Synthesis of Allyl and Dienyl Sulphones *via* Iodosulphonylation of Conjugated Dienes

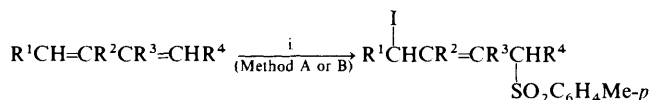José Barluenga,* José M. Martínez-Gallo, Carmen Nájera, Francisco J. Fañanás, and Miguel Yus
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The iodosulphonylation of conjugated dienes with sodium or mercury(II) toluene-*p*-sulphinate and iodine yields δ-iodoalkenyl sulphones stereoselectively. These compounds undergo stereospecific dehydrohalogenation to afford dienyl sulphones and nucleophilic substitution of the iodine atom to give δ-functionalized alkenyl sulphones.
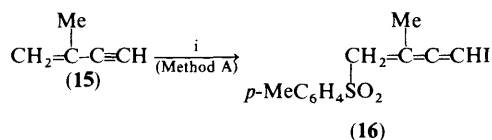
Sulphones are important compounds in organic synthesis and allyl sulphones in particular have been widely used in reactions for carbon-carbon bond formation.[1] These allylic derivatives are mainly prepared by displacement reactions of allylic halides or acetates with sodium arenesulphinates and by rearrangement of allylic sulphenates. On the other hand, the 1,4-addition of sulphonyl halides to conjugated dienes allows the synthesis of δ-halogenated alkenyl sulphones. In the case of sulphonyl chlorides the copper catalyzed 1,4-addition to conjugated dienes has been widely studied,[2-4] however, the same reaction with sulphonyl iodides has, in the case of buta-1,3-diene only been described.[5] In connection with our studies on the halogenofunctionalization of unsaturated systems[6-8] we report the application of the iodosulphonylation reaction of conjugated dienes to the synthesis of allyl and dienyl sulphones.

Results and Discussion

Iodosulphonylation of Conjugated Dienes.—Conjugated dienes (1)—(6) undergo exclusive 1,4-addition of the *in situ* generated tosyl iodide to give δ-iodoalkenyl sulphones (7)—(14) (Scheme 1). Iodosulphonylation has been carried out with sodium (method A) or mercury(II) (method B) toluene-*p*-sulphinate and iodine in dichloromethane at 0 °C, the isolation

Table 1. Iodosulphonylation of dienes

Diene	Method[a]	Product	Reaction time	Yield (%)[b]
(1)	A	(7)	6 h	99 (93)
(1)	B	(7)	2 h	90
(2)	A	(8)	1 d	99 (95)
(2)	B	(8) + (9)[c]	1 h	86
E-(3)	A	(10) + (11)[d]	1 d	91 (82)
E-(3)	B	(10) + (11)[d]	1 h	75
(4)	A	(12)	1 d	83 (77)
(4)	B	(12)	1 h	89
(5)	A	(13)[e]	1 d	98 (94)
(5)	B	(13)[e]	2 h	99
(6)	A	(14)	1 d	94 (88)

[a] A: sodium toluene-*p*-sulphinate and iodine, B: mercury(II) toluene-*p*-sulphinate and iodine. [b] Yield of isolated crude products. Yield after purification in parentheses (see Experimental section). Based on iodine. [c] (8):(9) 5:1 Mixture of regioisomers by n.m.r. Compound (8) was obtained as a 1:4 mixture of *Z*:*E* isomers. [d] (10):(11) 9:1 Mixture of regioisomers by n.m.r. Mixture of *cis*:*trans* stereoisomers (*ca.* 1:1).

of tosyl iodide[5] being avoided (Table 1). The reaction time is clearly shorter by method B than by method A, but better results were generally obtained by the latter. With symmetrical acyclic dienes such as buta-1,3-diene (1) and 2,3-dimethylbuta-1,3-diene (4), the corresponding δ-iodobut-2-enyl sulphones (7) and (12) were obtained respectively. In the case of asymmetrical acyclic dienes *e.g.*, isoprene (2) or (*E*)-piperylene (3) mixtures of regioisomeric products (8) and (9) or (10) and (11) respectively were isolated when method B was used. However, the iodosulphonylation of isoprene (2) with sodium toluene-*p*-sulphinate and iodine afforded only compound (8). The observed regiochemistry in the iodosulphonylation of conjugated systems using method B is in contrast with our previous results[7] where mainly 1,2-addition products were obtained when buta-1,3-diene was treated with iodine and mercury(II) acetate, chloride, or nitrate. Competition with a possible sulphonylmercuriation process[9] in method B is rejected because in that case 1,2-addition was only observed.

The *E* configuration of the acyclic δ-iodo sulphones (7)—(12) was established according to described physical data for compound (7)[5] and [1]H n.m.r. data for compounds (8) and (10). Only in the case of isoprene did iodosulphonylation by method B lead to a mixture of *Z*/*E* stereoisomers for compound (8).

