Intramolecular Diels–Alder reactions of 1-phenylsulfonylalka-1,2,(ω − 3),(ω − 1)-tetraenes

James R. Bull,* Richard Gordon and Roger Hunter

Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

Received (in Cambridge, UK) 27th June 2000, Accepted 25th July 2000
Published on the Web 1st September 2000

Methods are described for conversion of a series of (*E*)-alka-(ω − 3),(ω − 1)-dienals **2**, *via* ethynylation to the corresponding alkadienynols **3**, followed by sequential [2,3] sigmatropic rearrangement of their derived phenylsulfenate esters and chemoselective oxidation, into 1-phenylsulfonylalka-1,2,(ω − 3),(ω − 1)-tetraenes **5**, which are used to study the influence of tether length and peripheral substitution upon intramolecular cycloaddition reactivity and selectivity. It is demonstrated that (6*E*)-1-phenylsulfonylnona-1,2,6,8-tetraene **5c** and substrates featuring an analogous ethylene linkage between the functional termini, display exceptionally high intramolecular Diels–Alder (IMDA) reactivity, accompanied by *exo*-diastereoselectivity. Comparative studies are described, which delineate structure–reactivity trends and demonstrate the unique capacity of the dienophilic allenyl terminus to impose reactivity-enhancing conformational constraints upon IMDA processes in favourable cases. Preliminary investigations into substrates incorporating cyclic dienyl substructures are reported, and a novel approach to spiro[4.5]decanoid ring systems is described.

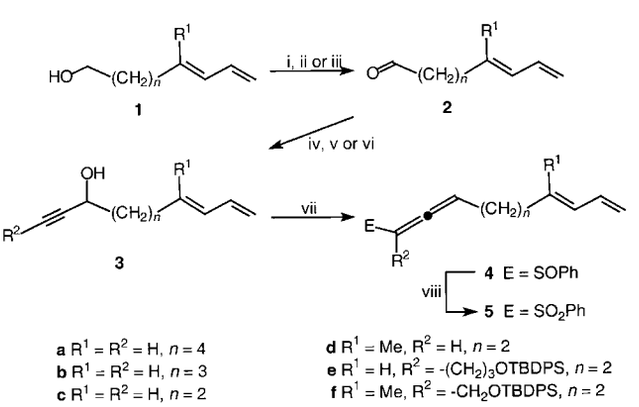
Introduction

Intramolecular Diels–Alder (IMDA) reaction methodology constitutes a key strategic step in the synthesis of many complex polycyclic molecules, and continues to receive attention as a vehicle for evaluating and applying emerging principles of reactivity and selectivity.[1] As part of our investigations into the reactivity of allenyl dienophiles in cycloaddition methodology,[2] we became interested in the scope for incorporating a phenylsulfonylallenyl dienophilic terminus into substrates for IMDA reactions. Phenylsulfonylallene is a useful reactant in intermolecular cycloaddition methodology,[3] and we sought to take advantage of the favourable reactivity associated with this functionality and, most importantly, to prepare the way for exploiting axial chirality as a tool for conducting IMDA reactions leading to enantiocontrolled synthesis of cyclic products.

Allenyl functionality has featured in a limited number of studies on intramolecular cycloaddition, both as the dienophilic terminus[4] and as part of the diene substructure.[5] It has been shown[6] that certain thermally induced cycloadditions involving 3-phenylsulfonylallenyl-terminated substrates are characterised by competition between [2 + 2] and [2 + 4] pathways, which are sensitive to peripheral structural features, and do not necessarily engage the dienophilically activated π-bond of the allenyl group. Additionally, evidence has emerged for an ene pathway in reactions of a presumed 1-phenylsulfonylallenyl olefin,[7] thus complementing the foregoing cycloaddition modes of ring formation. The underlying factors responsible for dictating alternative reaction outcomes are not evident from these reports, suggesting much scope for systematic exploration of IMDA reaction methodology in this area. Accordingly, we set out to test structure–reactivity trends associated with 1-phenylsulfonylallenyl-terminated substrates, and to ascertain whether useful levels of diastereoselectivity and periselectivity could be achieved. The first phase of this investigation addresses the question of the roles of 1-phenylsulfonyl substitution and of tether length on thermal reactivity of alka-1,2,(ω − 3),(ω − 1)-tetraenyl templates.[8]

Results and discussion

A general synthetic approach to model substrates for this investigation was envisaged through ethynylation of (*E*)-alka-(ω − 3),(ω − 1)-dienals **2**, and exploitation of the familiar [2,3] sigmatropic rearrangement[9] of derived propargylic phenylsulfenate esters (propargyl = prop-2-ynyl) to the corresponding terminal phenylsulfinylallenes **4**, followed by chemoselective oxidation to the 1-phenylsulfonylalka-1,2,(ω − 3),(ω − 1)-tetraenes **5** (Scheme 1). An early objective was to synthesise



Scheme 1 *Reagents and conditions*: (i) Swern oxidation; (ii) PCC, CH_2Cl_2, 20 °C; (iii) Dess–Martin periodinane, CH_2Cl_2, 20 °C; (iv) HC≡CMgBr, THF, 20 °C; (v) TBDPSO$(CH_2)_3$C≡CH, *n*-BuLi, THF, 0 °C; (vi) TBDPSOCH_2C≡CH, *n*-BuLi, THF, 0 °C; (vii) PhSCl, NEt_3, CH_2Cl_2, −78 °C; (viii) MCPBA, CH_2Cl_2, 0–25 °C.

the parent tetraenes **5a**–**5c** ($R^1 = R^2 = H$), distinguished respectively by tetramethylene, trimethylene and ethylene linkages between the functional termini, in order to ascertain the role of tether length upon intramolecular reactivity and periselectivity. Ensuing investigations were influenced by the outcome of these preliminary experiments, and entailed synthesis of ethylene-tethered tetraenes **5d**–**5f**, incorporating chain extension at C-1 and/or alkyl substitution at C-6.

DOI: 10.1039/b005146m

Table 1 Summary of reaction conditions and cycloadduct distributions

		Reaction conditions		Product(s)		
Tetraene	% *E*	Temp./°C	Time/h	Total[a]	Distribution[b]	
5a	88	180	24	34	**6** (100)	
5b	97	80	20	73	**7** (25)	**8** (75)
5c[c]	95	≤30	0.5	71	**9** (21)	**10** (79)
5d	100	150	2	58	**11** (22)	**12** (78)
5e	95	50	2	79	**13** (100)	
5f	100	150	2	0[c]	—	

[a] 'Total' refers to % yield of IMDA product(s) corrected for exclusive participation by the (*E*)-isomer. [b] Distribution of isomers, showing relative proportions of isolated products in parentheses. [c] Data based upon **4c** as starting material (see text).

Synthesis of starting materials

The starting (*E*)-alkadienols **1** were synthesised using routine literature methodology, with some minor adaptations designed to optimise yields and *E*-selectivity. For example, hexane-1,6-diol was converted into nona-6,8-dien-1-ol **1a**[10] (88% *E*) over five standard steps, and Swern oxidation gave aldehyde **2a**,[11] which was ethynylated to give dienynol **3a**. The aldehyde **2a** (as well as the structural analogues **2b**–**2d**) proved to be labile and highly volatile, which necessitated immediate conversion into the more tractable **3a**, which displayed the expected spectroscopic properties, most notably, distinctive ^{1}H NMR multiplets for the propargylic functionality at δ 2.47 (dd, *J* 2.3 and 0.8, 1-H) and δ 4.40 (td, *J* 2 × 6.3 and 2.3, 3-H).

Reaction of propargyl alcohol **3a** with benzenesulfenyl chloride[12] and triethylamine at −78 °C gave the 1-phenylsulfinylallene **4a** in 77% yield, arising from the formation of the intermediate phenylsulfenate ester and subsequent [2,3] sigmatropic rearrangement.[9] Spectrosopic examination revealed that **4a** occurs as the expected mixture of diastereomeric sulfoxides and, although partial chromatographic separation was possible, the mixture was preferably oxidised with *m*-chloroperbenzoic acid (MCPBA) to give the derived 1-phenylsulfonylundeca-1,2,8,10-tetraene **5a** (66%), full characterisation of which confirmed the structure, and thereby also those of the precursors. ^{1}H NMR spectroscopy of **5a** displayed diagnostic signals for the allenyl protons at δ 6.19 (dt, *J* 6.2 and 2 × 3.1, 1-H) and δ 5.83 (td, *J* 2 × 7.0 and 6.2, 3-H), in addition to those of the 8*E*,10-dienyl protons. Although MCPBA oxidation of **4a** displayed satisfactory chemoselectivity, attempts to force this and related reactions to completion through use of excess reagent and longer reaction times resulted in loss of material, presumably through intrusion of competing olefinic bond epoxidation.

Octa-5,7-dien-1-ol **1b** (97% *E*; prepared from 2-allyltetrahydropyran according to a procedure described by Schlosser *et al.*[13]) was similarly subjected to successive oxidation (to **2b**) and ethynylation to give propargyl alcohol **3b** in 67% overall yield. Phenylsulfenylation–rearrangement followed by oxidation afforded 1-phenylsulfonyldeca-1,2,7,9-tetraene **5b**.

Orthoester Claisen rearrangement of penta-1,4-dien-3-ol,[14] followed by reduction of the resultant ethyl hepta-4,6-dienoate with diisobutylaluminium hydride (DIBAL-H) gave hepta-4,6-dien-1-ol **1c** (95% *E*) in an overall yield of 86%. An alternative preparation of **1c** entailed reaction of pent-4-yn-1-yl *tert*-butyldiphenylsilyl (TBDPS) ether with zirconocene hydrogen chloride (Schwartz's reagent[15]), followed by treatment with iodine. Stille coupling[16] of the resulting vinyl iodide with vinyltributyltin resulted in highly selective formation of essentially pure (*E*)-dienol **1c**. The latter reaction sequence, although lower yielding than the former, provided a more versatile general approach to structural variants (*e.g.* **1d**, below) of the ethylene-linked tetraene prototype. Conversion of **1c** (*via* **2c** and **3c**) into 1-phenylsulfinylnona-1,2,6,8-tetraene **4c** proceeded routinely, but MCPBA oxidation of **4c** failed to furnish isolable 1-phenylsulfonyl derivative **5c**, owing to an unavoidable further reaction, which is discussed in the context of the IMDA reactions. 4-Methylhepta-4,6-dien-1-ol **1d**[17] was similarly converted into 1-phenylsulfinyl-6-methylnona-1,2,6,8-tetraene **4d** which, in contrast to **4c**, furnished the isolable and readily characterised 1-phenylsulfonyl compound **5d** upon oxidation with MCPBA.

Finally, two further model substrates featuring attachment of functionalised alkyl groups at C-1 of a 1-phenylsulfonylnona-1,2,6,8-tetraenyl substructure, were synthesised *via* alkynylation of **2c** and **2d**, followed by the standard rearrangement–oxidation sequence, to give **5e** and **5f** respectively. These low-yield procedures have not been optimised, but provided sufficient material upon which to test the influence of these substitution patterns on reactivity.

IMDA reactions of 1-phenylsulfonylalka-1,2,(ω − 3),(ω − 1)-tetraenes 5a–5f

With the selected range of 1-phenylsulfonylalkatetraenes **5** in hand for evaluation of their cycloaddition behaviour, a solution of each compound was heated under nitrogen in a sealed tube, at a temperature chosen to promote the desired reaction course whilst minimising adventitious decomposition as revealed by TLC and/or NMR monitoring. As far as possible, the reported reaction conditions represent minimum temperatures and times for complete consumption of starting material. Although these results were reproducible, no attempt was made to explore the scope for optimisation of reaction duration and yields through variations in solvent and concentration. The results of these experiments are outlined in Scheme 2, and summarised for comparison in Table 1.

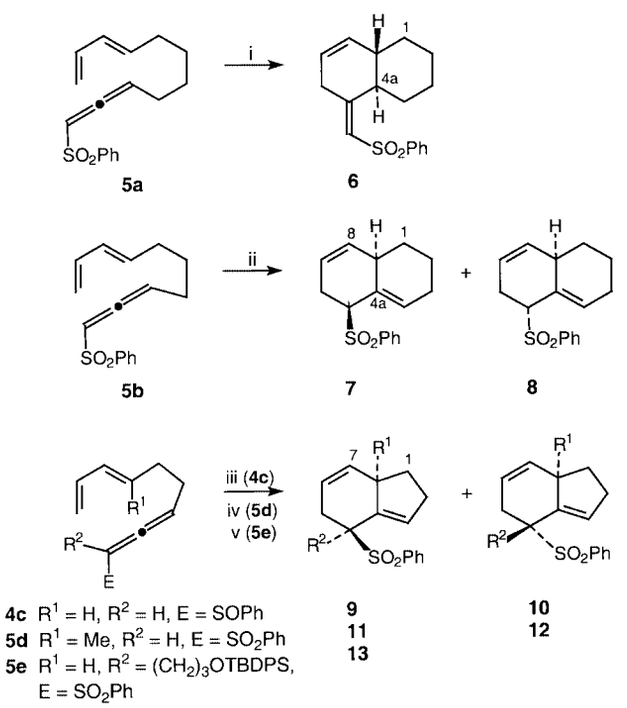
Certain distinctive features of specific reactions warrant comment. In the first place, the inefficiency of the IMDA process for 1-phenylsulfonylundeca-1,2,8,10-tetraene **5a** is noteworthy. Experiments performed at 120 and 150 °C resulted only in slow but progressive deterioration of substrate integrity, without formation of discrete products. However, the elevated temperature (180 °C) at which formation of product **6** was observed, was also accompanied by extensive decomposition. On the other hand, the IMDA reaction of 1-phenylsulfonyldeca-1,2,7,9-tetraene **5b** proceeded cleanly at 80 °C. The extraordinary IMDA reactivity of 1-phenylsulfonylnona-1,2,6,8-tetraene **5c** was inferred from the failure to isolate the compound following oxidation of the precursor **4c** at 0 °C. As a consequence, the oxidation mixture was maintained at 30 °C for 20 min, which resulted in completion of the IMDA process.

