Synthesis of Medium Ring Azacycles *via* Allene-based Cyclisations: Evaluation of Possible Mechanistic Pathways

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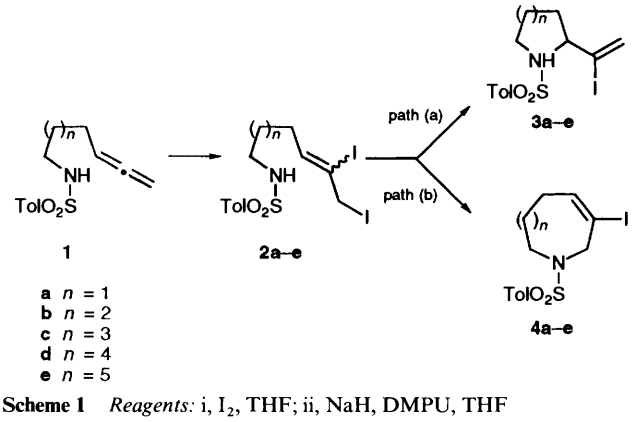
Two pathways have been evaluated to account for the I_2-mediated cyclisation of the allenic sulfonamides **1a–e** based on (i) the steric demands of the allenic unit and (ii) the ambident reactivity of the sulfonamide anion. The 1,3-disubstituted allenic sulfonamides **6** and **7** have been prepared and both undergo a facile cyclisation, without the need of an external base, to give the smaller of the two possible ring sizes **8** and **11**, respectively. In the case of **7**, the intermediate allylic iodides **9** and **10** have been observed and steric factors appear to play a decisive role in determining the preference for ring size in this cyclisation sequence. A possible role for the sulfonamide unit acting as an ambident nucleophile by undergoing initial *O*-alkylation has also been examined. The sulfonimidates **15a–c** undergo thermal [3,3]-rearrangement to give the corresponding sulfonamides **16a–c** but the conditions required to achieve this *O*- to *N*-migration step would preclude involvement of this pathway in the I_2-mediated cyclisation of allenic sulfonamides.

In the preceding paper we described a general synthesis of medium (8–11-membered) ring azacycles based on the I_2-mediated cyclisation of allenic sulfonamides.[1] This process, which is summarised in Scheme 1, involves a two-step sequence. In the first step, I_2-addition to the allenic sulfonamide **1** takes place across the terminal π-bond of the allene moiety to give the isolable allylic iodides (*E*/*Z*)-**2**; the other regioisomer of **2** resulting from I_2-addition across the internal π-bond of **1** was not observed. Cyclisation was then achieved by treatment of **2** with NaH in the presence of *N*,*N*′-dimethylpropyleneurea [DMPU; 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one] a polar, aprotic co-solvent. Two modes of cyclisation are possible based on the ambident electrophilic character of the allylic iodides **2**, leading to either the smaller ring **3** or the larger ring **4** *via* path (a) or path (b) respectively.



Scheme 1 *Reagents:* i, I_2, THF; ii, NaH, DMPU, THF

While the sulfonamide **1a** gave predominantly the corresponding pyrrolidine **3a** (an 8 : 1 mixture of the five-membered ring **3a** and 7-membered ring **4a** was isolated), in all other cases, the larger ring **4b–e** was either the *major* or *exclusive* product obtained. Similar observations—a preference for the formation of the larger of two possible rings—have recently been reported by Tsuda and co-workers[2] in reactions involving addition of a sulfonamide nucleophile to a π-allylpalladium intermediate, a reactive species that, like **2a–e**, should be viewed as an ambident electrophile.

In this paper we describe the results of experiments that were designed (i) to probe the mechanistic pathways available for the cyclisation sequence shown in Scheme 1 and (ii) to identify the factors that control the size of ring being formed, *i.e* path (a) *vs.* path (b). Two mechanistic avenues have been examined and each of these will be described in turn. The most obvious source of selectivity for the outcome of the sequence shown in Scheme 1 is a kinetic preference for an "S_N2" [path (b) involving a primary site] rather than "S_N2'" [path (a) involving a secondary site] mode of attack by the sulfonamide anion on the allylic iodide or related intermediate. Clearly, the balance of factors associated with this preference (steric, entropic, strain, *etc.*) must be such as to overcome the well-established barriers associated with generating medium-sized rings.[3] The most straightforward method of evaluating this proposal was to make both ends of the ambident electrophile—the allylic iodide or an intermediate iodonium species—similar in terms of the steric demands that are made on a subsequent nucleophilic displacement. This proposal has been examined using sulfonamides incorporating a 1,3-disubstituted allenyl unit.

