Tetrahedron Vol 47, No 35, pp 7489-7500, 1991
Printed in Great Britain

0040-4020/91 $3 00+.00
Pergamon Press plc

REGIO- AND STEREO-CHEMISTRY OF THE COUPLING REACTION OF PHENYLSULPHENYL-, PHENYLSULPHINYL- AND PHENYLSULPHONYL-PENTADIENYL METALS

E. Epifani,[b] S. Florio,*[a] G. Ingrosso,[b] L. Ronzini,[b]
R. Sgarra,[b] and L. Troisi.[b]

a) Dipartimento Farmaco-Chimico, Facoltà di Farmacia, Università di Bari, Traversa 200 Re David, 4, 70125 Bari, Italy.
b) Laboratorio di Chimica Organica, Dipartimento di Biologia, Università di Lecce, Via Monteroni, 73100 Lecce, Italy.

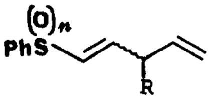
(*Received in UK* 20 *May* 1991)

Summary: The coupling reaction of phenylsulphenyl-, phenylsulphinyl- and phenylsulphonyl-pentadienyl metals 3a-g has been studied showing that while 3c-g couple in any case regioselectively and stereoselectively, the coupling of 3a-b is countercation and electrophile dependent. The α-regioisomeric coupling products of phenylsulphenylpentadienyl metals may undergo [1,5] sigmatropic rearrangement, those of phenylsulphinyl- and phenylsulphonyl-pentadienyl metals give fast double [3,2] sigmatropic isomerization.

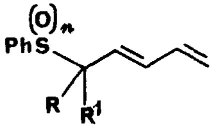
The coupling reactions of metallated pentadienyl sulphides, sulphoxides and sulphones have not been extensively investigated with reference to the inherent regio- and stereo-chemistry, notwithstanding their remarkable synthetic potential for the preparation of functionalized dienes which are important as such and as substrates for Diels-Alder cyclization.

In a recent paper[1] we reported on the coupling reaction of phenylsulphenylpentadienyl metals with C-electrophiles showing that the regiochemistry and stereochemistry much depend upon the nature of the metal and the electrophile. Indeed, the coupling reaction of 3a-b turned out to be completely α-regioselective and (Z)-diastereoselective with MeI and cyclopentanone but was poorly regio- and diastereo-selective with aldehydes.

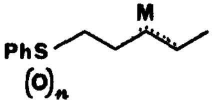
As an extension of such an investigation we decided to study in more details the coupling reaction of 3a-b with C-electrophiles and to compare it with that of the corresponding phenylsulphinyl- and phenylsulphonyl-pentadienyl derivatives. We have first investigated the C-C bond forming reactions of phenylsulphenylpentadienyllithium 3a. As reported,[1] 3a can be readily produced by lithiation of the phenylpentadienyl sulphide 1a. It could be trapped by methylation either with MeI or with bistrimethylsilylperoxide. Interestingly, trapping with MeI afforded α-regioselectively the sulphide 2e (E), whereas trapping with bistrimethylsilylperoxide (BTMSPO) led to the sulphide 4 (geometric isomers). Moreover, trapping of 3a with MeOD led to a 70 to 30 ratio of the monodeuterated isomeric sulphides 2f (>95% deuteration, E) and 1d (50% deuteration).



1a: n=0; R=H
1b: n=1; R=H
1c: n=2; R=H
1d: n=0; R=D

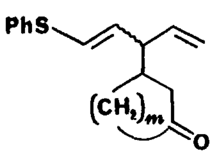


2a: n=2; R=H; R^1=Me
2b: n=2; R=R^1=Me
2c: n=2; R=R^1=H
2d: n=1; R=R^1=H
2e: n=0; R=H; R^1=Me
2f· n=0; R=H; R^1=D

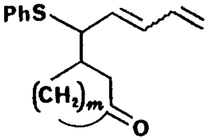


3a: n=0; M=Li
3b: n=0; M=ZnB
3c: n=1; M=Li
3d: n=1; M=Cu
3e: n=1; M=ZnB
3f: n=1; M=MgB
3g: n=2; M=Li

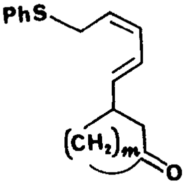
4



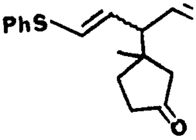
5a: m=2;
5b: m=3;



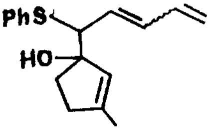
6a: m=2 (Z)
6b: m=2 (E)
6c: m=3 (Z)



