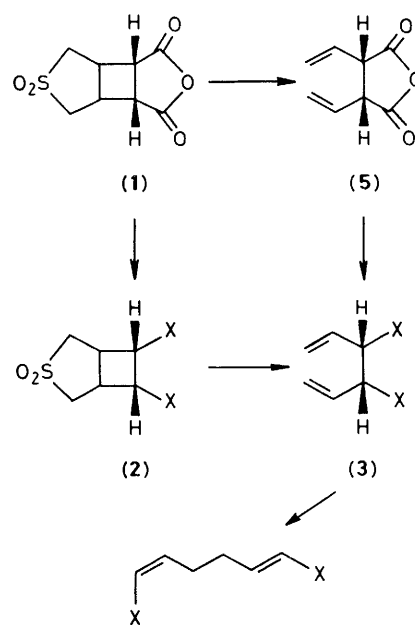


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1982A Simple, Stereocontrolled Synthesis of *E,Z*-1,5-Dienes†J. I. G. Cadogan,*^a Caroline M. Buchan,^b Ian Gosney,*^b Brendan J. Hamill,^b and Leo M. McLaughlin^b^a B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, U.K.^b Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

The readily available 3,3-dioxide (1) of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride acts as a general synthetic precursor for *E,Z*-1,5-dienes such as (4a—e) via functionalisation followed by thermal extrusion of SO₂.

Of the methods currently available for the synthesis of compounds with the *E,Z*-divinylethane grouping,¹ none allows the stereospecific construction of the carbon-carbon double bonds in a single step from a readily available precursor. We now report the realisation of this goal, exemplified by the preparation of the *E,Z*-1,5-dienes (4a—e)‡ in yields ranging from 30 to 87%.

The stereochemical course of our procedure, outlined in Scheme 1, relies on the usual chair-like transition state in the Cope rearrangement² of *meso*-1,2-divinyl compounds (3), generated by thermal extrusion of SO₂ from derivatives of the 3,3-dioxide (1) of *exo*-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride.§³ In a typical synthetic sequence, hydrolysis of (1) with boiling water, followed by esterification of the resulting diacid [(2a); 89%; m.p. 189–190 °C; ¹³C n.m.r. (CD₃SOCD₃) δ 173.66, 54.00, 43.87, and 33.79 p.p.m.] afforded the *cis*-diester [(2e); 91%; m.p. 126.5–127.5 °C; ¹³C n.m.r. (CD₃SOCD₃) δ 171.92, 53.17, 51.88, 43.00, and 33.29 p.p.m.] which on flash vacuum pyrolysis (550 °C at 10⁻³ mm Hg) gave the known *E,Z*-diene [(4e); 87%] in a purity of 85–90% (containing *ca.* 10% of the *E,E*-isomer)¶ as confirmed by ¹H n.m.r. spectral comparison with literature data⁴ and ¹³C n.m.r. spectroscopy [10 signals at δ(CDCl₃) 166.58, 166.28, 147.91, 147.54, 121.53, 120.29, 51.15, 50.81, 31.13, and 26.98 p.p.m.; *cf.* *E,E*-isomer, 5 signals at δ(CDCl₃)



- (4) a; X = CO₂H (34%)
 b; X = CH₂OH (39%)
 c; X = CH₂OMe (47%)
 d; X = CH₂OAc (30%)
 e; X = CO₂Me (87%)

Scheme 1

† Delivered at the Annual Congress of the Chemical Society, Durham, 9–11 April 1980 (*Chem. Br.*, 1980, 16, 385).

‡ All new compounds gave satisfactory microanalytical and spectral data.

§ The *exo*-configuration in this case is the one in which the two 5-membered rings are on opposite sides of the central cyclobutane ring.

¶ The product composition was quantitatively analysed by g.l.c. (10% Pega at 180 °C). Preparative g.l.c. under similar conditions allowed the isolation of the individual dienes in pure form for unequivocal identification.

166.25, 146.77, 121.57, 50.98, and 30.02 p.p.m.]. Alternatively, (4e) could be prepared by pyrolytic conversion of (1) into (5),³ esterification to give *meso*-dimethyl 2,3-divinylsuccinate [(3e); m.p. 36–37 °C; ¹³C n.m.r. (CDCl₃) δ 171.38, 132.61, 119.04, 52.49, and 51.51 p.p.m.], and subsequent

thermal rearrangement either under flash vacuum conditions (580 °C; 51%), or by heating at elevated temperatures for a short period of time.⁵

Similar pyrolyses of other derivatives obtained from (1) or (5) by conventional synthetic methods produced the dienes (4a–d) with a high degree of stereospecificity (>90%) in 30–47% yield. The stereochemistry of these products was validated by ¹³C n.m.r. spectroscopy, and in the case of the diacid [(4a); m.p. 111–113 °C; lit.⁶ 113–114 °C], by thermally induced isomerization to the *E,E*-form, m.p. 257 °C (decomp.) (lit.⁷ 256 °C). Subsequent conversion of the latter into its dimethyl ester gave a sample identical to that obtained by isomerization of (4e) in boiling heptane in the presence of iodine.

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Addendum (Received, 19th January 1982). After this work had been completed and following the submission of this communication, Williams and Lin⁸ confirmed our previously reported³ synthesis of *cis*-1,2-divinyl derivatives from the 3-thiabicyclo[3.2.0]heptane 3,3-dioxide ring system, and went on to claim that heating of these compounds, *e.g.* (3e), causes a Cope rearrangement leading cleanly to *E,E*-1,5-dienes in high yields. This is at variance with our results described above and those of others,^{2,5} which show that *meso*-1,2-divinyl compounds rearrange, upon thermolysis, with a remarkably high degree of stereoselectivity to *E,Z*-1,5-dienes. In actuality, *E,E*-1,5-dienes are the major products from the thermal re-

arrangement of (\pm)-1,2-divinyl intermediates. Evidence on this point, which also invalidates the claim of Williams and Lin, derives from our observation that conversion of (2e) with 1,5-diazabicyclo[5.4.0]undec-5-ene into its epimer [two ¹³C carbonyl resonances in CDCl₃ (δ 172.00 and 170.44 p.p.m.)], followed by pyrolysis in the usual way, gives a mixture of dimethyl octa-2,6-dienedioates containing 83% of the *E,E*-isomer (*cf.* ref. 5).

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