

3-Thiabicyclo[3.2.0]hept-6-ene 3,3-Dioxide: A Novel Synthon for *cis*-1,2-Divinyl Intermediates and Derived Seven-membered Ring Systems

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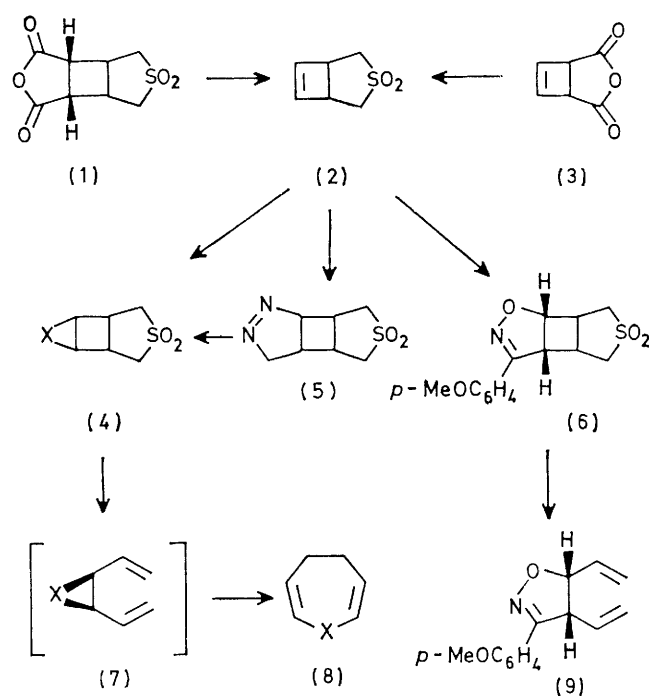
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Functionalisation of the 6,7-double bond in the novel bicyclic sulphone, 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide, followed by thermal extrusion of SO₂, allows direct entry into seven-membered ring systems via a Cope rearrangement of the resulting *cis*-1,2-divinyl intermediates.

A lack of regio-control in the functionalisation of the central double bond in *cis*-hexa-1,3,5-triene frustrates what is conceptually an attractive and potentially general approach to *cis*-1,2-divinyl compounds, a group of highly valued intermediates whose prime utility in organic chemistry lies in their propensity to undergo Cope rearrangements.¹ We report here a simple stratagem that not only circumvents the problem of regio-control, but also provides a convenient synthesis of seven-membered ring systems [*e.g.*, (8; X = O, NCO₂Et, CH₂)]. The method uses the novel bicyclic sulphone (2) as a masked form of *cis*-hexa-1,3,5-triene and involves two steps: structural elaboration of its 6,7-double bond as illustrated in Scheme 1 and subsequent elimination of SO₂ by flash vacuum pyrolysis.

The key synthon (2) was obtained as a colourless crystalline solid [m.p. 71–72 °C; ¹H n.m.r. (CDCl₃) δ 6.18 (2H,s), 3.7–3.6 (2H,m), and 3.2–2.9 (4H,m)][†] by two different routes, one involving oxidative bisdecarboxylation of the diacid of readily obtained (1)² either with lead tetra-acetate³ or by electrolysis,⁴ and the other from cyclobutene-3,4-dicarboxylic anhydride (3)⁵ using known methods.⁶ All reactions occurred in good preparative yields.

When (2) was subjected to flash vacuum pyrolysis at 400 °C and 10⁻³ mmHg, a *ca.* 1:1 mixture of *cis*-hexa-1,3,5-triene and its electrocyclised product, cyclohexa-1,3-diene, was obtained in virtually quantitative yield. Longer contact times by pyrolysis through a packed silica tube led exclusively to the latter. We have used this particular transformation to synthesize seven-membered ring systems. Thus, conversion of (2) into the epoxide (4; X = O) (m.p. 118–119 °C; 39%) by treatment with performic acid (55 °C; 48 h) followed by pyrolysis at 580 °C and 10⁻³ mmHg gave 4,5-dihydro-oxepin (8; X = O) (55%) as shown by comparison of ¹H and ¹³C



Scheme 1

n.m.r. spectra with literature data.^{7,8} Similar pyrolysis of the aziridine (4; X = NCO₂Et) (m.p. 142–143 °C),[‡] prepared in 31% yield by photolysis of (2) with neat ethyl azidoformate, produced the corresponding dihydro-azepine (8; X = NCO₂-

[†] All new compounds were characterised by combustion analysis as well as by ¹H and ¹³C n.m.r., i.r., and mass spectroscopy.

[‡] Compound (4; X = NCO₂Et) could also be obtained in 35% yield by base-induced elimination from Lwowski's salt (ref. 9), but only under phase-transfer conditions (ref. 10).

Et) which was isolated as a light-yellow oil [^1H n.m.r. (CDCl_3) δ 6.75 (2H,d, J 10 Hz), 5.4–5.2 (2H,m), 4.30 (2H,q), 2.35–2.25 (4H,m), and 1.25 (3H,t)] in 10% yield after preparative t.l.c.

Compound (2) also undergoes cycloaddition reactions with 1,3-dipoles, including diazomethane, which gave the adduct (5) (m.p. 157–158 °C) in 82% yield. Photolysis of (5) in acetonitrile yielded the cyclopropyl compound (4; $\text{X} = \text{CH}_2$) (m.p. 94–95 °C; 50%) which on pyrolysis at 475 °C and 10^{-3} mmHg afforded an 85% yield of C_7H_{10} hydrocarbons containing 94% of cyclohepta-1,4-diene as determined by g.l.c. (10% Pega at 55 °C) vs. authentic¹¹ pure compound.

The formation of these seven-membered ring compounds is envisaged as arising via an amply precedented^{12–14} Cope rearrangement of the transient *cis*-1,2-divinyl intermediates (7; $\text{X} = \text{O}$, NCO_2Et , CH_2), formed by cheletropic elimination of SO_2 . This behaviour is in contrast with the pyrolysis of the cycloadduct (6) (m.p. 182–184 °C), prepared in 45% yield from anisonitrile oxide, which at 500 °C and 10^{-3} mmHg gave the novel *cis*-1,2-divinyl derivative (9) (m.p. 58–60 °C; 33%) as the only product. Apparently, the ease with which cyclic *cis*-1,2-divinyl compounds undergo the Cope reaction depends on the size of the attached ring and for 5-membered ring systems such as (9), rearrangement is precluded.

Added in proof: Compound (2) also reacts with tetrachlorothiophene 1,1-dioxide¹⁵ to give the expected adduct in 34% yield, but pyrolysis of this compound at 550 °C in the usual way results in the exclusive formation of 1,2,3,4-tetrachlorobenzene by the unexpected loss of both SO_2 and butadiene. In this transformation, (2) acts as a dienophilic acetylene equivalent, a type of reagent that has aroused considerable recent interest.¹⁶

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