Phthalimidesulfenyl Chloride. Part 4.[1] Addition to Acetylenes and Synthetic Utilization of their Adducts

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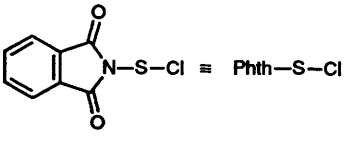
Both the stereo- and regio-chemical reactivity of the phthalimidesulfenyl chloride **1** towards symmetrical and terminal acetylenes and the reactivity of the adducts **3** and **5** with various nucleophiles has been investigated. Nucleophilic substitution of the phthalimide residue was achieved with MeLi, PhLi, Bu^{t}Li, $(Me_3Si)_2NNa$ and Me_3SiSMe. The synthesis of β-chlorovinyl tributylstannyl sulfides **14** is also described. The synthetic potential of the new sulfur compounds is discussed.

Whilst several functionalized sulfenyl chlorides have been described in the literature,[2,3] the reactivity of only a few has been well studied. The interest of these sulfenic species lies in the reactivity of the sulfur–chlorine bond coupled with that of the second functionality present.[2]

In studying the behaviour of the phthalimidesulfenyl chloride **1**[4,5] we found only two papers dealing with its chemistry: namely, its addition to cyclic alkenes[6] and its reaction with arylsilylamines.[7]



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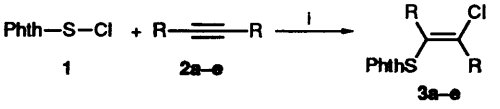
Following our studies on the chemistry of sulfenic species[8] we report here the reactivity of the phthalimidesulfenyl chloride **1** towards symmetrical and terminal alkynes, and the reactivity of the adducts formed with various nucleophiles.[4,5]

Results and Discussion

Compound **1** reacted with symmetrical alkynes in dichloromethane at 0 °C to give, as a single adduct in good yield, a new class of unsaturated phthalimide sulfenamides, to which the *E* configuration was assigned by analogy with the *anti*-addition observed in the reactions of non-functionalized sulfenyl chlorides with symmetrical alkynes.[2,3,9] A variety of *E* dialkyl and diaryl substituted vinyl sulfenamides were so synthesized (see Scheme 1). Addition of the phthalimidesulfenyl chloride **1**



1 **2a–e** **3a–e**

2a, 3a R = Me
2b, 3b R = Et
2c, 3c R = Ph
2d, 3d R = *p*-Tol
2e, 3e R = $PhCH_2$

Scheme 1 *Conditions:* i, CH_2Cl_2, 0 °C

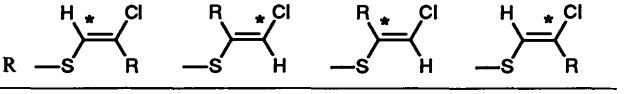
to terminal alkynes may give rise to two different *E* regioisomers: namely, the Markovnikov (M) and the *anti*-Markovnikov (*a*M). Several authors showed[2,3,9,10] that in the addition of alkane- or arene-sulfenyl chlorides to terminal alkyl acetylenes, steric hindrance is the most important factor driving the addition; *i.e.* the *anti*-Markovnikov regioisomer

Table 1

Compd.	R	*a*M:M[a]	δ_H(*a*M)	δ(M)
4a,5a	Me	89:11	6.66	6.38
4b,5b	Et	90:10	6.71	6.36
4c,5c	Bu	89:11	6.70	6.35
4d,5d	Bu^t	>99:1	6.43	—
4e,5e	Ph	85:15 (15:85)[b]	6.94	6.47

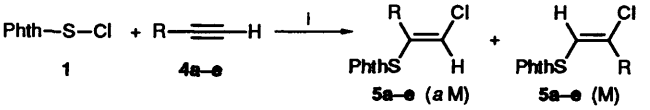
[a] Measured by ^{1}H NMR in CH_2Cl_2. [b] In $MeCO_2H$.

Table 2 Vinylic ^{13}C chemical shifts in Markovnikov and *anti*-Markovnikov isomers **5**



Me	119.67	121.67	133.84	142.91
Et	119.25	122.36	139.92	143.02
Bu	119.37	122.90	138.79	146.71
Bu^t	—	119.50	145.00	—
Ph	123.54	119.38	138.45	135.40

predominates in the reaction mixture. However, in the addition of non-functionalized sulfenyl chlorides to phenylacetylene the regioisomeric distribution was subject to a solvent effect.[10] The reaction of phthalimidesulfenyl chloride **1** with a large number of 1-alkylacetylenes and phenylacetylene in dichloromethane at 0 °C gave in each case the two possible *E* regioisomers although the *anti*-Markovnikov derivatives predominated (Scheme 2 and



1 **4a–e** **5a–e** (*a*M) **5a–e** (M)

Scheme 2 *Conditions:* i, CH_2Cl_2, 0 °C

Table 1). In contrast, addition of compound **1** to phenylacetylene in acetic acid gave a predominance of Markovnikov regioisomer. Thus, the regiochemistry of the addition of compound **1** to alk-1-ynes parallels that observed in the addition of non-functionalized sulfenyl chlorides to the same acetylenes. This is not an obvious result since very often the presence of electron withdrawing groups adjacent to the sulfenic sulfur can shift the preferred orientation to the Makovnikov regioisomer.[2]

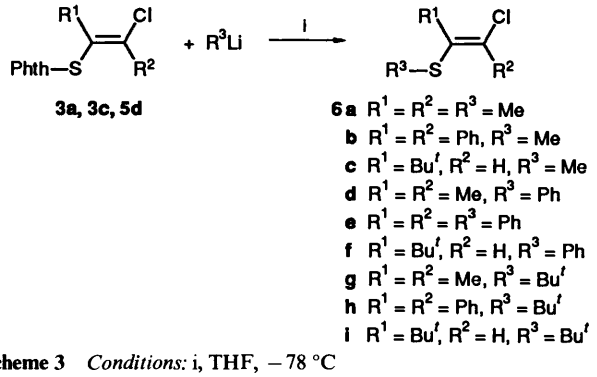
The regiochemical distribution of the adducts obtained in the addition of compound **1** to terminal acetylenes was assigned using ^{1}H NMR techniques (see Table 1), the ^{13}C chemical shifts

of the vinylic carbons in both isomers being diagnostic for the regiochemical assignments. In particular (see Table 2), in the products obtained by addition of compound **1** to 1-alkylacetylenes, the tertiary vinylic carbons in the Markovnikov adducts resonate at higher field than the corresponding tertiary carbons of the *anti*-Markovnikov ones; a reverse situation was found for the chemical shifts of the quaternary carbons in the two regioisomers. Moreover, the ^{13}C chemical shifts of the vinylic carbons of the adducts obtained in the reaction of compound **1** with phenylacetylene follow a reversed trend (Table 2). Such behaviour has been reported for similar compounds, *e.g.* β-chloro vinyl aryl sulfides.[11,12]

