Aziridination of *N*-sulfonylimines with a stabilized sulfonium ylide: simple preparation of *N*-sulfonyl-2-[(*E*)-2-(alkoxycarbonyl)ethenyl]-3-arylaziridines

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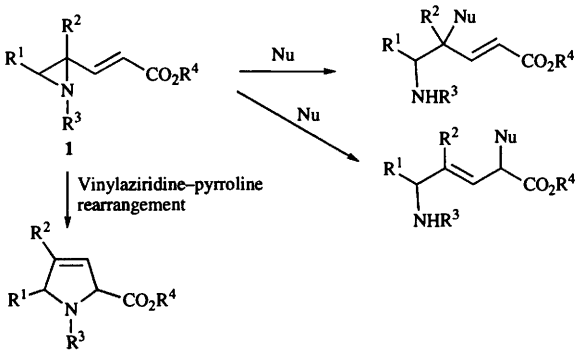
***N*-Sulfonyl-2-[(*E*)-2-(alkoxycarbonyl)ethenyl]-3-arylaziridines 1 are efficiently prepared either by the reaction of *N*-sulfonylimines 2 with 3-(alkoxycarbonyl)allyldimethylsulfonium bromide 3 in the presence of potassium carbonate in acetonitrile at room temperature or by the reaction of compounds 2 with preformed dimethylsulfonium 3-(alkoxycarbonyl)allylides 4 at −78 °C in moderate to good yields. The *cis*/*trans* value of the product ranged from 1/1 to 8/1.**

Introduction

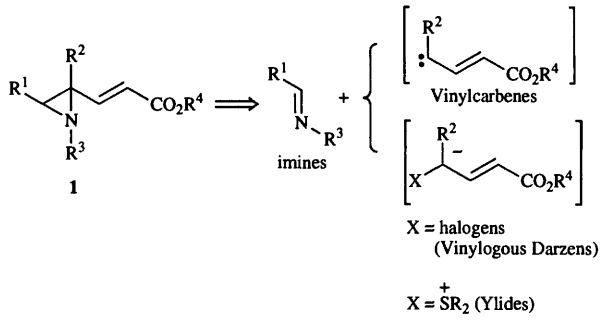
By various rearrangements[1] and ring-opening reactions,[2] β-aziridinyl-α,β-unsaturated esters **1** have found extensive applications in the synthesis of many biologically important substances, like pyrrolizidine alkaloids,[1,3] (*E*)-alkene dipeptide isosteres[2a,b,d] and α,β-unsaturated δ-amino esters or β,γ-unsaturated δ-amino esters[2c] (Scheme 1).



Scheme 1

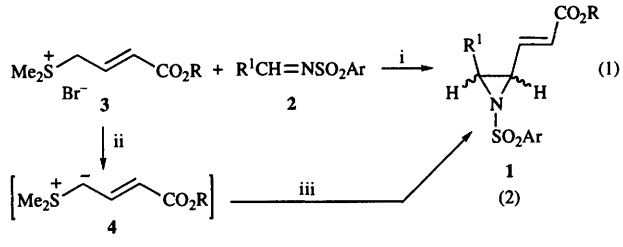
The recorded routes for the preparation of β-aziridinyl-α,β-unsaturated esters are chiefly by an intramolecular azide–diene cycloaddition[3] or from corresponding epoxides[2c] or aziridinyl esters[2a,b] *via* a multi-step sequence. It can be seen that, in the above methods, the preparation of precursors for further transformation to the desired unsaturated aziridinyl esters might suffer from the strict reaction conditions and low overall yields due to a long synthetic route, although these methods have been used for obtaining the said aziridines **1** in optically active form. By retrosynthetic analysis, compound **1** can be disconnected at the nitrogen-containing three-membered ring into an imine and a C_4-synthon, which may be a carbene, vinylogous Darzens reagent or an ylide (Scheme 2).

