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Synthesis and Chemistry of Acyl Silanes

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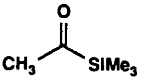
1 Introduction

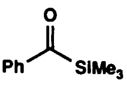
Acyl silanes exhibit unusual spectroscopic behaviour and possess interesting chemistry. In general they enjoy poor stability, particularly towards basic conditions and light. Early work, perhaps spurred by the green or yellow-green colour of simple acyl silanes, concentrated on spectroscopic properties, and indeed the structure and bonding of acyl silanes is a subject still worthy of discussion in the literature. Crystallographic studies have only added to the argument. More recently the chemistry of acyl silanes has been investigated resulting both in valuable new reactions and in improved methods of synthesis of acyl silanes of several types.[1] This survey covers the major developments in all areas of acyl silane chemistry since the first isolation in 1968, beginning with a simple descriptive spectroscopy section; readers are referred to publications cited in the text for a more thorough treatment of the structure and bonding aspects of acyl silane chemistry.

2 Structure and Spectroscopy of Acyl Silanes

A. Infrared Spectroscopy.—Early work on acyl silanes[2–4] mainly concerned their interesting and unusual spectroscopic properties. For example, the alkyl acyl silane (1) and the aryl acyl silane (2) have carbonyl stretching absorption frequencies at *ca.* 1645 cm^{-1} and 1620 cm^{-1} respectively in their infrared spectra (Table 1, entries 6 and 7).



(1)



(2)

This lowering of the carbonyl stretching frequency in the infrared spectrum relative to simple ketones is usually explained as an inductive effect: electron

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[1] A. Ricci and A. Degl'Innocenti, *Synthesis*, 1989, 647.

[2] A. G. Brook, *J. Am. Chem. Soc.*, 1957, **79**, 4373; A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, 1960, **82**, 5102.

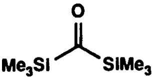
[3] V. Bazant, V. Chvalovsky, and J. Rathousky, in 'Organosilicon Compounds', Academic Press, New York, 1965; V. Chvalovsky, in 'Handbook of Organosilicon Compounds—Advances Since 1961', Marcel Dekker, New York, 1974.

[4] A. G. Brook and R. J. Mauris, *J. Am. Chem. Soc.*, 1957, **79**, 971; A. G. Brook and G. J. D. Peddle, *Can. J. Chem.*, 1963, **41**, 2351.

release from the silicon atom towards the carbonyl group should favour polarization of the carbonyl group, and so resonance structure (3) should be expected to have a more significant contribution than in a simple ketone, thus weakening the bond.[5]

(3)

The position of the carbonyl absorption of acyl silanes is not significantly altered by changing the type of group attached to the silicon atom, similar absorptions being observed for trimethyl, triphenyl, and tris-(*para*-substituted) phenylsilanes, the last showing a linear correlation of Hammett constants. Further, whereas ketone carbonyl absorptions shift to lower frequency on increasing the polarity of the medium in which they are measured, the position of acyl silane carbonyl absorptions is relatively independent of medium polarity.[6] The large σ inductive effect is caused by the low electronegativity of silicon (1.8) relative to carbon (2.5), and by the larger mass of silicon. Ground state mesomeric effects acting between silicon *d* orbitals and the carbonyl group [π (π–d) bonding] would be expected to give rise to absorption at higher frequency. However, differences in electronegativity producing significant inductive release of electron density towards the carbonyl group would be expected to lead to a decrease in the frequency, as is indeed the case.[5,6]



(4)

Acyl silanes and acyl germanes exhibit lower frequency absorptions than α-silyl ketones, which in turn absorb at lower frequency than β-silyl ketones. β-Silyl ketones absorb at similar frequency to their carbon analogues (Table 1, entries 2—4). This pattern is consistent with a strong inductive release of electrons, an effect which is less apparent in the α-metallo ketones, where it must operate through an extra methylene group, and which has no apparent effect through two methylene groups. The strong inductive release in acyl silanes is approximately additive as shown by the pink-coloured bis-(trimethylsilyl) ketone (4), where the infrared stretching frequency is shifted by approximately 80 cm^{-1} to lower frequency compared with pivaloyl trimethylsilane (Table 1, entries 32 and 33).[5]

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[5] A G Brook, *Adv Organomet Chem*, 1968, **7**, 96

[6] A G Brook, R Kıvıskık, and G E Le Grow, *Can J Chem*, 1965, **43**, 1175

Table 1 *Infrared C═O absorption of selected acyl metalloids and related compounds*

