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Intramolecular Diels-Alder Reactions of Sulphonyl-substituted Trienes. Stereospecific Formation of *cis*-Fused Bicyclo[4.3.0] and -[4.4.0] Systems Possessing a Bridgehead Sulphonyl Group

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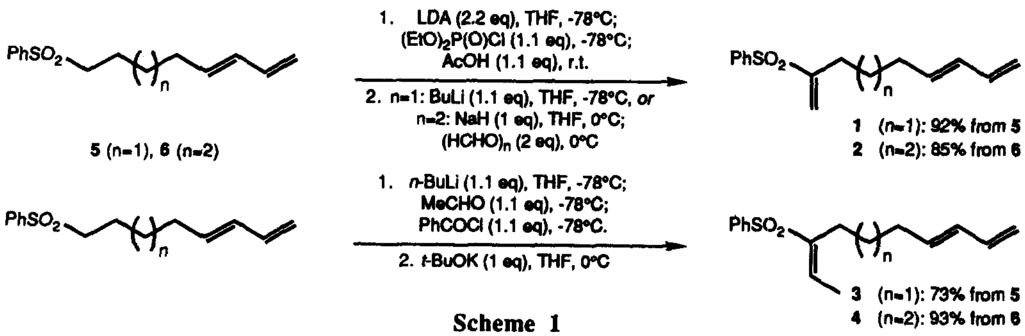
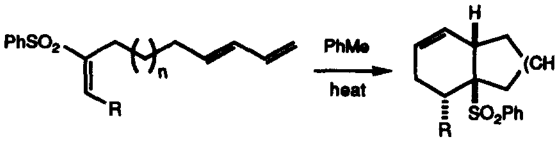
Abstract: The synthesis and thermal intramolecular Diels-Alder reactions of (*E*)-2-(phenylsulphonyl)-1,6,8-nonatriene **1**, (*E*)-2-(phenylsulphonyl)-1,7,9-decatriene **2**, (2*E*, 7*E*)-3-(phenylsulphonyl)-2,7,9-decatriene **3**, and (2*E*, 8*E*)-3-(phenylsulphonyl)-2,8,10-undecatriene **4** are described. The reactions are highly selective for the *cis*-fused bicyclic products, whose structures are assigned by X-ray crystallography. Substrate **2** undergoes competitive diene isomerization–IMDA reaction to give a bicyclo[4.3.0] cycloadduct.

The stereochemical outcome of the intramolecular Diels-Alder (IMDA) reaction is governed by several factors. These include the length of the chain linking diene and dienophile; the presence of substituents and/or heteroatoms within the tether; the nature and degree of substitution in the diene and dienophile.[1] For reactive substrates which undergo IMDA reaction at relatively low temperatures, *endo*-orientation of the dienophile with respect to the diene may be observed. Such secondary orbital effects may enhance or suppress any inherent preferences for *cis*- or *trans*-ring fusion resulting from the asynchronous nature of the cycloaddition. At higher temperatures, secondary orbital overlap becomes insignificant, and steric effects control product distribution to a greater extent. We recently reported[2] that a series of 1-(phenylsulphonyl) trienes undergo *exo*-selective thermal IMDA reaction. This was explained in terms of a preferred transition-state orientation of the bulky phenylsulphonyl group in the least sterically encumbered *exo*-environment. In this Letter, we describe thermal IMDA reactions of trienes substituted with a sulphonyl group at the internal position of the dienophile.

Trienes **1-4** were synthesized from (*E*)-1-(phenylsulphonyl)-5,7-octadiene **5** or (*E*)-1-(phenylsulphonyl)-6,8-nonadiene **6**[3] (Scheme 1). Application of the Wadsworth-Emmons route used for the preparation of **1** and **2** to the synthesis of **3** and **4** gave mixtures of vinyl sulphone geometric isomers. The alternative aldol-dehydration sequence shown typically gave **3** and **4** with *E*:*Z* ratios greater than 17:1.



