

Journal of Organometallic Chemistry, 437 (1992) 111–125
 Elsevier Sequoia S.A., Lausanne
 JOM 22698

Addition of sulphenyl halides to alkenyl–metal compounds

III *. Arenesulphenyl chloride additions to triethoxy- and triphenylvinylsilanes and to triphenylvinylgermanium. Crystal structure of (4-Me-2-O₂NC₆H₃S)CH(SiPh₃)CH₂Cl **

R. Alan Howie, Gavin M. Spencer, James L. Wardell

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE (UK)

and John N. Low

Department of Applied Physics and Electronic and Manufacturing Engineering, The University of Dundee, Dundee DD1 4HN (UK)

(Received February 11, 1992)

Abstract

Additions of arenesulphenyl chlorides (*e.g.* ArSCl = *p*-XC₆H₄SCl; X = Me or Cl; 4-Y-2-O₂NC₆H₄SCl; Y = H, Me or NO₂) to R₃MCH=CH₂ [R₃M=Ph₃Si, (EtO)₃Si or Ph₃Ge] can provide both possible adducts: R₃MCHSArCH₂Cl (the *anti*-Markovnikov adducts) and R₃MCHClCH₂SAr (the Markovnikov adducts). In reactions in CH₂Cl₂ at room temperature, the former adducts always dominate (> 77%) and can be the exclusive products. The ratio of [R₃MCHSArCH₂Cl]:[R₃MCHClCH₂SAr] increases in the sequences Ar = *p*-ClC₆H₄ > *o*-O₂NC₆H₄ > 2,4-(O₂N)₂C₆H₃; (Me₃SiCH=CH₂) > Ph₃SiCH=CH₂ > (EtO)₃SiCH=CH₂; and Ph₃SiCH=CH₂ > Ph₃GeCH=CH₂.

A crystal structure determination of (4-Me-2-O₂NC₆H₃S)CH(SiPh₃)CH₂Cl revealed a slightly distorted tetrahedral geometry about Si with a staggered conformation about the central C–C bond (Si–C–C–Cl dihedral angle is 167°). There is a short S···O intramolecular distance of 2.781 Å.

Introduction

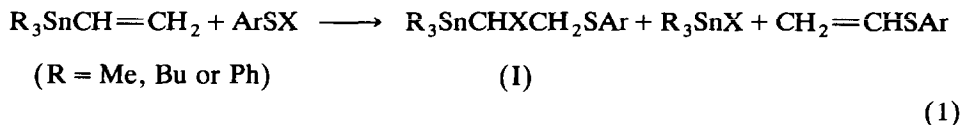
Sulphenyl halides, as electrophilic reagents, take part in addition reactions with alkenes [1–3]. Earlier, we reported [4] that ArSX (and ArSSCN) react with vinylstannanes to give both addition and cleavage products, eq. 1. The only adducts

Correspondence to: Dr. J.L. Wardell.

* For Part I, see ref. 4; for Part II, see ref. 5.

** Dedicated to Professor Alwyn G. Davies, as a friend, and in recognition of his important contributions to organometallic chemistry.

obtained had Markovnikov orientations; none of the *anti*-Markovnikov adducts ($R_3SnCHSArCH_2X$) were detected.

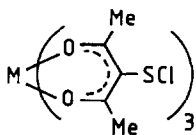


The ratio of addition to cleavage products depended on the Ar and R groups. Confirmations of the Markovnikov structures for two adducts, *viz.* o - $O_2NC_6H_4SCH_2CH(SCN)SnPh_3$ and $(4\text{-Me-}2\text{-}O_2NC_6H_3S)CH_2CHClSnPh_3$, were obtained from crystal structure determinations [5].

In contrast to the findings with the vinylstannanes, trimethylvinylsilane and $ArSCl$ were reported [6] to provide only the *anti*-Markovnikov adducts, eq. 2. Additions of more elaborate sulphenyl halides to $Me_3SiCH=CH_2$ have also been



studied: $(^tBuCH_2O)_2P(S)SBr$ was surprisingly reported to provide solely the Markovnikov adduct, $Me_3SiCHBrCH_2SP(S)(OCH_2^tBu)_2$ [7], while it appears [8] that both possible adducts are obtained from 3-*cis*-pentan-1,4-dionato-metal complexes (II).



(II), M = Cr, Co or Al)

To investigate the effects of substituents R in $R_3SiCH=CH_2$, reactions of $Ph_3SiCH=CH_2$ and $(EtO)_3SiCH=CH_2$ with $ArSCl$ have been carried out. A few reactions of $Ph_3GeCH=CH_2$ with $ArSCl$ have also been studied. In addition, the crystal structure of one adduct, $(4\text{-Me-}2\text{-}O_2NC_6H_3S)CH(SiPh_3)CH_2Cl$, has been determined.

Results and discussion

Addition of $ArSCl$ to vinylsilanes

Reactions of $ArSCl$ with $R_3SiCH=CH_2$ (R = Ph or EtO) in chlorocarbon solvents only produced adducts—no cleavage products were detected. Two sets of reaction conditions were adopted: (i) on a preparative scale for further study of the adducts and which involved refluxing solutions for several hours and (ii) on a NMR scale, at ambient temperature, to determine the kinetic product distribution. The latter reactions required days to go to completion.

As reported in the Introduction, $Me_3SiCH=CH_2$ and $ArSCl$ produced only the *anti*-Markovnikov adducts in dichloromethane in reactions at temperatures, initially at $-78^\circ C$ but finally at $20^\circ C$. In contrast, from reactions of $Ph_3SiCH=CH_2$ or

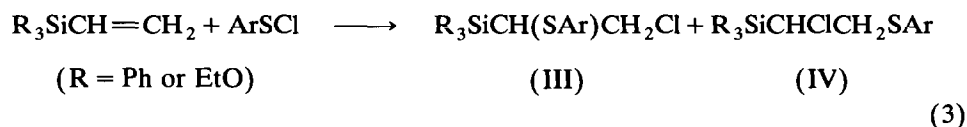
Table 1

Adducts of reaction of $R_3MCH=CH_2$ and $ArSCl$ in CH_2Cl_2 solutions at $25^\circ C$

$R_3MCH=CH_2$	$ArSCl$	$[R_3MCHSArCH_2Cl]:[R_3MCHClCH_2SAr]$
$Ph_3SiCH=CH_2$	$p\text{-ClC}_6\text{H}_4\text{SCl}$	100:0
	$2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{Cl}$	90:10
$(EtO)_3SiCH=CH_2$	$o\text{-O}_2\text{NC}_6\text{H}_4\text{SCl}$	85:15
	$2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{SCl}$	77:23
		63:37 ^a
$Ph_3GeCH=CH_2$	$p\text{-ClC}_6\text{H}_4\text{SCl}$	92:8
	$o\text{-O}_2\text{NC}_6\text{H}_4\text{SCl}$	83:17
	$2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{SCl}$	82:18

^a In CCl_4 solution.