Entry	*Compound*	ν(M═C)	ν(M═Si)	ν(M═Ge)	ν(M═Sn)	*Ref.*
1	$\mathrm{Ph_3MCOCH_3}$		1645	1669	1670	5
2	$\mathrm{Ph_3MCOPh}$	1692	1618	1629	1627	5, 7
3	$\mathrm{Ph_3MCH_2COPh}$	1698	1667	1661		5
4	$\mathrm{Ph_3MCH_2CH_2COPh}$	1692	1692			5
5	$\mathrm{PhMe_2MCOPh}$		1620			5, 7
6	$\mathrm{Me_3MCOPh}$	1675	1620	1629		5, 7
7	$\mathrm{Me_3MCOCH_3}$	1710	1645			5, 7
8	$\mathrm{Bu^tMe_2MCOCH_3}$		1630, 1640			8
9	$\mathrm{Me_3MCO(CH_2)_4CH_3}$	1700	1640			7, 9, 10
10	$\mathrm{(Me_3MCOCH_2CH_2)_2}$		1640			11
11	$\mathrm{Me_3MCOCH_2Ph}$		1635	1660	1656	12
12	$\mathrm{Et_3MCOCH_2CH_3}$		1640			13
13	$\mathrm{Pr^n{}_3MCOCH_2CH_3}$		1640			13
14	$\mathrm{Bu^tMe_2MCOCH_2CH_3}$		1630, 1640			8, 13
15	$\mathrm{Bu^tMe_2MCO(CH_2)_6CH_3}$		1630			8
16	$\mathrm{Me_3MCOCHCl(CH_2)_3CH_3}$		1650			14
17	$\mathrm{Me_3MCOCHBr(CH_2)_3CH_3}$		1645, 1652			7, 14
18	$\mathrm{Me_3MCOCH{=}CH_2}$		1635, 1641			15, 16
19	$\mathrm{Me_3MCOCH{=}CHCH_3}$		1642	1644	1648	12
20	$\mathrm{Me_3MCOC(CH_3){=}CH_2}$		1630			16
21	$\mathrm{PhMe_2MCOC(CH_3){=}CH_2}$		1620			17
22	$\mathrm{Me_3MCOCH{=}C(CH_3)_2}$		1640	1645	1640	12
23	$\mathrm{Me_3MCOCH{=}CH(CH_2)_3CH_3}$		1620			18—21
24	$\mathrm{Bu^tMe_2MCOCCl{=}C(CH_3)_2}$		1640			17
25	(21a)		1640			11
26	(21b), (21c)		1610			11
27	(21d)		1620			11
28	(21e), X = O		1590			22
29	(21e), X = S		1580			22
30	(21e), X = NMe		1575			22
31	$\mathrm{Bu^tMe_2MCOC{\equiv}CCH_3}$		1605			15
32	$\mathrm{Me_3MCOCMe_3}$		1636			5
33	$\mathrm{Me_3MCOMMe_3}$		1556, 1570			23
34	$\mathrm{Ph_3MCOMPh_3}$		1558 + 1592	1616		5
35	$\mathrm{Me_3MCOCOCH_3}$		1713 + 1658			7, 15
36	$\mathrm{Me_3MCOCOPh}$		1680 + 1610			7
37	$\mathrm{Me_3MCOCO_2Me}$		1660			24
38	$\mathrm{PhMe_2MCOCO_2Me}$		1660			24
39	$\mathrm{Me_3MCONEt_2}$	1620	1560			25
40	$\mathrm{(Me_3Si)_3MCO_2H}$		1630			26
41	$\mathrm{(Me_3Si)_3MCO_2Me}$		1655			26
42	$\mathrm{(Me_3Si)_3MCOAd}$*		1620	1640		27, 28
43	$\mathrm{Me(Me_3Si)_2MCOAd}$*		1613			29
44	$\mathrm{Bu^t(Me_3Si)_2MCOAd}$*		1622			29
45	$\mathrm{Ph(Me_3Si)_2MCOAd}$*		1609			29

* Ad = adamantyl

B. ^{13}C NMR Spectroscopy.—In comparison with the corresponding ketones, the ^{13}C signals of the carbonyl groups in acyl silanes are dramatically shifted downfield (Table 2).[30–31a] Carbonyl groups in acyl silanes have chemical shifts differing by between *ca.* 25 and 100 ppm from those of the analogous ketones;[31a] the effect is approximately additive (Table 2, entry 16).

