A Stable Enediol Sulphite: an Example of Steric Protection of Unstable Compounds

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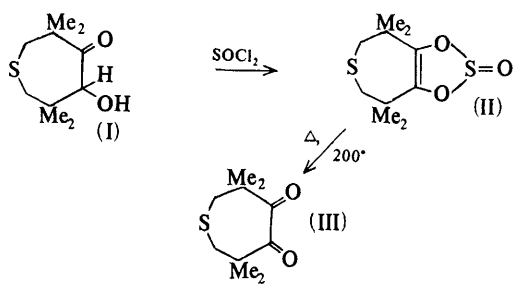
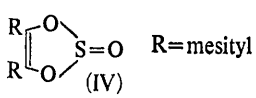
DURING our studies on the 3,3,6,6-tetramethylthiepan system[1,2] we attempted to prepare 5-chloro-3,3,6,6-tetramethyl-4-oxothiepan, by refluxing the hydroxy-ketone (I)[1] for 2 hr. with thionyl chloride and dimethylaniline, in chloroform as solvent. Instead of the chloro-ketone, the enediol sulphite (II) was isolated as a stable solid (m.p. 86—88°, 84% yield) which was characterized as 4,5,7,8-tetrahydro-4,4,8,8-tetramethylthiepino[4,5,-*d*]-1,3,2-dioxathiole 2-oxide by elemental analysis ($C_{10}H_{16}O_3S_2$) and by spectra. The i.r. spectrum showed an absorption at 1670 cm.$^{-1}$, indicating a double bond. The n.m.r. spectrum (10%, CCl_4) showed a singlet at τ 7·36 (4 methylene protons) and two singlets at τ 8·73 and 8·68 (12 methyl protons). The u.v. spectrum showed no absorption above 220 mμ. The mass spectrum showed a parent peak at 248 and the fragmentation pattern is in accord with the assigned structure. Pyrolysis of the enediol sulphite at 200—225° gave the diketone (III)[1] in 75% yield.



Enediol sulphites were postulated as intermediates in the reaction of benzoin with thionyl chloride by Fieser and Okumura.[3] The latter[4] prepared the dimesityl compound (IV) which showed an absorption maximum at 260 mμ (ϵ 10650). This, however, is attributable to the *cis*-hexamethylstilbene chromophore (*cf.* refs. 5 and 6), rather than to the enediol sulphite group, as was suggested by Okumara.[4]



The remarkable stability of compound (II), the first known example of a stable alicyclic enediol sulphite, is an example of stabilisation by steric protection such as the reported protection by t-butyl groups or α-*gem*-dimethyl groups of several reactive compounds.[7]

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