A New Synthesis of Vinyl Sulphides by Lewis Acid Promoted Reaction of [Chloro(arylthio)methyl]trimethylsilanes with Trisubstituted Alkenes

Hiroyuki Ishibashi,* Hiroshi Nakatani, Hiroshi Sakashita, and Masazumi Ikeda

Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 607, Japan

Treatment of the α-chloro-α-silyl sulphides (**1**) or (**5**) with trisubstituted alkenes (**6**) in the presence of $SnCl_4$ gave the vinyl sulphides (**7**) or (**8**), the formation of which involves a carbenium ion rearrangement controlled by the silyl group.

In our earlier work,[1] we showed that [chloro(4-chlorophenylthio)methyl]trimethylsilane (**1**) reacts with the terminal alkenes (**2**) in the presence of $SnCl_4$ to give the ene type products (**4**) *via* the cationic species (**3**). Here we report the sharply contrasting reaction of the chloride (**1**) or (**5**) with trisubstituted alkenes (**6**) which provides a high yield synthesis of the vinyl sulphides (**7**) or (**8**).

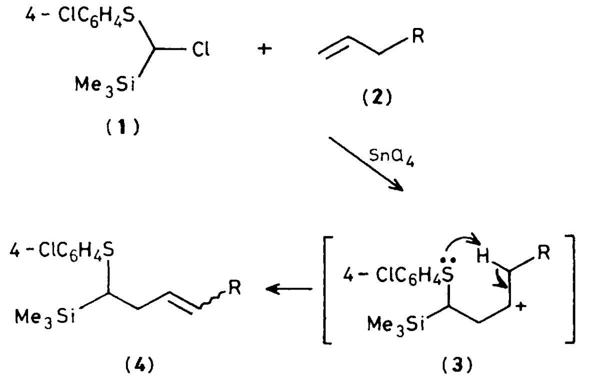
When a mixture of the chloride (**1**) and 2-methylbut-2-ene (**6a**) was treated with $SnCl_4$ (1 equiv.) in CH_2Cl_2 at −20 °C for 30 min, the vinyl sulphide (**7a**)† was obtained in 80% yield as a single stereoisomer with the thiochroman derivative (**9a**) (13%) (Scheme 1). Formation of (**9a**) was suppressed by the use of the dichlorophenyl compound (**5**); reaction with (**6a**) gave the vinyl sulphide (**8a**) (see Table 1) and the thiochroman (**10a**) in 94 and 4% yields, respectively. Additional examples of the reactions of (**5**) with (**6**) are in Table 1.‡ A mechanistic rationalization of the formation of the vinyl sulphides (**7**) or (**8**) involves initial attack of the alkene (**6**), with the aid of $SnCl_4$, on the chloride (**1**) or (**5**) to form the carbenium ion intermediate (**11**) (Scheme 2). This is followed by a 1,2-

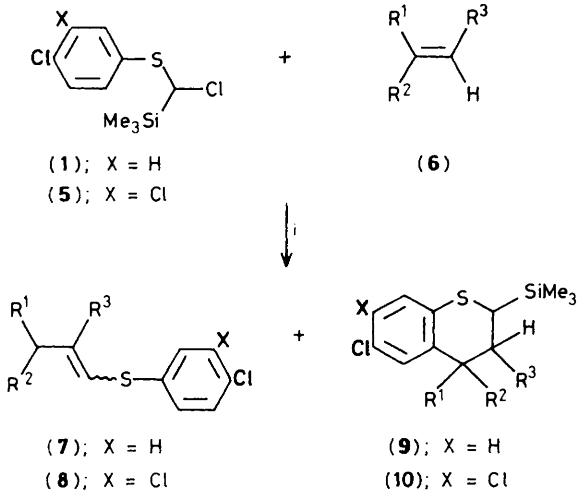
---

† Satisfactory elemntal analyses and spectroscopic data were obtained for all new compounds.

(**7a**), oil, δ ($CDCl_3$) 1.05 (6H, d, *J* 7 Hz), 1.80 (3H, br.s), 2.42 (1H, sept., *J* 7 Hz), 5.80—5.95 (1H, m), and 7.15 (4H, s).

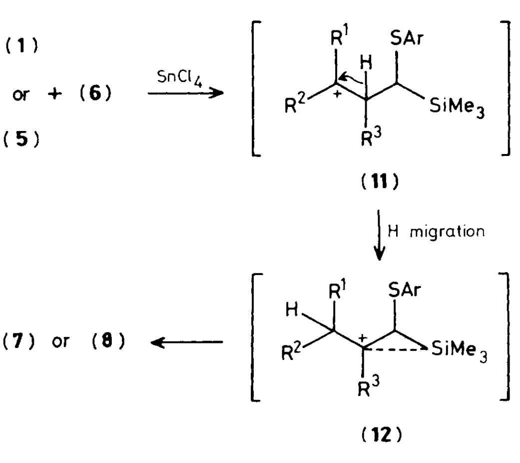
‡ Reaction of (**5**) with cyclohexene also gave the vinyl sulphide (**8**), but in low yield (25%), along with the ene product (**4**) (30%). With methylenecyclohexane the thiochroman derivative (**10**) was obtained in 66% yield.





a; $R^1 = R^2 = R^3 = Me$
b; $R^1 = R^2 = Me, R^3 = Et$
c; $R^1, R^3 = -[CH_2]_3-, R^2 = Me$
d; $R^1, R^3 = -[CH_2]_4-, R^2 = Me$
e; $R^1, R^2 = -[CH_2]_5-, R^3 = Me$

Scheme 1. *Reagents and conditions:* i, $SnCl_4$ (1 equiv.), CH_2Cl_2, −20 °C, 30 min.