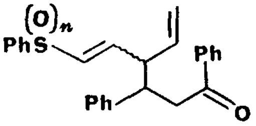
7a: m=2
7b: m=3



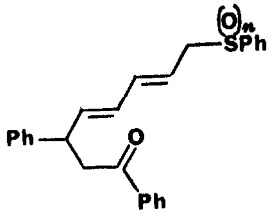
8



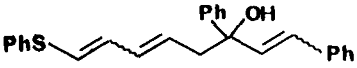
9



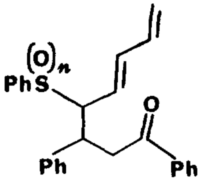
10: n=0
22· n=1



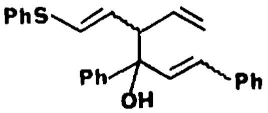
11: n=0
20: n=1
24: n=2



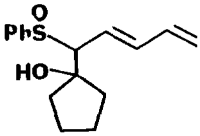
12



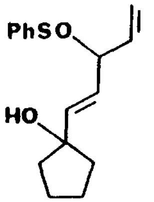
13: n=0
21: n=1
23· n=2



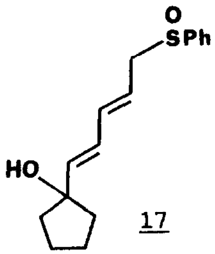
14



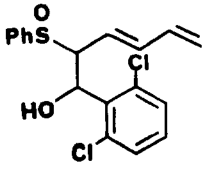
15



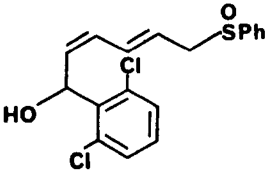
16



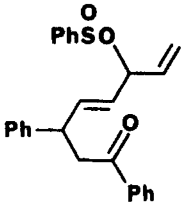
17



18



19



25

Phenylsulphenylpentadienyllithium 3a reacts with 2-cyclopentenone in a highly regioselective (either with respect to 3a and to the enone), but poorly diastereoselective manner yielding the γ-regioisomer 5a (E/Z=2/1) togheter with small percentages of the (Z)-α-regioisomer 6a, which tends to undergo a [1,5] sigmatropic rearrangement to 7a, and the (E)-α-regioisomer 6b. It was worthy noting that 6b, in contrast with 6a, does not rearrange presumably for not having the proper geometry required for the [1,5] sigmatropic rearrangement.[1] Such a coupling proved to be metal dependent as the reaction of 3b (generated in situ upon transmetallation of 3a with $ZnBr_2$) with 2-cyclopentenone afforded very poor yield of the α- and γ-regioisomer 5a, and 6b and 7a.

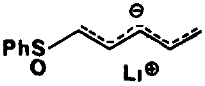
Similarly, 3a reacted with 2-cyclohexenone to give yet in γ-regioselective manner the 1,4 addition product 5b (E+Z) togheter with compound 7b likely arising from the [1,5] sigmatropic rearrangement of the α-regioisomer 6c (Z).

The coupling reaction of 3a with 3-methyl-2-cyclopentenone looses in regioselectivity giving a mixture of the γ-1,4-addition product 8 (E+Z) and the α-1,2-addition compound 9 (Z+E) with a 66 to 34 regioisomeric ratio. Still more complex turned out to be the reaction of 3a with chalcone that afforded a 5.7:1:3.3 mixture of the γ-1,4-addition product 10 (E+Z), the isomerized α-1,4-addition product 11 (E,E) and the ε-1,2-addition adduct 12 (geometric isomers).

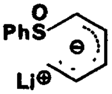
The reaction of 3b with chalcone was completely α-regioselective as for as the 1,4-addition giving a mixture of 13 (E) and 11 (E,E) and γ-regioselective with reference to the 1,2-addition producing 14 (geometric isomers).

The outcome of the above reactions of 3a-b confirms the previous observations that the coupling of phenylthiopentadienyl metals actually depends upon the nature of the countercation and the electrophile, while the heteroatom function does not seem to affect such a coupling.

The m-chloroperbenzoic acid (MCPBA) oxidation of phenylpentadienyl sulphide 1a[1] (E/Z=1/4) furnished a mixture (E/Z=2/3) of phenylpentadienyl sulphoxide 1b. The geometric isomers could be separated by column chromatography and assigned the configuration on the basis of coupling constants between the two hydrogens belonging to the internal double bond (J = 9.55 Hz for the Z isomer versus J = 15.14 Hz for the E isomer). Lithiation of 1b (E or Z or the mixture of the two) with n-BuLi at -78°C gave phenylsulphinylpentadienyllithium 3c, which could not be trapped by methylation neither with MeI or bistrimethylsilylperoxide[2] and the quenching with aqueous NH$_4$Cl afforded the conjugate (E)-phenyl-2,4-pentadienyl sulphoxide 2d. It is interesting to note that 2d adopts an exclusive trans geometry around the internal C-C double bond and this presumably because the lithiated precursor 3c prefers the W shaped (A) rather than the U shaped structure (B).



(A)



(B)

Treatment of 3c with cyclopentanone led to the allylic alcohols 17, adopting an E,E configuration, which presumably originates from a double [3,2] sigmatropic rearrangment of the homoallylic alcohol 15 through the sulphinate intermediate 16. The alcohol 15 corresponds to the α-regioisomer of the coupling reaction between 3c and cyclopentanone. Attempts to isolate and characterized 15 failed. The trans geometry around the central C-C double bond of the chain of 15 would make the fast double [3,2] sigmatropic rearrangment easy to occur. Moreover, the bias of 15 to undergo the sigmatropic rearrangment above, which is synthetically interesting and not unprecedented,[4] might be ascribed to the internalization of the diene unit that provides sufficient stabilization to 17.[4]

Comparable results have been obtained when phenylsulphinylpentadienyl copper 3d and phenylsulphinylpentadienylzinc bromide 3e, easily achievable by transmetallation of 3c with CuI and ZnBr$_2$ respectively, were reacted with cyclopentanone leading finally to the allylic alcohol 17 (E,E). Also highly regio- and stereo-selective was the coupling reactions of 3c, 3d, 3e and 3f (from transmetallation of 3c with MgBr$_2$·Et$_2$O) with 2,6-dichlorobenzaldehyde that furnished in all cases the allylic alcohol 19, which is likely the result of the sigmatropic rearrangement of the α-regioisomer 18, that however could not be isolated.

The reaction of 3c with chalcone yielded the ketones 20 (E,E) as the major product and the γ-regioisomer 22 (20/22=82/18). Probably, compound 20 comes from the rearrangement of the α-regioisomer 21.

Table. Reactions of 3a-g with electrophiles in THF at -78°C.

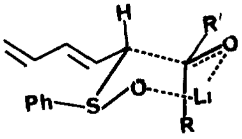
Pentadienyl metal	Electrophile	Reaction product (%)	Overall yield %
3a	2-cyclopentenone	5a (85)	66
		7a (11)	
		6b (4)	
3b	"	5a	(trace)
		7a+6b	(trace)
3a	2-cyclohexenone	5b (76)	77
		7b (24)	
3a	3-methyl-2-cyclopentenone	8 (66)	58
		9 (34)	
3a	chalcone	10 (57)	58
		11 (10)	
		12 (33)	
3b	"	13 (50)	40
		11 (25)	
		14 (25)	
3c	cyclopentanone	17	40
3d	"	17	55
3e	"	17	11[a]
3c	2,6-dichlorobenzaldehyde	19	40[a]
3d	"	19	47
3e	"	19	25[a]
3f	"	19	43[a]
3c	chalcone	20 (82)	73
		22 (18)	
3g	MeI (1 equiv.)	2a (55)	83
		2b (13)	
		2c (32)	
3g	MeI (excess)	2a (26)	75
		2b (74)	
3g	cyclopentanone	2c	47
3g	2,6-dichlorobenzaldehyde	2c	77
3g	chalcone	23[b]	55

a) The precursor of 3e, 3f and 3c (that is 1b) was recovered as the isomer 2d. b) Compound 23 undergoes isomerization to 24 during crystallization.