$(EtO)_3SiCH=CH_2$ in CH_2Cl_2 at $20^\circ C$, both possible adducts, III and IV, were usually obtained (eq. 3).



An exception was the reaction between $Ph_3SiCH=CH_2$ and $p\text{-ClC}_6\text{H}_4\text{SCl}$, which provided solely the *anti*-Markovnikov adduct III (R = Ph; Ar = $p\text{-ClC}_6\text{H}_4$). The *anti*-Markovnikov adducts III were always the major products in these reactions (> 77%) (Table 1). As the electron releasing ability of the Ar group increases, so does the ratio of III:IV, *i.e.* the more reactive $ArSCl$ provides the most selective reaction. The proportion of the Markovnikov adduct increases in the sequence $p\text{-ClC}_6\text{H}_4\text{SCl} < o\text{-O}_2\text{HC}_6\text{N}_4\text{SCl} < 2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{SCl}$ for the same $R_3MCH=CH_2$. Less selectivity was obtained in CCl_4 than in CH_2Cl_2 (Table 1). NMR spectral data for adducts are listed in Table 2.

Spectral assignments of the $=CH-CH_2-$ protons were aided by $^1H-^{13}C$ COSY experiments. As can be seen, the CH_2 protons in both types of adducts are diastereotopic.

It is generally accepted [1] that the rate determining step in addition of R^2SX to an alkene is the formation of the episulphonium ion V in Scheme 1. Under kinetically controlled conditions, the products obtained are governed by the ease of approach of X^- to the two carbon centres in V; for bulky R' groups, the predominant products are the *anti*-Markovnikov adducts [9–10], *e.g.* $Me_3CC-H=CH_2$ and $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{SCl}$ ($ArSCl$) in CH_3CO_2H at $25^\circ C$ provides a 95:5 molar ratio of $Me_3CCHSArCH_2Cl:Me_3CCHClCH_2SAr$ [9]. Such kinetically controlled ratios can have prolonged stabilities at ambient temperatures: it is only at higher temperatures that isomerisations occur to give thermodynamic (equilibrium) ratios, rich in the Markovnikov adducts. Clearly the vinyl-metal compounds studied here can be considered to be alkenes bearing bulky substituents R' [$R' = Ph_3Si, (EtO)_3Si$ or Ph_3Ge]. For less bulky R' groups, the relative amounts of products VI and VII depend much more on the electronic effects of R' .

With the more electron withdrawing R^2 groups, the episulphonium ion V becomes less stable and some positive charge will be transferred from sulphur to

Table 2
NMR spectral data for adducts in CD₂Cl₂

	R ₃ MCH _a SArCH _b H _c Cl	δH _a [J(H _a -H _c)]	δH _b [J(H _b -H _c)]	δH _c [J(H _a -H _b)]	δH _{aryl} +others	δ ¹³ CH	δ ¹³ CH ₂
A							
R = Ph, M = Si	Ar = <i>p</i> -ClC ₆ H ₄	3.59 [8.69]	3.86 [11.66]	4.10 [3.73]	7.80-7.20(m)	38.71	49.32
R = Ph; M = Si	Ar = 4-Me-2-O ₂ NC ₆ H ₃ ^a	3.76 [9.30]	3.86 [11.27]	4.14 [3.40]	7.83(s), 7.60(m), 7.40(m) aryl 2.40(s, Me)	36.50	48.32
R = Ph; M = Si	Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	3.9(m) + 4.24(m)			8.94(d, J 2.50), 8.36(dd, J 2.50, J 9.06) 7.99(d, J 9.06), 7.65(m, <i>o</i> -Ph ₃ Si), 7.45(m, <i>m</i> + <i>p</i> -Ph ₃ Si)	36.67	48.84
R = EtO, M = Si	Ar = <i>o</i> -O ₂ NC ₆ H ₄	3.12 [7.35]	3.77 [11.37]	ca. 4.0 [5.87]	8.14(dd, J 1.3, J 8.2), 7.66(m), 7.34(m) (aryl) 3.96(q, J 7.0), 1.28(t, J 7.0) (EtO)	33.65	46.22
R = EtO; M = Si	Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	3.16 [8.52]	3.74 [11.73]	4.07 [5.21]	9.02(d, J 2.49), 8.36(dd, J 2.49, J 9.10) 7.86(d, J 9.10) (aryl) 3.96(q, J 7.0), 1.27(t, J 7.0) (EtO)	33.60	45.39
R = Ph; M = Ge	Ar = <i>p</i> -ClC ₆ H ₄	3.74 [7.36]	3.88 [11.48]	3.98 [4.44]	7.60-7.20(m)		
R = Ph; M = Ge	Ar = <i>o</i> -O ₂ NC ₆ H ₄ ^a	4.08 [7.69]	3.98 [10.56]	4.18 [3.97]	8.09(dd, J 1.42, J 8.20), 7.80-7.20(m)	36.58	47.99

R = Ph; M = Ge	Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	4.08 [9.05]	3.95 [11.17]	4.19 [3.83]	8.97(d, <i>J</i> 2.50), 8.37(dd, <i>J</i> 2.50, <i>J</i> 9.10), 7.96(d, <i>J</i> 9.10), 7.62(m, <i>o</i> -Ph ₃ Ge), 7.50(m, <i>m</i> - + <i>p</i> -Ph ₃ Ge)	38.4	45.5
B	R ₃ MCH ₆ ClCH ₆ H ₆ SAr						
R = Ph; M = Si	Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	4.26 [2.23]	3.45 [13.65]	3.71 [12.10]	9.04(d, <i>J</i> 2.50), 8.17(dd, <i>J</i> 2.50, <i>J</i> 9.04) 7.13(d, 9.04), 7.65(m, <i>o</i> -Ph ₃ Si), 7.45(m, <i>m</i> - + <i>p</i> -Ph ₃ Si)	37.51	42.94
R = EtO; M = Si	Ar = <i>o</i> -O ₂ NC ₆ H ₄	ca. 3.7 [ca. 3]	ca. 3.33 [ca. 13]	ca. 3.5 [ca. 11]	8.18(dd), 7.7–7.3 (aryl) 3.70(g, <i>J</i> 7.0), 1.28(t, <i>J</i> 7.0) (EtO)	37.24	41.41
R = EtO; M = Si	Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	3.74 [2.32]	3.35 [12.70]	3.47 [11.27]	9.08(d, <i>J</i> 2.51), 8.40(dd, <i>J</i> 2.51, <i>J</i> 9.03), 7.64(d, <i>J</i> 9.03) (aryl) 3.68(g, <i>J</i> 7.0), 1.27(t, <i>J</i> 7.0) (EtO)		
R = Ph, M = Ge	Ar = <i>p</i> -ClC ₆ H ₄	4.20 [2.58]	3.27 [14.51]	3.61 [11.89]	7.60–7.20(m)		
R = Ph; M = Ge	Ar = <i>o</i> -O ₂ NC ₆ H ₄ ^a	4.41 [2.85]	3.53 [13.89]	3.77 [11.50]	8.36(dd, <i>J</i> 1.39, <i>J</i> 8.20), 7.80–7.70(m)	38.83	46.46
R = Ph; M = Ge	Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	4.37 [2.81]	3.56 [13.64]	3.77 [11.66]	9.04(d, <i>J</i> 2.50), 8.19(dd, <i>J</i> 2.52, <i>J</i> 9.02), 7.21(d, 9.02), 7.62(m, <i>o</i> -Ph ₃ Ge), 7.50(m) <i>m</i> - + <i>p</i> -Ph ₃ Ge		
R = Ph; M = Sn	Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃ ^b	4.35 [8.7]	3.79 [13.6]	3.72 [6.4]	9.00(d, <i>J</i> 2.50), 8.23(dd, <i>J</i> 2.5, 8.9), 7.34(d, 8.9), 7.63(m, <i>o</i> -Ph ₃ Sn), 7.46(m), <i>m</i> - + <i>p</i> -Ph ₃ Sn		

