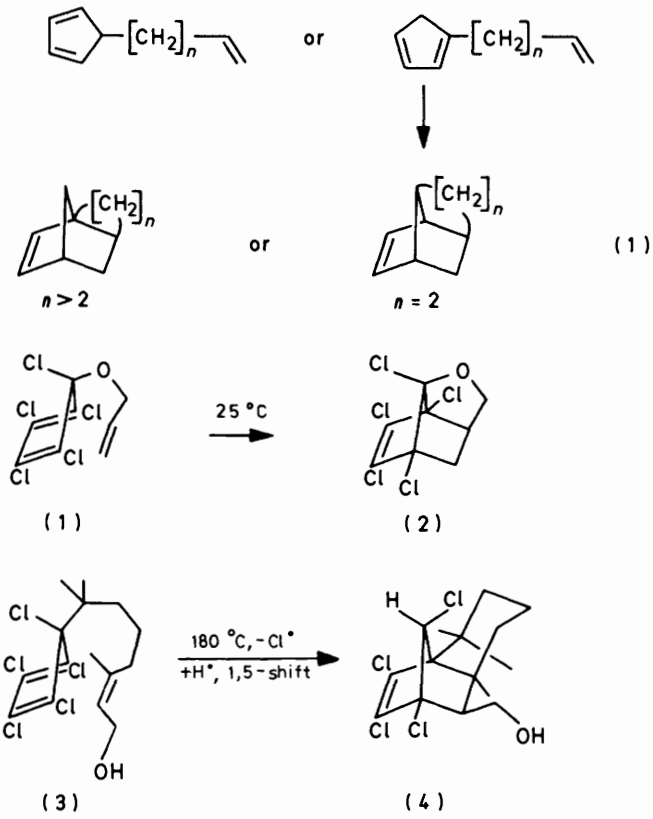
An Investigation of the Chemistry of Phenylsulphonylcyclopentadiene

Alexander J. Bridges * and John W. Fischer
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, USA

Phenylsulphonylcyclopentadiene (7) exists mainly as the 1-isomer, and the assigned structure of its dimer (6) has been corroborated by n.m.r. decoupling experiments. Both the diene (7) and its cyclopentadienide anion (8) were unusually unreactive, although anion (8) rapidly perdeuteriates and undergoes Michael addition, α to the sulphonyl group, to methyl vinyl ketone, albeit in very low yield to form adduct (11). On being heated to 65 °C compound (11) rearranges, and two consecutive 1,5-shift products have been tentatively identified by n.m.r. spectroscopy.

Diels–Alder reactions of cyclopentadienes have great synthetic utility in the preparation of norbornenes.[1] 5-Substituted cyclopentadienes can react efficiently to form 7-substituted norbornenes,[2] but only if the temperature is kept low enough to prevent 1,5-H shifts from preceding the Diels–Alder reaction.[3] With intramolecular Diels–Alder reactions [4] the conditions are always drastic enough to allow 1,5-H shifts to precede cycloaddition, and the products of cycloaddition are normally dependent only on the chain length separating diene and dienophile,[5] and not on the initial cyclopentadiene isomer. If the chain length is two atoms the product is exclusively the 1,7-bridged norbornene,[6,7] and if the chain length is >2 atoms the product is exclusively the 1,2-bridged isomer [8–10] as shown in equation (1). These preferences appear to be very strong. For example the pentachlorocyclopentadiene (1) cyclises readily at 25 °C to form the highly strained 2,7-bridged tricyclic compound (2),[11] but the pentachlorocyclopentadiene (3) cyclises to the 1,2-bridged compound (4) only at 180 °C after it has dechlorinated.[12] Several natural products are 2,7-bridged norbornanes with a three-carbon (*e.g.* sativene) or four-carbon (*e.g.* longifolene) bridge, and are therefore logical targets for synthesis *via* intramolecular Diels–Alder reactions. Two strategies exist to ensure that the correct adduct is formed. One is to expand the two-carbon-bridge adduct, as was done by Snowden in an elegant synthesis of sativene.[13] The other is to block the 1,5-shifts with some group of low migratory aptitude, although Glass's experience [12] with diene (3) suggests that approach would not be easy.



We decided to investigate the chemistry of phenylsulphonylcyclopentadiene to see whether the phenylsulphonyl group would be a suitable blocking group for such intramolecular Diels–Alder reactions. We chose the phenylsulphonyl group for three reasons. Its strong electron-withdrawing effect should direct alkylation of the corresponding cyclopentadiene anion to the 5-position.[14] Although little appears to be known about the sigmatropic migratory aptitude of the sulphone group [15] we believed that it would be low. Lastly, the unactivated sulphone group should be easily removed by reduction [16] after cyclisation.

