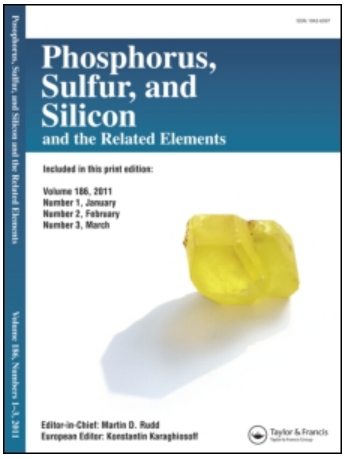

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A PETERSON OLEFINATION REACTION USING SILYL-SUBSTITUTED SULFONAMIDE CARBANIONS. SYNTHESIS OF VINYLIC SULFONAMIDES

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A PETERSON OLEFINATION REACTION USING SILYL-SUBSTITUTED SULFONAMIDE CARBANIONS. SYNTHESIS OF VINYLIC SULFONAMIDES

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α-Trimethylsilyl-substituted sulfonamides $RCH(SiMe_3)SO_2N(CH_3)_2$ (**3**), (R=H, CH_3 and C_6H_5) are synthetized in almost quantitative yields. Their lithium derivatives **4** undergo a smooth Peterson olefination reaction with nonenolisable carbonyl compounds to give good to excellent yields of vinylsulfonamides **6**. With R=H, the reaction is highly *E*-stereoselective. Moderate stereoselectivity is obtained in the cases of $R=CH_3$ and $R=C_6H_5$.

Key words: Peterson olefination reaction; *N,N*-dimethyl α-trimethylsilylsulfonamides; α-trimethylsilyl-substituted sulfonamide carbanions; vinylic sulfonamides; stereochemistry.

INTRODUCTION

α-Silyl-substituted carbanions have been found to be effective reagents in the conversion of carbonyl compounds to functionalized alkenes. This very useful alternative to the Wittig reaction, known after its discoverer[1] as Peterson reaction or Peterson olefination,[2] has been used to prepare a wide variety of α,β-unsaturated compounds such as, carboxylic acids,[3] esters,[4–8] lactams,[9] aldehydes,[10,11] amides,[9,12,13] ethers,[14,15] nitriles,[16,17] oximes,[18] phosphonates,[19] phosphinesulfides,[1] sulfides,[1,19,20] sulfoxides,[21] sulfones,[22,23,24] thiol esters[25] etc.

We report here our studies on the interaction of carbanions of *N,N*-dimethyl α-trimethylsilylsulfonamides with carbonyl compounds yielding a series of substituted vinylsulfonamides.

RESULTS AND DISCUSSION

N,N-Dimethyl α-trimethylsilylsulfonamides **3a–c** are prepared by deprotonation of sulfonamides **1a–c** and reaction of the carbanions formed with trimethylsilyl chloride according to Equation 1, Scheme 1. As silicon stabilizes adjacent carbon-metal bonds,[26] the ease of metallation of **3** increases with respect to sulfonamide **1**. The exchange reaction (Equation 2, Scheme 1) is rapid enough to compete with

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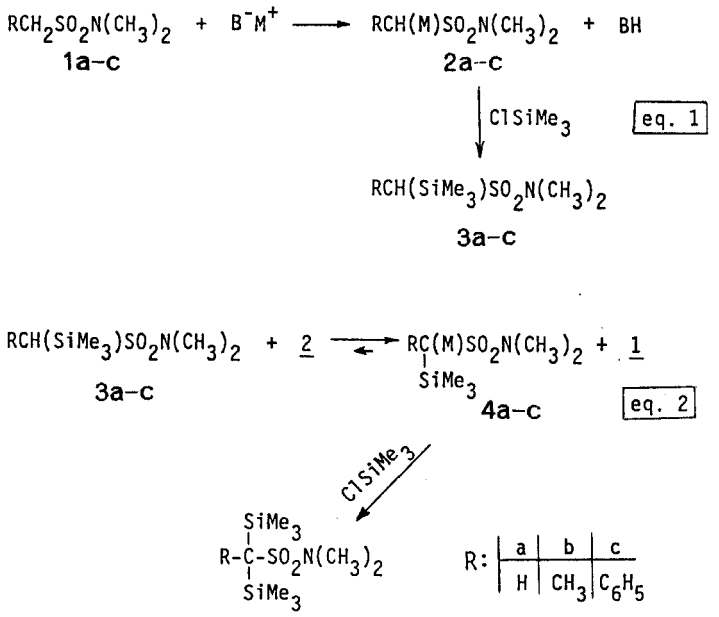


SCHEME 1

the formation of the desired compound **3** contaminating it by the starting sulfonamide **1** and its *bis*(trimethylsilyl) derivative. Two deprotonating agents, lithium diisopropylamide and sodium bis(trimethylsilyl)amide, and different reaction temperatures, solvents and concentrations are checked in order to avoid this competitive reaction. It is essential to minimize the coexistence time of the carbanion **2** and the trimethylsilyl-sulfonamide **3**, creating conditions for an instantaneous and complete reaction of **2** with Me_3SiCl.

