Synthesis of 1,6-Dioxa-6a-thiapentalenes: Sulphur–Oxygen Coupling by Thallium(III) Trifluoroacetate

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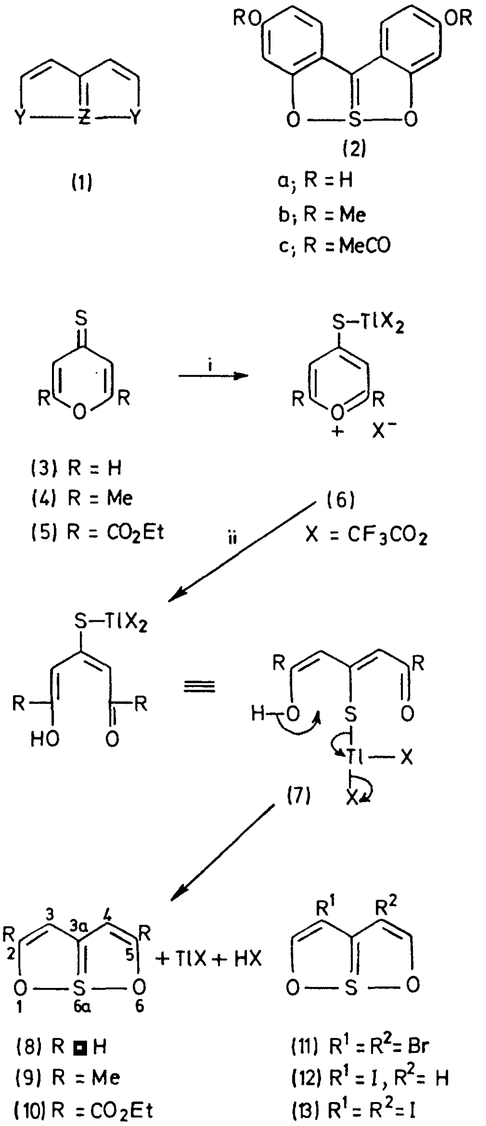
Summary 4*H*-Pyran-4-thiones react with thallium(III) trifluoroacetate to form thallium-containing pyrylium trifluoroacetates which are ring-opened by water; the resulting intermediates spontaneously lose thallium(I) trifluoroacetate, with concomitant sulphur–oxygen bond formation, to give 1,6-dioxa-6a-thiapentalenes.

Several hypervalent[1] heterocyclic systems (**1**) related to 6a-thiathiophthen have recently been synthesised,[2] in which Y and Z are heteroatoms of Groups V and VI and Z is theoretically capable of valence-shell expansion. The simplest possible system (**1**; Y = O, Z = S) has hitherto remained unknown except in the form of the dibenzo-derivative (**2a**),[3] and the corresponding dimethyl ether (**2b**) and diacetate (**2c**). We report here a two-step synthesis o- 1,6-dioxa-6a-thiapentalenes from γ-pyrones, involving sulf phur–oxygen coupling by thallium(III) trifluoroacetate.

Addition of thallium(III) trifluoroacetate in acetonitrile to



Reagents: i, TlX_3; ii, H_2O

a solution of 4H-pyran-4-thione (**3**)[4] in acetonitrile at room temperature gave immediately a pale brown solution containing the labile pyrylium salt (**6**; R = H) which was not isolated. Addition of water after 1 min and conventional work-up afforded 1,6-dioxa-6a-thiapentalene (**8**) (61%), m.p. 61—62·5°; M^+ 127·993097; λ_{max} (cyclohexane) 339 (log ϵ 4·06), 257 (3·35), 222 (3·38), and 198 nm (3·78); δ (100 MHz; $CDCl_3$; Me_4Si internal reference) 6·90 (2H, d, $J_{3,2(4,5)}$ 2·8 Hz, 3- and 4-H) and 8·64 p.p.m. (2H, d, $J_{2,3(5,4)}$ 2·8 Hz, 2- and 5-H). The C_{2v}-symmetrical pattern of the ^{1}H n.m.r. spectrum remained unchanged down to $-50°$. Compound (**8**) showed no i.r. absorption in the double bond region above 1510 cm^{-1}. By the same procedure the thione (**4**)[5] was converted into the dioxathiapentalene (**9**) (9%), m.p. 70—71°. Also, the ester (**5**)[6] gave the pale yellow diester (**10**) (61%), m.p. 97—98·5°.

Water is sufficiently nucleophilic to open the pyrylium ring in the intermediates (**6**); yields of products were not significantly different when 1M-sodium hydroxide was used. The driving force for sulphur–oxygen bond formation, for which very few methods exist, is the well established,[7] energetically favourable $Tl^{III} \rightarrow Tl^{I}$ process [structure (**7**)]. The scope of this new method is being investigated.

Conversion of 4H-pyran-4-thiones into 1,6-dioxa-6a-thiapentalenes completes a two-step synthesis of 1,6-dioxa-6a-thiapentalenes from γ-pyrones, since 4H-pyran-4-thiones are readily obtained by thionation of γ-pyrones.

Preliminary experiments reveal a high reactivity of 1,6-dioxa-6a-thiapentalenes in substitution reactions. 1,6-Dioxa-6a-thiapentalene (**8**) reacted immediately at room temperature with bromine in carbon tetrachloride to give the pale yellow dibromo-derivative (**11**) (79%), m.p. 133—135° (decomp.), δ 8·66 (2- and 5-H) p.p.m. Iodination (I_2–AgOAc) could be controlled to give either the pale yellow iododioxathiapentalene (**12**) (73%), m.p. 74—75°, or di-iodo-dioxathiapentalene (**13**) (59%), m.p. 153—156°. Satisfactory analyses were obtained for all new compounds. Crystallographic structure determinations of selected 1,6-dioxa-6a-thiapentalenes are in progress.

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