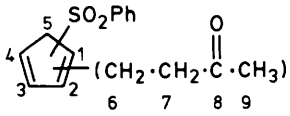
Phenylsulphonylcyclopentadiene was prepared by the method of Hartke and Gleim.[17] Benzenesulphenyl chloride was added to cyclopentadiene to give *trans*-3-chloro-4-phenylthiocyclopentene in quantitative yield. Oxidation with 2 equiv. of *m*-CPBA (*m*-chloroperbenzoic acid) gave the corresponding chlorosulphone (5), which is reported to dehydrohalogenate with DBN (1,5-diazabicyclo[4.3.0]non-5-ene) to give the dicyclopentadiene (6), presumably *via* the desired diene (7) (Scheme 1). The cyclopentadienide anion (8), characterized by n.m.r. spectroscopy, was obtained by treatment of the chloride (5) with excess of sodium hydride in [$^2H_6$]DMSO.*

We found that treatment of (5) with either 2 equiv. of n-butyl-lithium or sodium hydride, both in THF (tetrahydrofuran), followed by a mild acid quench, gave diene (7) in 50—80% yield. Perhaps surprisingly, chloro-sulphone (5), in the presence of catalytic tetra-n-butylammonium bromide (which is presumably acting only as a detergent) dissolves in aqueous 2.5M sodium hydroxide. Washing the aqueous layer with diethyl ether, followed by acidification of the aqueous phase and extraction with diethyl ether, gave diene (7) rather cleanly in 85% yield.

Diene (7) is a white crystalline solid which dimerises quite rapidly in the solid phase, there being essentially no monomer left after 16 h at −20 °C. As a 1M solution in $CDCl_3$ the mono-

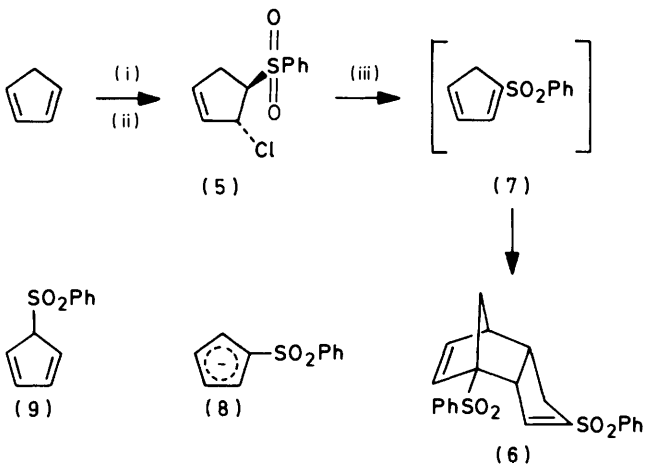
* DMSO is dimethyl sulphoxide.

Table 1. Chemical shifts (δ) of cyclopentadiene derivatives



Carbon	Diene (7)		Diene (9) [a]	Diene (11)		Diene (12)	Diene (13)
	^1H	[^{13}C]	^1H	^1H	[^{13}C]	^1H	^1H
1	—	145.7	6.42	6.26	136.8	—	—
2	7.47	142.7	6.42	6.26	134.8	6.08	—
3	6.50	131.6	6.42	6.26	134.8	6.26	6.41
4	6.73	140.9	6.42	6.26	136.8	6.26	6.65
5	3.30	41.2	4.76	—	82.8	4.60	3.37
6				2.2—2.45	20.8	*b*	2.95—3.25
7				2.6—2.85	37.5	*b*	2.6—2.9
8				—	206.9	—	—
9				2.05	29.9	2.16	2.16

[a] Highly tentative assignments. [b] Since compound was never obtained pure accurate δ-values could not be determined.



