



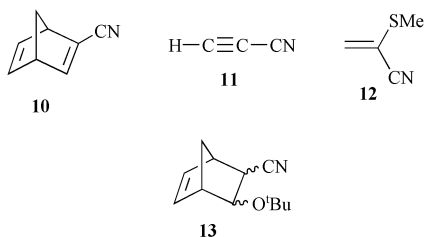
**Table 1** Reactions of (*E*)-3-phenylsulfonylprop-2-enitrile with furan

Dienophile 1/g	Furan/g	Solvent/cm <sup>3</sup>	T/°C	Time	Ratio 6 : 7
0.09	1.4	None	rt	25 h	2.3
0.09	1.4	None	rt	48 h	1.9
0.19	2.1	None	Reflux	4 h	1.5
0.14	1.4	None	0	5 d	6.3
0.15	2.1	None	-20	14 d	1.8
0.15	2.1	Benzene (2)	rt	8 d	2.3

**Table 2** Reactions of (*E*)-3-phenylsulfonylprop-2-enitrile with cyclopentadiene

Dienophile 1/g	Cyclopentadiene/g	Solvent/cm <sup>3</sup>	T/°C	Time	Ratio 8 : 9
0.19	0.16	Acetone (2)	-20	5 d	4.0
0.19	0.16	Benzene (2)	0	5 d	4.0
3.76	2.66	Acetone (35)	rt	7 h	4.5
3.86	2.66	Acetone (15)	rt	10 min	7.3
1.94	0.83	Acetone (15)	0	24 h	4.5
0.15	2.1	Benzene (2)	rt	8 d	2.3

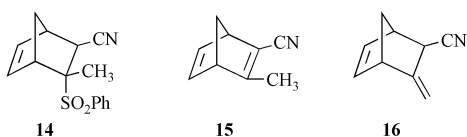
diene, and our dienophile **1** can thus act as a cyanoacetylene equivalent in this [4 + 2 $\pi$ ] cycloaddition reaction. 2-(Methylthio)prop-2-enitrile **12** is a related synthon,<sup>20</sup> but two steps are required for the transformation of its cycloadducts into bicyclo[2.2.1]hepta-2,5-dienes.



When the mixture of cycloadducts **8** and **9** was treated with an excess of potassium *tert*-butoxide in tetrahydrofuran compound **10** could not be isolated from the reaction mixture. Instead, a mixture of the isomeric ethers **13**, which could also be obtained from **10** by its reaction with the alkoxide, was formed. Addition of the poorly nucleophilic *tert*-butoxide ion to strained, reactive Michael acceptors has occasionally been observed.<sup>21</sup>

Alkylation of the carbanion derived from the major cyclopentadiene cycloadduct **8** was next investigated. The p*K*<sub>a</sub> values for methine hydrogens adjacent to nitrile<sup>22</sup> and phenylsulfonyl<sup>23</sup> substituents are rather similar, but we anticipated that low-temperature deprotonation of **8** would lead largely to the  $\alpha$ -sulfonyl carbanion due to the relative accessibility of the relevant *exo*-proton.

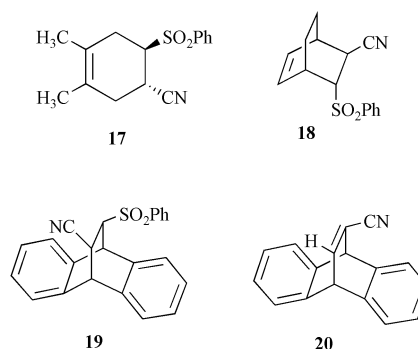
When the sulfone **8** was treated with *n*-BuLi in THF at -78 °C a dark coloured solution of the anion was formed. Addition of iodomethane led to discharge of this colour, and work up gave the methylated product **14** in moderate yield. The NMR spectrum of **14** was consistent with retention of stereochemistry at the sulfonyl carbon. Accompanying **14** was the unstable unsaturated nitrile **15** together with a significant amount of unreacted starting material **8**. Since **15** clearly arises *via* competing base-catalysed elimination of benzenesulfonic acid from the primary product **14**, the overall yield of the latter compound is necessarily reduced.



Use of lithium diisopropylamide as base led to a product mixture which did not contain any of the diene **15** but which contained the  $\beta,\gamma$ -unsaturated nitrile **16** as well as the desired product **14**. Attempted alkylation of **8** using allyl bromide or allyl chloride as electrophile gave poor yields of mixtures of products.

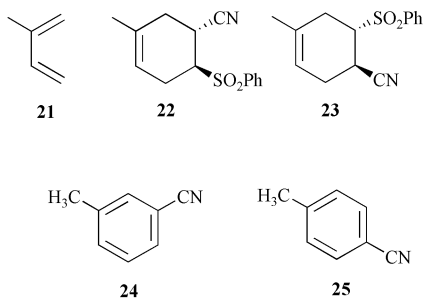
Attempted conversion of the sulfonyl function of **8** into a carbonyl group *via* reaction<sup>24</sup> of its anion with bis(trimethylsilyl) peroxide was similarly unsuccessful.

2,3-Dimethylbutadiene, cyclohexa-1,3-diene and anthracene all reacted with **1** to yield, respectively, the expected cycloadducts **17**, **18** and **19**. Only the *endo*-phenylsulfonyl adduct, identifiable by the characteristic downfield shift of the proton  $\alpha$  to the sulfonyl group, was obtained from cyclohexa-1,3-diene, although this diene has been reported<sup>25</sup> to react with phenylsulfonyl ethene to give an 81 : 19 mixture of *endo*- and *exo*-adducts. The anthracene adduct **19** could be converted into the unsaturated nitrile **20** *via* potassium *tert*-butoxide-catalysed elimination of benzenesulfonic acid. No Michael adducts analogous to the *tert*-butyl ethers **13** were observed in this instance.