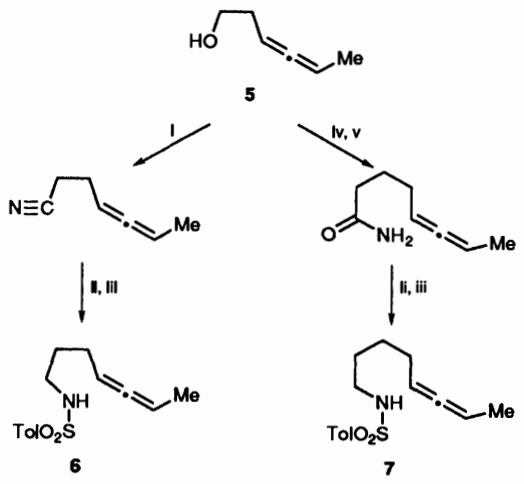
Starting from hexa-3,4-dien-1-ol **5**,[4] two 1,3-disubstituted allenic sulfonamides **6** and **7** have been prepared (Scheme 2).

Under I_2-mediated cyclisation conditions, the sulfonamide **6** is capable of forming either a 5- or 7-membered ring (*cf.* **1a**), with 5-ring formation being expected to predominate. The sulfonamide **7** can, by analogy, lead to either a 6- or 8-membered ring but, based on our initial studies, 8-ring formation should compete effectively in this situation.

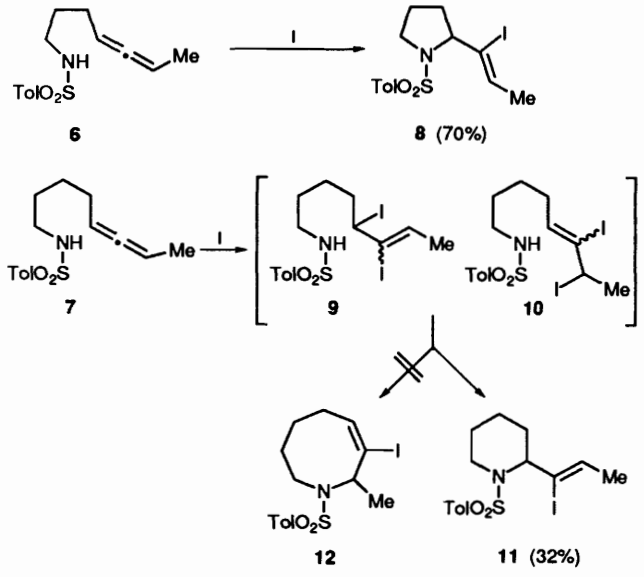
The regiochemical outcome of the I_2-addition step must also be considered, since, unlike the chemistry shown in Scheme 1, the sulfonamides **6** and **7** would be expected to produce regioisomeric allylic iodides derived from addition of I_2 across either π-bond of the allene unit.[5] In the event, the sulfonamide **6** underwent facile addition of I_2 (Scheme 3), but after 20 min at room temperature (RT) the *only* product observed was the pyrrolidine **8** which was isolated in 70% yield; no intermediate allylic iodides could be detected in this reaction by TLC.†

The homologous sulfonamide **7** also displayed a significantly higher degree of reactivity than had been expected. Addition of

† The alkene geometries of the alkenyl iodides **8–11** have not been assigned but all were obtained as single geometrical isomers.



Scheme 2 *Reagents:* i, TsCl (Ts = 4-$MeC_6H_4O_2S$), py, then KCN; ii, $LiAlH_4$; iii, TsCl, py; iv, TsCl, py, then NaI, Me_2CO; v, $AcNHSiMe_3$, BuLi