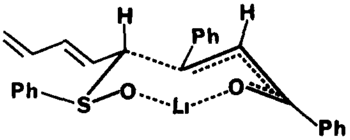
It is also noteworthy that 3c gives α-1,4-addition on chalcone as γ-1,4-addition has been reported for lithiated allylic sulphoxide.[5] Therefore, the coupling of phenylsulphinylpentadienyl metals 3c-f is always α-regio- and diastereo-selective whatever the countercation M and electrophile.

The α-regioselectivity of the coupling reactions of 3c-f might be interpreted in terms of a higher negative charge density in the α position due to the sulphinyl group that provides stabilization to the carbanionic species with its electronic and coordinating effects. Moreover, such an α-regioselectivity might be rationalized by assuming that the coupling reaction to give the α regioisomer proceeds through the relatively stable six-membered chair-like transition state (C) in the case of saturated carbonyls and a eight-membered crown-like transition state

(D) in the case of unsaturated carbonyls.



(C)

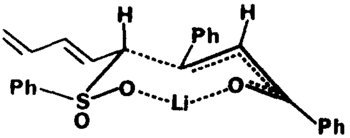


(D)

(E+Z)-Phenyl-1,4-pentadienyl sulphone 1c, promptly available by MCPBA oxidation of the corresponding sulphide 1a, has been lithiated to give 3g upon treatment with n-BuLi at -78°C. Lithiated sulphone 3g has been found to couple α-regioselectively with MeI to produce both the trans-monomethylated compound 2a and the trans-dimethylated diene 2b togheter with some isomerized trans-phenyl-2,4-pentadienyl sulphone 2c. In contrast, no coupling occurred when 3g was treated with cyclopentanone and 2,6-dichlorobenzaldehyde; after quenching with aqueous NH_4Cl it was just recovered the (E)-diene sulphone 2c.[6]

Coupling reaction occurred when 3g was treated with chalcone to give still α-regioselectively the carbonyl sulphone 23 (E+Z) which is prone to undergo isomerization to 24 (E). We presume that the conversion 23-->24 can be considered as a double [3,2] sigmatropic rearrangement passing through the sulphinate 25. Such a conversion is noteworthy in view of the fact that, as for as we know, no [1,5] like rearrangement of pentadienylsulphones has ever been reported so far.[7,8]

As in the coupling reaction of phenylsulphinylpentadienyllithium 3c, the α-regioselectivity observed in the reaction of phenylsulphonylpentadienyllithium 3g with chalcone might be explained by assuming a higher negative charge density in the α position due to the proximity of the sulphonyl group and by considering that the coupling through the α carbon of 3g would pass through a eight-membered crown-like transition state (E) of relatively low energy.



(E)

In conclusion, our work shows that while regio- and stereo-chemistry of the coupling reaction of phenylsulphenylpentadienyl metals much depends upon the countercation M and the electrophile with the sulphenyl group apparently not affecting the coupling, that of phenylsulphinyl- and phenylsulphonyl-dienyl metals is substantially unaffected by either the metal and the electrophile being whatsoever α-regioselective with the sulphinyl and the sulphonyl group playing a major role in determining the regiochemistry of the reaction. This sounds interesting from the synthetic viewpoint as regio- and stereo-defined functionalized dienes can be prepared and these can rather easily be rearranged to other stereodefined dienes.

More work is in progress in order to rationalize the different behaviour of phenylsulphenyl-, phenylsulphinyl- and phenylsulphonyl-pentadienyl metals with respect to C-electrophile and to get structural information on such dienyl metals.

EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Varian XL-200 or EM 360A spectrometer; chemical shifts are reported in part per million (δ) from internal standard using $CDCl_3$ as solvent. IR spectra were recorded on a Perkin-Elmer spectrometer model 598 and refer to films. GC analyses were carried out with a Hewlett-Packard HP-5890 series II gaschromatograph (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.); GC-MS spectrometry analyses were performed on a HP-5890A gaschromatograph equipped with a HP-5970B Mass Selective Detector operating at 70 eV (E.I.). Melting points, taken on an Electrothermal apparatus, and boiling points were uncorrected. Flash chromatographies were done with Merck 230-400 mesh silica gel.

Materials: Tetrahydrofuran (THF) and diethyl ether of commercial grade (RS, C. Erba) were purified by distillation (twice) from sodium wire in N_2 atmosphere. Petroleum ether refers to the 40-60°C boiling fraction. All other chemicals were of commercial grade and used without further purification or eventually distilled or crystallized prior to use. (Z)-1-bromo-2-phenylthioethene[9] and bis-trimethylsilylperoxide[2] were prepared as reported.

1-Phenylsulphenyl-1,4-pentadiene 1a: a mixture of (Z)-1-bromo-2-phenylthioethene (6.5 gr, 30 mmol) and [1,2-Bis(diphenylphosphino)ethane]nickel(II) chloride [$NiCl_2$(dppe)] (0.57 gr, 1.1 mmol) in 150 ml of ether was treated with 36 mmol of allylmagnesium bromide in ether at room temperature under N_2 and stirring. After 5 h a solution of aqueous NH_4Cl was slowly added and the mixture extracted with Et_2O (3 x 100 ml), washed with H_2O and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure gave a residue that was distilled (b.p. 55-57°C/1 mm Hg) to give 4.6 gr (87% yield) of 1a (Z/E = 80/20).
^{1}H-NMR (200 MHz) δ: 2.88-3.10 (m, 2H), 5.04-5.22 (m, 2H), 5.77-6.05 (m, 2H), 6.18-6.35 (m, 1H), 7.17-7.49 (m, 5H). I.R. 3080, 3000, 1480 cm^{-1}.