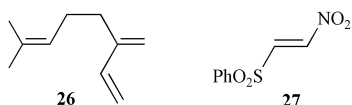


We next investigated the regioselectivity of the Diels–Alder reaction of **1** with unsymmetrical dienes. Isoprene **21** gave an unresolvable mixture of products **22** and **23**. These had similar <sup>1</sup>H NMR spectra but were clearly differentiated by <sup>13</sup>C NMR spectroscopy. Reaction of the mixture of **22** and **23** with potassium *tert*-butoxide in DMSO or in THF gave, *via* elimination of benzenesulfonic acid, the toluonitriles **24** and **25** formed by aerial oxidation or by disproportionation of the primary elimination products. The regioselectivity of the Diels–Alder reaction of **1** with isoprene was not improved in the presence of Lewis acids (ZnCl<sub>2</sub>, BF<sub>3</sub>·Et<sub>2</sub>O), indeed, as others have also noted,<sup>26</sup> overall yields were actually reduced.

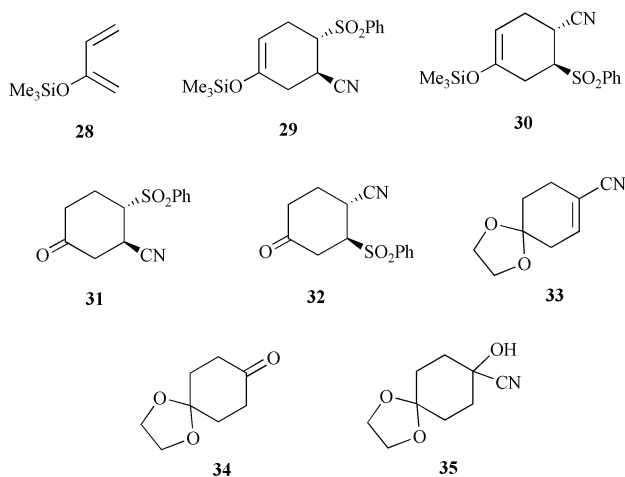
Similar poor regioselectivity was observed when **1** was reacted with myrcene **26**.



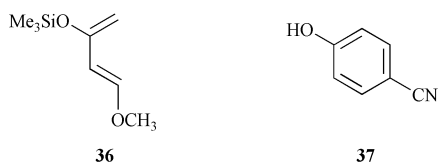
These results parallel those of Ono,<sup>9</sup> who found that 1-nitro-2-phenylsulfonylethene **27** also reacted with the two dienes **21** and **26** to give mixtures of products in which neither regioisomer predominated.



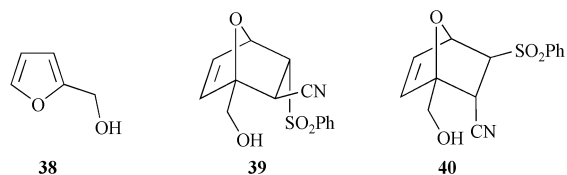
When **1** was reacted with the electronically biased 2-trimethylsilyloxybuta-1,3-diene **28** a 1 : 2 mixture of the two regioisomeric cycloadducts **29** and **30** was formed. These were unstable towards chromatography, and were converted into the corresponding ketones **31** and **32** by hydrolysis with aqueous acetic acid. These ketones could be separated by column chromatography, the minor isomer **31** being eluted first. The NMR spectra of **31** and **32**, although different, did not permit unambiguous assignment of their structures, and the ketone **32** was therefore converted into its ethylene acetal which was treated with potassium *tert*-butoxide to give the nitrile **33**. An authentic specimen of this nitrile was prepared from cyclohexane-1,4-dione monoacetal **34** which was converted *via* its bisulfite compound into the cyanohydrin **35** using aqueous potassium cyanide and then dehydrated using thionyl chloride in pyridine to give **33**.



Reaction of **1** with Danishefsky's diene **36** gave a mixture of adducts which could not be separated and which were desilylated using aqueous acetic acid. The resulting crude mixture of unstable keto-nitriles gave 4-hydroxybenzonitrile **37** as the sole product when it was treated with potassium *tert*-butoxide.



Cycloaddition of **1** with furfuryl alcohol **38** proceeded in a regioselective manner to yield the diastereoisomeric adducts **39** and **40** whose structures were elucidated on the basis of their <sup>1</sup>H NMR shifts and coupling patterns.



## Conclusion

Thus, the unsaturated sulfonylnitrile **1** is an easily prepared reactive dienophile. The facile base-induced elimination of benzenesulfonic acid from its cycloadducts with cyclopentadiene and with anthracene demonstrate its application as a cyanoacetylene equivalent. Alkylation reactions of the  $\alpha$ -sulfonyl anions of the cycloadducts are of limited value because of competing elimination of benzenesulfonate ion from the reaction products. Inadequate regiocontrol is observed in cycloaddition reactions with simple unsymmetrical dienes, but excellent results were obtained with Danishefsky's diene and with furfuryl alcohol. However, spontaneous crystallisation of the reaction products from solution may be an important factor in the latter instance.

## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained for solutions in CDCl<sub>3</sub> unless otherwise stated using JEOL PMX-60, Bruker WP-80 or Bruker MSL-300 spectrometers. *J* values are given in Hz. IR spectra were recorded using Perkin-Elmer 298, Perkin-Elmer 883 or Paragon FT-IR instruments. Melting points were obtained using a Stuart Scientific SMP2 apparatus and are uncorrected. GLC analysis was carried out using a Varian 3300–3400 gas chromatograph. TLC was performed using Merck 60F<sub>254</sub> silica-coated plates. Column chromatography was carried out using Merck Kieselgel 60. All solvents were distilled before use. Elemental analyses were performed by the Micro-analytical Laboratory, University College Dublin.

### 2-Chloro-3-phenylsulfonylpropanenitrile **3**

Sodium benzenesulfinate (24.7 g) was dissolved in a mixture of water (50 cm<sup>3</sup>) and acetic acid (20 cm<sup>3</sup>). 2-Chloroprop-2-enenitrile **2** (13.1 g) was added, followed by methanol (50 cm<sup>3</sup>). After 10 min, the solid product **3** (26.16 g; 76%) was collected by filtration, mp 104 °C (lit.<sup>13</sup> 105–106 °C);  $\delta_{\text{H}}$  3.70 (2H, dd, *J* 14.0 and 6.8, -CH<sub>2</sub>CH-), 5.01 (1H, t, *J* 6.8, -CH<sub>2</sub>CH-) and 7.4–8.15 (5H, m, Ar-) ppm [Found C 47.10, H 3.45, N 6.12. C<sub>9</sub>H<sub>8</sub>ClNO<sub>2</sub>S requires C 47.06, H 3.48, N 6.10%].

### (*E*)-3-Phenylsulfonylprop-2-enenitrile **1**

The crude chloro-compound **3** (24.71 g) was dissolved in chloroform (175 cm<sup>3</sup>) and the solution was cooled in an ice-salt bath. Triethylamine (15 cm<sup>3</sup>; 0.11 mol) was added dropwise and the mixture was kept at 0 °C during 10 min. It was then washed sequentially with dilute aqueous hydrochloric acid and with sodium hydrogen carbonate solution. Evaporation of solvent after drying over anhydrous magnesium sulfate yielded a solid which was recrystallised from 70 : 30 ethyl acetate-hexane (charcoal) to give the unsaturated sulfone **1** (12.5 g; 64%), mp 93–94 °C (lit.<sup>14</sup> 103–104 °C from H<sub>2</sub>O);  $\nu_{\text{max}}$  (Nujol) 3060, 2225, 1310 and 1150 cm<sup>-1</sup>;  $\delta_{\text{H}}$  6.43 (1H, d, *J* 15.4, -CH=CHCN), 7.15 (1H, d, *J* 15.4, -CH=CHSO<sub>2</sub>Ph) and 7.3–7.9 (5H, m, Ar-) ppm [Found C 55.60, H 3.52, N 7.03. C<sub>9</sub>H<sub>7</sub>NO<sub>2</sub>S requires C 55.96, H 3.63, N 7.25%].

**(Z)-3-Phenylsulfonylprop-2-enitrile 4.** This was sometimes formed as a minor product (*ca.* 3%), and it could be separated from **1** by chromatography on silica gel using 40 : 60 ethyl acetate–hexane as eluant. It crystallised from 70 : 30 ethyl acetate–hexane as *needles*, mp 77.5–78 °C;  $\nu_{\max}$  (Nujol) 3040, 2210, 1300 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  6.05 (1H, d,  $J$  11.2 Hz,  $-\text{CH}=\text{CHCN}$ ), 7.08 (1H, d,  $J$  11.2 Hz,  $-\text{CH}=\text{CHSO}_2\text{Ph}$ ) and 7.60–8.23 (5H, m, Ar-) ppm [Found C 55.50, H 3.61, N 7.00.  $\text{C}_9\text{H}_7\text{NO}_2\text{S}$  requires C 55.96, H, 3.63, N 7.25%].

### 3-endo-Phenylsulfonyl-7-oxabicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **6** and 3-exo-phenylsulfonyl-7-oxabicyclo[2.2.1]hept-5-ene-2-endo-carbonitrile **7**

(*E*)-3-Phenylsulfonylprop-2-enitrile **1** (0.19 g) was dissolved in furan **5** (3  $\text{cm}^3$ ) and the solution was heated at 30 °C during 4 h. Excess furan was evaporated and the residue was chromatographed on silica gel using 30 : 70 ethyl acetate–hexane as eluant.

First eluted was 3-endo-phenylsulfonyl-7-oxabicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **6** (0.16 g; 60%), which was recrystallised from 60 : 40 ethyl acetate–hexane to give a *solid*, mp 93–94 °C;  $\nu_{\max}$  (Nujol) 2240, 1305 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 2.87 (1H, d,  $J$  4.7, H-3), 3.98 (1H, apparent t,  $J$  4.7 and 4.7, H-2), 5.32 (2H, m, H-1 and H-4), 6.66 (2H, m, H-5 and H-6), 7.7 (3H, m, *meta*- and *para*-ArH) and 7.9 (2H, m, *ortho*-ArH) ppm [Found: C 59.48, H 4.15, N 5.46.  $\text{C}_{13}\text{H}_{11}\text{NO}_2\text{S}$  requires C 59.77, H 4.21, N 5.36%].