Scheme 1



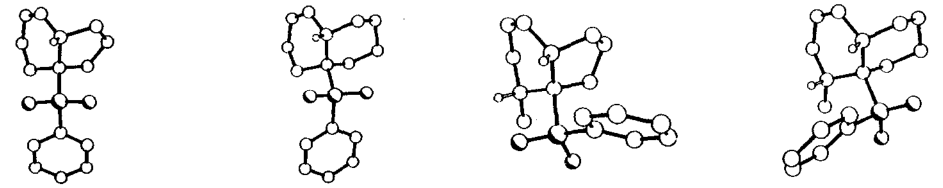
1 - 4 **7 - 10**

Scheme 2

Triene	Product	n	R	T(°C)	t (h)	yield (%)[4]
1	7	1	H	180	4.5	88
2	8	2	H	180	36	53[5]
3	9	1	CH_3	162	90	73[6]
4	10	2	CH_3	180	54	5

Table

The IMDA reactions of trienes **1** - **4** were performed on carefully degassed, dilute (*ca.* 0.02M) toluene solutions in $HN(SiMe_3)_2$-washed Carius tubes. Reaction times were determined on small-scale reactions of d_8-toluene solutions in sealed nmr tubes prior to carrying out the preparative experiments. Products were examined in all cases by ^1H nmr analysis (500 MHz) of the crude reaction mixtures after removal of solvent under reduced pressure. The structures of **7** - **10** were established by X-ray analysis of single crystals (Figure).[7]



X-ray structure of **7** X-ray structure of **8** X-ray structure of **9** X-ray structure of **10**

Figure

All four of the cycloaddition processes were found to be *cis*-specific (Scheme 2, Table). As with our earlier investigations of terminally dienophile-activated sulphonyl-substituted trienes,[2] we explain this stereospecificity in terms of a favoured *exo*-disposition of the sterically demanding phenylsulphonyl group. It may be noted from the Table that a 4-carbon linking chain (compare trienes **1** and **2**, **3** and **4**) and the presence of a β-methyl group on the dienophile (compare trienes **1** and **3**, **2** and **4**) both greatly attenuate reactivity, to the extent that triene isomerization may compete with cycloaddition. We are currently investigating IMDA reactions of substrates related to **1** - **4** possessing additional electron-withdrawing groups within the linking chain. The results of these studies will be reported in due course.

Acknowledgements

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References and notes

1. For a review of the IMDA reaction, and leading references, see: Craig, D. *Chem. Soc. Rev.* **1987**, 187.
2. Craig, D.; Fischer, D. A.; Kemal, Ö.; Marsh, A.; Plessner, T.; Slawin, A. M. Z.; Williams, D. J. *Tetrahedron* **1991**, *47*, 3095. Preliminary communication: Craig, D.; Fischer, D. A.; Kemal, Ö.; Plessner, T. *Tetrahedron Lett.* **1988**, *29*, 6367.
3. Dienyl sulphones **5** and **6** were prepared from (*E*)-5,7-nonadienol and (*E*)-6,8-nonadienol respectively, *via* sequential mesylation, bromide displacement, and reaction with sodium phenylsulphinate–DMSO. The dienols were prepared analogously to a published procedure: Lin, Y.-T.; Houk, K. N. *Tetrahedron Lett.* **1985**, *26*, 2269.
4. Yields are for pure materials isolated by flash chromatography on silica gel. All new compounds gave nmr and ir data, and elemental combustion analyses in accord with the proposed structures.
5. Bicycle **8** was formed together with *ca.* 22% of the product of IMDA reaction of (*E*)-2-(phenylsulphonyl)-1,6,8-decatriene, presumably formed *via* isomerization of **2** *in situ.*
6. *Ca.* 10% of (2*E*, 6*E*, 8*E*)-3-(phenylsulphonyl)-2,6,8-decatriene was formed in this reaction, presumably *via* isomerization of **3**. Bicycle **9** was obtained in 60% yield after fractional crystallization (benzene-petrol).
7. We thank Dr D. J. Williams and Ms A. M. Z. Slawin (Imperial College) for these determinations.

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