Radical-chain reactions of sulfonyl azides and of ethyl azidoformate with allylstannanes: homolytic allylation at nitrogen

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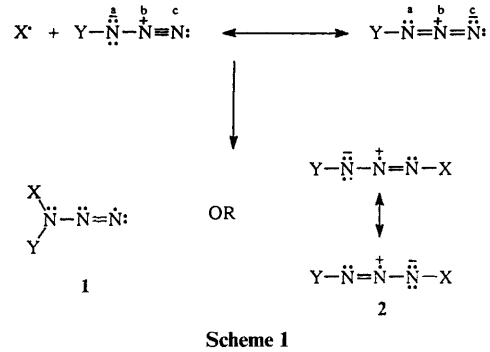
4-Methylbenzenesulfonyl azide reacts with allyltriphenylstannane (ATPS) in refluxing benzene, in the presence of 2,2′-azobis(2-methylpropionitrile) as initiator, to give *N*-allyl-4-methylbenzenesulfonamide in good yield after hydrolytic work-up. Small amounts of allyl 4-methylphenyl sulfone were also formed. The reaction follows a free-radical chain mechanism which involves competitive addition of $Ph_3Sn^{\cdot}$ to N^a and to N^c of the azido group in $ArSO_2N^aN^bN^c$. Addition to N^a followed by loss of nitrogen gives $ArSO_2\dot{N}SnPh_3$, the precursor of the *N*-allylarenesulfonamide, while addition to N^c leads to the formation of $Ar\dot{S}O_2$ and thence to the allyl aryl sulfone. Allyltrimethylstannane behaves in a similar way to ATPS, but allyltributylstannane gives only a low yield of *N*-allylarenesulfonamide and the major product is the unsubstituted sulfonamide $MeC_6H_4SO_2NH_2$, which results because the radical $ArSO_2\dot{N}SnBu_3$ undergoes intramolecular 1,5-hydrogen-atom transfer in preference to adding to the allylstannane. 2-Methylallyltriphenylstannane reacts in an analogous way to ATPS, but allylstannanes containing non-terminal double bonds do not react successfully. The arenesulfonyl azides $4\text{-}XC_6H_4SO_2N_3$ (X = H, MeO, F) react in a similar way to tosyl azide, but the reaction is very sluggish when X = NO_2. With 1-octanesulfonyl azide, reaction with $Ph_3Sn^{\cdot}$ is much less selective and products arising from attack at N^a and N^c are formed in comparable yields. Ethyl azidoformate reacts with allylstannanes in a similar manner to, although more slowly than, tosyl azide and gives good yields of the corresponding allylic carbamates.

The available evidence indicates that homolytic addition to an azide $YN^aN^bN^c$ can take place at either N^a or N^c to give a 3,3-triazenyl radical **1** or a 1,3-triazenyl radical **2**, respectively (see Scheme 1).[1] It is sometimes not clear to which end of the azido



Scheme 1

group addition occurs, because the ultimate products could plausibly arise from either intermediate triazenyl radical.[2] For example, aryl, acyl and sulfonyl azides undergo induced decomposition when heated in propan-2-ol at 50–80 °C in the presence of diethyl peroxydicarbonate initiator and the key step was thought to involve reaction of $Me_2\dot{C}OH$ with the azide according to eqn. (1).[3] It was proposed[3] that addition of

$$Me_2\dot{C}OH + YN_3 \longrightarrow Y\dot{N}H + Me_2CO + N_2 \quad (1)$$

$Me_2\dot{C}OH$ takes place initially at N^c to give a 1,3-triazenyl radical, followed by intramolecular hydrogen-atom transfer from oxygen to N^a with concerted elimination of acetone and molecular nitrogen. However, it seems equally possible that the 3,3-triazenyl radical $YN(H)\text{–}N{=}N^{\cdot}$ is formed initially, by hydrogen-atom transfer from oxygen in $Me_2\dot{C}OH$, followed by loss of nitrogen to give $Y\dot{N}H$. Indeed, we have proposed that the reaction between $Me_2\dot{C}OH$ and a primary alkyl azide RCH_2N_3 to give the aminyl radical $Me_2C(OH)CH_2\dot{N}R$ also involves attack at N^a, except that here 1,2-migration of the alkyl group R to nitrogen takes place in preference to hydrogen-atom transfer from oxygen.[1]

However, we have also reported that the EPR spectra observed during the generation of triorganosilyl radicals in the presence of a variety of types of azide are best interpreted as arising from 1,3-triazenyl adducts of the type $Y\dot{N}N\dot{N}SiR_3$.[1] The largest value of $a(^{14}N)$ for these radicals arises from hyperfine coupling to the central nitrogen atom and the unpaired electron resides in a σ molecular orbital symmetric to reflection in the NNN plane, as it does in the related 1,3-dialkyltriazenyl radicals.[4] On the other hand, the reaction of trichloromethyl radicals with aryl azides to give $Ar\dot{N}CCl_3$ would appear much more likely to proceed by way of a 3,3-triazenyl adduct, rather than *via* an intermediate 1,3-triazenyl radical $ArN\dot{N}NCCl_3$, as originally suggested.[5]