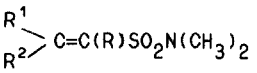
At sufficiently low temperature lithium and sodium derivatives **2** do not react noticeably with Me_3SiCl.[27] Pure **3a–c** can be obtained in almost quantitative (94–97%) yields if under these conditions Me_3SiCl is added at once under good mechanical stirring to **2** and if then the reaction mixture is rapidly warmed up to room temperature (see experimental section).

The structures of the previously unknown compounds **3a–c** are confirmed by microanalytical and spectroscopic data (Table II). The α-trimethylsilylsulfonamides proved to be rather inert towards carbonyl compounds. For example, no addition of **3a** to benzaldehyde is observed in the presence of $TiCl_4$ in CH_2Cl_2 at $-78°C$, or with TBAF in THF for 24 h at room temperature. In both cases the α-trimethylsilylsulfonamide **3a** is recovered quantitatively. On the contrary, as compounds **3** can be readily metallated, they could be utilized in a Peterson olefination reaction.

In order to outline the scope and limitations of the Peterson reaction of sulfonamides we studied the interaction of lithium derivatives of *N,N*-dimethylamides of three α-trimethylsilyl-substituted sulfonic acids, **3** (R=H, CH_3 and C_6H_5), with a number of aldehydes and two ketones of different nature and steric requirements (Table I).

TABLE I

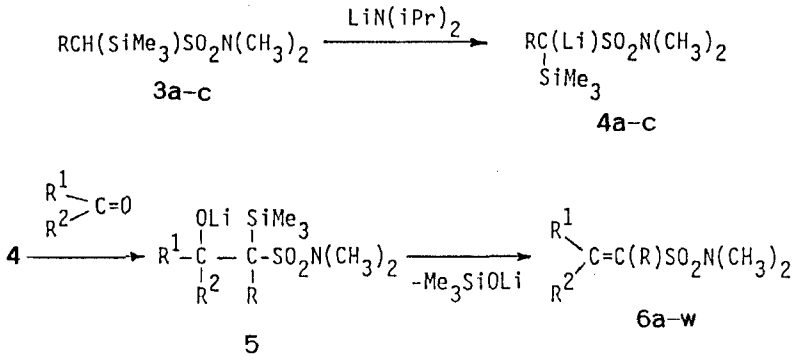
Preparation of *N,N*-Dimethyl vinylsulfonamides **6**



Entry	6	R	Compound R^1	R^2	Yield (%)	*E/Z* (*EE/ZE*)*	Reaction conditions**
1	**a**	H	C_6H_5	H	86	100,-	A
2	**a**	H	C_6H_5	H	84	82/18	B
3	**b**	H	2-$CH_3C_6H_4$	H	91	95/5	A
4	**c**	H	4-$CH_3C_6H_4$	H	88	100,-	A
5	**d**	H	4-CH_3O-C_6H_4	H	94	100,-	A
6	**e**	H	3,4-$(CH_3O)_2C_6H_3$	H	95	98/2	A
7	**f**	H	3,4-(-OCH_2O-)C_6H_3	H	83	100,-	A
8	**g**	H	3-ClC_6H_4	H	81	100,-	A
9	**h**	H	4-ClC_6H_4	H	81	100,-	A
10	**i**	H	4-BrC_6H_4	H	80	100,-	A
11	**j**	H	4-NCC_6H_4	H	87	90/10	A
12	**k**	H	4-$O_2NC_6H_4$	H	70	80/20	C
13	**l**	H	1-naphthyl	H	85	100,-	A
14	**m**	H	2-furyl	H	78	88/12	D
15	**n**	H	*E*-C_6H_5CH=CH	H	85	76/24*	A
16	**o**	H	$(CH_3)_3C$	H	70	100,-	A
17	**o**	H	$(CH_3)_3C$	H	90	80/20	B
18	**p**	H	$(CH_3)_2CH$	H	40	60/40	A
19	**q**	H	C_6H_5	C_6H_5	87	-	A
20	**r**	CH_3	C_6H_5	H	83	33/67	A
21	**s**	CH_3	4-$CH_3OC_6H_4$	H	71	40/60	A
22	**t**	CH_3	*E*-C_6H_5CH=CH	H	75	15/85*	A
23	**u**	C_6H_5	C_6H_5	H	74	80/20	B
24	**v**	C_6H_5	4-$CH_3OC_6H_4$	H	68	75/25	E
25	**w**	C_6H_5	*E*-C_6H_5CH=CH	H	68	40/60*	B

** In all cases one equiv. of R^1COR^2 is added to **4** at -60°C then the reaction mixture is stirred at the corresponding temperature: A: ether, 24 h, reflux; B: THF, 24 h, r.t.; C: ether+20% THF,24 h reflux; D: ether, 24 h, r.t.; E:THF, 48 h, from -50° to -30°C.