1-Phenylsulphinyl-1,4-pentadiene 1b: phenylpentadienylsulphide 1a (3.40 gr, 19 mmol, Z/E = 80/20) was dissolved in chloroform (100 ml) and cooled in a ice bath. m-Chloroperbenzoic acid (4.00 gr, 22.8 mmol) in 40 ml of chloroform was then dropped in with constant stirring. The reaction was complete in 2 h (monitored by TLC E.E./E.P.=8/2). The reaction mixture was washed successively with sodium thiosulphate, sodium bicarbonate (twice) and water, then dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude sulphoxide (3.16 gr, 87% yield) was column chromatographed (E.E./E.P.=8/2) yielding 1b as the Z (2.0 gr) and the E isomer (1.0 gr).

(Z)-1-phenylsulphinyl-1,4-pentadiene 1b: oil. ^{1}H-NMR (200 MHz) δ: 3.00-3.05 (m, 2H), 4.79-4.86 (m, 2H), 5.49-5.62 [m, 1H, when irradiated at 3.02 δ the multiplet changed to a double doublet: 5.55 (dd, J=9.77 Hz, J= 17.73 Hz)], 5.85-5.98 [m, 2H, when irradiated at 3.02 δ the multiplet gave two doublets: 5.89 (d, 1H, J=9.55 Hz), 5.95 (d, 1H, J=9.52 Hz)], 7.11-7.34

(m, 5H). I.R. 3060, 3010, 1040 cm^{-1}.

(E)-1-phenylsulphinyl-1,4-pentadiene 1b: oil. ^{1}H-NMR (200 MHz) δ: 2.83-2.90 (m, 2H), 4.94-5.05 (m, 2H), 5.59-5.79 [m, 1H, when irradiated at 2.87 δ the multiplet changed to a double doublet: 5.69 (dd, J=9.65 Hz, J=17.47 Hz)], 6.13-6.22 [m, 1H, when irradiated at 2.87 δ the multiplet became a doublet: 6.18 (d, J=15.14 Hz)], 6.55 (dt, 1H, J=6.35 Hz, J=15.14 Hz, when irradiated at 2.87 δ the dt changed to a doublet), 7.37-7.55 (m, 5H). I.R.: 3060, 3010, 1040 cm^{-1}.

1-Phenylsulphonyl-1,4-pentadiene 1c: to a solution of 6.7 gr (38.0 mmol) of sulphide 1a in 80 ml of $CHCl_3$ was added (0°C) a solution of 16 gr (95 mmol) of MCPBA in 120 ml of $CHCl_3$; then the mixture was refluxed for 15 h and workup as above gave 9.2 gr of crude product which was column chromatographed (ether) to obtain a Z/E=2/1 mixture of sulphone 1c, 6.5 gr (82% yield). I.R. 3070, 1310, 1140 cm^{-1}. The ^{1}H-NMR (200 MHz) spectra were extracted from that of the isomeric mixture: for (Z)-1-phenylsulphonyl-1,4-pentadiene δ: 3.28-3.35 (m, 2H), 4.86-5.00 (m, 2H), 5.52-5.73 (m, 1H), 6.09-6.31 [m, 2H, when irradiated at 3.31 δ the multiplet transformed in two doublets: 6.15 (d, 1H, J=10.82 Hz), 6.24 (d, 1H, J=10.83 Hz)], 7.35-7.53 (m, 5H); for (E)-1-phenylsulphonyl-1,4-pentadiene δ: 2.80-2.87 (m, 2H), 4.86-5.00 (m, 2H), 5.52- 5.73 (m, 1H), 6.23-6.30 [m, 1H, when irradiated at 2.83 δ the multiplet became a doublet: 6.26 (d, J=15.13 Hz)], 6.88 (dt, 1H, J=6.11 Hz, J=15.14 Hz, when irradiated at 2.83 δ the dt changed to a doublet), 7.73-7.88 (m, 5H).

General metallation procedure: To a solution of diene 1a or 1b or 1c (1.6-2.3 mmol) in THF under N_2, stirred and cooled at -78°C were added dropwise 1.1 molar equiv of n-BuLi in hexane. After 30 min the pentadienyllithium 3a, 3c and 3g were formed. Addition of CuI or $ZnBr_2$, or $MgBr_2 \cdot Et_2O$ (1.3 equiv) in THF to a 3a or 3c solution led to the transmetallated species 3b, 3d, 3e and 3f.

Reactions of phenylsulphenylpentadienyllithium 3a: a) Methylation with methyliodide: A 2.3 mmol sample of 3a in 20 ml of THF at -78°C, under N_2 and stirring, was added with MeI (4.6 mmol) in 10 ml of THF. After 30 min (monitored by GC) quenching with NH_4Cl, usual workup and column chromatography (by petroleum ether) gave 0.38 gr (88% yield) of (E)-5-phenylsulphenyl-1,3-hexadiene 2e: oil. ^{1}H-NMR (200 MHz) δ: 1.42 (d, 3H, J=6.8 Hz, when irradiated at 3.80 δ, the doublet became a singlet), 3.77-3.84 (m, 1H), 5.00-5.14 (m, 2H), 5.70 (dd, 1H, J=7.9 Hz, J=15.10 Hz, when irradiated at 3.80 δ the double doublet became a doublet J=15.1 Hz), 5.94 (dd, 1H, J=10.00 Hz, J=15.00 Hz), 6.28 (dt, 1H, J=10.00 Hz, J=17.05 Hz), 7.24-7.44 (m, 5H).

b) Methylation with bis-trimethylsilylperoxide: to 1.7 mmol of 3a in 20 ml of THF at -78°C, under N_2 and with stirring were added 3.4 mmol of BTMSPO in 10 ml of THF and the mixture stirred for 1h, then quenched with sat NH_4Cl, extracted with Et_2O (30 ml x 3), and dried over $MgSO_4$. The removal of the solvent under reduced pressure gave an oil, which was purified by short column chromatography on silica gel (petroleum ether) to give 1-phenylsulphenyl-1,3-hexadiene 4 (0.26 gr, 80% yield) as an isomeric mixture. ^{1}H-NMR (200 MHz) δ: 1.04-1.14 (m, 3H), 2.13-2.26 (m, 2H), 5.69-6.57 (m, 4H), 7.21-7.45 (m, 5H). MS m/e (rel. int.): 190 (M^+, 100), 175 (8), 161 (16), 109 (20), 81 (91). A small amount of PhSSPh (5%) was also isolated.

c) Deuteration: a solution of 1.7 mmol of 3a in 20 ml of THF was treated at -78°C with 1.0 ml of CH_3OD (99.8%) in 5 ml of THF. After 30 min usual workup yielded the monodeuterated sulphides 2f (E): 0.1 gr, 33% yield (95% deuteration) and 1d (E+Z): 0.2 gr, 66% yield (50% deuteration), which were separated by column chromatography on silica gel (ether/petroleum ether=1/50).