The carbene route has not been reported for this type of aziridine. We have tried a vinylogous Darzens reaction of various imines, including *N*-alklyl- or -aryl-imines and *N*-tosylimines, with methyl 4-bromocrotonate. Negative results were gained in all cases although such a reaction worked well with carbonyl compounds.[4] In our previous work to prepare vinylaziridines *via* an ylide route,[5] we found that, in contrast to *N*-alkyl- or *N*-aryl-imines, *N*-tosylimines react with a variety of semi-stabilized allylic sulfonium, telluronium and arsonium ylides to form vinylaziridines in high yields generally within



Scheme 2

several minutes under phase-transfer conditions. These results encouraged us to explore the possibility of preparing aziridine **1** by the reaction of *N*-tosylimines **2** with a stabilized allylic sulfonium ylide, dimethylsulfonium 3-(alkoxycarbonyl)allylides **4** (Scheme 3). Since stabilized sulfonium ylides and semi-



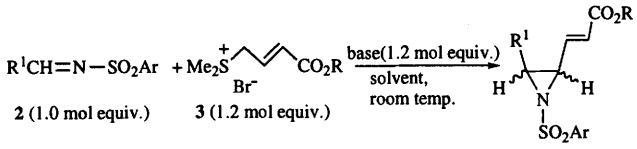
Scheme 3 *Reagents and conditions:* i, K_2CO_3, MeCN, room temp.; ii, $KN(SiMe_3)_2$, THF, −78 °C; iii, $R^1CH{=}NSO_2Ar$, −78 °C to room temp.

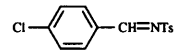
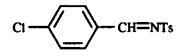
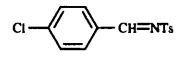
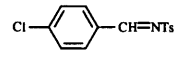
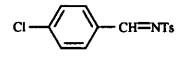
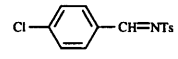
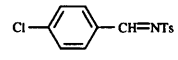
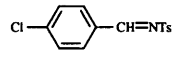
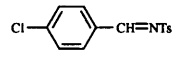
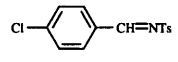
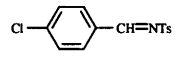
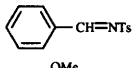
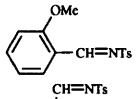
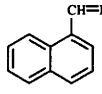
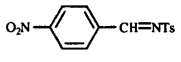
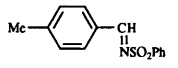
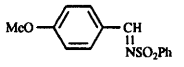
stabilized ones usually show very different reactivity in many reactions (for example, semi-stabilized allylic sulfonium ylides can react very efficiently with aldehydes to form epoxides under phase-transfer conditions,[6] but the stabilized ones cannot[7]) it will be very interesting to investigate the reaction of a stabilized sulfonium ylide with tosylated imines.

Results and discussion

When sulfonium salt **3**, *N*-sulfonylimines **2** and a base were mixed in acetonitrile, β-aziridinyl-α,β-unsaturated esters **1** were obtained in moderate yields after several minutes at room temperature through a reaction of *N*-tosylimines **2** and dimethylsulfonium 3-(alkoxycarbonyl)allylides **4**, generated *in situ* from

Table 1 Preparation of *N*-sulfonyl-2-[(*E*)-2-(alkoxycarbonyl)ethenyl]aziridines **1** by the reaction of *N*-sulfonylimines **2** and 3-(alkoxycarbonyl)-allyldimethylsulfonium bromide **3** under phase-transfer conditions[a]