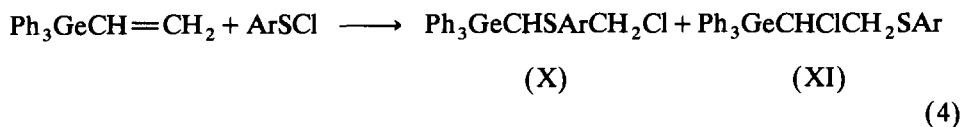
^a In CDCl₃. ^b Ref. 5.

carbon, with even the formation of open carbonium ions (VIII or IX). Greater proportions of the *anti*-Markovnikov adducts of non-metallated alkenes have been obtained from ArSCL having the more electron releasing Ar groups [10]. This parallels our findings with $R_3MCH=CH_2$. The stabilisation of VIII and IX clearly becomes important in deciding product ratios. For vinylsilanes, an important factor is the well-known β -effect, *i.e.* the stabilisation of silylethyl cations, $R_3Si-\overset{\overset{|}{C}}{\underset{|}{C}}^+$ via hyperconjugation involving the σ -(C-Sn) orbital and the empty *p*-orbital at the β -positive centre. The silylethyl cation has been calculated to be 38 kcal mol⁻¹ more stable than the ethyl cation [11a]; σ^+ values for Me_3SiCH_2 and $(EtO)_3SiCH_2$ (-0.54 and -0.19 respectively) also reflect this [11b]. The stabilisation of the $R_3SiCH(SAr)CH_2^+$ cation enhances formation of the *anti*-Markovnikov adducts (and thereby supplements the consequences of the steric effects of the R_3Si groups).

Relatively greater amounts of $R_3SiCHClCH_2SAr$ (Markovnikov adducts) in the vinylsilane reactions are also obtained in the sequence $R_3Si = (Me_3Si <)Ph_3Si < (EtO)_3Si$ for the same ArSCL. The σ^+ values for Me_3Si and $(EtO)_3Si$ are -0.13 and +0.01 respectively [11b]; thus there is a greater difference in σ^+ values for Me_3SiCH_2 and Me_3Si (0.41) than there is for $(EtO)_3SiCH_2$ and $(EtO)_3Si$ (0.20). The smaller difference for $(EtO)_3SiCH_2/(EtO)_3Si$ suggests that there should be less discrimination between adducts of $(EtO)_3SiCH=CH_2$ than of $Me_3SiCH=CH_2$, *i.e.* there should be a reduced $[R_3SiCHSArCH_2Cl]:[R_3SiCHClCH_2SAr]$ ratio for $R = EtO$ compared to that for $R = Me$, as found.

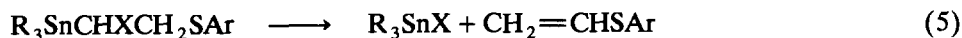
Additions to $Ph_3GeCH=CH_2$

It is apparent from the results in Table 1, that $Ph_3GeCH=CH_2$ provides results much more similar to those for vinylsilanes than for vinylstannanes. As with $R_3SiCH=CH_2$, $Ph_3GeCH=CH_2$ gave both adducts, with the major ones being the *anti*-Markovnikov compounds, eq. 4; no cleavage products (*i.e.* Ph_3GeCl and $CH_2=CHSAr$) were detected. The ratio of X:XI increased with the reactivity of ArSCL.

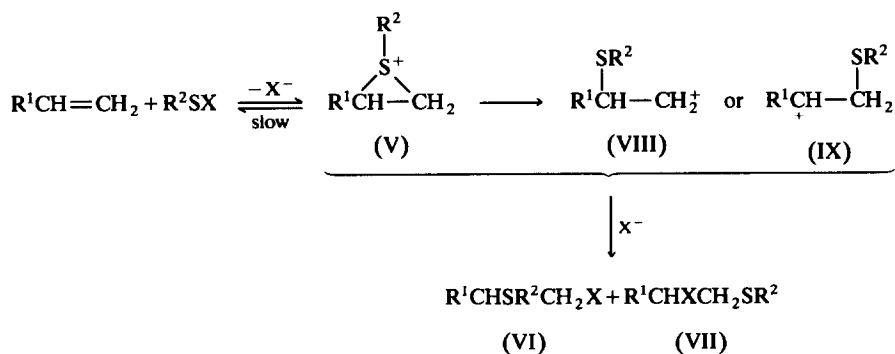


Reactions of the adducts

All adducts of $R_3SiCH=CH_2$ ($R = EtO$ or Ph) and $Ph_3SiCH=CH_2$ were stable in chlorocarbon solvents over a long period at 20°C. This contrasts markedly with the instability (eq. 5) of $R_3SnCHXCH_2SAr$ over similar times [4]. However the adduct $Ph_3SiCH(SC_6H_4Me-p)CH_2Cl$, was converted to $Ph_3SiCH(SC_6H_4Me-p)CH_2OH$ on chromatography on Al_2O_3 .

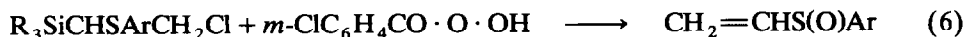


Magnus *et al.* [6] showed that $Me_3SiCHSArCH_2Cl$ could be converted to synthetically useful $CH_2=CHS(O)Ar$ by oxidative cleavage using $m-ClC_6H_4CO \cdot O$



Scheme 1.