Scheme 1. *Reagents*: (i) PhSCl; (ii) *m*-CPBA; (iii) DBN

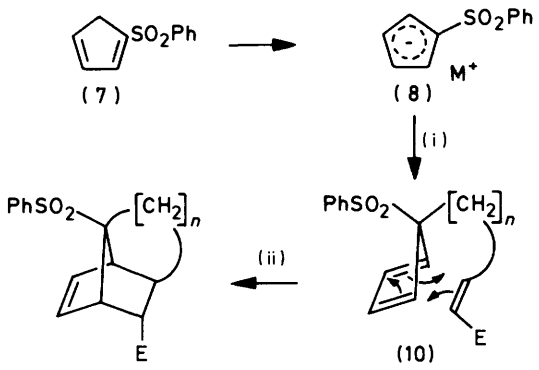
mer (7) was less than 10% dimerised after 3 h at 0 °C, and we were able to characterize it fully by n.m.r. and i.r. spectroscopy. The proton spectrum shows quite clearly that one isomer is the major (>90%) component present, and that this isomer is the 1-isomer (7).[18] As well as the typical phenylsulphonyl absorbance in the δ 7.5—8.2 region, compound (7) shows a two-proton quartet at δ 3.30, *J* 1.5 Hz, a much broadened two-proton AB quartet, *J* 7 Hz at δ 6.50 and 6.73, and a one-proton multiplet at δ 7.47. For assignments see Table 1. The shifts are almost identical to those of 1-cyanocyclopentadiene,[19] and visually the ring portion of the spectrum is very similar to that published for 1-acetylcyclopentadiene.[20] In addition there were always small but variable quantities of two singlets at δ 4.76 and 6.42, in a *ca.* 1 : 4 ratio, which may be due to the 5-isomer (9), in which case it is present in 1—2.5% amounts. (See Table 1 for chemical shifts and multiplicities of other 5-sulphonylcyclopentadienes.) The ^{13}C spectrum shows absorbances at δ_C 41.2, 131.6, 140.9, 142.7, and 145.7 p.p.m. for the cyclopentadiene ring. The three highly deshielded vinyl carbon atoms are highly indicative of the directly conjugated 1-isomer (7) rather than the cross-conjugated 2-isomer, or the unconjugated 5-isomer (9).

Diene (7) is quite acidic and could be completely extracted into 1M sodium hydroxide solution, but it extracts only partially into a potassium carbonate buffer, pH 10.1, from an equal volume of diethyl ether. We therefore estimate that the p*K*- of compound (7) to be 10 or slightly below. This high acidity of diene (7) meant that it could be purified conveniently by base extraction.

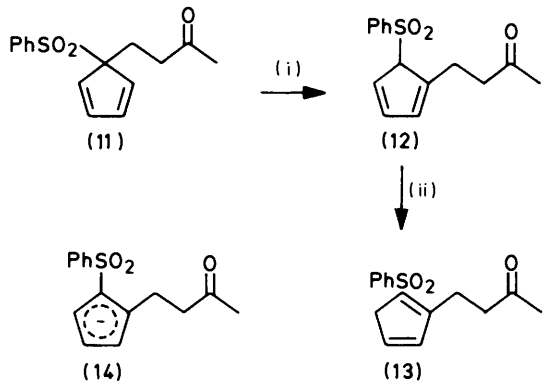
Diene (7) in $CDCl_3$ did not deuteriate with D_2O under mild base catalysis (pH 8) or acid catalysis (0.1M CF_3CO_2H). However, diene (7) in [$^2H_6$]DMSO was deuteriated at all five ring positions immediately on treatment with D_2O, under basic, neutral, or acidic conditions. This rather unexpected dependence on solvent rather than on pH can be explained readily assuming that deuteriation only occurs *via* anion (8). In a good ionising medium such as DMSO–water, anion (8) is formed so rapidly that deuteriation is completed, *via* multiple non-regiospecific protonations of (8), well within the timeframe of an n.m.r. experiment (*ca.* 2 min). Presumably the deuteriation under acidic conditions is much slower than under neutral or basic conditions, but still rapid enough for equilibration to occur within the n.m.r. experimental time. In $CDCl_3$ the anion (8) is not readily formed so that deuteriation is so slow that it does not compete with dimerisation.

Although diene (7) exists predominately as the 1-isomer, rather than the desired 5-isomer (9), we examined the Diels–Alder reaction of (7) to see whether the less stable, but potentially more reactive, isomer (5) might be trapped in the same way that 1-methoxycarbonylcyclopentadiene is reported to be trapped as the 5-isomer in Thiele's ester [21] and by maleic anhydride.[22] However, treatment of diene (7) with both *N*-phenyldihydrotriazoledione and *N*-phenylmaleimide led only to dimer (6), showing no indication that any ' crossed ' Diels–Alder reaction had occurred. An attempt to do an inverse-electron-demand Diels–Alder reaction with ethoxyethene also failed.

