Silicon-containing Carbonyl Equivalents

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1 Introduction

Despite the advances made in the field of organosilicon chemistry and the numerous synthetic methods which rely on the properties of silicon, the use of this element in acyl anion equivalents has received little attention compared to other elements such as sulphur. Indeed, the area of acyl anion equivalents and other *umpolung*[1] reagents has been dominated by sulphur compounds.[2–4] It is the aim of this review to discuss the use of silicon reagents in this role; general organosilicon chemistry will not be considered as there are already many excellent reviews.[5–11] For the purposes of this article, only compounds which have the silicon atom bonded directly or through one heteroatom to the carbon atom which is to become the carbonyl carbon and are *umpolung* reagents have been considered. This means that *O*-silylcyanohydrins are looked at but *O*-silylenol ethers have been omitted.[11]

2 Vinylsilanes and α,β-Epoxysilanes

Vinylsilanes as carbonyl equivalents was one of the first uses for these compounds in organic methodology.[12] The large number of methods of preparation and reactions of these compounds[13] has made vinylsilanes useful synthetic tools besides providing a method for the synthesis of carbonyl compounds *via* α,β-epoxysilanes.

Vinylsilanes (1) have been prepared from acetylenes by a variety of routes which are summarized in Scheme 1. Silanes have been added to acetylenes in the presence

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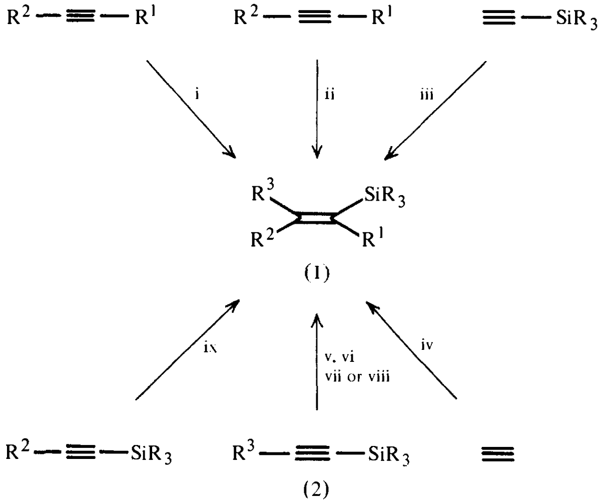
[1] D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 639; 1979, **18**, 239.
[2] B.-T. Gröbel and D. Seebach, *Synthesis*, 1977, 357.
[3] O. W. Lever, *Tetrahedron*, 1976, **32**, 1943.
[4] S. F. Martin, *Synthesis*, 1979, 633.
[5] I. Fleming, *Chem. Ind.*, 1975, 449.
[6] T. H. Chan, *Acc. Chem. Res.*, 1977, **10**, 442.
[7] E. W. Colvin, *Chem. Soc. Rev.*, 1978, **7**, 15.
[8] I. Fleming in 'Comprehensive Organic Chemistry' ed. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979. vol III, p. 541*ff.*
[9] I. Fleming, *Chimica*, 1980, **34**, 265.
[10] P. Magnus, *Aldrichimica Acta*, 1980, **13**, 43.
[11] I. Fleming, *Chem. Soc. Rev.*, 1981, **10**, 83.
[12] G. Stork and E. Colvin, *J. Am. Chem. Soc.*, 1971, **93**, 2080.
[13] T. H. Chan and I. Fleming, *Synthesis*, 1979, 761.

of a platinum catalyst,[12,14–19] but because of the lack of regioselectively a terminal acetylene which leads to a 1-silylalkene, or symmetrical acetylene have normally been used. The cuprate derived from dimethylphenylsilyl-lithium added to acetylenes with some regioselective control; this method has the added advantage that the resultant vinylcopper compound can react with a variety of electrophiles to give functionalized vinylsilanes.[20] Other organometallic reagents which have been added to silylacetylenes (2) or acetylenes and the resultant vinylmetallic reagent treated with a silyl halide are organocuprates,[21,22] organoboranes,[16,23,24] organoaluminium compounds,[25,26] and Grignard reagents catalysed by nickel.[27]



Reagents: (i) $R^1 = R^3 = H$ or $R^1 = R^2$, $R^3 = H$; R_3SiH, H_2PtCl_6 (ref. 12, 14—18). (ii) $R^1 = R^2$ or $R^2 = H$; (*a*) $(PhMe_2Si)_2CuLi.LiCN/THF/0\,°C$, (*b*) R^3X (ref. 20). (iii) $R^1 = R^3 = H$; (*a*) $R^2{}_2CuMgX$ or $R^2CuX.MgX/THF$, (*b*) H_2O (ref. 21). (iv) $R^1 = R^2 = H$; (*a*) $R^2{}_2CuLi$, (*b*) Me_3SiCl (ref. 22). (v) $R^1 = R^2 = H$; (*a*) $(c\text{-}C_6H_{11})BH/THF$, (*b*) $AcOH/\Delta$ (*c*) $H_2O_2/{}^-OH$ (ref. 23). (vi) $R^2 = H$; (*a*) $(c\text{-}C_6H_{11})BH/THF$, (*b*) MeLi, (*c*) CuI, (*d*) $P(OEt)_3/HMPA/R^1X$ (ref. 24). (vii) $R^2 = H$; (*a*) $Dibal\text{-}H/R^4{}_3N$, (*b*) MeLi, (*c*) R^1X (ref. 25). (viii) $R^2 = Me$; (*a*) $Ni(acac)_2/Me_3Al/MeMgBr/THF$, (*b*) R^1X (ref. 27). (ix) $R^3 = H$; (*a*) Dibal-H, (*b*) MeLi, (*c*) R^1X (ref. 25, 26).

Scheme 1

[14] R. A. Benkeser, M. L. Burrows, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, 1961, **83**, 4385.

[15] G. Stork, M. E. Jung, E. Colvin, and Y. Noel, *J. Am. Chem. Soc.*, 1974, **96**, 3685.

[16] P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, 1975, **40**, 2263.

[17] P. F. Hudrlik and C.-N. Wan, *Synth. Commun.*, 1979, **9**, 333.

[18] K. Yamamoto, O. Nunokawa, and J. Tsuji, *Synthesis*, 1977, 721.

[19] G. H. Wagner, *U. S. Patent*, 2 637 738; *Chem. Abs.*, 1954, **48**, 8254.

[20] I. Fleming and F. Roessler, *J. Chem. Soc., Chem. Commun.*, 1980, 276; I. Fleming, T. W. Newton, and F. Roessler, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2527.

[21] H. Westmijze, J. Meijer, and P. Vermeer, *Tetrahedron Lett.*, 1977, 1823.

[22] A. Alexakis, G. Cahiez, and J. F. Normant, *Synthesis*, 1979, 826.

[23] R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 1974, 543.

[24] K. Uchida, K. Utimoto, and H. Nozaki, *J. Org. Chem.*, 1976, **41**, 2941; *Tetrahedron*, 1977, **33**, 2987.

[25] J. J. Eisch and G. Damasevitz, *J. Org. Chem.*, 1976, **41**, 2941.

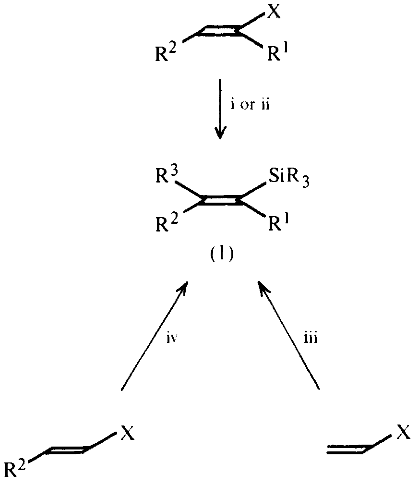
[26] K. Uchida, K. Utimoto, and H. Nozaki, *J. Org. Chem.*, 1976, **41**, 2215.

[27] B. B. Snider, M. Karras, and R. S. E. Conn, *J. Am. Chem. Soc.*, 1978, **100**, 4624.

Silylacetylenes have been reduced to the vinylsilane by hydrogenation in the presence of a poisoned palladium catalyst[12] or Raney nickel.[28] Vinylsilanes have also been prepared by a Diels–Alder reaction of a silylacetylene with a diene[29] or of a silyl-substituted diene with an appropriate dienophile.[30]

Vinyl halides have been used as precursors to vinylsilanes; the required transformation has been achieved by Wurtz coupling[15,31–33] *via* the vinyl-lithium[34,35] (this method has been used to prepare functionalized vinylsilanes[36]), high temperatures,[37] or palladium catalysis[38] (see Scheme 2).

Elimination of a hydrogen halide,[39–42] water,[43] or an ester[44] from an appropriately substituted silane leads to vinylsilanes. The most useful reaction of this type



Reagents: (i) R = Me, R^3 = H; Na/Et_2O/Me_3SiCl (ref. 31—33). (ii) R = Me, R^3 = H; (*a*) t-BuLi/low temp., (*b*) Me_3SiCl (ref. 34, 35). (iii) R = Cl, $R^1 = R^2 = R^3$ = H; Si/$SnCl_2$ or CuCl/550 °C (ref. 37). (iv) R = Me_nCl_{3-n}; $(Cl_{3-n}Me_nSi_2)$/$Pd(PPh_3)_4$ (ref. 38).

Scheme 2

[28] K. Atsumi and I. Kuwajima, *Tetrahedron Lett.*, 1977, 2001.

[29] R. F. Cunico, *J. Org. Chem.*, 1971, **36**, 929.

[30] J. W. Ryan and J. L. Speier, *J. Org. Chem.*, 1966, **31**, 2698.

[31] M. Kanazashi, *Bull. Chem. Soc. Jpn.*, 1953, **26**, 493.

[32] A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev, *Zh. Obshch. Khim.*, 1957, **27**, 1535; *Chem. Abs.*, 1958, **52**, 3668*g*.

[33] G. Nagendrappa, *Synthesis*, 1980, 704.

[34] D. Seebach and H. Neumann, *Chem. Ber.*, 1974, **107**, 847.

[35] H. Neumann and D. Seebach, *Tetrahedron Lett.*, 1976, 4839; *Chem. Ber.*, 1978, **111**, 2785.

[36] For example: J. S. Swenton and E. L. Fritzen, *Tetrahedron Lett.*, 1979, 1951 and references cited therein; C. Shih and J. S. Swenton, *Tetrahedron Lett.*, 1981, **22**, 4217.

[37] C. O. Strother and G. H. Wagner, *U. S. Patent*, 2 532 430; *Chem. Abs.*, 1951, **45**, 2968*e*.

[38] H. Matsumoto, S. Nagashima, T. Kato, and Y. Nagai, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 279.

[39] F. K. Cartledge and J. P. Jones, *Tetrahedron Lett.*, 1971, 2193.

[40] C. L. Agre and W. Hilling, *J. Am. Chem. Soc.*, 1952, **74**, 3895.

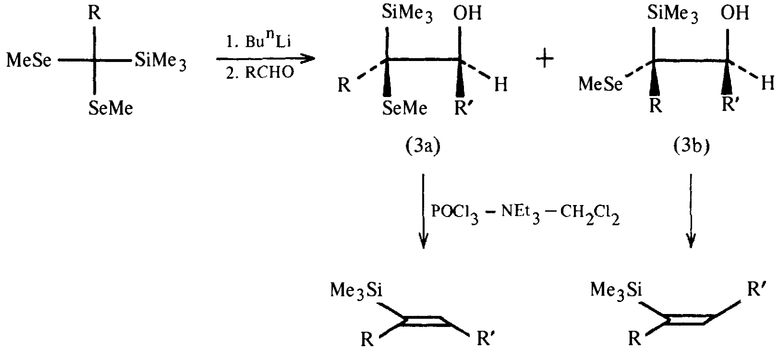
[41] L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *J. Am. Chem. Soc.*, 1948, **70**, 2869.