Entry	Imine **2**	R	Base/solvent	Time (min)	Product (yield %)[b]	*trans*/*cis* **1**[c]
1		Et	K_2CO_3/CH_3CN	4	**1a** (48)	36/64
2		Et	K_2CO_3/THF	8	**1a** (29)	31/69
3		Et	K_2CO_3/CH_2Cl_2	12	**1a** (42)	31/69
4		Et	K_2CO_3/toluene	26	**1a** (7)	41/59
5		Et	KOH/CH_3CN	2	**1a** (40)	36/64
6		Et	$NaOH/CH_3CN$	2	**1a** (35)	42/58
7		Et	50% aq. $NaOH/CH_3CN$	3	**1a** (22)	42/58
8		Et	$KF{\cdot}Al_2O_3/CH_3CN$	4	**1a** (25)	36/64
9		Et	$LiOH{\cdot}H_2O/CH_3CN$	12	**1a** (46)	34/66
10		Et	NEt_3/CH_3CN	5	**1a** (22)	39/61
11		Me	K_2CO_3/CH_3CN	4	**1b** (42)	26/74
12		Me	K_2CO_3/CH_3CN	3	**1c** (45)	34/66
13		Me	K_2CO_3/CH_3CN	3	**1d** (52)	26/74
14		Me	K_2CO_3/CH_3CN	3	**1e** (40)	58/42
15		Me	K_2CO_3/CH_3CN	2	**1f** (35)	31/69
16		Me	K_2CO_3/CH_3CN	3	**1g** (49)	41/59
17		Me	K_2CO_3/CH_3CN	3	**1h** (50)	33/67

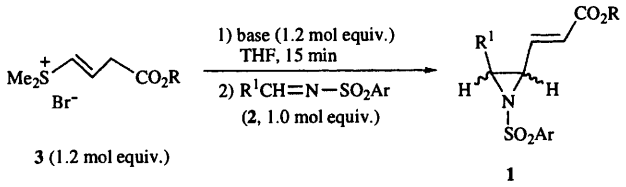
[a] All reactions were carried out with the proportions imine: sulfonium salt: base = 1 : 1.2 : 1.2 on a 0.5-mmol scale in a solvent at room temperature. [b] Isolated yields based on imine. [c] Determined by 300 MHz ^1H NMR analysis.

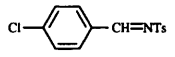
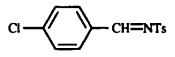
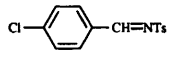
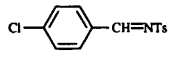
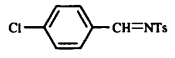
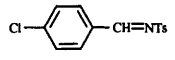
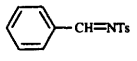
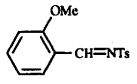
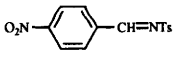
sulfonium salt **3** by a base. Some results are summarized in Table 1.

This reaction was complete generally within several minutes under such mild conditions. Among the solvents and bases examined for this reaction, acetonitrile was clearly the best solvent and potassium carbonate was the most suitable base. A variety of substituted *N*-tosylarylimines are useful for this reaction. In addition to the aziridine, aldehyde, the hydrolysed product, was usually found as a by-product. Although only moderate yields and a *trans*/*cis* value of 1 : 1–1 : 3 were achieved, this work may represent a direct entry of convenience to β-aziridinyl-α,β-unsaturated esters, a type of very useful intermediate for the synthesis of biologically important substances.

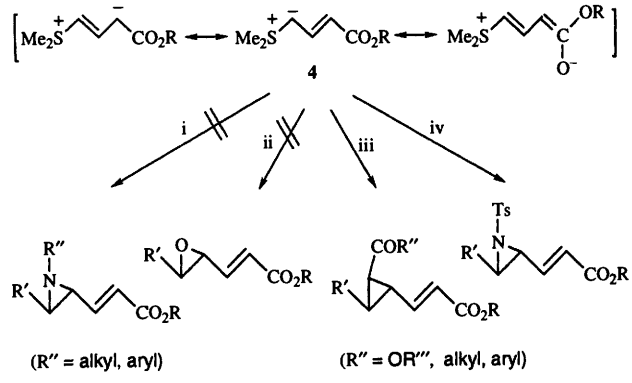
It should be pointed out that ylide **4** in Scheme 3 is a resonance-stabilized sulfonium ylide (Scheme 4). As stated before, it did not react with aldehydes to form epoxides, but react with Michael acceptors to furnish cyclopropanes.[7] It was reasonable that we found ylide **4** did also not react with *N*-alkyl- or -aryl-imines, which were commonly recognized to be less reactive than aldehydes. However, it was not true for *N*-tosylimines, which have been shown to be more reactive than aldehydes in our ylide aziridination reactions with semi-stable