(E)-1-Phenylsulphenyl-1-deutero-2,4-pentadiene 2f: oil. ^{1}H-NMR (200 MHz) δ: 3.57 (d, 1H, J=5.61 Hz), 5.01-5.17 (m, 2H), 5.74 (dd, 1H, J=7.02 Hz, J= 14.70 Hz, when irradiated at 3.56 δ this dd produced a doublet J=14.40 Hz), 6.04-6.39 (m, 2H), 7.14-7.36 (m, 5H).

d) Reaction with 2-cyclopentenone: to a solution of 3a in THF (20 ml) (2.8 mmol) was added a THF solution (10 ml) of 2-cyclopentenone (3.4 mmol) at -78°C, under N$_2$. After 5 min usual workup left an oil residue of four main compounds. They were separated by column chromatography using diethyl ether-petroleum ether mixture of increasing polarity starting from petroleum ether. The first eluted compound was (E)-1-phenylsulphenyl-1-(3-oxocyclopentyl)-2,4-pentadiene 6b as an oil (2% yield). ^{1}H-NMR (200 MHz): δ 1.9-2.5 (m, 7H), 3.5 (dd, 1H, J=9.3 Hz, J=7.5 Hz), 5.0-5.2 (m, 2H), 5.6 (dd, 1H, J=9.2 Hz, J=15.2 Hz), 5.8 (dd, 1H, J=15.2 Hz, J=12.5 Hz), 6.1-6.3 (m, 1H), 7.2-7.4 (m, 5H).

The second eluted compound was: (Z)-1-phenylsulphenyl-3-(oxocyclopentyl)-1,4-pentadiene 5a (18% yield). Oil. ^{1}H-NMR (200 MHz): δ 1.9-2.4 (m, 7H), 3.24 (ddd, 1H, J=6.9 Hz, J=7.1 Hz, J= 9.4 Hz), 5.06-5.2 (m, 2H), 5.7 (ddd, 1H, J=10.3 Hz, J=7.1 Hz, J=16.9 Hz), 5.71 (dd, 1H, J=9.4 Hz, J=9.4 Hz), 6.34 (d, 1H, J=9.4 Hz), 7.1-7.4 (m, 5H). I.R. 1740 cm^{-1} (C=O).

The third eluted compound was (E)-5a (36% yield). Oil. ^{1}H-NMR (200 MHz): δ 1.9-2.4 (m, 7H), 2.7-2.8 (m, 1H), 5.0-5.2 (m, 2H), 5.6-5.9 (m, 2H), 6.2 (d, 1H, J=15.1 Hz), 7.1-7.5 (m, 5H).

The fourth eluted compound was 5-phenylsulphenyl-1-(3-oxocyclopentyl)-1,3-pentadiene 7a (8% yield): oil., ^{1}H-NMR (200 MHz): δ 1.9-2.4 (m, 6H), 2.80-2.85 (m, 1H), 3.6 (d, 2H, J=7.0 Hz), 5.6 (dd, 1H, J=6.8 Hz, J=14.3 Hz), 5.7 (dt, 1H, J=7.0 Hz, J=14.0 Hz), 6.0 (dd, 1H, J=8.3 Hz, J=14.0 Hz), 6.1 (dd, 1H, J=8.3 Hz, J=14.3 Hz), 7.2-7.4 (m, 5H). I.R. 1740 cm^{-1} (C=O).

e) Reaction with 2-cyclohexenone: to a THF solution (20 ml) of 3a (2.8 mmol) was added a THF solution (10 ml) of 2-hexenone (3.4 mmol) at -78°C under N$_2$. After 5 min usual workup left an oil residue of three main compounds, which were separated by column chromatography using a 1:1 diethyl ether-petroleum ether mixture as eluting system.

The first eluted product was 1-phenylsulphenyl-3-(3-oxocyclohexyl)-1,4-pentadiene 5b [(E+Z), oil, 59% yield]. The ^{1}H-NMR (200 MHz) spectra were extracted from that of the isomeric mixture; for (Z)-5b: δ 1.8-2.5 (m, 9H), 3.11-3.23 (m, 1H), 4.98-5.14 (m, 2H), 5.55-5.7 (m, 2H), 6.3 (d, 1H, J=9.3 Hz), 7.1-7.4 (m, 5H). For (E)-5b: δ 1.8-2.5 (m, 9H), 2.68-2.8 (m, 1H), 5.0-5.1 (m, 2H), 5.5-5.7 (m, 2H), 6.15 (d, 1H, J=14.7 Hz), 7.1-7.4 (m, 5H).

The second eluted compound was 5-phenylsulphenyl-1-(3-oxocyclohexyl)-1,3-pentadiene 7b. Oil (18% yield). ^{1}H-NMR (CCl$_4$, 60 MHz): δ 1.5-2.6 (m, 9H), 3.6 (d, 2H, J=7.0 Hz), 5.4-6.4 (m, 4H), 7.2-7.5 (m, 5H).

f) Reaction with 3-methyl-2-cyclopentenone: to a stirred THF solution (20 ml) of 3a (2.8 mmol) was added a THF solution (10 ml) of 3-methyl-2-cyclopentenone (3.4 mmol) at -78°C, under N$_2$. After 20 min usual workup afforded an oil residue of three main compounds. They were separated by column chromatography (1:9 diethyl ether/petroleum ether) and are described in order of increasing retention time.