[42] S. N. Ushakov and A. M. Itenberg, *J. Gen. Chem.*, 1937, 7, 2495; *Chem. Abs.*, 1938, **32**, 2083.

[43] H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, 1959, **81**, 1107.

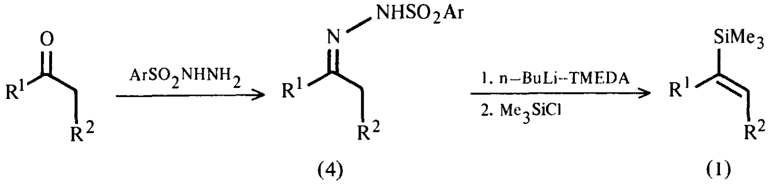
[44] F. A. Carey and J. R. Toler, *J. Org. Chem.*, 1976, **41**, 1966.

is shown in Scheme 3, although it should be noted that the isomers of the β-hydroxyselenide (3a and 3b) have to be separated.[45]



Scheme 3[45]

Vinylsilanes have been prepared from ketones *via* the corresponding sulphonylhydrazones (4)[46–48] (see Scheme 4) and, hence, it is possible to protect a ketone as a vinylsilane.



Scheme 4[46–48]

In addition to the anions produced by the addition of organometallic reagents to silylacetylenes (2) (*vide supra*), anions derived from vinylsilanes have been used to synthesize other vinylsilanes by reaction with alkyl halides,[49–55] carbonyl

[45] W. Dumont, D. Van Ende, and A. Krief, *Tetrahedron Lett.*, 1979, 485.

[46] T. H. Chan, A. Baldassare, and D. Massuda, *Synthesis*, 1976, 801.

[47] R. T. Taylor, C. R. Degenhardt, W. P. Melega, and L. A. Paquette, *Tetrahedron Lett.*, 1977, 159.

[48] A. R. Chamberlin, J. E. Stemke, and F. T. Bond, *J. Org. Chem.*, 1978, **43**, 147.

[49] B.-T. Gröbel and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 83.

[50] B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 1977, **112**, 867.

[51] A. G. Brook, J. M. Duff, and W. F. Reynolds, *J. Organomet. Chem.*, 1976, **121**, 293.

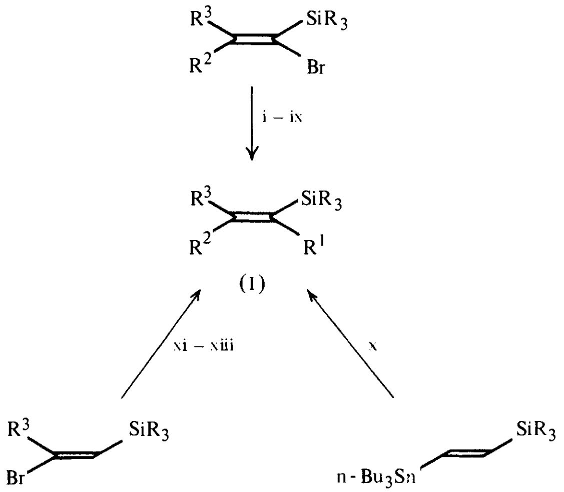
[52] D. Seyferth, J. L. Lefferts, and R. L. Lambert, *J. Organomet. Chem.*, 1977, **142**, 39.

[53] G. Zweifel and W. Lewis, *J. Org. Chem.*, 1978, **43**, 2739.

[54] R. F. Cunico and F. J. Clayton, *J. Org. Chem.*, 1976, **41**, 1480.

[55] C. Huynh and G. Linstrumelle, *Tetrahedron Lett.*, 1979, 1073.

compounds,[49,56–61] α,β-unsaturated carbonyl compounds,[55,62–64] acid anhydrides,[65] or epoxides[66] (see Scheme 5).



Reagents: (i) $R^3 = H$; (*a*) BuLi, (*b*) R^1X (ref. 49—53). (ii) $R = Me$, $R^2 = H$; $R^1{}_2CuLi$ (ref. 53). (iii) $R = Me$; (*a*) Mg, (*b*) Cu^I/R^1X (ref. 55). (iv) $R^2 = R^3 = H$; $R^1 = R^4R^5C(OH)—$; (*a*) BuLi, (*b*) R^4R^5CO (ref. 49, 56, 57, 61). (v) $R = Me$, $R^2 = H$, $R^1 = CH_2R^4$; (*a*) t-BuLi, (*b*) R^3CHO, (*c*) SO_2Cl_2, (*d*) $R^4{}_2CuLi$ (ref. 58, 59). (vi) $R = Me$, $R^3 = H$, $R^1 = CH_2R^4$; (*a*) t-BuLi, (*b*) R^2CHO, (*c*) AcCl/AgCN, (*d*) $R^4{}_2CuLi$ (ref. 58, 60). (vii) $R = Me$. $R^1 = R^6C(O)CH_2CR^4R^5—$; (*a*) t-BuLi or Mg, (*b*) CuI, (*c*) $R^4R^5C{=}CHC(O)R^6$ (ref. 55. 62—64). (viii) $R^1 = R^4CO$; (*a*) t-BuLi or Mg, (*b*) $(R^4CO)_2O$ (ref. 65). (ix) $R = Me$; $R^2 = R^3 = H, R^1 = —CH(R^4)C(OH)R^5R^6$; (*a*) Mg, (*b*) $R^4\overline{CHCR^5R^6O}$ (ref. 66). (x) $R = Me$; $R^1 = R^3 = H$; (*a*) n-BuLi/ – 70 °C, (*b*) R^2X (ref. 54). (xi) as (iii) but with R^2X (ref. 55). (xii) as (vii) but $R^2 = R^6C(O)CH_2CR^4R^5$ (ref. 55, 62—64). (xiii) as (viii) but $R^2 = R^4CO$ (ref. 65).

Scheme 5

The Peterson reaction,[67] the silicon equivalent of the Wittig reaction, provides another method for the preparation of vinylsilanes. The required α-silylanions have been prepared from the parent silane,[49,68] by addition of an alkyl-lithium to a

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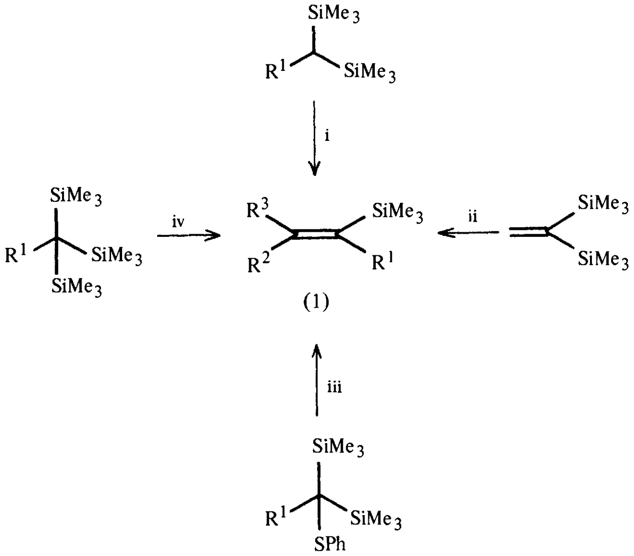
[56] T. H. Chan, W. Mychajlowskij, B. S. Ong, and D. N. Harpp, *J. Organomet. Chem.*, 1976, **107**, Cl.
[57] T. H. Chan, B. S. Ong, and W. Mychajlowskij, *Tetrahedron Lett.*, 1976, 3253.
[58] W. Mychajlowskij and T. H. Chan, *Tetrahedron Lett.*, 1976, 4439.
[59] T. H. Chan and B. S. Ong, *J. Org. Chem.*, 1978, **43**, 2994.
[60] R. Amouroux and T. H. Chan, *Tetrahedron Lett.*, 1978, 4453.
[61] T. H. Chan, W. Mychajlowskij, B. S. Ong, and D. N. Harpp, *J. Org. Chem.*, 1978, **43**, 1526.
[62] R. K. Boeckman and K. J. Bruza, *Tetrahedron Lett.*, 1974, 3365.
[63] R. K. Boeckman and M. Ramaiah, *J. Org. Chem.*, 1977, **42**, 1581.
[64] R. K. Boeckman and K. J. Bruza, *J. Org. Chem.*, 1979, **44**, 4781.
[65] A. G. Brook and J. M. Duff, *J. Organomet. Chem.*, 1973, **51**, 2024.
[66] I. Matsuda, *Chem. Lett.*, 1978, 773.
[67] D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.
[68] B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 1977, **110**, 852.

vinylsilane[49,69] and by displacement of a suitable group[70,71] (see Scheme 6). This method, however, has the disadvantage that the anions only react cleanly with non-enolizable carbonyl compounds, but this can be overcome by the presence of other functional groups on the anion.[70,72]



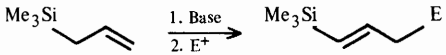
Reagents: (i) R^1 = H or $SiMe_3$; (*a*) R^4Li, (*b*) R^2R^3CO (ref. 49, 68). (ii) R^2 or R^3 = H; R^1 = R^4CH_2; (*a*) R^4Li, (*b*) R^2CHO (ref. 49, 69). (iii) (*a*) LiNaph/THF/−78 °C, (*b*) R^2R^3CO (ref. 70). (iv) R^1 = H or $SiMe_3$; (*a*) NaOMe/HMPA, (*b*) R^2R^3CO (ref. 71).

Scheme 6

Other routes to vinylsilanes are provided by the allyl anion of allyltrimethylsilane (5)[73–77] (see Scheme 7), nucleophilic substitution of 1- and 3-trimethylsilylallyl acetates (6) and (7)[78] (see Scheme 8), anions derived from α,β-epoxysilanes (8),[79] reduction of an α-silyl ester[80] or thioacetal of an enal,[81] a Diels–Alder

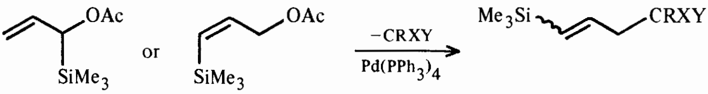
[69] D. Seebach, R. Bürstinghaus, B.-T. Gröbel, and M. Kolb, *Annalen*, 1977, 830.
[70] D. J. Ager, *J. Org. Chem.*, submitted.
[71] H. Sakurai, K.-i. Nishiwaki, and M. Kira, *Tetrahedron Lett.*, 1973, 4193.
[72] K. Sachdev, *Tetrahedron Lett.*, 1976, 4041.
[73] D. Ayalon-Chass, E. Ehlinger, and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 1977, 772.
[74] K. Yamamoto, M. Ohta, and J. Tsuji, *Chem. Lett.*, 1979, 713.
[75] E. Ehlinger and P. Magnus, *J. Am. Chem. Soc.*, 1980, **102**, 5004.
[76] R. J. P. Corriu, C. Guerin, and J. M'Boula, *Tetrahedron Lett.*, 1981, **22**, 2985.
[77] M. A. Tius, *Tetrahedron Lett.*, 1981, **22**, 3335.
[78] T. Hirao, J. Enda, Y. Ohshiro, and T. Agawa, *Tetrahedron Lett.*, 1981, **22**, 3079.
[79] J. J. Eisch and J. E. Gable, *J. Am. Chem. Soc.*, 1976, **98**, 4646.
[80] J.-P. Picard, J. Dunoguès, N. Duffaut, and R. Calas, *J. Chem. Res(S)*, 1977, 54.
[81] D. Pandy-Szekeres, G. Dèlèris, J.-P. Picard, J.-P. Pillot, and R. Calas, *Tetrahedron Lett.*, 1980, **21**, 4267.

reaction,[82] and rearrangement of silyl substituted cyclopropanes (9)[83] (see Scheme 9).