$\cdot\text{OH}$. By similar means, $\text{R}_3\text{SiCHSArCH}_2\text{Cl}$ ($\text{R} = \text{EtO}$ or Ph) were shown to be equally good precursors of $\text{CH}_2=\text{CHS(O)Ar}$ (eq. 6).



Molecular structure of (4-Me-2-O₂NC₆H₃S)CHSiPh₃CH₂Cl (XII)

The atomic numbering system and atomic arrangements are shown in Fig. 1. The atom coordinates and bond angles and lengths are in Tables 3 and 4.

The geometry about Si in XII is tetrahedral with C–Si–C angles ranging from 106.2(3) to 112.8(3)°. The C–Si bond lengths [Si–C_{alkyl} 1.916(6) and Si–C_{aryl} 1.870(6)–1.888(6)] are normal. The solid state conformation is staggered about the C(1)–C(2) bond with a Si–C–C–Cl dihedral angle of 167° (Fig. 2).

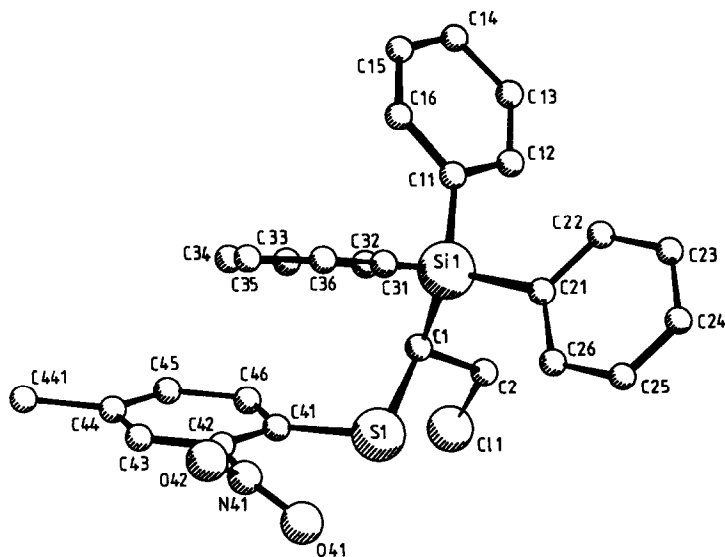


Fig. 1. Atomic arrangements and numbering systems for XII.

Table 3

Coordinates $\times 10^4$ for non-hydrogen atoms and $U_{eq} \times 10^3$ with e.s.d.s in parentheses

	x	y	z	U_{eq}^a
Si(1)	2407(2)	9149(1)	1539(1)	37(1)
S(1)	1864(2)	8069(1)	498(1)	46(1)
Cl(1)	-2237(2)	9116(2)	347(1)	84(1)
C(1)	751(8)	8697(5)	986(2)	40(2)
C(2)	-436(9)	9647(6)	770(2)	62(3)
C(11)	1171(8)	9294(5)	2082(2)	40(2)
C(12)	-109(9)	10114(6)	2096(2)	51(2)
C(13)	-1087(10)	10159(6)	2483(3)	61(3)
C(14)	-789(9)	9397(6)	2872(3)	57(3)
C(15)	482(10)	8589(6)	2865(3)	60(3)
C(16)	1468(9)	8534(5)	2482(2)	46(2)
C(21)	3526(8)	10520(5)	1429(2)	39(2)
C(22)	3685(9)	11410(6)	1776(3)	55(2)
C(23)	4601(11)	12385(6)	1698(3)	71(3)
C(24)	5392(11)	12493(7)	1280(4)	74(3)
C(25)	5295(10)	11629(7)	935(3)	71(3)
C(26)	4346(8)	10647(6)	1011(2)	54(2)
C(31)	4041(8)	7978(5)	1662(2)	34(2)
C(32)	5790(9)	8224(6)	1734(2)	57(2)
C(33)	7033(10)	7335(7)	1820(3)	71(3)
C(34)	6522(10)	6235(7)	1832(2)	59(3)
C(35)	4803(10)	5965(6)	1762(2)	56(2)
C(36)	3575(9)	6810(5)	1683(2)	44(2)
C(41)	1417(8)	6585(5)	551(2)	35(2)
C(42)	2666(8)	5760(6)	494(2)	36(2)
N(41)	4327(8)	6090(5)	357(2)	51(2)
O(41)	4360(7)	6893(4)	68(2)	78(2)
O(42)	5605(6)	5550(5)	531(2)	78(2)
C(43)	2416(8)	4593(5)	561(2)	43(2)
C(44)	853(9)	4210(6)	677(2)	39(2)
C(441)	524(8)	2938(5)	746(2)	53(2)
C(45)	-415(8)	5014(5)	725(2)	42(2)
C(46)	-161(8)	6183(5)	660(2)	42(2)

$$^a U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

A feature of the structure of XII is the short S(1)···O(41) intramolecular distance [2.781(6) Å] and the C(1)–S(1)–O(41) valency angle of 159.2(6)°. This S···O distance is less than the sum of the van der Waal radii (3.25 Å). Table 5 provides values of S···O distances in some *o*-nitrophenylsulphido compounds, R-2-O₂NC₆H₃SY [12–14]. The Y–S···O angles are all close to 180° and as can be seen the S···O distance varies with the electronegativity of the bonding atom in Y. The S···O distances are similar in MeSC₆H₄NO_{2-*o*} and in XII, despite the (H₃)C–S···O angle in MeSC₆H₄NO_{2-*o*} being greater than that in XII [173.9(21) *vs.* 159.2(6)°] (Fig. 3). The greater deviation from 180° in XII rises as a consequence of the bulk of the additional substituents in XIII, *i.e.* the Ph₃Si and Cl groups.