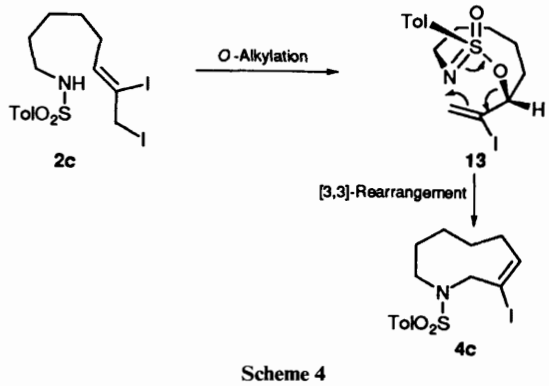
Scheme 3 *Reagents:* i, I_2, THF

I_2 proceeded rapidly to give a mixture of products (as judged by TLC). After 96 h (at RT) the piperidine **11** was isolated in 32% yield. This reaction was repeated but with the I_2 addition step being carried out at 0 °C. After 15 min, three components (present in approximately equal amounts) were observed by ^1H NMR analysis, one of which was the piperidine **11**. Two other signals [δ_H 6.00 (1 H, q, *J* 7) and 5.88 (1 H, t, *J* 7)] have been assigned to the alkenyl protons of the isomeric I_2-addition products **9** and **10**, respectively. It was not possible to isolate or purify these intermediates but when this mixture was redissolved in THF and allowed to stand at RT for 96 h, the piperidine **11** was again the only product observed; the corresponding 8-membered ring **12** was *not* detectable (by ^1H NMR analysis) in the crude product mixture.

It is evident that incorporation of a 1,3-disubstituted allene in the sulfonamides **6** and **7** results in a facile I_2-mediated cyclisation process and formation of the azacycles **8** and **11** requires neither a base nor a polar co-solvent to be present*—NaH and DMPU had been required for the cyclisation of the simpler variants **2**—and the increased reactivity of **6** and **7** must be associated with the activating (cation-stabilising) influence of the additional methyl residue.† This type of substitution pattern is known[6] to lead to a significant increase in the reactivity of simple allylic halides towards nucleophiles. As a result, steric factors associated with the environment of the allylic iodide moiety are suggested to be significant in terms of the selectivity for ring size observed in both Schemes 1 and 3. In Scheme 1, the preference for the larger ring size **4** relates to the ease of nucleophilic displacement at the primary rather than secondary site of the intermediate allylic iodide **2**. However, once the steric demands at each end of the ambident electrophile have been equalised as in **9** and **10**, the cyclisation process is now more facile and becomes heavily biased towards formation of the smaller (5- and 6-membered) rather than the larger (7- and 8-membered) rings. No definitive statements can be made about the relative reactivity of the isomeric allylic iodides **9** and **10**, however, the presence of iodide ion would be expected to mediate an equilibration between these two reactive intermediates.

While a direct "S_N2" or "S_N2'" mode of reactivity is considered to be the most reasonable explanation for the I_2-mediated cyclisation of the allenic sulfonamides **1a–e** as well as **6** and **7**, an alternative pathway, based on the ambident nucleophilicity of the sulfonamide moiety, has also been considered in this study.

The proposal, which is illustrated in Scheme 4 for the



Scheme 4

conversion of the allylic iodide **2c** into the 9-membered ring **4c**, would involve initial *O*-alkylation of the sulfonamide anion to generate the *O*-allylated sulfonimidate **13**. Given the flexibility associated with a sufficiently large ring, [3,3]-sigmatropic rearrangement of the sulfonimidate **13** to give the observed medium ring azacyle becomes feasible.

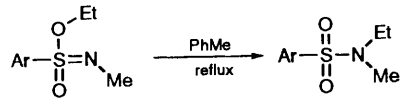
While participation of this reaction pathway in the cyclisation sequences shown in Schemes 1 and 3 appears to be unlikely (see below), the novelty of the *O*- to *N*-rearrangement (sulfonimidate to sulfonamide) was felt to merit further study. The ambident nucleophilic character of sulfonamides has been recognised, but examples of this reactivity and the correspond-

* Under the conditions used previously[1] to achieve cyclisation of compounds **2a–e** (NaH, DMPU), the pyrrolidine **8** and the piperidine **11** both undergo elimination of HI to give the alkynyl-substituted heterocycles **I** and **II** in 71 and 38% yields respectively (see Experimental section).

I **II**

† The accelerating influence of additional methyl substitution has been reported.[6] 4-Chloropent-2-ene undergoes solvolysis approximately 10^3 times faster than 4-chlorobut-2-ene.