We have reported the reactivity of the β-chlorovinylsulfenamides **2** and **3** towards nucleophiles such as hydride[13] or lithium acetylides,[1] reactions which give a new class of vinylthio thiiranes[13] and provide easy access of alkynyl vinyl sulfides.[1]

The key step of these reactions was the nucleophilic substitution of the phthalimide residue; in fact, polarization of the nitrogen–sulfur bond in the sulfenamides provides an opportunity for nucleophilic attack at sulfur, and several examples of this reactivity are described in the literature.[14–18] We describe here the reactions of three adducts **3a**, **3c** and **5d**, which are representative of all the types of sulfenamides synthesized, towards various nucleophiles.[5]

First, we considered the reaction of the adducts **3a**, **3c** and **5d** with MeLi, PhLi and Bu^{t}Li in THF at −78 °C by addition of the latter to a solution of the former (Scheme 3). In each case the



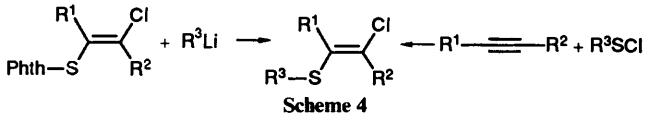
3a, 3c, 5d

6a $R^1 = R^2 = R^3 = Me$
b $R^1 = R^2 = Ph$, $R^3 = Me$
c $R^1 = Bu^t$, $R^2 = H$, $R^3 = Me$
d $R^1 = R^2 = Me$, $R^3 = Ph$
e $R^1 = R^2 = R^3 = Ph$
f $R^1 = Bu^t$, $R^2 = H$, $R^3 = Ph$
g $R^1 = R^2 = Me$, $R^3 = Bu^t$
h $R^1 = R^2 = Ph$, $R^3 = Bu^t$
i $R^1 = Bu^t$, $R^2 = H$, $R^3 = Bu^t$

Scheme 3 *Conditions:* i, THF, −78 °C

substitution products were isolated by column chromatography and purified by distillation or recrystallization; acceptable elemental analysis and spectroscopic data were obtained (see Experimental section).

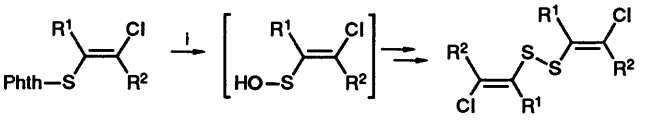
Where possible, the β-chlorovinyl sulfides **6** were also identified by comparison of their physical and spectroscopic data with those of the corresponding products synthesized by alternative routes. In fact, the products obtained by substitution of the phthalimide residue with the carbanionic group of MeLi or PhLi are those that can be synthesized by reaction of methane- or benzene- sulfenyl chloride with the same alkynes (Scheme 4).



Scheme 4

The sulfides obtained by reaction of **3a**, **3c** and **5d** with Bu^{t}Li cannot be identified by comparison because of the instability of *tert*-sulfenyl chloride.[19] Therefore, the phthalimide sulfenyl chloride can be considered as a synthetic equivalent of this elusive species.

We showed that the yields of these reactions are very sensitive to 'free' LiOH in the lithium carbanion solution, the presence of which decreased the yield of the substitution products. The observed formation of divinyl disulfides **8** as by-products, probably arise by decomposition of the unstable sulfenic acid **7**. The disulfides **8** are the reduced counterpart of this process, but we could detect no oxidised product.[2] In fact, minute amounts of the symmetrical divinyl disulfides **8a** and **8b** were always detected in the reaction of the lithium carbanions with **3a** and **3c**. Moreover, alkaline hydrolysis (aqueous sodium hydroxide–dichloromethane) of the latter leads to the formation of the corresponding divinyl disulfides **8a** and **8b** (Scheme 5). The



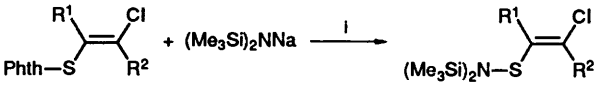
3a, 3c **7** **8a** $R^1 = R^2 = Me$ **8b** $R^1 = R^2 = Ph$

Scheme 5 *Reagents and conditions:* i, NaOH (0.1 mol dm^{-3}; 1 equiv.)–CH_2Cl_2

corresponding *tert*-butyl derivative was not detected in the reaction of compound **5d** with the same reagents, probably because of its instability.[13]

A further interesting feature of the reactivity of phthalimidesulfenamides **3** towards carbanions was shown by treating **3a** and **3c** with Grignard reagents, when the major product was the corresponding divinyl disulfide **8**, there being no trace of substitution product.

Although the reactivity of several amines with sulfenamides has been described in the literature,[16] we found that the bis(trimethylsilyl)amine, failed to substitute the phthalimide residue of the phthalimidesulfenamides **3** and **5**, probably because of its low basicity and nucleophilicity. However, use of sodium bis(trimethylsilyl)amide as a nucleophile with the sulfenamides **3a**, **3c** and **5d** in THF at −78 °C (see Scheme 6)

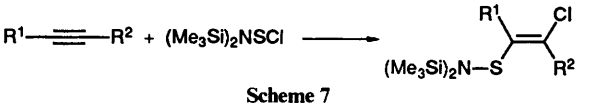


3a, 3c, 5d

9a $R^1 = R^2 = Me$
9b $R^1 = R^2 = Ph$
9c $R^1 = Bu^t$, $R^2 = H$

Scheme 6 *Conditions:* i, THF, −78 °C

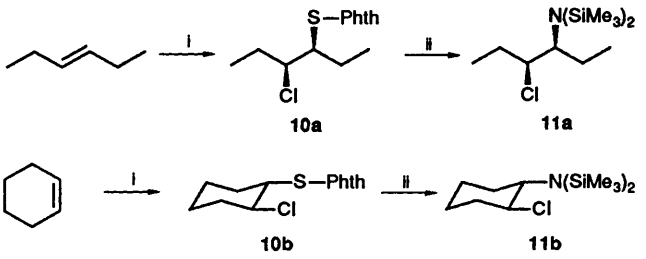
gave good yields of the silylated sulfenamides **9**. This new class of compounds are of interest because of the various functionalities present. Moreover, the reaction sequence–addition of compound **1** to acetylenes and substitution of the phthalimide residue suggests that phthalimidesulfenyl chloride may be considered as a synthetic equivalent of bis(trimethylsilyl)-aminosulfenyl chloride, another inaccessible sulfenic species (Scheme 7). The methodology, used to synthesize the *N*,*N*-