Cyclic conjugated dienes also gave the 1,4-addition products (13) and (14). Cyclohexa-1,3-diene (5) yielded 1-iodo-4-tosyl-cyclohex-2-ene (13) as a mixture (*ca.* 1:1) of *cis* and *trans* isomers, whereas compound (14) from cyclo-octa-1,3-diene (6) was isolated as a single stereoisomer, presumably, *trans* as discussed below. These results contrast with the chlorosulphonyl-

$$R^1CH=CR^2CR^3=CHR^4 \xrightarrow[\text{(Method A or B)}]{i} R^1\overset{I}{C}HCR^2=CR^3CHR^4$$
$$SO_2C_6H_4Me\text{-}p$$

(1); $R^1 = R^2 = R^3 = R^4 = H$
(2); $R^1 = R^2 = R^4 = H$, $R^3 = Me$
(*E*)-(3); $R^1 = Me$, $R^2 = R^3 = R^4 = H$
(4); $R^1 = R^4 = H$, $R^2 = R^3 = Me$
(5); R^1-$R^4 = (CH_2)_2$, $R^2 = R^3 = H$
(6); R^1-$R^4 = (CH_2)_4$, $R^2 = R^3 = H$

(7); $R^1 = R^2 = R^3 = R^4 = H$
(8); $R^1 = R^2 = R^4 = H$, $R^3 = Me$
(9); $R^1 = R^3 = R^4 = H$, $R^2 = Me$
(10); $R^1 = Me$, $R^2 = R^3 = R^4 = H$
(11); $R^1 = R^2 = R^3 = H$, $R^4 = Me$
(12); $R^1 = R^4 = H$, $R^2 = R^3 = Me$
(13); $R^1 = R^4 = (CH_2)_2$, $R^2 = R^3 = H$
(14); $R^1 = R^4 = (CH_2)_4$, $R^2 = R^3 = H$

$$\underset{(15)}{CH_2=\overset{Me}{\underset{|}{C}}-C\equiv CH} \xrightarrow[\text{(Method A)}]{i} \underset{(16)}{CH_2=\overset{Me}{\underset{|}{C}}-C=C=CHI}$$
$$p\text{-MeC}_6H_4SO_2$$

Scheme 1. *Reagents:* i, $p\text{-MeC}_6H_4SO_2M\text{-}I_2$ (M = Na: Method A; M = 1/2Hg: Method B)

Table 2. Dehydrohalogenation of δ-iodoalkenyl sulphones

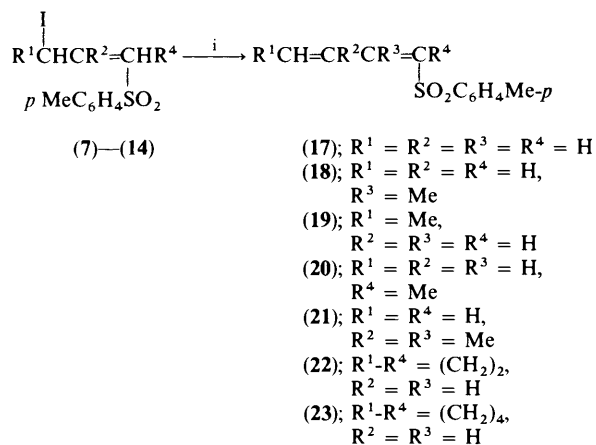| Iodo sulphone	Dienyl sulphone	Yield (%)[a]
(7)	(17)	70 (64)
(8)	(18)[b]	86
(10) + (11)	(19) + (20)[c]	95 (89)[d]
(12)	(21)	81 (78)
(13)	(22)	96 (91)
(14)	(23)	50

[a] Isolated crude yields. Yield after purification in parentheses (see Experimental section). Based on crude iodo sulphones. [b] 1:1 Mixture of Z:E isomers (ca. 1:1) from [1]H n.m.r. (lit.[4]). [c] 19:1 Mixture of regioisomers starting from a 9:1 mixture of (10) and (11) (deduced from [13]C n.m.r.). [d] Referred to the starting (E)-piperylene (3).

ation of both dienes[3] where only the opposite stereochemistry results were obtained.

The iodosulphonylation of 3-methylbut-3-en-1-yne (15) by method A afforded exclusively the allenic derivative (16) in 70% yield corresponding also to a 1,4-addition reaction (Scheme 1). However, method B led to an intractable mixture of products.

The chemical behaviour of the prepared δ-iodoalkenyl sulphones (7)—(14) in elimination and nucleophilic substitution reactions was also tested.

Reactivity of δ-Iodoalkenyl Sulphones.—The reaction of iodo sulphones (7)—(14) with triethylamine (TEA) in a solution of tetrahydrofuran–water (1:1) at room temperature gave α, β, γ, δ-unsaturated sulphones (17)—(23) (Scheme 2 and Table 2).

$$
\begin{array}{c}
\overset{\displaystyle I}{\underset{\displaystyle p\text{-MeC}_6\text{H}_4\text{SO}_2}{R^1\text{CHCR}^2\text{=CHR}^4}} \xrightarrow{\ i\ } R^1\text{CH=CR}^2\text{CR}^3\text{=CR}^4 \\
\underset{\displaystyle \text{SO}_2\text{C}_6\text{H}_4\text{Me-}p}{}
\end{array}
$$

(7)—(14)

(17); R[1] = R[2] = R[3] = R[4] = H
(18); R[1] = R[2] = R[4] = H,
      R[3] = Me
(19); R[1] = Me,
      R[2] = R[3] = R[4] = H
(20); R[1] = R[2] = R[3] = H,
      R[4] = Me
(21); R[1] = R[4] = H,
      R[2] = R[3] = Me
(22); R[1]-R[4] = (CH₂)₂,
      R[2] = R[3] = H
(23); R[1]-R[4] = (CH₂)₄,
      R[2] = R[3] = H