Table 2 Preparation of *N*-sulfonyl-2-[(*E*)-2-(alkoxycarbonyl)ethenyl]aziridines **1** by the reaction of *N*-sulfonylimines **2** and preformed dimethylsulfonium 3-(alkoxycarbonyl)allylides **4**[a]



Entry	Imine **2**	R	Base	Temperature (°C)	Product (yield %)[b]	*trans*/*cis* **1**[c]
1		Et	NaH	20	**1a** (36)	43/57
2		Et	BuLi	−78	**1a** (34)	25/75
3		Et	$NaN(SiMe_3)_2$	−78	**1a** (32)	19/81
4		Et	$LiN(SiMe_3)_2$	−78	**1a** (15)	32/68
5		Et	Bu^{t}OK	−78	**1a** (47)	29/71
6		Et	$KN(SiMe_3)_2$	−78	**1a** (46)	17/83
7		Me	$KN(SiMe_3)_2$	−78	**1c** (62)	25/75
8		Me	$KN(SiMe_3)_2$	−78	**1d** (62)	11/89
9		Me	$KN(SiMe_3)_2$	−78	**1e** (58)	41/59
10		Me	$KN(SiMe_3)_2$	−78	**1f** (42)	26/74

[a] All reactions were carried out with the proportions imine: sulfonium salt: base = 1: 1.2: 1.2 on a 0.5-mmol scale in THF. [b] Isolated yields based on imine. [c] Determined by 300 MHz ^{1}H NMR analysis.



Scheme 4 *Reagents:* i, R′CH=NR″; ii, R′CHO; iii, R′–CH=CHCOR″; iv, R′CH=NTs

sulfonium allylides.[5] Such a result was also noted in a very recent work of Matano *et al.*[8] in the preparation of aziridinyl ketones with bismuthonium ylides.

It is noteworthy that the ylide aziridination has never been achieved with resonance-stabilized sulfonium ylides before.[9] In several reports on the reaction of stabilized sulfonium ylides and *N*-alkyl- or -aryl-imines, only enamines,[10a,b] cyclopropanes,[10b] or a more complex product[10c] were obtained. So, the present work may illustrate a successful example of the realization of aziridination with the resonance-stabilized sulfonium ylides.

Considering that good stereoselectivity was often achieved in a low-temperature reaction by changing the reaction conditions, the above phase-transfer aziridination was also carried out with preformed ylides at low temperature [equation (2) in Scheme 3 and Table 2]. As expected, both the yield and *trans*/*cis* value of the product were improved when $KN(SiMe_3)_2$ was used as the base to generate ylides (entries 1, 12–15 in Table 1 *vs.* 6–10 in Table 2). In some cases, the *cis*/*trans* value could reach 8/1 (entry 8 in Table 2). Further improvement of the *cis*/*trans* value of our products may be achieved by using a Pd-catalysed isomerization method.[11]

Experimental

All reagents and solvents, unless otherwise specified, were bought from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled immediately prior to use from sodium–benzophenone ketyl under nitrogen. Proton magnetic resonance spectra were recorded on a Bruker AMX-300 (300 MHz) spectrometer. *J* Values are in Hz. Mass spectra, including high-resolution mass measurements, were taken using HP5989A and Finnigan MAT mass spectrometers, respectively. *N*-Sulfonylimines **2**[12] and sulfonium salts **3** (ref. 7 for methyl ester and ref. 10*a* for ethyl ester) were prepared, according to literature methods, in reasonable yields.

General procedure for phase-transfer reactions

Imine (**2**, 1.0 mol equiv.), sulfonium salt (**3**, 1.2 mol equiv.) and anhydrous K_2CO_3 (1.2 mol equiv.) were sequentially added to stirred acetonitrile (4 cm^3, reagent grade, need not be dried

before use). After the reaction was complete, the reaction mixture was filtered on a short silica gel column to remove inorganic salts. The filtrate was concentrated, and chromatographed on a silica gel column with a mixture of light petroleum (60–90 °C) *and* ethyl acetate (4 : 1) as the eluent to give pure product **1** as a *cis*/*trans* mixture.