The latter result influenced the decision to extend the study, by incorporating the core substructure of **5c** into further-substituted substrates. Introduction of a 6-methyl group resulted in a significant suppression of the IMDA reactivity of **5d** (requiring 2 h at 150 °C for consumption of starting material) as well as loss of yield, whereas chain extension at C-1 enabled the compound **5e** to be prepared and characterised with ease, but nevertheless to display impressive IMDA reactivity in $CDCl_3$ at 50 °C (solvent chosen to facilitate NMR

Table 2 Comparative ^{1}H NMR data for the cycloadducts **7**–**13**[a]

	Olefinic proton signals				$CHSO_2Ph$			
Cpd	δ	Mult.	J/Hz	position	δ	Mult.	J/Hz	position
7	6.55	br d	2	4-H	3.82	ddd	9.4, 3.5, 1.3	5-H
	5.52	ddt	9.9, 7.7, 2.4. 2.4	7-H				
	5.43	br d	9.9	8-H				
8	5.25	m	$W_{\frac{1}{2}}$ 4.4	4-H	3.72	d	8.4	5-H
	5.65	dddd	10.4, 6.4, 4.8, 2.4	7-H				
	5.57	br d	10.4	8-H				
9	6.42	t	2.3, 2.3	3-H	3.78	m	W 21.7	4-H
	5.18	ddt	9.8, 5.0, 2.4, 2.4	6-H				
	5.41	br d	9.8	7-H				
10	5.37	br d	2.4	3-H	4.04	d	8.4	4-H
	5.57	ddt	10.0, 4.4, 2.7, 2.7	6-H				
	5.57	dq	10.0, 2.4, 2.4, 2.4	7-H				
11	6.1	br d	1.8	3-H	3.92	m	W 20.7	4-H
	5.38	ddd	9.9, 5.3, 2.3	6-H				
	5.65	dd	9.9, 2.7	7-H				
12	5.6	m	$W_{\frac{1}{2}}$ 1.7	3-H	4.14	m	W 16	4-H
	5.55	dt	10.0, 3.7, 3.7	6-H				
	5.82	br d	10.0	7-H				
13	5.4	br s		3-H				
	5.63	ddd	9.9, 7.4, 2.5	6-H				
	5.7	br d	9.9	7-H				

[a] All spectra recorded at 400 MHz in $CDCl_3$. See Experimental for details.



Scheme 2 *Reagents and conditions*: (i) $C_6H_5CH_3$, 180 °C, 24 h; (ii) $C_6H_5CH_3$, 80 °C, 20 h; (iii) (a) MCPBA, CH_2Cl_2, 0 °C, 30 min, then quenched by aq. $NaHCO_3$; (b) CH_2Cl_2, 30 °C, 20 min; (iv) $C_6H_5CH_3$, 150 °C, 2 h; (v) $CDCl_3$, 50 °C, 2 h.

monitoring, which showed complete reaction after 2 h). Combination of the foregoing structural features, exemplified by the 1,6-disubstituted substrate **5f**, resulted in loss of IMDA reactivity comparable to that of **5d**, and apparent loss of selectivity, suggested by the conversion of substrate into an intractable mixture after 2 h at 150 °C.

The structural assignments of the cycloadducts **6**–**13** were based largely upon extensive ^{1}H and ^{13}C NMR spectroscopy, supported by COSY techniques. In general, the gross structures of the cycloadducts were readily discerned from the presence, the chemical shifts and the coupling relationships of signals for the olefinic protons and, where applicable, for those of the methine proton α- to the $PhSO_2$ group (Table 2). Aspects of the stereochemical assignments demanded interpretative analysis of spectrosopic results, aided by mechanistic inferences.

The ensuing comments identify salient features of these assignments. The bicyclo[4.4.0]decene substructure of **6** was evident from a self-consistent pattern of COSY correlations, supported by evidence for a phenylsulfonylmethylene group, and a *trans*-ring junction was assigned owing to the diagnostic width of the 4a-proton signal. The latter assignment conferred obligatory *Z*-orientation on the 5-substituent. Differentiation of the cycloadducts **7** and **8** followed from a comparison of the 5-H signals, which revealed the expected multiplicities and coupling magnitudes associated with vicinal and allylic couplings in the appropriate conformers of each epimer, supported by orientationally sensitive anisotropic deshielding of 4-H by the $PhSO_2$ group in **8**. Similar patterns of differentiation were discerned in both pairs of bicyclo[4.3.0]nonadiene epimers **9**/**10** and **11**/**12**, and the C-4 configuration of **13** was based on analogy.

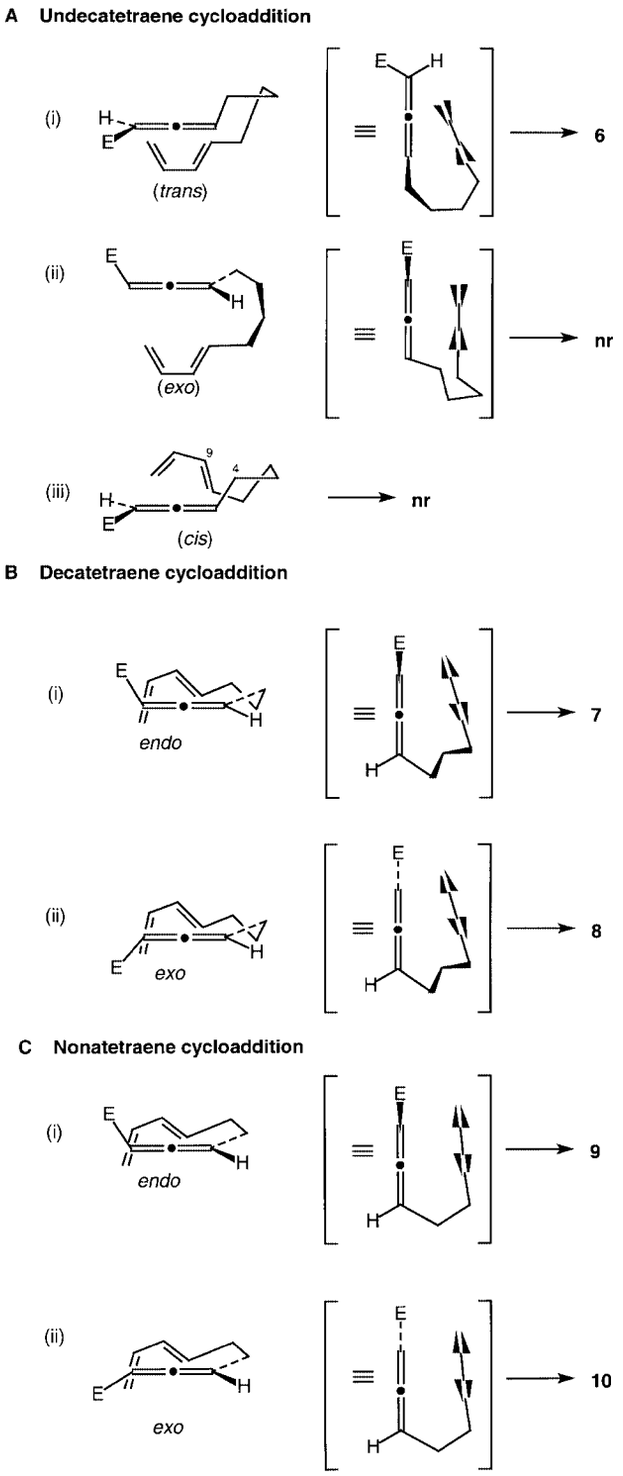
Finally, an X-ray crystal structure determination on a representative cycloadduct **8** confirmed the assignment[8] and, by extension, those of the epimer **7** and of the cycloadducts assigned by comparative NMR analysis. Notably, the conformation of **8** was indeed revealed to confer a nearly orthogonal torsion angle relationship (88.9°) on 5β-H and 6α-H, thereby rationalising the absence of vicinal coupling observed in the NMR spectra of this and similarly assigned cycloadducts.

Mechanism and selectivity

A common feature of the foregoing experiments was the exclusive pattern of [4 + 2] cycloaddition behaviour in all cases. Although the sometimes moderate yields of characterisable products suggest that alternative or competing modes of reaction may intervene in certain cases, we have not found evidence to support this. Secondly, the relationship between tether length and reactivity is compellingly demonstrated in the comparison of reaction outcomes for **5a**, **5b** and **5c**.

The poor result for the undecatetraene **5a** is instructive, since it clearly illustrates limited IMDA reactivity associated with a tetramethylene tether, and preference for generation of a 6,6- rather than a 6,7-fused ring system, consistent with the richly exemplified former pathway in aliphatic triene substrates.[1] However, the extent to which IMDA reaction occurs, with attendant participation of the unactivated Δ^2-bond of the

phenylsulfonylallenyl terminus, suggests that transition state alignment of the reaction centres rather than nascent ring size is decisive, even in the presence of the more reactive Δ^1-bond. Thus, the observed reaction course accommodates a chair-like tether orientation, whereas engagement of the Δ^1-bond can only proceed *syn* to C(3)–C(4), and thus encounters sterically demanding or orientationally improbable juxtapositions of reaction centres (Scheme 3). The isolation of *trans*-fused product only, is not readily prefigured by comparison of the respective *exo*- and *endo*-transition state alignments, but this may not be meaningful in the light of poor overall recovery of product.



Scheme 3 Conformational perspectives of IMDA alignments for undecatetraene **5a** (**A**), decatetraene **5b** (**B**), and nonatetraene **5c** (**C**) (E = SO_2Ph).

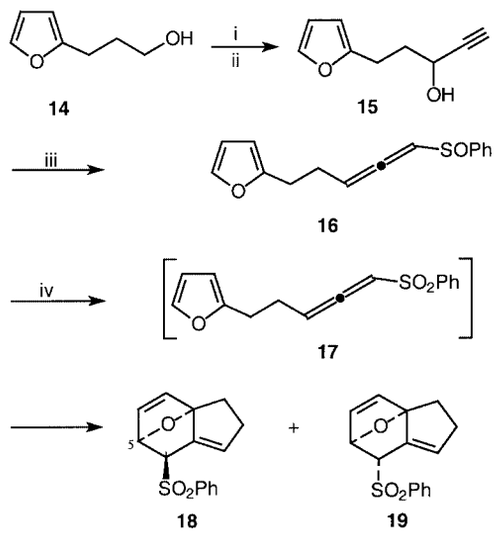
The IMDA reaction rate for the decatetraene **5b** is considerably higher than that reported for the structurally analogous 1-phenylsulfonyldeca-1,7,9-triene,[18] which requires treatment at 140 °C for 44 h to furnish a single product arising from *exo*-oriented cycloaddition. It is evident that the additional geometrical constraint imposed by the inner π-bond of the phenylsulfonylallenyl group of **5b**, not only necessitates bond formation *syn* to C(3)–C(4), but also facilitates favourable alignment of the reaction termini. This constraint also appears to relieve steric interactions between the $PhSO_2$ and dienyl groups, or within the tether, to an extent that allows some competing participation by an *endo*-transition state (Scheme 3), although *exo*-selectivity remains preponderant (~3 : 1). The dienophilic reactivity of the phenylsulfonylallenyl terminus is most dramatically manifested by the facility with which the nonatetraene **5c** undergoes IMDA reaction. It is inferred that the factors responsible for reactivity in the foregoing example are amplified here through highly advantageous juxtaposition of reaction termini (Scheme 3) and by conservation of those steric features which favour the *exo*-transition state leading to a similar diastereomer distribution (~4 : 1). This level of reactivity and stereoselectivity contrasts even more sharply with that of 1-phenysulfonylnona-1,6,8-triene,[18] which required treatment at 140 °C for 44 h to give a ~1 : 1 mixture of *exo*- and *endo*-derived cycloadducts.

Not surprisingly, the exceptional reactivity of **5c** is somewhat suppressed in the 6-methylnonatetraene **5d**, owing to the introduction of an additional steric impediment at one reaction terminus. Nevertheless, the substrate must enjoy a similar intramolecular alignment of reaction centres during IMDA reaction, since the isomer distribution for **5d** is similar to that of **5c**, although overall yields are reduced. The IMDA reaction rate of compound **5e**, which features a 1-alkyl chain attached to the nonatetraene substructure, is also diminished in comparison with **5c**, but remarkably little for this level of substitution at the dienophilic terminus. Furthermore, the reaction is highly efficient and stereoselective, implying that the *endo*-relationship between the 1-alkyl chain and the diene terminus imposes no adverse steric effects upon the *exo*-transition state [*cf.* conformational drawing C(ii), Scheme 3], but rather, reinforces it. A practical implication of the latter IMDA reaction is that it offers a superior strategy for synthesis of 4-alkylhydrindanes (hydrindane = hexahydroindane), since attempted base-mediated alkylation of cycloadducts **9** or **10** proceeds with poor diastereoselectivity. The evident complexity of the reaction outcome involving the 1,6-dialkylnonatetraene **5f**, suggests that this level of substitution and attendant steric crowding result in diminished reactivity and selectivity.