Next eluted was 3-exo-phenylsulfonyl-7-oxabicyclo[2.2.1]hept-5-ene-2-endo-carbonitrile **7** (0.1 g; 40%) which was recrystallised from 50 : 50 ethyl acetate–hexane to give a *solid*, mp 103–104 °C;  $\nu_{\max}$  (Nujol) 2240, 1297 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 3.38 (2H, m, H-2 and H-3), 5.36 (1H, m, H-4), 5.52 (1H, apparent t,  $J$  0.98 and 0.98, H-1), 6.63 (2H, m, H-5 and H-6), 7.62 (3H, m, *meta*- and *para*-ArH) and 7.9 (2H, m, *ortho*-ArH) ppm [Found: C 60.23, H 3.96, N 5.31.  $\text{C}_{13}\text{H}_{11}\text{NO}_2\text{S}$  requires C 59.77, H 4.21, N 5.36%].

### 3-endo-Phenylsulfonylbicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **8** and 3-exo-phenylsulfonylbicyclo[2.2.1]hept-5-ene-2-endo-carbonitrile **9**

Freshly distilled cyclopentadiene (0.83 g) was added to a solution of (*E*)-3-phenylsulfonylprop-2-enitrile **1** (1.94 g) in acetone (15  $\text{cm}^3$ ) and the mixture was kept at 0 °C during 24 h. Solvent and excess cyclopentadiene were evaporated and the residue (2.64 g) was chromatographed on silica gel using chloroform–hexane–diethyl ether (30 : 50 : 30) as eluant.

First eluted was 3-exo-phenylsulfonylbicyclo[2.2.1]hept-5-ene-2-endo-carbonitrile **9** (0.46 g; 18%), which was recrystallised from 60 : 40 ethyl acetate–hexane to give a *solid*, mp 137–138 °C;  $\nu_{\max}$  (Nujol) 2240, 1580, 1305 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 1.61 (1H, dd,  $J$  9.5 and 1.5, H-7<sub>a</sub>), 2.09 (1H, d,  $J$  9.5, H-7<sub>b</sub>), 3.06–3.49 (4H, m, H-1, H-2, H-3 and H-4), 6.40 (2H, m, H-5 and H-6), 7.53–7.78 (3H, m, *meta*- and *para*-ArH) and 7.92 (2H, m, *ortho*-ArH) ppm [Found: C 64.46, H 4.86, N 5.26.  $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$  requires C 64.85, H 5.05, N 5.40%].

Next eluted was 3-endo-phenylsulfonylbicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **8** (2.1 g; 82%), which was recrystallised from 50 : 50 ethyl acetate–hexane to give a *solid*, mp 121–123 °C;  $\nu_{\max}$  (Nujol) 2240, 1580, 1305 and 1148  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 1.43–1.84 (2H, m, H-7<sub>a</sub> and H-7<sub>b</sub>), 2.71 (1H, dd,  $J$  1.7 and 5.4, H-2), 3.26–3.47 (2H, m, H-1 and H-4), 3.83 (1H, dd,  $J$  5.4 and 3.2, H-3), 6.36 (2H, m, H-5 and H-6), 7.48–7.77 (3H, m, *meta*- and *para*-ArH) and 7.84 (2H, m, *ortho*-ArH) ppm [Found: C 64.92, H 5.08, N 5.35.  $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$  requires C 64.85, H 5.05, N 5.40%].

### Bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **10**<sup>19</sup>

A mixture of the cycloadducts **8** and **9** (0.86 g) was dissolved in THF (30  $\text{cm}^3$ ) with freshly-sublimed potassium *tert*-butoxide

(0.44 g; 1.3 eq.). After 15 min the yellow reaction mixture was diluted with water and extracted with ether to give bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **10** as an oil (0.29 g; 75%),  $\delta_{\text{H}}$  (80 MHz) 2.06–2.26 (2H, m, 2H-7), 3.63–3.87 (2H, m, H-1 and H-4), 6.50–6.87 (2H, m, H-5 and H-6) and 7.49 (1H, m, H-3) ppm.

### 3-*tert*-Butoxybicyclo[2.2.1]hept-5-ene-2-carbonitrile **13**

A mixture of the cycloadducts **8** and **9** (0.26 g) was dissolved in THF (10  $\text{cm}^3$ ) with freshly-sublimed potassium *tert*-butoxide (0.47 g; 4.2 eq.). After 20 min the yellow reaction mixture was diluted with water and extracted with ether to give a mixture of isomers of 3-*tert*-butoxybicyclo[2.2.1]hept-5-ene-2-carbonitrile **13** as an oil (0.14 g; 74%), bp 74–75 °C/15 mmHg;  $\delta_{\text{H}}$  (60 MHz) 1.21 (9H, s, *tert*-Bu group; both isomers), 1.5–1.9 (2H, m, 2H-7; both isomers), 2.37 (~0.5H, dd,  $J$  ~ 3.0, H-2; one isomer), 2.67 (1H, m, H-4; both isomers), 2.8–3.2 (~2.5H, m, H-1 (both isomers) and H-2; one isomer), 3.74 (1H, m, H-3; both isomers) and 5.97–6.35 (2H, m, H-5 and H-6; both isomers) ppm [Found: C 74.68, H 9.66, N 7.48.  $\text{C}_{12}\text{H}_{19}\text{NO}$  requires C 74.61, H 9.84, N 7.25%].