Ethyl (2*E*)-5-(4-chlorophenyl)-4,5-[(4-methylphenyl)sulfonylimino]pent-2-enoate 1a. *cis*-**1a**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.20 (3 H, t, *J* 7.1, CH_2CH_3), 2.43 (3 H, s, $ArCH_3$), 3.70 (1 H, dd, *J* 7.5 and 7.4, C*H*-CH), 4.05 (2 H, q, *J* 7.0, CH_2CH_3), 4.14 (1 H, d, *J* 6.8, CH-C*H*), 6.09 (1 H, d, *J* 15.7, =$CHCO_2$), 6.30 (1 H, dd, *J* 7.6 and 15.6, CHC*H*=), 7.10–7.36 (6 H, m, ArH) and 7.87 (2 H, d, *J* 8.2, ArH); *m/z* (EI) 250.0669 (M^+ − Ts. $C_{13}H_{13}ClNO_2$ requires *m/z*, 250.0635), 405 (M^+, 0.5%), 360 (1.5), 334 (2.4), 332 (6), 252 (39), 250 (100), 224 (5.2), 222 (16.5), 204 (13), 178 (15), 155 (7.5), 139 (46), 125 (6), 115 (13), 91 (25), 89 (14), 85 (23), 77 (3.4), 65 (10.4) and 47 (5.7). *trans*-**1a**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.31 (3 H, t, *J* 7.2, CH_2CH_3), 2.40 (3 H, s, $ArCH_3$), 3.32 (1 H, dd, *J* 3.8 and 10.2, C*H*-CH), 4.12 (1 H, d, *J* 3.4, CH-C*H*), 4.22 (2 H, q, *J* 7.1, CH_2CH_3), 6.21 (1 H, d, *J* 15.5, =$CHCO_2$), 7.11–7.36 (7 H, m, ArH + CHC*H*=) and 7.83 (2 H, dd, *J* 6.8 and 1.4, ArH).

Methyl (2*E*)-5-(4-chlorophenyl)-4,5-[(4-methylphenyl)sulfonylimino]pent-2-enoate 1b. *cis*-**1b**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.45 (3 H, s, $ArCH_3$), 3.64 (3 H, s, CO_2CH_3), 3.69 (1 H, dd, *J* 7.4 and 7.4, C*H*-CH), 4.14 (1 H, d, *J* 7.2, CH-C*H*), 6.08 (1 H, d, *J* 15.6, =$CHCO_2$), 6.30 (1 H, dd, *J* 7.6 and 15.7, CHC*H*=), 7.10–7.37 (6 H, m, ArH) and 7.87 (2 H, dd, *J* 8.5 and 1.8, ArH); *m/z* (EI) 236.0492 (M^+ − Ts. $C_{12}H_{11}ClNO_2$ requires *m/z*, 236.0478), 391 (M^+, 0.54%), 332 (6.8), 280 (2.7), 238 (35.3), 236 (100), 208 (10.8), 178 (3), 155 (1.8), 139 (1.5), 111 (0.7), 91 (4), 73 (30.8), 57 (1.1) and 44 (2.3). *trans*-**1b**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.41 (3 H, s, $ArCH_3$), 3.30 (1 H, dd, *J* 3.8 and 10.2, C*H*-CH), 3.78 (3 H, s, CO_2CH_3), 4.11 (1 H, d, *J* 3.7, CH-C*H*), 6.21 (1 H, d, *J* 15.6, =$CHCO_2$), 7.10–7.37 (7 H, m, ArH + CHC*H*=) and 7.82 (2 H, d, *J* 8.3, ArH).