Intramolecular addition of aryl[6] or alkyl[7] radicals to an azido function evidently takes place preferentially at N^a to give intermediate 3,3-triazenyl radicals, which undergo subsequent loss of nitrogen to give cyclic aminyl radicals, and this reaction shows promise for organic synthesis. The reactions[8–12] of tributylstannyl radicals with alkyl and acyl azides appear to give stannylaminyl radicals of the type $Y\dot{N}SnBu_3$. It seems likely that these radicals are formed following addition of $Bu_3Sn^{\cdot}$ to N^a, although addition to N^c cannot be ruled out entirely because metallotropic interconversion of 1,3- and 3,3-triazenyl adducts could be rapid and it is even possible that the tin atom could bridge between N^a and N^c to form an intermediate containing a four-membered ring.

Alkyl radicals react with alkane- and arene-sulfonyl azides at elevated temperatures to displace the corresponding sulfonyl radical [eqn. (2)],[13] presumably *via* an intermediate 1,3-

$$R^{\cdot} + ArSO_2N_3 \longrightarrow RN_3 + Ar\dot{S}O_2 \quad (2)$$

triazenyl radical adduct. Thus, we conclude that quite subtle

factors determine the relative rates of homolytic addition to N^a and N^c of the azido function and the balance can be tipped in either direction depending on the nature of the azide and of the attacking radical. For some reactant pairs, reversibility of addition to N^c could also be important.

The diazo group $-CH=N_2$ is isoelectronic with the azido group $-N=N_2$ and we have reported recently that α-diazocarbonyl compounds react with allyltributylstannane (ATBS) by a radical-chain mechanism to bring about allylation at carbon [eqn. (3)].[14] Here $Bu_3Sn^\bullet$ evidently adds to the

$$RC(O)CH=N_2 + Bu_3SnCH_2CH=CH_2 \longrightarrow RC(O)CH(SnBu_3)CH_2CH=CH_2 + N_2 \quad (3)$$

carbon atom of the $-CH=N_2$ group (analogous to N^a of the azido group) to form a diazenyl radical, followed by rapid loss of nitrogen to give $RC(O)\dot{C}HSnBu_3$ which then reacts with ATBS. The Bu_3Sn group in the ultimate product [eqn. (3)] is readily replaced hydrolytically by H and thus the reaction of ATBS with α-diazo carbonyl compounds provides a new radical-mediated method for allylation at carbon α to a carbonyl group under non-basic conditions.

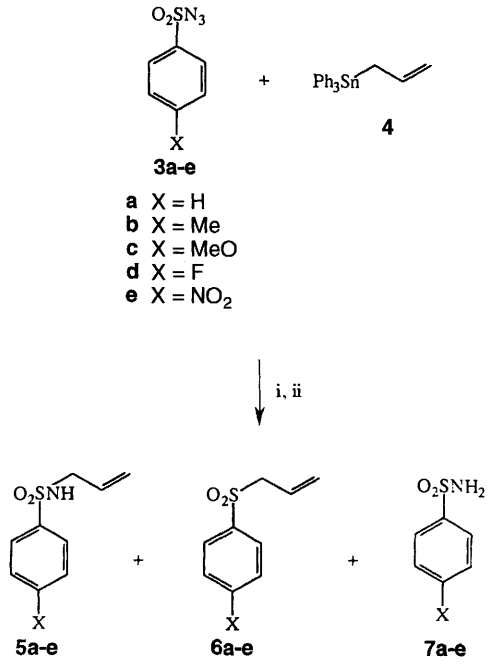
Against this background, we have now investigated the reactions of sulfonyl azides with allylstannes [15–18] with the aim of developing new methods for homolytic allylation at nitrogen. The corresponding reactions of benzoyl azide and of ethyl azidoformate have also been studied.