The carbon–sulphur bond lengths in XII are 1.845(6) C_{alkyl}–S and 1.779(6) Å, C_{aryl}–S, compared to values in MeSC₆H₄NO_{2-*o*} of 1.809(6) and 1.774(6) Å and MeSPh of 1.803(13) and 1.749(12) Å respectively [15]. Taking into account the 2

Table 4

Interatomic distances (Å) and angles (deg)

<i>Interatomic distances</i>			
C1...Si1	1.916(6)	C11...Si1	1.888(6)
C21...Si1	1.871(6)	C31...Si1	1.870(6)
C1...S1	1.846(6)	C41...S1	1.779(6)
C2...C11	1.799(6)	C2...C1	1.512(7)
C12...C11	1.391(8)	C16...C11	1.402(8)
C13...C12	1.390(8)	C14...C13	1.380(9)
C15...C14	1.373(8)	C16...C15	1.385(8)
C22...C21	1.399(8)	C26...C21	1.394(8)
C23...C22	1.379(8)	C24...C23	1.378(10)
C25...C24	1.375(9)	C26...C25	1.399(8)
C32...C31	1.384(8)	C36...C31	1.416(7)
C33...C32	1.403(9)	C34...C33	1.370(9)
C35...C34	1.368(8)	C36...C35	1.373(8)
C42...C41	1.397(7)	C46...C41	1.392(8)
N41...C42	1.454(7)	C43...C42	1.393(8)
O42...N41	1.229(6)	O42...N41	1.219(6)
C44...C43	1.381(8)	C441...C44	1.525(7)
C45...C44	1.386(8)	C46...C45	1.396(7)
<i>Angles</i>			
C11-Si1-C1	106.2(3)	C21-Si1-C1	112.9(3)
C21-Si1-C11	110.6(3)	C31-Si1-C1	107.9(3)
C31-Si1-C11	109.8(3)	C31-Si1-C21	109.4(3)
C41-S1-C1	102.1(3)	S1-C1-Si1	110.0(3)
C2-C1-Si1	114.3(4)	C2-C1-S1	109.7(4)
C1-C2-C11	112.2(4)	C12-C11-Si1	122.4(5)
C16-C11-Si1	120.5(5)	C16-C11-C12	117.1(6)
C13-C12-C11	121.6(6)	C14-C13-C12	120.6(7)
C15-C14-C13	118.4(7)	C16-C15-C14	121.7(7)
C15-C16-C11	120.6(7)	C22-C21-Si1	121.8(5)
C26-C21-Si1	120.2(5)	C26-C21-C22	117.8(6)
C23-C22-C21	120.5(7)	C24-C23-C22	120.6(8)
C25-C24-C23	120.8(8)	C26-C25-C24	118.6(8)
C25-C26-C21	121.7(7)	C32-C31-Si1	120.7(5)
C36-C31-Si1	122.6(5)	C36-C31-C32	116.7(6)
C33-C32-C31	121.4(7)	C34-C33-C32	119.9(7)
C35-C34-C33	120.1(7)	C36-C35-C34	120.5(7)
C35-C36-C31	121.4(6)	C42-C41-S1	121.0(5)
C46-C41-S1	122.5(5)	C46-C41-C42	116.5(5)
N41-C42-C41	120.6(6)	C43-C42-C41	123.2(6)
C43-C42-N41	116.1(6)	O41-N41-C42	118.0(6)
O42-N41-C42	118.5(6)	O42-N41-O41	123.5(7)
C44-C43-C42	119.5(6)	C441-C44-C43	121.0(6)
C45-C44-C43	118.1(6)	C45-C44-C441	120.9(6)
C46-C45-C44	122.3(6)	C45-C46-C41	120.3(6)

lone pairs on sulphur, trigonal bipyramidal geometries for MeSC₆H₄NO₂-*o* and for XII are attained with C_{alkyl} and O both axial and C_{aryl} and the two lone pairs equatorial.

The S(1)-C(41)-C(42)-N(41)-O(41) unit in XII is not planar; N(41) and O(41) are -0.09 and -0.79 Å distant from a "best" plane defined by C(41), C(42) and S(1).

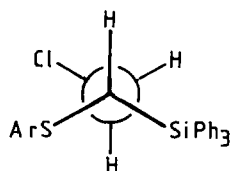


Fig. 2. Solid state conformation of XII.

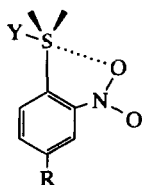
Conformations in solutions

The anti-Markovnikov adducts can have the staggered conformations XIII–XV in solution, while for the Markovnikov adducts, the possible staggered conformations are XVI–XVIII (Fig. 4). The populations of the conformers in solution of each adduct can be calculated from values of the overall coupling constants, ${}^3J(\text{H}_a\text{--H}_c)$ and ${}^3J(\text{H}_c\text{--H}_b)$ (Table 2). Some estimates are required for the individual 3J coupling constants for each of the conformers. Previously, values of ${}^3J(\text{H--H}) = 2.5$ and 13.5 Hz were chosen for *gauche* and *trans* arrangements of hydrogens respectively for 2,4-(O_2N) $_2\text{C}_6\text{H}_3\text{SCH}_2\text{CHClPh}$ [16] (and subsequently [9] for $\text{Ph}_3\text{SnCHClCH}_2\text{SAr}$). Use of these values for the *anti*-Markovnikov adducts, $\text{R}_3\text{MCHSArCH}_2\text{Cl}$, provide the populations quoted in Table 6. Populations calculated using ${}^3J(\text{H--H})$ *gauche* = 2 Hz are also listed in Table 6. As can be seen, the major conformations in solution are similar to that found for (4-Me-2- $\text{O}_2\text{NC}_6\text{H}_3\text{S}$) $\text{CH}(\text{SiPh}_3)\text{CH}_2\text{Cl}$ in the solid state.

For the Markovnikov adducts, $\text{R}_3\text{MCHClCH}_2\text{SAr}$, a lower ${}^3J(\text{H--H})$ *gauche* value has to be used, since overall ${}^3J(\text{H}_a\text{--H}_b)$ values of below 2.5 Hz are obtained. If a value of ${}^3J(\text{H--H})$ *gauche* = 2.0 Hz is chosen along with ${}^3J(\text{H--H})$ *trans* = 13.5 Hz, the populations calculated for $\text{R}_3\text{MCHClCH}_2\text{SAr}$ are those listed in Table 6. The major conformation in solution for the Markovnikov adducts,

Table 5

Values of $\text{S}\cdots\text{O}$ distances and $\text{Y--S}\cdots\text{O}$ angles in selected $\text{R-2-O}_2\text{NC}_6\text{H}_3\text{SY}$ compounds



Compound		(S \cdots O) (Å)	Y-S \cdots O (deg)	Ref.
Y	R			
Cl ^a	H	2.414(11)	177.8(19)	12
Cl ^b	H	2.379(5)	176.9(3)	13
		2.408(5)	178.5(3)	
MeO ^b	H	2.458(2)	176.4(2)	13
Me ^a	H	2.769(7)	173.9(21)	14
$\text{ClCH}_2\text{CH}(\text{SiPh}_3)$ ^b	Me	2.781(6)	159.2(6)	This study
$\text{Ph}_3\text{CHClCH}_2$ ^b	Me	2.715(8)	178.2(3)	5
$\text{Ph}_3\text{SnCHSCNCH}_2$ ^b	H	2.655(5)	172.7(3)	5

^a By e.d. ^b By X-ray.