### Alkylation of 3-endo-phenylsulfonylbicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **8**

(a) Using *n*-BuLi as base:

The sulfone **8** (0.51 g; 1.97 mmol), in THF (15  $\text{cm}^3$ ) at –78 °C, was stirred and treated dropwise with *n*-BuLi (1.15 M in hexane; 1.7  $\text{cm}^3$ ; 1 eq.). After 1 h iodomethane (0.3  $\text{cm}^3$ ; 2.5 eq.) was added to the brown solution and the mixture was allowed to warm to rt over 45 min. After a further 2 h, aqueous ammonium chloride was added to the yellow solution which was then extracted with ether to give an oil (0.46 g) which was chromatographed on silica gel using 30 : 70 ethyl acetate–hexane as eluant. 3-Methylbicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **15** (10 mg; 4%) was obtained as an unstable brown oil,  $\delta_{\text{H}}$  (60 MHz) 1.8–2.1 (2H, m, 2H-7), 2.08 (3H, s,  $-\text{CH}_3$ ), 3.5 (1H, m, H-1), 3.7 (1H, m, H-4) and 6.6–6.9 (2H, m, H-5 and H-6) ppm. This was followed by 3-endo-phenylsulfonyl-3-exo-methylbicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **14** (0.22 g; 41%), mp 142 °C (diethyl ether);  $\nu_{\max}$  (Nujol) 2273 and 1148  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 1.55 (3H, s,  $-\text{CH}_3$ ), 1.70 (1H, ddd,  $J$  2, 2 and 10, H-7<sub>a</sub>), 1.91 (1H, d,  $J$  10, H-7<sub>b</sub>), 3.0–3.15 (1H, m, H-2), 3.25–3.45 (2H, m, H-1 and H-4), 6.33 (1H, dd,  $J$  5.6 and 3, H-5 or H-6), 6.52 (1H, dd,  $J$  5.6 and 2.7, H-6 or H-5), 7.50–7.73 (3H, m, *meta*- and *para*-ArH) and 7.82 (2H, m, *ortho*-ArH) ppm [Found: C 65.33, H 5.97, N 5.24.  $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$  requires C 65.45, H 6.18, N 5.09%].

(b) Using LDA as base:

A solution of LDA, prepared by adding *n*-BuLi (1.37 M in hexane; 6.5  $\text{cm}^3$ ) to diisopropylamine (1.25  $\text{cm}^3$ ) in THF (10  $\text{cm}^3$ ) at –78 °C, was added dropwise to a stirred solution of the sulfone **8** (1.05 g; 4 mmol) and iodomethane (0.5  $\text{cm}^3$ ; 7.7 mmol) in THF (25  $\text{cm}^3$ ) at –78 °C. After 1.5 h the mixture was allowed to warm to rt. It was then diluted with water and extracted with ether to give a brown oil (0.88 g) which was chromatographed on silica gel using 20 : 50 ethyl acetate–hexane as eluant. A fraction which was enriched in 3-methylidenebicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **16** was obtained and had  $\delta_{\text{H}}$  (60 MHz) 1.5–1.75 (2H, m, 2H-7), 2.9 (1H, m, H-2), 3.25–3.57 (2H, m, H-1 and H-4), 5.10 (2H, d,  $J$  7.0,  $-\text{C}=\text{CH}_2$ ) and 6.25–6.40 (2H, m, H-5 and H-6) ppm. Attempts to obtain an analytically pure sample of **16** were unsuccessful. Another fraction (0.13 g) contained (NMR) a mixture of the nitriles **10** and **14** in the ratio 9 : 2, and a third fraction (0.47 g) was identified as being the sulfone **8**.

### 6-Phenylsulfonyl-3,4-dimethylcyclohex-3-enecarbonitrile **17**

(*E*)-3-Phenylsulfonylprop-2-enitrile **1** (2.95 g) was dissolved in acetone (60  $\text{cm}^3$ ) with 2,3-dimethylbuta-1,3-diene (4.14 g; 3.4

eq.) and the mixture was refluxed during 23 h. Evaporation of solvent yielded an oil which soon solidified. Recrystallisation from 40 : 60 ethyl acetate–hexane afforded 6-phenylsulfonyl-3,4-dimethylcyclohex-3-enecarbonitrile **17** (3.98 g; 95%) as a solid, mp 90–91 °C;  $\nu_{\max}$  (Nujol) 2240, 1310 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 1.62 (6H, s,  $-\text{CH}_3$  groups), 2.35–2.5 (4H, m,  $-\text{CH}_2$  groups), 2.9–3.23 (2H, m, H-1 and H-2), 7.67 (3H, m, *meta*- and *para*-ArH) and 7.89 (2H, m, *ortho*-ArH) ppm [Found: C 65.44, H 6.27, N 5.01.  $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$  requires C 65.45, H 6.18, N 5.09%].

### 3-endo-Phenylsulfonylbicyclo[2.2.2]oct-5-ene-2-exo-carbonitrile **18**

(*E*)-3-Phenylsulfonylprop-2-enenitrile **1** (0.19 g) was dissolved in acetone (2  $\text{cm}^3$ ) with cyclohexa-1,3-diene (0.24  $\text{cm}^3$ ; 2.5 eq.) in a small pressure tube. The contents of the tube were frozen and the tube was sealed and then heated at 80 °C during 15 h. Removal of solvent gave a solid which was a single diastereoisomer (NMR). Recrystallisation from diethyl ether gave 3-endo-phenylsulfonylbicyclo[2.2.2]oct-5-ene-2-exo-carbonitrile **18** (0.16 g; 60%), mp 123–125 °C;  $\nu_{\max}$  (Nujol) 2235, 1305 and 1145  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 1.23–2.05 (4H, m,  $-\text{CH}_2-\text{CH}_2-$ ), 2.75–3.33 (3H, H-1, H-2 and H-4), 3.38 (1H, dd, *J* 6.5 and 1.4, H-3), 6.30 (2H, m, H-5 and H-6), 7.45–7.75 (3H, m, *meta*- and *para*-ArH) and 7.82 (2H, m, *ortho*-ArH) ppm [Found: C 66.21, H 5.73, N 5.01.  $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{S}$  requires C 65.91, H 5.53, N 5.12%].