The lithium reagents **4a–c** are easily prepared by metallation of **3a–c** with LDA in ether or THF, then allowed to react with carbonyl compounds to yield the corresponding vinylic sulfonamides **6** (Scheme 2). The reaction conditions (Table I) are chosen on the basis of a more detailed study of the reaction of the lithium reagent of **3a** with two aldehydes-benzaldehyde and pivalaldehyde. The addition reaction (aldol step) is very rapid in both ether and THF even at low temperature, but the second step, the β-elimination of the elements of lithium trimethylsilanoxide, needs much longer time. The elimination reaction is faster in THF, because



SCHEME 2

THF has greater solvation ability than ether and therefore the oxygen-lithium bond is more polarized, then in ether. So, in THF the elimination step is complete after 24 h at room temperature, whereas in ether the desired product **6** is obtained after the same reaction time as a mixture with certain amounts of β-hydroxy-α-trimethylsilyl sulfonamide. When the elimination is carried out in ether under reflux for 24 h, only traces or none of β-hydroxy-α-trimethylsilyl sulfonamide is found in the crude reaction product.

In general, the Peterson reaction has a relatively low stereoselectivity.[2b] For instance, mixtures of equal amounts of *E*- and *Z*-isomers are obtained in the reaction of carbanions of α-trimethylsilyl-substituted methane,[1,28] acetic acid[3a] or its trimethylsilylester,[3b] propionitriles,[16] aldimines,[10] phenylsulfinylmethane[21] and phenylmethylsulfone[23] with carbonyl compounds. The reactions of lithium *bis*(trimethylsilyl)methane[29] and the Reformatsky reagent of α-trimethylsilyl-acetonitrile[17] are fairly stereoselective, and with lithium ethyl α-trimethylsilyl-acetate[7,30] the stereoselectivity is dependent on the reaction conditions. High stereoselectivity has been reported for the synthesis of vinyl thiol esters.[25]

Our studies show temperature-independent stereochemical results in THF, both with PhCHO and *t*-BuCHO—the addition step carried out at −10° or at −60°C (entries 2 and 17, Table I) always results in the same *E*/*Z*-ratio—82/18 for the benzaldehyde and 80/20 for the pivalaldehyde. On the contrary, in ether the stereochemistry of the products depends on the reaction temperature of the aldol step: a ratio of 87/13 for **6** is obtained when PhCHO or *t*-BuCHO is added to **4a** at −10°C, but at −60°C the *E*-isomers are formed exclusively (entries 1 and 16). In order to obtain better stereoselectivity in the preparation of **6** we adopted, in most cases presented in Table I, the following reaction conditions: ether as a solvent, addition of the carbonyl compound to **4** at −60°C followed by reflux of the reaction mixture, under stirring, for 24 h. Different reaction conditions will be explained specifically. So a series of α,β-unsaturated sulfonamides **6** are prepared, most of these not previously described.

As can be seen from Table I excellent yields are obtained with R=H or CH_3. The yields are moderate with R=Ph (*vide infra*).

Only 40% of the desired vinylsulfonamide **6p** (entry 18) is obtained from *iso*-butyraldehyde and **4a** due to competing abstraction by the **4a** acting as a base, of an α-hydrogen from this enolisable aldehyde. **6p** was isolated, as a mixture of geometrical isomers E/Z = 60/40, by means of preparative TLC. Attempts to carry out the reaction with acetophenone failed. Due to the fact that steric constraints are more important in the case of ketones as compared to aldehydes it is not surprising that in this case only enolisation occurs; to the contrary, 87% of the desired product is obtained with nonenolisable benzophenone (entry 19). Although the Peterson reaction is usually applicable to enolisable carbonyl compounds (see for example Reference 3a, 4, 5, 16, 23, 31). Some results similar to ours have been described in the literature. Thus, low yields are obtained with enolisable aldehydes: 30% with butyraldehyde and *bis*(trimethylsilyl)methyllithium,[29] 25% with *iso*-butyraldehyde and 1-trimethylsilyl-1-(phenylsulphinyl)methyllithium.[21] A failure of the reaction of lithium *tert*-butyl *bis*(trimethylsilyl)acetate with enolisable ketones like cyclohexanone[5] is reported.

The reaction of the lithium derivative of α-trimethylsilylsulfonamide **3a** with three aldehydes with higher steric requirements, 2-methylbenzaldehyde, 1-naphthaldehyde, and pivalaldehyde, is studied in order to establish the role of steric factors. High stereoselectivity and good yields are observed in all three cases (entries 3, 13, 16) giving the *E*-product, the one with higher J_{HH} of the vinylic protons in the ^{1}H-NMR spectra. Steric factors are thus shown to be of little importance. Although the Me_3Si group is quite large, its steric effect is often less relevant than expected, due to the fact that the bond C—Si is long (1.89 Å) as compared to C—C.

The experiments with various benzaldehydes having polar substituents (entries 1, 3–12) show that electronic effects do not influence both the yield and the stereoselectivity of the reaction. 2-Furaldehyde reacts in a similar way with **4a** (entry 14) affording in 78% yield β-(α-furyl)vinylsulfonamide **6m**, showing good stereoselectivity in favour of the *E*-isomer.

