Photocycloaddition of 2,5-Dihydrothiophen *SS*-Dioxides to α,β-Unsaturated Cyclic Anhydrides. Synthesis of 10-Hydroxygeraniol[1]

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Summary 10-Hydroxygeraniol (**6c**) was synthesized from 2,5-dihydro-3-methylthiophen *SS*-dioxide (**1b**) and citraconic anhydride (**2b**) in 48% overall yield *via* irradiation followed by thermal extrusion of SO$_2$ from the intermediate photoadduct (**3b**) and a Cope rearrangement of the resulting divinyl diester (**5b**).

THE photocycloaddition of substituted cyclobutenes to chiral cyclohexenones has afforded a convenient entry into the stereospecific synthesis of a large number of sesquiterpenes including elemane, germacrane, cadinane, eudesmane, and guaiane skeletons.[2] We sought a cheap and more readily available isoprene synthon than 1-methylcyclobutene, and now report the stereospecific synthesis of *cis*-1,2-divinyl systems by the thermal extrusion of sulphur dioxide from dihydrothiophen *SS*-dioxide photoadducts. Furthermore, heating the *cis*-1,2-divinyl intermediates causes a Cope rearrangement leading cleanly to *trans,trans*-1,5-dienes in high yields. By using appropriate substituents on the photoadduct, these two steps may be combined and flash vacuum pyrolysis of the dihydrothiophen *SS*-dioxide photoadducts yields *trans,trans*-1,5-dienes in high yields. This methodology has been used to synthesize 10-hydroxygeraniol (**6c**).

Photocycloaddition† of the *SS*-dioxide (**1b**) with citraconic anhydride (**2b**) afforded the photoadduct (**3b**)‡ in 80% yield; (**3a**) was prepared as described previously *via* photosensitization.[3] Treatment of (**3b**) with diazomethane (MeOH–Et$_2$O, 1 : 5) gave the diester (**4b**), m.p. 138—139 °C, in 72% yield. Flash vacuum pyrolysis of (**4b**) at 500 °C and 0·5 mmHg afforded *trans,trans*-dimethyl 2,6-dimethylocta-2,6-diene-1,8-dicarboxylate (**6b**)[4] in 87% yield; ν_{max} (film) 1720 and 1640 cm^{-1}. The ^{13}C n.m.r. spectrum displayed 12 signals attesting to its stereoisomeric purity. Aluminium

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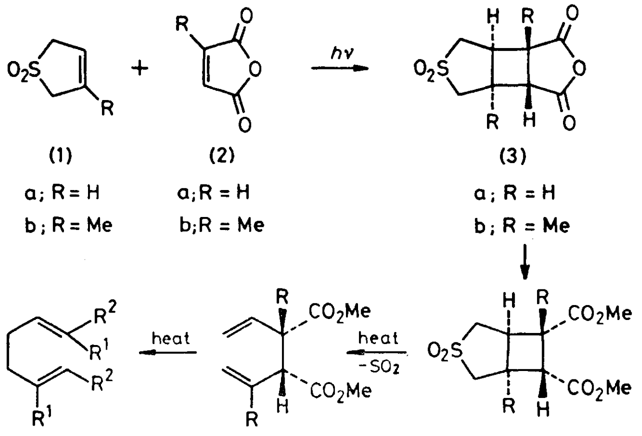
† In CH$_2$Cl$_2$ under nitrogen at −78 °C using a 450 W Hanovia lamp in a quartz tube for 30 h.

‡ Compound (**3b**) crystallizes in two forms, m.p. 194—196 and 210—211 °C; ν_{max} (KBr) 1860, 1780, 1310, 1012, and 917 cm^{-1}; ^{1}H n.m.r. (CD$_3$SOCD$_3$) 3·80—2·90 (m, 6 H), 1·46 (s, 3 H), and 1·32 (s, 3 H). All new compounds gave satisfactory analytical and spectral data.

hydride reduction of the diester (**6b**)[4] gave the diol (**6c**) in 97% yield or 48% overall yield based on (**1b**). 10-Hydroxygeraniol (**6c**) has been synthesized previously[4–6] and shown to be the biosynthetic precursor for loganin[4,6] and iridodial.[5]



(1)
a; R = H
b; R = Me

(2)
a; R = H
b; R = Me

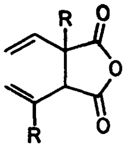
(3)
a; R = H
b; R = Me

(6)
a; R^1 = H, R^2 = CO_2Me
b; R^1 = Me, R^2 = CO_2Me
c; R^1 = Me, R^2 = CH_2OH

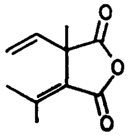
(5)
a; R = H
b; R = Me

(4)
a; R = H
b; R = Me

To prepare the *cis*-1,2-divinyl system stereospecifically, the anhydride photoadduct (**3a**) was flash-vacuum pyrolysed at 700 °C and 0·5 mmHg pressure to yield (**7a**) in 81% yield, in agreement with the recent work of Cadogan *et al.*[7] Apparently when the anhydride ring is present the Cope rearrangement does not occur. However, when the anhydride (**7a**) was esterified with diazomethane (MeOH–Et_2O, 1 : 5) to yield the diester (**5a**), thermolysis at 290 °C of (**5a**) afforded (**6a**) in 78% yield. When the dimethyl analogue (**3b**) was subjected to flash-vacuum pyrolysis a mixture of the *cis*-3,4-divinyl anhydride (**7b**) and the conjugated isomer (**8**) was obtained.



(7)
a; R = H
b; R = Me



(8)

When (**3a**) was thermolysed in toluene at 290 °C for 5 h in a sealed tube a complex mixture of products was obtained; however, the dimethyl analogue (**3b**) gave (**8**) in 87% yield. Presumably the sulphur dioxide being liberated in the sealed tube is causing (**7a**) to react further under these vigorous conditions.

Thus, dihydrothiophen *SS*-dioxides offer an alternative method to the use of cyclobutenes for the stereospecific synthesis of *cis*-1,2-divinyl systems and ***trans-trans*** acyclic 1,5-dienes.

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