Scheme 2. *Reagent:* i, (C₂H₅)₃N

Better yields were observed under these conditions than in benzene as was described for the dehydrohalogenation of the corresponding chlorosulphones.[3,4] Elimination took place almost instantaneously and with good yields; only compound (23), derived from cyclo-octa-1,3-diene, was obtained in lower yield after *ca.* 2 days. This fact supports a possible *trans* stereochemistry for the starting iodo sulphone (14) as it also occurs in the dehydrohalogenation of *trans*-1-iodo-2-(aryl-sulphonyl)cyclohexanes.[10]

The stereochemistry of the resulting dienyl sulphone (17) derived from buta-1,3-diene (1) was E and E,E for compound (19) arising from the iodo sulphone (10) derivative of (E)-piperylene (3) (deduced from [1]H n.m.r. data which are in agreement with those of the described phenyl derivatives[11]). The E stereochemistry for the dienyl sulphone (21) arising from 2,3-dimethylbuta-1,3-diene (4) was deduced from the chemical
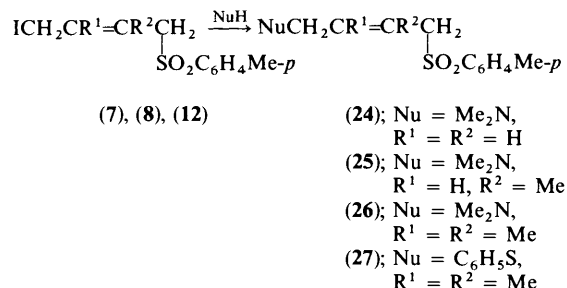
Table 3. Nucleophilic substitution of δ-iodoalkenyl sulphones

Iodo sulphone	Nucleophile	Product	Yield (%)[a]
(7)	Me₂NH	(24)	90
(8)	Me₂NH	(25)	90
(14)	Me₂NH	(26)	90 (83)
(14)	C₆H₅SH	(27)	97 (75)

[a] Isolated crude yields. Yield after purification in parentheses (see Experimental section). Based on crude iodo sulphones.

shift of the methyl group in the beta position to the sulphone function which appears at 2.2 p.p.m. in the [1]H n.m.r., as has been deduced for the dienyl sulphones derived from isoprene.[4] Only the described dienyl sulphone of isoprene (18)[4] resulting from the iodo sulphone (8) [corresponding to the iodosulphonylation (method A) of isoprene (2)] was obtained as a Z/E mixture (ca. 1:1), as in the case of the chloro sulphones.[4] The elimination reaction of hydrogen iodide from iodo sulphones (7)—(14) was therefore stereospecific except for compound (8). These dienic systems have already been used in the synthesis of linear polyenes[12] and terpenoids[13] by conjugated addition of carbanionic compounds.

When iodo sulphones (7), (8), and (12) were allowed to react with dimethylamine or thiophenol, compounds (24)—(27), resulting from the nucleophilic displacement of the iodine atom, were obtained (Scheme 3 and Table 3).

$$
\begin{array}{c}
\underset{\displaystyle \text{SO}_2\text{C}_6\text{H}_4\text{Me-}p}{\text{ICH}_2\text{CR}^1\text{=CR}^2\text{CH}_2} \xrightarrow{\ \text{NuH}\ } \underset{\displaystyle \text{SO}_2\text{C}_6\text{H}_4\text{Me-}p}{\text{NuCH}_2\text{CR}^1\text{=CR}^2\text{CH}_2}
\end{array}
$$

(7), (8), (12)

(24); Nu = Me₂N,
      R[1] = R[2] = H
(25); Nu = Me₂N,
      R[1] = H, R[2] = Me
(26); Nu = Me₂N,
      R[1] = R[2] = Me
(27); Nu = C₆H₅S,
      R[1] = R[2] = Me

Scheme 3.

The substitution reaction took place instantaneously on addition of the nucleophile to a solution of the freshly prepared iodo sulphone in dichloromethane at 0 °C. No competition with the corresponding elimination reaction was observed when the iodine atom was attached to a primary carbon. However, when the iodo sulphone (10) derived from piperylene (3) was treated with dimethylamine only the corresponding dienyl sulphone (19) was obtained.

Attempts to achieve substitution with alcohols or acetate failed, but with sodium methoxide compound (12) afforded the sulphone (28) in 68% yield resulting from an isomerization of the previously formed dienyl sulphone (21) (Scheme 4).