Scheme 7

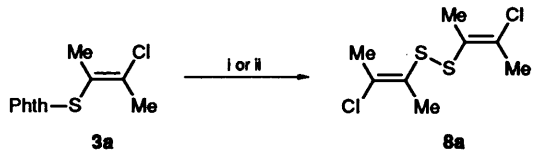
bis(trimethylsilyl)sulfenamides **9** appears to be general, since the cyclohexyl and hexyl derivatives **10a** and **10b** (obtained by reaction of phthalimidesulfenyl chloride **1** with the corresponding alkenes) reacted with sodium bis(trimethylsilyl)amide in dry THF at −78 °C to give the corresponding β-alkyl phthalimidesulfenamides **11a,b** (Scheme 8).

Following the same strategy, we attempted to substitute the phthalimide residue in the β-chlorovinyl sulfenamides **3** by generating anionic species such as Me_3Si^- and Bu_3Sn^-.



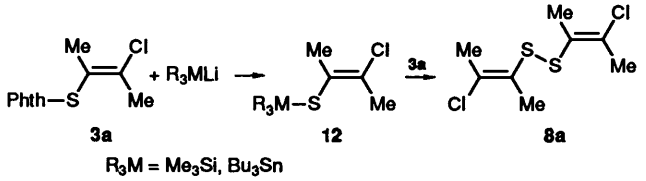
Scheme 8 *Reagents and conditions:* i, Phth–S–Cl, CH_2Cl_2, 0 °C; ii, $(Me_3Si)_2NNa$, THF, −78 °C

Unfortunately the reaction of Me_3SiLi and Bu_3SnLi with the sulfenamide **3a** gave the corresponding divinyl disulfide **8a** as the sole product (Scheme 9). Although this result might be



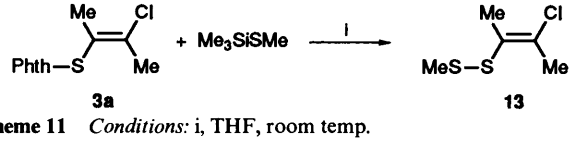
Scheme 9 *Reagents and conditions:* i, Me_3SiLi, THF–HMPA, −78 °C; ii, Bu_3SnLi, THF, 0 °C

considered to involve the formation of thiosilylated or thiostannylated species **12** as intermediates, the attack of which on a further molecule of starting material, could give the disulfide **8a** (Scheme 10), this hypothesis may be ruled out for at



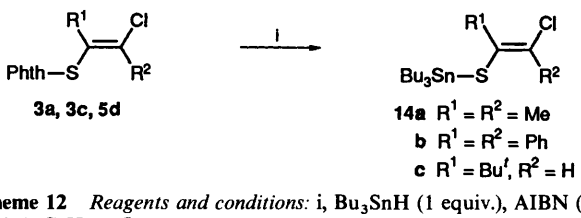
Scheme 10

least two reasons. First, the reactivity of thiosilylated compounds towards S–N bonds is a well known phenomenon,[20] while the corresponding thiostannylated species are reported to be unreactive.[20] Furthermore, we observed that the formation of the disulfide **13** in the reaction of **3a** with methylthiotrimethyl silane needed several hours at room temperature (Scheme 11), whilst (see Scheme 9) **8a** is formed instantaneously on reaction of Me_3SiLi with **3a** at −78 °C.



Scheme 11 *Conditions:* i, THF, room temp.

The stannylated vinyl thiols were, finally, synthesized by a different approach in which substitution of the phthalimide residue by the tributyltin group occurred upon treatment of the sulfenamides **3a**, **3c** and **5d** with tributyltin hydride in the presence of a catalytic amount of AIBN to give compounds **14a–c** (Scheme 12). The latter, tin-protected vinyl thiols, can be



Scheme 12 *Reagents and conditions:* i, Bu_3SnH (1 equiv.), AIBN (0.1 equiv.), C_6H_6, reflux

also considered to be generated by addition of an unknown stannanesulfenyl chloride to the corresponding alkynes.

In summary, phthalimidesulfenyl chloride **1** reacts stereo- and regio-chemically with alkynes as a non-functionalized sulfenyl chloride to give a new class of vinylsulfenamides, useful and versatile intermediates in the synthesis of a large number of sulfur compounds.[1,13] In addition, since nucleophilic substitution may take place on the phthalimide residue the phthalimidesulfenyl chloride may be considered as the synthetic equivalent of a series of inaccessible sulfenyl chlorides.

Experimental

Reactions were carried out under a dry nitrogen atmosphere. Reagents were of commercial quality from freshly opened containers. Dichloromethane was washed with water, dried (calcium chloride) and freshly distilled from calcium chloride before use. THF was freshly distilled once from sodium and twice from lithium aluminium hydride before use. Methyllithium, *tert*-butyllithium and phenyllithium were purchased from Aldrich and titrated before use. Phthalimidesulfenyl chloride **1**,[6] trimethylsilyllithium,[21] and tributylstannyllithium[22] were prepared following literature procedures. Silica gel (E. Merk 230–400 Mesh) and TLC plates (Merck 60 F_{254}) were used for chromatographic purifications. M.p.s (Büchi 510) are uncorrected. In the case of Kugelrohr distillations (Büchi GKR 50) the oven temperature is given. All ^1H NMR spectra were obtained in $CDCl_3$ and were recorded at 200 MHz on a Varian Gemini 200; residual $CHCl_3$ was used as reference at 7.26 ppm. ^{13}C NMR spectra were recorded at 50 MHz and chemical shifts were referenced to the central peak of the solvent ($CDCl_3$) at 77.00 ppm. *J*-Values in Hz. GCMS spectra were performed with a Auto-Hrgc-Ms QMD 1000 Carlo Erba. Microanalyses were obtained with an Elementary Analyzer 245 Perkin-Elmer.