Results and discussion

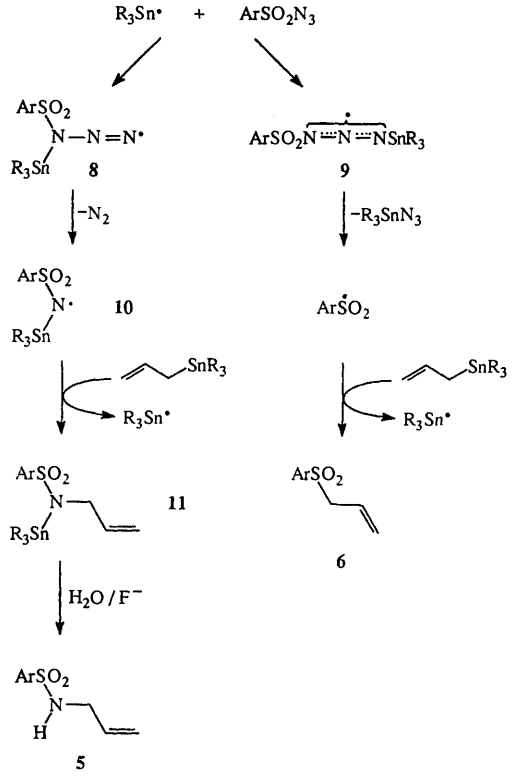
Reactions of sulfonyl azides

All reactions between sulfonyl azides and allylstannanes were carried out in refluxing benzene, under an atmosphere of nitrogen or argon, and were initiated by thermal decomposition of 2,2′-azobis(2-methylpropionitrile) (AIBN; 5 mol% based on sulfonyl azide). The reaction between benzenesulfonyl azide **3a** and two molar equivalents of allyltriphenylstannane (ATPS) **4** was carried out under these conditions for 3 h, after which the mixture was treated with saturated aqueous potassium fluoride. After removal of Ph_3SnF and a standard work-up, the crude product mixture was examined by ^1H NMR spectroscopy. No sulfonyl azide remained and the only detectable products were *N*-allylbenzenesulfonamide **5a** and allyl phenyl sulfone **6a**, together with a trace amount of benzenesulfonamide **7a** (see Scheme 2). The products were separated by flash chromatography on silica gel and their identities were confirmed by comparison with the authentic compounds. No reaction took place in the absence of AIBN and, in the presence of initiator, the reaction could be inhibited with the nitroxide 2,2,6,6-tetramethylpiperidine-*N*-oxyl (5 mol% based on sulfonyl azide), confirming the involvement of a free-radical chain mechanism. The proposed propagation sequence for the formation of the *N*- and *S*-allylation products is shown in Scheme 3 and involves competitive addition of the triphenylstannyl radical to N^a and to N^c of the azide, to give the 3,3-triazenyl radical **8** or the 1,3-triazenyl radical **9**, respectively. Loss of nitrogen from the triazenyl radical **8** gives the electrophilic *N*-stannylsulfonamidyl radical **10**, which then adds to the allylstannane, followed by β-scission of the adduct radical to give the *N*-allyl-*N*-stannylsulfonamide **11**, hydrolysis of which yields the allylsulfonamide **5**. Fragmentation of the 1,3-triazenyl radical **9** to give stannyl azide and an arenesulfonyl radical is followed by addition of the latter to the allylstannane [19] and β-scission of the adduct to give the allyl aryl sulfone **6**.

The reaction was repeated with the 4-substituted benzenesulfonyl azides **3b–d**, each of which was consumed completely under the reaction conditions, to give the corresponding *N*-allylarenesulfonamide **5b–d** and allyl aryl sulfone **6b–d**, along with small amounts of unsubstituted arenesulfonamide **7b–d**, as the only detectable products (see Scheme 2). The yields of



Scheme 2 *Reagents and conditions:* i, AIBN, benzene, reflux; ii, KF–H_2O



Scheme 3

the sulfonamides **7a–d** were determined by quantitative chromatographic isolation and, assuming that **5–7** are the only products deriving from the azides, the yields of *N*-allylarenesulfonamides **5a–d** and allyl arene sulfones **6a–d** were estimated from the ^1H NMR spectra of the crude reaction products. The reaction of 4-nitrobenzenesulfonyl azide **3e** proceeded only to a small extent and most of the original azide was recovered unchanged; a 15% yield of the *N*-allylarenesulfonamide **5e** was isolated by flash chromatography. The results are summarised in Table 1.

Broadly similar results were obtained when allyltrimethylstannane (ATMS) was used in place of ATPS under otherwise identical conditions. For each of the azides **3a–d** there was a

Table 1 Yields of products from the reactions of arenesulfonyl azides 4-$XC_6H_4SO_2N_3$ **3a–e** with allyltriorganostannanes $R_3SnCH_2CH{=}CH_2$

3	R (stannane)	Yield (%)[a] 5	6	7
a X = H	Ph	91	5	4
	Me	81	12	7
	Bu	6	30	64
b X = Me	Ph	89	8	3
	Me	83	11	6
	Bu	7	32	61
c X = MeO	Ph	86	10	4
	Me	82	14	4
	Bu	4	37	59
d X = F	Ph	83	12	5
	Me	72	20	8
	Bu	14	21	65
e X = NO_2	Ph	15	*b*	*b*
	Bu	*c*	*c*	*c*

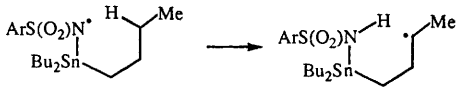
[a] Based on arenesulfonyl azide. [b] Only traces present. [c] No significant reaction.

modest decrease in the product ratio **5**:**6**, although the *N*-allylarenesulfonamide **5** was still by far the major product, on going from ATPS to ATMS and again small amounts of the arenesulfonamide **7** were obtained. Although the major fate of the *N*-stannylsulfonamidyl radical **10** is addition to the allylstannane (Scheme 3), it appears that **10** also abstracts hydrogen to a small extent to give the *N*-stannylsulfonamide **12** [eqn. (4)], which would yield **7** after treatment with aqueous

$$ArS(O_2)\dot{N}SnR_3 + H\text{–}Z \longrightarrow ArS(O_2)N(H)SnR_3 + Z^{\bullet} \quad (4)$$
12

fluoride. The most probable hydrogen-atom donor H–Z would appear to be ATPS or ATMS, since the allylic C–H bonds in these compounds will be relatively weak.