^{13}C studies also expose some interesting resonance features of acyl silanes. The carbonyl group of an alkyl phenyl ketone (*e.g.* Ph–CO–Bu^t) displays a ^{13}C chemical shift close to its aliphatic analogue (*i.e.* Me–CO–Bu^t); however, the difference between the two corresponding silicon species (*e.g.* Ph–CO–SiMe$_3$ and CH$_3$–CO–SiMe$_3$) is a little more marked. Benzoyltrimethylsilane (2) exhibits a carbonyl shift *ca.* 11—14 ppm upfield of that displayed by acetyltrimethylsilane (1) (Table 2, entries 2 and 5). This could be ascribed to participation of resonance structures such as (5) which, by reducing the amount of positive charge on the carbonyl carbon atom, increase its shielding, thus displacing the chemical shift upfield relative to the aliphatic analogue where such an effect cannot operate.

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[9] G Zweifel and J A Miller, *Synthesis*, 1981, 288

[10] C Heathcock and J Lampe, *J Org Chem*, 1983, **48**, 4330

[11] A Capperucci, A Degl'Innocenti, C Faggi, A Ricci, P Dembech, and G Seconi, *J Org Chem*, 1988, **53**, 3612

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[15] H J Reich, M J Kelly, R E Olson, and R C Holtan, *Tetrahedron*, 1983, **39**, 949, H J Reich and M J Kelly, *J Am Chem Soc*, 1982, **104**, 1119

[16] R L Danheiser, D M Fink, K Okano, Y-M Tsai, and S W Szczepanski, *J Org Chem*, 1985, **50**, 5393

[17] H J Reich, E K Eisenhart, R E Olson, and M J Kelly, *J Am Chem Soc*, 1986, **108**, 7791, H J Reich and E K Eisenhart, *J Org Chem*, 1984, **49**, 5282

[18] R Mantione and Y Leroux, *Tetrahedron Lett*, 1971, **12**, 591

[19] R G Visser, L Brandsma, and H J T Bos, *Tetrahedron Lett*, 1981, **22**, 2827

[20] K J H Kruithof and G W Klumpp, *Tetrahedron Lett*, 1982, **23**, 3101

[21] J C Clinet and G Linstrumelle, *Tetrahedron Lett*, 1980, **21**, 3987

[22] A Ricci, A Degl'Innocenti, S Chimichi, M Fiorenza, G Rossini, and H J Bestmann, *J Org Chem*, 1985, **50**, 130

[23] A Ricci, M Fiorenza, A Degl'Innocenti, G Seconi, P Dembech, K Witzgall, and H J Bestmann, *Angew Chem, Int Ed Engl*, 1985, **24**, 1068

[24] A Sekiguchi, Y Kabe, and W Ando, *Tetrahedron Lett*, 1979, **20**, 871

[25] G J D Peddle and R W Walsingham, *J Chem Soc, Chem Commun*, 1969, 462

[26] A G Brook and L Yau, *J Organomet Chem*, 1984, **271**, 9

[27] A G Brook, J W Harris, J Lennon, and M El Sheikh, *J Am Chem Soc*, 1979, **101**, 83, A G Brook, S C Nyburg, W F Reynolds, Y C Poon, Y-M Chang, J-S Lee, and J-P Picard, *J Am Chem Soc*, 1979, **101**, 6750, A G Brook, S C Nyburg, F Abdesaken, B Gutekunst, G Gutekunst, R K M R Kallury, Y C Poon, Y-M Chang, and W Wong-Ng, *J Am Chem Soc*, 1982, **104**, 5667

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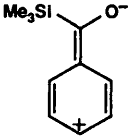
[30] E M Dexheimer, G L Buell, and C le Croix, *Spectroscopy Lett*, 1978, **11**, 751

[31] (*a*) F Bernardi, L Lunazzi, A Ricci, G Seconi, and G Tonachini, *Tetrahedron*, 1986, **42**, 3607, (*b*) S Fliszar, G Cardinal, and M T Beraldin, *J Am Chem Soc*, 1982, **104**, 5287

Table 2 *^{13}C Carbonyl group chemical shifts of selected acyl silanes and related compounds*