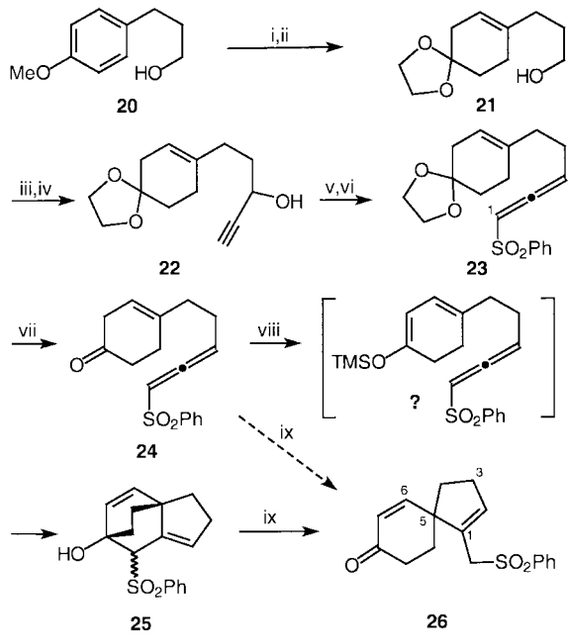
Further synthetic applications

The foregoing results invited exploration of reactants in which the 1-phenylsulfonylallenyl terminus is linked *via* an ethylene tether to more elaborate dienyl substructures. In particular, it was of interest to examine the scope for achieving IMDA closure onto cyclic dienyl systems, in order to prepare more elaborate bridged polycyclic structures. The record of successful IMDA reactions involving furanyl dienes ('IMDAF' reactions) with appropriately linked dienophilic allenyl groups[19] suggested that the synthesis and IMDAF reaction of 5-(2-furyl)-1-phenylsulfonylpenta-1,2-diene **17** would be an instructive first objective (Scheme 4).

3-(2-Furyl)propan-1-ol **14**[20] was converted, *via* sequential oxidation, ethynylation and rearrangement, into the 1-phenylsulfinylpenta-1,2-dienyl intermediate **16**, in an overall yield of 42%. Treatment of the sulfoxide **16** with MCPBA at −10 °C for 30 min revealed evidence (TLC) of the expected oxidation accompanied by further reaction, and a low-temperature quench and work-up procedure was adopted in an attempt to intercept the intermediate as well as derived



Scheme 4 *Reagents and conditions*: (i) Dess–Martin periodinane, CH_2Cl_2, 20 °C; (ii) HC≡CMgBr, THF, 20 °C; (iii) PhSCl, NEt_3, −78 °C; (iv) MCPBA, CH_2Cl_2, −10 °C; work-up at 0 °C.



Scheme 5 *Reagents and conditions*: (i) Li, NH_3, EtOH; (ii) $(CH_2OH)_2$, $BF_3{\cdot}OEt_2$, THF; (iii) Dess–Martin periodinane, CH_2Cl_2, 25 °C; (iv) HC≡CMgBr, THF, 25 °C; (v) PhSCl, NEt_3, CH_2Cl_2, −78 °C; (vi) MCPBA, CH_2Cl_2, 25 °C; (vii) (a) TFA, 25 °C; (b) $NaHCO_3$, 0 °C; (viii) LDA, TMSCl, −78 °C→25 °C; (ix) KOH, THF–H_2O–MeOH, 25 °C.

products. An ^{1}H NMR spectrum of the isolate revealed a three-component mixture (10:2:1), in which the major product **19** (see below) was accompanied by components displaying signals tentatively assigned to the obligatory phenylsulfonyl intermediate **17** [δ 5.87 (td, J 2 × 7.0 and 6.2, 3-H) and 6.20 (dt, J 6.2 and 2 × 3.1, 1-H)] and an *endo*-cycloadduct **18** [δ 5.45 (m, 3-H), 4.42 (d, J 3.6, 4-H), 5.30 (dd, J 3.6 and 1.7, 5-H), 6.57 (dd, J 5.6 and 1.7, 6-H) and 6.54 (d, J 5.6, 7-H)].

Chromatography of the crude reaction product resulted in isolation of the pure major product only (63%), the structure of which was assigned as the *exo*-cycloadduct **19**, on the basis of convincing ^{1}H NMR evidence. In addition to the readily identified olefinic proton signals at δ 5.75 (dt J 3.3 and 2 × 1.9, 3-H), 6.41 (dd, J 5.7 and 2.1, 6-H) and 6.50 (d, J 5.7, 7-H), those at δ 3.65 (dt, J 3.4 and 2 × 1.9, 4-H) and 5.38 (d, J 2.1, 5-H) were assigned with the aid of COSY correlations, which also revealed an absence of vicinal coupling between 4-H and 5-H, thereby confirming the orthogonal relationship between the bridgehead and neighbouring *endo*-proton in the 7-oxanorbornanoid substructure. Further supporting evidence for the assignment stemmed from the unexpected complexity of the signal for 4-H, which displayed long range coupling to 2-H_2 and to 3-H, as verified through COSY correlations. Homoallylic coupling is known to occur between allylic protons separated by a π-bond,[21] and typically ranges between 1.9 and 3.5 Hz for cyclic systems, maximised by orthogonality between the coupling partners. The conformation of **19** is compatible with the assignment of 4-H multiplicity to homoallylic couplings $^5J_{2\beta,4}$ 3.4 and $^5J_{2\alpha,4}$ 1.9, together with an allylic coupling, $^4J_{3,4}$ 1.9.

The outcome of this experiment further demonstrates the exceptional IMDA reactivity associated with the nonatetraenyl structural motif, and the synthetic potential of this approach to assembly of polycyclic ring systems. A further application was suggested by the known facility with which cycloadducts derived from phenyl vinyl sulfone and terminally oxygenated dienes undergo base-mediated fragmentation,[22] and entailed synthesis of a 1-oxy-4-(5-phenylsulfonylpenta-3,4-dienyl)cyclohexa-1,3-dienyl derivative, upon which to test the potential for exploiting an IMDA–fragmentation sequence to synthesise functionalised spiro[4.5]decanes (Scheme 5).

3-(4-Anisyl)propan-1-ol **20**[23] (prepared routinely from 4-allylanisole) was subjected to sequential Birch reduction and hydrolysis–ketalisation. Dess–Martin oxidation of the resultant alcohol **21**, followed by ethynylation furnished the propargyl alcohol **22** in good overall yield. Phenylsulfenylation–rearrangement, and subsequent MCPBA oxidation, without isolation of the intermediate, gave the expected phenylsulfonylallene **23**. The modest overall yield (41%) was ascribed to losses through competitive epoxidation of the isolated olefinic bond. Deprotection of **23** with TFA proceeded smoothly to give the 4-substituted cyclohexenone **24** (92%), but ensuing enolisation (LDA–THF, −78 °C), followed by attempted trapping with chlorotrimethylsilane resulted in formation of a complex mixture, chromatography of which furnished a minor fraction (12%) displaying ^{1}H NMR signals consistent with a diastereomeric mixture (~5:1) of desilylated cycloadducts **25**. Evidence for the structure of the major component included signals at δ 4.90 (q, J 3 × 2.2, 3-H), 6.12 (d, J 8.6, 6-H) and 6.10 (d, J 8.6, 7-H) for the olefinic protons and at 4.05 (br s) for 4-H, whereas the minor component displayed a similar pattern of signals at δ 5.65 (q, J 3 × 2.0, 3-H), 6.12 (d, J 8.6, 6-H), 5.60 (d, J 8.6, 7-H) and 4.15 (br s, 4-H).

Although isolation of this minor fraction implies that the putative tetraenyl substrate is indeed formed and readily undergoes IMDA reaction, several sources of interference militate against a preparatively useful outcome. Inadequate regiocontrol during deprotonation–trapping, competitive isomerisation, inefficient trapping and substrate lability may all be contributory, and attempts to improve the reaction sequence through variations in reaction conditions and trapping agents have hitherto failed. Nevertheless, the validity of this overall strategy for synthesis of the target spiro system was demonstrated through treatment of **25** with aqueous alkali to give 1-(phenylsulfonylmethyl)spiro[4.5]deca-1,6-dien-8-one **26** (70%), the structure of which was fully supported by analytical and spectrosopic data. This product proved to be identical to a minor by-product, noted during the exploratory phase of the deprotection of the ketal **23** into the cyclohexenone intermediate **24**, and raised the intriguing possibility that an IMDA–fragmentation mediated protocol might be superfluous. Indeed, deprotection of the ketal **23** with TFA, followed by immediate treatment of the reaction mixture with aqueous alkali furnished the spiro compound **26** (85%), in a simple and efficient one-pot process, *via* a dienolate-initiated intramolecular Michael

reaction. Although tangential to the thrust of the IMDA investigation, this serendipitous finding not only circumvents the troublesome features of the former process, but opens a new synthetic route to spiro[4.5]decanoid systems.

In conclusion, this study has shown that IMDA processes mediated by a dienophilic 1-phenylsulfonylallenyl terminus display strong dependence upon tether length, and that an ethylene linker to the dienyl moiety imposes an ideal conformational constraint for extraordinarily facile reaction in which *exo*-product formation predominates. Extension of the model study, to substrates featuring substitution or skeletal modification of the nonatetraenyl substructure, reveals much potential for further development and synthetic applications. Furthermore, the 1-phenylsulfonylallenyl grouping offers scope for exploiting axial chirality to perform diastereocontrolled IMDA reactions, in a novel approach to enantiopure cyclic intermediates for synthesis. Indeed, preliminary investigations support this contention, and will form the subject of a forthcoming publication.

Experimental

Melting points were determined using a Reichert-Jung Thermovar hot-stage microscope and are uncorrected. Infrared spectra were recorded as chloroform solutions on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR were recorded on a Varian VXR-200 instrument at 200 MHz, a Varian Mercury at 300 MHz or a Varian Unity spectrometer at 400 MHz. All ^{1}H NMR spectra were recorded at 200 MHz and ^{13}C at 50 MHz in deuteriochloroform, unless otherwise stated, using $CHCl_3$ (δ 7.26) as internal standard. Chemical shifts are reported as δ/ppm from tetramethylsilane, and J values are given in Hz, using conventional descriptors for multiplicities. Elemental analyses were performed using a Fison's Instruments Elemental Analyser EA1108. Mass spectra were recorded on a VG micromass 16F spectrometer and accurate mass determinations were performed on a Kratos Limited MS9/50 spectrometer. All mass spectra data were obtained using electron impact techniques unless otherwise stated. Silica gel refers to Merck Kieselgel 60, 63–200 μm for gravity chromatography and 40–60 μm for flash chromatography. Unless otherwise stated, column chromatography was performed using a substrate–adsorbent ratio of ~1 : 100 and indicated solvent mixtures as eluents.

Synthesis of dienols 1

Compound 1a. Hexane-1,6-diol was converted, *via* sequential mono-benzoylation, Swern oxidation, allylidenation, isomerisation and deprotection, into nona-6,8-dien-1-ol, which displayed analytical and spectroscopic properties consistent with the (6*E*)-isomer **1a**,[10] containing 12% of the (6*Z*)-isomer.

Compound 1b. Octa-5,7-dien-1-ol **1b** (97% *E*) was prepared from 2-allyltetrahydropyran following the procedure of Schlosser *et al.*[13]

Compound 1c. *Method 1.* Orthoester Claisen rearrangement of penta-1,4-dien-3-ol with triethyl orthoacetate, following a literature procedure,[14] gave ethyl hepta-4,6-dienoate (95% *E*). The ester (560 mg, 3.6 mmol) in THF (5 cm^3) at 0 °C was treated with diisobutylaluminium hydride (4 cm^3, 6 mmol, 1.5 M solution in toluene) for 1 h, the reaction was quenched with 1 M HCl, and the resultant mixture was extracted (EtOAc). The organic phase was washed (water, brine), dried ($MgSO_4$) and evaporated under reduced pressure to give hepta-4,6-dien-1-ol **1c** (350 mg, 86%; 95% *E*) as a colourless oil whose physical and spectroscopic properties were in agreement with reported data.[14,24]

Method 2. Pent-4-yn-1-yl *tert*-butyldiphenylsilyl (TBDPS) ether (1.54 g, 4.78 mmol; prepared from the reaction of pent-4-yn-1-ol and *tert*-butyldiphenylchlorosilane in the presence of pyridine) was added to a slurry of zirconocene hydrogen chloride (1.23 g, 4.78 mmol) in dichloromethane (20 cm^3) in a vessel protected from sunlight. The resulting homogeneous solution was stirred at room temperature for 4 h, then iodine (1.34 g, 5.3 mmol) in dichloromethane (15 cm^3) was added and the mixture was stirred for a further 1 h. Water was added and the mixture was extracted (Et_2O). The extract was washed ($Na_2S_2O_3$, water, brine), dried ($MgSO_4$) and evaporated under reduced pressure to yield crude 5-iodopent-4-en-1-yl TBDPS ether (2.05 g) as a yellow oil, δ_H 1.05 (9H, s, Bu^t), 1.65 (2H, m, 2-H$_2$), 2.20 (2H, m, 3-H$_2$), 3.66 (2H, t, J 6.1, 1-H$_2$), 5.97 (1H, br d, J 14.3, 5-H), 6.50 (1H, dt, J 14.3 and 2 × 7.1, 4-H) and 7.40–7.80 (10H, m, 2 × Ph), which was used directly in the next step.