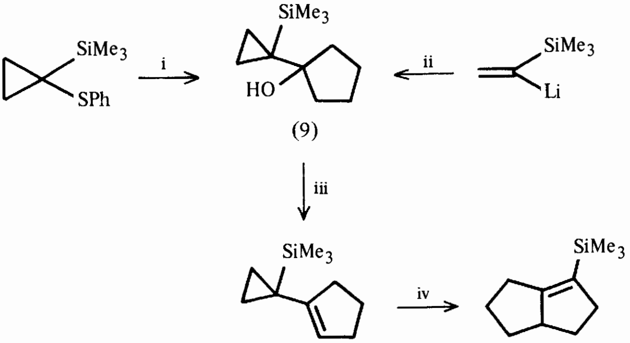
(5)

Scheme 7



(6) (7)

Scheme 8[78]



Reagents: (i) (*a*) LiNaph, (*b*)  (ref. 84), (ii) (*a*)  , (*b*) EtZnI/CH_2I_2/25 °C, (*c*) NH_4Cl/H_2O (ref. 84). (iii) TsOH/C_6H_6/20 °C (ref. 84), (iv) Δ (ref. 83).

Scheme 9

α,β-Epoxysilanes (8) have been prepared by epoxidation of the vinylsilane (1) with a peracid[57,59,85] which is commonly *m*-chloroperoxybenzoic acid (MCPBA).[12,16,64,75,86–89] The epoxide (8) was formed stereospecifically[16,85,89]

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[82] I. Fleming and R. V. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1981, 684.

[83] L. A. Paquette, G. J. Wells, K. A. Horn, and T.-H. Yan, *Tetrahedron Lett.*, 1982, **23**, 263.

[84] L. A. Paquette, K. A. Horn, and G. J. Wells, *Tetrahedron Lett.*, 1982, **23**, 259.

[85] J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 1976, **41**, 2615.

[86] G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, 1974, **96**, 3682.

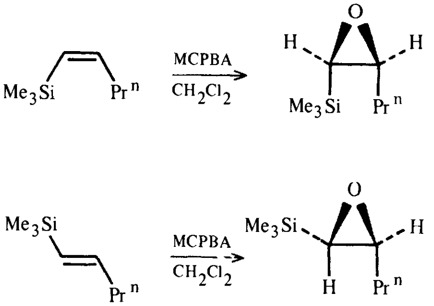
[87] T. H. Chan, M. P. Li, W. Mychajlowskij, and D. N. Harpp, *Tetrahedron Lett.*, 1974, 3511.

[88] T. H. Chan, P. W. K. Lau, and M. P. Li, *Tetrahedron Lett.*, 1976, 2667.

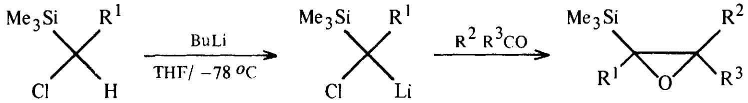
[89] M. Obayaski, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, 1977, 1807.

(see Scheme 10). It has been found that ketones must be protected during this oxidation.[62,63]

The epoxides (8) have also been prepared by the use of anions derived from α-chlorosilanes (10); epoxide formation was the preferred pathway rather than elimination of the silyl group *via* a Peterson reaction[10,90,91] (see Scheme 11). The anions of some α,β-epoxysilanes have been obtained by direct deprotonation.[92]



Scheme 10[16]



(10)

R = H or Me

(8)

Scheme 11

α,β-Epoxysilanes (8) have been hydrolysed to the corresponding carbonyl compounds by acid catalysed hydrolysis (see Scheme 12). Many acids have been used[10,12,62,63,75,93] and in some cases the hydrolysis may proceed *via* the acetal. In cyclic cases, for example, 1,2-epoxy-1-trimethylsilylcyclohexane (11), the diol (12) was formed upon hydrolysis, instead of the ketone[94,95] (see Scheme 13). These results show that vinylsilanes can only be used as masked carbonyl compounds in acyclic cases and suggest that the hydrolysis proceeds by the mechanism shown in Scheme 12 rather than by a concerted attack at the silyl group and ring opening.[12]

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[90] C. Burford, F. Cooke, E. Ehlinger, and P. D. Magnus, *J. Am. Chem. Soc.*, 1977, **99**, 4536.

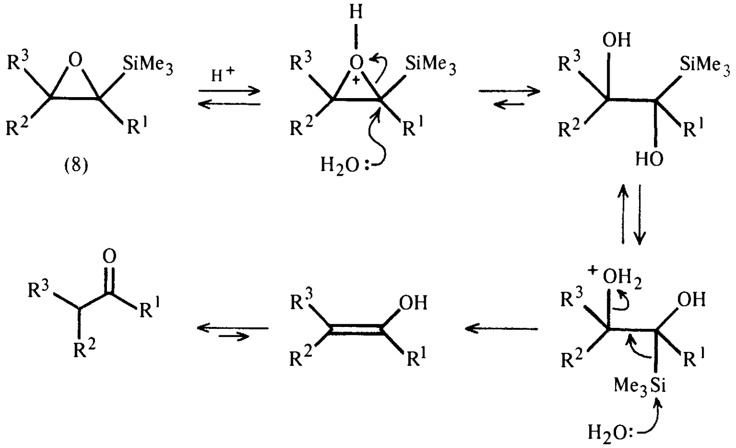
[91] F. Cooke and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 1977, 513.

[92] J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, 1976, **98**, 4646.

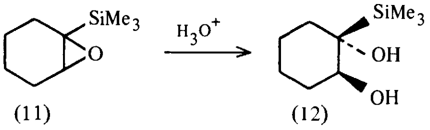
[93] G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, 1974, **96**, 3682.

[94] C. M. Robbins and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 1976, 697; A. P. Davis, G. J. Hughes, P. R. Lowndes, C. M. Robbins, E. J. Thomas, and G. H. Whitman, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1934.

[95] P. F. Hudrlik, J. O. Arcoleo, R. H. Schwartz, R. N. Misra, and R. J. Rona, *Tetrahedron Lett.*, 1977, 591.

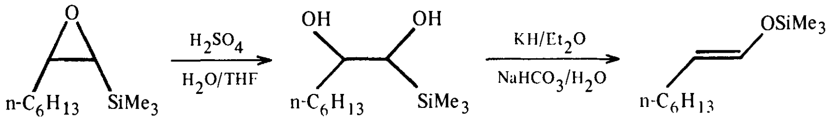


Scheme 12



Scheme 13

The diols (13) have been converted into trimethylsilyl enol ethers by reaction with potassium hydride[96] (see Scheme 14). In addition, α,β-epoxysilanes have been converted directly or indirectly into carbonyl compounds by pyrolysis[97–99] or magnesium salt induced rearrangement[100,101] but these methods usually produce a mixture of products, the major one leading to a carbonyl compound in which the carbonyl carbon was not derived from the carbon atom to which the silicon was originally bonded.



Scheme 14[96]

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[96] P. F. Hudrlik, R. H. Schwartz, and A. K. Kulkami, *Tetrahedron Lett.*, 1979, 2233.

[97] P. F. Hudrlik, C.-N. Wan, and G. P. Withers, *Tetrahedron Lett.*, 1976, 1449.

[98] A. R. Bassindale, A. G. Brook, P. Chen, and J. Lennon, *J. Organomet. Chem.*, 1975, **94**, C21.

[99] P. F. Hudrlik and C.-N. Wan, *Synth. Commun.*, 1979, **9**, 333.

[100] P. F. Hudrlik, R. N. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona, and J. P. Arcoleo, *Tetrahedron Lett.*, 1976, 1453.

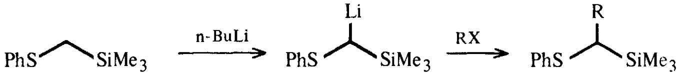
[101] M. Obayashi, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, 1977, 1807.

The use of α,β-epoxysilanes has been illustrated by the synthesis of (R)-(+)-frontalin.[10,102]

3 α-Silylsulphides and β-Siloxysulphides

Unlike acyl anion equivalents which are based solely on sulphur, such as 1,3-dithianes, and are often difficult to hydrolyse,[2,103] silicon analogues may be hydrolysed under mild conditions (*vide infra*). The parent compound for this series is phenylthiotrimethylsilylmethane (14). This silane (14) has been prepared by the reaction of sodium thiophenoxide with trimethylsilylmethyl chloride[104] or by phenylthiomethyl-lithium with chlorotrimethylsilane.[105–107]

Phenylthiotrimethylsilylmethyl-lithium (15) has been prepared in quantitative yield from the silane (14) with n-butyl-lithium as the base in THF[105] or N,N,N',N'-tetramethylethylenediamine (TMEDA)-hexane[106,107] as solvents, and alkylated in high yield by primary alkyl bromides and iodides (see Scheme 15); secondary alkyl halides gave only poor to moderate yields, indeed with cyclohexyl bromide, elimination was the only reaction pathway observed.



(14) (15) (16)

Scheme 15

The masked aldehydes (16) have also been made by the addition of alkyl-lithiums to 1-phenylthio-1-trimethylsilylethene (17),[108] reaction of bis(phenylthio)acetals (18) with lithium naphthalenide followed by chlorotrimethylsilane,[109] and by silylation of α-thioanions[110] and allyl anions derived from appropriately substituted sulphur compounds[111–114] (but 1-thio-3-silyl compounds may also be formed[112,113]). The reactions are summarized in Scheme 16.

Phenylthiotrimethylsilylmethyl-lithium (15) has been treated with a wide variety of electrophiles;[115] some will be seen below. The reaction of the anion with

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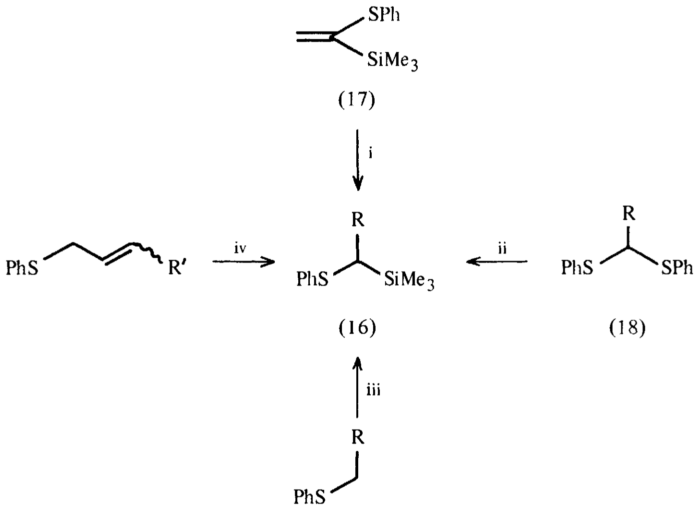
[102] P. D. Magnus and G. Roy, *J. Chem. Soc., Chem. Commun.*, 1978, 297.
[103] D. Seebach, *Synthesis*, 1969, 17.
[104] G. D. Cooper, *J. Am. Chem. Soc.*, 1954, **76**, 3713.
[105] P. J. Kocienski, *Tetrahedron Lett.*, 1980, **21**, 1559.
[106] D. J. Ager and R. C. Cookson, *Tetrahedron Lett.*, 1980, **21**, 1667.
[107] D. J. Ager, *J. Chem. Soc., Perkin Trans. 1*, in press.
[108] D. J. Ager, *Tetrahedron Lett.*, 1981, **22**, 587.
[109] D. J. Ager, *Tetrahedron Lett.*, 1981, **22**, 2923.
[110] T. M. Dolak and T. A. Bryson, *Tetrahedron Lett.*, 1977, 1961.
[111] K. Hiroi and L.-M. Chen, *J. Chem. Soc., Chem. Commun.*, 1982, **23**, 1945.
[112] I. Fleming and R. V. Williams, Unpublished results.
[113] D. J. Ager, Unpublished results.
[114] A. Itoh, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1979, 1783.
[115] D. J. Ager, *Tetrahedron Lett.*, 1981, **22**, 2803.