Spectroscopic data for compounds **3a**, **3b**, **5a**, **5d** and **8a** have been published elsewhere.[13,14]

General Procedure for the Synthesis of the Phthalimidesulfenamides **3**, **5** *and* **10**.—To a solution of the alkyne or alkene (3 mmol) in dry dichloromethane (5 cm^3) at 0 °C a solution of compound **1** (3 mmol) in dry dichloromethane (10 cm^3) was added *via* a syringe. After 15 min the mixture was allowed to warm to room temperature when the reagents had completely disappeared (TLC) (15 min for dialkyl and terminal acetylenes, 24 h for diarylacetylenes). The mixture was then diluted with dichloromethane (50 cm^3), washed twice with saturated aqueous sodium hydrogen carbonate and twice with brine, dried (Na_2SO_4) and evaporated to dryness. The resulting crude product was analysed (^1H and ^{13}C NMR) to measure the regioisomeric distribution (when necessary). Column chromatography and recrystallization gave the pure predominant regioisomer.

N-(2-*Chloro*-1,2-*diphenylvinylthio*)*phthalimide* **3c**. 82%, m.p. 172–175 °C (dichloromethane–hexane) (Found: C, 67.5; H, 3.7; N, 3.2. $C_{22}H_{14}ClNO_2S$ requires C, 67.44; H, 3.58; N, 3.58%); δ_H(200 MHz, $CDCl_3$) 7.00–7.18 (3 H, m, Ar), 7.25–7.34 (2 H, m, Ar), 7.35–7.49 (3 H, m, Ar) and 7.56–7.75 (6 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 128.05, 128.48, 128.51, 129.13, 129.30, 129.59 (d, Ar), 134.69, 137.15 (s, Ar), 127.16, 135.09 (s, vinylic), 123.49, 134.37 (d, Phth), 131.38 (s, Phth) and 166.95 (s, C=O); *m/z* 391 (M^+, 17%), 244 (M^+ − Phth, 27), 178 (78) and 104 (100).

N-(2-*Chloro*-1,2-*di*-p-*tolylvinylthio*)*phthalimide* **3d**. 83%, m.p. 157–159 °C (dichloromethane–hexane) (Found: C, 68.5; H, 4.2; N, 3.2. $C_{24}H_{18}ClNO_2S$ requires C, 68.66; H, 4.29; N, 3.34%); δ_H(200 MHz, $CDCl_3$) 2.14, 2.39 (3 H, s, Me), 6.60–6.99 (2 H, m, Ar), 7.21–7.28 (4 H, m, Ar) and 7.59–7.72 (6 H, m, Ar);

δ_C(50 MHz, $CDCl_3$) 21.13, 21.42 (q, Me), 128.73, 129.00, 129.16, 129.53 (d, Ar), 131.73, 134.58, 138.38, 139.59 (s, Ar), 127.20, 134.42 (s, vinylic), 123.47, 134.28 (d, Phth), 131.48 (s, Phth) and 167.05 (s, C=O); *m/z* 366 (M^+ − 53, 10%), 272 (M^+ − Phth, 30) and 206 (100).

N-(1,2-*Dibenzyl*-2-*chlorovinylthio*)*phthalimide* **3e**. 81%, m.p. 118–120 °C (hexane) (Found: C, 68.6; H, 4.3; N, 3.3. $C_{24}H_{18}ClNO_2S$ requires C, 68.41; H, 4.20; N, 3.12%); δ_H(200 MHz, $CDCl_3$), 3.98, 4.54 (s, CH_2), 6.92–7.02 (2 H, m, Ar), 7.08–7.16 (2 H, m, Ar), 7.25–7.41 (5 H, m, Ar) and 7.65–7.78 (4 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 40.10, 43.50 (t, CH_2), 125.97, 127.68, 128.13, 128.60, 128.83, 140.79 (d, Ar), 131.10, 136.78 (s, Ar), 126.88, 137.26 (s, vinylic), 123.67, 134.25 (d, Phth), 131.65 (s, Phth) and 167.47 (s, C=O).

N-(2-*Chloro*-1-*ethylvinylthio*)*phthalimide and* N-(2-*chloro*-2-*ethylvinylthio*)*phthalimide* **5b**. 96.5%, m.p. 113 °C (hexane) (Found: C, 54.0; H, 3.7; N, 5.7. $C_{12}H_{10}ClNO_2S$ requires C, 53.83; H, 3.76; N, 5.23%); δ_H(200 MHz, $CDCl_3$) 2.18 (3 H, t, *J* 7.43), 2.34 (2 H, q, *J* 7.43), 6.71 (1 H, s), 7.72–7.85 (2 H, m, Ar) and 7.86–8.00 (2 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 11.72 (q, Me), 24.00 (t, CH_2), 122.36 (d, vinylic), 139.92 (s, vinylic), 124.03, 134.77 (d, Phth), 131.74 (s, Phth) and 167.56 (s, C=O); *m/z* 267 (M^+, 0.40%), 253 (27) and 179 (100).

N-(1-*Butyl*-2-*chlorovinylthio*)*phthalimide and* N-(2-*butyl*-2-*chlorovinylthio*)*phthalimide* **5c**. 86% m.p. 60–63 °C (hexane) (Found: C, 57.0; H, 4.9; N, 5.05. $C_{14}H_{14}ClNO_2S$ requires C, 56.85; H, 4.77; N, 4.73%); δ_H(200 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 7.59, Me), 1.31 (2 H, sext, *J* 7.59), 1.61 (2 H, quint, *J* 7.59), 2.30 (2 H, t, *J* 7.59), 6.70 (1 H, s), 7.72–7.85 (2 H, m, Ar) and 7.86–8.00 (2 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 13.62 (q, Me), 22.00, 29.00, 30.01 (t, CH_2), 122.90 (d, vinylic), 138.79 (s, vinylic), 124.11, 134.87 (d, Phth), 131.86 (s, Phth) and 167.00 (s, C=O); *m/z* 295 (M^+, 18%), 253 (5), 148 (M^+ − Phth, 100).