To test the possibilities of synthesis of sulfonamides with extended conjugation we carried out the reaction of **4a–c** with *E*-cinnamic aldehyde. As for the Peterson reaction with other α-silyl-substituted carbanions,[16,21] no Michael-type addition occurs. The reaction proceeds smoothly in a 1,2-fashion (entries 15, 22, and 25) with 85%, 75% and 68% yield of the corresponding 1-substituted 4-phenylbuta-1,3-dienesulfonamides with H (**6n**), CH_3 (**6t**) and C_6H_5 (**6w**) as substituents in the 1-position. The geometry at the newly formed double bond is established by ^{1}H-NMR N.O.E. experiments. With R=H, the 1*E*,3*E*-isomer is predominant in the crude reaction mixture while in the cases of R=CH_3 and R=C_6H_5 the stereoselectivity is in favour of 1*Z*,3*E*-isomers. It is of interest to note that a higher stereoselectivity, especially with R=H and CH_3, is observed in our case compared to nitriles[16] and sulfoxides[21] where ca. 1:1 mixtures of the two isomers are obtained.

A comparison of the data in Table I shows somewhat lowered yields and stereoselectivities in the direction of R=H, CH_3, C_6H_5. The lower stereoselectivities in both latter cases (the configurations are established on the basis of N.O.E. experiments) could be explained with steric interference of CH_3 and Ph groups. The steric difference between the Me_3Si group and H is large enough to determine a high kinetic stereoselectivity of the aldol step for R=H. The Me_3Si—CH_3 and Me_3Si—Ph differences are less significant than Me_3Si—H, and that reduces the

differences in the transition stage energies of the diastereoisomer pairs with R=CH_3 or Ph relative to R=H which reflects in lower stereoselectivities. With R=Ph, a certain influence of thermodynamic factor must be taken into consideration. In this case the yields are more significantly lowered. Solubility problems in these cases are the reason to carry out the reactions in THF. With R=H or CH_3, no side products are formed, while with R=Ph the target product, vinylsulfonamide **6**, is obtained as a mixture with sulfonamide **1c**. The amount of the latter depends considerably on the reaction conditions, temperature and reaction time. The reaction of **4c** and benzaldehyde (entry 23, conditions B) gives the sulfonamide **6u** in 74% yield, and the stereoselectivity is favouring the *E*-isomer (*E*/*Z* = 80/20), while in the crude reaction mixture 10% of **1c** and traces of **3c** and **5c–u** (H instead of Li) are found. Reflux in ether/THF has the same stereochemical result, but the yields are considerably lower and the target product is contaminated by ca. 40% **1c**. *E*-Cinnamaldehyde reacts similar to benzaldehyde yielding 68% of **6w**; the amount of **1c** is 24% (entry 25). With anisaldehyde, the reaction mixture, when hydrolysed after 24 h at ambient temperature, contains still considerable amounts of α-trimethylsilylsulfonamide **3c** and the β-hydroxy-α-trimethylsilyl-substituted product **5c–v** (H instead of Li) along with the vinylsulfonamide **6v** (a mixture of stereoisomers, *E*/*Z* = 75/25), and **1c**. With a longer reaction time (48 h) the crude reaction mixture no longer shows the above silyl-containing compounds but the yield of **6v** is only 40%, and ca. 55% **1c** is isolated. The lowered yield and the considerable amount of desilylated sulfonamide as the side product are obviously caused by the reversibility of the reaction. The β-elimination step of the Peterson reaction in sulfonamides proved to be much slower than with a large number of other α-silyl-substituted carbanions. On the other hand, we have previously reported[32] that the products of the addition reactions of the phenylmethanesulfonamide carbanion **2c** to aldehydes and ketones show a greater tendency to retroaldol reaction than that of **1a** and **1b**, especially in THF. So, the intermediate **5c** (Scheme 2) is sufficiently long-lived to permit a retroaldol decomposition. The lithium reagent **4c**, is insufficiently stable under these conditions and undergoes other changes. This shifting of the reaction equilibrium has the result of lowered target product yields, in particular at higher temperature. The last statement is based on the observation that from **4c**, after 48 h at room temperature, and subsequent hydrolysis only 55% of **3c** was formed besides 30% phenylmethanesulfonamide **1c** and 14% *bis*(trimethylsilyl)phenylmethanesulfonamide. Lower reaction temperature (reaction conditions E; entry 24) results in higher yields of **6v**, up to 68%, due to more difficult retroaldol decomposition, on the one hand, and higher stability of **4c**, on the other. In this case the reaction mixture contains ca. 7% **1c**, traces of β-hydroxy-α-trimethylsilylsulfonamide (**5c–v**, with H instead of Li) and 18% α-trimethylsilylsulfonamide **3c**. The Si-containing compounds are easily removed by simple washing of the crude product with *n*-hexane.

The results described herein demonstrate that the interaction of α-trimethylsilyl-substituted sulfonamide carbanions with nonenolisable aldehydes and ketones provides an efficient method for the synthesis of vinylic sulfonamides. This interaction proceeds smoothly without side reactions and in high yields when the thermodynamic factor does not interfere. The stereoselectivity, ranging from moderate to very high, is dependent on the substituent R.

TABLE II

$(CH_3)_3SiCH(R)SO_2N(CH_3)_2$, **3**, prepared according to Scheme 1.