Entry	*Compound*	δ(M=Si)	δ(M=C)	*Ref.*
1	$Me_3MCOCMe_3$	249.0	215.1	31*a*
2	Me_3MCOCH_3	244.3, 247.6	210.4	31*a*, 32
3	$Me_3MCO(CH_2)_5CH_3$	251.2		7
4	(112)	246.7		33
5	Me_3MCOPh	233.6, 237.5	207.8, 209.1	31*a*, 32
6	$Me_3MCOCH{=}CH_2$	236.7, 237.9		15, 16
7	$Me_3MCOC(CH_3){=}CH_2$	237.3		16
8	$Me_3MCOCH{=}CH(CH_2)_6CH_3$	236.4		16
9	(21d)	236.0		11
10	(21e), X = O	220.7		22
11	(21e), X = S	223.1		22
12	(21e), X = NMe	220.0		22
13	$Bu^tMe_2MCOC{\equiv}CCH_3$	225.7		15
14	$Me_3MCOCHBr(CH_2)_4CH_3$	234.8		7
15	$Me_3MCOCHBr(CH_2)_3Cl$	235.2		7
16	$Me_3MCOSiMe_3$	318.2, 318.8	249.0	23, 31*a*
17	$Me_3M\mathit{CO}CO(CH_2)_4CH_3$	235.1		7
18	$Me_3M\mathit{CO}COPh$	220.4		7
19	$Me_3M\mathit{CO}COCH_3$	235.5		15
20	Ph_3MCOCH_3	240.1		34
21	$(Me_3Si)_3MCOPh$	233.8		34
22	$(Me_3Si)_3MCOC(CH_3)_3$	244.6		34



(5)

C. ^1H NMR Spectroscopy.—^1H NMR data indicate that protons attached to the α carbon atom of acyl silanes and acyl germanes are generally somewhat deshielded relative to their carbon analogues (Table 3). This property no doubt results from differences in electronegativity and magnetic anisotropy. Interestingly, α,β-unsaturated acyl silanes appear to be an exception to this rule (entry 16).

D. ^{29}Si NMR Spectroscopy.—The ^{29}Si NMR properties of acyl silanes[30] indicate that the acyl group has a moderate shielding effect upon the silicon atom compared with the situation in tetramethylsilane similar in magnitude to that observed in vinyl trimethylsilane (Table 4).

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[32] G. A. Olah, A. L. Berrier, L. D. Field, and G. K. Surya Prakash, *J. Am. Chem. Soc.*, 1982, **104**, 1349.
[33] B. Frei and M. E. Scheller, *Helv. Chim. Acta*, 1984, **67**, 1734.
[34] A. G. Brook, F. Abdesaken, G. Gutekunst, and N. Plavac, *Organometallics*, 1982, **1**, 994.

Table 3 ^{1}H *Chemical shifts at α-carbon atom of selected acyl metalloids*

Entry	*Compound*	δ(M=C)	δ(M=Si)	δ(M=Ge)	δ(M=Sn)	*Ref.*
1	$\mathrm{Me_3MCOC}H_2\mathrm{Ph}$		3.77	3.73	3.80	12
2	$\mathrm{Me_3MCOCH_3}$	2.07	2.18, 2.20			5, 7
3	$\mathrm{Ph_3MCOCH_3}$	2.01	2.30	2.38		5
4	$\mathrm{Bu^tMe_2MCOCH_3}$		2.32			8
5	$\mathrm{Me_3MCOC}H_2\mathrm{(CH_2)_3CH_3}$	2.33	2.50			7, 9, 10
6	$\mathrm{Me_3MCOC}H\mathrm{(CH_2CH_3)_2}$		2.50			8
7	$\mathrm{Bu^tMe_2MCOC}H_2\mathrm{CH_3}$		2.64			8, 13
8	$\mathrm{Et_3MCOC}H_2\mathrm{CH_3}$		2.60			13
9	$\mathrm{Pr^n{}_3MCOC}H_2\mathrm{CH_3}$		2.60			13
10	$\mathrm{Me_3MCOC}H\mathrm{PhCH_2CH_3}$		3.86			8
11	$\mathrm{Me_3MCOCOC}H_3$		2.03			7, 15
12	$\mathrm{Me_3MCOCOC}H_2\mathrm{(CH_2)_3CH_3}$		2.55			7
13	$\mathrm{Me_3MCOCOC}H_2\mathrm{(CH_2)_2CH_3}$		2.58			7
14	$\mathrm{Me_3MCOC}H\mathrm{Cl(CH_2)_3CH_3}$		4.11			14
15	$\mathrm{Me_3MCOC}H\mathrm{Br(CH_2)_3CH_3}$		4.39, 4.33			7, 14
16	$\mathrm{Me_3MCOC}H\mathrm{{=}CH_2}$	6.88	6.28, 6.38			7, 15, 16, 35
17	$\mathrm{Me_3MCOC}H\mathrm{{=}CHCH_3}$		6.78	6.62	6.39	7, 12
18	$\mathrm{Me_3MCOC}H\mathrm{{=}C(CH_3)_2}$		6.56	6.32	6.40	12

The nature of the groups attached to the silicon moiety also affects the chemical shift of the silicon atom (Table 4), although it is difficult to see any reliable pattern except in the cases of acyl tris-(trimethylsilyl) silanes and acyl alkyl bis-(trimethylsilyl) silanes (entries 11–23).

