# Flash Vacuum Pyrolysis of the 3-Thiabicyclo[3.2.0]heptane 3,3-Dioxide Ring System: a New Stereospecific Synthesis of *cis*-1,2-Divinyl Derivatives

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*Summary* A short and stereospecific route to *cis*-1,2-divinyl compounds from derivatives of the readily available 3,3-dioxide (**1**) of 3-thiabicyclo[3 2 0]heptane-6,7-dicarboxylic anhydride by cheleotropic elimination of $SO_2$ is reported

THE considerable interest in *cis*-1,2-divinyl systems now current[1] is tempered by difficulties in synthetic access through existing methods[2] which usually give mixtures of *cis*- and *trans*-isomers We now report a simple, stereospecific, and general route to novel *cis*-1,2-divinyl systems by thermal extrusion of $SO_2$ from derivatives of the 3,3-dioxide (**1**) of 3-thiabicyclo[3 2 0]heptane-6,7-dicarboxylic anhydride, easily prepared by photolysis of 2,5-dihydrothiophen 1,1-dioxide and maleic anhydride for 24 h in anhydrous acetone [3]

Thus, esterification of (**1**) followed by reduction with $LiAlH_4$ and subsequent cyclisation[4] of the resulting diol (**2**) afforded 4 oxa-9-thiatricyclo[5 3 0 $0^{2,6}$]decane 9,9-dioxide (**3**, X=O, m p 129—130 °C)† which on pyrolysis under

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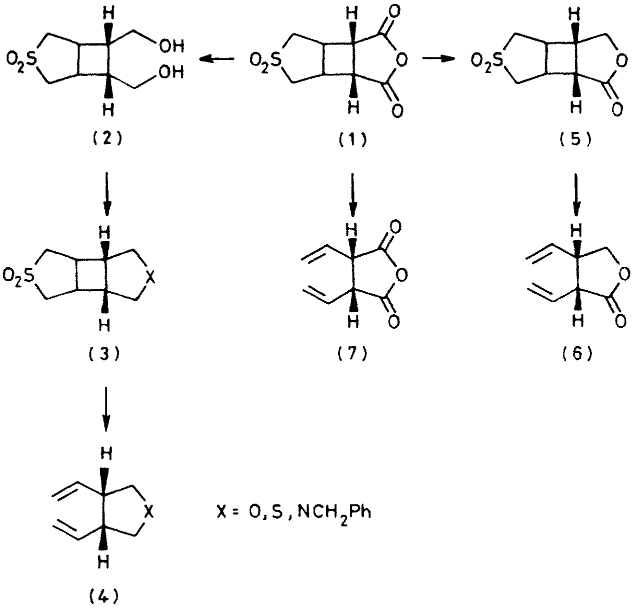
† All new compounds were fully characterised by $^1H$ and $^{13}C$ n m r , i r and mass spectral and microanalytical data



flash vacuum conditions (625 °C at $10^{-3}$ mmHg) gave exclusively *cis*-3,4-divinyltetrahydrofuran (**4**, X=O; b.p. 40 °C at 41 mmHg; 62%). Similar pyrolysis of the lactone (**5**); m.p. 157—158 °C, prepared by reduction of (**1**) with $NaBH_4$ in dimethylformamide, afforded the corresponding *cis*-1,2-divinyl derivative (**6**; b.p. 75 °C at 0·1 mmHg) in 31% overall yield from (**1**). Further transformations of (**1**), which serve to illustrate the potential of our procedure, have been effected leading to (**4**, X=S; b.p. 140 °C at 16 mmHg; 25%) and (**4**, X=$NCH_2Ph$; b.p. 100 °C at 0·01 mmHg; 67%) by pyrolysis of (**3**, X=S; m.p. 195—196 °C) [conversion of (**2**) into its dimethanesulphonate and treatment with $Na_2S$–aq.EtOH; 82%] and (**3**, X=$NCH_2Ph$; m.p. 132—135 °C) [reaction of the ditosylate of (**2**) with benzylamine; 56%] respectively. We have also shown that flash vacuum pyrolysis of (**1**) gave *cis*-hexa-1,5-diene-3,4-dicarboxylic anhydride (**7**; b.p. 65 °C at 0·1 mmHg; 80%) from which *cis*-1,2-divinyl systems of type (**4**) could be obtained by conventional synthetic methods.

Stereospecificity in all cases exceeded 99·9% and the *cis*-stereochemistry, which is a consequence of the symmetrical structure of the starting anhydride (**1**), was validated by the essentially quantitative chemical transformation of (**7**) into *meso*-2,3-diethylsuccinic acid, m.p. 190—191 °C (decomp.) (lit.[5] 192 °C; *cf*. racemic acid, m.p. 129 °C) by hydrolysis with boiling water and subsequent hydrogenation over 10% palladium–charcoal at room temperature.

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