Compound 3, R	Yield[a](%)	b.p.°C/Torr[b] m.p.°C	Molecular formula[c]	IR (KBr)	1H-NMR ($CDCl_3$, TMS), δ (ppm), J (Hz)
3a, H	95	94/0.05 38-40	$C_6H_{17}NO_2SSi$ (195.3)	1321, 1254, 1151, 951, 849	0.24 (s, 9H) ; 2.38 (s, 2H) ; 2.76 (s, 6H).
3b, CH_3	94	85/0.02	$C_7H_{19}NO_2SSi$ (209.4)	[d]1321, 1265, 1217, 1022, 847	0.22 (s, 9H) ; 1.30 (d, 3H, J = 7.3) ; 2.77 (q, 1H, J = 7.3) ; 2.90 (s, 6H).
3c, C_6H_5	97	107-108 (Et_2O/n-C_6H_{14})	$C_{12}H_{21}NO_2SSi$ (271.4)	1335, 1292, 1138, 964, 854	0.20 (s, 9H) ; 2.54 (s, 6H) ; 4.04 (s, 1H) ; 7.30-7.39 (m, 5H).

[a] Based on starting sulfonamide.

[b] B.p.s. and m.p.s. are uncorrected.

[c] Elemental analyses and $(M + H)^+$ peaks in the CI-MS are in good agreement with the theoretical values.

[d] In $CHCl_3$.

TABLE III

Constants and ^{1}H-NMR data of *N,N*-dimethylvinylsulfonamides **6**

Compound	m.p. (°C)[a]	Molecular formula[b]	^{1}H-NMR ($CDCl_3$, TMS), δ (ppm), J (Hz)
6a, E	104–105[c]		2.84 (*s*, 6H); 6.69 (*d*, 1H, *J* = 15.5); 7.47 (*d*, 1H, *J* = 15.5); 7.40–7.50 (*m*, 5H).
6a, Z	78–79	$C_{10}H_{13}NO_2S$ (211.3)	2.74 (*s*, 6H); 6.24 (*d*, 1H, *J* = 12.1); 7.13 (*d*, 1H, *J* = 12.1); 7.35–7.39 (*m*, 3H); 7.59–7.63 (*m*, 2H).
6b, E	81–82	$C_{11}H_{15}NO_2S$ (225.3)	2.44 (*s*, 3H); 2.84 (*s*, 6H); 6.59 (*d*, 1H, *J* = 15.5); 7.29–7.51 (*m*, 4H); 7.72 (*d*, 1H, *J* = 15.5).
6b, Z	—		[d]2.30 (*s*, 3H); 2.68 (*s*, 6H); 6.34 (*d*, 1H, *J* = 11.7).
6c, E	120–121	$C_{11}H_{15}NO_2S$ (225.3)	2.39 (*s*, 3H); 2.82 (*s*, 6H); 6.63 (*d*, 1H, *J* = 15.5); 7.21 (*d*, 2H, *J* = 8.0); 7.39 (*d*, 2H, *J* = 8.0); 7.44 (*d*, 1H, *J* = 15.5).
6d, E	109–110	$C_{11}H_{15}NO_3S$ (241.3)	2.82 (*s*, 6H); 3.85 (*s*, 3H); 6.54 (*d*, 1H, *J* = 15.6); 6.92 (*d*, 2H, *J* = 8.7); 7.40 (*d*, 1H, *J* = 15.6); 7.45 (*d*, 2H, *J* = 8.7).
6e, E	115–116	$C_{12}H_{17}NO_4S$ (271.3)	2.83 (*s*, 6H); 3.93 (*s*, 6H); 6.55 (*d*, 1H, *J* = 15.3); 6.89 (*d*, 1H, *J* = 8.3); 7.0 (*d*, 1H, *J* = 2.0); 7.10 (dd, 1H, *J* = 8.3 and 2.0); 7.40 (*d*, 1H, *J* = 15.3).
6e, Z	—		[d]2.80 (*s*, 6H); 3.91 (*s*, 6H); 6.08 (*d*, 1H, *J* = 12.3).
6f, E	166–167	$C_{11}H_{13}NO_4S$ (255.3)	2.82 (*s*, 6H); 6.03 (*s*, 2H); 6.50 (*d*, 1H, *J* = 15.4); 6.83 (*d*, 1H, *J* = 8.4); 6.98 (*s*, 1H); 7.01 (*d*, 1H, *J* = 8.4); 7.36 (*d*, 1H, *J* = 15.4).
6g, E	91–92	$C_{10}H_{12}ClNO_2S$ (245.7)	2.85 (*s*, 6H); 6.70 (*d*, 1H, *J* = 15.6); 7.35–7.50 (*m*, 4H); 7.41 (*d*, 1H, *J* = 15.6).
6h, E	129–130[c]		2.84 (*s*, 6H); 6.67 (*d*, 1H, *J* = 15.5); 7.42 (*d*, 1H, *J* = 15.5); 7.39 (*d*, 2H, *J* = 8.7); 7.44 (*d*, 2H, *J* = 8.7).
6i, E	132–134	$C_{10}H_{12}BrNO_2S$ (290.2)	2.84 (*s*, 6H); 6.69 (*d*, 1H, *J* = 15.6); 7.37 (*d*, 2H, *J* = 8.4); 7.40 (*d*, 1H, *J* = 15.6); 7.56 (*d*, 2H, *J* = 8.4)
6j, E	162–163	$C_{11}H_{12}N_2O_2S$ (236.3)	2.87 (*s*, 6H); 6.82 (*d*, 1H, *J* = 15.5); 7.47 (*d*, 1H, *J* = 15.5); 7.61 (*d*, 2H, *J* = 8.3); 7.72 (*d*, 2H, *J* = 8.3).
6j, Z	—		[d]2.78 (*s*, 6H); 6.38 (*d*, 1H, *J* = 12.2); 7.15 (*d*, 1H, *J* = 12.2); 7.60–7.75 (*m*, 4H).
6k, E	181–182	$C_{10}H_{12}N_2O_4S$ (256.3)	2.88 (*s*, 6H); 6.85 (*d*, 1H, *J* = 15.5); 7.52 (*d*, 1H, *J* = 15.5); 7.66 (*d*, 2H, *J* = 8.7); 8.28 (*d*, 2H, *J* = 8.7).
6k, Z	—		[d]2.80 (*s*, 6H); 6.42 (*d*, 1H, *J* = 12.0); 7.20 (*d*, 1H, *J* = 12.0); 7.68 (*d*, 2H, *J* = 8.8); 8.23 (*d*, 2H, *J* = 8.8).
6l, E	121–122	$C_{14}H_{15}NO_2S$ (261.3)	2.89 (*s*, 6H); 6.77 (*d*, 1H, *J* = 15.3); 7.47–7.63 (*m*, 3H); 7.11 (*d*, 1H, *J* = 7.5); 7.92 (brt, 2H); 8.10 (*d*, 1H, *J* = 7.8); 8.28 (*d*, 1H, *J* = 15.3).
6m, E	71–72	$C_8H_{11}NO_3S$ (201.2)	2.82 (*s*, 6H); 6.50 (dd, 1H, *J* = 3.4 and 1.7); 6.56 (*d*, 1H, *J* = 15.2); 6.60 (*d*, 1H, *J* = 3.4); 7.22 (*d*, 1H, *J* = 15.2); 7.51 (*d*, 1H, *J* = 1.7).
6m, Z	—		[d]5.96 (*d*, 1H, *J* = 13.0); 6.90 (*d*, 1H, *J* = 13.0).
6n, ZE	146–147	$C_{12}H_{15}NO_2S$ (237.3)	2.83 (*s*, 6H); 5.93 (*d*, 1H, *J* = 11.1); 6.84 (*d*, 1H, *J* = 15.2); 6.91 (dd, 1H, *J* = 11.1 and 11.4); 7.30–7.50 (*m*, 5H); 7.87 (dd, 1H, *J* = 15.2 and 11.4).
6n, EE	92–93[c]		2.80 (*s*, 6H); 6.26 (*d*, 1H, *J* = 14.7); 6.77 (dd, 1H, *J* = 15.5 and 10.3); 6.95 (*d*, 1H, *J* = 15.5); 7.25 (dd, 1H, *J* = 14.7 and 10.3); 7.31–7.49 (*m*, 5H).