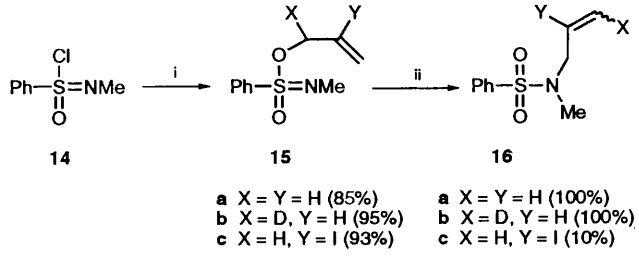
ing *O*- to *N*-alkyl rearrangement are rare.[8,9] Challis has shown (i) that sulfonimidates undergo alkyl (ethyl) group migration under thermal conditions [eqn. (1)] and (ii) that this process,



(1)

which obviously does not involve [3,3]-sigmatropic rearrangement, is slow ($t_{1/2}$ *ca.* 20 days at 110 °C).[9]

To test the hypothesis outlined in Scheme 4, the *O*-allyl sulfonimidate **15a** was prepared *via* the *N*-methylsulfonimidoyl chloride[10] **14** (Scheme 5). Thermal rearrangement of **15a** was



Scheme 5 *Reagents and conditions:* i, NaOCH(X)C(Y)=CH_2, PhMe; ii, PhMe, reflux

achieved in toluene (at reflux) to give a quantitative yield of the corresponding sulfonamide **16a**.

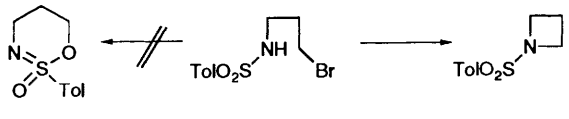
To confirm that this model reaction was a [3,3]-sigmatropic rearrangement, the deuterio derivative **15b** was prepared in an analogous fashion and underwent thermolysis to give **16b**. The influence of an alkenyl iodide moiety has also been examined and, using 2-iodoprop-2-en-1-ol, the sulfonimidate **15c** was prepared and subjected to thermolysis. Rearrangement was observed to give the sulfonamide **16c**, but in low (10%) yield, and this reaction was accompanied by a significant amount of decomposition.

In summary, the conditions requiried for the *O*- to *N*-allyl migration reactions shown in Scheme 5 exclude participation of this pathway in the I_2-mediated cyclisation of allenic sulfonamides shown in Schemes 1 and 3, a process that takes place at room temperature. Direct *N*-alkylation of the sulfonamide moiety *via* nucleophilic substitution—which is sensitive to the steric environment of the participating allylic iodide—appears to be the most reasonable explanation for the ring selectivities observed and is also consistent with the conclusions reached by Challis on the preferred mode of reaction of sulfonamide nucleophiles.* Further work in this area is being focused on exploiting and extending the synthetic utility of the heterocyclic alkenyl iodides available using the I_2-mediated cyclisation methodology.

Experimental

General experimental details have been described earlier.[1b]

* Tosyl(3-bromopropyl)amine undergoes cyclisation under basic conditions (NaH, THF) to provide the corresponding azetidine.[10] We have confirmed this observation and, upon examination of the crude product by ^{1}H NMR spectroscopy, were unable to detect any evidence for the presence of the 6-ring sulfonimidate **III**.



III

Hepta-4,5-dienenitrile.—To an ice-cold solution of hexa-3,4-diene-1-ol **5**[4] (1.07 g, 10.9 mmol) in pyridine (5 cm^3) was added tosyl chloride (2.51 g, 13.2 mmol). After 30 min, the mixture was allowed to warm to room temperature with further stirring for 1 h, followed by storage overnight at −15 °C. The mixture was then diluted with ether (50 cm^3) and washed with aqueous HCl (2 mol dm^{-3}; 3 × 15 cm^3). The aqueous washings were back-extracted with ether (30 cm^3) after which the combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure to give hexa-3,4-dienyl tosylate as a colourless oil which was used without further purification.

To the crude tosylate in DMSO (5 cm^3) was added sodium cyanide (1.3 g, 27 mmol). After being stirred overnight the mixture was diluted with water and extracted with ether (4 × 25 cm^3). The combined extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure and the residue was purified by flash chromatography (EtOAc–light petroleum, 5 : 95) to give hepta-4,5-dienenitrile (0.81 g, 69%) as a colourless oil (Found: M^+, 107.0732. C_7H_9N requires *M*, 107.0735); ν_{max}(neat)/cm^{-1} 2210 and 1950; δ_H(60 MHz) 5.4–4.9 (2 H, m), 2.6–2.0 (4 H, m) and 1.7 (3 H, dd, *J* 6, 4); *m/z* (EI) 107 (M^+).