N-(2-*Chloro*-1-*phenylvinylthio*)*phthalimide and* N-(2-*chloro*-2-*phenylvinylthio*)*phthalimide* **5e**. 87%, m.p. 108–109 °C (hexane) (Found: C, 60.8; H, 3.2; N, 4.2. $C_{16}H_{10}ClNO_2S$ requires C, 60.85; H, 3.19; N, 4.43%); δ_H(200 MHz, $CDCl_3$) 6.94 (1 H, s), 7.20–7.36 (3 H, m, Ar), 7.48–7.58 (2 H, m, Ar), 7.66–7.75 (2 H, m, Ar) and 7.76–7.86 (2 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 128.20, 129.25, 129.72 (d, Ar), 132.25 (s, Ar), 119.38 (d, vinylic), 138.45 (s, vinylic), 123.87, 134.60 (d, Phth) 131.55 (s, Phth) and 167.01 (s, C=O); *m/z* 315 (M^+, 100%), 280 (M^+ − 35, 43), 168 (M^+ − Phth, 98).

N-(4-*Chlorohexan*-3-*ylthio*)*phthalimide* **10a**. 88%, m.p. 133–135 °C (hexane) (lit.,[6] 138–140 °C); δ_H(200 MHz, $CDCl_3$) 1.30–1.80 (6 H, m), 2.00–2.20 (1 H, m), 2.30–2.50 (1 H, m), 3.37 (1 H, m), 4.06 (1 H, m), 7.72–7.85 (2 H, m, Ar) and 7.86–8.00 (2 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 23.33, 23.59, 28.05, 34.06 (t, CH_2), 55.17, 61.91 (d, CH), 123.82, 134.59 (d, Phth), 131.74 (s, Phth), 168.33 (s, C=O); *m/z* 295 (M^+, 0.80%), 259 (M^+ − 36, 14), 148 (M^+ − 147, 20), 76 (100).

N-(2-*Chlorocyclohexylthio*)*phthalimide* **10b**. 97%, m.p. 104–106 °C (hexane) (Found: C, 56.4; H, 5.45; N, 4.4. $C_{14}H_{16}ClNO_2S$ requires C, 56.46; H, 5.41; N, 4.70%); δ_H(200 MHz, $CDCl_3$) 1.06 (3 H, t, *J* 7.24), 1.22 (3 H, q, *J* 7.30), 1.40–1.70 (1 H, m), 1.80–2.20 (3 H, m), 3.04 (1 H, m), 4.07 (1 H, m), 7.70–7.84 (2 H, m, Ar) and 7.86–8.00 (2 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 10.96, 11.58 (q, Me), 22.81, 28.85 (t, CH_2), 59.93, 67.38 (d, CH), 123.93, 134.74 (d, Phth), 132.09 (s, Phth) and 168.64 (s, C=O); *m/z* 261 (M^+ − 36, 15%), 226 (54), 169 (M^+ − 128, 100).

Reaction of N-*Chlorothiophthalimide* **1** *with Phenylacetylene* **4e** *in Acetic Acid.*—A solution of compound **1** (426 mg, 2 mmol) in acetic acid (20 cm^3) was added dropwise to a solution of compound **4e** (205 mg, 2 mmol) in acetic acid (5 cm^3). After 15 min the mixture was diluted with dichloromethane (100 cm^3) and washed with water, saturated sodium hydrogen carbonate (basified) and with brine to neutral pH. The organic phase was dried (sodium sulfate) and evaporated to give the crude product **5e** which was analysed (^1H and ^{13}C NMR) to measure the regioisomeric distribution (see Scheme 2, Table 1). Purification by column chromatography gave compound **5e** (315 mg, 50%) as a mixture of M and *a*M in the same distribution as that measured in the crude mixture. Various attempts to obtain the pure Markovnikov regioisomer by recrystallization were unsuccessful.

General Procedure for the Synthesis of the Thiovinyl Chlorides **6**.—A solution of the commercial lithium carbanion (2 mmol) was added *via* a syringe to a solution of the sulfenamide (2 mmol) in dry THF (10 cm^3) at − 78 °C. After 15 min the mixture was allowed to warm to room temperature. After dilution with diethyl ether (50 cm^3) the mixture was washed twice with saturated ammonium chloride and twice with brine and the organic layer was dried (sodium sulfate) and evaporated to give a crude product which was purified by column chromatography using light petroleum as eluent. The sulfides **6** were further purified by recrystallization or distillation.

1,2-*Dimethyl*-2-*methylthiovinyl chloride* **6a**. 51%, b.p. 70 °C, 27 Torr* (lit.,[23] 50 °C, 10 Torr); δ_H(200 MHz, $CDCl_3$), 2.01 (3 H, t, *J* 1.53), 2.20 (3 H, s) and 2.43 (3 H, q, *J* 1.53); δ_C(50 MHz, $CDCl_3$), 15.82, 19.90 (q, Me), 23.86 (q, MeS), 126.18 and 128.15 (s, vinylic).

1,2-*Diphenyl*-2-*methylthiovinyl chloride* **6b**. 33%, m.p. 72 °C (methanol) (Found: C, 68.7; H, 5.0. $C_{15}H_{15}ClS$ requires C, 69.09; H, 5.02%); δ_H(200 MHz, $CDCl_3$) 1.81 (3 H, s), 7.30–7.50 (6 H, m, Ar) and 7.55–7.65 (4 H, m, Ar); *m/z* 260 (M^+, 62%), 245 (M^+ − 15, 6) and 210 (M^+ − 50, 100).

2-tert-*Butyl*-2-*methylthiovinyl chloride* **6c**. 49%, oil; δ_H(200 MHz, $CDCl_3$) 1.35 (9 H, s), 2.20 (3 H, s), 5.48 (1 H, s), [lit.,[24] 1.36 (9 H, s), 2.21 (3 H, s), 5.51 (1 H, s)]; *m/z* 164 (M^+, 88%), 149 (M^+ − 35, 15) and 41 (100).

1,2-*Dimethyl*-2-*phenylthiovinyl chloride* **6d**. 48%, b.p. 60 °C, 0.3 Torr (Found: C, 60.3; H, 5.7. $C_{10}H_{14}ClS$ requires C, 60.44; H, 5.58%); δ_H(200 MHz, $CDCl_3$) 2.06 (3 H, q, *J* 1.53), 2.44 (3 H, q, *J* 1.53) and 7.15–7.38 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 21.71, 24.48 (q, Me), 124.00, 134.88 (s, vinylic), 126.35, 129.01, 129.09 (d, Ar) and 134.15 (s, Ar); *m/z* 198 (M^+, 64%), 163 (M^+ − 35, 81) and 147 (100).