In order for diene (7) to be useful in the overall scheme shown in Scheme 2 its cyclopentadienide anion (8) must be capable of being alkylated α to the sulphone substituent to form (eventually) a 5,5-disubstituted derivative of type (10) which must in turn undergo a Diels–Alder reaction, in preference to both thermal rearrangement and dimerisation. The reaction of anion (8) with several electrophiles was investigated. The sodium cyclopentadienide anion (8; M = Na) did not react with dimethyl sulphate even in hexamethylphosphoric triamide HMPA, or with benzyl bromide in dimethylformamide (DMF) at 50 °C. When this reaction was repeated at 100 °C anion (8) decomposed. Attempts to silylate



Scheme 2. *Reagents*: (i) $X[CH_2]_nCH{=}CHE$; (ii) heat



Scheme 3. *Reagents and conditions*: (i) 65 °C; (ii) 65 °C or base

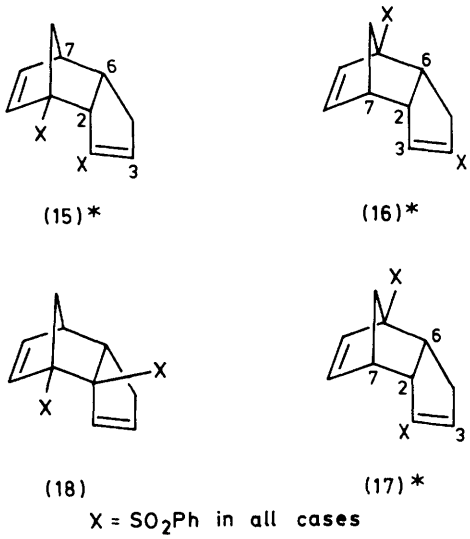
anion (8) with both chlorotrimethylsilane and trimethylsilyl trifluoromethanesulphonate were also unsuccessful. However, anion (8) in DMF did react with 1 equiv. of acetyl chloride, but the reaction mixture consisted largely of dimer (6), and showed several acetyl peaks in the n.m.r., suggesting that a mixture of polyacylation products had been formed in low yield. An attempt to drive the reaction to completion with 5 equiv. of acetyl chloride and sodium hydride led only to polymerisation. The lithium cyclopentadienide (8; M = Li) reacted instantly with 1 equiv. of bromine at −78 °C, but the reaction mixture consisted mainly of dimer (6) with several (poly)bromo compounds which were not further identified. Diene (7) itself also reacts with 1 equiv. of bromine to form a similar product mixture. Anion (8) also failed to form a ferrocene [23] under classical conditions.[24]

When anion (8; M = Na, Li) was treated with the Michael acceptors methyl vinyl ketone (MVK), acrolein, and acrylonitrile it polymerised them. However, when the MVK reaction was run in the presence of excess of chlorotrimethylsilane some product was discernible in a very dirty reaction mixture. Silica-gel chromatography gave a reasonably clean adduct in 15% yield, but after further purification on preparative t.l.c. (p.l.c.) the yield of the simple Michael adduct (11) dropped to 6%, indicating that adduct (11) is not very stable to silica gel. Attempts were made to improve the yield of (11), but they gave variable results and no yields >10%. We surmised that the reaction might be a radical- or single-electron-transfer process but addition of traces of *m*-CPBA or $CuI{\cdot}P(OMe)_3$ did not improve yields at all.

The structure of adduct (11) was evident from the n.m.r. spectrum (Table 1). The four vinyl protons appear as a broad singlet at δ 6.26 and the methylene groups of the side-chain as typical A_2B_2 pattern at δ 2.3 and 2.7 .In the ^{13}C n.m.r. spectrum only two vinyl signals are present at δ_C 134.8 and 136.8 p.p.m., which are reasonable values for an allylic sulphone, and which confirm the plane of symmetry in the cyclopentadiene ring. At room temperature adduct (11) appeared to be indefinnitely stable, showing no signs of rearrangement or dimerisation. However, on being heated to 65 °C in $CDCl_3$, adduct (11) had a half-life of *ca.* 1 h. This was clearly seen in the methyl region of the spectrum where a new singlet grew in at δ 2.16. Initially new peaks also appeared at δ 4.60, a slightly broadened singlet, and 6.08, a much broadened singlet, and the vinyl singlet at δ 6.26 remained much larger than expected because the new compound also has an absorbance at that δ-value. The A_2B_2 system also began to shift downfield into the δ 2.9—3.2 region. After 3 h these changes were much more pronounced and new peaks began to appear, a triplet at δ 3.37 (*J ca.* 1 Hz) and an AB quartet, *J* 5.5 Hz at δ 6.41 and 6.65. After 6 h very little starting material remained, and the two sets of peaks were in a *ca.* 1 : 1 ratio. (The spectrum was now complex enough to show at least 20% of unassignable broadened signals presumably due to polymerisation products.) Treatment of the sample with 1 μl of *N*-ethyldi-isopropylamine, led to an immediate disappearance of the peaks at δ 4.60, 6.08, and 6.26 and an increase in intensity of those at δ 3.37, 6.41, and 6.65. The sample was extracted with base and, after acidification and extraction with ether, an n.m.r. spectrum was taken on the remaining material. It was the second product, showing the above quoted peaks and an A_2B_2 pattern at δ 2.6—2.9 and 2.95—3.25.