N-(p-*Tolylsulfonyl*)*hepta*-4,5-*dienylamine* **6**.—To an ice-cold suspension of $LiAlH_4$ (0.60 g, 16 mmol) in ether (50 cm^3) under nitrogen was added hepta-4,5-dienenitrile (0.78 g, 7.3 mmol) in ether (5 cm^3) over 5 min. After 30 min, the mixture was diluted with CH_2Cl_2 (20 cm^3) and the reaction mixture quenched by the dropwise addition to it of saturated aqueous ammonium chloride. The resulting suspension was dried (Na_2SO_4) and filtered through Celite, the solids being washed with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure to give hepta-4,5-dienylamine which was used without further purification; δ_H(60 MHz) 7.3 (2 H, s), 5.2–4.7 (2 H, m), 2.6 (2 H, m) and 2.2–1.1 (7 H, m).

To an ice-cold solution of the crude amine in pyridine (5 cm^3) was added tosyl chloride (1.44 g, 7.6 mmol) over 10 min. The mixture was stirred for 2 h at 0 °C and then allowed to stand at −15 °C overnight. The suspension was then diluted with ether (50 cm^3) and washed with aqueous HCl (2 mol dm^{-3}; 3 × 15 cm^3). The aqueous washings were then back-extracted with ether (30 cm^3). The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure and the residue was purified by flash chromatography (EtOAc–light petroleum, 1 : 9) to afford the *title compound* **5** (1.11 g, 58%) as a colourless oil (Found: M^+ + H, 266.1215. $C_{14}H_{19}NO_2S$ requires *M*, 266.1214); ν_{max}(neat)/cm^{-1} 3250, 1950 and 1310; δ_H(270 MHz) 7.77 (2 H, d, *J* 8), 7.29 (2 H, d, *J* 8), 5.32 (1 H, t, *J* 6), 5.05–4.90 (2 H, m), 2.95 (2 H, q, *J* 7), 2.41 (3 H, s), 1.99–1.92 (2 H, m) and 1.62–1.51 (5 H, m); δ_C(67.8 MHz, $CDCl_3$) 204.4, 142.9, 136.7, 129.3, 126.8, 88.7, 85.9, 42.4, 28.4, 25.3, 21.2 and 14.1; *m/z* (CI) 266 (M^+ + H).

1-*Iodohexa*-3,4-*diene*.[12]—Hexa-3,4-dienyl tosylate [from hexa-3,4-dien-1-ol (1.02 g, 10.4 mmol)] was dissolved in acetone (30 cm^3) and treated with NaI (4.64 g, 31 mmol). After being stirred at room temperature for 72 h, the mixture was diluted with pentane (50 cm^3), washed with saturated aqueous sodium thiosulfate, dried and concentrated under reduced pressure to give 1-iodohexa-3,4-diene (1.38 g, 64%) as a colourless oil, b.p. 125 °C (14 mmHg).

Octa-5,6-*dienamide*.—To an ice-cold solution of butyllithium (1.6 mol dm^{-3} in hexane; 2.0 cm^3, 3.2 mmol) in THF (20 cm^3) was slowly added a solution of *N*-(trimethylsilyl)acetamide (189 mg, 1.44 mmol) in THF (1 cm^3). After 30 min a solution of 1-iodohexa-3,4-diene (360 mg, 1.6 mmol) in THF (1 cm^3) was

slowly added to the mixture which was then stirred overnight under nitrogen. After this, the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride and then evaporated. The residual solids were extracted with CH_2Cl_2 (25 cm^3) and the combined extracts were washed with water (2 × 5 cm^3); the aqueous washings were then back-extracted with CH_2Cl_2 (5 cm^3). The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure and the residue was purified by flash chromatography (EtOAc) to give the *title compound* (15 mg, 7%) as an oil which slowly crystallised (Found: M^+, 139.0982. $C_8H_{13}NO$ requires *M*, 139.0997); $\nu_{max}(CHCl_3)/cm^{-1}$ 3380, 1955 and 1675; δ_H(270 MHz) 5.79 (1 H, br s), 5.52 (1 H, br s), 5.13–4.99 (2 H, m), 2.27 (2 H, t, *J* 7), 2.04 (2 H, qd, *J* 7, 3.5), 1.76 (2 H, pentet, *J* 7) and 1.65 (3 H, dd, *J* 7, 3.5); *m/z* 139 (M^+).