Methyl (2*E*)-4,5-[(4-methylphenyl)sulfonylimino]-5-phenylpent-2-enoate 1c. *cis*-**1c**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.44 (3 H, s, $ArCH_3$), 3.62 (3 H, s, CO_2CH_3), 3.68 (1 H, dd, *J* 7.4 and 7.4, C*H*-CH), 4.18 (1 H, d, *J* 7.2, CH-C*H*), 6.08 (1 H, d, *J* 15.8, =$CHCO_2$), 6.34 (1 H, dd, *J* 7.7 and 15.7, CHC*H*=), 7.16–7.36 (7 H, m, ArH) and 7.88 (2 H, d, *J* 8.3, ArH); *m/z* (EI) 357.1027 (M^+. $C_{19}H_{19}NO_4S$ requires M, 357.1035), 358 (M^+ + 1, 3%), 357 (M^+, 0.8), 326 (2.3), 298 (3.7), 280 (1), 260 (0.8), 202 (100), 174 (36), 170 (12), 155 (5), 143 (11.8), 128 (1.5), 115 (17), 104 (8.8), 91 (20.4), 77 (3.8), 65 (8.7) and 51 (2.4). *trans*-**1c**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.40 (3 H, s, $ArCH_3$), 3.33 (1 H, dd, *J* 3.9 and 10.1, C*H*-CH), 3.78 (3 H, s, CO_2CH_3), 4.14 (1 H, d, *J* 3.8, CH-C*H*), 6.20 (1 H, d, *J* 15.6, =$CHCO_2$), 7.16–7.36 (8 H, m, ArH + CHC*H*=) and 7.84 (2 H, d, *J* 8.3, ArH).

Methyl (2*E*)-5-(2-methoxyphenyl)-4,5-[(4-methylphenyl)sulfonylimino]pent-2-enoate 1d. *cis*-**1d**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.44 (3 H, s, $ArCH_3$), 3.62 (3 H, s, CO_2CH_3), 3.72 (1 H, dd, *J* 7.0 and 7.7, C*H*-CH), 3.78 (3 H, s, OCH_3), 4.29 (1 H, d, *J* 7.3, CH-C*H*), 6.03 (1 H, d, *J* 15.2, =$CHCO_2$), 6.31 (1 H, dd, *J* 7.5 and 15.7, CHC*H*=), 6.80 (1 H, d, *J* 7.0, ArH), 6.85 (1 H, m, ArH), 7.12 (1 H, dd, *J* 7.5 and 1.5, ArH), 7.20–7.38 (3 H, m, ArH) and 7.89 (2 H, dd, *J* 1.9 and 8.7, ArH); *m/z* (EI) 387.1153 (M^+. $C_{20}H_{21}NO_5S$ requires M, 387.1140), 387 (M^+, 0.5), 356 (0.7), 328 (0.3), 291 (0.7), 232 (100), 204 (29.6), 185 (12), 172 (15), 145 (11), 134 (16), 107 (11), 91 (60), 77 (14), 65 (24), 59 (8) and 51 (9) (Found: C, 61.9; H, 5.5; N, 3.9. $C_{20}H_{21}NO_5S$ requires C, 62.00; H, 5.46; N, 3.62%). *trans*-**1d**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.42 (3 H, s, $ArCH_3$), 3.27 (1 H, dd, *J* 4.0 and 7.5, C*H*-CH), 3.62 (3 H, s, CO_2CH_3), 3.80 (3 H, s, OCH_3), 4.42 (1 H, d, *J* 3.9, CH-C*H*), 6.20 (1 H, d, *J* 15.6, =$CHCO_2$), 6.94 (1 H, d, *J* 7.7, ArH), 7.20–7.38 (6 H, m, ArH + CHC*H*=) and 7.86 (2 H, dd, *J* 1.5 and 9.8, ArH).