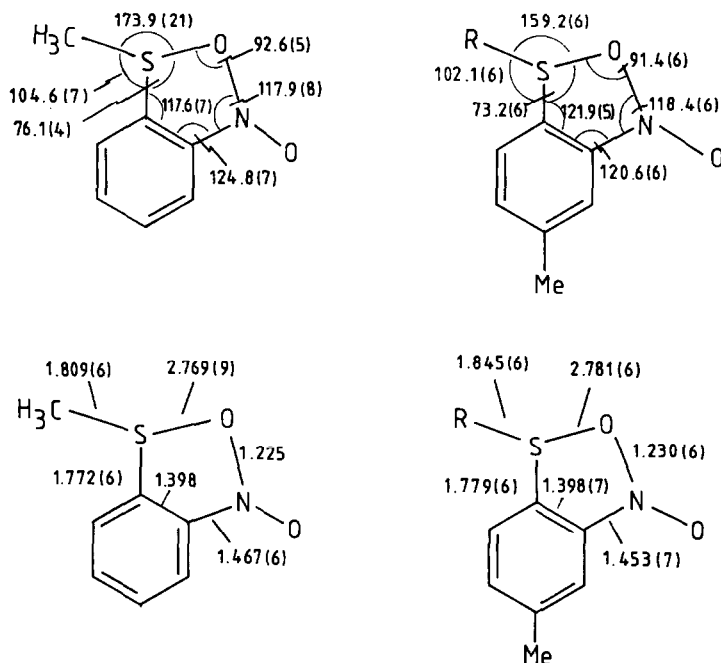
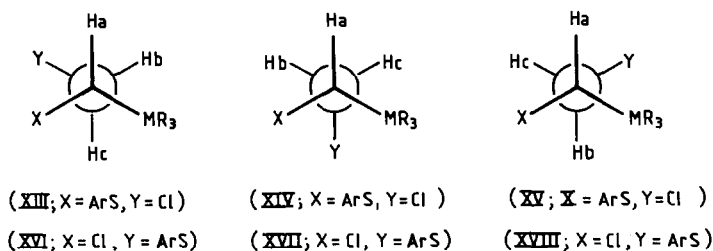


Fig. 3. Comparison of structures of $\text{MeSC}_6\text{H}_4\text{NO}_2\text{-}o$ and XII.

$\text{R}_3\text{MCHClCH}_2\text{SAr}$ ($\text{M} = \text{Si}$ or Ge) is clearly XVI, the other two conformers having only minor populations. This situation is in marked contrast to that calculated for $\text{Ph}_3\text{SnCHClCH}_2\text{SAr}$, for which XVIII had a considerable presence. The solid state conformations of $(o\text{-O}_2\text{NC}_6\text{H}_4\text{S})\text{CH}_2\text{CH}(\text{SCN})\text{SnPh}_3$ and $(4\text{-Me-}2\text{-O}_2\text{NC}_6\text{H}_3\text{S})\text{CH}_2\text{CHClSnPh}_3$ were determined [8] also to be XVIII and suggested some weak $\text{Sn} \cdots \text{S}(\beta)$ interactions. It appears that $\text{Si} \cdots \text{S}(\beta)$ and $\text{Ge} \cdots \text{S}(\beta)$ interactions must be considerably weaker.



Population

a

b

c

$$a + b + c = 1$$

Fig. 4. Conformers in solutions.

Table 6

Populations of conformers of adducts in CH₂Cl₂ solution at 25°C

	XIII ^a (a)	XIV ^a (b)	XV ^a (c)
<i>R</i> ₃ <i>MCHSArCH₂Cl</i>			
R = Ph; Ar = C ₆ H ₄ Cl- <i>p</i>	56[58]	32[27]	12[15]
M = Si			
R = Ph; Ar = 4-Me-2-O ₂ NC ₆ H ₃	62[64]	30[24]	8[12]
M = Si			
R = EtO; Ar = <i>p</i> -ClC ₆ H ₄	44[47]	25[20]	31[33]
M = Si			
R = EtO; Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	55[57]	21[16]	24[27]
M = Si			
R = Ph; Ar = <i>p</i> -ClC ₆ H ₄	44[47]	38[32]	18[21]
M = Ge			
R = Ph; Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	59[61]	28[23]	13[16]
M = Ge			
	XVI ^b (a)	XVII ^b (b)	XVIII ^b (c)
<i>R</i> ₃ <i>MCHClCH₂SAr</i>			
R = Ph; Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	[88]	[10]	[2]
M = Si			
R = EtO; Ar = <i>o</i> -O ₂ NC ₆ H ₄	[78]	[13]	[9]
M = Si			
R = EtO; Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	[81]	[17]	[2]
M = Si			
R = Ph; Ar = <i>p</i> -ClC ₆ H ₄	[86]	[9]	[5]
M = Ge			
R = Ph; Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	[84]	[9]	[7]
M = Ge			
R = Ph; Ar = 2,4-(O ₂ N) ₂ C ₆ H ₃	52 ^c	4 ^c	44 ^c
M = Sn			

^a Calculations using ³*J*(H, H) *gauche* = 2.5 and 2.0 Hz []. ^b Calculations using ³*J*(H, H) *gauche* = 2.0 Hz. ^c Ref. 5.

Experimental

Melting points are uncorrected and were obtained by use of a Kofler hotstage. NMR spectra were recorded on a Bruker 250 MHz instrument. Solvents were dried by standard methods prior to use.

p-Chlorobenzenesulphenyl chloride was a redistilled sample from a previous study [17]. *o*-Toluenesulphenyl chloride, b.p. 74–78°C/2 mmHg [18], *o*-nitrobenzenesulphenyl chloride, m.p. 69–71°C [19], 2,4-dinitrobenzenesulphenyl chloride, m.p. 96–98°C [20] and 4-methyl-2-nitrobenzenesulphenyl chloride, m.p. 88–89°C [21] were prepared by chlorination of the appropriate diaryl disulphide.

Triphenylvinylsilane. Obtained from Ph₃SiCl (17 g) and the Grignard reagent, made from CH₂=CHBr (12 g) and Mg (2.75 g) in THF. After hydrolysis, separation of the organic layer and removal of the solvent, the residue was chromatographed on Al₂O₃ with CCl₄ as eluant, and the first fraction yielded Ph₃SiCH=CH₂ (9.1 g), m.p. 64°C. Lit. value [22] 71–72°C.

^1H NMR (250 MHz, CD_2Cl_2): δ 5.84 (dd, 1H, J 3.75, J 20.16 Hz), 6.38 (dd, 1H, J 3.73, J 14.58 Hz), 6.77 (dd, 1H, J 14.58; J 20.16 Hz), 7.44 (m, 12H, m - and p -H of Ph_3Si), 7.56 (m, 8H, o -H of Ph_3Si).