### trans-12-Phenylsulfonyl-9,10-ethanoanthracene-11-carbonitrile **19**

Anthracene (2.85 g; 16 mmol) and (*E*)-3-phenylsulfonylprop-2-enenitrile **1** (1.03 g; 5.3 mmol) in toluene (58  $\text{cm}^3$ ) were refluxed together during 29 h. The mixture was cooled and excess anthracene was removed by filtration. After evaporation of solvent the residue was chromatographed on silica gel using 50 : 50 ethyl acetate–hexane as eluant to give a crude solid (1.96 g), some of which was purified by sublimation (200 °C/0.3 mmHg) to give *trans*-12-phenylsulfonyl-9,10-ethanoanthracene-11-carbonitrile **19**, mp 83–84 °C;  $\nu_{\max}$  (Nujol) 2240, 1310 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 3.34 (1H, dd, *J* 6.0 and 2.2, H-2), 3.55 (1H, dd, *J*, 6.0 and 2.2, H-3), 4.59 (1H, d, *J* 2.2, H-1), 4.97 (1H, d, *J* 2.0, H-4) and 7.12–7.89 (13H, m, ArH) ppm [Found: C 74.51, H 4.64, N 3.79.  $\text{C}_{23}\text{H}_{17}\text{NO}_2\text{S}$  requires C 74.37, H 4.61, N 3.77%].

### (*E*)-9,10-Ethanoanthracene-11-carbonitrile **20**

The above adduct **19** (0.35 g), in THF (20  $\text{cm}^3$ ), was treated with potassium *tert*-butoxide (0.21 g; 2 eq.) at rt. After 15 min the mixture was diluted with water and the product was extracted using ether to give (*E*)-9,10-ethanoanthracene-11-carbonitrile **20** (0.13 g; 59%), mp 186–188 °C (lit.<sup>27</sup> mp 194–196 °C);  $\nu_{\max}$  (Nujol) 2200  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 5.17–5.26 (2H, m,  $-\text{CHCH}=\text{C}(\text{CN})\text{CH}-$ ), 6.91–7.37 (8H, m, ArH) and 7.66 (1H, dd, *J* 6.2 and 1.8,  $-\text{CH}=\text{C}(\text{CN})-$ ) ppm.

### Reaction of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** with isoprene **21**

A solution of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** (0.29 g) with isoprene **21** (0.3  $\text{cm}^3$ ; 2 eq.) in acetone (3  $\text{cm}^3$ ) in a small pressure tube was frozen and sealed under vacuum and then heated at 80 °C during 14 h. Solvent was evaporated to yield an oil (0.32 g) which was chromatographed on silica gel using 7 : 13 ethyl acetate–hexane to give a mixture of *trans*-4-phenylsulfonyl-1-methylcyclohexene-5-carbonitrile **22** and *trans*-5-phenylsulfonyl-1-methylcyclohexene-4-carbonitrile **23** as a solid (0.31 g; 80%) which could not be further separated into its components.  $\nu_{\max}$  (Nujol) 2240, 1305 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$

(80 MHz) 1.69 (3H, br s,  $-\text{CH}_3$  groups), 2.17–2.65 (4H, m,  $-\text{CH}_2$  groups), 2.9–3.7 (2H, overlapping ms,  $-\text{CHCN}$ - and  $-\text{CHSO}_2\text{Ph}$ ), 5.2–5.4 (1H, m, vinyl), 7.33–7.65 (3H, m, *meta*- and *para*-ArH) and 7.84 (2H, m, *ortho*-ArH) ppm;  $\delta_{\text{C}}$  (75 MHz) 25.31 and 25.79 ( $\text{CH}_3$ ), 24.06 ( $\text{CH}_2$ ), 25.31 and 25.79 ( $\text{CHCN}$ ), 28.22, 28.61 and 32.77 ( $\text{CH}_2$ ), 59.72 and 60.47 ( $\text{CHSO}_2\text{Ph}$ ), 117.85 and 118.67 ( $-\text{CH}=\text{C}$ ), 119.89 (CN), 131.45 and 131.57 ( $-\text{CH}=\text{C}$ ), 129.47, 129.9 and 134.84 (ArCH) and 137.85 (quaternary) ppm [Found: C 64.19, H 5.83, N 5.729.  $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}$  requires C 64.37, H 5.75, N 5.36%].

### Elimination of benzenesulfinic acid from **22** and **23**

A mixture of the cyclohexenes **22** and **23** (0.27 g; 1.03 mmol) in THF (12  $\text{cm}^3$ ) was treated with potassium *tert*-butoxide (0.56 g; 4.99 mmol). After 10 min the red solution was diluted with water and extracted using ether to give an oil (0.1 g) that was (by NMR comparison with authentic specimens) a mixture of starting materials and the *m*- and *p*-toluonitriles **24** and **25**.