Methyl (2*E*)-4,5-[(4-methylphenyl)sulfonylimino]-5-(1-naphthyl)pent-2-enoate 1e. *cis*-**1e**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.45 (3 H, s, $ArCH_3$), 3.49 (3 H, s, CO_2CH_3), 3.94 (1 H, dd, *J* 7.3 and 7.3, C*H*-CH), 4.62 (1 H, d, *J* 7.1, CH-C*H*), 6.06 (1 H, d, *J* 15.7, =$CHCO_2$), 6.20 (1 H, dd, *J* 7.6 and 15.8, CHC*H*=), 7.26–7.39 (5 H, m, ArH), 7.48–7.56 (3 H, m, ArH), 7.77 (1 H, d, *J* 7.8, ArH) and 7.95 (2 H, m, ArH); *m/z* (EI) 407.1218 (M^+. $C_{23}H_{21}NO_4S$ requires M, 407.1191), 407 (M^+, 2.6%), 348 (4.5), 311 (3.6), 252 (100), 220 (54), 192 (69), 180 (4.5), 165 (55), 154 (38.5), 139 (35), 127 (21), 115 (8), 99 (5), 91 (60), 77 (12), 65 (30) and 44 (26) (Found: C, 67.9; H, 5.2; N, 3.6. $C_{23}H_{21}NO_4S$ requires C, 67.79; H, 5.19; N, 3.44%). *trans*-**1e**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.41 (3 H, s, $ArCH_3$), 3.35 (1 H, dd, *J* 4.1 and 10.3, C*H*-CH), 3.83 (3 H, s, CO_2CH_3), 4.69 (1 H, d, *J* 4.0, CH-C*H*), 6.26 (1 H, d, *J* 15.5, =$CHCO_2$), 7.26–7.39 (6 H, m, ArH + CHC*H*=), 7.48–7.56 (3 H, m, ArH), 7.86 (1 H, m, ArH) and 7.91 (2 H, m, ArH).

Methyl (2*E*)-4,5-[(4-methylphenyl)sulfonylimino]-5-(4-nitrophenyl)pent-2-enoate 1f. *cis*-**1f**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.46 (3 H, s, $ArCH_3$), 3.63 (3 H, s, CO_2CH_3), 3.74 (1 H, dd, *J* 7.2 and 7.8, C*H*-CH), 4.22 (1 H, d, *J* 7.5, CH-C*H*), 6.07 (1 H, d, *J* 15.8, =$CHCO_2$), 6.26 (1 H, dd, *J* 7.5 and 15.5, CHC*H*=), 7.24–7.42 (4 H, m, ArH), 7.88 (2 H, d, *J* 8.1, ArH) and 8.15 (2 H, d, *J* 8.5, ArH); *m/z* (EI) 402.0894 (M^+. $C_{19}H_{18}N_2O_6S$ requires M, 402.0886), 403 (M^+ + 1, 0.5%), 402 (M^+, 1.7), 343 (15.6), 247 (74), 219 (55), 215 (15), 187 (8), 169 (12), 155 (33), 139 (20), 130 (7.1), 115 (22.6), 103 (11), 91 (100), 77 (18), 71 (21), 65 (49), 51 (13.5) and 44 (10.5). *trans*-**1f**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.42 (3 H, s, $ArCH_3$), 3.32 (1 H, dd, *J* 3.6 and 10.1, C*H*-CH), 3.79 (3 H, s, CO_2CH_3), 4.20 (1 H, d, *J* 3.6, CH-C*H*), 6.22 (1 H, d, *J* 15.4, =$CHCO_2$), 7.24–7.42 (5 H, m, ArH + CHC*H*=), 7.83 (2 H, d, *J* 8.3, ArH) and 8.15 (2 H, d, *J* 8.5, ArH).