1,2-*Diphenyl*-2-*phenylthiovinyl chloride* **6e**. 15%, m.p. 93 °C (methanol) [lit.,[25] m.p. 93–94 °C (methanol)]; δ_H(200 MHz, $CDCl_3$) 7.15–7.70 (m, Ar); *m/z* 322 (M^+, 33%), 287 (M^+ − 35, 42) and 178 (100).

2-tert-*Butyl*-2-*phenylthiovinyl chloride* **6f**. 57.5%, b.p. 75 °C, 0.02 Torr (Found: C, 63.6; H, 6.7. $C_{12}H_{15}ClS$ requires C, 63.56; H, 6.67%); δ_H(200 MHz, $CDCl_3$) 1.35 (9 H, s), 6.37 (1 H, s) and 7.20–7.40 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 29.16 (q, Me), 38.25 (s), 120.83 (d, vinylic), 139.92 (s, vinylic), 124.84, 129.28, 129.44 (d, Ar) and 136.66 (s, Ar); *m/z* 226 (M^+, 7%), 190 (M^+ − 36, 7), 57 (100).

2-tert-*Butylthio*-1,2-*dimethylvinyl chloride* **6g**. 56%, oil (Found: C, 54.2; H, 8.7. $C_8H_{15}ClS$ requires C, 54.83; H, 8.46%); δ_H(200 MHz, $CDCl_3$), 1.34 (9 H, s), 2.21 (3 H, q, *J* 1.58) and 2.43 (3 H, q); δ_C(50 MHz, $CDCl_3$) 25.30, 26.09 (q, Me, vinylic), 31.51 (q, Me, Bu^t), 48.28 (s, Bu^t), 124.90 and 138.70 (s, vinylic); *m/z* 178 (M^+, 10%), 122 (M^+ − 56, 93%) and 57 (100).

2-tert-*Butylthio*-1,2-*diphenylvinyl chloride* **6h**. 18%, m.p. 82–84 °C (Found: C, 71.6; H, 6.1. $C_{18}H_{19}ClS$ requires C, 71.38; H, 6.32%); δ_H(200 MHz, $CDCl_3$) 1.09 (9 H, s), 7.34–7.60 (10 H, m, Ar); *m/z* 302 (M^+, 20%) and 246 (M^+ − 56, 100).

2-tert-*Butyl*-2-tert-*butylthiovinyl chloride* **6i**. 8%, b.p. 110 °C, 0.3 Torr (Found: C, 58.1; H, 9.2. $C_{10}H_{19}ClS$ requires C, 58.08; H, 9.26%); δ_H(200 MHz, $CDCl_3$) 1.30 (9 H, s), 1.31 (9 H, s)

* 1 Torr ≈ 133 Pa.

and 6.58 (1 H, s); δ_C(50 MHz, $CDCl_3$) 29.79, 31.61 (q, Me, Bu^t), 37.16, 47.19 (s, Bu^t), 123.33 (d, vinylic) and 143.76 (s, vinylic); *m/z* 206 (M^+, 12%) and 150 ($M^+ - 56$, 100).

General Procedure for the Synthesis of the Silyl Sulfenamides **9** *and* **11**.—A solution of the adduct (2 mmol) in dry THF (10 cm^3) was added *via* a syringe to a suspension of bis(trimethylsilyl)-sodium amide (2 mmol) in dry THF (10 cm^3) at −78 °C and after 15 min the mixture was allowed to warm to room temperature and diluted with freshly distilled pentane (100 cm^3). The *N*-sodiumphthalimide precipitated was filtered off and the solvent evaporated to dryness. The crude silyl derivatives obtained were purified by distillation.

N-(2-*Chloro*-1,2-*dimethylvinylthio*)*bis*(*trimethylsilyl*)*amine* **9a**. 89%, b.p. 60 °C, 0.01 Torr (Found: C, 42.0; H, 8.9; N, 5.3. $C_{10}H_{24}ClNSSi_2$ requires C, 42.59; H, 8.57; N, 4.96%); δ_H(200 MHz, $CDCl_3$) 0.18 (18 H, s), 1.95 (3 H, q, *J* 1.48) and 2.18 (3 H, q, *J* 1.48); δ_C(50 MHz, $CDCl_3$) 1.86 (q, MeSi), 16.19, 22.60 (q, Me, vinylic), 118.68 and 134.06 (s, vinylic); *m/z* 281 (M^+, 11%), 212 (11) and 73 (100).

N-(2-*Chloro*-1,2-*diphenylvinylthio*)*bis*(*trimethylsilyl*)*amine* **9b**. 67%, b.p. 125 °C, 0.01 Torr (Found: C, 59.0; H, 7.0; N, 3.6. $C_{20}H_{28}ClNSSi_2$ requires C, 59.15; H, 6.95; N, 3.45%); δ_H(200 MHz, $CDCl_3$) −0.06 (18 H, s) and 7.26–7.60 (10 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 1.89 (q, MeSi), 127.50, 127.69, 127.97, 128.92, 129.69, 130.13 (d, Ar), 137.59, 138.18 (s, Ar), 126.12 and 141.76 (s, vinylic); *m/z* 405 (M^+, 62%), 285 ($M^+ - 30$, 12) and 178 (100).

N-(1-tert-*Butyl*-2-*chlorovinylthio*)*bis*(*trimethylsilyl*)*amine* **9c**. 95%, b.p. 70 °C, 0.01 Torr (Found: C, 46.7; H, 9.3; N, 4.7. $C_{12}H_{28}ClNSSi_2$ requires C, 46.48; H, 9.10; N, 4.51%); δ_H(200 MHz, $CDCl_3$) 0.18 (18 H, s), 1.23 (9 H, s) and 5.34 (1 H, s); δ_C(50 MHz, $CDCl_3$) 1.51 (q, MeSi), 27.77 (q, Me, Bu^t), 36.48 (s, Bu^t), 102.81 (d, vinylic) and 148.79 (s, vinylic); *m/z* 309 (M^+, 23%), 146 (17) and 73 (100).

N-(4-*Chlorohexan*-3-*yl*)*bis*(*trimethylsilyl*)*amine* **11a**. 70%, b.p. 135 °C, 0.015 Torr (Found: C, 46.2; H, 9.0; N, 4.7. $C_{12}H_{28}ClNSSi_2$ requires C, 46.48; H, 9.10; N, 4.51%); δ_H(200 MHz, $CDCl_3$) 0.19 (18 H, s), 1.45–1.65 (4 H, m), 1.70–1.85 (2 H, m), 2.00–2.20 (2 H, m), 2.92 (1 H, m) and 4.25 (1 H, m); *m/z* 309 (M^+, 10%), 177 (34) and 73 (100).