Triphenylvinylgermanium. Prepared from Ph_3GeCl by a procedure similar to that used for $\text{Ph}_3\text{SiCH}=\text{CH}_2$. It was recrystallised from ethanol, m.p. 61–63°C. Lit. value [23] 62–64°C. ^1H NMR (250 Mhz, CD_2Cl_2): δ 5.83 (dd, 1H, J 3.03, J 19.92 Hz), 6.35 (dd, 1H, J 3.03, J 13.44 Hz), 6.79 (dd, 1H, J 13.44, J 19.92 Hz), 7.44 (m, 12H, m - and p -H of Ph_3Ge), 7.53 (m, 8H, o -H of Ph_3Ge).

Tri(ethoxy)vinylsilane was a gift from Professor G.G. Cameron.

^1H NMR (250 Mhz, CD_2Cl_2) 1.20 (t, 9H, J 7.00 Hz), 3.80 (q, 6H, J 7.00 Hz), 5.85 (dd, J 13.18, J 20.55 Hz), 5.94 (dd, J 5.80, J 20.55 Hz), 6.06 (dd, 1H, J 5.80, J 13.18 Hz).

Formation of adducts

Reaction of triphenylvinylsilane and 4-methyl-2-nitrobenzenesulphenyl chloride. A solution of $\text{Ph}_3\text{SiCH}=\text{CH}_2$ (1.11 g) and 4-Me-2- $\text{O}_2\text{NC}_6\text{H}_3\text{SCl}$ (0.79 g) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (30 ml) was refluxed for 2 h. The solvent was removed to leave an oil, which after addition of light petroleum (b.p. 60–80°C), solidified on scraping (yield 1.60 g). Repeated recrystallisation from ethanol gave pure (4-Me-2- $\text{O}_2\text{NC}_6\text{H}_3\text{S}$) $\text{CHSiPh}_3\text{CH}_2\text{Cl}$ as a yellow solid, m.p. 142–145°C. Anal. Found: C, 65.7; H, 5.1; Cl, 7.0; S, 6.7; N, 2.9. $\text{C}_{27}\text{H}_{24}\text{ClNO}_2\text{SSi}$ calc.: C, 66.0; H, 4.9; Cl, 7.2; S, 6.5; N, 2.8%.

^1H NMR see Table 2. ^{13}C NMR (62.9 MHz, CDCl_3): δ 20.55 (Me), 36.50 (CH), 48.32 (CH_2), 125.77, 128.17, 129.37, 130.33, 131.55, 132.61, 133.98, 136.05, 136.38, 148.35.

In a similar fashion, yellow (o - $\text{O}_2\text{NC}_6\text{H}_4\text{S}$) $\text{CHSiPh}_3\text{CH}_2\text{Cl}$, m.p. 119–121°C, was isolated from $\text{Ph}_3\text{SiCH}=\text{CH}_2$ (1.00 g) and o - $\text{O}_2\text{NC}_6\text{H}_4\text{SCl}$ (0.66 g). ^1H NMR (CDCl_3 , 100 MHz): δ 3.80 (m, 2H), 4.10 (m, 1H), 7.2–8.0 (m, 19H, aryl). Anal. Found: C, 65.7; H, 4.9; Cl, 7.5; S, 6.5; N, 2.7. $\text{C}_{26}\text{H}_{22}\text{ClNO}_2\text{SSi}$ calc.: C, 65.4; H, 4.6; Cl, 7.4; S, 6.7; N, 2.9%.

A mixture of $\text{Ph}_3\text{SiCH}=\text{CH}_2$ (1.37 g) and p - $\text{MeC}_6\text{H}_4\text{SCl}$ (0.76 g) in CCl_4 (25 ml) was refluxed for 3 h. The solvent was removed to leave a solid residue which was chromatographed on Al_2O_3 with light petroleum using chloroform as eluant. Hydrolysis occurred during chromatography as shown by the appearance of a broad new absorption at δ 3.9 in the ^1H NMR spectrum of the major component.

Small scale reactions

Reactions between the vinyl metallic compound and ArSCl were carried out on a 2 mmol scale in CD_2Cl_2 (0.5 ml). The mixtures were maintained at 20°C and monitored by ^1H NMR spectroscopy. NMR spectral data and isomer proportions are given in Tables 1 and 2.

Reaction between (o - $\text{O}_2\text{NC}_6\text{H}_4\text{S}$) $\text{CH}(\text{SiPh}_3)\text{CH}_2\text{Cl}$ and m - $\text{ClC}_6\text{H}_4\text{CO} \cdot \text{O} \cdot \text{OH}$. To a solution of (o - $\text{O}_2\text{NC}_6\text{H}_4\text{S}$) $\text{CH}(\text{SiPh}_3)\text{CH}_2\text{Cl}$ (0.0953 g) in CH_2Cl_2 (10.0 ml) was added m - $\text{ClC}_6\text{H}_4\text{CO} \cdot \text{O} \cdot \text{OH}$ (0.0350 g). The solution was left overnight, then washed successively with a saturated solution of aqueous NaHCO_3 (5 ml), aqueous sodium bisulphite solution (5 ml), and aqueous sodium chloride solution (5 ml), and the organic layer was dried and the solvent removed. The residue was chromatographed on Al_2O_3 with using CHCl_3 as eluant to give o -

Table 7

Crystal data for (4-Me-2-O₂NC₆H₃S)CH(SiPh₃)CH₂Cl

Formula	C ₂₇ H ₂₄ ClNO ₂ SSi	μ (mm ⁻¹)	0.31
<i>M</i>	490.08	θ range (deg)	0–30
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>h</i> range	0–10
<i>a</i> (Å)	7.822(5)	<i>k</i> range	0–15
<i>b</i> (Å)	11.688(9)	<i>l</i> range	–35 to 35
<i>c</i> (Å)	27.283(11)	Standard reflections checked	
α (deg)	90.0	after every 50	1, 0, –12
β (deg)	98.24(4)	Intensity variation (%)	< 2
γ (deg)	90.0		and 1, 1, 5
<i>V</i> (Å ³)	2468.6		< 2
<i>Z</i>	4	Scan speed (deg s ⁻¹)	variable
<i>D</i> _c (Mg m ⁻³)	1.319	Scan width (deg)	0.6 (ω scan)
Reflections for lattice parameters	{ number 14 θ -range (deg) 7.5–9.0	No. of measured reflections	4699
		Condition for observed reflections	$F \geq 6\sigma F$
Radiation	Mo-K α	No. of reflections used in the refinement	1729
Wavelength λ (Å)	0.71069	No. of refined parameters	301
<i>F</i> (000)	1024	$R = \sum \Delta F / \sum F_o $ (%)	5.32
Temperature (K)	298	$R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$ (%)	4.40
Crystal size (mm ³)	0.1 × 0.6 × 0.14	$w = 1.7798 / (\sigma^2 F + 0.00011 F^2)$	
Diffractionmeter	Nicolet P3	Max shift/esd	< 0.02
		Max $\Delta\rho$	{ 0.29 e Å ³ –0.29 e Å ³
		Min $\Delta\rho$	

O₂NC₆H₄S(O)CH=CH₂ (0.029 g, 74%), m.p. 71–72°C (Lit. value [6] 68–69°C). ¹H NMR (250 MHz, CDCl₃): δ 5.81 (d, 1H, *J* 9.44 Hz), 6.31 (d, 1H, *J* 16.31 Hz), 4.00 (dd, 1H, *J* 9.44, *J* 16.31 Hz), 7.5 (m) and 7.8 (m).