N-(p-*Tolylsulfonyl*)*octa*-5,6-*dienylamine* **7**.—To a stirred solution of octa-5,6-dienamide (51 mg, 0.37 mmol) in ether (4 cm^3) at 0 °C was added $LiAlH_4$ (30 mg, 0.79 mmol) and the mixture allowed to warm to room temperature over 2 h. The suspension was diluted with CH_2Cl_2 (5 cm^3) and the reaction mixture quenched by the addition of saturated aqueous ammonium chloride. The resulting mixture was dried (Na_2SO_4) and filtered through Celite, the solids being washed with CH_2Cl_2. The filtrate and washings were evaporated under reduced pressure to give octa-5,6-dienylamine which was used without further purification: δ_H(60 MHz) 5.2–4.8 (2 H, m), 2.8–2.4 (2 H, br s) and 2.2–1.1 (11 H, m).

To a solution of crude amine prepared above in pyridine (2 cm^3) under nitrogen was added tosyl chloride (50 mg, 0.26 mmol) and the mixture stirred overnight. The solution was diluted with ether (20 cm^3) and washed with aqueous HCl (2 mol dm^{-3}; 2 cm^3). The aqueous washings were back-extracted with ether (3 × 5 cm^3) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure. Purification of the residue by flash chromatography (EtOAc–light petroleum, 1:9) gave the *title compound* **7** (24 mg, 23%) as a colourless oil (Found: M^+, 279.1593. $C_{15}H_{21}NO_2S$ requires *M*, 279.1293); $\nu_{max}(CHCl_3)/cm^{-1}$ 3350, 1955 and 1320; δ_H(270 MHz) 7.75 (2 H, d, *J* 8), 7.31 (2 H, d, *J* 8), 5.07–4.91 (2 H, m), 4.49 (1 H, br s), 2.94 (2 H, q, *J* 6.5), 2.43 (3 H, s), 1.91 (2 H, qd, *J* 7, 3.5), 1.62 (3 H, dd, *J* 6.5, 3.5) and 1.55–1.33 (4 H, m); δ_C(67.8 MHz) 204.6, 136.8, 129.5, 127.0, 89.5, 85.7, 42.9, 28.8, 25.7, 21.4 and 14.4; *m/z* (CI) 280 ($M + H^+$).

(Z)-2-(1-*Iodoprop*-1-*enyl*)-1-(p-*tolylsulfonyl*)*pyrrolidine* **8**.—To a solution of the sulfonamide **6** (258 mg, 0.97 mmol) in THF (20 cm^3) under nitrogen was added a solution of iodine (255 mg, 1.0 mmol) in THF (10 cm^3) over 20 min. After a further 20 min, solvents were removed under reduced pressure and the crude product was dissolved in EtOAc (20 cm^3) and the solution was washed with saturated aqueous sodium thiosulfate (20 cm^3) and water (20 cm^3). The aqueous washings were back-extracted with EtOAc (10 cm^3) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure. Purification of the residue by flash chromatography (EtOAc–light petroleum, 1:9) gave the *title compound* **8** (273 mg, 70%) as colourless crystals, m.p. 98.5–100 °C (ether) (Found: C, 42.9; H, 4.65; N, 3.5. $C_{14}H_{18}INO_2S$ requires C, 43.0; H, 4.64; N, 3.58%); ν_{max}(Nujol)/cm^{-1} 1590, 1440 and 1335; δ_H(270 MHz) 7.71 (2 H, d, *J* 7), 7.31 (2 H, d, *J* 7), 6.01 (1 H, qd, *J* 6.5, 1), 4.24 (1 H, dd, *J* 7.5, 4), 3.52–3.34 (2 H, m), 2.43 (3 H, s), 1.96–1.59 (4 H, m) and 1.76 (3 H, dd, *J* 6.5, 1); δ_C(67.8 MHz) 143.3, 131.2, 129.4, 127.4, 127.3, 112.8, 68.2, 49.5, 33.0 and 21.5; *m/z* 391 (M^+).