6o, E	109–110	$C_8H_{17}NO_2S$ (191.3)	1.13 (*s*, 9H); 2.76 (*s*, 6H); 5.98 (*d*, 1H, *J* = 15.3); 6.78 (*d*, 1H, *J* = 15.3).
6o, Z			[f]1.29 (*s*, 9H); 2.83 (*s*, 6H); 5.83 (*d*, 1H, *J* = 12.8); 6.20 (*d*, 1H, *J* = 12.8).
6p, E	Oil	$C_7H_{15}NO_2S$ (177.2)	[d]1.10 (*d*, 6H, *J* = 6.8); 2.55 (*m*, 1H); 2.76 (*s*, 6H); 6.03 (dd, 1H, *J* = 15.2 and 1.4); 6.75 (dd, 1H, *J* = 12.2 and 6.4).
6p, Z			[d]1.04 (*d*, 6H, *J* = 6.5); 2.75 (*m*, 1H); 2.79 (*s*, 6H); 5.88 (*d*, 1H, *J* = 11.0); 6.12 (*d*, 1H, *J* = 11.0).
6q	142–143[g]		2.67 (*s*, 6H); 6.69 (*s*, 1H); 7.20–7.53 (*m*, 10H).
6r, E	88–89[h]	$C_{11}H_{15}NO_2S$ (225.3)	2.22 (*d*, 3H, *J* = 1.3); 2.88 (*s*, 6H); 7.38–7.46 (*m*, 5H); 7.49 (*q*, 1H, *J* = 1.3).
6r, Z	69–70[h]		2.20 (*d*, 3H, *J* = 1.4); 2.59 (*s*, 6H); 7.01 (*q*, 1H, *J* = 1.4); 7.29–7.40 (*m*, 5H).
6s, E	Oil	$C_{12}H_{17}NO_3S$ (255.3)	[d]2.22 (*d*, 3H, *J* = 1.2); 2.86 (*s*, 6H); 3.84 (*s*, 3H); 6.93 (*d*, 2H, *J* = 8.8); 7.36 (*d*, 2H, *J* = 8.8); 7.43 (*q*, 1H, *J* = 1.2).
6s, Z			[d]2.18 (*d*, 3H, *J* = 1.4); 2.65 (*s*, 6H); 3.81 (*s*, 3H); 6.84 (*d*, 2H, *J* = 8.8); 6.95 (*q*, 1H, *J* = 1.4); 7.39 (*d*, 2H, *J* = 8.8).
6t, ZE	158–159	$C_{13}H_{17}NO_2S$ (251.3)	2.12 (brs, 3H); 2.86 (*s*, 6H); 6.63 (brd, 1H, *J* = 11.4); 6.70 (*d*, 1H, *J* = 15.5); 7.37–7.47 (*m*, 3H); 7.49–7.52 (*m*, 2H); 7.85 (dd, 1H, *J* = 15.5 and 11.4).
6t, EE	*i*		2.13 (*d*, 3H, *J* = 1.2); 2.84 (*s*, 6H); 6.90 (*m*, 2H); 7.12 (*m*, 1H); 7.28–7.40 (*m*, 4H); 7.43–7.50 (*m*, 2H).
6u, E	155–156[j]		2.63 (*s*, 6H); 7.02–7.25 (*m*, 5H); 7.44 (*s*, 5H); 7.68 (*s*, 1H).
6u, Z	—		[d]2.47 (*s*, 6H).
6v, E	135–136	$C_{17}H_{19}NO_3S$ (317.4)	2.62 (*s*, 6H); 3.75 (*s*, 3H); 6.69 (*d*, 2H, *J* = 8.8); 6.99 (*d*, 2H, *J* = 8.8); 7.44 (*s*, 5H); 7.61 (*s*, 1H).
6v, Z	—		[d]2.47 (*s*, 6H); 3.72 (*s*, 3H); 7.19 (*s*, 1H).
6w, ZE	135–135.5	$C_{18}H_{19}NO_2S$ (313.4)	2.60 (*s*, 6H); 6.81 (*d*, 1H, *J* = 11.5); 6.84 (*d*, 1H, *J* = 15.5); 7.34–7.42 (*m*, 6H); 7.52–7.56 (*m*, 4H); 8.10 (dd, 1H, *J* = 15.5 and 11.5).
6w, EE	*i*		2.59 (*s*, 6H); 6.63 (dd, 1H, *J* = 15.6 and 11.2); 6.98 (*d*, 1H, *J* = 15.6); 7.27–7.34 (*m*, 6H); 7.42–7.50 (*m*, 5H).