E. *X*-Ray Diffraction Studies.—Single-crystal *X*-ray analyses of both acetyl triphenylsilane[37] and acetyl triphenylgermane[38a] have been completed. In both cases the three phenyl groups and the acetyl group are located tetrahedrally around the metalloid centre. For the acyl silane, whereas the phenyl–Si bond length is 1.864 Å, the Si–CO (acetyl) bond length is significantly longer, at 1.926 Å; a typical value for a saturated carbon–silicon single bond would be 1.84—1.87 Å. However, the C=O bond length, which might have been expected to be abnormally long (reflecting the unusually long wavelength carbonyl absorption and the enhanced basicity) was found to be 1.21 Å—approximately the same as that normally found in ketones. The bond angles involving the carbonyl group were approximately the theoretical 120° and the CH_3–CO bond length of 1.50 Å was normal. The structure of acetyl triphenylgermane is very similar to its silicon analogue and shows a lengthening of the Ge–C (acetyl) bond by 0.066 Å compared with the Ge–Ph bond.

Trotter ascribes the lengthening of the metalloid–carbon (acetyl bond) to a contribution to the structure not only of canonical forms (6) and (7), whose carbon analogues contribute to the structure of ordinary ketones, but also (8) in

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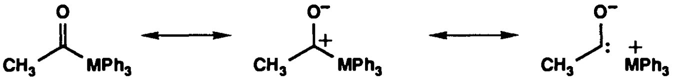
[35] I. Naito, A. Kanishita, and T. Yonenitsu, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 339.

Table 4 ^{29}Si *Chemical shifts of selected acyl silanes and related compounds*

Entry	*Compound*	δ(Si)/ppm	*Ref.*
1	$Me_3SiCOMe$	−10.1	32
2	$Ph_3SiCOMe$	−30.4	34
3	$(Me_3Si)_4\mathit{Si}$	−135.5	34
4	$Ph_3SiCOPh$	−28.3	34
5	$Et_3SiCOPh$	−28.3	34
6	$Me_3SiCOPh$	−7.4, −15.1	32, 34
7	$Me_3SiCOSiMe_3$	−14.4	23
8	(21e), X = O	−6.3	22
8	(21e), X = S	−6.9	22
9	(21e), X = NMe	−8.8	22
10	$Me_3SiCH{=}CH_2$	−7.6	36
11	$(Me_3Si)_3GeCO$-Ad*	−5.24	28
12	$(Me_3Si)_3\mathit{Si}CO$-Ad*	−78.8	34
13	$(Me_3\mathit{Si})_3SiCO$-Ad*	−11.5	34
14	$Me(Me_3Si)_2\mathit{Si}CO$-Ad*	−50.38	29
15	$Me(Me_3\mathit{Si})_2SiCO$-Ad*	−13.72	29
16	$Bu^t(Me_3Si)_2\mathit{Si}CO$-Ad*	−32.24	29
17	$Bu^t(Me_3\mathit{Si})_2SiCO$-Ad*	−15.48	29
18	$Ph(Me_3Si)_2\mathit{Si}CO$-Ad*	−44.75	29
19	$Ph(Me_3\mathit{Si})_2SiCO$-Ad*	−13.45	29
20	$(Me_3Si)_3\mathit{Si}CO_2H$	−73.84	26
21	$(Me_3\mathit{Si})_3SiCO_2H$	−6.15	26
22	$(Me_3Si)_3\mathit{Si}CO_2Me$	−74.45	26
23	$(Me_3\mathit{Si})_3SiCO_2Me$	−6.34	26

* Ad = adamantyl

which there is no formal bond between the metalloid atom and the acetyl carbon atom, a structure considered possible as a contributing resonance form because of the considerable differences in electronegativity between the metalloids and carbon.[37,38a] The acetyl triphenylgermane molecule is therefore represented by Trotter as (9), a structure said to represent both the basicity of the ketone oxygen atom and the long germanium–carbonyl carbon bond.[37]



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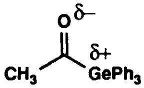

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[36] E. Lippmaa, M. Mägi, V. Chvalovsk'y, and J. Schraml, *Coll. Czech. Chem. Commun.*, 1977, **42**, 318.