Vinyltributyltin (1.26 cm^3, 4.3 mmol) was added to bis(triphenylphosphine)palladium(II) chloride (170 mg, 0.24 mmol) in *N*,*N*-dimethylformamide (20 cm^3) at 25 °C, followed by the vinyl iodide (2.05 g), and the resulting solution was stirred at room temperature for 72 h. Ammonium hydroxide (10% v/v, 20 cm^3) was added and the reaction mixture was extracted (Et_2O). The extract was washed (water, brine), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel using ethyl acetate–hexane (1 : 19) as eluent to yield hepta-4,6-dien-1-yl TBDPS ether (1.16 g, 70%) as a pale-yellow oil, δ_H 1.05 (9H, s, Bu^t), 1.68 (2H, m, 2-H$_2$), 2.20 (2H, m, 3-H$_2$), 3.66 (2H, t, J 6.1, 1-H$_2$), 4.95 (1H, br d, J 10.3, 7-H$_{cis}$), 5.08 (1H, br d, J 17.0 , 7-H$_{trans}$), 5.65 (1H, dt, J 15.2 and 2 × 6.6, 4-H), 6.05 (1H, dd, J 15.2 and 10.3, 5-H), 6.30 (1H, dt, J 17.0 and 2 × 10.3, 6-H) and 7.40–7.80 (10H, m, 2 × Ph). Treatment of the TBDPS ether (1.10 g, 3.14 mmol) in THF (10 cm^3) with tetrabutylammonium fluoride (3.2 cm^3, 1 M solution in THF, 3.2 mmol) at room temperature for 2 h, followed by addition of brine and extraction (Et_2O) gave material which was chromatographed on silica gel [ethyl acetate–hexane (1 : 3)] to give hepta-4,6-dien-1-ol **1c** (147 mg, 42%; 100% *E*).

Compound 1d. Pent-4-yn-1-ol was subjected to sequential zirconocene chloride mediated coupling followed by Stille coupling with vinyltributyltin, using a procedure of Wender and Tebbe,[17] to give 4-methylhepta-4,6-dien-1-ol **1d** (68% over 2 steps; 100% *E*).

Synthesis of dienynols 3

Compound 3a. A mixture of oxalyl chloride (0.2 cm^3, 1.0 mmol) and dimethyl sulfoxide (0.15 cm^3, 2.0 mmol) in dichloromethane (5 cm^3) was stirred at −78 °C for 30 min, then alcohol **1a** (250 mg, 1.0 mmol) was added. After 30 min at −78 °C, triethylamine (1.5 cm^3, 10 mmol) was added, and the solution was warmed to room temperature, water was added and the mixture was extracted (CH_2Cl_2). The organic phase was washed (water, brine), dried ($MgSO_4$) and evaporated under reduced pressure to give nona-6,8-dienal **2a** (206 mg, 83%) as an oil, whose spectroscopic properties were in agreement with reported data.[11]

Dry acetylene was bubbled vigorously through THF (40 cm^3). After 30 min, a solution of hot ethylmagnesium bromide [prepared by refluxing a mixture of magnesium (166 mg, 7.2 mmol), bromoethane (0.53 cm^3, 7.2 mmol) and iodine (cat.) in THF (40 cm^3) for 2 h] was added, whilst maintaining the passage of acetylene. After 30 min, the aldehyde **2a** (520 mg, 3.77 mmol) was added and the mixture was stirred at room temperature for 2 h. Sat. aqueous NH_4Cl was added and the mixture was extracted (Et_2O). The organic phase was washed (dil. HCl, water, brine), dried ($MgSO_4$) and evaporated under reduced pressure to yield *undeca-8,10-dien-1-yn-3-ol* **3a** (540 mg, 87%; 88% *E*), ν_{max}/cm^{-1} 3684 (OH) and 3305 (C≡C); δ_H (400 MHz) 1.60–1.80 (6H, m, 4-, 5- and 6-H$_2$), 2.15 (2H, m, 7-H$_2$),

2.47 (1H, dd, *J* 2.3 and 0.8, 1-H), 4.40 (1H, td, *J* 2 × 6.3 and 2.3, 3-H), 4.95 (1H, dd, *J* 10.2 and 2.7, 11-H_{cis}), 5.10 (1H, dd, *J* 17.0 and 2.7, 11-H_{trans}), 5.70 (1H, dt, *J* 15.1 and 2 × 6.8, 8-H), 6.05 (1H, br dd, *J* 15.1 and 10.3, 9-H) and 6.32 (1H, dt, *J* 17.0 and 2 × 10.3, 10-H); δ_C (100 MHz) 24.5 and 28.7 (C-5 and C-6), 32.3 (C-7), 37.4 (C-4), 62.1 (C-3), 72.8 (C-1), 84.9 (C-2), 114.7 (C-11), 131.1 (C-9), 134.9 (C-8) and 137.2 (C-10); *m*/*z* 164 (M^+).

Compound 3b. Alcohol **1b** (150 mg, 1.19 mmol) in dichloromethane (2 cm^3) was added to a stirred solution of pyridinium chlorochromate (384 mg, 1.78 mmol) in dichloromethane (2 cm^3) and the resulting mixture was stirred at room temperature for 16 h. The supernatant was poured into a separate flask and the residue was washed repeatedly with ether. The washings were combined and the solvent evaporated to give octa-5,7-dienal **2b** (140 mg, 95%) as a volatile oil whose spectroscopic properties were in agreement to those reported in the literature.[10,14]

Ethynylation of the crude aldehyde **2b** (2.4 g, 19 mmol) as described in the foregoing experiment gave *deca-7,9-dien-1-yn-3-ol* **3b** (1.92 g, 67%; 97% *E*) as a colourless oil, ν_{max}/cm^{-1} 3684 (OH) and 3305 (C≡C); δ_H 1.50–1.80 (4H, m, 4 and 5-H_2), 2.15 (2H, q, *J* 6.7, 6-H_2), 2.47 (1H, d, *J* 2.3, 1-H), 4.38 (1H, td, *J* 2 × 6.3 and 2.3, 3-H), 4.95 (1H, dd, *J* 10.2 and 2.7, 10-H_{cis}), 5.10 (1H, dd, *J* 17.0 and 2.7, 10-H_{trans}), 5.70 (1H, dt, *J* 15.2 and 2 × 6.7, 7-H), 6.05 (1H, dd, *J* 15.1 and 10.3, 8-H) and 6.32 (1H, dt, *J* 17.0 and 2 × 10.2, 9-H); δ_C 24.6 (C-5), 32.1 (C-6), 37.1 (C-4), 62.1 (C-3), 73.0 (C-1), 84.8 (C-2), 115.0 (C-10), 131.9 (C-8), 134.4 (C-7) and 137.0 (C-9); *m*/*z* 150 (M^+).

Compound 3c. A solution of the alcohol **1c** (890 mg, 7.95 mmol) and Dess–Martin periodinane (4.45 g, 10.5 mmol) in dichloromethane (25 cm^3) was stirred at room temperature for 1 h. Saturated aq. $NaHCO_3$–$Na_2S_2O_3$ (5:1) was added and the solution was stirred for a further 1 h. The mixture was extracted (Et_2O) and the organic phase was washed ($NaHCO_3$, water, brine), dried ($MgSO_4$) and evaporated under reduced pressure to yield hepta-4,6-dienal (800 mg, 92%) as a pungent volatile oil, whose spectroscopic properties corresponded to those reported.[24] The aldehyde was used directly without further purification. Ethynylation of the crude aldehyde **2c** as described previously, gave *nona-6,8-dien-1-yn-3-ol* **3c** (900 mg, 91%; 95% *E*) as a colourless oil, ν_{max}/cm^{-1} 3684 (OH) and 3305 (C≡C); δ_H (400 MHz) 1.60 (2H, m, 4-H_2), 2.30 (2H, q, *J* 6.7, 5-H_2), 2.48 (1H, d, *J* 1.8, 1-H), 4.40 (1H, br t, *J* 5.8, 3-H), 4.95 (1H, dd, *J* 10.2 and 2.7, 9-H_{cis}), 5.10 (1H, dd, *J* 17.0 and 2.7, 9-H_{trans}), 5.70 (1H, dt, *J* 15.2 and 2 × 6.7, 6-H), 6.10 (1H, dd, *J* 15.5 and 10.2, 7-H) and 6.32 (1H, dt, *J* 17.0 and 2 × 10.3, 8-H); δ_C (100 MHz) 28.0 (C-5), 36.9 (C-4), 61.7 (C-3), 73.2 (C-1), 84.6 (C-2), 115.4 (C-9), 131.9 (C-7), 133.4 (C-6) and 136.9 (C-8); *m*/*z* 136.0868 (M^+. $C_9H_{12}O$ requires *M*, 136.0888).

Compound 3d. Sequential Dess–Martin oxidation of **1d**, followed by ethynylation, as described in the previous experiment, gave *6-methylnona-6,8-dien-1-yn-3-ol* **3d** (74% over two steps; 100% *E*), ν_{max}/cm^{-1} 3687 (OH) and 3305 (C≡C); δ_H (400 MHz) 1.78 (3H, br s, 6-Me), 1.86 (2H, m, 4-H_2), 2.26 (2H, t, *J* 7.8, 5-H_2), 2.48 (1H, d, *J* 2.0, 1-H), 4.37 (1H, m, 3-H), 5.00 (1H, br d, *J* 10.6, 9-H_{cis}), 5.12 (1H, dd, *J* 16.9 and 1.8, 9-H_{trans}), 5.90 (1H, dd, *J* 10.6 and 0.9, 7-H) and 6.58 (1H, dt, *J* 16.9 and 2 × 10.6, 8-H); δ_C (100 MHz) 16.6 (C-Me), 35.0, 35.6 (C-4 and C-5), 61.8 (C-3), 73.2 (C-1), 84.6 (C-2), 115.2 (C-9), 126.1 (C-8), 133.0 (C-6) and 138.0 (C-7); *m*/*z* 150.1035 (M^+. $C_{10}H_{14}O$ requires *M*, 150.1044).

Compound 3e. Pent-4-yn-1-yl TBDPS ether (0.9 g, 2.8 mmol) was added to ethylmagnesium bromide [prepared by treatment of magnesium (62 mg, 2.6 mmol) with bromoethane (0.2 cm^3, 2.6 mmol) in THF (5 cm^3), in the presence of iodine (catalytic) and stirring for 1 h], followed by hepta-4,6-dienal **2c** (330 mg, 3 mmol), and the resulting solution was stirred at room temperature for 30 min. Saturated aq. NH_4Cl was added and the mixture was extracted (Et_2O). The extract was washed (dil. HCl, water, brine), dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel [ethyl acetate–hexane (1:9)] to afford the starting material (730 mg, 81%) followed by *dodeca-9,11-dien-4-yne-1,6-diol 1-TBDPS ether* **3e** (149 mg, 14%; 95% *E*) as a colourless oil, ν_{max}/cm^{-1} 3674 (OH) and 2228 (C≡C); δ_H (400 MHz) 1.05 (9H, s, Bu^t), 1.60 (4H, m, 2-H_2 and 7-H_2), 2.24 (2H, q, *J* 6.6, 8-H_2), 2.36 (1H, td, *J* 2 × 7.0 and 2.0, 3-H_2), 3.74 (2H, t, *J* 6.0, 1-H_2), 4.36 (1H, m, 6-H), 4.95 (1H, br d, *J* 10.2, 12-H_{cis}), 5.10 (1H, dd, *J* 17.1 and 1.1, 12-H_{trans}), 5.70 (1H, dt, *J* 15.1 and 2 × 6.6, 9-H), 6.10 (1H, dd, *J* 15.1 and 10.2, 10-H), 6.32 (1H, dt, *J* 17.1 and 10.2, 11-H) and 7.40–7.70 (10H, m, Ph); δ_C (100 MHz) 15.1 (C-2), 19.2 (CMe_3), 26.8 (CMe_3), 28.2 (C-8), 31.4 (C-3), 37.3 (C-7), 62.0, 62.3 (C-1 and C-6), 81.1 (C-4), 85.3 (C-5), 115.1 (C-12), 127.6 (Ph), 129.5 (Ph), 131.5 (C-10), 133.7 (C-9), 133.8 (Ph), 135.5 (Ph) and 137.0 (C-11); *m*/*z* 375 ($M^+ - Bu^t$).

Compound 3f. *n*-BuLi (0.95 cm^3, 2.4 mmol, 2.5 M solution in hexanes) was added to prop-2-yn-1-yl TBDPS ether (705 mg, 2.4 mmol) in THF (20 cm^3) at −78 °C, followed by 4-methylhepta-4,6-dienal **2d** (300 mg, 2.4 mmol). After 1 h at −78 °C, 1 M HCl was added and the product was isolated by extraction (Et_2O) as above, and chromatographed on silica gel [ethyl acetate–hexane (1:9)] to yield *7-methyldeca-7,9-dien-2-yne-1,4-diol 1-TBDPS ether* **3f** (420 mg, 42%; 100% *E*), ν_{max}/cm^{-1} 3603 (OH) and 2252 (C≡C); δ_H (400 MHz) 1.05 (9H, s, Bu^t), 1.72 (2H, m, 5-H_2), 1.74 (3H, s, 7-Me), 2.18 (2H, t, *J* 7.8, 6-H_2), 4.27 (1H, br, *W* 10, 4-H), 4.38 (2H, d, *J* 1.6, 1-H_2), 4.98 (1H, br d, *J* 10.6, 10-H_{cis}), 5.09 (1H, dd, *J* 16.7 and 1.8, 10-H_{trans}), 5.85 (1H, br d, *J* 10.9, 8-H), 6.56 (1H, dt, *J* 16.7 and 2 × 10.6, 9-H) and 7.40–7.70 (10H, m, Ph); δ_C (100 MHz) 16.6 (Me), 19.2 (CMe_3), 26.7 (CMe_3), 35.0, 35.6 (C-5 and C-6), 52.7 (C-1), 62.0 (C-4), 83.6 (C-2), 86.0 (C-3), 115.1 (C-10), 126.0 (C-8), 127.7 (Ph), 129.8 (Ph), 133.0 (C-9), 133.3 (Ph), 135.7 (Ph) and 138.3 (C-7); *m*/*z* 361 ($M^+ - Bu^t$).