The stereochemistry of the δ-functionalized allyl sulphones (24)—(27) appears to be E according to the [1]H n.m.r. data for the vinylic protons of compound (25), derived from isoprene, which appear at 5.25 p.p.m.* In the Z isomers of δ-chloro[4] or δ-iodo derivatives however, the signals appear at 5.8—5.9 p.p.m. No appreciable changes in [1]H- and ^{13}C-n.m.r. spectra were observed for any compounds. Moreover the i.r. spectrum of compound (24) derived from buta-1,3-diene shows the corresponding band for *trans* 1,2-disubstituted alkenes. Consequently

* This value has been also observed in the corresponding (E)-hydroxy sulphone[14] at 5.38 p.p.m. for the (E)-chloro sulphone[4] and 5.40 p.p.m. for the (E)-iodo derivative (see Experimental section).
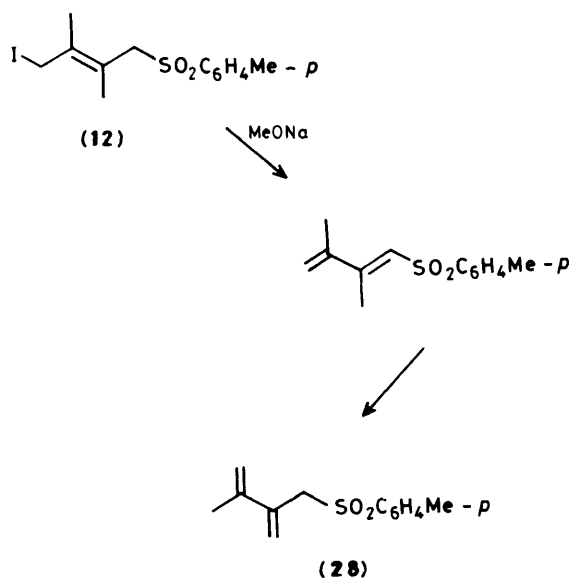
Scheme 4.

the nucleophilic displacement of δ-iodo sulphones obtained by iodosulphonylation of conjugated dienes is also stereospecific with retention of the configuration of the double bond. The synthetic interest of this type of δ-functionalised allyl sulphone lies in their use as d^4- or a^4-reagents[14,15] (according to Seebach's nomenclature[16]) mainly in reactions involving carbon-carbon bond formation. Possible applications of δ-functionalized allyl sulphones in organic synthesis are still in progress.

Experimental

The experimental techniques and spectroscopic instrumentation employed in the course of this work were as described in ref. 8.

Iodosulphonylation Reaction.—The following procedures are typical: *Method A.* Iodine (0.76 g, 3 mmol) at 0 °C was added to a suspension of diene* or 3-methylbut-3-en-1-yne (3 mmol) and sodium toluene-*p*-sulphinate (0.54 g, 3 mmol) in dichloromethane (10 ml). The reaction mixture was stirred for *ca.* 1 day at room temperature and then diluted with water. The organic layer was washed with aqueous sodium thiosulphate (0.1M), dried (Na$_2$SO$_4$), and evaporated under reduced pressure (15 torr) to give pure (^{13}C n.m.r.) products (**7**)—(**14**) and (**16**). Compounds (**7**) and (**8**) were crystallized in hexane at −20 °C since they decompose on warming. Compounds (**12**)—(**14**) and (**16**) were further purified by recrystallization, and compounds (**10**) and (**11**) by column chromatography on silica gel.

Method B. Iodine (0.76 g, 3 mmol) was added to a suspension of diene* (3 mmol) and mercury(II) toluene-*p*-sulphinate[7] in dichloromethane (20 ml) at 0 °C. The reaction mixture was stirred at 0 °C until decolouration of iodine was achieved and then the mercury(II) iodide was filtered off. The filtrate was washed with aqueous sodium thiosulphate (0.1M) and saturated aqueous potassium iodide, dried, and evaporated as in method A, to give compounds (**7**)—(**13**). (*E*)-1-Iodo-4-tosylbut-2-ene (**7**) m.p. 67—69 °C (lit.,[5] 68—69 °C), ν$_{max.}$(neat) 3 030, 1 650, 1 300, 970 (HC=CH), 1 320, and 1 150 (SO$_2$) cm^{-1}; δ$_H$(CCl$_4$) 2.35 (3 H, s, Me), 3.55, 3.7 (4 H, 2 × d, *J* 6 Hz, 2 × CH$_2$), 5.6 (2

H, m, 2 × C*H*CH$_2$), 7.2, and 7.6 (4 H, 2 d, *J* 8 Hz, ArH); δ$_C$(CCl$_4$) 4.4 (CI), 21.6 (Me), 58.85 (CH$_2$S), 120.4, 136.7 (*C*HCH$_2$), 128.3, 129.8, 135.65, and 144.4 (ArC) p.p.m.; *m/z* 208 (*M*$^+$ − HI, 3%), 139 (46), 127 (2), 92 (49), 91 (100), 89 (53), 65 (42), 54 (34), 53 (29), 32 (24), and 28 (60).

(*E*)-*1-Iodo-3-methyl-4-tosylbut-2-ene* (**8**) (Found: C, 40.5; H, 4.0. C$_{12}$H$_{15}$IO$_2$S requires C, 41.15; H, 4.30%) m.p. 63—64 °C, ν$_{max.}$(Nujol) 1 300 and 1 130 (SO$_2$) cm^{-1}; δ$_H$(CDCl$_3$) 1.7 (3 H, s, *Me*CCH$_2$), 2.4 (3 H, s, *Me*Ar), 3.7 (2 H, s, CH$_2$S), 3.85 (2 H, m, CH$_2$I), 5.4 (1 H, t, *J* 9 Hz, C*H*CH$_2$), 7.3, and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); δ$_C$(CCl$_4$) 1.4 (CI), 16.7 (*Me*CCH$_2$), 21.8 (*Me*Ar), 65.5 (CH$_2$S), 128.5, 130.8, 135.8, 144.6 (ArC), 129.5, and 131.4 (CH=C) p.p.m.; *m/z* 223 (*M*$^+$ − I, 46%), 195 (20), 159 (21), 155 (50), 127 (4), 91 (100), 68 (34), 67 (35), and 65 (31). (*E*)-1-Iodo-2-methyl-4-tosylbut-2-ene (**9**) was identified in the mixture with product (**8**) when method B was used (see text and Table 1); δ$_H$(CDCl$_3$) 1.5 (s, *Me*CCH$_2$I).†