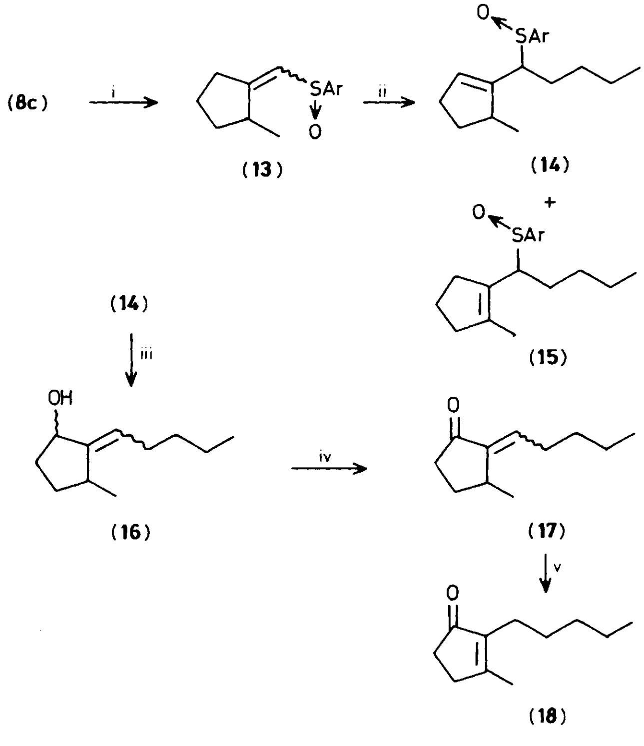


Scheme 2

Table 1. Preparation of the vinyl sulphides (**8**) from (**5**) and (**6**).[a]

Vinyl sulphide (% yield)	Ratio of stereoisomers
(**8a**) (94)	*ca.* 100:0
(**8b**) (88)	*ca.* 2:1
(**8c**) (90)	*ca.* 2:1
(**8d**) (96)	*ca.* 4:1
(**8e**) (75)	*ca.* 10:1

[a] The reactions of (**5**) with (**6a**), (**6b**), and (**6e**) formed a small amount of the thiochroman derivatives (**10**).



Ar = $3,4-Cl_2C_6H_3$

Scheme 3. *Reagents:* i, MCPBA, CH_2Cl_2; ii, LDA, hexamethylphosphoramide (HMPA), tetrahydrofuran (THF), −78 °C, then Bu^{n}I, −40 °C; iii, $(MeO)_3P$, Me_2NH_2Cl, THF–MeOH (3:1), 60 °C; iv, PCC, CH_2Cl_2; v, conc. HCl, Bu^{n}OH, 90 °C.

hydride shift to give the stabilised carbenium ion (**12**), which loses the trimethylsilyl group to furnish the vinyl sulphides (**7**) or (**8**). Apparently, the driving force for this 1,2-hydride shift arises from the powerful stabilising effect of the trimethylsilyl group on a β-carbenium ion.[2] On the other hand, the formation of the thiochromans (**9**) or (**10**) appears to be the result of intramolecular nucleophilic attrack by an aromatic ring of the arylthio group on the carbenium ion (**11**).[3]

Vinyl sulphides are useful intermediates in organic synthesis,[4] and we have synthesised dihydrojasmone (**18**) from the sulphide (**8c**). Oxidation of (**8c**) with *m*-chloroperbenzoic acid

(MCPBA) gave a mixture of (*E*)- and (*Z*)-vinyl sulphoxides (**13**) in 91% total yield (Scheme 3). This mixture was deconjugated with lithium di-isopropylamide (LDA) and then quenched with n-butyl iodide to give two isomeric allyl sulphoxides (**14**) [δ 5.4—5.9 (1H, m, =CH)] and (**15**) in 46 and 26% yields. Compound (**14**) then underwent the allylic sulphoxide–sulphenate rearrangement[5] in the presence of $(MeO)_3P$ and Me_2NH_2Cl at 60 °C to give the allylic alcohol (**16**) in 94% yield. Pyridinium chlorochromate (PCC) oxidation of (**16**) gave, in 58% yield, the exocyclic methylene ketone (**17**), whose isomerisation to dihydrojasmone (**18**) with concentrated HCl has been reported.[6]

Received, 23rd October 1986; Com. 1518

References

1 H. Ishibashi, H. Nakatani, Y. Umei, W. Yamamoto, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, in the press.

2 For other examples of a carbenium ion rearrangement controlled by a silyl group, see H. Sakurai, T. Imai, and A. Hosomi, *Tetrahedron Lett.*, 1977, 4045; I. Fleming and S. K. Patel, *ibid.*, 1981, **22**, 2321.

3 For analogous cycloadditions of phenylthiomethyl chlorides with substituted alkenes, see H. Ishibashi, M. Okada, K. Sato, M. Ikeda, K. Ishiyama, and Y. Tamura, *Chem. Pharm. Bull.*, 1985, **33**, 90.

4 B. M. Trost and A. C. Lavoie, *J. Am. Chem. Soc.*, 1983, **105**, 5075, and references therein.

5 J. R. Bull and K. Bischofberger, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2723, and references therein.

6 D. Liotta, C. S. Barnum, and M. Saindane, *J. Org. Chem.*, 1981, **46**, 4301.