Phenylsulfenylation–[2,3]sigmatropic rearrangement of propargylic alcohols 3

General method. Triethylamine (3.74 mmol) was added to a stirred solution of dienynol **3** (3.29 mmol) in THF (5 cm^3) at −78 °C, followed by benzenesulfenyl chloride (3.74 mmol). After 1 h at −78 °C the solution was allowed to warm to room temperature, aq. NH_4Cl was added and the mixture was extracted (EtOAc). The extract was washed (brine), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel to give the phenylsulfinyltetraene **4** as a mixture of *S*-diastereomers.

1-Phenylsulfinylundeca-1,2,8,10-tetraene 4a. (77%) Eluent ethyl acetate–hexane (1:9); ν_{max}/cm^{-1} 1948 (C=C=C) and 1042 (SO); δ_H (400 MHz) 1.60–1.90 (4H, m, 5- and 6-H_2), 2.15–2.25 (4H, m, 4- and 7-H_2), 4.98 (1H, dd, *J* 10.2 and 2.7, 11-H_{cis}), 5.10 (1H, dd, *J* 17.0 and 2.7, 11-H_{trans}), 5.67 (1H, dt, *J* 15.1 and 2 × 6.7, 8-H), 5.68–5.73 (1H, m, 3-H), 6.05 (2H, m, 1-, and 9-H), 6.30 (1H, dt, *J* 17.0 and 2 × 10.2, 10-H) and 7.52–7.90 (5H, m, SOPh); δ_C (100 MHz) 27.9 and 28.1 (C-5 and C-6), 28.4 (C-4), 32.0 (C-7), 99.1 (C-1), 102.7 (C-3), 114.8 (C-11), 124.2 (SOPh), 129.1 (SOPh), 130.9 (SOPh), 131.2 (C-9), 134.7 (C-8), 137.1 (C-10), 144.8 (SOPh) and 203.7 (C-2); *m*/*z* 272.1140 (M^+. $C_{17}H_{20}OS$ requires *M*, 272.1130).

1-Phenylsulfinyldeca-1,2,7,9-tetraene 4b. (65%) Eluent ethyl acetate–hexane (1:10); ν_{max}/cm^{-1} 1950 (C=C=C) and 1037 (SO); δ_H 1.65 (2H, m, 5-H_2), 2.10–2.25 (4H, m, 4- and 6-H_2), 4.96 (1H,

dd, *J* 10.2 and 2.7, 10-H_{cis}), 5.10 (1H, dd, *J* 17.0 and 2.7, 10-H_{trans}), 5.70 (2H, m, 3-H and 7-H), 6.05 (2H, m, 1-H and 8-H), 6.30 (1H, dt, *J* 17.0 and 10.2, 9-H) and 7.50 (5H, m, SOPh); δ_C (C-5), 28.5 (C-4), 31.7 (C-6), 98.9 (C-1), 102.8 (C-3), 115.2 (C-10), 124.2 (SOPh), 129.1 (SOPh), 130.9 (SOPh), 131.2 (C-8), 134.7 (C-7), 137.0 (C-9), 144.8 (SOPh) and 203.7 (C-2); *m*/*z* 258.1070 (M^+. $C_{16}H_{18}OS$ requires *M*, 258.1077).

1-Phenylsulfinylnona-1,2,6,8-tetraene 4c. (69%) Eluent ethyl acetate–hexane (1 : 4); ν_{max}/cm^{-1} 1950 (C=C=C) and 1037 (SO); δ_H (400 MHz) 2.25 (4H, m, 4- and 5-H_2), 5.00 (1H, dd, *J* 10.2 and 2.7, 9-H_{cis}), 5.12 (1H, dd, *J* 17.0 and 2.7, 9-H_{trans}), 5.60–5.75 (2H, m, 3-H and 6-H), 6.05 (2H, m, 1-H and 7-H), 6.30 (1H, dt, *J* 17.0 and 2 × 10.3, 8-H) and 7.50–7.65 (5H, m, SO*Ph*); δ_C (100 MHz, $CDCl_3$) 27.7 (C-4) 31.5 (C-5), 98.5 (C-1), 103.1 (C-3), 115.7 (C-9), 124.2 (SOPh), 129.1 (SOPh), 130.9 (SOPh), 132.3 (C-7), 132.7 (C-6), 136.9 (C-8), 144.8 (SOPh) and 203.6 (C-2), *m*/*z* 245 (M^+ + H).

6-Methyl-1-phenylsulfinylnona-1,2,6,8-tetraene 4d. (57%) Eluent ethyl acetate–hexane (1 : 4); ν_{max}/cm^{-1} 1949 (C=C=C) and 1037 (SO); δ_H (400 MHz) 1.75 (3H, s, 6-Me), 2.15–2.30 (4H, m, 4-H_2 and 5-H_2), 5.02 (1H, br d, *J* 9.9, 9-H_{cis}), 5.12 (1H, m, 9-H_{trans}), 5.60 (1H, m, 3-H), 5.85 (1H, m, 7-H), 6.05 (1H, dt, *J* 5.7 and 2 × 2.7, 1-H), 6.30 (1H, m, 8-H) and 7.50–7.65 (5H, m, SOPh); δ_C (100 MHz) 16.5 (Me), 26.5 (C-4), 38.5 (C-5), 98.6 (C-1), 103.0 (C-3), 115.4 and 115.6 (C-9), 124.2 and 124.3 (SOPh), 126.6 (C-7), 129.2 (SOPh), 130.9 and 131.0 (SOPh), 133.0 and 132.9 (C-8), 137.3 (C-6), 144.9 (SOPh) and 203.5 (C-2); *m*/*z* 258.1066 (M^+. $C_{16}H_{18}OS$ requires *M*, 258.1078).

1-(*tert*-Butyldiphenylsilyloxy)-4-phenylsulfinyldodeca-4,5,9,11-tetraene 4e. (68%) Eluent ethyl acetate–hexane (1 : 10); ν_{max}/cm^{-1} 1956 (C=C=C) and 1045 (SO); δ_H (400 MHz) 0.95 (9H, s, Bu^t), 3.58 (2H, m, 1-H_2), 4.95 (1H, m, 12-H_{cis}), 5.10 (1H, m, 12-H_{trans}), 5.66 (2H, m, 6-H and 9-H), 6.07 (1H, m, 10-H), 6.28 (1H, m, 11-H) and 7.40–7.70 (15H, m, Ph) as a colourless oil, which was used directly in the next step.

1-(*tert*-Butyldiphenylsilyloxy)-2-phenylsulfinyl-7-methyldeca-2,3,7,9-tetraene 4f. (28%) Eluent ethyl acetate–hexane (1 : 5); ν_{max}/cm^{-1} 1956 (C=C=C) and 1038 (SO); δ_H (400 MHz) 0.93 (9H, s, Bu^t), 1.71, 1.73 (3H, s, 7-Me), 4.20 (1H, m, 1-H), 4.43 (1H, m, 1-H), 4.98 (1H, br m, 10-H_{cis}), 5.09 (1H, br m, 10-H_{trans}), 5.65 (1H, m, 3-H), 5.85 (1H, br m, 8-H), 6.52 (1H, br m, 9-H) and 7.30–7.60 (15H, m, Ph); *m*/*z* 469 (M^+ − Bu^t).

Oxidation of the phenylsulfinyltetraenes 4

General procedure. *m*-Chloroperbenzoic acid (MCPBA) (1.1 mmol) was added to a solution of the phenylsulfinyltetraene **4** (1.1 mmol) in dichloromethane (15 cm^3) at 0 °C, and the mixture was allowed to warm to room temperature. After 1 h at room temperature, aq. NH_4Cl was added and the mixture was extracted (EtOAc). The organic phase was washed (dil. HCl, water, brine), dried ($MgSO_4$) and evaporated under reduced pressure, and the residue was chromatographed on silica gel to give the phenylsulfonyltetraene **5**.

1-Phenylsulfonylundeca-1,2,8,10-tetraene 5a. (66%) Eluent ethyl acetate–hexane (1 : 4); ν_{max}/cm^{-1} 1955 (C=C=C), 1319 and 1148 (SO); δ_H (400 MHz) 1.38–1.43 (4H, m, 5- and 6-H_2), 2.15–2.25 (4H, m, 4- and 7-H_2), 4.96 (1H, dd, *J* 10.2 and 2.7, 11-H_{cis}), 5.10 (1H, dd, *J* 17.0 and 2.7, 11-H_{trans}), 5.66 (1H, dt, *J* 15.1 and 2 × 6.7, 8-H), 5.83 (1H, td, *J* 2 × 7.0 and 6.2, 3-H), 6.05 (1H, br dd, *J* 15.1 and 10.2, 9-H), 6.19 (1H, dt, *J* 6.2 and 2 × 3.1, 1-H), 6.30 (1H, dt, *J* 17.0 and 2 × 10.2, 10-H) and 7.50–7.90 (5H, m, SO_2Ph); δ_C (100 MHz) 27.5 and 27.8 (C-5 and C-6), 28.3 (C-4), 32.0 (C-7), 101.0 (C-1), 101.2 (C-3), 114.9 (C-11), 127.2 (SO_2Ph), 129.1 (SO_2Ph), 131.2 (C-9), 133.3 (SO_2Ph), 134.6 (C-8), 137.1 (C-10), 141.3 (SO_2Ph) and 205.5 (C-2); *m*/*z* 288.1091 (M^+. $C_{17}H_{20}O_2S$ requires *M*, 288.1079).

1-Phenylsulfonyldeca-1,2,7,9-tetraene 5b. (53%) Eluent ethyl acetate–hexane (1 : 5); ν_{max}/cm^{-1} 1956 (C=C=C), 1307 and 1149 (SO); δ_H (400 MHz) 1.49 (2H, quintet, *J* 4 × 7.5, 5-H_2), 2.10–2.15 (4H, m, 4- and 6-H_2), 4.96 (1H, dd, *J* 10.2 and 2.7, 10-H_{cis}), 5.10 (1H, dd, *J* 17.0 and 2.7, 10-H_{trans}), 5.60 (1H, dt, *J* 15.2 and 2 × 6.7, 7-H), 5.85 (1H, td, *J* 2 × 7.0 and 6.2, 3-H), 6.05 (1H, dd, *J* 15.2 and 10.2, 8-H), 6.20 (1H, dt, *J* 6.2 and 2 × 3.1, 1-H), 6.28 (1H, dt, *J* 17.0 and 2 × 10.2, 9-H) and 7.56–7.90 (5H, m, SO_2Ph); δ_C (100 MHz) 27.0 (C-5), 27.7 (C-4), 31.6 (C-6), 100.9 (C-1), 101.2 (C-3), 115.2 (C-10), 127.6 (SO_2Ph), 129.1 (SO_2Ph), 131.7 (SO_2Ph), 133.3 (C-8), 133.8 (C-7), 137.0 (C-9), 141.4 (SO_2Ph) and 205.7 (C-2); *m*/*z* 275 (M^+ + H).

6-Methyl-1-phenylsulfonylnona-1,2,6,8-tetraene 5d. (50%) Eluent ethyl acetate–hexane (1 : 5); ν_{max}/cm^{-1} 1956 (C=C=C), 1320 and 1148 (SO); δ_H (400 MHz) 1.72 (3H, s, 6-Me), 2.16 (2H, t, *J* 7.6, 5-H_2), 2.28 (2H, m, 4-H_2), 5.02 (1H, br d, *J* 10.5, 9-H_{cis}), 5.08 (1H, dd, *J* 16.9 and 2.0, 9-H_{trans}), 5.85 (2H, m, 7-H), 5.87 (1H, td, *J* 2 × 6.9 and 6.0, 3-H), 6.20 (1H, dt, *J* 6.0 and 2 × 3.0, 1-H), 6.54 (1H, dt, *J* 16.9 and 2 × 10.5, 8-H) and 7.50–7.95 (5H, m, SO_2Ph); δ_C (100 MHz) 16.5 (Me), 26.0 (C-4), 38.2 (C-5), 100.5 (C-1), 101.5 (C-3), 115.6 (C-9), 126.6 (C-7), 127.6 (SO_2Ph), 129.1 (SO_2Ph), 132.9 (C-8), 133.4 (SO_2Ph), 137.1 (C-6), 141.4 (SO_2Ph) and 205.6 (C-2); *m*/*z* 274 (M^+).