(*E*)-*4-Iodo-1-tosylpent-2-ene* (**10**) and (*E*)-*1-iodo-4-tosylpent-2-ene*‡ (**11**). *R*$_F$ 0.4 and 0.5 [hexane–ether (1:2)] respectively; ν$_{max.}$(neat) 3 020, 1 640, 960 (HC=CH), 1 310, and 1 140 (SO$_2$) cm^{-1}; δ$_H$ for compound (**10**) (CDCl$_3$) 1.5 (3 H, d, *J* 7 Hz, *Me*CH), 2.45 (3 H, s, *Me*Ar), 3.7 (2 H, d, *J* 7 Hz, CH$_2$S), 4.75 (1 H, quint., *J* 7 Hz, CHI), 5.5 (1 H, dt, *J* 15 and 7 Hz, C*H*CH$_2$S), 5.8 (1 H, dd, *J* 15 and 8 Hz, C*H*CHI), 7.35, and 7.7 (4 H, 2 d, *J* 8 Hz, ArH); δ$_C$ for compound (**10**) (CDCl$_3$) 20.1 (*Me*Ar), 22.0 (CHI), 25.6 (*Me*CH), 57.1 (CH$_2$), 114.3, 142.3 (2 × CH=), 126.6, 128.2, 153.3 and 142.8 (ArC) p.p.m.; *m/z* for compound (**10**) 223 (*M*$^+$ − I, 3%), 157 (22), 155 (21), 139 (42), 113 (100), 91 (72), 85 (20), 67 (21), 65 (43), 43 (73), and 39 (20). Compound (**11**) was identified in the mixture with product (**10**) by method A or B (see Table 1): δ$_H$(CDCl$_3$) 1.4 (d, *Me*CHS); δ$_C$(CDCl$_3$) 2.7 (CH$_2$I), 11.5 (*Me*CHS), and 60.7 (CHS) p.p.m.; *m/z* after tandem g.c.–m.s. 223 (*M*$^+$ − I, 8%).

(*E*)-*1-Iodo-2,3-dimethyl-4-tosylbut-2-ene* (**12**) (Found: C, 42.4; H, 4.5. C$_{13}$H$_{17}$IO$_2$S requires C, 42.87; H, 4.70%) m.p. 118—119 °C (from hexane–CHCl$_3$), ν$_{max.}$(Nujol) 1 305 and 1 140 (SO$_2$) cm^{-1}; δ$_H$(CDCl$_3$) 1.45, 1.75 (6 H, 2 s, 2 × *Me*CCH$_2$), 2.5 (3 H, s, *Me*Ar), 3.8, 3.85 (4 H, 2 × s, 2 × CH$_2$), 7.3, and 7.7 (4 H, 2 d, *J* 8 Hz, ArH); δ$_C$(CDCl$_3$) 9.3 (CI), 17.2, 19.1 (2 × *Me*CCH$_2$), 21.4 (*Me*Ar), 62.1 (CH$_2$S), 122.05 (*C*CH$_2$I), 128.0, 129.7, 135.7, 135.8, and 144.5 (ArC and *C*CH$_2$S) p.p.m.; *m/z* 237 (*M*$^+$ − I, 39%), 209 (20), 173 (23), 155 (34), 139 (35), 131 (20), 127 (3), 91 (100), 82 (69), 81 (20), 67 (71), 66 (55), 37 (28), and 39 (40).

cis- and *trans*-4-Iodo-4-tosylcyclohex-2-ene (**13**) m.p. 107—109 °C (of a *ca.* 1:1 mixture, dec., from hexane–CHCl$_3$); *R*$_F$ 0.27, 0.16 [hexane–ether (2:1)]; ν$_{max.}$(neat) 3 030 1 400, 710 (CH=CH), 1 305, and 1 140 (SO$_2$) cm^{-1}; δ$_H$(CDCl$_3$) 1.5—2.6 (7 H, 2 × m with s at 2.4, 2 × CH$_2$ and Me), 3.95 (1 H, m, CHS), 5.0 (1 H, m, CHI), 5.5—6.6 (2 H, m, CH=CH), 7.45, and 7.85 (4 H, 2 d, *J* 8 Hz, ArH); δ$_C$(CDCl$_3$) 20.1, 20.7 (*C*H$_2$CI), 22.1 (Me), 25.2, 25.4 (CHI), 29.8, 31.6 (*C*H$_2$CHS), 59.5, 62.0 (CHS), 119.2, 120.0 (*C*HCHI), 129.0, 129.2, 129.25, 130.1, 133.5, 145.1 (ArC), 137.2, and 138.3 (*C*HCHS) p.p.m.