[a] M.p.s. (uncorrected) are taken on a Kofler hot-stage microscope, the products were recrystallised from $CHCl_3$/hexane.

[b] Elemental analyses are in good agreement with the theoretical values.

[c] Lit. 104° for **6a** and 126° for **6h**, A. Bongini, D. Savoia and A. Umani-Ronchi, *J. Organometal. Chem.*, **112,** 1 (1976).

[d] From a mixture of the geometrical isomers.

[e] Literature 91° (unknown configuration), L. A. Paquette, M. Rosen, *J. Am. Chem. Soc.*, **89,** 4102 (1967).

[f] From a mixture of **6o**, Z and **1a**.

[g] Literature: 141–142.5°, E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87,** 1345 (1965); 144°, W. Chodkiewicz, P. Cadiot and A. Willemart, *Bull. Soc. Chim. Fr.*, **1958,** 1586.

[h] From C_2H_5OH/H_2O.

[i] Amorphous solids. Their chemical and geometrical purities are secured by TLC analyses combined with ^{1}H-NMR and CI-mass spectroscopy.

[j] Lit. 153°, B. B. Jarvis, W. P. Tong, H. L. Ammon, *J. Org. Chem.*, **40,** 3189 (1975).

EXPERIMENTAL

All synthetic experiments are carried out under dry argon or nitrogen. Ether and THF are freshly distilled over $LiAlH_4$ prior to use. The aldehydes are purified by washing with a bicarbonate solution followed by distillation (resp. recrystallization). The sulfonamides **1a–c** are prepared according to Reference 33.

IR spectra are measured on a Bruker IFS 113 V Fourier spectrometer. The ^{1}H-NMR spectra as well as N.O.E. difference experiments are recorded on a Bruker WM spectrometer at 250 MHz and on a Bruker AC 200 E spectrometer with TMS as internal standard.

1. *Synthesis of N,N-dimethyl α-trimethylsilylsulfonamides* **3a–c**. The yields, physical and spectroscopic data of compounds **3a–c** are presented in Table II.

a) Synthesis of **3a,b**

The deprotonating agents, $LiN[CH(CH_3)_2]_2$ and $NaN[Si(CH_3)_3]_2$ are prepared in 1.3 N solution in a mixture of ether-THF (1:1) in the presence of α-methylstyrene as electron acceptor from lithium and diisopropylamine, resp. sodium and hexamethyldisilazane according to Reference 34, 27.