1-(*tert*-Butyldiphenylsilyloxy)-4-phenylsulfonyldodeca-4,5,9,11-tetraene 5e. (70%) Eluent ethyl acetate–hexane (1 : 10); ν_{max}/cm^{-1} 1960 (C=C=C), 1306 and 1149 (SO); δ_H (400 MHz) 1.10 (9H, s, Bu^t), 2.16 (2H, m, 8-H_2), 2.18–2.36 obsc. (2H, m, 2-H_2), 2.38 (2H, td, *J* 2 × 7.0 and 2.0, 3-H_2), 3.60 (2H, t, *J* 6.2, 1-H_2), 4.95 (1H, br d, *J* 10.2, 12-H_{cis}), 5.10 (1H, dd, *J* 17.1 and 1.1, 12-H_{trans}), 5.65 (1H, dt, *J* 15.1 and 2 × 7.0, 9-H), 5.70 (1H, m, 6-H), 6.02 (1H, dd, *J* 15.1 and 10.2, 10-H), 6.28 (1H, dt, *J* 17.1 and 10.2, 11-H) and 7.30–7.70 (15H, m, Ph); δ_C (100 MHz) 19.1 (C-2), 23.3 (CMe_3), 26.8 (CMe_3), 27.7 (C-7), 30.5, 31.3 (C-3 and C-8), 62.5, (C-1), 100.7 (C-6), 113.7 (C-4), 115.6 (C-12), 122.8, 127.6, 128.0, 129.5 (Ph), 130.5 (C-10), 132.1 (Ph), 133.0, 133.2 (Ph), 133.7 (C-9), 135.5 (Ph), 136.7 (C-11), 140.4 (Ph) and 203.8 (C-5); *m*/*z* (Electrospray) 579 (M^+ + Na).

1-(*tert*-Butyldiphenylsilyloxy)-2-phenylsulfonyl-7-methyldeca-2,3,7,9-tetraene 5f. (48%) Eluent acetate–hexane (1 : 10); ν_{max}/cm^{-1} 1959 (C=C=C), 1307 and 1151 (SO); δ_H (400 MHz) 0.93 (9H, s, Bu^t), 1.72 (3H, s, 7-Me), 2.12 (2H, t, *J* 7.8, 6-H_2), 2.25 (2H, m, 5-H_2), 4.48 (2H, m, 1-H_2), 4.98 (1H, br d, *J* 10.6, 10-H_{cis}), 5.10 (1H, dd, *J* 16.7 and 1.8, 10-H_{trans}), 5.80 (2H, m, 4-H and 8-H), 6.53 (1H, dt, *J* 16.7 and 2 × 10.6, 9-H) and 7.30–7.90 (15H, m, Ph); δ_C (100 MHz) 16.5 (C-Me), 19.1 (CMe_3), 26.2 (C-5), 26.6 (CMe_3), 38.4 (C-6), 60.3 (C-1), 100.8 (C-4), 113.4 (C-2), 115.5 (C-10), 126.5 (C-8), 127.7, 127.8, 129.8, 132.7 (Ph), 132.9 (C-9), 133.1 (Ph), 133.3 (Ph), 135.4 (Ph), 137.4 (C-7) and 205.3 (C-3); *m*/*z* 542 (M^+).

Intramolecular Diels–Alder reactions of the phenylsulfonyltetraenes 5

Compound 6. A solution of undecatetraene **5a** (100 mg, 0.35 mmol) in toluene (2 cm^3) was flushed with nitrogen and heated at 180 °C (sealed tube) for 20 h. The solvent was evaporated and the residue was chromatographed on silica gel [ethyl acetate–toluene (1 : 50)] to yield *(5Z,4aR*,8aR*)-5-(phenylsulfonyl)-methylene-1,2,3,4,4a,5,6,8a-octahydronaphthalene* **6** (30 mg, 30%) as a gum, ν_{max}/cm^{-1} 1321 and 1146 (SO); δ_H (400 MHz, C_6D_6) 1.20–1.85 (8H, m, 1-, 2-, 3- and 4-H_2), 2.12 (1H, dd, *J* 15.1 and 6.1, 6α-H), 2.27 (1H, ddt, *J* 15.1, 4.8 and 2 × 2.9, 6β-H), 2.70 (1H, br m, *W* 29, 4a-H), 5.43 (1H, dddd, *J* 8.8, 6.1, 4.8 and 2.9, 7-H), 5.52 (1H, dt, *J* 8.8 and 2.9, 8-H), 5.85 (1H, m,

W 4.5, 1′-H) and 6.84–7.82 (5H, dd, *J* 7.6 and 1.3, SO_2Ph); δ_C (100 MHz, C_6D_6) 26.3, 26.8, 31.6, 33.4 (t, C-1, C-2, C-3 and C-4), 36.5 (t, C-6), 42.3 (d, C-8a), 45.1 (d, C-4a), 124.0 (d, C-1′), 124.6 (d, C-8), 127.0 (d, SO_2Ph), 128.6 (d, SO_2Ph), 132.1 (d, SO_2Ph), 135.9 (d, C-7), 143.7 (s, SO_2Ph) and 160.7 (s, C-5); *m*/*z* 288.1192 (M^+. $C_{17}H_{20}O_2S$ requires *M*, 288.1183).

Compounds 7 and 8. A solution of decatetraene **5b** (400 mg, 1.46 mmol) in toluene (30 cm^3) was flushed with nitrogen and heated at 80 °C (sealed tube) for 20 h. The solvent was evaporated and the residue was chromatographed on silica gel [ethyl acetate–toluene (1 : 50)] to give *(5S*,8aR*)-5-phenylsulfonyl-1,2,3,5,6,8a-hexahydronaphthalene* **7** (70 mg, 18%), mp 110–113 °C (from isopropyl alcohol) (Found: C, 70.0; H, 6.5; S, 11.6%; M^+, 274. $C_{16}H_{18}O_2S$ requires C, 70.1; H, 6.6; S, 11.7%; *M*, 274); ν_{max}/cm^{-1} 1306 and 1142 (SO); δ_H (400 MHz) 1.18 (1H, qd, *J* 3 × 12.9 and 2.8, 1β-H), 1.50 (1H, qdd, *J* 3 × 12.9, 6.3 and 2.8, 2α-H), 1.75 (1H, m, *W* 29, 2-H), 1.90 (1H, m, *W* 25, 5-H), 2.20 (3H, m, 6-H and 3-H_2), 2.61 (1H, m, *W* 36, 6-H), 2.76 (1H, br m, $W_{\frac{1}{2}}$ 7.0, 8a-H), 3.82 (1H, ddd, *J* 9.4, 3.5 and 1.3, 5-H), 5.43 (1H, br d, *J* 9.9, 8-H), 5.52 (1H, dddt, *J* 9.9, 7.7 and 2 × 2.4, 7-H), 6.55 (1H, br d, *J* 2.0, 4-H) and 7.55–7.90 (5H, m, SO_2Ph); δ_C (100 MHz) 21.4 (t, C-2), 25.5 (t, C-6), 28.8 (t, C-3), 30.2 (t, C-1), 37.6 (d, C-8a), 64.5 (d, C-5), 122.4 (d, C-7), 125.1 (d, C-4), 128.6 (d, SO_2Ph), 128.8 (s, C-4a), 128.9 (d, SO_2Ph), 132.2 (d, C-8), 133.5 (d, SO_2Ph) and 139.1 (s, SO_2Ph). Further elution furnished *(5R*,8aR*)-5-phenylsulfonyl-1,2,3,5,6,8a-hexahydronaphthalene* **8** (214 mg, 54%), mp 123–125 °C (from ethanol) (Found: C, 70.2; H, 6.7; S, 11.9%; M^+, 274. $C_{16}H_{18}O_2S$ requires C, 70.1; H, 6.6; S, 11.7%; *M*, 274); ν_{max}/cm^{-1} 1302 and 1146 (SO); δ_H (400 MHz) 0.95 (1H, qd, *J* 3 × 12.4 and 2.4, 1β-H), 1.49 (1H, qdd, *J* 3 × 12.4, 5.6 and 2.8, 2α-H), 1.80–1.95 (4H, m, 1-H, 2-H and 3-H_2), 2.55 (1H, dddd, *J* 19.8, 8.4, 6.4 and 2.4, 6β-H), 3.00 (1H, dd, *J* 19.8 and 4.8, 6α-H), 3.06 (1H, m, $W_{\frac{1}{2}}$ 7.0, 8a-H), 3.72 (1H, d, *J* 8.4, 5-H), 5.25 (1H, m, $W_{\frac{1}{2}}$ 4.4, 4-H), 5.57 (1H, br d, *J* 10.4, 8-H), 5.65 (1H, dddd, *J* 10.4, 6.4, 4.8 and 2.4, 7-H) and 7.50–7.85 (5H, m, SO_2Ph); δ_C (100 MHz) 21.0 (t, C-2), 24.5 (t, C-6), 26.0 (t, C-3), 29.8 (t, C-1), 33.7 (d, C-8a), 67.9 (d, C-5), 121.4 (d, C-7), 128.6 (d, SO_2Ph), 128.9 (s, SO_2Ph), 129.2 (s, C-4a), 130.9 (d, C-8), 132.2 (d, C-4), 133.3 (d, SO_2Ph) and 137.6 (s, SO_2Ph).

Compounds 9 and 10. The phenylsulfinyl nonatetraene **4c** (350 mg, 1.43 mmol) in dichloromethane (50 cm^3) at 0 °C was treated with MCPBA (370 mg, 67%, 1.43 mmol). After 30 min at 0 °C, aq. $NaHCO_3$ was added, and the mixture was extracted (CH_2Cl_2). The organic phase was washed (brine), dried ($MgSO_4$) and evaporated under reduced pressure, and the residue was dissolved in dichloromethane (20 cm^3) and kept at 30 °C for 20 min. Evaporation of the solvent and flash chromatography of the residue on silica gel [ethyl acetate–hexane (1 : 50)] yielded a fraction comprising a mixture of cycloadducts (~4 : 1 by NMR), which was rechromatographed on silica gel with ethyl acetate–toluene (1 : 49) as eluent to give *(4S*,7aR*)-4-phenylsulfonyl-2,4,5,7a-tetrahydro-1H-indene* **9** (63 mg, 18%), mp 114–116 °C (from ethanol) (Found: C, 69.1; H, 6.2; S, 12.1%; $M^+ - SO_2Ph$, 119. $C_{15}H_{16}O_2S$ requires C, 69.2; H, 6.2; S, 12.3%; *M*, 260); ν_{max}/cm^{-1} 1307 and 1146 (SO); δ_H (400 MHz, C_6D_6) 1.36 (1H, dq, *J* 19.5 and 3 × 9.8, 1β-H), 1.80 (1H, br m, *W* 29.5, 1α-H), 2.15 (3H, m, 2-H_2 and 5-H), 2.60 (1H, m, $W_{\frac{1}{2}}$ 36.7, 5α-H), 2.80 (1H, m, $W_{\frac{1}{2}}$ 17.5, 7a-H), 3.78 (1H, m, *W* 21.7, 4-H), 5.18 (1H, ddt, *J* 9.8, 5.0 and 2 × 2.4, 6-H), 5.41 (1H, br d, *J* 9.8, 7-H), 6.42 (1H, t, *J* 2.3, 3-H) and 7.00–7.78 (5H, m, SO_2Ph); δ_H (400 MHz, $CDCl_3$) 1.40 (1H, dq, *J* 19.5 and 3 × 9.8, 1β-H), 2.20–2.45 (5H, m, 1α-H, 2-H_2 and 5-H_2), 3.20 (1H, m, $W_{\frac{1}{2}}$ 17.5, 7a-H), 4.00 (1H, m, *W* 21.7, 4-H), 5.45 (1H, ddt, *J* 9.8, 5.0 and 2 × 2.4, 6-H), 5.41 (1H, br d, *J* 9.8, 7-H), 6.42 (1H, t, *J* 2.3, 3-H) and 7.00–7.78 (5H, m, SO_2Ph); δ_C (100 MHz, C_6D_6) 28.4 (C-5), 30.7 (C-1), 32.5 (C-2), 46.5 (C-7a), 61.8 (C-4), 122.6 (C-6), 126.3 (SO_2Ph), 127.9 (SO_2Ph), 128.1 (C-7), 132.2 (C-3), 133.0 (SO_2Ph), 134.1 (C-3a) and 140.0 (SO_2Ph), followed by *(4R*,7aR*)-4-phenylsulfonyl-2,4,5,7a-tetrahydro-1H-indene* **10** (175 mg, 50%), mp 76–78 °C (from ethanol) (Found: C, 69.3; H, 6.2; S, 12.1%; M^+ + H, 261. $C_{15}H_{16}O_2S$ requires C, 69.2; H, 6.2; S, 12.3%; *M*, 260); ν_{max}/cm^{-1} 1334 and 1148 (SO); δ_H (400 MHz) 1.40 (1H, dq, *J* 12.7 and 11.0, 1β-H), 2.20 (3H, m, 1α-H and 2-H_2), 2.53 (1H, ddq, *J* 19.5, 8.4 and 3 × 2.7, 5β-H), 3.00 (1H, ddq, *J* 19.5, 4.4 and 3 × 2.3, 5α-H), 3.38 (1H, m, $W_{\frac{1}{2}}$ 10.5, 7a-H), 4.04 (1H, d, *J* 8.4, 4β-H), 5.37 (1H, br d, *J* 2.4, 3-H), 5.57 (1H, ddt, *J* 10.0, 4.4 and 2 × 2.7, 6-H), 5.73 (1H, dq, *J* 10.0 and 3 × 2.4, 7-H) and 7.57–7.82 (5H, m, SO_2Ph); δ_C (100 MHz) 24.7 (t, C-5), 31.5 (t, C-1), 31.6 (t, C-2), 41.0 (d, C-7a), 62.0 (d, C-4), 121.7 (d, C-6), 128.7 (d, SO_2Ph), 128.8 (d, SO_2Ph), 131.3 (d, C-7), 132.7 (d, C-3), 133.5 (d, SO_2Ph), 135.0 (s, C-3a) and 137.7 (s, SO_2Ph).