Reagents: (i) $R = R^1CH_2$; (*a*) R^1Li/TMEDA/Et_2O/0 °C, (*b*) NH_4Cl/H_2O (ref. 108). (ii) (*a*) LiNaph/THF/−78 °C, (*b*) Me_3SiCl (ref. 109). (iii) (*a*) t-BuLi/THF/HMPA/−78 °C, (*b*) Me_3SiCl (ref. 110). (iv) (*a*) base, (b) Me_3SiCl (ref. 111—114).

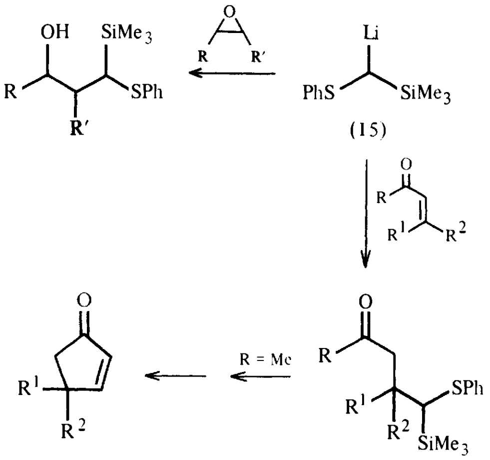
Scheme 16

epoxides[105,115,116] and α,β-unsaturated ketones[115,117,118] provide useful methods for introducing an aldehyde group (see Scheme 17). The phenylthiotrimethylsilylmethyl group has been introduced by the reaction of phenylthiotrimethylsilylmethyl bromide (19a) or chloride (19b) with trimethylsilylenol ethers[119-121] (see Scheme 18).

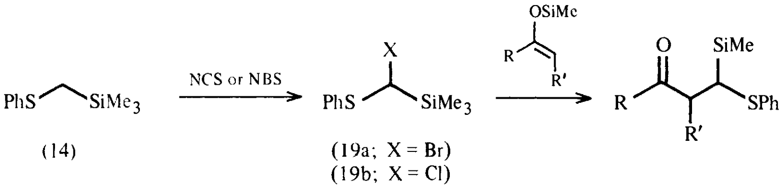
α-Silylsulphides (16) have also been prepared from the dianion of benzylthiol[122] and base-induced ring-opening of trimethylsilylmethyl substituted 1,3-dithianes.[123] β,γ-Unsaturated aldehyde derivatives (20) have been prepared by the rearrangement reaction outlined in Scheme 19.[124]

Phenylthiotrimethylsilylmethyl-lithium (15) reacted with carbonyl compounds to give vinylsulphides (21) (see Scheme 20), which are themselves masked aldehydes[115,125,126] and useful precursors to olefins.[127]

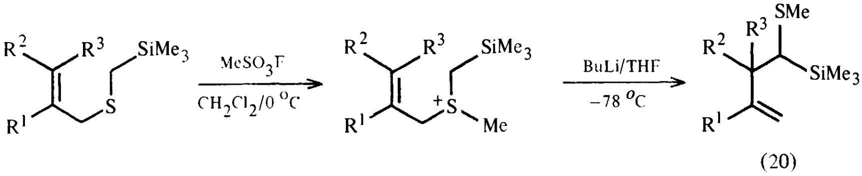
[116] I. Fleming and C. D. Floyd, *J. Chem. Soc., Perkin Trans. 1*, 1981, 969.
[117] D. J. Ager, *J. Org. Chem.*, submitted.
[118] D. J. Ager, *J. Chem. Soc., Perkin Trans. 1*, submitted.
[119] I. Fleming and S. K. Patel, *Tetrahedron Lett.*, 1981, **22**, 2321.
[120] I. Fleming and D. A. Perry, *Tetrahedron*, 1981, **37**, 4027.
[121] D. J. Ager, *Tetrahedron Lett.*, in press.
[122] K.-H. Geiβ, D. Seebach, and B. Seuring, *Chem. Ber.*, 1977, **110**, 1833.
[123] T. A. Hase and L. Lahtinen, *Tetrahedron Lett.*, 1981, **22**, 3285.
[124] P. J. Kocienski, *J. Chem. Soc., Chem. Commun.*, 1980, 1096.
[125] F. A. Carey and A. S. Court, *J. Org. Chem.*, 1972, **37**, 939.
[126] T. Agawa, M. Ishikawa, M. Komatsu, and Y. Ohshiro, *Chem. Lett.*, 1980, 335.
[127] B. M. Trost and P. L. Ornstein, *Tetrahedron Lett.*, 1981, **22**, 3463.



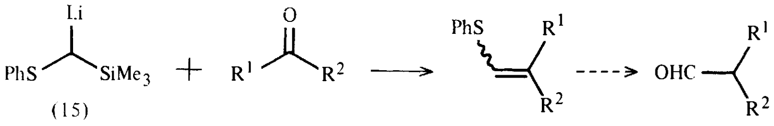
Scheme 17



Scheme 18



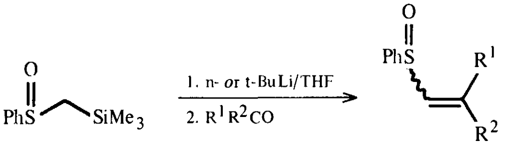
Scheme 19[124]



R^2 = alkyl or NR^3_2

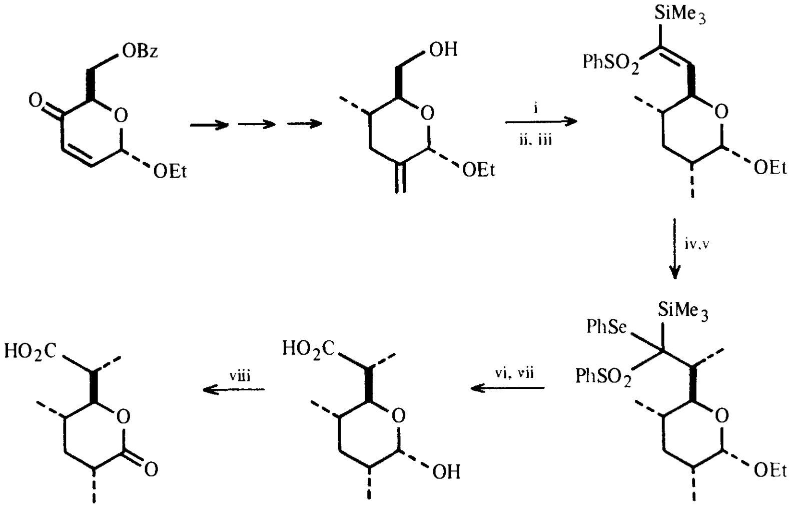
Scheme 20

Other oxidation states of sulphur have also been used to prepare these systems. 1-Trimethylsilyl-1-phenylsulphinylmethyl-lithium reacted with carbonyl compounds (see Scheme 21)[128] but could only be alkylated with methyl iodide.[128,129] α-Silylsulphoxides have also been prepared by treatment of a methyl sulphinate with a Grignard reagent.[130]



Scheme 21

α-Silylsulphones have been used as masked carboxylic acids and employed in a synthesis of Prelog–Djerassi lactonic acid (22). The relevant steps are summarized in Scheme 22 and a mechanism for the key oxidation step is shown in Scheme 23.[131]



(22)

Reagents: (i) $(COCl)_2/DMSO/NEt_3$, (ii) $PhS(Me_3Si)_2CLi$, (iii) MCPBA, (iv) MeLi, (v) PhSeCl, (vi) $H_2O_2/H_2O/THF$, (vii) H_3O^+, (viii) $Br_2/NaOAc/H_2O/DMF$.

Scheme 22

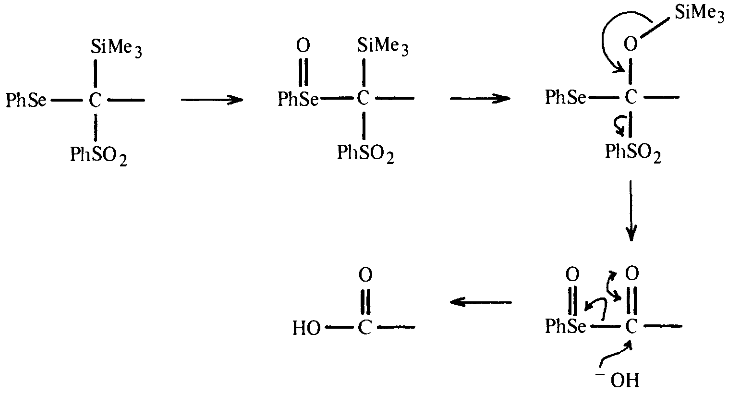
---

[128] F. A. Carey and O. Hernandez, *J. Org. Chem.*, 1973, **38**, 2670.

[129] This reaction is under investigation at present as it would provide a direct method for the preparation of aldehydes (ref. 113).

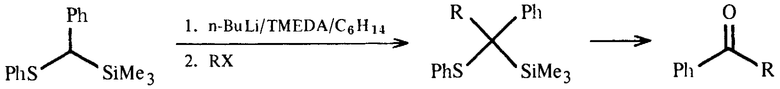
[130] A. G. Brook and D. G. Anderson, *Can. J. Chem.*, 1968, **46**, 2115.

[131] M. Isobe, Y. Ichikawa, and T. Goto, *Tetrahedron Lett.*, 1981, **22**, 4287.



Scheme 23

In contrast to 1,3-dithianes, 1-phenylthio-1-trimethylsilylalkanes (16) cannot be used as precursors to ketones because treatment with a base did not produce the correct anion. Direct deprotonation may be used, however, for the preparation of phenylketones (23) as the correct anion is obtained in this case[132] (see Scheme 24).



(23)

Scheme 24[132]

This problem has been alleviated by the use of indirect methods for the preparation of the acyl anion equivalent and are summarized in Scheme 25. They consist of the addition of an alkyl-lithium to 1-phenylthio-1-trimethylsilylethene (17)[133] in a manner similar to that used for the synthesis of aldehydes, and displacement of a tin[134] or sulphur group.[135,136] The last method also provides alternative routes and a solution to the problem of diastereoisomers which can occur with the other methods.