The most likely interpretation of these data is that adduct (11) undergoes an initial 1,5-sulphone shift (giving the first qualitative data for the migratory aptitude of the sulphone group in sigmatropic rearrangements) to form the 5-sulphonylcyclopentadiene (12). The 3- and 4-H vinyl protons would be expected to retain a similar chemical shift to that in compound (11) as they are still allylic to a sulphone group. The 2-H peak, however, should move upfield as the alkene becomes more substituted, and it should also broaden due to the allylic coupling. The A_2B_2 system of the side-chain should also move downfield as the C-6 methylene group becomes allylic. Since Table 1 shows exactly these changes, we assign structure (12) to the first intermediate. On continued heating a slower 1,5-H shift takes place to produce the thermodynamic product (13) (Scheme 3). Electron-withdrawing halogen substituents are reported to slow down the 1,5-H shift in cyclopentadiene [25] so these relative rates are not surprising. Equilibration of (12) and (13) is much faster in base *via* the corresponding cyclopentadienide anion (14) where facile formation allows for the basic extraction of (13) to be successful. Thus the base-induced behaviour of both (12) and (13) adds chemical evidence to the structural assignments as both must clearly be 5-hydrogen-substituted cyclopentadienes to explain their evidently high acidity. The structure of (13) also rests strongly on n.m.r. evidence. As can be seen from Table 1 the ring resonances of (13) are very similar to those of an authentic 1-sulphonylcyclopentadiene (7) with the exceptions that (i) the system shows slightly lesser multiplicity and (ii) the 2-H vinyl proton at δ 7.47 is missing. Again the C-6 methylene group is shifted downfield from that in diene (11) as anticipated, and the C-9 methyl is unsurprisingly the same as in the ring isomer (12).

This study convinced us that, although the phenylsulphonyl group does show some of the anticipated properties, the low reactivity of anion (8) and the relatively low thermal stability of adduct (11) make it unsuitable for its original purpose. It is interesting, however, to contrast the chemistry of anion (8), which appears to be unreactive towards most electrophiles, but which does alkylate α to the sulphone, with that of the far more acidic cyclopentadienyltriphenylphosphorane,[26] which



reacts with quite a wide range of electrophiles, but forms 1,2-disubstituted cyclopentadienes.

We then turned our attention to the high point of the chemistry of diene (7), its dimerisation to form the dicyclopentadiene (6). Hartke and Gleim [17] assigned structure (6) on the basis of a partial n.m.r. analysis, and by analogy with the minor isomer of Thiele's ester.[27] Since, allowing for free 1,5-H shifts, there are 72 possible structures for dimer (6), and the literature does not unequivocally prove the structure [27] to which dimer (6) is compared, and is replete with examples of the complexity of dimerisation reactions of electron-deficient cyclopentadienes,[20,28] we carried out an n.m.r. analysis of this reaction. Diene (7) (>95% pure after basic extraction) was allowed to dimerise in *ca.* 1M $CDCl_3$ solution at 30 °C, and the reaction was followed by n.m.r. spectroscopy. Diene (7) disappeared completely over a period of a week, and a very complex set of signals appeared. Recrystallisation of this analytically pure material gave a crystalline solid with the literature m.p.,[17] and an n.m.r. spectrum superimposable on the pre-recrystallisation spectrum. Despite this the material was clearly not completely pure, with the proton spectrum showing three multiplets, each of *ca.* 0.1 proton intensity, at δ 5.4—5.6, 3.05—3.25, and 1.3, which must belong to a minor component although both the ^1H and ^{13}C spectra suggest that the dimer is ⩾90% one compound. Our data were not good enough to allow us to determine whether the impurity was a second dimer, perhaps produced initially, or in equilibrium with the major dimer.