Compounds 11 and 12. A solution of the 6-methylnonatetraene **5d** (60 mg, 0.21 mmol) in toluene (2 cm^3) was flushed with nitrogen and heated at 150 °C (sealed tube) for 2 h. The solvent was evaporated and the residue was chromatographed on silica gel [ethyl acetate–toluene (1 : 99)] to yield *(4S*,7aR*)-7a-methyl-4-phenylsulfonyl-2,4,5,7a-tetrahydro-1H-indene* **11** (8 mg, 13%) as an oil, ν_{max}/cm^{-1} 1307 and 1146 (SO); δ_H (400 MHz) 1.60 (3H, s, 7a-Me), 1.69 (1H, td, *J* 2 × 12.3 and 9.6, 1β-H), 1.78 (1H, ddd, *J* 12.3, 7.1 and 1.4, 1α-H), 2.20 (1H, dtd, *J* 16.4, 2 × 5.3 and 1.4, 5-H), 2.38 (1H, m, 2-H), 2.50–2.70 (2H, m, 2-H and 5-H), 3.92 (1H, m, *W* 20.7, 4-H), 5.38 (1H, ddd, *J* 9.9, 5.3 and 2.3, 6-H), 5.65 (1H, dd, *J* 9.9 and 2.7, 7-H), 6.10 (1H, br d, *J* 1.8, 3-H) and 7.40–7.80 (5H, m, SO_2Ph); δ_C (100 MHz) 24.8 (Me), 28.5 (C-5), 30.3 (C-1), 37.7 (C-2), 49.4 (C-7a), 59.9 (C-4), 119.7 (C-6), 124.3 (SO_2Ph), 128.5 (SO_2Ph), 129.1 (SO_2Ph), 133.6 (C-3), 137.6 (C-7), 138.7 (s, SO_2Ph) and 138.7 (C-3a); *m*/*z* 274.1012 (M^+. $C_{16}H_{18}O_2S$ requires *M*, 274.1023).

Further elution furnished *(4R*,7aR*)-7a-methyl-4-phenylsulfonyl-2,4,5,7a-tetrahydro-1H-indene* **12** (27 mg, 45%) as a gum, ν_{max}/cm^{-1} 1306 and 1146 (SO); δ_H (400 MHz) 1.15 (3H, s, 7a-Me), 1.75 (1H, td, *J* 2 × 11.7 and 8.7, 1β-H), 1.83 (1H, dd, *J* 11.7 and 6.7, 1α-H), 2.18 (1H, ddd, *J* 16.5, 8.7 and 3.5, 2β-H), 2.45 (2H, m, 2α-H and 5-H), 2.75 (1H, br d, *J* 18.3, 5-H), 4.14 (1H, m, *W* 16, 4-H), 5.55 (1H, dt, *J* 10.0 and 2 × 3.7, 6-H), 5.60 (1H, m, $W_{\frac{1}{2}}$ 1.7, 3-H), 5.82 (1H, br d, *J* 10.0, 7-H) and 7.50–7.90 (5H, m, SO_2Ph); δ_C (100 MHz) 23.5 (q, Me), 23.8 (t, C-5), 29.6 (t, C-1), 40.9 (t, C-2), 46.0 (s, C-7a), 61.6 (d, C-4), 120.0 (d, C-6), 128.9 (d, SO_2Ph), 129.2 (d, SO_2Ph), 133.3 (d, C-3), 133.5 (d, SO_2Ph), 137.7 (s, C-3a), 138.0 (d, C-7) and 138.3 (s, SO_2Ph); *m*/*z* 274.1008 (M^+. $C_{16}H_{18}O_2S$ requires *M*, 274.1023).

Compound 13. The dodecatetraene **5e** (57 mg, 0.1 mmol) in $CDCl_3$ (2 cm^3) was heated in a sealed NMR tube at 50 °C for 2 h, whereupon NMR monitoring revealed that reaction was complete. The solvent was evaporated, and the residue was chromatographed on silica gel [ethyl acetate–toluene (1 : 49)] to yield *(4′R*,7a′R*)-3-(4-phenylsulfonyl-2,4,5,7a-tetrahydro-1H-inden-4-yl)propan-1-yl TBDPS ether* **13** (43 mg, 75%), ν_{max}/cm^{-1} 1308 and 1141 (SO); δ_H (400 MHz) 0.95 (9H, s, Bu^t), 1.00 (3H, m, 1′β-H and 3-H_2), 1.40 (2H, m, 2-H_2), 1.98 (1H, ddd, *J* 9.9, 6.5 and 3.0, 1′α-H), 2.25 (3H, m, 2′-H_2 and 5′-H), 3.00 (1H, dt, 18.7 and 2 × 2.5, 5′-H), 3.25 (1H, br, $W_{\frac{1}{2}}$ 14, 7a′-H), 3.60 (2H, m, 1-H_2), 5.40 (1H, br s, 3′-H), 5.63 (1H, ddd, *J* 9.9, 7.4 and 2.5, 6′-H), 5.70 (1H, br d, *J* 9.9, 7′-H) and 7.35–7.80 (15H, m, Ph); δ_C (100 MHz) 19.2 (s, CMe_3), 26.6, (t, C-3), 26.8 (q, C–C(Me_3)$_3$), 28.6 (t, C-5′), 31.2 (t, C-1′), 31.7 (t, C-2′), 31.9 (t, C-2), 43.4 (d, C-7a′), 63.6 (t, C-1), 67.5 (s, C-4′), 122.9 (d, C-6′), 127.6, 128.2, 129.6 (d, Ph), 131.8 (d, C-7′), 132.0 (d, Ph), 133.4 (d, C-3′), 133.7 (s, Ph), 134.8 (d, Ph), 135.2 (s, C-3a′) and 135.5, 137.6 (s, Ph); *m*/*z* (Electrospray) 579 (M^+ + Na).

5-(2-Furyl)pent-1-yn-3-ol 15

Dess–Martin oxidation of 3-(2-furyl)propan-1-ol **14**[20] followed

by ethynylation, as described in previous experiments, gave the *pentynol* **15** (85% over two steps) as a colourless oil, ν_{max}/cm^{-1} 3687 (OH) and 3305 (C≡C); δ_H (400 MHz) 2.05 (2H, m, 4-H$_2$), 2.48 (1H, d, *J* 2.1, 1-H), 2.80 (2H, t, *J* 7.6, 5-H$_2$), 4.40 (H, br m, 3-H), 6.00 (1H, dd, 3.1 and 0.9, 5′-H), 6.28 (1H, dd, *J* 3.1 and 1.8, 4′-H) and 7.31 (1H, dd, *J* 1.8 and 0.9, 3′-H); δ_C (100 MHz) 23.5 (C-5), 35.8 (C-4), 61.4 (C-3), 73.3 (C-1), 84.3 (C-2), 105.3 (C-3′), 110.0 (C-4′), 141.0 (C-5′) and 154.7 (C-2′); *m*/*z* 150.0697 (M$^+$. $C_9H_{10}O_2$ requires *M*, 150.0681).

5-(2-Furyl)-1-phenylsulfinylpenta-1,2-diene 16

Treatment of compound **15** (50 mg, 0.33 mmol) with triethylamine (50 µl, 0.37 mmol) and benzenesulfenyl chloride (38 µl, 0.37 mmol) followed by work-up and chromatography on silica gel [ethyl acetate–hexane (3:7)] gave the *1-phenylsulfinylallene* **16** (42 mg, 49%) as a colourless oil, ν_{max}/cm^{-1} 1951 (C=C=C) and 1036 (SO); δ_H (400 MHz) 2.45 (2H, m, $W_{\frac{1}{2}}$ 10.8, 4-H$_2$), 2.75 (2H, t, *J* 7.5, 5-H$_2$), 5.75 (1H, td, *J* 2 × 7.0 and 6.2, 3-H), 6.02 (1H, dq, 3.1 and 0.9, 5′-H), 6.05 (1H, dt, *J* 6.2 and 2 × 3.1, 1-H), 6.27 (1H, dd, *J* 3.1 and 1.8, 4′-H), 7.30 (1H, dd, *J* 1.8 and 0.9, 3′-H) and 7.52–7.62 (5H, m, SOPh); δ_C (100 MHz) 26.8 (C-4), 27.1 (C-5), 98.1 (C-1), 103.2 (C-3), 105.7 (C-3′), 110.2 (C-4′), 124.3 (SOPh), 129.2 (SOPh), 131.0 (SOPh), 141.2 (C-2′), 144.8 (SOPh), 154.2 (C-5′) and 203.6 (C-2); *m*/z 258 (M$^+$).

Oxidation–IMDA cyclisation of the furyl compound 16

The phenylsulfinylallene **16** (230 mg, 0.89 mmol) was treated with MCPBA (230 mg, 67%, 0.89 mmol) in dichloromethane (30 cm^3) at −10 °C for 30 min. The reaction was quenched with aq. $NaHCO_3$–ice, and the mixture was extracted (CH_2Cl_2). The organic phase was washed (brine), dried ($MgSO_4$) and evaporated under reduced pressure, maintaining the temperature ~0 °C throughout the work-up. A ^{1}H NMR spectrum of the reaction mixture showed the presence of three species in the ratio ~10:2:1. The major component **19** was isolated (see below), whereas the minor components were characterised by the following spectroscopic data of the mixture, δ_H (400 MHz) **17**: 2.45 (2H, m, 4-H$_2$), 2.70 (2H, t, *J* 7.5, 5-H$_2$), 5.87 (1H, td, *J* 2 × 7.0 and 6.2, 3-H), 6.00 (1H, dq, 3.1 and 0.9, 5′-H), 6.20 (1H, dt, *J* 6.2 and 2 × 3.1, 1-H), 6.27 (1H, dd, *J* 3.1 and 1.8, 4′-H), 7.30 (1H, dd, *J* 1.8 and 0.9, 3′-H) and 7.50–7.90 (5H, m, SO_2Ph); **18**: 4.42 (1H, d, *J* 3.6, 4-H), 5.30 (1H, dd, *J* 3.6 and 1.7, 5-H), 5.45 (1H, m, 3-H), 6.54 (1H, d, *J* 5.6, 7-H) and 6.57 (1H, dd, *J* 5.6 and 1.7, 6-H).

Flash chromatography of the mixture on silica gel [ether–hexane (3:2)] furnished *(4S*,5R*,7aS*)-4-phenylsulfonyl-5,7a-epoxy-2,4,5,7a-tetrahydro-1H-indene* **19** (150 mg, 63%), mp 87–90 °C (from dichloromethane–ether) (Found: C, 66.1; H, 5.1; S, 11.4%; M$^+$, 274. $C_{15}H_{14}O_3S$ requires C, 65.7; H, 5.1; S, 11.7%; *M*, 274); ν_{max}/cm^{-1} 1307 and 1141 (SO); δ_H (400 MHz) 1.85 (1H, ddd, *J* 13.9, 9.6 and 8.2, 1β-H), 2.28 (1H, ddd, *J* 13.9, 7.4, and 1.6, 1α-H), 2.70–2.90 (2H, m, 2-H$_2$), 3.65 (1H, dt, *J* 3.4 and 2 × 1.9, 4-H), 5.38 (1H, d, *J* 2.1, 5-H), 5.75 (1H, dt, *J* 3.3 and 2 × 1.9, 3-H), 6.41 (1H, dd, *J* 5.7 and 2.1, 6-H), 6.50 (1H, d, *J* 5.7, 7-H) and 7.55–7.87 (5H, m, SO_2Ph); δ_C (100 MHz) 26.3 (t, C-1), 37.1 (t, C-2), 66.7 (d, C-4), 83.8 (d, C-5), 101.1 (s, C-7a), 124.4 (d, C-3), 128.7 (d, SO_2Ph), 129.5 (d, SO_2Ph), 133.8 (d, SO_2Ph), 135.0 (d, C-6), 137.8 (s, C-3a) and 137.8 (SO_2Ph) and 140.3 (d, C-7).

3-(4,4-Ethylenedioxycyclohex-1-en-1-yl)propan-1-ol 21

3-(4-Anisyl)propan-1-ol **20**[23] (830 mg, 5 mmol) in THF (10 mmol) was added to stirred liquid ammonia (30 cm^3) and ethanol (20 cm^3), followed by sodium (1 g, 43 mmol, in small portions). The solution was stirred for 30 min, then NH_4Cl (s) was added and the ammonia was allowed to evaporate. The remaining solvent was evaporated under reduced pressure, the residue was taken up with dichloromethane, and the organic phase was washed (water), dried ($MgSO_4$) and evaporated under reduced pressure to yield an oily residue (783 mg, 93%), a portion (700 mg, 4.06 mmol) of which was dissolved in THF (20 cm^3) and treated at 0 °C with ethylene glycol (0.66 cm^3, 10 mmol) and BF_3·OEt_2 (0.2 cm^3, 1.6 mmol) for 1 h. The mixture was poured into aq. $NaHCO_3$–ice, and the product was extracted (CH_2Cl_2). The combined extract was washed (water, brine), dried ($MgSO_4$) and evaporated under reduced pressure, and the residue was chromatographed on silica gel [ethyl acetate–hexane (2:3)] to yield *3-(4,4-ethylenedioxycyclohex-1-en-1-yl)propan-1-ol* **21** (489 mg, 61%), ν_{max}/cm^{-1} 3621 (OH); δ_H (400 MHz) 1.70 (2H, m, 2-H$_2$), 1.74 (2H, t, *J* 6.7, 6′-H$_2$), 2.07 (2H, t, *J* 7.2, 3-H$_2$), 2.18 (2H, m, 5′-H$_2$), 2.24 (2H, br s, 3′-H$_2$), 3.62 (2H, t, *J* 6.4, 1-H$_2$), 3.95 (4H, s, O-(CH$_2$)$_2$O) and 5.35 (1H, br s, 2′-H); δ_C (100 MHz) 27.5 (t, C-5′), 30.6 (t, C-2), 31.1 (t, C-6′), 33.6 (t, C-3), 35.6 (t, C-3′), 62.8 (t, C-1), 64.4 (t, O(CH$_2$)$_2$O), 108.1 (s, C-4′), 118.5 (d, C-2′) and 137.1 (s, C-1′); *m*/*z* 198.1250 (M$^+$. $C_{11}H_{18}O_3$ requires *M*, 198.1250).