Very different results were obtained from the corresponding reactions of allyltributylstannane (ATBS) with sulfonyl azides. Compared with reactions involving ATPS or ATMS, the yields of the *N*-allylarenesulfonamides **5** are dramatically reduced, the yields of allyl aryl sulfones **6** (resulting from attack of the triorganostannyl radical at N^c) are increased, and there are large increases in the yields of the arenesulfonamides **7**. We propose that the increase in the yield of **7** at the expense of **5** arises because the intermediate *N*-stannylsulfonamidyl radical **10** now undergoes relatively rapid *intramolecular* 1,5-hydrogen-atom transfer, involving a butyl group attached to tin [eqn. (5)], to give the radical **13** which subsequently undergoes



(5)

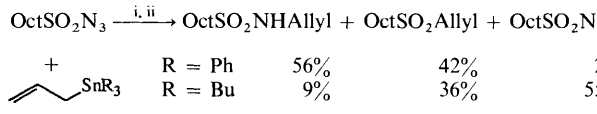
13

radical–radical reactions or allylation by ATBS to give an *N*-stannylsulfonamide and thence **7** after treatment with aqueous fluoride.

The rapidity of the inter- and intra-molecular reactions of the *N*-stannylsulfonamidyl radical **10** implies that this species is more reactive than an *N*-alkylsulfonamidyl radical.[20] This would parallel the increased reactivity of *N*-trialkylsilylaminyl radicals compared with the corresponding radicals containing *N*-alkyl groups.[21,22] For example, the reactivity of the bis(trimethylsilyl)aminyl radical $(Me_3Si)_2N^{\bullet}$ is much greater than that of $Me_2N^{\bullet}$ and more like that of an alkoxyl radical.[21]

Provided that only the reactions shown in Scheme 3 are involved and that reversibility of any addition process may be neglected, the yields of *N*-allylsulfonamide **5** and allyl aryl sulfone **6** will reflect directly the relative rates of addition of $R_3Sn^{\bullet}$ to N^a and N^c in the original sulfonyl azide. Inspection of Table 1 shows that, apart from 4-nitrobenzenesulfonyl azide which is unsatisfactory presumably because of interference by the nitrophenyl group with the propagation cycle, the electronic properties of the 4-substituent on the arenesulfonyl azide have little effect on the relative rates of attack of $R_3Sn^{\bullet}$ at N^a compared with N^c. Of the triorganostannyl radicals, the tendency to add to N^a (leading to *N*-allylation) decreases along the series $Ph_3Sn^{\bullet} > Me_3Sn^{\bullet} > Bu_3Sn^{\bullet}$, and the reaction of the crystalline 4-methylbenzenesulfonyl azide **3b** with ATPS would appear to be the most suitable system for preparative *N*-allylation.

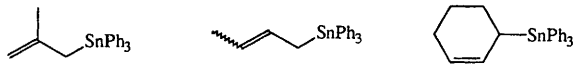
In order to compare the behaviour of an alkanesulfonyl azide, the reactions of octane-1-sulfonyl azide ($OctSO_2N_3$) with two molar equivalents of ATPS or ATBS were carried out under the same conditions; the results are summarised in Scheme 4.† The product yields indicate that both $Ph_3Sn^{\bullet}$ and



Scheme 4 *Reagents and conditions:* i, AIBN, benzene, reflux; ii, KF–H_2O

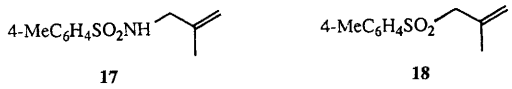
$Bu_3Sn^{\bullet}$ attack N^a and N^c at quite similar rates and thus the alkanesulfonyl azide is less suitable for selective *N*-allylation at nitrogen.

In order to explore the limitations of *N*-allylation using arenesulfonyl azides and allylstannanes, the reactions of 4-methylbenzenesulfonyl azide with the three allyltriphenylstannanes **14**–**16** were carried out under the standard conditions



14 **15** **16**

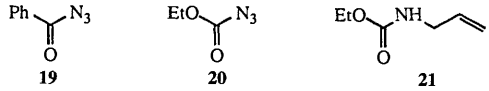
in refluxing benzene. Unfortunately, significant reaction took place with only the 2-methylallyl derivative **14**, indicating that a terminal double bond is necessary to achieve a sufficiently high rate of radical addition to the allylstannane to maintain the chain. With the allylstannane **14**, the azide was completely consumed and the *N*-2-methylallylsulfonamide **17** (86%) and the 2-methylallyl sulfone **18** (9%) were isolated by flash chromatography, together with a small amount of the sulfonamide **7b**.