[37] P. C. Chieh and J. Trotter, *J. Chem. Soc.*, 1969, 1778.

[38] (*a*) R. W. Harrison and J. Trotter, *J. Chem. Soc.*, 1968, 258; (*b*) F. Agolini, S. Klemenko, I. G. Csizmadia, and K. Yates, *Spectrochim. Acta*, 1968, **24a**, 169; (*c*) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, 1955, **77**, 4462; (*d*) R. West, R. H. Baney, and D. L. Powell, *J. Am. Chem. Soc.*, 1960, **82**, 6269; (*e*) N. A. Matwiyoff and R. S. Drago, *J. Organomet. Chem.*, 1965, **3**, 393.

F. Ultraviolet and Visible Spectroscopy.—Acyl silanes display most unusual ultraviolet and visible spectral characteristics (Table 5)[39, 44] Several acyl metalloids, including acetyl trimethylsilane and acetyl trimethylgermane, have been studied by photoelectron spectroscopy,[41] and a range of *ab initio* and semiempirical calculations have been carried out[41, 42] Acyl silanes show absorptions due to $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions, as do simple ketones However, the $n \longrightarrow \pi^*$ excitation of alkyl acyl silanes occurs around 370 nm, a shift of about 100 nm to longer wavelength compared with the analogous carbon compound pinacolone (ν_{max} 279 nm) This translates into a *ca* 25 kcal mol^{-1} lowering in the energy of the $n \longrightarrow \pi^*$ transition Comparison of extinction coefficients of acetyl trimethylsilane and pinacolone ($\varepsilon = 126$ and 21 respectively) shows that absorption for the silicon derivative is far more intense In addition, considerable fine structure is observed, usually consisting of three main bands, sometimes with two additional shoulders at lower wavelengths[5] The persistence of this vibrational structure in polar solvents, an effect not commonly observed in ketones, is not clearly understood In aryl acyl silanes, which may be lime green in colour, and in α,β-unsaturated acyl silanes, the $n \longrightarrow \pi^*$ transition occurs around 420 nm, again shifted to longer wavelength by about 100 nm than in the corresponding carbon compounds In the yellow α-carboxyacyl silanes the transition appears at 455 nm, and in α-ketoacyl silanes around 520 nm, accounting for the deep crimson colour of this species, bis-(trimethylsilyl) ketone (4) is also pink-coloured The $\pi \longrightarrow \pi^*$ transition for the carbonyl group in aryl acyl silanes produces a fairly intense absorption band in the range 250—260 nm The position and extinction coefficient of such transitions does not vary greatly, regardless of substituents on the silyl group, although slight red shifts are observed in polar solvents as would be expected for conjugated carbonyl group transitions

As is seen for ketones, a third absorption is observed in the region 185—195 nm For acyl silanes with aromatic substituents this could either be ascribed to a primary benzene band or to a second $\pi \longrightarrow \pi^*$ transition, whereas for other acyl silanes this transition (195 nm, $\varepsilon = 4200$ for acetyl trimethylsilane) is presumably the latter In general the nature of the groups (other than acyl) attached to the silicon atom has little effect on the energies of $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions[5]

3 Synthesis of Acyl Silanes

A. Simple Acyl Silanes.—(i) *Formyl Silanes* Formyl silanes have been investigated only briefly, due primarily to their instability After several years of speculation

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[39] R West, *J Organomet Chem*, 1965, **3**, 314

[40] D F Harnish and R West, *Inorg Chem*, 1963, **2**, 1082

[41] B G Ramsey, A G Brook, A R Bassindale, and H Bock, *J Organomet Chem*, 1974, **74**, C41

[42] E B Nadler, Z Rappoport, E Arad, Y Apeloig, *J Am Chem Soc*, 1987, **109**, 7873

[43] L E Orgel, in 'Volatile Silicon Compounds', ed E A V Ebsworth, Pergamon Press, Oxford, 1963, p 81