1-Iodo-4-tosylcyclo-oct-2-ene (**14**) (Found: C, 45.7; H, 5.1. C$_{15}$H$_{19}$IO$_2$S requires C, 46.16; H, 4.91%) m.p. 118—120 °C (decomp., from hexane–CH$_2$Cl$_2$), ν$_{max.}$(Nujol) 3 040, 1 600, 840 (Ar), 1 300, and 1 140 (SO$_2$) cm^{-1}; δ$_H$(CDCl$_3$) 1.3—2.6 (11 H, 2 × m with s at 2.5, 4 × CH$_2$ and Me), 4.0 (1 H, m, CHS), 4.75 (1 H, m, CHI), 5.5 (1 H, dd, *J* 12 and 10 Hz, C*H*CHS), 6.2 (1 H, dd, *J* 11 and 9 Hz, C*H*CHI), 7.35, and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); δ$_C$(CDCl$_3$) 21.0 (Me), 23.1 (CI and CH$_2$), 27.1, 28.6, 41.6 (3 × CH$_2$), 62.3 (CHS), 120.9, 138.15 (CH=CH), 128.1, 129.2, 134.1, and 144.1 (ArC) p.p.m.

1-Iodo-3-methyl-4-tosylbuta-1,2-diene (**16**) (Found: C, 41.8; H, 3.5. C$_{12}$H$_{13}$IO$_2$S requires C, 41.39; H, 3.76%) m.p. 70—72 °C

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* In the case of buta-1,3-diene the gas was bubbled through the suspension of the toluene-*p*-sulphinate and iodine during 6 or 2 h (see Table 1).

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† The same data as in the case of chlorosulphonyl derivative.[4]
‡ Stereochemistry tentatively assigned.

(from hexane–CHCl₃), $v_{max.}$(Nujol) 1 940, 870 (C=C=CH), 1 300, and 1 130 (SO₂) cm⁻¹; δ_H(CCl₄) 2.0 (3 H, s, MeCCH₂), 2.5 (3 H, s, MeAr), 3.7 (2 H, s, CH₂S), 5.4 (1 H, s, CHI), 7.4, and 7.8 (4 H, 2 d, J 8 Hz, ArH); δ_C(CCl₄) 19.0 (MeCCH₂), 22.4 (MeAr), 37.0 (CHI), 60.4 (CH₂S), 128.1, (CCH₂), 128.85, 130.6, 136.3, 145.2 (ArC), and 192.0 (C=CH) p.p.m.

Dehydrohalogenation of δ-Iodoalkenyl Sulphones. General Procedure.—To a solution of δ-iodoalkenyl sulphone (7)—(14) (2 mmol) in THF (5 ml) and water (5 ml) was added triethylamine (1.1 ml, 8 mmol). The solution was stirred at room temperature for 1 h [2 days for compound (14)] and extracted with dichloromethane (2 × 20 ml). The organic layer was washed with water, dried, and evaporated to afford crude dienyl sulphones (17)—(23). These compounds were purified by column chromatography on silica gel or by recrystallization.

(E)-1-*Tosylbuta*-1,3-*diene* (17), oil, R_F 0.35 [hexane–ether (1:1)] (lit.,[11] neither physical nor spectroscopic data reported); $v_{max.}$(neat) 3 040, 1 635, 1 300, 1 000, 960, 930 (CH=CH), 1 315, and 1 140 (SO₂) cm⁻¹; δ_H(CCl₄) 2.35 (3 H, s, Me), 5.45 (1 H, dd, J 9 and 0.5 Hz, 4-H), 5.6 (1 H, dd, J 15 and 0.5 Hz, 4-H), 6.15—6.55 (2 H, m, with d at 6.3, J 15 Hz, 1-H and 3-H), 7.1 (1 H, dd, J 15 and 10 Hz, 2-H), 7.2 and 7.6 (4 H, 2 × d, J 8 Hz, ArH); δ_C(CCl₄) 21.65 (Me), 127.7, 130.2, 138.2, 144.3 (ArC), 128.1, 132.05, 142.3 (3 × CH=), and 132.9 (CH₂) p.p.m.; m/z 208 (M⁺, 9%) and 139 (100).

(E,E)-1-*Tosylpenta*-1,3-*diene* (19) and 4-*tosylpenta*-1,3-*diene* (20) m.p. 113—115 °C (of a 10:1 mixture, from hexane–CCl₄); R_F for compound (19) 0.44 [hexane–ether (1:2)]; $v_{max.}$(neat) 3 040, 1 645, 1 300, 990 (CH=CH), 1 315, and 1 140 (SO₂) cm⁻¹; δ_H for compound (19) (CDCl₃) 1.8 (3 H, d, J 5.5 Hz, MeCH); 2.3 (3 H, s, MeAr), 5.8—6.4 (3 H, m, with d at 6.15, J 15 Hz, 1-H, 3-H, and 4-H), 7.2 (1 H, dd, J 15 and 10 Hz, 2-H), 7.25, and 7.7 (4 H, 2 d, J 8 Hz, ArH); δ_C for compound (19) (CDCl₃) 19.0 (MeCH), 21.9 (MeAr), 127.7, 130.2, 136.8, 144.5 (ArC), 127.9, 128.4, 130.2, and 142.4 (4 × CH=) p.p.m.; m/z for compound (19) 222 (M⁺, 10%), 143 (29), 139 (64), 92 (36), 91 (61), 89 (20), 83 (29), 77 (32), 67 (29), 66 (56), 65 (100), 63 (31), 55 (31), 53 (20), 51 (23), 41 (46), and 39 (69). Compounds (20) was identified in the mixture with product (19): δ_H(CDCl₃) 1.7 (s, MeCS) p.p.m.; m/z after tandem g.c.–m.s. 222 (M⁺, 12%).