5-(4,4-Ethylenedioxycyclohex-1-en-1-yl)pent-1-yn-3-ol 22

Sequential Dess–Martin oxidation–ethynylation of **21**, as described in previous experiments, gave *pentynol* **22** (54% over two steps), ν_{max}/cm^{-1} 3691 (OH) and 3305 (C≡C); δ_H (400 MHz) 2.44 (1H, d, *J* 2.1, 1H), 3.95 (4H, s, O-(CH$_2$)$_2$O), 4.45 (1H, td, *J* 2 × 6.4 and 2.1, 3-H) and 5.35 (1H, br, *W* 10.2, 2′-H); δ_C (100 MHz) 27.5 (C-5′), 31.1 (C-6′), 32.4 (C-5), 35.4 (C-4), 35.6 (C-3′), 62.0 (C-3), 64.4 [O(CH$_2$)$_2$O], 73.0 (C-1), 84.7 (C-2), 108.1 (C-4′), 119.0 (C-2′) and 136.4 (C-1′); *m*/*z* 222.1257 (M$^+$. $C_{13}H_{18}O_3$ requires *M*, 222.1256).

5-(4,4-Ethylenedioxycyclohex-1-en-1-yl)-1-phenylsulfonylpenta-1,2-diene 23

Treatment of compound **22** (900 mg, 4.05 mmol) with triethylamine (0.85 cm^3, 6.08 mmol) and benzenesulfenyl chloride (0.58 cm^3, 5 mmol) in dichloromethane (40 cm^3) at −78 °C, followed by oxidation of the resulting crude phenylsulfinylallene (1.07 g, 3.24 mmol) with MCPBA (912 mg, 3.24 mmol) in dichloromethane (40 cm^3) at 0 °C, as described in previous experiments, gave the *phenylsulfonylallene* **23** (461 mg, 41%), ν_{max}/cm^{-1} 1956 (C=C=C), 1308 and 1148 (SO); δ_H (400 MHz) 1.73 (2H, t, *J* 6.6, 5′-H$_2$), 2.03 (2H, br t, *J* 7.5, 5-H$_2$), 3.94 (4H, s, O-(CH$_2$)$_2$O), 5.26 (1H, br s, *W* 8.2 Hz, 2′-H), 5.85 (1H, td, *J* 2 × 7.0 and 6.0, 3-H), 6.18 (1H, dt, *J* 6.0 and 2 × 3.0, 1-H) and 7.40–7.90 (5H, m, SO_2Ph); δ_C (100 MHz) 25.8 (t, C-6′), 27.5 (t, C-4), 31.0 (t, C-5), 35.5, 35.6 (t, C-3′ and C-5′), 64.4 (t, O(CH$_2$)$_2$O), 100.6 (d, C-1), 101.3 (d, C-3), 107.9 (s, C-4′), 119.4 (d, C-2′), 127.6 (d, SO_2Ph), 129.1 (d, SO_2Ph), 133.4 (d, SO_2Ph), 135.6 (s, C-1′), 141.4 (s, SO_2Ph) and 205.5 (s, C-2); *m*/*z* 346.1234 (M$^+$. $C_{19}H_{22}O_4S$ requires *M*, 346.1234).

4-(5-Phenylsulfonylpenta-3,4-dienyl)cyclohex-3-en-1-one 24

The ketal **23** (200 mg, 0.58 mmol) in trifluoroacetic acid (1.5 cm^3) was stirred at room temperature for 30 min, then the solution was cooled to 0 °C and neutralised with aq. $NaHCO_3$. The mixture was extracted (Et_2O), and the extract was washed (water, brine), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel [ethyl acetate–hexane (2:3)] to yield the *ketone* **24** (161 mg, 92%), ν_{max}/cm^{-1} 1956 (C=C=C), 1713 (CO), 1308 and 1149 (SO); δ_H (400 MHz) 2.20 (2H, t, *J* 2 × 7.4, 1′-H$_2$), 2.30 (2H, m, *W* 25, 2H$_2$), 2.35 (2H, td, *J* 2 × 6.8 and 1.2, 5-H$_2$), 2.50 (2H, td, *J* 2 × 6.8 and 0.8, 6-H$_2$), 2.82 (2H, m, 2′-H$_2$), 5.46 (1H, m, 3-H), 5.85 (1H, td, *J* 2 × 6.8 and 5.9, 3′-H), 6.20 (1H, dt, *J* 5.9 and 2 × 2.9, 5′-H) and 7.56–7.62 (5H, m, SO_2Ph); δ_C (100

MHz) 25.7 (t, C-5), 27.8 (t, C-2′), 35.5 (t, C-1′), 38.4 (t, C-6), 39.5 (t, C-2), 100.4 (d, C-3′), 101.5 (d, C-5′), 119.3 (d, C-3), 127.6 (d, SO_2Ph), 129.2 (d, SO_2Ph), 133.4 (SO_2Ph), 136.7 (d, SO_2Ph), 141.3 (s, SO_2Ph), 155.4 (s, C-4) and 205.6 (s, C-4′), 210.4 (s, C-1); *m/z* 302.0981 (M^+. $C_{17}H_{18}O_3S$ requires *M*, 302.0977).

1-(Phenylsulfonylmethyl)spiro[4.5]deca-1,6-dien-8-one 26

From compound 24. The ketone **24** (200 mg, 0.66 mmol) was added to a solution of lithium diisopropylamide [from *n*-BuLi (0.28 cm^3, 0.7 mmol, 2.5 M solution in THF) and diisopropylamine (92 µl, 0.7 mmol)] in THF (5 cm^3) at −78 °C and the mixture was stirred for 15 min, then trimethylchlorosilane (0.11 cm^3, 0.55 mmol) was added. After a further 30 min at −78 °C, the mixture was warmed to room temperature, then stirred for 2 h. Pentane was added, the solution was washed ($NaHCO_3$), and the solvent was evaporated under reduced pressure. Flash chromatography of the residue on silica gel [ethyl acetate–hexane (3:7)] gave a fraction (23 mg, 12%) comprising a mixture of isomers **25** (~5:1 by NMR), δ_H (400 MHz) *major component*: 4.05 (1H, br s, 4-H), 4.45 (1H, br s, OH), 4.90 (1H, q, *J* 3 × 2.2, 3-H), 6.10 (1H, d, *J* 8.6, 7-H), 6.12 (1H, d, *J* 8.6, 6-H), 7.60–7.95 (5H, m, SO_2Ph); *minor component*: 4.15 (1H, br s, 4-H), 4.95 (1H, br s, OH), 5.60 (1H, d, *J* 8.6, 7-H), 5.65 (1H, q, *J* 3 × 2.0, 3-H), 6.12 (1H, d, *J* 8.6, 6-H), 7.45–7.70 (5H, m, SO_2Ph). A portion (10 mg, 0.33 µmol) of this fraction in THF–EtOH (1 cm^3, 1:1) was treated with aq. 1 M KOH (1 cm^3, 1 mmol) at room temperature for 30 min, water was added, and extraction (Et_2O) of the mixture furnished the *spiro compound* **26** (7 mg, 70%) as a colourless oil, ν_{max}/cm^{-1} 1674 (CO), 1309 and 1152 (SO); δ_H (400 MHz) 1.70–1.90 (3H, 4-H and 10-H_2), 2.85 (4H, m, 3-H_2 and 9-H_2), 3.68 (1H, dd, *J* 14.4 and 1.2, CH_2S), 3.77 (1H, dd, *J* 14.4 and 1.6, CH_2S), 5.91 (1H, dd, *J* 10.0 and 0.8, 7-H), 6.19 (1H, m, 2-H), 6.50 (1H, dd, *J* 10.0 and 1.6, 6-H) and 7.56–7.90 (5H, m, SO_2Ph); δ_C (100 MHz) 30.7, 30.9, 34.2 (t, C-3, C-4 and C-10), 35.1 (t, C-9), 52.5 (s, C-5), 54.6 (t, CSO_2Ph), 128.5 (d, SO_2Ph), 129.2 (d, SO_2Ph), 129.3 (d, C-7), 133.9 (d, SO_2Ph), 134.3 (s, SO_2Ph), 136.5 (d, C-2), 139.3 (s, C-1), 154.9 (d, C-6) and 199.0 (s, C-8); *m/z* 302.0971 (M^+. $C_{17}H_{18}O_3S$ requires *M*, 302.0977).

From compound 23. The phenylsulfonylallene **23** (460 mg, 1.33 mmol) was stirred in trifluoroacetic acid (4 cm^3) at room temperature for 1 h, an excess of 1 M KOH was added, and the solution was stirred for a further 1 h. Aq. NH_4Cl was added and the product was extracted (EtOAc). The extract was washed (NH_4Cl, brine), dried ($MgSO_4$) and evaporated under reduced pressure, and the residue was chromatographed on silica gel [ethyl acetate–hexane (2:3)] to yield compound **26** (340 mg, 85%).

Acknowledgements

We thank the National Research Foundation and AECI Ltd for financial support.

References

1 (*a*) A. G. Fallis, *Can. J. Chem.*, 1984, **62**, 183; (*b*) D. Craig, *Chem. Soc. Rev.*, 1987, 187; (*c*) W. R. Roush, in *Comprehensive Organic Synthesis*, ed. I. Fleming and B. Trost, Pergamon Press, Oxford, 1991; (*d*) D. Craig, in *Stereoselective Synthesis*, ed. G. Helmchen, R. W. Hoffmann, J. Mulzer and E. Schaumann, Thieme, Stuttgart, 1996, E21, vol. 5, 2872; (*e*) A. G. Fallis, *Acc. Chem. Res.*, 1999, **32**, 464.
2 J. R. Bull, N. S. Desmond-Smith, S. J. Heggie, R. Hunter and F.-C. Chang, *Synlett*, 1998, 900.
3 N. S. Simpkins, *Sulfones in Organic Synthesis*, Pergamon, Oxford, 1993, ch. 6 and references cited therein.
4 (*a*) L. Henn, G. Himbert, K. Diehl and M. Kaftory, *Chem. Ber.*, 1986, **119**, 1953 and references cited therein; (*b*) C. P. Dell, E. H. Smith and D. Wharburton, *J. Chem. Soc.*, *Perkin Trans. 1*, 1985, 747; (*c*) S.-K. Yeo, M. Shiro and K. Kanematsu, *J. Org. Chem.*, 1994, **59**, 1621 and references cited therein.
5 M. L. Curtin and W. H. Okamura, *J. Org. Chem.*, 1990, **55**, 5278 and references cited therein.
6 A. Padwa, M. Meske, S. S. Murphree, S. H. Watterson and Z. Ni, *J. Am. Chem. Soc.*, 1995, **117**, 7071 and references cited therein.
7 C. Bintz-Giudicelli, O. Weymann, D. Uguen, A. de Cian and J. Fisher, *Tetrahedron Lett.*, 1997, **38**, 2841; C. Bintz-Giudicelli and D. Uguen, *Tetrahedron Lett.*, 1997, **38**, 2973.
8 A preliminary account of aspects of this investigation has been published: J. R. Bull, R. S. Gordon and R. Hunter, *Synlett*, 1999, 599.
9 S. Braverman and H. Mechoulam, *Tetrahedron*, 1974, **30**, 3883; G. Smith and C. J. M. Stirling, *J. Chem. Soc.* (*C*), 1971, 1530 and references cited therein.
10 W. D. Wulff and T. S. Powers, *J. Org. Chem.*, 1993, **58**, 2381.
11 W. R. Roush and S. E. Hall, *J. Am. Chem. Soc.*, 1981, **103**, 5200.
12 P. B. Hopkins and P. L. Fuchs, *J. Org. Chem.*, 1978, **43**, 1208.
13 C. Margot, M. Rizzolio and M. Schlosser, *Tetrahedron*, 1990, **46**, 2411.
14 W. R. Roush, H. R. Gillis and A. J. Ako, *J. Am. Chem. Soc.*, 1982, **104**, 2269.
15 J. Schwartz and J. A. Labinger, *Angew. Chem.*, *Int. Ed. Engl.*, 1976, **15**, 333 and references cited therein.
16 J. K. Stille, *Angew. Chem.*, *Int. Ed. Engl.*, 1986, **25**, 508.
17 P. D. Wender and M. J. Tebbe, *Synthesis*, 1991, 1089.
18 D. Craig, N. J. Geach, C. J. Pearson, A. M. Slawin, A. J. P. White and D. J. Williams, *Tetrahedron*, 1995, **51**, 6071.
19 C. O. Kappe, S. S. Murphree and A. Padwa, *Tetrahedron*, 1997, **53**, 14179.
20 P. DeShong, R. E. Waltermine and H. L. Ammon, *J. Am. Chem. Soc.*, 1988, **110**, 1901.
21 H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed., VCH Publishers, Weinheim, 1993, ch. 3.
22 J. R. Bull, M. A. Sefton and R. I. Thomson, *S. Afr. J. Chem.*, 1990, **43**, 42.
23 A. Goosen, C. F. Marais, C. W. McCleland and F. Rinaldi, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 1227.
24 C. Spino, J. Crawford and J. Bishop, *J. Org. Chem.*, 1995, **60**, 844.