1-Phenylsulphenyl-3-(1-methyl-3-oxocyclopentyl)-1,4-pentadiene 8: 38% yield. (Z)-8: oil. ^{1}H-NMR (200 MHz): δ 1.07 (s, 3H), 1.9-2.4 (m, 6H), 3.27 (dd, 1H, J=8.5 Hz, J=9.6 Hz), 5.15-5.19 (m, 2H), 5.6-5.9 (m, 1H), 5.8 (dd, 1H, J=9.6 Hz, J=9.7 Hz), 6.37 (d, 1H, J=9.7 Hz), 7.1-7.4 (m, 5H). I.R 1740 cm^{-1} (C=O).

(E)-8. Oil. ^{1}H-NMR (200 MHz)· δ 1.0 (s, 3H), 1.8-2.4 (m, 6H), 2.8 (dd, 1H, J=8.0 Hz, J=8.1 Hz), 5.0-5.2 (m, 2H), 5.7-6.0 (m, 2H), 6.2 (d, 1H, J=15.0 Hz), 7.15-7.3 (m, 5H). I.R. 1740 cm^{-1} (C=O).

(E)-1-phenylsulphenyl-1-(1-hydroxy-3-methyl-2-cyclopentenyl)-2,4-pentadiene 9, oil (20% yield). ^{1}H-NMR (CCl$_4$, D$_2$O, 60 MHz): δ 1.75 (s, 3H), 1.8-2.3 (m, 4H), 3.7 (d, 1H, J=(8.0 Hz), 4.8-5.2 (m, 2H), 5.3-6.3 (m, 4H), 7.1-7.6 (m, 5H). I.R. 3650-3150 cm^{-1} (OH).

g) Reaction with chalcone: to a THF solution (20 ml) of 3a (2.8 mmol) was added a THF solution (10 ml) of chalcone (3.4 mmol) at -78°C, under N$_2$. After 30 min usual workup left a crude oil residue of three main compounds, which were separated by column chromatography using 1:9 diethyl ether/petroleum ether mixture as eluent.

The first eluted compound was 1,3-diphenyl-4-vinyl-6-phenylsulphenyl-5-hexen-1-one 10 [(E+Z), 33% yield]. The ^{1}H-NMR (200 MHz) spectra were extracted from that of the isomers mixture. For (Z)-10: δ 3.2-3.7 (m, 4H), 4.9-5.1 (m, 2H), 5.55-5.95 (m, 2H), 6.32 (d, 1H, J=9.7 Hz), 7.1-8.0 (m, 15H). For (E)-10: δ 3.2-3.7 (m, 4H), 4.9-5.1 (m, 2H), 5.55-5.95 (m, 2H), 6.17 (d, 1H, J=15.1 Hz), 7.1-8.0 (m, 15H).

The second eluted compound was 1,3-diphenyl-8-phenylsulphenyl-4,6-octadien-1-one 11. Oil (6% yield). ^{1}H-NMR (200 MHz): δ 3.4 (d, 2H, J=6.9 Hz), 3.54 (d, 2H, J=7.1 Hz), 4.15 (dt, 1H, J=6.9 Hz, J=6.8 Hz), 5.62 (dt, 1H, J=14.4 Hz, J=7.1 Hz), 5.82 (dd, 1H, J=14.5 Hz, J=6.8 Hz), 5.9-6.15 (m, 2H), 7.1-8.0 (m, 15H).

The third eluted compound was: 1,3-diphenyl-8-phenylsulphenyl-1,5,7-octatrien-3-ol 12, oil (19% yield). ^{1}H-NMR (200 MHz): δ 2.5 (s, 1H, exhange with D_2O), 2.86-2.97 (m, 2H), 5.5-5.9 (m, 1H), 6.2-6.4 (m, 2H), 6.5-6.9 (m, 3H), 7.2-7.6 (m, 15H). I.R. 3600-3200 cm^{-1} (OH).

Reactions of phenylsulphenylpentadienylzinc bromide 3b:

a) Reaction with 2-cyclopentenone: to a THF solution (5 ml) of 3b (0.6 mmol) was added a THF solution (5 ml) of 2-cyclopentenone (0.7 mmol) at -78°C, under N_2. After 4h TLC analysis showed only trace of 5a, 7a and 6b.

b) Reaction with chalcone: to a THF solution (20 ml) of 3b (1.7 mmol) was added a THF solution (10 ml) of chalcone (1.9 mmol) at -78°C under N_2. After 20 min usual workup afforded an oil residue of three compounds. They were separated by column chromatography using 15:85 diethyl ether-petroleum ether mixture as eluent. The first eluted compound was 1,3-diphenyl-4-phenylsulphenyl-5,7-octadien-1-one 13: oil (20% yield). ^{1}H-NMR (200 MHz): δ 3.3-3.65 (m, 2H), 3.7-3.85 (m, 1H), 3.9-4.0 (m, 1H), 4.9-5.1 (m, 2H), 5.6 (dd, 1H, J=15.1 Hz, J=9.3 Hz), 5.8 (dd, 1H, J=15.1 Hz, J=10.1 Hz), 6.1-6.35 (m, 1H), 7.2-8.0 (m, 15H).

The second eluted compound was 11: oil (10% yield). The third eluted compound was 1,3-diphenyl-6-phenylsulphenyl-4-vinyl-1,5-hexadien-3-ol 14: oil (10% yield). ^{1}H-NMR (200 MHz): δ 2.4 (s, 1H, which exhange with D_2O), 4.0-4.1 (m, 1H), 5.1-5.3 (m, 2H), 5.6-6.4 (m, 3H), 6.6-6.8 (m, 2H), 7.1-8.0 (m, 15H).