17 **18**

Reactions of benzoyl azide and of ethyl azidoformate

The analogous reactions of benzoyl azide **19** and of ethyl azidoformate **20** with ATPS were also investigated under

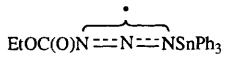


19 **20** **21**

similar conditions (2 molar equivalents of ATPS, AIBN initiator, refluxing benzene). Benzoyl azide gave mainly 1,3-

† The product yields were estimated as described for the arenesulfonyl azides.

diphenylurea after work-up, which presumably arises from hydrolysis of phenyl isocyanate, itself formed by thermally-induced Curtius rearrangement of the azide. Ethyl azidoformate, like the sulfonyl azides, does not undergo such rearrangement and ethyl *N*-allylcarbamate **21** was isolated in 45% yield from the reaction with ATPS (2.5 h reflux) after work-up with saturated aqueous potassium fluoride. However, *ca.* 50% of the azide remained unreacted and thus the reaction to give **21** is clean, but relatively slow. The allylcarbamate presumably arises by a route analogous to that shown in Scheme 3 for the formation of the *N*-allylsulfonamide **5** and involves attack of $Ph_3Sn^{\bullet}$ at N^a of the azido group. Competitive addition to N^c would give the 1,3-triazenyl radical **22** which



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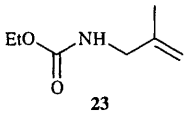

23

does not break down readily to give $EtO\dot{C}{=}O$, in contrast to the corresponding sulfonyl azide adduct **9** which readily loses $Ar\dot{S}O_2$. One probable fate of **22** is reversion to the azidoformate and $Ph_3Sn^{\bullet}$, but the triazenyl radical could also act as a scavenger for chain-carrying radicals, thereby inhibiting the formation of the *N*-allyl-*N*-stannylcarbamate and thus reducing the yield of **21**.

Under more forcing conditions (9 h total reaction time, with further additions of 3 mol% AIBN after 3 h and after 6 h), essentially all the azidoformate was consumed and the isolated yield of **21** increased to 74%. Under the same conditions, the reaction of ethyl azidoformate with the 2-methylallylstannane **14** afforded the *N*-allylic urethane **23** in an isolated yield of 78%. Since the free amine may be readily obtained by hydrolysis of such urethanes, the radical-chain reaction of allyltriphenylstannanes containing terminal double bonds with alkyl azidoformates could provide a useful synthetic route to allylic amines.

Experimental

NMR spectra were recorded using a Varian VXR-400 instrument (400 MHz for ^1H). The solvent was $CDCl_3$ and chemical shifts are reported relative to Me_4Si; *J* values are quoted in Hz. Column chomatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel 60 F_{254} aluminium-backed precoated plates, respectively. All manipulations and reactions of air-sensitive compounds were carried out under an atmosphere of dry argon or nitrogen and all extracts were dried over anhydrous $MgSO_4$. Petroleum refers to light petroleum (bp 40–60 °C).

Materials

Benzene was heated under reflux over metallic sodium, then distilled and stored over 4 Å molecular sieves under argon. AIBN (Merck-BDH) was recrystallised from dichloromethane–petroleum. Allyltributylstannane (ATBS) and allyltriphenylstannane (ATPS) (both Aldrich) were used as received. Allyltrimethylstannane (ATMS),[23] 2-methylallyltriphenylstannane[23] **14** and 1-triphenylstannylbut-2-ene[19] **15** (*cis* + *trans* mixture) were prepared by a modified Grignard method[23] and 3-triphenylstannylcyclohexene[23] **16** was prepared from 3-lithiocyclohexene, as described previously. Benzoyl azide[24] and ethyl azidoformate[25] [δ_H 1.30 (3 H, t, *J* 7.1) and 4.25 (2 H, q, *J* 7.1); δ_C 14.0, 64.5 and 157.5] were prepared by literature methods.

Sulfonyl azides

These were prepared in 87–96% yield by the reaction of the corresponding sulfonyl chloride (50 mmol) with sodium azide (55 mmol) in aqueous ethanol, following the standard procedure.[26]

Benzenesulfonyl azide[27] **3a.** Obtained as an oil which solidified on standing at 5 °C; δ_H 7.62 (2 H, m), 7.74 (1 H, m) and 7.96 (2 H, m); δ_C 127.4, 129.7, 134.8 and 138.4.