2-(*Prop*-1-*ynyl*)-N-(p-*tolylsulfonyl*)*pyrrolidine*.—To a solution of the pyrrolidine **6** (23 mg, 0.44 mmol) in THF (3 cm^3) under nitrogen was added NaH (60% dispersion in mineral oil; 10 mg, 0.25 mmol). After 1.5 h, further NaH (10 mg) was added to the mixture which was then stirred for 72 h. After this, the mixture was diluted with CH_2Cl_2 (10 cm^3), quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (10 cm^3). The extracts were washed with water (2 × 5 cm^3) and brine, dried (Na_2SO_4), and evaporated under reduced pressure to give the *title compound* (11 mg, 71%) as a colourless oil (Found: M^+, 263.0958. $C_{14}H_{17}NO_2S$ requires *M*, 263.0980); $\nu_{max}(CHCl_3)/cm^{-1}$ 2280 and 1340; δ_H(270 MHz) 7.76 (2 H, d, *J* 7), 7.30 (2 H, d, *J* 7), 4.50 (1 H, m), 3.34 (2 H, dd, *J* 7.5, 6), 2.42 (3 H, s), 2.07–1.74 (4 H, m) and 1.68 (3 H, s); *m/z* 263 (M^+).

(Z)-2-(1-*Iodoprop*-1-*enyl*)-1-(p-*tolylsulfonyl*)*piperidine* **11**.—To a solution of the sulfonamide **7** (5 mg, 0.18 mmol) in THF (0.5 cm^3) at 0 °C under nitrogen was added a solution of iodine (6 mg, 0.24 mmol) in THF (0.5 cm^3). After 96 h, the mixture was extracted with CH_2Cl_2 (10 cm^3) and the extract washed with saturated aqueous sodium thiosulphate (1 cm^3) and water (2 cm^3). The aqueous washings were back-extracted with CH_2Cl_2 (5 cm^3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the residue by flash chromatography (EtOAc–light petroleum, 1:9) gave the *title compound* **11** (2.5 mg, 32%) as an oil (Found: $M^+ + H$, 406.0338. $C_{15}H_{21}INO_2S + H$ requires *M*, 406.0338) $\nu_{max}(CHCl_3)/cm^{-1}$ 1715, 1600, 1435 and 1335; δ_H(270 MHz) 7.72 (2 H, d, *J* 7), 7.29 (2 H, d, *J* 8), 5.80 (1 H, qd, *J* 6.5, 2), 4.74 (1 H, br s), 3.77–3.72 (1 H, m), 3.13–3.08 (1 H, m), 2.43 (3 H, s), 1.75 (3 H, dd, *J* 6.5, 2) and 1.56–1.25 (6 H, m); δ_C(67.8 MHz), 143.0, 138.0, 132.0, 129.5, 127.0, 109.5, 60.4, 41.8, 28.3, 23.7, 22.6, 21.4 and 18.1; *m/z* (CI) 406 ($M + H^+$).

2-(*Prop*-1-*ynyl*)-1-(p-*Tolylsulfonyl*)*piperidine*.—Under the same conditions as described for compound **6**, the sulfonamide **7** gave the *title compound* as a colourless oil (38%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1330; δ_H(270 MHz) 7.69 (2 H, d, *J* 7), 7.28 (2 H, d, *J* 8), 4.81 (1 H, br s), 3.66–3.62 (1 H, m), 2.80–2.72 (1 H, m), 2.42 (3 H, s), 1.73–1.56 (6 H, m) and 1.44 (3 H, d, *J* 2); *m/z* 277 (M^+). We were unable to obtain satisfactory high-resolution mass data for this product.

Allyl N-*Methylbenzenesulfonimidate* **15a**.—*N*-Methylbenzenesulfonimidoyl chloride **14**[10] (1.22 g, 6.4 mmol) in CCl_4 (10 cm^3) was added to a stirred suspension of the sodium salt of allyl alcohol (8 g, 0.13 mol) in toluene (10 cm^3) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and then quenched with ether (20 cm^3). It was then filtered and the filtrate concentrated under reduced pressure, to give the *title compound* **15a** (1.1 g, 85%) as a pale yellow oil which was used without purification (Found: $M^+ + H$, 212.075. $C_{10}H_{13}NO_2S + H$ requires *M*, 212.0745); ν_{max}(neat)/cm^{-1} 1440, 1290 and 1185; δ_H(300 MHz) 7.92–8.00 (2 H, m), 7.46–7.60 (3 H, m), 5.80 (1 H, m), 5.25 (1 H, d, *J* 16), 5.18 (1 H, d, *J* 10), 4.31–4.40 (2 H, m) and 2.95 (3 H, s); *m/z* (CI) 212 ($M^+ + H$).