X-ray structure determination of (4-Me-2-O₂NC₆H₃S)CHSiPh₃CH₂Cl

Table 7 lists the crystal data. A direct method (SHELXS-86 [24]) revealed all atoms of the structure. Refinement of the structure was carried out by full matrix least squares using SHELXL-76 [25]. Initially all non-hydrogen atoms were refined using isotropic thermal parameters and then, after inclusion of the hydrogen atoms in calculated positions, the non-hydrogen atoms were refined using anisotropic thermal parameters. All hydrogen atoms were allowed to ride on their parent atoms except for those of the methyl group which was refined as a rigid group. All hydrogen atoms were given a fixed isotropic thermal parameter approximately 1.5 times that of their parent atoms. Atomic scattering factors, corrected for anomalous dispersion were taken from *International Tables for X-ray Crystallography* [26]. The PLUTO program was also used [27].

Tables of hydrogen atom positions, anisotropic thermal parameters and structure factors are available from the corresponding author.

References

- (a) G.H. Schmid and D. Garrett, in S. Patai (Ed.), *The Chemistry of the Functional Groups. The Chemistry of Double-bonded Functional Groups*, Wiley, Chichester, Part 2, 1977, p. 828; (b) G.H.

- Schmid, in S. Patai (Ed.), *The Chemistry of the Functional Groups, Supplement A: The Chemistry of Double-bonded Functional Groups, Vol. 2, Part A*, Wiley, Chichester, 1989, Chap. 11.
- 2 G. Capozzi, G. Modena and L. Pasquato, in S. Patai (Ed.), *The Chemistry of the Functional Groups: The Chemistry of Sulphenic Acids and their Derivatives*, Wiley, Chichester, 1990, Chap. 10.
 - 3 E. Kuhle, *The Chemistry of the Sulphenic Acids*, George Thieme, Stuttgart, 1973.
 - 4 J.L. Wardell, *J. Chem. Soc., Dalton Trans.*, (1975) 1786.
 - 5 R.A. Howie, J.L. Wardell, E. Zanetti, P.J. Cox and S.M.S.V. Doidge-Harrison, *J. Organomet. Chem.*, 431 (1992) 27.
 - 6 F. Cooke, R. Moerck, J. Schwindeman and P. Magnus, *J. Org. Chem.*, 45 (1980) 1046.
 - 7 A. Lopusinski, J. Michalski and M. Potrzebowski, *J. Chem. Soc., Chem. Commun.*, (1982) 1362.
 - 8 G.M. Svistunov, V.P. Shapkin, V.I. Razov and V.Yu. Glushchenko, *Zh. Obshch. Khim.*, 60 (1990) 1359.
 - 9 G.M. Beverly and D.R. Hogg, *Chem. Commun.*, (1966) 138.
 - 10 W.H. Mueller and P.E. Butler, *J. Am. Chem. Soc.*, 88 (1966) 2866; *ibid.*, 90 (1968) 2075; W.A. Thaler, W.H. Mueller and P.E. Butler, *ibid.*, 90 (1968) 2069; W.H. Mueller, *Angew. Chem., Int. Ed. Engl.*, 8 (1969) 482; W.H. Mueller, R.M. Rubin and P.E. Butler, *J. Org. Chem.*, 31 (1966) 3537; W.H. Mueller and P.E. Butler, *ibid.*, 32 (1967) 2925.
 - 11 (a) I. Fleming, J. Dunogues and R. Smithers, *Org. React.*, 37 (1989) 57; (b) A.N. Egorochkin, M.A. Lopatin, S.E. Skobeleva, V.I. Zhun and V.D. Steludyakov, *Metallorg. Chem.*, 1 (1988) 350.
 - 12 G. Shultz, I. Hargittai, I. Kapovits and A. Kucsman, *J. Chem. Soc., Faraday Trans. 2*, 83 (1987) 2113.
 - 13 G. Schultz, I. Hargittai, I. Kapovits, and A. Kucsman, *J. Chem. Soc., Faraday Trans. 2*, 80 (1984) 273.
 - 14 A. Kucsman, I. Kapovits, M. Czugler, L. Parkanyi and A. Kalman, *J. Mol. Struct.*, 198 (1989) 339.
 - 15 K.M. Zaripov, *Zh. Strukt. Khim.*, 17 (1976) 741.
 - 16 A.V. Borisov, A.I. Lutsenko, L.V. Chumakov, V.A. Smith and I.V. Bodrikov, *Bull. Acad. Sci. USSR*, 32 (1983) 2114.
 - 17 D.W. Grant, D.R. Hogg and J.L. Wardell, *J. Chem. Res.*, (S) (1987) 392; (M) (1987) 3123.
 - 18 F. Kurzer and J.R. Powell, *Org. Synth.*, 4 (1963) 934.
 - 19 T. Zincke and F. Farr, *Ann.*, 391 (1912) 55.
 - 20 N. Kharasch, G.J. Gleason and C.M. Buess, *J. Am. Chem. Soc.*, 72 (1950) 1796.
 - 21 T. Zincke and H. Rose, *Ann.*, 406 (1914) 103.
 - 22 D. Seyferth and M.A. Weiner, *J. Am. Chem. Soc.*, 83 (1961) 3583.
 - 23 M.C. Henry and J.G. Noltes, *J. Am. Chem. Soc.*, 82 (1960) 555.
 - 24 G.M. Sheldrick, *Acta Crystallogr., Sect. A*, 46 (1990) 467.
 - 25 G.M. Sheldrick, *SHELX-76*, Program for Crystal Structure Determination, University of Cambridge, 1976.
 - 26 *International Tables for X-ray Crystallography, Vol. IV*, Kynoch Press, Birmingham, 1974.
 - 27 W.D.S. Motherwell and W. Clegg, *PLUTO*, Program for Plotting Molecular and Crystal Structures, University of Cambridge, 1978.