To a solution of $NaN[Si(CH_3)_3]_2$, prepared from 0.072 g at. Na, a solution of 0.065 mole of **1a** in 65 ml THF (for **3a**) or 0.065 mole of **1b** in 35 ml THF (for **3b**) is added dropwise at −20°C. The reaction mixture is allowed to warm and is stirred at room temperature for 90 min. Then the mixture is cooled to −65°C and 0.085 mole of $(CH_3)_3SiCl$ is introduced at once under vigorous mechanical stirring. The reaction mixture is rapidly warmed to room temperature using a water bath. After 15 min the precipitate is filtered off on Celite, and washed with dry ether. From the filtrate, after removal of the solvent in vacuo and distillation of the residue **3a** and **3b** are isolated in pure form.

When LDA is used instead of $NaN[Si(CH_3)_3]_2$ in a similar procedure, the results are almost the same.

It is of interest to note that failure to maintain the above-mentioned conditions, gives a mixture of **1a** and **3a**, and the latter compound can easily be isolated and purified by simple washing with water, in which **1a** is very soluble. This is not possible when R=CH_3 or C_6H_5.

b) Synthesis of **3c**

To a solution of 0.04 mole of $LiN[CH(CH_3)_2]_2$ (prepared from 16 ml 2.5 N *n*-BuLi in hexane and 4.04 g of diisopropylamine in 6.5 ml THF) 0.035 mole of **1c** dissolved in 72 ml THF are added dropwise at −20°C. The reaction mixture is maintained at room temperature for 90 min, then cooled at −90°C and 0.052 mole $(CH_3)_3SiCl$ is added at once under good mechanical stirring (the temperature reaches −70°C). After stirring at −70°C for 10 min the mixture is rapidly warmed to room temperature. The precipitate is filtered off and washed with CCl_4. The combined filtrates, after removal of the solvents in vacuo give 97% yield of **3c**, pure enough to be used in further syntheses. Analytically pure **3c** is obtained by recrystallization from dry ether/*n*-hexane 1:2. The synthesis of **3c** may be carried out by metallating agent $NaN[Si(CH_3)_3]_2$, but requires larger volumes of solvent before adding $(CH_3)_3SiCl$.

2. *Synthesis of vinylsulfonamides* **6**. The IR spectra (KBr) of compounds **6** show bands for conjugated carbon-carbon double bonds ($\nu_{C=C}$) in the region 1630–1600 cm^{-1} and intense bands caracteristic for sulfonamides[35] in the intervals: 1371–1321 cm^{-1} and 1184–1134 cm^{-1} (asymmetric and symmetric SO_2 stretching vibrations), 987–951 cm^{-1} (symmetric C—N stretching vibrations), 790–714 cm^{-1} (C—S stretching vibrations) and 591–542 cm^{-1} (SO_2 scissoring vibrations).

The constants and ^{1}H-NMR data are presented in Table III.

In a typical procedure, 5.5 mmole of 1.6 N solution of *n*-BuLi in *n*-hexane is added to 5.5 mmole diisopropylamine in 1 ml of ether at −35° to −40°C with stirring. Then 5 mmole of **3** dissolved in 5 ml of the corresponding solvent is added dropwise and after stirring for 1 h at −20°C, the mixture is cooled to −65°C. A solution of 5 mmole of the corresponding carbonyl compound (concentration depending on its solubility; due to the very poor solubility of 4—O_2N—C_6H_4CHO, it is introduced in the reaction mixture as a suspension in ether-THF, conditions C) is added dropwise in order to keep the reaction temperature at −60°C. After additional 15 min at this temperature the reaction mixture is gradually warmed in order to allow the β-elimination to occur and then maintained for a time as listed in Table I. For **6m** heating is to be avoided due to considerable darkening of the reaction mixture and lower yields at reflux (conditions D). After hydrolysis with diluted HCl (1:1) the reaction mixture is extracted with ether or ethylacetate. Aliquots of the crude products are subjected to ^{1}H-NMR determination of the *E*/*Z*-ratio. In the majority of cases the crude reaction product, obtained after evaporation of the solvent, gives pure **6** (within the limits of the NMR measurement) by simple washing with *n*-hexane (8 to 10 ml). Where mixtures of isomers are obtained, the *E*-isomers of **6a–q** and the 1*Z*,3*E*-isomers of **6n**, **6t** and **6w**, are isolated in analytically pure form by recrystallization from chloroform/*n*-hexane, and the residual isomers by preparative TLC on silica gel (eluent ether/*n*-hexane 1:1 for *Z*-**6a**; 1,2-dichloroethane/*n*-hexane 2:1 for 1*E*,3*E*-isomers of **6n**, **6t** and **6w**). *E*-**6r** and *Z*-**6r** are separated by fractional recrystallization from ethanol/water.

In the case of **6p**, ether/*n*-hexane 1:1 is used as an eluent for the preparative TLC separation of the mixture of *E*/*Z*-isomers from *iso*-butyraldehyde autocondensation products.

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