(E)-2,3-*Dimethyl-1-tosylbuta*-1,3-*diene* (21) (Found: C, 65.8; H, 6.7. C₁₃H₁₆O₂S requires C, 66.07; H, 6.82%) m.p. 97—98 °C (from hexane–CCl₄); $v_{max.}$(Nujol) 3 050, 1 620, 1 290, 930, 800 (CH=CH), 1 300, and 1 130 (SO₂) cm⁻¹; δ_H(CDCl₃) 1.8 (3 H, s, MeCCH₂), 2.2 (3 H, s, MeCCH), 2.4 (3 H, s, MeAr), 5.1, 5.3 (2 H, 2 × s, CH₂), 6.2 (1 H, s, CH), 7.25, and 7.75 (4 H, 2 d, J 8 Hz, ArH); δ_C(CDCl₃) 12.15 MeCMe), 18.1 (MeCCH), 19.2 (MeAr), 117.3 (CH₂), 124.9, 128.35, 137.2, 140.3, 141.8, 149.3 (ArC and C=C), and 125.3 (CHS) p.p.m.; m/z 236 (M⁺, 17%), 157 (100), 142 (23), 139 (30), 105 (53), 91 (61), 81 (21), 79 (78), 77 (29), 65 (66), 41 (53), and 39 (72).

1-*Tosylcyclohexa*-1,3-*diene* (22) (Found: C, 66.1; H, 6.3. C₁₃H₁₄O₂S requires C, 66.64; H, 6.02%), m.p. 112—114 °C (decomp., from ethanol); $v_{max.}$(Nujol) 1 400, 720 (CH=CH), 1 300, and 1 150 (SO₂) cm⁻¹; δ_H(CDCl₃) 2.25 (4 H, s, 2 × CH₂), 2.35 (3 H, s, Me), 6.0, 6.95 (3 H, d, and m, J 4 Hz, 3 × CH=), 7.25, and 7.7 (4 H, 2 d, J 8 Hz, ArH); δ_C(CDCl₃) 20.6, 23.4 (2 × CH₂), 22.0 (Me), 123.2, 131.7, 133.8 (3 × CH=), 128.3, 129.3, 130.4, 137.15, and 144.7 (ArC and CH₂CS) p.p.m.; m/z 157 (M⁺ − C₆H₅, 10%), 139 (10), 107 (50), 106 (17), 91 (64), 79 (100), 78 (43), 77 (35), and 70 (31).

1-*Tosylcyclo-octa*-1,3-*diene* (23), oil, $v_{max.}$(neat) 1 620, 710 (CH=CH), 1 300, and 1 140 (SO₂) cm⁻¹; δ_H(CCl₄) 1.0—2.5 (11 H, 2 × m with s at 2.35, 4 × CH₂ and Me), 5.85 (2 H, m, CH=CH), 7.15 (1 H, m, CH=C), 7.3, and 7.75 (4 H, 2 d, J 8 Hz, ArH); δ_C(CCl₄) 21.4 (Me), 22.0, 23.1, 25.9, 28.9 (4 × CH₂),

122.7, 134.4, 136.8 (3 × CH), 128.9, 129.75, 137.2, 143.8 (ArC), and 141.2 (CCH₂) p.p.m.

Nucleophilic Displacement of δ-Iodoalkenyl Sulphones. General Procedure.—A solution of the δ-iodoalkenyl sulphone (7), (8), or (12) (2 mmol) in dichloromethane (10 ml) was treated with the nucleophile (20 mmol) at 0 °C. The reaction mixture was stirred for 1 h and then washed with water and in the case of thiophenol, with aqueous sodium hydroxide (0.5M), dried, and then evaporated to give pure compounds (24)—(27). Compounds (24) and (25) decomposed when they were purified by column chromatography on silica gel. (E)-N,N-*Dimethyl-4-tosylbut-2-enylamine* (24) yellow oil, R_F 0.32 [hexane–ether (1:1)]; $v_{max.}$(neat) 3 040, 1 300, 970 (CH=CH), 1 310, and 1 140 (SO₂) cm⁻¹; δ_H(CDCl₃) 2.05 (6 H, s, 2 × MeN), 2.35 (3 H, s, MeAr), 2.8 (2 H, d, J 5 Hz, CH₂N), 3.7 (2 H, d, J 5 Hz, CH₂S), 5.4 (2 H, m, 2 × CHCH₂), 7.15, and 7.55 (4 H, 2 d, J 8 Hz, ArH); δ_C(CCl₄) 21.5 (MeAr), 44.9 (2 × MeN), 59.5, 61.0 (2 × CH₂), 119.35, 137.6 (2 × CHCH₂), 128.4, 129.5, 136.4, and 143.8 (ArC) p.p.m.; m/z 253 (M⁺, 2%), 208 (2), 98 (100), 97 (46), 91 (30), 82 (28), 65 (24), 58 (41), 55 (20), 44 (25), and 42 (33).