### Reaction of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** with myrcene **26**

A solution of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** (0.39 g; 2.02 mmol) and freshly distilled myrcene **26** (1.0  $\text{cm}^3$ ; 4.41 mmol) in benzene (7  $\text{cm}^3$ ) was refluxed during 4 h. Solvent was evaporated and the residue was chromatographed on silica gel using 50 : 50 ethyl acetate–hexane to yield an oil (0.58 g; 88%),  $\nu_{\max}$  (liquid film) 2240, 1308 and 1148  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (60 MHz) 1.60 (3H, br s,  $-\text{CH}_3$ ), 1.67 (3H, br s,  $-\text{CH}_3$ ), 1.9–2.1 (4H, m,  $-\text{CH}_2$  groups), 2.9–3.7 (2H, overlapping ms,  $-\text{CHCN}$ - and  $-\text{CHSO}_2\text{Ph}$ ), 4.8–5.2 (1H, m, vinyl), 5.23–5.45 (1H, m, vinyl) and 7.3–8.0 (5H, ArH) ppm.

### Reaction of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** with 2-trimethylsilyloxybuta-1,3-diene **28**

2-Trimethylsilyloxybuta-1,3-diene (0.72 g; 5.06 mmol) and (*E*)-3-phenylsulfonylprop-2-enenitrile **1** (0.85 g; 4.4 mmol) were refluxed together in benzene (10.5  $\text{cm}^3$ ) under nitrogen during 26 h. Evaporation of solvent and of excess reagent afforded an oily mixture (1.46 g; 93%) of the adducts **29** and **30**,  $\delta_{\text{H}}$  (80 MHz) 0.10 (9H,  $-\text{SiMe}_3$ ), 2.13–2.67 (4H, m,  $-\text{CH}_2$  groups), 4.71 (1H, m,  $-\text{CH}=\text{C}$ ), 7.32–7.68 (3H, m, *meta*- and *para*-ArH) and 7.82 (2H, d, *J* 8.0, *ortho*-ArH) ppm.

A mixture of the adducts **29** and **30** (2.02 g) was dissolved in aqueous acetic acid (80%; 15  $\text{cm}^3$ ). After 1 h at rt the mixture was diluted with water and extracted using chloroform to give a crude product mixture which was chromatographed on silica gel using 7 : 13 ethyl acetate–hexane as eluant.

First eluted was *trans*-4-phenylsulfonyl-3-cyanocyclohexanone **31** (0.17 g; 10%), mp 149–150 °C (ethyl acetate–hexane);  $\nu_{\max}$  (Nujol) 2235, 1722, 1310 and 1155  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (60 MHz) 2.4–2.67 (8H, m,  $-\text{CH}_2$  and  $-\text{CH}$  groups), 7.5–7.77 (3H, m, *meta*- and *para*-ArH) and 7.95 (2H, d, *J* 8.1, *ortho*-ArH) ppm [Found: C 59.02, H 4.98, N 5.17.  $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{S}$  requires C 59.30, H 4.98, N 5.32%].

Next eluted was *trans*-3-phenylsulfonyl-4-cyanocyclohexanone **32** (0.46 g; 28%), mp 158–159 °C (ethyl acetate–hexane);  $\nu_{\max}$  (Nujol) 2240, 1715, 1305 and 1150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (80 MHz) 2.35–2.81 (6H, m,  $-\text{CH}_2$  groups), 3.63–3.86 (2H, m, H-3 and H-4), 7.51–8.04 (5H, m, ArH) ppm [Found: C 59.41, H 5.00, N 5.12.  $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{S}$  requires C 59.30, H 4.98, N 5.32%].

### 1,4-Dioxaspiro[4.5]dec-7-ene-7-carbonitrile **33** from **32**

The ketone **32** (80 mg) was refluxed in benzene (10  $\text{cm}^3$ ) with toluene-*p*-sulfonic acid (12 mg) and ethylene glycol (0.7  $\text{cm}^3$ ) during 12 h. The usual work-up followed by chromatography on silica gel using 20 : 30 ethyl acetate–hexane as eluant

afforded *trans*-7-phenylsulfonyl-1,4-dioxaspiro[4.5]decane-8-carbonitrile (80 mg; 85%) as a solid, mp 76–77 °C;  $\delta_{\text{H}}$  (80 MHz) 1.26–2.84 (7H, m,  $-\text{CH}_2$  groups and  $-\text{CH}(\text{CN})-$ ), 3.54 (1H, ddd,  $J$  12.8, 11.3 and 4.0,  $-\text{CHSO}_2\text{Ph}$ ), 3.94 (4H, br s,  $-\text{OCH}_2\text{CH}_2-\text{O}$ ) and 7.58–8.03 (5H, m, ArH) ppm. This acetal (80 mg), in THF (5 cm<sup>3</sup>), was treated with potassium *tert*-butoxide (0.1 g) during 15 min at rt. The reaction mixture was diluted with water, extracted with ether and chromatographed over silica gel, eluting with 10 : 90 ethyl acetate–hexane, to yield 1,4-dioxaspiro[4.5]dec-7-ene-7-carbonitrile **33** as an oil (65 mg) which slowly solidified and which was then sublimed at atmospheric pressure to give crystals, mp 30–31 °C;  $\nu_{\text{max}}$ (Nujol) 2210 and 1640 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (60 MHz) 1.65–1.95 (2H, m,  $-\text{CH}_2-\text{C}=\text{C}-$ ), 2.28–2.65 (4H, m,  $-\text{CH}_2$  groups), 4.00 (4H, s,  $-\text{OCH}_2\text{CH}_2-\text{O}$ ) and 6.51 (1H, m, H-8) ppm [Found: C 65.67, H 6.87, N 8.34%. C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub> requires C 65.45, H 6.66, N 8.48%].