Reactions of phenylsulphinylpentadienyllithium 3c:

a) With MeI or BTMSPO: a 1.6 mmol sample of 3c in 10 ml of THF at -78°C under N_2 and stirring was added with MeI or BTMSPO (4.6 mmol) in 10 ml of THF and the reaction allowed to stirr for 6h and additional 3h at room temperature, then quenched with sat NH_4Cl; usual workup afforded 0.27 gr (90% yield) of (E)-phenylsulphinyl-2,4-pentadiene 2d: oil; ^{1}H-NMR (200 MHz) δ: 3.30-3.50 (m, 2H), 4.91-5.04 (m, 2H), 5.23-5.39 [m, 1H, when irradiated at 3.41 δ the multiplet was transformed in a doublet: 5.32 (d, J= 14.95 Hz)], 5.85-6.20 (m, 2H), 7.29-7.46 (m, 5H). I.R. 3060, 2920, 1040 cm^{-1}.

b) With cyclopentanone: to a solution of 1.6 mmol of 3c in 10 ml of THF at -78°C, under N_2 and stirring was added 0.16 ml (1.8 mmol) of cyclopentanone in 10 ml of THF. After 15 min the mixture was quenched with sat NH_4Cl and extracted with ether (3 x 30 ml), washed with water, dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product (0.32 gr) was chromatographed on column (silica gel, ether) to give 0.18 gr of (E,E)-5-phenylsulphinyl-1-(1-hydroxycyclopentyl)-1,3-pentadiene 17 (40% yield). ^{1}H-NMR (200 MHz), $CDCl_3/D_2O$ δ: 1.56-1.95 (m, 8H), 3.41-3.62 (m, 2H), 5.13-5.48 (m, 2H), 6.02-6.43 (m, 2H), 7.43-7.65 (m, 5H). I.R. 3450, 1040 cm^{-1}.

c) With 2,6-dichlorobenzaldehyde· a 1.6 mmol sample of 3c in 10 ml of THF at -78°C, under N_2 and stirring, was added with 0.31 gr (1.76 mmol) of 2.6-dichlorobenzaldehyde in 10 ml of THF. After 30 min the mixture was quenched with sat NH_4Cl and workedup as usual. The crude mixture (0.45 gr) was separated by column chromatography on silaca gel (ether) to give 0.15

gr (50% yield) of 2d and 0.24 gr (40% yield) of 6-phenylsulphinyl-1-(2,6-dichlorophenyl)-2,4-hexadien-1-ol 19: oil; ^{1}H-NMR (200 MHz) δ: 3.38-3.57 (m, 2H), 3.61-3.75 (m, 1H, OH), 5.30-5.46 [m, 1H, when irradiated at 3.47 δ the multiplet changed to a double doublet: 5.38 (dd, J=2.0 Hz, J=14.1 Hz)], 5.90-6.19 (m, 4H), 7.03-7.51 (m, 8H). I.R.: 3350, 1030 cm^{-1}.

d) with chalcone: the lithium derivative 3c (1.6 mmol) in 10 ml of THF cooled at -78°C, under N$_2$ and stirring was added with 0.37 gr (1.76 mmol) of chalcone in 10 ml of THF. The reaction was over in 2.0 h. Quenching and usual workup gave 0.71 gr of crude material that was column chromatographed (ether) to yield three fractions. The first eluted compound was 1,3-diphenyl-4-vinyl-6-phenylsulphinyl-5-hexen-1-one 22 (0.07 gr, 11% yield), oil, ^{1}H-NMR (200 MHz): 2.68 (dt, 1H, J=4.6 Hz, J=9.5 Hz), when irradiated at 3.26 δ this dt turned to a doublet J=9.4 Hz), 3.20-3.33 (m, 2H), 4.94-5.27 (m, 3H), 6.09- 6.38 (m, 2H), 7.18-7.65 (m, 14H), 8.01-8.09 (m, 2H). I.R. 3070, 2940, 1670, 1020 cm^{-1}.

The second eluted compound was chalcone (0.05 gr) and the third eluted product was 1,3-diphenyl-8-phenylsulphinyl-4,6-octadien-1-one 20 (0.4 gr, 62% yield). Oil, ^{1}H-NMR (200 MHz) δ: 3.37 (d, 2H, J=7.8 Hz), 3.43- 3.51 (m, 2H), 4.09-4.20 (m, 1H), 5.26-5.41 (m, 1H), 5.79-6.10 (m, 3H), 7.14-7.56 (m, 13H), 7.87-7.91 (m, 2H). I.R.: 3020, 2940, 1680, 1040 cm^{-1}.

Reactions of phenylsulphinylpentadienylcopper 3d: These reactions were performed in the same conditions of the corresponding lithiated derivative 3c starting from 3d and a) Cyclopentanone to give, after 1 h, 0.25 gr (55% yield) of product 17.

b) 2,6-dichlorobenzaldehyde to give after 30 min 0.28 gr (47% yield) of product 19.

Reactions of phenylsulphinylpentadienylzinc bromide 3e: These reactions were performed in the same conditions of the corresponding lithiated derivative 3c starting from 3e and a) cyclopentanone to give after 30 min and column chromatography (EE/EP=8/2) 0.05 gr (11% yield) of product 17 and 0.15 gr (50% yield) of starting material recovered as the isomer 2d.

b) 2,6-dichlorobenzaldehyde to give after 2 h 0.12 gr (40% yield) of starting material recovered as the isomer 2d and 0.15 gr (25% yield) of compound 19.

Reaction of phenylsulphinylpentadienylmagnesium bromide 3f with 2,6-dichlorobenzaldehyde: starting from 3f and 2,6-dichlorobenzaldehyde in the above reported conditions, we obtained after 20 min 0.06 (20% yield) of product 2d and 0.26 gr (43% yield) of product 19.

Reactions of phenylsulphonylpentadienyllithium 3g: a) with methyliodide (1 equiv). To a solution of 3g (1.4 mmol) in 10 ml of THF at -78°C, under N$_2$ and stirring were added 0.09 ml (1.54 mmol) of MeI in 10 ml of THF. After 30 min the reaction was quenched, extracted, washed, dried and evaporated in the usual manner to give 0.4 gr of a residue that was chromatographed (silica gel, ethyl acetate/petroleum ether=1/4) to give three fractions. The first eluted compound was (E)-5-methyl-5-phenylsulphonyl-1,3-hexadiene 2b (0.032 gr, 10% yield): oil, ^{1}H-NMR (200 MHz): δ 1.43 (s, 6H), 5.07-5.18 (m, 2H), 5.75 (d, 1H, J= 15.5 Hz), 5.94 (dd, 1H, J=9.85 Hz, J=15.5 Hz), 6.16-6.38 (m, 1H), 7.44-7.84 (m, 5H). The second eluted product was 5-phenylsulphonyl-1,3-hexadiene 2a (0.13 gr, 41% yield): oil, ^{1}H-NMR (60 MHz): δ 1.52 (d, 3H, J=7.0 Hz), 3.6-4.0 (m, 1H), 5.0-6.7 (m, 5H), 7.6-8.2 (m, 5H). The third product was (E)-5-phenylsulphonyl-1,3-pentadiene 2c (0.11 gr, 32% yield): oil, ^{1}H-NMR (200 MHz): δ 3.81 (d, 2H, J=7.62 Hz), 5.07-5.18 (m, 2H), 5.49-5.64 [m, 1H, when irradiated at 3.81 δ the multiplet became a double doublet: 5.58 (dd, J=0.68 Hz, J=15.08 Hz)], 5.95-6.37 (m, 2H), 7.48-7.67 (m,3H), 7.81-7.87 (m, 2H).

