-2-t-butyl-1,3-oxathiolan-5-one gave exclusively the sulphoxide (I; R = Bu^t), m.p. 114—115°, whereas oxidation of 2-ethyl-2-methyl-1,3-oxathiolan-5-one gave again a mixture of isomers (I: II = 65: 35; R = Et) of which only isomer (I; R = Et), m.p. 87—89°, has thus far been isolated in the pure state.

The reaction of each of the above sulphoxides with acetic anhydride (1·1 mol. equiv.) in dichloromethane (*cf.* ref. 7) at ambient temperatures (48 hr.) and catalysed with a trace of toluene-*p*-sulphonic acid, afforded (80—90%) the corresponding 4-acetoxy-1,3-oxathiolan-5-ones. The ratios of the isomeric acetoxy-compounds (III and IV) thus formed were established by examination of the signal areas at *ca.* τ 3·5 for their 4-protons. In all cases it was found that the rearrangement proceeded with 85—90% stereoselectivity, and that the acetoxy-group was introduced on the side of the oxathiolan ring formerly accommodating the sulphoxide bond, irrespective of the relative thermodynamic stabilities (see below) of the products. The configurations of the 4-acetoxyoxathiolanones (III and IV) were determined following their equilibration by heating their solutions in benzene (6 hr.) in the presence of toluene-*p*-sulphonic acid, when the thermodynamically preferred (III) predominated (*e.g.* III: IV = 65 : 35 at equilibrium; R = Bu^t).

We feel that under these experimental conditions, the high stereoselectivity observed in this reaction can best be accounted for by an intramolecular process, possibly proceeding *via* the acetoxysulphonium ion[3] (V) and the ion-pair (VI) to the 4-acetoxyoxathiolanone (III).



(V) (VI)

Although the reaction of the sulphoxides (I and II) with, *e.g.*, HCl, $SOCl_2$, and AcCl gave rise to good yields of isomeric mixtures of 4-chloro-oxathiolanones, there was no obvious relationship between the ratios of the products formed and the stereochemistry of the sulphoxides, and we feel unable to comment upon the mechanistic aspects of this reaction other than to note that rapid racemisation of sulphoxides has been observed[8] to be catalysed by HCl.

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