Another approach which has been used, is to employ the phenylsulphone group to stabilize the anion.[137] Carey and Court,[125] as mentioned above, found that the sulphoxide was difficult to alkylate but this may be due to the ease of the sila-Pummerer rearrangement (*vide infra*)[113] which does not occur in the sulphone series. Again, a variety of pathways are available and are summarized in Scheme 26;

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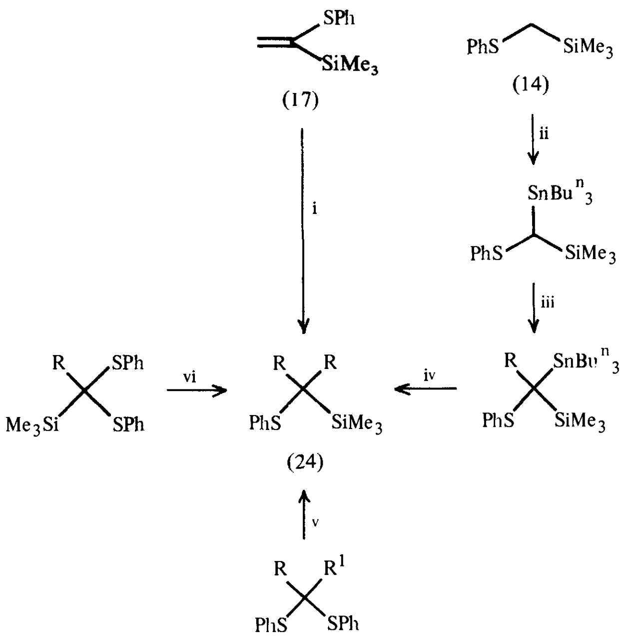
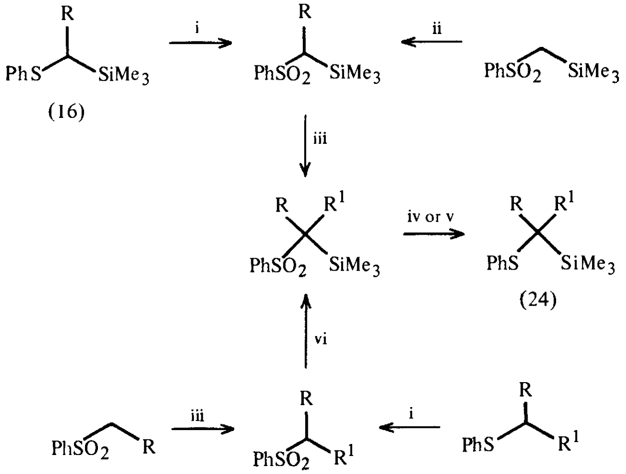
[132] D. J. Ager, *Tetrahedron Lett.*, 1980, **21**, 4759.
[133] D. J. Ager, *Tetrahedron Lett.*, 1983, **24**, 95.
[134] D. J. Ager, *Tetrahedron Lett.*, submitted.
[135] D. J. Ager, *Tetrahedron Lett.*, submitted.
[136] D. J. Ager, *Tetrahedron Lett.*, submitted.



Reagents: (i) R = R^2CH_2 ; (*a*) $R^2Li/Et_2O/TMEDA/0\,°C$, (*b*) R^1X (ref. 133). (ii) (*a*) n-BuLi/THF, (*b*) n-Bu_3SnCl (ref. 115). (iii) (*a*) LDA or KDA/THF/$-78\,°C$, (*b*) RX (ref. 134). (iv) (*a*) n-BuLi, (*b*) R^1X (ref. 134). (v) LiNaph/THF/$-78\,°C$, (*b*) Me_3SiCl (ref. 136). (vi) (*a*) LiNaph/THF/$-78\,°C$, (*b*) R^1X (ref. 136).

Scheme 25

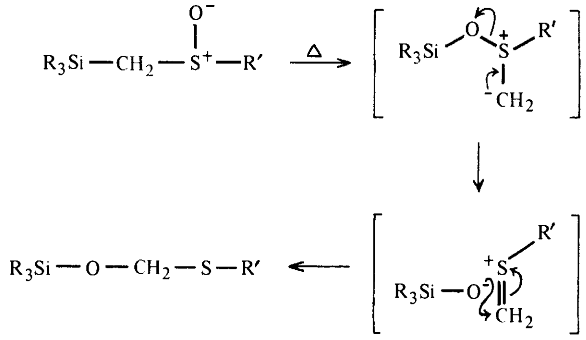


Reagents: (i) 2.2 equiv. MCPBA/CH_2Cl_2. (ii) (*a*) n-BuLi/THF, (*b*) RX. (iii) (*a*) n-BuLi/THF, (*b*) R^1X. (iv) Dibal-H/THF. (v) $LiAlH_4$/THF. (vi) (*a*) n-BuLi/THF, (*b*) Me_3SiCl.

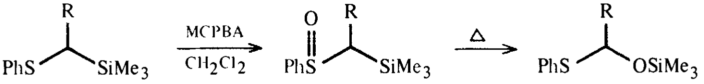
Scheme 26[137]

in addition, it seems to be possible to add alkyl-lithiums to 1-phenylsulphonyl-1-trimethylsilylalkenes and alkylate the resultant anion.[113] The disadvantage of the sulphone methods is that two extra steps—an oxidation and reduction—are introduced, even though both are invariably high yielding.[137]

The masked aldehydes (16) and ketones (24) have been converted into the corresponding carbonyl compounds by a sila-Pummerer rearrangement. The mechanism, as proposed by Brook[130] is given in Scheme 27. The reaction provides an excellent method for the conversion of 1-phenylthio-1-trimethylsilylalkanes (16) into 1-phenylthio-1-trimethylsiloxyalkanes (25),[105–107,138] (see Scheme 28).



Scheme 27[130]



(16) (25)

Scheme 28

In a manner similar to the Pummerer rearrangement itself,[139] the sila-Pummerer rearrangement is subject to stereo and electronic effects[138] and, therefore, in some ketone cases the vinylsulphide (21) becomes the major product instead of the required siloxythioacetal (26) (see Scheme 29); this phenomenon has also been observed in the aldehyde series.[105] Although vinylsulphides may be hydrolysed to carbonyl compounds,[2] the conditions required are not as mild as those required for the hydrolysis of the acetal (26). This means that the synthesis of branch-chained ketones has two major drawbacks; the alkylations with a secondary halide are only moderate to low yielding and the sila-Pummerer rearrangement can lead to the vinylsulphide (21) as the major product.

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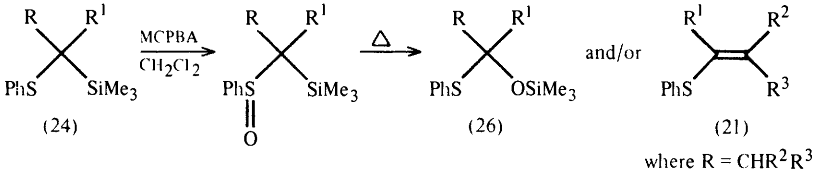
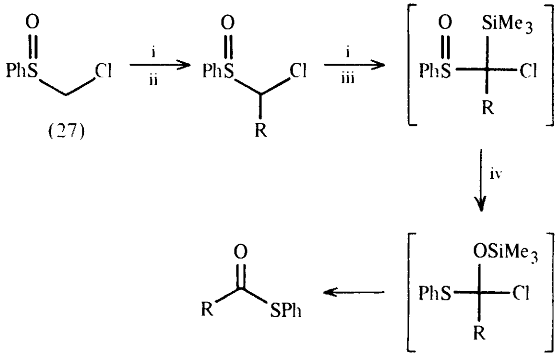
[137] D. J. Ager, *Tetrahedron Lett.*, submitted.

[138] E. Vedejs and M. Mullins, *Tetrahedron Lett.*, 1975, 2017.



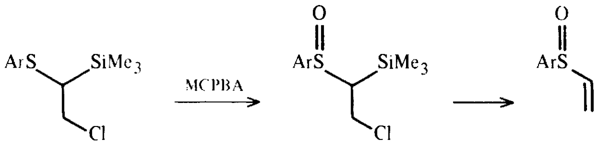
Scheme 29[140]

The sila-Pummerer rearrangement has been used to prepare thiol esters (27) from chloromethyl phenyl sulphoxide (28) (see Scheme 30);[141] the rearrangement failed when the chlorine was in the 2-position (see Scheme 31), although alternative mechanisms are available in this case.[75] It has also been used for the synthesis of enals (29) from 3-trimethylsilylallylic alcohols as shown in Scheme 32.[142]



Reagents: (i) LDA/THF/−78 °C. (ii) RX. (iii) Me_3SiCl. (iv) −78 → 60 °C.

Scheme 30[141]



Scheme 31[75]

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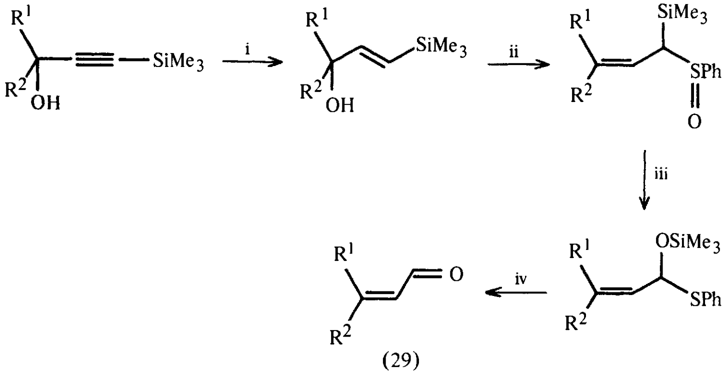
[139] G. A. Russell and G. J. Mikal in 'Mechanisms of Molecular Migrations' ed. B. S. Thyagarajam. Interscience, New York, 1968, vol. 1, p. 157; T. Durst, *Adv. Org. Chem.*, 1969, **6**, 356; T. Durst in 'Comprehensive Organic Chemistry', ed. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 3, p. 137, and E. Block in 'Reactions of Organosulphur Compounds', Academic, New York, 1978, p. 154.

[140] D. J. Ager, *Tetrahedron Lett.*, submitted.

[141] K. M. More and J. Wemple, *J. Org. Chem.*, 1978, **43**, 2713.

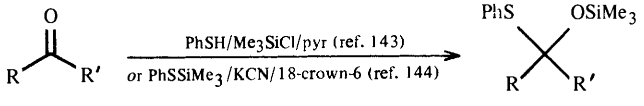
[142] I. Cutting and P. J. Parsons, *Tetrahedron Lett.*, 1981, **22**, 2021.



Reagents: (i) $LiAlH_4/THF/\Delta$. (ii) $PhSCl/NEt_3/Et_2O$. (iii) r.t. (iv) $AgNO_3/H_2O/MeCN$.