The proton spectrum of dimer (6) was investigated in some detail, with extensive decoupling, both by ordinary double resonance and spectrum-subtraction techniques. The chemical shifts determined for dimer (6) are given in Table 2, and the determined coupling constants in Table 3. In each table the literature values for *endo*-dicyclopentadiene [29] are given for comparison. The decoupling experiments allow all the protons to be assigned as shown in Table 2, and demonstrate that dimer (6) is an *endo*-dicyclopentadiene with sulphone substituents on one of the bridgehead norbornene atoms, and one of the cyclopentene vinyl carbons, but do not unequivocally decide between structures (6), (15),* (16),* and (17.* However, there are some indications in the spectrum to discount structures (15)—(17). There should be a coupling constant of 2—3 Hz between 6-H and 7-H in structures (6) and (15) or between 2-H and 7-H in structures (16) and (17). Despite a careful search no such coupling was found, which would be expected if 7-H (δ 2.96) were next to 6-H (δ 2.9—3.35) but surprising if it were next to 2-H (δ 3.91). In the sulphone dimer 2-H and 6-H are 0.79 and 0.48 p.p.m., respectively, further downfield than they are in dicyclopentadiene. Therefore, 2-H rather than 6-H is likely to be more proximate to the electron-withdrawing sulphone group. Both of these facts point towards structures (6) and (15) for the sulphone dimer rather than (16) and (17). Atom 3-H has coupling constants of 2.3 Hz with 2-H and 1.5 Hz with 5a- and 5b-H. This would fit structure (6) better than (15), but the range of vinylic and allylic coupling constants in cyclopentenes does not allow for an unequivocal assignment.

On chemical grounds there are also reasons to prefer structure (6) over structures (15)—(17). Structures (6) and (16) are dimers of the stable 1-isomer (7), whereas structures (15) and (17) are ' crossed ' dimers requiring the 2-isomer, for which we saw no evidence. Furthermore, structures (15) and (17) require the 2-isomer to act as the dienophilic component in a Diels–Alder reaction, and an examination of the Diels–Alder reactions of carboxymethylcyclopentadiene shows that, despite the fact that all three isomers can serve as dienic components in Diels–Alder reactions, only the 1-isomer acts as a dienophilic component.[27,28,30] FMO theory [31] also supports the assigned structure (6), since it is the FMO-predicted 1,1-dimer, rather than (16). For a 1,2-dimer FMO theory predicts the 1,2-disubstituted dimer (18) (which is disfavoured sterically by the vicinal phenylsulphonyl substituents) rather than either (15) or (17).

Experimental

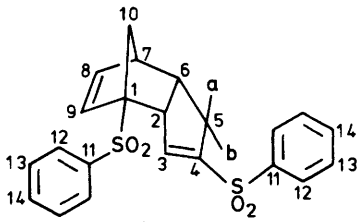
General.—All n.m.r. spectra were recorded on an IBM NR80 spectrometer as dilute solutions in $CDCl_3$ unless otherwise stated. I.r. spectra were recorded on a Pye-Unicam 3-200 grating i.r. spectrophotometer as KBr discs. M.p.s were recorded on a Fisher–Johns m.p. apparatus and are uncorrected. Ether refers to diethyl ether.

1-*Phenylsulphonylcyclopentadiene* (7).—*Method A.* n-Butyllithium (1.4 ml, 2 mmol) was added dropwise to a stirred solution of *trans*-3-chloro-4-phenylsulphonylcyclopentene (5) [17] (0.24 g, 1 mmol) in THF (3 ml) at −78 °C under N_2. After 1 h at −78°C the mixture was poured onto aqueous sodium dihydrogen phosphate (1M; 10 ml) and extracted with ether (2 × 25 ml). The combined extracts were extracted with aqueous sodium hydroxide (1M; 2 × 10 ml). The basic layers were combined and acidified with dilute hydrochloric acid and then extracted with ether (3 × 10 ml). The combined extracts were washed in turn with water (10 ml) and saturated brine (10 ml), and were then dried ($MgSO_4$). The solvent was removed under reduced pressure to yield 1-phenylsulphonylcyclopentadiene (0.17 g, 82%) as a light brown solid.

Method B. *trans*-3-Chloro-4-phenylsulphonylcyclopentene (5) (0.24 g, 1 mmol) was added to vigorously stirred aqueous sodium hydroxide (2.5M; 2 ml), containing tetra-n-butylammonium bromide (10 mg) under N_2 at 20 °C. After 15 min all the solid had dissolved, and the pale brown solution was diluted with water (10 ml) and washed with ether (20 ml). The aqueous solution was acidified with dilute hydrochloric acid (3M; 2 ml) and was extracted with ether (2 × 10 ml). The combined extracts were washed with saturated brine (10 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give 1-phenylsulphonylcyclopentadiene (7) (0.18 g, 85%) as a white solid, $\nu_{max.}$ 1 575, 1 440, 1 200, 1 150, 1 000, 760, 720, and 680 cm^{-1}; δ 7.56—8.2 (5 H, m), 7.47 (1 H, m),

* The numbering schemes adopted for these structures refer only to the position numbers in Tables 2 and 3, and are meant only to facilitate the fitting of the spectroscopic data to the four possible dimer structures.