4-Methylbenzenesulfonyl azide[28] **3b.** Obtained as an oil which solidified on standing at 5 °C, mp 20 °C (lit.,[28] mp 19–20 °C); δ_H 2.48 (3 H, s), 7.42 (2 H, d, *J* 8.4) and 7.83 (2 H, d, *J* 8.4); δ_C 21.7, 127.4, 130.2, 135.3 and 146.2.

4-Methoxybenzenesulfonyl azide[29] **3c.** Recrystallised from CH_2Cl_2–petroleum, mp 54 °C (lit.,[29] mp 55 °C); δ_H 3.91 (3 H, s), 7.05 (2 H, d, *J* 9.0) and 7.90 (2 H, d, *J* 9.0); δ_C 55.8, 114.7, 114.9, 129.9 and 164.6.

4-Fluorobenzenesulfonyl azide[30] **3d.** Recrystallised from CH_2Cl_2–petroleum, mp 35–36 °C; δ_H 7.31 (2 H, dd, J_{HH} 8.45, J_{HF} 8.33) and 8.00 (2 H, dd, J_{HH} 8.45, J_{HF} 4.98); δ_C 117.1 (d, J_{CF} 23.0), 130.5 (d, J_{CF} 9.8), 134.4 (d, J_{CF} 3.1) and 166.3 (d, J_{CF} 257.2).

4-Nitrobenzenesulfonyl azide[31] **3e.** Recrystallised from CH_2Cl_2–petroleum as pale yellow needles, mp 101–102 °C (lit.,[31] mp 101.5–102 °C); δ_H 8.17 (2 H, m) and 8.46 (2 H, m); δ_C 124.9, 128.9, 143.7 and 151.2.

1-Octanesulfonyl azide. Prepared in 85% yield following the method used for the arenesulfonyl azides; it was an oil which solidified on standing at 5 °C; δ_H 0.88 (3 H, t, *J* 6.7), 1.31 (8 H, m), 1.45 (2 H, m), 1.91 (2 H, m) and 3.30 (2 H, m); δ_C 14.0, 22.5, 23.3, 27.9, 28.8(2), 28.8(4), 31.6 and 55.9 (Found: C, 43.8; H, 7.9; N, 19.2. $C_8H_{17}N_3O_2S$ requires C, 43.8; H, 7.8; N, 19.2%).

General procedure for reactions of sulfonyl azides with allyltriorganostannanes

A solution containing the sulfonyl azide (2.0 mmol), the allylstannane (4.0 mmol) and AIBN (17 mg, 0.10 mmol) in benzene (6 cm^3) was heated under reflux for 3 h under an atmosphere of argon. The reaction mixture was allowed to cool to room temperature, diluted with diethyl ether (15 cm^3) and shaken vigorously with saturated aqueous potassium fluoride (15 cm^3). The precipitate was removed by filtration and washed with diethyl ether. The organic layer was separated from the filtrate and the aqueous layer was extracted with diethyl ether (3 × 20 cm^3). The combined organic phase was washed with saturated brine, dried and the solvent removed under reduced pressure. The residue was examined by ^1H NMR spectroscopy to determine the relative yields of *N*-allylarenesulfonamide and allyl aryl sulfone, by integration of the characteristic signals from the allylic protons. The residue was subjected to flash chromatography, eluting successively with petroleum (to remove unreacted ATMS or ATBS) or petroleum–diethyl ether (10:1) (to remove ATPS), followed by petroleum–diethyl ether (5:1) to obtain the allylsulfonamides **5** and allyl aryl sulfones **6**, followed by petroleum–diethyl ether–CH_2Cl_2 (2:1:1) to obtain the sulfonamides **7**. The yields are given in Table 1 and the analytical data are given below.

***N*-Allylbenzenesulfonamide**[32] **5a.** A viscous oil; δ_H 3.60 (2 H, m), 4.81 (1 H, br t, *J ca.* 6, N*H*), 5.08 (1 H, dd, *J* 10.3, 1.2), 5.16 (1 H, dd, *J* 16.0, 1.2), 5.70 (1 H, ddt, *J* 16.0, 10.3, 6.1), 7.51 (2 H, m), 7.58 (1 H, m) and 7.88 (2 H, m); δ_C 45.7, 117.7, 127.0, 129.1, 132.7, 132.8 and 139.9.

***N*-Allyl-4-methylbenzenesulfonamide**[33] **5b.** Mp 63–65 °C (lit.,[33] mp 65–66 °C); δ_H 2.43 (3 H, s), 3.57 (2 H, m), 4.82 (1 H, br t, *J ca.* 6.1, N*H*), 5.08 (1 H, dd, *J* 10.3, 1.3), 5.16 (1 H, dd, *J* 17.1, 1.3), 5.70 (1 H, ddt, *J* 17.1, 10.3, 6.0), 7.30 (2 H, d, *J* 8.0) and 7.76 (2 H, d, *J* 8.0); δ_C 21.5, 45.7, 117.6, 127.1, 129.7, 132.9, 136.8 and 143.4.