Scheme 32[142]

Siloxythioacetals [(25) and (26)] have also been prepared from the parent carbonyl compounds by treatment with thiophenol and chlorotrimethylsilane in pyridine[143] or a thiosilane in the presence of an anionic initiation[144] (this method is not, however, general for ketones) (see Scheme 33). They have also been prepared by the photochemical addition of α-trimethylsiloxythiols to olefins.[145]



(26)

Scheme 33

The acetals [(25) and (26)] are more stable to hydrolysis than would be expected from analogous systems. They were, however, cleaved by acid or base hydrolysis or hydrolysis catalysed by metal ions such as copper, silver, and mercury.[105,142,146] Reaction of [(25) or (26)] with an alkyl-lithium in an ethereal solvent yielded the parent carbonyl compound but when the reaction was carried out in HMPA or TMEDA, the thio-group was displaced to give the alcohol (30).[107,148] The acetals [(25) and (26)] have also been converted into α-iodosulphides, vinylsulphides,[147]

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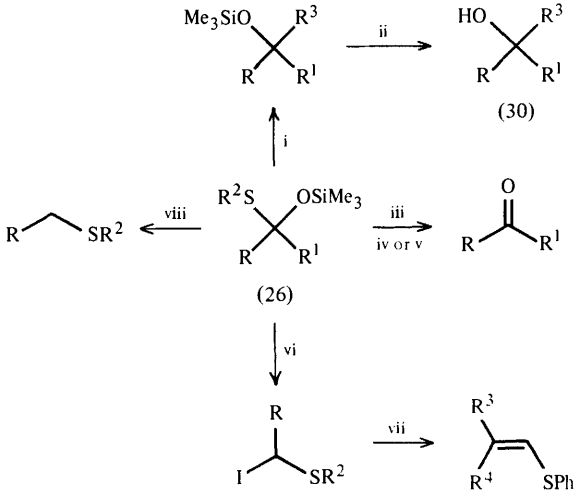
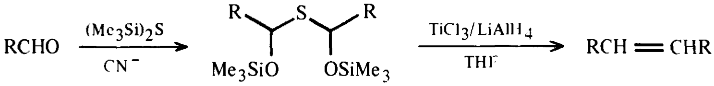
[143] T. H. Chan and B. S. Ong, *Tetrahedron Lett.*, 1976, 319.
[144] D. A. Evans, L. K. Truesdale, K. G. Grimm, and S. L. N. Nesbitt, *J. Am. Chem. Soc.*, 1977, **99**, 5009.
[145] T. Aida, T. H. Chan, and D. N. Harpp, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 691.
[146] D. J. Ager, *Tetrahedron Lett.*, submitted.
[147] T. Aida, D. N. Harpp, and T. H. Chan, *Tetrahedron Lett.*, 1980, **21**, 3247.
[148] R. S. Glass, *Synth. Commun.*, 1976, **6**, 47.

and sulphides[148] (see Scheme 34) while α,α′-bis(trimethylsiloxy)sulphides[149] have been converted into olefins[150] (see Scheme 35).



Reagents: (i) R^3Li/HMPA or THF/TMEDA (ref. 107, 143). (ii) H_2O. (iii) HCl/H_2O/THF (ref. 143, 146). (iv) $NaOH/H_2O$/THF (ref. 146). (v) MX_n/H_2O/THF, MeCN or Et_2O (ref. 105, 142, 146). (vi) $Me_3SiI/CHCl_3$ (ref. 147, 149). (vii) NEt_3 or $NaOH/H_2O/R_4NX$ (ref. 147). (viii) $LiAlH_4/AlCl_3/Et_2O$ (ref. 148).

Scheme 34



Scheme 35[149,150]

The advantages of employing the sulphur–carbon–silicon system as an acyl-anion equivalent are that the hydrolysis is very mild and can be achieved in acidic, neutral, or basic conditions whereas, in contrast, the parent α-thiosilanes are stable to a variety of reagents.[118] When further transformations of the carbonyl group are required, the system can be converted directly into an alcohol, vinylsulphide, sulphide, acetal, or olefin without isolation of the carbonyl compound. The main disadvantages of the system are that a chiral centre is introduced although the use of bis(phenylthio)acetals may alleviate this to some extent, oxidations in the presence of sulphur can be troublesome and the method cannot be used to synthesize hindered ketones.

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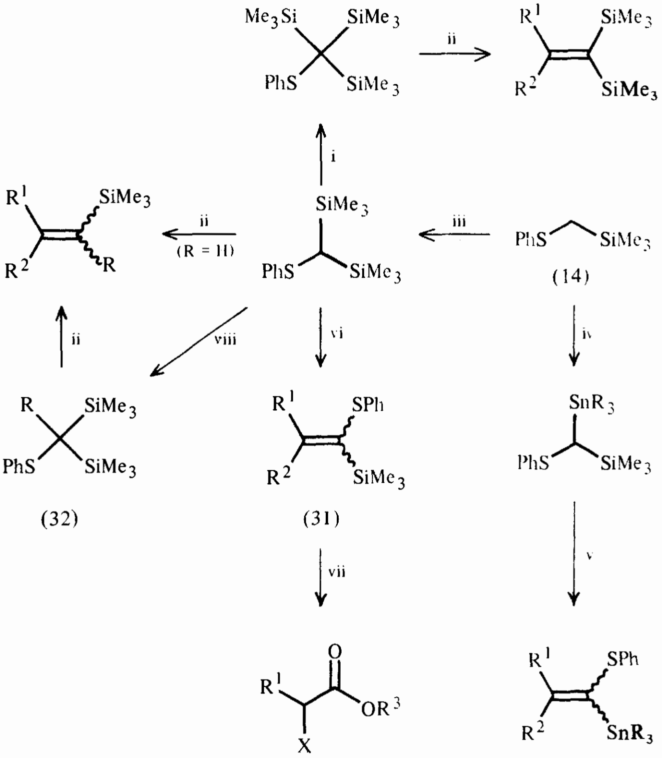
[149] T. Aida, T. H. Chan, and D. N. Harpp, *Tetrahedron Lett.*, 1981, **22**, 1089.
[150] T. H. Chan, J. S. Li, T. Aida, and D. N. Harpp, *Tetrahedron Lett.*, 1982, **23**, 837.



Reagents: (i) (*a*) n-BuLi/THF, (*b*) Me_3SiCl (ref. 70). (ii) (*a*) LiNaph/THF/−78 °C, (*b*) R^1R^2CO (ref. 70). (iii) (*a*) n-BuLi, (*b*) Me_3SiCl (ref. 115). (iv) R = Me or Bu^n; (*a*) n-BuLi, (*b*) R_3SnCl (ref. 68, 115). (v) LDA or KDA/THF, (*b*) R^1R^2CO (ref. 68, 115). (vi) (*a*) n-BuLi/THF, (*b*) R^1R^2CO (ref. 68, 151). (vii) R^2 = H; NCS/R^3OH (ref. 151). (viii) (*a*) n-BuLi, (*b*) RX (ref. 152).

Scheme 36

The reactions of anions with two silicon groups and one sulphur group attached to one carbon atom are summarized in Scheme 36, and those for one silicon and two sulphur groups are shown in Scheme 37. As can be seen, a wide variety of products are available, such as vinylsilanes (*vide supra*), vinylsulphides, thiol esters,

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[151] B.-T. Gröbel, R. Bürstinghaus, and D. Seebach, *Synthesis*, 1976, 121.

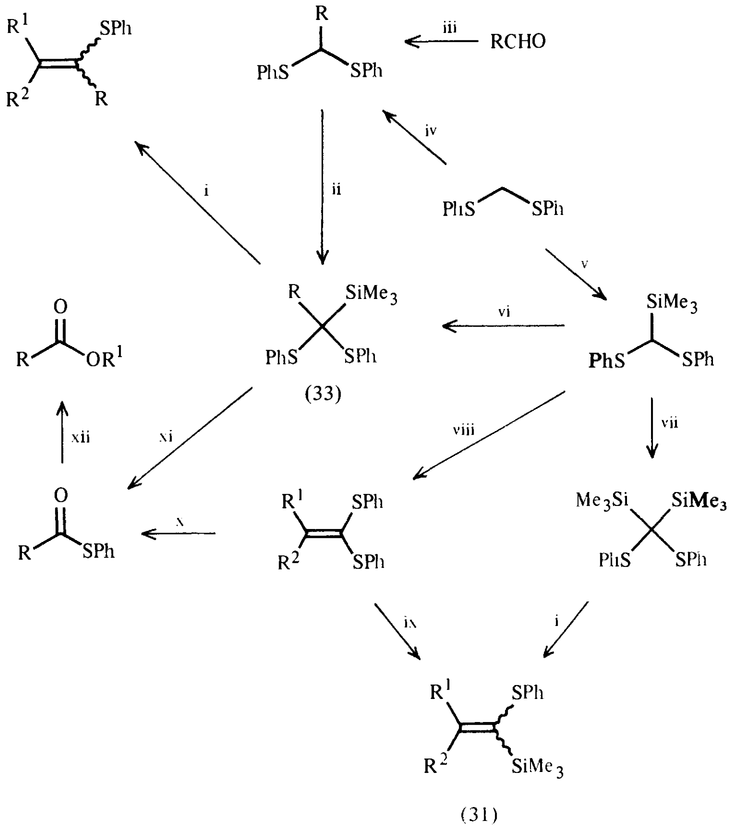
[152] D. J. Ager, *Tetrahedron Lett.*, submitted.

[153] *c.f.* D. J. Ager, *Tetrahedron Lett.*, 1980, **21**, 4763; I. Kuwajima, T. Abe, and K. Atsumi, *Chem. Lett.*, 1978, 383.

[154] E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4097.

[155] P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1074.

[156] D. Seebach, M. Kolb, and B.-T. Gröbel, *Chem. Ber.*, 1973, **106**, 2277.



Reagents: (i) (*a*) LiNaph, (*b*) R^1R^2CO (ref. 70), (ii) (*a*) n-BuLi/TMEDA (*b*) Me_3SiCl (ref. 113, 153). (iii) $PhSH/H^+$ (ref. 154, 155). (iv) (*a*) n-BuLi, (*b*) RX (ref. 154). (v) n-BuLi, (*b*) Me_3SiCl (ref. 152, 156). (vi) as (iv) (ref. 152). (vii) as (v) (ref. 70). (viii) (*a*) n-BuLi, (*b*) R^1R^2CO (ref. 152, 156) (for reactions of anions derived from 1,3-dithianes see ref. 157). (ix) (*a*) LiNaph, (*b*) Me_3SiCl (ref. 113, 158). (x) TFA (ref. 159, 160), (xi) (*a*) MCPBA, (*b*) Δ, (*c*) hydrolysis (ref. 152). (xii) Ag^I or Cu^{II}/R^1OH (ref. 161).

Scheme 37

[157] F. A. Carey and A. S. Court, *J. Org. Chem.*, 1972, 37, 1926; D. Seebach, B.-T. Gröbel, A. K. Beck, M. Braun, and K.-H. Geiss, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 443; P. F. Jones and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1972, 526; P. F. Jones, M. F. Lappert, and A. C. Szany, *J. Chem. Soc., Perkins Trans. 1*, 1973, 2272; N. H. Anderson, Y. Yamamoto, and A. D. Denniston, *Tetrahedron Lett.*, 1975, 4547; S. Danishefsky, R. McKee, and R. K. Singh, *J. Org. Chem.*, 1976, **41**, 2934; R. S. Brinkmeyer, *Tetrahedron Lett.*, 1979, 207.