Table 2. Chemical shift values for dimer (6) and *endo*-dicyclopentadiene [29]



(6)

Position		1	2	3	4	5	6	7
Dimer (6)	^{1}H	—	3.91	6.54	—	a 2.45 b 1.81	2.9—3.55	2.96
	^{13}C	79.1	54.6	140.7	147.8	32.6	45.7	44.5
	Off resonance	(s)	(d)	(d)	(s)	(t)	(d)	(d)
endo-Dicyclopentadiene ^{1}H		2.85	3.18	5.45	5.45	a 2.15 b 1.60	2.67	2.8

Position		8	9	10	11	12	13	14
Dimer (6)	^{1}H	5.85	5.97	1.65	—		7.4—8.3	
	^{13}C	131.2	135.6	52.1	139.6,	129.4,	129.2,	134.3,
	Off resonance	(d)	(d)	(t)	137.6	129.3	128.1	133.8
endo-Dicyclopentadiene ^{1}H		5.92	5.92	1.27, 1.45				

Table 3. Coupling constants (Hz) for dimer (6) and dicyclopentadiene [29]

Coupled protons	2,3	2,5a	2,5b	2,6	3,5a	3,5b	5a,5b	5a,6	7,8	7,10	8,9
Dimer (6)	2.3	1.5	3	8	1.5	1.5	17	10	3	*ca.* 2	6
endo-Dicyclopentadiene							17	10			

6.73 and 6.50 (1 H, and 1 H, broadened ABq, J 5.5 Hz), and 3.30 (2 H, q, J 1.5 Hz); δ_C 145.7, 142.7, 141.5, 140.9, 133.27, 131.57, 129.4, 127.6, and 41.2 p.p.m.

endo-1,4-*Bis*(*phenylsulphonyl*)*tricyclo*[5.2.1.0^{2,6}]*deca*-3,8-*diene* (6).—n-Butyl-lithium (1.4M in hexane; 7 ml, 10 mmol) was added dropwise to a stirred solution of *trans*-3-chloro-4-phenylsulphonylcyclopentene (5) (1.21 g, 5 mmol) in THF (10 ml) under N_2 at − 78 °C. After 1 h the reaction mixture was poured onto aqueous sodium dihydrogen phosphate (1M, 15 ml) and was extracted with ether (2 × 10 ml). The combined extracts were re-extracted with aqueous sodium hydroxide (1M; 20 ml). The aqueous phase was acidified with dilute hydrochloric acid and extracted with ether (3 × 10 ml). The combined ethereal extracts were washed in turn with water (10 ml) and saturated brine (10 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a light brown solid (0.57 g 55%) which was kept in a vacuum desiccator at 20 °C for 4 d to give the dicyclopentadiene (6) as a light brown solid, m.p. 172—175 °C (Found: C, 64.1; H, 4.95. Calc. for $C_{22}H_{20}O_4S_2$: C, 64.05; H, 4.90%, $\nu_{max.}$ 1 440, 1 297, 1 150, 1 080, 753, 740, 715, and 684 cm^{-1}. See Tables 2 and 3, and text for both proton and carbon spectra. A sample of (6) recrystallised from benzene–hexane had m.p. 180—182 °C (lit.,[17] 180 °C) and an identical ^{1}H n.m.r. spectrum to that shown prior to recrystalisation.