***N*-Allyl-4-methoxybenzenesulfonamide**[34] **5c.** Mp 45 °C (lit.,[34] mp 45–47 °C); δ_H 3.56 (2 H, m), 3.86 (3 H, s), 4.71 (1 H, br t, *J ca.* 6, NH), 5.08 (1 H, dd, *J* 10.3, 2.3), 5.15 (1 H, dd, *J* 18.5, 2.3), 5.71 (1 H, ddt, *J* 18.5, 10.3, 5.9), 6.97 (2 H, d, *J* 9.0) and 7.80 (2 H, d, *J* 9.0); δ_C 45.7, 55.6, 114.2, 117.6, 129.2, 131.4, 133.0 and 162.9.

***N*-Allyl-4-fluorobenzenesulfonamide 5d.** Mp 53 °C; δ_H 3.60 (2 H, m), 4.73 (1 H, br t, *J ca.* 6, N*H*), 5.09 (1 H, dd, *J* 10.3, 1.2),

5.16 (1 H, dd, *J* 17.1, 1.2) and 5.70 (1 H, ddt, *J* 17.1, 10.3, 6.0); δ_C 45.7, 116.3 (d, J_{CF} 22.5), 117.9, 129.8 (d, J_{CF} 9.4), 132.7, 136.0 (d, J_{CF} 3.2) and 165.0 (d, J_{CF} 254.7) (Found: C, 50.2; H, 4.7; N, 6.5. $C_9H_{10}FNO_2S$ requires C, 50.2; H, 4.7; N, 6.5%).

***N*-Allyl-4-nitrobenzenesulfonamide**[35] **5e.** Mp 112–113 °C (lit.,[35] mp 113–113.5 °C); δ_H 3.70 (2 H, m), 4.75 (1 H, br t, *J ca.* 6, N*H*), 5.15 (1 H, dd, *J* 10.2, 1.1), 5.19 (1 H, dd, *J* 17.1, 1.1), 5.73 (1 H, ddt, *J* 17.1, 10.2, 6.7), 8.10 (2 H, m) and 8.45 (2 H, m); δ_C 45.9, 118.4, 124.5, 128.4, 132.4, 146.1 and 152.3.

***N*-Allyl-1-octanesulfonamide.** Mp 43 °C; δ_H 0.87 (3 H, t, *J* 7.1), 1.27 (8 H, m), 1.39 (2 H, m), 1.78 (2 H, m), 3.00 (2 H, m), 3.73 (2 H, m), 4.78 (1 H, br m, N*H*), 5.18 (1 H, dd, *J* 10.1, 1.1), 5.28 (1 H, dd, *J* 17.1, 1.1) and 5.85 (1 H, ddt, *J* 17.1, 10.1, 5.9); δ_C 14.0, 22.6, 23.6, 28.2, 28.9, 29.0, 31.7, 45.6, 53.2, 117.6 and 133.7 (Found: C, 56.6; H, 10.0; N, 6.0. $C_{11}H_{23}NO_2S$ requires C, 56.6; H, 9.9; N, 6.0%).

Allyl phenyl sulfone[36] **6a.** An oil; δ_H 3.80 (2 H, d, *J* 7.3), 5.13 (1 H, dd, *J* 17.0, 1.2), 5.32 (1 H, dd, *J* 10.1, 1.2), 5.78 (1 H, ddt, *J* 17.0, 10.1, 7.3), 7.55 (2 H, m), 7.65 (1 H, m) and 7.87 (2 H, m); δ_C 60.8, 121.4, 124.7, 128.4, 129.0, 133.7 and 137.0.

Allyl 4-methylphenyl sulfone[37] **6b.** Mp 59 °C (lit.,[37] mp 58 °C); δ_H 2.42 (3 H, s), 3.77 (2 H, d, *J* 7.4), 5.13 (1 H, dd, *J* 17.1, 1.0), 5.31 (1 H, dd, *J* 10.1, 1.0), 5.76 (1 H, ddt, *J* 17.1, 10.1, 7.4), 7.32 (2 H, d, *J* 8.4) and 7.72 (2 H, d, *J* 8.4); δ_C 21.6, 60.8, 124.6, 128.4, 129.4, 129.7, 135.2 and 144.7.

Allyl 4-methoxyphenyl sulfone[38] **6c.** An oil; δ_H 3.77 (2 H, d, *J* 7.4), 3.87 (3 H, s), 5.13 (1 H, dd, *J* 17.1, 1.1), 5.30 (1 H, dd, *J* 10.2, 1.1), 5.77 (1 H, ddt, *J* 17.1, 10.2, 7.4), 7.00 (2 H, d, *J* 8.9) and 7.77 (2 H, d, *J* 8.9); δ_C 55.6, 61.1, 114.2, 124.4, 124.9, 129.2, 130.6 and 163.7.