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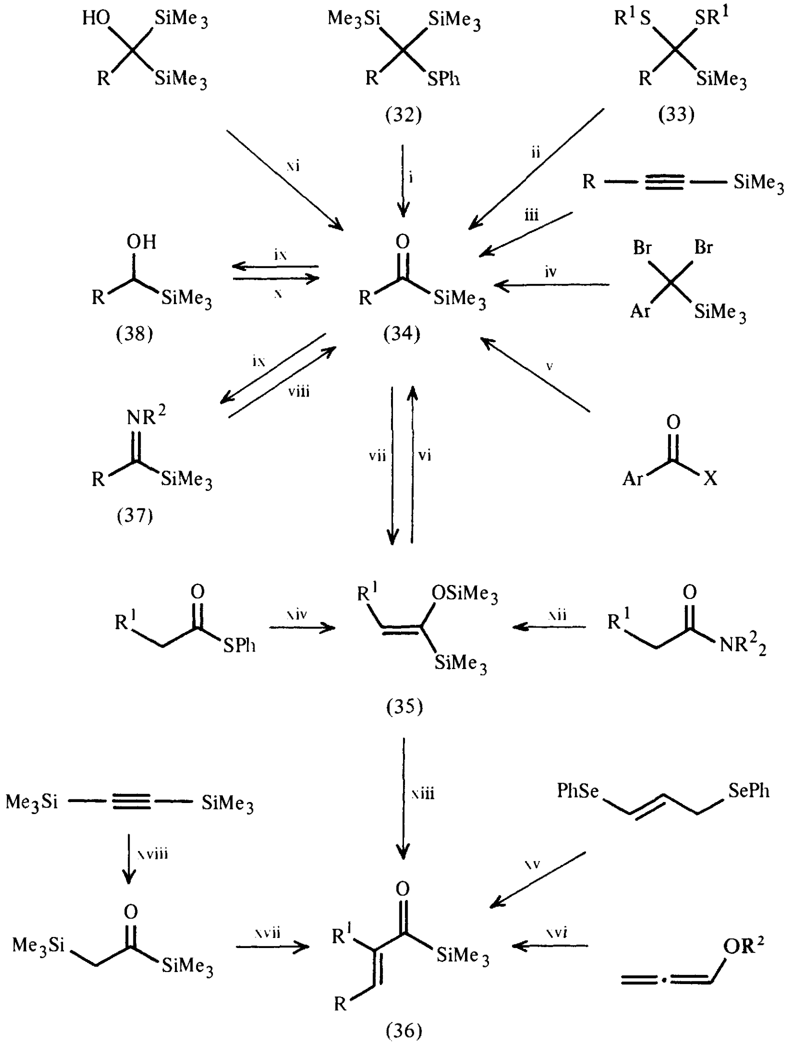
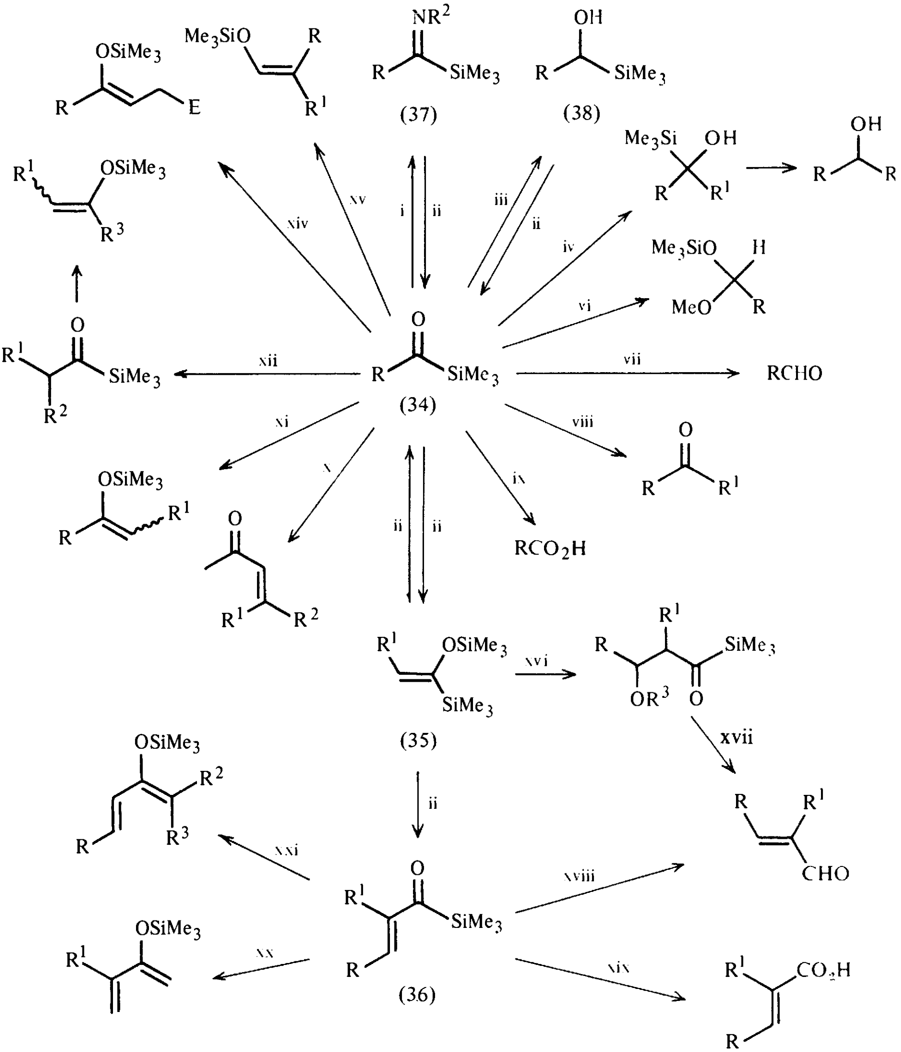


Reagents: (i) (*a*) MCPBA, (*b*) Δ, (*c*) hydrolysis (ref. 152, for the selenium analogue see ref. 163). (ii) hydrolysis, *e.g.* $HgCl_2/MeCN/H_2O$ (ref. 152, 164—166). (iii) $HBCl_2$, (*b*) $Me_3NO.2H_2O/C_6H_6$ (ref. 167). (iv) R = Ar; $AgOAc/Me_2CO/EtOH/H_2O$ (ref. 168) or SiO_2 (ref. 169). (v) R = Ar; X = OR^2. (*a*) $Me_3SiCl/Mg/HMPA$, (*b*) H_3O^+ (ref. 170); X = Cl, $Me_3SiSiMe_3/[(\eta^3\text{—}C_3H_5)PdCl]_2/P(OEt)_3$ (ref. 171). (vi) H_3O^+ (ref. 172). (vii) (*a*) LDA, (*b*) Me_3SiCl (ref. 173). (viii) H_3O^+ (ref. 174, 175). (ix) see Scheme 39. (x) DCC/DMSO (ref. 176) or CrO_3/pyr (ref. 162). (xi) t-$BuOCl/CCl_4$ (ref. 177). (xii) $Mg/Me_3SiCl/HMPA$ (ref. 172). (xiii) (*a*) PhSCl, (*b*) MCPBA, (*c*) xylene/Δ (ref. 178). (xiv) (*a*) LDA, (*b*) Me_3SiCl, (*c*) Na/Me_3SiCl (ref. 179). (xv) R^1 = H; (*a*) LDA, (*b*) Me_3SiCl, (*c*) $LiNEt_2$, (*d*) RX, (*e*) AcOH (ref. 180). (xvi) R^1 = H, R^2 = Me or EtOCH(Me)—, (*a*) BuLi, (*b*) Me_3SiCl, (*c*) BuLi, (*d*) RX, (*e*) TFA or $H_2SO_4/H_2O/THF$ (ref. 181, 182). (xvii) (*a*) LDA, (*b*) R^1X, (*c*) RCHO (ref. 185). (xviii) (*a*) $BH_3.SMe_2$, (*b*) Me_3NO, (*c*) H_2O (ref. 184).

Scheme 38



Reagents: (i) $TsNHNH_2/EtOH/AcOH$ (ref. 185) or $N_2H_4/AcOH$ (ref. 186). (ii) see Scheme 38. (iii) $LiAlH_4/Et_2O$ (ref. 176, 187, 188). (iv) R^1Li (ref. 176). (v) KH/HMPA (ref. 170) (This is the Brook rearrangement for further examples see ref. 180 and 189). (vi) $h\nu$/MeOH (ref. 190). (vii) R = Ar; ^-OH or ^-OEt (ref. 168, 191) or $KF/H_2O/DMSO$ or HMPA (ref. 192, 193) (viii) R = Ar; KF/18-crown-6/R^1X (ref. 194) or KF/R^1I/DMSO or HMPA (ref. 192). (ix) HO_2^- (ref. 195), (x) (*a*) $R^1{-}{\equiv}{-}Li$, (*b*) R^2X, (*c*) hydrolysis (ref. 180). (xi) $PhSO_2CHLiR^1$ or $R^1CHLiCN$/THF (ref. 175). (xii) $R{=}R^1CH_2$; (*a*) LDA, (*b*) R^2X (ref. 173). (xiii) $R^2 = PhS$; R^3Li/Et_2O (ref. 173). (xiv) (*a*) $CH_2 = CHLi/Et_2O$, (*b*) E^+ (ref. 180). (xv) Δ (ref. 196). (xvi) $RCH(OR^3)_3/BF_3.Et_2O$ (ref. 197). (xvii) NBu_4OH (ref. 197). (xviii) $NBu_4F/HCO_2H/$ 75 °C (ref. 183, 198). (xix) $H_2O_2/NaOH/THF/H_2O$ (ref. 183). (xx) R = H, $R^1 = PhSe$; $PhS(O)CH_2Li$ (ref. 173). (xxi) R^1H; $PhSO_2CLiR^1R^2$ (ref. 182).

Scheme 39

and esters. Both of the systems have been used to prepare acylsilanes (34)[162] whose methods of preparation are summarized in Scheme 38. Acylsilanes (34) are not strictly *umpolung* reagents but the numerous synthetic methods which stem from them (see Scheme 39) despite their labile nature,[8] makes them worthy of inclusion.

4 α-Silylselenides

Unlike α-silylsulphides, α-silylselenides have not found such a widespread application as acyl-anion equivalents. This is due to the selenium analogue of the sila-Pummerer rearrangement leading to the vinylsilane rather than the required *O*-trimethylsilylselenoacetal for ketone derivatives.[163] Despite this, α-silylselenides have been used to prepare aldehydes, olefins, and ketones (see Scheme 40) as well as carboxylic acids (see Scheme 23). The synthesis of olefins from α-silylselenides,

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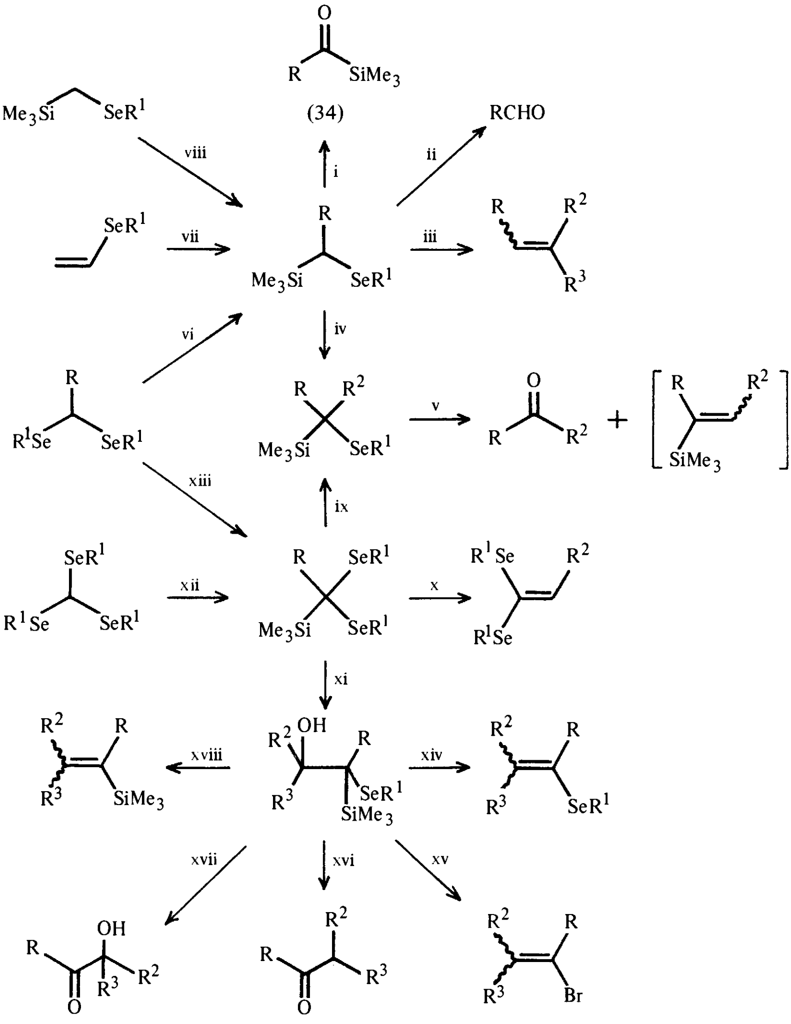