4-(1-*Phenylsulphonylcyclopenta*-2,4-*dienyl*)*butan*-2-*one* (11).—n-Butyl-lithium (1.6M in hexane; 12.5 ml, 20 mmol) was added dropwise to a stirred solution of 1-phenylsulphonylcyclopentadiene (7) (2.42 g, 10 mmol) in THF (25 ml) at −78 °C under nitrogen. After 30 min, chlorotrimethylsilane (2.4 ml, 20 mmol) was added at −78 °C. Ten minutes after the addition was completed, MVK (1.85 ml, 20 mmol) was added dropwise to the stirred mixture. After a further 30 min the mixture was poured onto aqueous sodium dihydrogen phosphate (1M; 25 ml) and the layers were separated. The aqueous layer was extracted with ether (2 × 25 ml) and the combined organic layers were washed in turn with water (25 ml) and saturated brine (25 ml), and dried ($MgSO_4$). The solvent was removed under reduced pressure to yield a thick brown oil (3.65 g) which was purified on a silica-gel column (60 × 3 cm, 175 g; 175 ml fractions); elution was initially with 35% chloroform–hexane (450 ml), then 45% chloroform–hexane (450 ml), and finally 60% chloroform–hexane (9.5 l). Fractions 36—58 were combined and the solvent was removed under reduced pressure to give 4-(1-*phenylsulphonylcyclopenta*-2,4-*dienyl*)*butan*-2-*one* (11) (0.41 g, 15%) as a light yellow oil which was purified further by p.l.c. with ethyl acetate as developer to yield the desired compound (0.17 g, 6%) as a white-yellow solid. Recrystallisation from ethyl acetate–hexane gave white rod-like crystals (0.07 g, 2.5%), m.p. 116.5—118.5 °C (Found: C, 64.5; H, 6.2. $C_{15}H_{16}O_3S$ requires C, 65.18; H, 5.85%); $\nu_{max.}$ 1 705, 1 585, 1 450, 1 370, 1 310, 1 290, 740, and 725 cm^{-1}; δ 7.2—8.0 (5 H, m), 6.25 (4 H, brs), 2.6—2.85 (2 H, m), 2.2—2.45 (2 H, m), and 2.05 (3 H, s); δ_C 206.9, 136.8, 135.7, 134.8, 133.8, 130.1, 127.6, 82.8, 37, 29.9, and 20.8 p.p.m.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Research Corporation for partial support of this research.

References

1 R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hadec, *J. Chem. Soc.*, 1964, 3062.
2 E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Am. Chem. Soc.*, 1969, **91**, 5675.
3 I. Fleming and J. P. Micheal, *J. Am. Chem. Soc.*, 1978, **100**, 245.
4 G. Breiger and J. N. Bennett, *Chem. Rev.*, 1980, **80**, 63.
5 R. L. Snowden, *Tetrahedron Lett.*, 1981, **22**, 97
6 G. Breiger and D. R. Anderson, *J. Org. Chem.*, 1971, **36**, 243.
7 L. Paquette, M. Wyvratt, and J. Matthew, *J. Am. Chem. Soc.*, 1974, **96**, 4671.
8 G. Breiger, *J. Am. Chem. Soc.*, 1963, **85**, 3783.
9 E. J. Corey and R. S. Glass, *J. Am. Chem. Soc.*, 1967, **89**, 2600.
10 T. Olson and O. W. Wernerstrom, *Tetrahedron Lett.*, 1979, 1721.
11 M. E. Jung and L. A. Light, *J. Org. Chem.*, 1982, **47**, 1084.
12 R. S. Glass, J. O. Herzog, and R. L. Sobszak, *J. Org. Chem.*, 1978, **43**, 3209.
13 R. L. Snowden, *Tetrahedron Lett.*, 1981, **22**, 101.
14 P. T. Lansbury, R. W. Erwin, and D. A. Jeffrey, *J. Am. Chem. Soc.*, 1980, **102**, 1602.
15 C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.
16 P. A. Grieco and Y. Masaki, *J. Org. Chem.*, 1975, **40**, 150.
17 K. Hartke and H. V. Gleim, *Ann. Chem.*, 1976, 716.
18 D. Peters, *J. Chem. Soc.*, 1959, 1761.
19 O. W. Webster, *J. Am. Chem. Soc.*, 1966, **88**, 3046.
20 G. Grundke and H. M. R. Hoffmann, *J. Org. Chem.*, 1981, **46**, 5428.
21 J. Thiele, *Chem. Ber.*, 1901, **34**, 68.
22 G. L. Grunewald and D. P. Davis, *J. Org. Chem.*, 1978, **43**, 3074.
23 V. N. Drozd, V. A. Sazanova, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 1964, **159**, 591.
24 G. Wilkinson, *Org. Synth.*, Coll. Vol. IV, 1963, 473.
25 R. Breslow, J. H. Hoffman, and C. Perchonok, *Tetrahedron Lett.*, 1973, 3723.
26 Z. I. Yoshida, S. Yoneda, and Y. Murata, *J. Org. Chem.*, 1973, **38**, 3537.
27 W. E. Franklin, C. H. Mack, and S. P. Rowland, *J. Org. Chem.*, 1968, **33**, 626.
28 D. Peters, *J. Chem. Soc.*, 1961, 1042.
29 R. G. Foster and M. C. McIvor, *J. Chem. Soc. B*, 1969, 188.
30 D. Peters, *J. Chem. Soc.*, 1961, 1037.
31 See I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley, New York, 1976.

Received 28*th February* 1983; *Paper* 3/306