Methyl (2*E*)-5-(4-methylphenyl)-4,5-phenylsulfonyliminopent-2-enoate 1g. *cis*-**1g**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.30 (3 H, s, $ArCH_3$), 3.66 (3 H, s, CO_2CH_3), 3.69 (1 H, dd, *J* 7.6 and 7.4, C*H*-CH), 4.17 (1 H, d, *J* 7.2, CH-C*H*), 6.08 (1 H, d, *J* 15.7, =$CHCO_2$), 6.36 (1 H, dd, *J* 7.7 and 15.7, CHC*H*=), 7.03–7.11 (3 H, m, ArH), 7.25–7.33 (1 H, m, ArH), 7.46–7.65 (3 H, m, ArH) and 7.99 (2 H, dd, *J* 7.9 and 1.5, ArH); *m/z* (EI) 357.1035 (M^+. $C_{19}H_{19}NO_4S$ requires M, 357.1035), 357 (M^+, 0.7%), 326 (1.0), 298 (4.7), 266 (2), 216 (100), 188 (38), 184 (21), 156 (28), 141 (8), 129 (19), 118 (26), 103 (8.4), 91 (8.7), 77 (40), 71 (11), 59 (8), 51 (13) and 43 (4). *trans*-**1g**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.17 (3 H, s, $ArCH_3$), 3.35 (1 H, dd, *J* 3.9 and 10.1, C*H*-CH), 3.78 (3 H, s, =$CHCO_2$), 4.12 (1 H, d, *J* 3.9, CH-C*H*), 6.20 (1 H, d, *J* 15.5, =$CHCO_2$), 7.03–7.11 (4 H, m, ArH + CHC*H*=), 7.25–7.33 (1 H, m, ArH), 7.46–7.65 (3 H, m, ArH) and 7.95 (2 H, dd, *J* 9.0 and 1.2, ArH).

Methyl (2*E*)-5-(4-methoxyphenyl)-4,5-phenylsulfonyliminopent-2-enoate 1h. *cis*-**1h**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.64 (3 H, s, CO_2CH_3), 3.69 (1 H, dd, *J* 7.1 and 7.5, C*H*-CH), 3.76 (3 H, s, OCH_3), 4.16 (1 H, d, *J* 7.1, CH-C*H*), 6.07 (1 H, d, *J* 15.8, =$CHCO_2$), 6.36 (1 H, dd, *J* 7.7 and 15.5, CHC*H*=), 6.77–6.82 (1 H, m, ArH), 7.08–7.13 (2 H, m, ArH), 7.47–7.66 (4 H, m, ArH) and 8.00 (2 H, dd, *J* 7.4 and 1.2, ArH); *m/z* (EI) 373.0990 (M^+. $C_{19}H_{19}NO_5S$ requires M, 373.0984), 374 (M^+ + 1, 4.5%), 373 (M^+, 11.8), 314 (11.7), 276 (3.4), 250 (12.3), 231 (49), 216 (6), 200 (47), 185 (10), 173 (17), 158 (13), 141 (21), 135 (21), 125 (35), 109 (26), 97 (11), 77 (100), 69 (7), 65 (21) and 51 (42). *trans*-**1h**: δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.35 (1 H, dd, *J* 3.87 and 10.10, C*H*-CH), 3.64 (3 H, s, CO_2CH_3), 3.78 (3 H, s, OCH_3), 4.11 (1 H, d, *J* 3.9, CH-C*H*), 6.20 (1 H, d, *J* 15.5, =$CHCO_2$), 6.77–6.82 (2 H, m, ArH + CHC*H*=), 7.08–7.13 (2 H, m, ArH), 7.47–7.66 (4 H, m, ArH) and 7.95 (2 H, dd, *J* 8.6 and 1.1, ArH).

General procedure for low-temperature reactions

A solution of $KN(SiMe_3)_2$ (1.2 mol equiv.) in THF was introduced through a syringe into a suspension of sulfonium salt (**3**, 1.2 mol equiv.) in THF (5 cm^3) at −78 °C under N_2. After stirring of this mixture for 15 min, a solution of imine (**2**, 1.0 mol equiv.) in THF (3 cm^3) was added and the mixture was allowed to warm to room temperature within 2–3 h. After the reaction

was complete (TLC) the reaction mixture was filtered on a short silica gel column to remove inorganic salts and to destroy the active species. The filtrate was concentrated and chromatographed on a silica gel column with a mixture of light petroleum and ethyl acetate (4 : 1) as eluent to give pure produce **1** as a *cis*/*trans* mixture.

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