[44] K Yates and F Agolini, *Can J Chem*, 1966, **44**, 2229

Table 5 *UV/Visible absorption of selected metalloids and related compounds*

Entry	*Compound*	*n* ⟶ π*	π ⟶ π*	*Ref.*
		[λ_{max}/nm (ε)]		
1	Me_3CCOMe	278 (15)		5
2	$Me_3SiCOMe$	372 (126)		5
3	$Et_3GeCOMe$	365 (173)		5
4	$Me_3SiCO(CH_2)_4CH_3$	367 (129)		9
5	$Me_3SiCO(CH_2)_5CH_3$	357 (131)		7
6	$Me_3SiCOCHBr(CH_2)_4CH_3$	374 (142)		7
7	(112)	372 (16)		33
8	Ph_3CCOPh	329 (299)	251 (11 600)	5
9	$Ph_3SiCOPh$	424 (292)	257 (16 200)	5
10	$Ph_3GeCOPh$	417 (210)	254 (16 200)	5
11	$Ph_3SnCOPh$	435		5
12	$Me_3SiCOPh$	425 (127)	250 (14 500)	5, 7
13	$Me_3GeCOPh$	412 (120)	252 (10 700)	5
14	$Me_3SiCOCH_2Ph$	377 (113)		12
15	$Me_3GeCOCH_2Ph$	366 (124)		12
16	$Me_3SnCOCH_2Ph$	379		12
17	$Me_3SiCOCH{=}CH_2$	434 (96)	213 (8630)	15
18	$Me_3SiCOCH{=}CHCH_3$	424 (98)	224 (10 300)	7, 12
19	$Me_3GeCOCH{=}CHCH_3$	416 (109)	258 (11 300)	12
20	$Me_3SnCOCH{=}CHCH_3$	432	258	12
21	$Me_3SiCOCH{=}C(CH_3)_2$	439 (120)	249 (12 700)	12
22	$Me_3GeCOCH{=}C(CH_3)_2$	432 (140)		12
23	$Me_3SnCOCH{=}C(CH_3)_2$	453		12
24	$Me_3SiCOC(CH_3){=}CH_2$	425 (77)	222 (5900)	16
25	$Me_3SiCOCH{=}CH(CH_2)_6CH_3$	424 (68)	225 (10 358)	16
26	$Me_3SiCOC{\equiv}CCH_3$	420 (170)	227 (7450)	22
27	$Bu^tMe_2SiCOCO_2Me$	455 (100), 227 (254)		24
28	$Me_3SiCOCO_2Et$	455 (97), 230 (388)		24
29	$PhMe_2SiCOCO_2Me$	455 (213), 279 (620)		24
30	$Me_3SiCOCOCH_3$	535 (99)		15
31	$Me_3SiCOCO(CH_2)_4CH_3$	530 (96)		7
32	$Me_3SiCOCO(CH_2)_3CH_3$	528 (98)		7
33	$Me_3SiCOCOPh$	518 (117)	275 (6500)	7
34	$Me_3SiCONEt_2$	264 (270)		25
35	$Bu^t(Me_3Si)_2SiCO\text{-}Ad^*$	380 (200)		29
36	$Ph(Me_3Si)_2SiCO\text{-}Ad^*$	380 (200)		29

about these species,[5,45] Ireland and Norbeck obtained evidence for formyl trimethylsilane Me_3SiCHO by a trap with a Wittig reagent following Swern oxidation of trimethylsilyl methanol [see Scheme 9, Section 3A(v)].[46,47] Subse-

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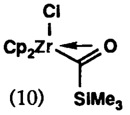
[45] L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, 1954, **76**, 1613.

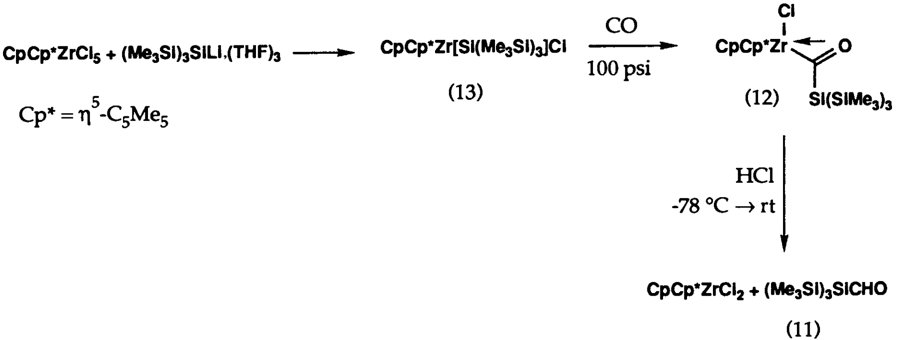
[46] A. J. Mancuso, D. S. Brownfain, and D. Swern, *J. Org. Chem.*, 1979, **44**, 4148.

[47] R. E. Ireland and D. W. Norbeck, *J. Org. Chem.*, 1985, **50**, 2198.