Allyl 4-fluorophenyl sulfone[39] **6d.** Mp 46 °C (lit.,[39] mp 47 °C); δ_H 3.81 (2 H, d, *J* 7.4), 5.15 (1 H, dd, *J* 17.1, 1.1), 5.35 (1 H, dd, *J* 10.1, 1.1), 5.79 (1 H, ddt, *J* 17.1, 10.0, 7.4), 7.23 (2 H, d, *J* 8.9, 8.4) and 7.89 (2 H, dd, *J* 8.9, 5.1); δ_C 61.0, 116.3 (d, J_{CF} 22.7), 124.7, 124.9, 131.3 (d, J_{CF} 9.6), 134.2 (d, J_{CF} 3.1) and 165.8 (d, J_{CF} 256.2).

Allyl oct-1-yl sulfone. An oil; δ_H 0.87 (3 H, t, *J* 6.6), 1.28 (8 H, m), 1.41 (2 H, m), 1.81 (2 H, m), 2.93 (2 H, m), 3.69 (2 H, d, *J* 7.4), 5.43 (1 H, dd, *J* 17.0, 1.0), 5.48 (1 H, dd, *J* 10.1, 1.0) and 5.93 (1 H, ddt, *J* 17.0, 10.1, 7.4); δ_C 14.0, 21.7, 22.5, 28.4, 28.9, 29.0, 31.7, 51.2, 57.6, 124.4 and 125.2 (Found: C, 60.6; H, 10.0. $C_{11}H_{22}O_2S$ requires C, 60.5; H, 10.2%).

Sulfonamides 7a–d. The melting points of the unsubstituted sulfonamides **7a–d** agreed with those given in the literature.[40] Benzenesulfonamide **7a**, mp 150–151 °C; 4-methylbenzenesulfonamide **7b**, mp 137–139 °C; 4-methoxybenzenesulfonamide **7c**, mp 110–112 °C and 4-fluorobenzenesulfonamide **7d**, mp 124–125 °C.

1-Octanesulfonamide. Mp 67–68 °C (lit.,[41] mp 68–69 °C).

***N*-(2-methylallyl)-4-methylbenzenesulfonamide**[42] **17.** Mp 49 °C (lit.,[42] mp 50–52 °C); δ_H 1.67 (3 H, s), 2.42 (3 H, s), 3.47 (2 H, d, *J* 6.5), 4.75 (1 H, br t, *J ca.* 6.5, N*H*), 4.81 (1 H, s), 4.85 (1 H, s), 7.72 (2 H, d, *J* 8.1) and 7.75 (2 H, d, *J* 8.1); δ_C 20.1, 21.5, 49.0, 112.7, 127.7, 130.0, 136.9, 140.5 and 143.4.

2-Methylallyl 4-methylphenyl sulfone[43] **18.** Mp 70–71 °C (lit.,[43] mp 70.5–71.5 °C); δ_H 1.85 (3 H, t, *J* 1.0), 2.44 (3 H, s), 3.73 (2 H, s), 4.68 (1 H, m), 5.02 (1 H, m), 7.33 (2 H, d, *J* 8.5) and 7.74 (2 H, d, *J* 8.5); δ_C 21.6, 22.7, 64.5, 120.6, 128.5, 129.6, 133.5, 135.4 and 144.6.

Reactions of ethyl azidoformate 20

A solution in benzene (6 cm^3) containing ethyl azidoformate (2 mmol), allyltriphenylstannane (4 mmol) and AIBN (0.1 mmol) was heated under reflux for 2.5 h, as described for the reactions of sulfonyl azides. After work-up as described before, ethyl *N*-allylcarbamate[44] **21** (45%) was obtained as an oil, together with unreacted azide (50%); δ_H 1.24 (3 H, t, *J* 7.0), 3.80 (2 H, br m), 4.12 (2 H, q, *J* 7.0), 4.79 (1 H, br s, N*H*), 5.12 (1 H, dd, *J* 10.3, 1.4), 5.18 (1 H, dd, *J* 17.2, 1.4) and 5.84 (1 H, ddt, *J* 17.2, 10.3, 6.8); δ_C 14.6, 43.3, 60.8, 115.8, 134.6 and 156.6.

When the reaction was repeated, but with an initial reflux time of 3 h, followed by addition of AIBN (0.06 mmol) and further heating for 3 h, then addition of more AIBN (0.06 mmol) and heating for an additional 3 h, the yield of urethane **21** was increased to 74%. Under these conditions, the reaction of ethyl azidoformate with 2-methylallyltriphenylstannane **14** afforded ethyl *N*-2-methylallylcarbamate[45] **23** in 78% yield; δ_H 1.21 (3 H, t, *J* 7.5), 1.70 (3 H, s), 3.68 (2 H, d, *J* 6.0), 4.09 (2 H, q, *J* 7.5) and 4.75–4.90 (3 H including NH, m); δ_C 14.7, 20.2, 46.6, 60.9, 110.6, 142.4 and 156.7.

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