Reagents: (i) (*a*) $LiNEt_2$, (*b*) Me_3SiCl, (*c*) H_2O_2 (ref. 163). (ii) H_2O_2 (ref. 200, 201). (iii) (*a*) n-BuLi, (*b*) R^2R^3CO, (*c*) H_3O^+ (ref. 202). (iv) R = Ph; (*a*) $LiNEt_2$, (*b*) R^2X (ref. 63). (v) (*a*) MCPBA, (*b*) Δ (ref. 163), (vi) (*a*) n-BuLi, (*b*) Me_3SiCl (ref. 202, 203) (vii) $R = R^2(CH_2)_2—$; (*a*) R^2Li/Et_2O, (*b*) Me_3SiCl (ref. 204). (viii) (*a*) LDA (*b*) RX (ref. 200, 201). (ix) (*a*) n-BuLi, (*b*) R^2X (ref. 201). (x) (*a*) LDA, (*b*) R^2CHO (ref. 68). (xi) (*a*) n-BuLi, (*b*) R^2R^3CO (ref. 201, 205). (xii) (*a*) LDA, (*b*) RX, (*c*) n-BuLi, (*d*) Me_3SiCl (ref. 201). (xiii) (*a*) LDA, (*b*) Me_3SiCl (ref. 68, 201). (xiv) $KOBu^t/THF$ (ref. 205). (xv) Br_2/CCl_4 (ref. 205). (xvi) $HgCl_2/MeCN$ (ref. 205). (xvii) H_2O_2 (ref. 205). (xviii) $POCl_3/NEt_3/CH_2Cl_2$ (ref. 205).

Scheme 40

in contrast to α-silylsulphides (*vide supra*), has the disadvantage of the α-silylanion formation step being low yielding.[199]

5 *O*-Silylcyanohydrins

O-Silylcyanohydrins [(39) and (40)] are readily available from aldehydes or ketones respectively (for a review see reference 206). Their use as acyl-anion equivalents has, however, been limited to the cyanohydrins derived from aromatic aldehydes. These reactions, together with some other useful transformations which do not strictly involve *O*-silylcyanohydrins as acyl-anion equivalents, are summarized in Scheme 41.

The *O*-trimethylsilylcyanohydrins of α,β-unsaturated aldehydes (41) have been alkylated to give, after hydrolysis, enones[225] (see Scheme 42). They have also been used as acyl-anion equivalents for a three-carbon annelation procedure[226] (see Scheme 43) and oxidized with pyridinium dichromate to Δ^2-butenolides[227] (see Scheme 44).

6 Other Methods

This section considers silicon-containing carbonyl equivalents which do not fall into any of the above sections.

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[224] G. L. Grunewald, W. J. Brouillette, and J. A. Finney, *Tetrahedron Lett.*, 1980, **21**, 219.

[225] V. Hertenstein, S. Hünig, and M. Öller, *Synthesis*, 1976, 416.

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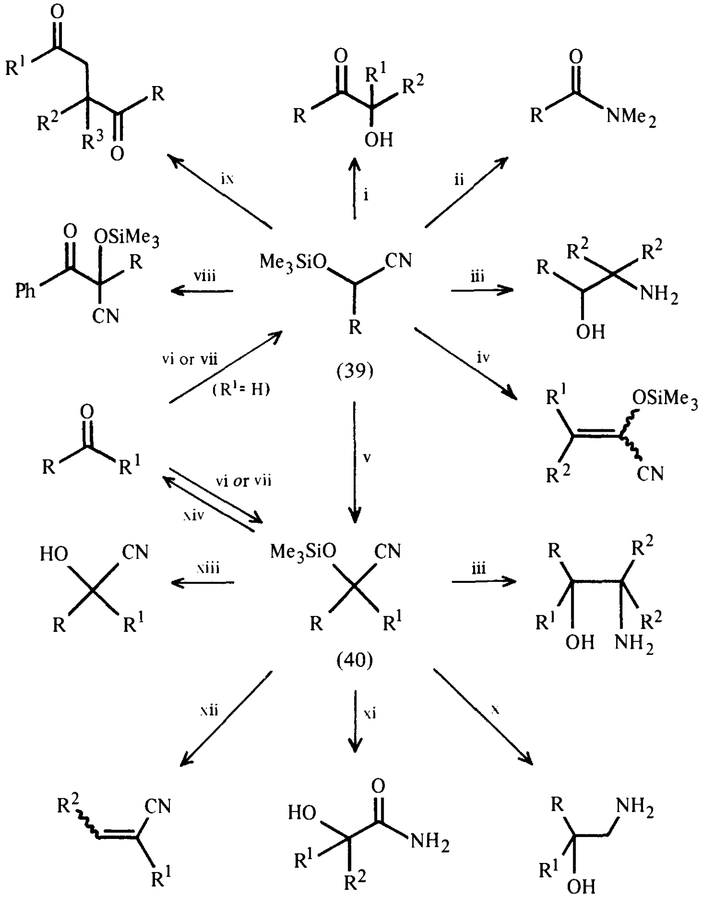
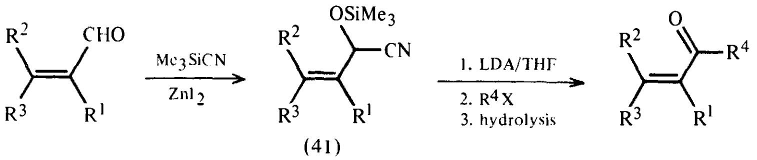
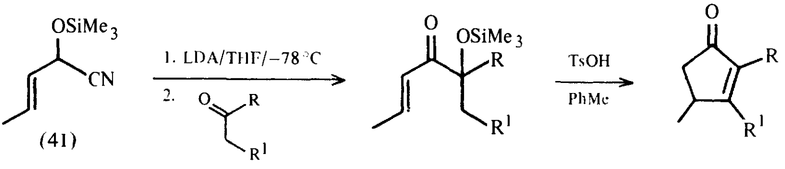


Reagents: (i) R = Ar; (*a*) LDA/DME, (*b*) R^1R^2CO, (*c*) H_2O (ref. 207, 208). (ii) R = Ar; (*a*) LDA, (*b*) $Ph_2P(O)ONMe_2$, (*c*) H_3O^+ (ref. 209). (iii) (*a*) R^2Li, (*b*) H_2O, (*c*) $AcOH/H_2O$ (ref. 210). (iv) $KHSO_4$/130—150 °C (ref. 211, 212). (v) R = Ar; (*a*) LDA/THF/-78 °C, (*b*) R^2X (ref. 213—215). (vi) $KCN/Me_3SiCl/MeCN$ or DMF/ZnI_2 (ref. 216). (vii) Me_3SiCN/CH_2Cl_2 or C_6H_6/ZnI_2 (ref. 206, 217, 218). (for a preparation of the t-butyldimethylsilyl derivative see ref. 219). (viii) R = Ar; (*a*) $LDA/Et_2O/-78$ °C, (*b*) PhCOCl (ref. 220). (ix) R = Ar; (*a*) LDA/Et_2O, (*b*) $R^1COCH{=}CR^2R^3$, (*c*) H_3O^+ (1,2-addition occurs when THF or DME used as solvent, see ref. 220, 221). (x) $LiAlH_4$/THF (ref. 222, 223). (xi) R = Ar; HCl (ref. 224) (for the t-butyldimethylsilyl analogue see ref. 219). (xii) R = R^2CH_2; $POCl_3$/pyr (ref. 218). (xiii) HCl/H_2O (ref. 217). (xiv) (*a*) H_3O^+ or R_3NHF, (*b*) HO^- (ref. 213, 215).

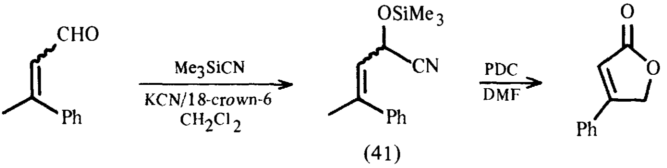
Scheme 41



Scheme 42[225]

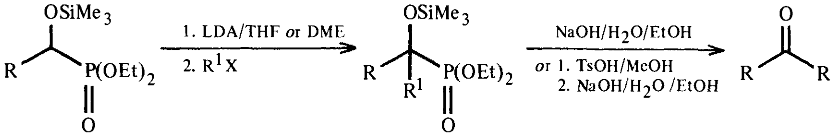


Scheme 43[226]



Scheme 44[227]

1-Trimethylsiloxyphosphonates[228,229] have been alkylated to give the ketone derivatives which, in turn, were easily hydrolysed[230] (see Scheme 45).



Scheme 45[230]

In addition to anions derived from α-chlorosilanes (*vide supra*), Magnus has employed the anion of methoxymethyltrimethylsilane (42) to prepare methyl enol ether, and consequently aldehydes[10,231] (see Scheme 46).

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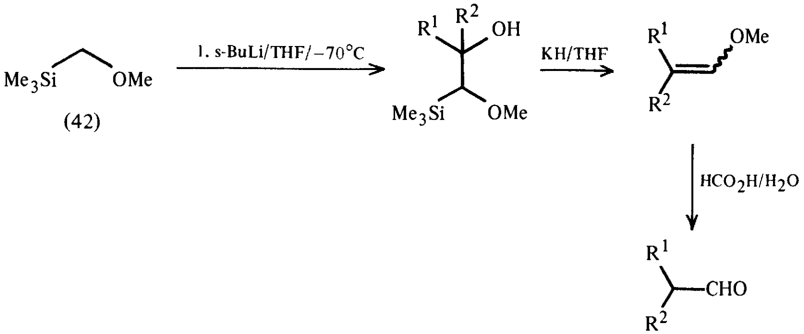
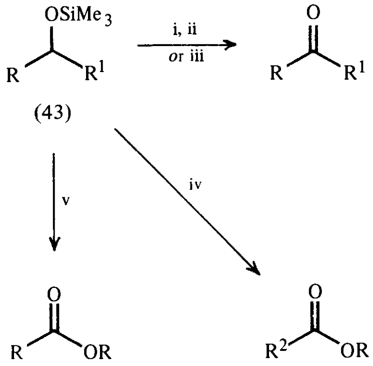


Scheme 46[231]

Trimethylsilyl ethers (43) although not *umpolung* reagents, may be regarded as carbonyl equivalents as they have been oxidized to the ketone by a variety of methods (see Scheme 47). Oxidation of the ethers (43) derived from primary alcohols gave the ester instead of the aldehyde.

Finally, it should be mentioned that a silyl group has been used as a masked anion for the preparation of non-silicon-containing acyl-anion equivalents.[235]



Reagents: (i) (*a*) Ph_3CBF_4/CH_2Cl_2, (*b*) H_2O (ref. 232). (ii) $NOBF_4/CH_2Cl_2$ (ref. 233). (iii) NBS/CCl_4/*hv* (ref. 234). (iv) R^1 = H; R^2CHO/NBS/CCl_4/*hv* (ref. 234). (v) R^1 = H; NBS/CCl_4/*hv* (ref. 200).

Scheme 47

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7 Conclusions

It has been seen that there are many methods which employ organosilicon reagents for the synthesis of carbonyl compounds. Some of these methods have distinct advantages over more traditional methods. It is to be hoped that silicon-containing carbonyl equivalents find widespread use alongside the more traditional reagents.