N-(2-*Chlorocyclohexyl*)*bis*(*trimethylsilyl*)*amine* **11b**. 89%, b.p. 125 °C, 0.01 Torr (Found: C, 46.0; H, 9.8; N, 4.7. $C_{12}H_{30}ClNSSi_2$ requires C, 46.19; H, 9.69; N, 4.49%); δ_H(200 MHz, $CDCl_3$) 0.21 (18 H, s), 1.00–1.20 (6 H, m), 1.40–2.00 (4 H, m), 2.60–2.80 (1 H, m) and 4.00–4.20 (1 H, m); δ_C(50 MHz, $CDCl_3$) 2.34 (q, MeSi), 11.89 , 12.64 (q, Me), 20.19, 29.77 (t), 59.12 and 66.12 (d); *m/z* 311 (M^+, 8%), 281 (21) and 73 (100).

General Procedure for the Synthesis of Tributylstannylsulfides **14**.—To a solution of the adduct (1 mmol) in freshly distilled benzene (10 cm^3) and azoisobutyronitrile (0.1 mmol), tributylstannyl hydride (1 mmol) was added *via* a syringe and the mixture heated to reflux 20 min. A white precipitate of phthalimide was formed during heating. The mixture was cooled at room temperature, diluted with freshly distilled pentane (50 cm^3) and the phthalimide filtered off. The stannyl derivatives obtained after evaporation of the solvent were purified by distillation.

2-*Tributylstannylthio*-1,2-*dimethylvinyl chloride* **14a**. 74%, b.p. 85 °C, 0.01 Torr (Found: C, 46.3; H, 8.3. $C_{16}H_{33}ClSSn$ requires C, 46.68; H, 8.08%); δ_H(200 MHz, $CDCl_3$) 0.90 (9 H, t, Me, *J* 7.06), 1.14 (6 H, t, *J* 7.06), 1.42–1.62 (6 H, m), 2.10 (3 H, q, vinylic Me, *J* 1.52) and 2.33 (3 H, q, vinylic Me, *J* 1.52); δ_C(50 MHz, $CDCl_3$) 13.40 [q, Me (Bu)], 14.29 (t, CH_2Sn), 26.90, 28.35 [t, CH_2 (Bu)], 24.85, 27.18 (q, Me, vinylic), 124.08 and 129.19 (s, vinylic); *m/z* 411 (M^+, 1%), 355 ($M^+ - 56$, 19), 177 (100).

2-*Tributylstannylthio*-1,2-*diphenylvinyl chloride* **14b**. 60%, b.p. 155 °C, 0.001 Torr (Found: C, 58.5; H, 7.1. $C_{26}H_{37}ClSSn$ requires C, 58.28; H, 6.96%); δ_H(200 MHz, $CDCl_3$) 0.70–1.70 (27 H, m); δ_C(50 MHz, $CDCl_3$) 13.59 [q, Me (Bu)], 14.46 (t, CH_2Sn), 26.94, 28.37 [t, CH_2 (Bu)], 127.75, 127.79, 127.85, 128.00, 128.06, 128.96 (d, Ar), 129.74, 129.96 (s, Ar), 127.72 and 143.36 (s, vinylic); *m/z* 478 ($M^+ - 57$, 19%) and 57 (100).

2-tert-*Butyl*-2-*tributylstannylthiovinyl chloride* **14c**. [Attempts to purify by distillation (130 °C, 0.001 Torr) resulted in *E*–*Z* isomerization; yield and elemental analysis refer to the mixture after distillation and spectroscopic data to the crude *E*-stannyl sulfide obtained from the reaction]. 71% (Found: C, 49.2; H, 8.1. $C_{18}H_{37}ClSSn$ requires C, 49.16; H, 8.48%); δ_H(200 MHz, $CDCl_3$) 0.89 (9 H, t, Me, *J* 7.18), 1.05–1.20 (6 H, m, CH_2Sn), 1.25–1.40 (6 H, m), 1.45–1.60 (6 H, m), 1.30 (9 H, s) and 6.14 (1 H, s); δ_C(50 MHz, $CDCl_3$) 15.05 [q, Me (Bu)], 16.69 (t, CH_2Sn), 27.07, 28.46 [t, CH_2 (Bu)], 28.46 [q, Me, Bu^t)], 39.93 (s, Bu^t), 117.21 (d, vinylic) and 148.93 (d, vinylic); *m/z* 383 ($M^+ - 56$, 26%), 269 (48) and 57 (100).

Alkaline Hydrolysis of Compounds **3a** *and* **3c**.—A solution of the adduct (1 mmol) in dichloromethane (10 cm^3) was stirred for 12 h in the presence of aqueous sodium hydroxide (0.1 mol dm^{-3}; 10 cm^3). The organic layer was separated, and the aqueous layer was washed twice with dichloromethane (20 cm^3). The organic layers were collected, washed with saturated ammonium chloride and brine and evaporated to dryness. The crude bis(2-chloro-1,2-dimethylvinyl) disulfide **8a** was purified (46%) by preparative TLC using light petroleum as eluent (spectroscopic identification).[13]

The crude bis(2-chloro-1,2-diphenylvinyl) disulfide **8b** was purified by column chromatography, using light petroleum–ethyl ether (3:1) as eluent, and recrystallized to give the pure product **8b** (38%), m.p. 117–118 °C (methanol) (Found: C, 68.9; H, 4.6. $C_{28}H_{20}Cl_2S_2$ requires C, 68.50; H, 4.11%); δ_H(200 MHz, $CDCl_3$) 7.00–7.10 (8 H, m, Ar) and 7.15–7.40 (12 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 127.91, 128.02, 128.07, 129.01, 129.57, 129.95 (d, Ar), 131.50, 134.74, 137.45 and 137.75 (s, Ar and vinylic); *m/z* 490 (M^+, 7%), 246 ($M^+ - 244$, 35) and 210 ($M^+ - 270$, 100).