(E)-N,N-3-*Trimethyl-4-tosylbut-2-enylamine* (25) yellow oil, R_F 0.58 [hexane–ether (1:4)]; $v_{max.}$(neat) 1 300 and 1 140 (SO₂) cm⁻¹; δ_H(CCl₄) 1.7 (3 H, s, MeCCH₂), 2.0 (6 H, s, 2 × MeN), 2.4 (3 H, s, MeAr), 2.7 (2 H, m, CH₂N), 3.65 (2 H, s, CH₂S), 5.25 (1 H, m, CHCH₂), 7.25, and 7.7 (4 H, 2 d, J 8 Hz, ArH); δ_C(CCl₄) 17.1 (MeCCH₂), 21.4 (MeAr), 45.3 (2 × MeN), 57.1 (CH₂N), 65.8 (CH₂S), 126.4 (CHCH₂), 128.5, 129.9, 133.5, 136.6, and 144.4 (ArC and CCH₂) p.p.m.

(E)-N,N,2,3-*Tetramethyl-4-tosylbut-2-enylamine* (26) (Found: C, 64.2; H, 8.0; N, 4.6. C₁₅H₂₃NO₂S requires C, 64.02; H, 8.24; N, 4.98%) m.p. 68—70 °C (from hexane–CCl₄); $v_{max.}$(Nujol) 1 320 and 1 140 (SO₂) cm⁻¹; δ_H(CCl₄) 1.3, 1.7 (6 H, 2 × s, 2 × MeCCH₂), 2.0 (6 H, s, 2 × MeN), 2.4 (3 H, s, MeAr), 2.65 (2 H, s, CH₂N), 3.6 (2 H, s, CH₂S), 7.2 and 7.6 (4 H, 2 d, J 8 Hz, ArH); δ_C(CDCl₃) 17.7, 19.3 (2 × MeCCH₂), 21.7 (MeAr), 45.3 (2 × CH₃N), 62.1, 62.25 (2 × CH₂), 120.4 (CCH₂N), 128.4, 129.8, 137.1, 137.25, and 144.8 (ArC and CCH₂S) p.p.m.; m/z 281 (M⁺, 2%), 237 (2), 126 (100), 96 (29), 91 (38), 65 (27), 58 (97), and 44 (28).

(E)-*Phenyl 4-tosyl-2,3-dimethylbut-2-enyl sulphide* (27) white solid decomposes on warming, R_F 0.19 [hexane–ether (5:1)]; $v_{max.}$(neat) 3 060, 1 600, 1 580, 820, 750, 690 (Ar), 1 320, and 1 150 (SO₂) cm⁻¹; δ_H(CCl₄) 1.35, 1.6 (6 H, 2 s, 2 × MeCCH₂), 2.35 (3 H, s, MeAr), 3.35, 3.6 (4 H, 2 s, 2 × CH₂), 7.15 (7 H, m, ArH), and 7.6 (2 H, d, J 8 Hz, ArH); δ_C(CDCl₃) 18.6, 19.5 (2 × MeCCH₂), 21.7 (MeAr), 29.1 (CH₂SPh), 61.85 (CH₂SO₂), 121.7, 126.5, 128.3, 128.7, 129.65, 130.5, 134.3, 136.5, 136.7, and 144.2 (ArC and 2 × CCH₂) p.p.m.; m/z 346 (M⁺, 3%), 218 (10), 192 (11), 191 (100), 190 (10), 109 (33), 91 (60), 81 (36), 79 (27), and 65 (40).

2-*Methyl-3-tosylbuta*-1,3-*diene* (28).—To a solution of (E)-1-iodo-2,3-dimethyl-4-tosylbut-2-ene (12) (0.91 g, 2.5 mmol) in dry THF (5 ml) was added a 5.4M methanolic solution of sodium methoxide (5 ml, 27 mmol) under an argon atmosphere at −20 °C. After 14 h, the solvents were evaporated off (15 torr) and the resulting residue hydrolysed with water, extracted with dichloromethane, the extracts dried, and evaporated to give compound (28) (0.4 g) (Found: C, 65.2; H, 6.5. C₁₃H₁₆O₂S requires C, 66.07; H, 6.82%) m.p. 50—52 °C (from hexane–ether), $v_{max.}$(Nujol) 3 100, 3 060, 910, 770 (CH=, CH₂=C), 1 300, and 1 150 (SO₂) cm⁻¹; δ_H(CDCl₃) 1.8 (3 H, s, MeCCH₂), 2.4 (3 H, s, MeAr), 4.0 (2 H, s, CH₂S), 5.0, 5.3 (4 H, 2 m, 2 × CH₂=C), 7.25, and 7.7 (4 H, 2 d, J 8 Hz, ArH); δ_C(CCl₄) 21.15, 21.7 (2 × Me), 67.5 (CH₂S), 121.0, 127.5 (2 × CH₂=C), 128.9, 129.7, 136.6, 136.7, 140.75, and 144.3 (ArC and 2 × C=CH₂)

p.p.m.; m/z 236 (M^+, 2%), 172 (17), 157 (90), 113 (21), 91 (72), 81 (33), 79 (100), 77 (22), 65 (58), 41 (33), and 39 (40).

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