#### 1,4-Dioxaspiro[4.5]dec-7-ene-7-carbonitrile **33** from cyclohexane-1,4-dione monoethylene acetal **34**

Cyclohexane-1,4-dione monoethylene acetal **34** (1.01 g) was added at rt to water (7.5 cm<sup>3</sup>) containing sodium metabisulfite (0.71 g). After 15 min water was evaporated at reduced pressure, the residue was triturated with ether and the solid bisulfite compound was collected by filtration. This was dissolved in water (28 cm<sup>3</sup>) layered with ether (28 cm<sup>3</sup>), and the two-phase mixture was stirred vigorously with potassium cyanide (0.66 g) during 15 min. Extraction with ether yielded the cyanohydrin **35** as a solid (1.0 g; 95%),  $\nu_{\text{max}}$  (Nujol) 3370 and 2240 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (60 MHz) 1.6–2.4 (8H, m,  $-\text{CH}_2$  groups), 3.75 (1H, br s, exch. D<sub>2</sub>O,  $-\text{OH}$ ) and 4.13 (4H, s,  $-\text{OCH}_2\text{CH}_2-\text{O}$ ) ppm. This cyanohydrin **35** (1.94 g) was dissolved in pyridine (40 cm<sup>3</sup>) at 0 °C and treated with thionyl chloride (0.8 cm<sup>3</sup>). After 12 h the mixture was worked up in the usual way to give 1,4-dioxaspiro[4.5]dec-7-ene-7-carbonitrile **33**, identical in every respect with material obtained from the ketone **32** as described above.

#### Reaction of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** with Danishefsky's diene **36**

1-Methoxy-3-trimethylsilyloxybuta-1,3-diene **36** (2.0 cm<sup>3</sup>; 1.05 mmol) was added to a solution of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** (1.76 g; 9.1 mmol) in benzene (35 cm<sup>3</sup>) under an atmosphere of nitrogen and the mixture was refluxed during 23 h. Evaporation of solvent yielded a solid (3.84 g). This (2.38 g) was treated with aqueous acetic acid (80%; 25 cm<sup>3</sup>) during 24 h at rt after which time extraction using ethyl acetate afforded an oil (1.9 g) which contained (NMR) 4-hydroxybenzoinitrile together with a mixture of diastereoisomers of 3-phenylsulfonyl-4-cyano-5-methoxycyclohexanone. This oil, in THF (17 cm<sup>3</sup>), was treated with potassium *tert*-butoxide (0.32 g) during 2 h and then worked up to give 4-hydroxybenzoinitrile **37** (0.94 g; 90% from **1**), spectroscopically identical with authentic material.

#### Reaction of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** with furfuryl alcohol **38**

Furfuryl alcohol **38** (1.4 cm<sup>3</sup>; 1.62 mmol) was added to a solution of (*E*)-3-phenylsulfonylprop-2-enenitrile **1** (0.54 g; 2.8 mmol) in benzene (7 cm<sup>3</sup>) at rt. After 6 h, the reaction products were collected by filtration and separated by fractional crystallisation from ethanol.

The major product, 3-endo-phenylsulfonyl-1-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile **39**, was obtained as a solid (0.49 g; 60%), mp 113–114 °C (ethanol);  $\nu_{\text{max}}$  (Nujol) 3450, 2240, 1300 and 1150 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (80 MHz; [<sup>2</sup>H<sub>6</sub>]acetone) 3.12 (1H, d,  $J$  5.1, H-2), 4.06–4.54 (4H, m,

$-\text{CH}_2\text{OH}$ ,  $-\text{OH}$  and H-3), 5.24 (1H, dd,  $J$  4.3 and 1.3, H-4), 6.63 (2H, m, H-5 and H-6) and 7.7–8.09 (5H, m, ArH) ppm. Deuterium exchange of the hydroxy proton simplified the multiplet at  $\delta$  4.06–4.54 which became 4.11 (2H, s,  $-\text{CH}_2\text{OH}$ ) and 4.36 (1H, dd,  $J$  5.0 and 4.4, H-4) ppm [Found: C 57.30, H 4.15, N 4.35%. C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>S requires C 57.72, H 4.50, N 4.81%].

The minor product, 3-exo-phenylsulfonyl-1-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene-2-endo-carbonitrile **40**, was obtained as a solid, (0.13 g; 16%), mp 122–122.5 °C (ethanol);  $\nu_{\text{max}}$  (Nujol) 3490, 2240, 1300 and 1147 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (80 MHz; [<sup>2</sup>H<sub>6</sub>]acetone) 3.16 (1H, br s, exch. D<sub>2</sub>O,  $-\text{OH}$ ), 3.52 (1H, d,  $J$  4.6, H-2), 3.78 (1H, d,  $J$  4.6, H-3), 4.09 (2H, s,  $-\text{CH}_2\text{OH}$ ), 5.43 (1H, d,  $J$  1.8, H-4), 6.60 (1H, d,  $J$  5.7, H-6), 6.77 (1H, dd,  $J$  5.7 and 1.8, H-5), 7.68–7.84 (3H, m, *meta*- and *para*-ArH) and 8.04 (2H, d,  $J$  8.0, *ortho*-ArH) ppm. Deuterium exchange of the hydroxy proton simplified the multiplet at  $\delta$  4.06–4.54 which became 4.11 (2H, m,  $-\text{CH}_2\text{OH}$ ) and 4.36 (1H, dd,  $J$  5.0 and 4.4, H-4) ppm [Found: C 57.71, H 4.58, N 4.33. C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>S requires C 57.72, H 4.50, N 4.81%].

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