[1-$^2H_1$]*Allyl* N-*Methylbenzenesulfonimidate* **15b**.—Using a similar procedure to that described for **15a**, *N*-methylbenzenesulfonimidoyl chloride **14**[10] was allowed to react with the sodium [2-$^2H_1$]prop-2-en-1-olate[13] to give the *title compound* **15b** (95%) (Found: $M^+ + H$, 213.082. $C_{10}DH_{12}NO_2S + H$ requires *M*, 213.081); ν_{max}(neat)/cm^{-1} 1440, 1290 and 1185; δ_H(300 MHz) 7.91–8.00 (2 H, m), 7.45–7.62 (3 H, m), 5.79 (1 H, ddd, *J* 6, 10, 16), 5.28 (1 H, d, *J* 16), 5.20 (1 H, d, *J* 10), 4.35 (1 H, m) and 2.95 (3 H, s); *m/z* (CI) 213 ($M^+ + H$).

2-*Iodoallyl* N-*Methylbenzenesulfonimidate* **15c**.—Using a similar procedure, *N*-methylbenzenesulfonimidoyl chloride **14**[10] reacted with the sodium 2-iodoprop-2-en-1-olate[14] to give the *title compound* **15c** (93%) (Found: $M^+ + H$, 337.972. $C_{10}H_{12}INO_2S + H$ requires *M*, 337.971); ν_{max}(neat)/cm^{-1} 1610, 1600, 1440, 1290 and 1170; δ_H(300 MHz) 7.48–8.00 (5 H, m), 6.30–6.50 (2 H, m), 4.48 (2 H, d, *J* 5) and 2.96 (3 H, s); *m*/*z* (CI) 338 ($M^+ + H$).

N-*Allyl*-N-*methylbenzenesulfonamide* **16a**.—A solution of the sulfonimidate **15a** (35 mg, 0.16 mmol) in toluene (20 cm^3) was heated at 110 °C for 40 h and then concentrated under reduced pressure to give the *title compound* **16a** (35 mg, 100%) as a colourless oil (Found: C, 57.2; H, 6.2; N, 6.7. $C_{10}H_{13}NO_2S$ requires C, 56.9; H, 6.2; N, 6.6%); ν_{max}(neat)/cm^{-1} 1440, 1335 and 1165; δ_H(300 MHz) 7.76–7.82 (2 H, m), 7.50–7.62 (3 H, m), 5.70 (1 H, m), 5.14–5.24 (2 H, m), 3.63 (2 H, d, *J* 5) and 2.67 (3 H, s); *m*/*z* (CI) 212 ($M^+ + H$). An authentic sample of **16a** was prepared by a literature procedure.[15]

N-[3-$^2H_1$]*Allyl*-N-*methylbenzenesulfonamide* **16b**.—Using a similar procedure to that described above, rearrangement of **15b** was conducted to give, without purification, the *title compound* **16b** in quantitative yield as a colourless oil (Found: $M^+ + H$, 213.082. $C_{10}DH_{12}NO_2S + H$ requires *M*, 213.081; ν_{max}(neat)/cm^{-1} 1620, 1580, 1340 and 1160; δ_H(300 MHz) 7.50–7.80 (5 H, m), 5.70 (1 H, m), 5.16 (1 H, m), 3.60 (2 H, d, *J* 5) and 2.68 (3 H, s); δ_C 137.4, 132.5, 132.3, 128.9, 127.3, 118.8 (dd, J_{CD} 24, 23), 52.9 and 34.1.

N-(2-*Iodoallyl*)-N-*methylbenzenesulfonamide* **16c**.—Using a similar procedure to that described above, rearrangement of **15c** was conducted to give, without purification, the *title compound* **16c** (10%) (Found: $M^+ + H$, 337.971. $C_{10}H_{12}INO_2S + H$ requires *M*, 337.971); δ_H(300 MHz) 7.75–7.82 (2 H, m), 7.50–7.62 (3 H, m), 6.46 (1 H, dt *J* 7.5, 1.5), 6.18 (1 H, dt *J* 7.5, 6.5), 3.77 (2 H, dd, *J* 6.25, 1.25) and 2.72 (3 H, s); *m*/*z* (CI) 338 ($M^+ + H$).

Acknowledgements

We thank Glaxo Research and Development Ltd. and Shell Research Ltd. for financial support and Drs. D. Lathbury and M. Anderson for helpful discussions.

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Paper 4/04916K
Received 10*th August* 1994
Accepted 6*th September* 1994