b) With methyliodide (excess): the reaction was effected in the same conditions as above. Treatment of 3g (1.4 mmol) with MeI (0.19 ml, 3.1 mmol). led to a mixture of 2b (0.18 gr, 56% yield) and 2a (0.06 gr, 20% yield).

c) With cyclopentanone or 2,6-dichlorobenzaldehyde: a 1.4 mmol sample of 3g in 10 ml of THF at -78°C, under N$_2$ and stirring, was added with cyclopentanone or 2,6-dichlorobenzaldehyde (1.54 mmol) in 10 ml of THF and the reaction allowed to stirr for 5 h and additional 2 h at room temperature, then quenched with sat NH_4Cl. Usual workup afforded to recover 0.14 gr (47% yield) or 0.23 gr (77% yield) of sulphone 2c.

d) with chalcone: lithium derivative 3g (2.4 mmol) in 10 ml of THF cooled at -78°C under N_2 and stirring was added with 0.55 gr (2.64 mmol) of chalcone in 10 ml of THF. The reaction was over in 1 h. Quenching with NH_4Cl and usual workup gave 0.7 gr of crude material that was purified by column chromatography (silica gel, EE/EP=4/6) to give 0.11 gr of chalcone and 0.53 gr (55% yield) of (E)-1,3-diphenyl-4-phenylsulphonyl-5,7-hexadien-1-one 23: oil. ^{1}H-NMR (200 MHz) δ: 3.58 (dd, 1H, J=11.17 Hz, J=17.09 Hz, when the signal at 4.43 δ was irradiated the dd became a doublet J=17.09 Hz), 3.73 (dd, 1H, J=3.12 Hz, J=10.07 Hz, when the signal at 4.43 δ was irradiated the dd became a doublet J=10.07 Hz), 3.96 (dd, 1H, J=3.28 Hz, J=17.09 Hz, when the signal at 4.43 δ was irradiated the dd transformed into a doublet J=17.09 Hz), 4.43 (dt, 1H, J=3.17 Hz, J=11.03 Hz), 4.99-5.14 [m, 2H, when the signal at 6.35 δ was irradiated the multiplet changed to a doublet: 5.07 (d, J=18.31 Hz)], 5.64 (dd, 1H, J=10.26 Hz, J=15.14 Hz, when the signal at 6.35 δ was irradiated the dd became a doublet J=15.14 Hz), 5.89 (dd, 1H, J=10.01 Hz, J=15.13 Hz), 6.35 (dt, 1H, J=10.26 Hz, J=16.84 Hz), 7.11-7.94 (m, 15H). I.R. 3060, 2910, 1680, 1380, 1150 cm^{-1}. Attempted crystallization of product 23 promoted partial rearrangement to 1,3-diphenyl-8-phenylsulphonyl-4,6-octadien-1-one 24. Separation by column chromatography (silica gel, CH_2Cl_2) afforded 0.31 gr (60%) of 23 and 0.2 gr (40%) of 24: thick oil, ^{1}H-NMR (200 MHz): δ 3.38 (d, 2H, J=7.08 Hz), 3.76 (d,2H, J=7.32 Hz), 4.10-4.20 (m, 1H), 5.37-5.51 (m, 1H), 5.79-6.02 (m, 3H), 7.14-7.94 (m, 15H). I.R.: 3030, 2910, 1675, 1310, 1150 cm^{-1}.

Acknowledgements: We tank Ministero Università e Ricerca (MURST) and Italian CNR (Roma) for financial support.

References

1) S. Florio, L. Ronzini and R. Sgarra, Tetrahedron Lett., 31, 2327(1990)
2) Bistrimethylsilylperoxide has been recently reported by us to act as a methylating agent of stabilized carbanions: S. Florio and L. Troisi, Tetrahedron Lett., 30, 3721(1989); E. Epifani,S. Florio and L. Troisi, Tetrahedron, 46, 4031 (1990).
3) This hypothesis is supported by the fact that similar pentadienyl metals have been reported to adopt the abovementioned W structure: G. Wolf, E.U. Würthwein, Tetrahedron Lett., 29, 3647 (1988). However, work has been planned in order to get, by NMR and X-Ray analysis, more insights into the structure of the sulphur stabilized pentadienyl carbanions.
4) Double [3,2] sigmatropic rearrangement of pentadienyl sulphoxide has been already reported: E.J. Corey and D.J. Hoover, Tetrahedron Lett., 23, 3465 (1982).
5) J.M. Fang, W.C. Chou, G.H. Lee, S.M. Peng, J.Org.Chem., 55, 5515(1990).
6) As in the case of sulphinyl pentadienyllithium 3c, also sulphonyl pentadienyllithium 3g likely adopts the W shape.
7) A more difficult (toluene, reflux) double [3,2] sigmatropic rearrangment has been reported for pentadienyl dithiocarbamate: T. Hayashi, I. Hori and T. Oishi, J. Am. Chem. Soc., 105, 2909 (1983).
8) During the preparation of the manuscript of the present paper we knew about an unprecedented sulphone [1,5] sigmatropic rearrangment:K.Ogura, N. Yahata, F. Fujimori, M. Fujita, Tetrahedron Lett., 31, 4621 (1990).
9) V. Fiandanese, G. Marchese, F. Naso and L. Ronzini, J. Chem. Soc. Perkin Trans I, 1115 (1985).
10) All new compounds showed consistent microanalytical data.