Reaction of Compound **3a** *with Trimethylsilyllithium*.—To a solution of trimethylsilyllithium[21] (1.25 mmol) and kept at −78 °C a solution of **3a** (267 mg, 1 mmol) in dry THF (3 cm^3) was added. After 15 min TLC showed the complete disappearance of the adduct **3a**. The mixture was allowed to warm to room temperature, quenched with saturated aqueous ammonium chloride (30 cm^3) and diluted with diethyl ether (30 cm^3). The organic layer was washed twice with saturated aqueous ammonium chloride (30 cm^3) and twice with brine (30 cm^3), dried (Na_2SO_4) and evaporated to dryness. The crude product was purified by column chromatography, using a light petroleum as eluent, to give compound **8a** (85 mg, 70%) as an oil identified by comparison with a pure sample.[13]

Reaction of Compound **3a** *with Tributylstannyllithium*.—To a solution of tributylstannyllithium[22] (1.25 mmol) at 0 °C a solution of compound **3a** (267 mg, 1 mmol) in dry THF (3 cm^3) was added. After 15 min TLC showed the complete disappearance of the adduct **3a**. The mixture was allowed to warm to room temperature, quenched with saturated aqueous ammonium chloride (30 cm^3) and diluted with diethyl ether (30 cm^3). The organic layer was washed twice with saturated aqueous ammonium chloride (30 cm^3) and twice with brine (30 cm^3), dried (Na_2SO_4) and evaporated to dryness. The crude product was purified by column chromatography, using light petroleum as eluent, to give compound **8a** (61 mg, 50%) as an oil identified by comparison with a pure sample.[13] Hexabutyldistannane (231 mg, 80%) was also isolated.

Reaction of Compound **3a** *with Methylthiotrimethylsilane.*—Methylthiotrimethylsilane (240 mg, 2 mmol) was added *via* a syringe to a solution of compound **3a** (534 mg, 2 mmol) in dry THF (20 cm^3) at room temperature. The reaction mixture was stirred until complete disappearance of compound **3a** occurred (24 h), and was then quenched with brine. The organic layer was separated, dried (Na_2SO_4) and evaporated to dryness. The crude product obtained was purified by chromatography on silica gel, using light petroleum as eluent, yielding 2-chloro-1,2-dimethylvinyl methyl disulfide **13** (193 mg, 71%) as an oil (Found: C, 35.8; H, 5.4. C_5H_9ClS requires C, 35.60; H, 5.38%); δ_H(200 MHz, $CDCl_3$) 2.22 (3 H, q, *J* 1.52), 2.36 (3 H, q, *J* 1.52) and 2.41 (3 H, s, MeS); δ_C(50 MHz, $CDCl_3$) 20.15, 24.18 (q, Me, vinylic), 23.35 (q, MeS), 127.32 and 131.46 (s, vinylic); *m/z* 168 (M^+, 37%), 120 (M^+ − 48, 30) and 59 (100).

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References

1 For part 3 see: E. Busi, G. Capozzi, S. Menichetti and C. Nativi, *Synthesis*, 1992, in the press.
2 G. Capozzi, G. Modena and L. Pasquato, in *The Chemistry of Functional Groups: The Chemistry of Sulphenic Acids and Their Derivatives*, ed. S. Patai, Wiley, Chichester, 1990, p. 403.
3 E. Kuele, in *The Chemistry of Sulphenic Acids*, Thieme, Stuttgart, 1970.
4 G. Capozzi, L. Gori and S. Menichetti, *Phosphorus, Sulphur Silicon Relat. Elem.*, 1991, **59**, 157.
5 G. Capozzi, L. Gori and S. Menichetti, *Tetrahedron Lett.*, 1990, **31**, 6213.
6 M. U. Bombala and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3013.
7 M. R. Bryce and P. C. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1990, 3225.
8 (*a*) G. Capozzi, V. Lucchini and G. Modena, *J. Chem. Soc., Perkin Trans. 2*, 1975, 361; (*b*) G. Capozzi, V. Lucchini and G. Modena, *J. Chem. Soc., Perkin Trans. 2*, 1975, 900; (*c*) G. Capozzi, O. De Lucchi, V. Lucchini and G. Modena, *Tetrahedron Lett.*, 1975, **16**, 2605; (*d*) G. Capozzi, O. De Lucchi, V. Lucchini and G. Modena, *Synthesis*, 1976, 677; (*e*) G. Capozzi, V. Lucchini, G. Modena and P. Scrimin, *Tetrahedron Lett.*, 1977, **18**, 912; (*f*) G. Capozzi, *Pure Appl. Chem.*, 1987, **59**, 989; (*h*) G. Capozzi, F. Capozzi and S. Menichetti, in *Reviews on Heteroatom Chemistry*, ed. S. Oae, Myu K.K., Tokyo, 1988, vol. 1, p. 178.
9 G. H. Schmid, in *The Chemistry of Functional Groups: The Chemistry of the Carbon–Carbon Triple Bonds*, ed. S. Patai, Wiley, Chichester, 1978, p. 306.
10 G. Capozzi, V. Lucchini and G. Modena, *Rev. Chem. Intermed.*, 1979, **2**, 347.
11 G. H. Schmid, A. Modro, F. Lenz, D. G. Garratt and K. Yates, *J. Org. Chem.*, 1976, **41**, 2331.
12 G. H. Schmid, A. Modro, D. G. Garratt and K. Yates, *Can. J. Chem.*, 1976, **54**, 3045.
13 G. Capozzi, L. Gori and S. Menichetti, *Tetrahedron*, 1991, **47**, 7185.
14 S. K. Boustany and B. A. Sullivan, *Tetrahedron Lett.*, 1970, **11**, 3547.
15 D. N. Harpp and G. T. Back, *J. Org. Chem.*, 1971, **36**, 3828.
16 D. H. R. Barton, G. Page and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 1970, 1466.
17 D. N. Harpp and G. T. Back, *Tetrahedron Lett.*, 1971, **12**, 4953.
18 S. J. Grosset and K. P. Dubey, *J. Chem. Soc., Chem. Commun.*, 1982, 1183.
19 W. A. Schulze, USP 2 123 083/1938.
20 D. A. Armitage and M. J. Clark, *J. Organomet. Chem.*, 1970, **24**, 629.
21 P. F. Hudrlik, M. A. Waugh and A. M. Hudrlik, *J. Organomet. Chem.*, 1984, **271**, 69.
22 W. Clark Still, *J. Am. Chem. Soc.*, 1978, **100**, 1481.
23 G. Capozzi, O. De Lucchi, V. Lucchini and G. Modena, *J. Chem. Soc., Chem. Commun.*, 1975, 248.
24 G. Capozzi, C. Caristi, V. Lucchini and G. Modena, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2197.
25 G. Capozzi, G. Melloni and G. Modena, *J. Chem. Soc. C*, 1970, 2625.

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