(10)

quently Tilley identified formyl trimethylsilane by NMR spectroscopy as the product of reaction of the zirconium η^2-sila-acyl complex $(\eta^5\text{-}C_5H_5)_2Zr\text{-}(\eta^2\text{-}COSiMe_3)Cl$ (10) with hydrochloric acid.[48] More recently, Tilley was able to prepare, isolate, and characterize the first stable formyl silane, formyl tris-(trimethylsilyl)silane $(Me_3Si)_3SiCHO$ (11), from the zirconium η^2-sila-acyl complex (12).[49] This complex was prepared in good yield by reaction of silyl zirconium species (13) with carbon monoxide at 100 psi. Treatment of complex (12) with anhydrous hydrogen chloride at −78 °C in toluene solution gave formyl silane (11), which was stable under an inert atmosphere and showed typical carbonyl group reactivity (Scheme 1a). Formyl silanes, formed *in situ*, have been used to prepare α,β-acetylenic acyl silanes by lithium acetylide addition and Swern oxidation.[50]



Scheme 1a

(ii) *Hydrolysis of Thioacetals.* The most general synthesis of acyl silanes is based on dithiane methodology, first investigated by Brook[51] and Corey[52] in the late 1960's. This route is outlined in Scheme 1b.

The major drawback of this synthesis lies in the final deprotection step; ease of hydrolysis of the silyl 1,3-dithiane (14) with retention of the silicon moiety is very dependent on the nature of R and on the size of the groups attached to silicon. In general, the larger these groups are, the more successful is the final deprotection. Initial methods of hydrolysis involved the use of mercury(II) salts, and although this process has been improved by the use of such reagents as chloramine T

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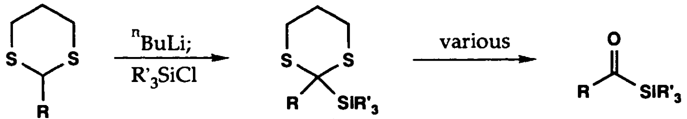
[48] B K Campion, J Falk, and T D Tilley, *J Am Chem Soc*, 1987, **109**, 2049

[49] F H Elsner, H-G Woo, and T D Tilley, *J Am Chem Soc*, 1988, **110**, 313

[50] R J Linderman and Y Suhr, *J Org Chem*, 1988, **53**, 31569

[51] A G Brook, J M Duff, P F Jones, and N R Davis, *J Am Chem Soc*, 1967, **89**, 4431

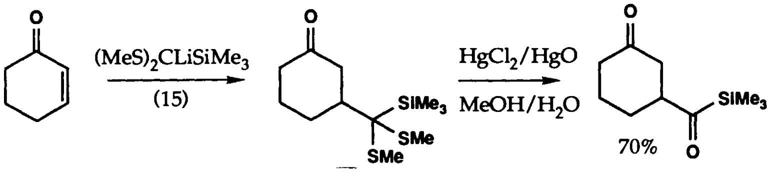
[52] E J Corey, D Seebach, and R Freedman, *J Am Chem Soc*, 1967, **89**, 434



(14)

Scheme 1b

hydrate,[53–56] this step still remains a significant problem, production of the corresponding aldehyde accounting for 10—100% of the product mixture.[7] To circumvent this difficulty a number of more readily hydrolysed thioacetals have been utilized, for example, lithio bis-(methylthio) methanes (15) (Scheme 2).[57] Some interesting cyclic acyl silanes such as (105) have been prepared using the dithiane method.[54]



Scheme 2

O-Trimethylsilyl hemithioacetals (16) have been used in the synthesis of bis-(trimethylsilyl) ketone (4) as hydrolysis of these compounds occurs under very mild conditions.[58] The route is outlined in Scheme 3; oxidation of methyl tris-(trimethylsilyl) methyl thioether (17) with *meta*-chloroperbenzoic acid gives the unstable sulphoxide species (18), which readily undergoes a sila-Pummerer rearrangement, perhaps due to relief of steric compression, to give the intermediate hemithioacetal (16).[59] This hemithioacetal reacts with the Pummerer intermediate to give a 1:1 mixture of bis-(trimethylsilyl) ketone (4) and the thioketal (19). However, this route suffers from difficulties in the purification of the acyl silane product and in preparation of the highly functionalized starting materials (17). The sila-Pummerer rearrangement of bis-(trimethylsilyl) phenylselenenyl phenyl methane, induced by hydrogen peroxide, has also been used to prepare benzoyl trimethylsilane in 46% yield.[60]

A much better synthesis of acyl silanes is based on methoxy phenylthio trialkylsilyl methane (20), which acts as an α-silyl acyl anion equivalent

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[53] D. W. Emerson and H. Wynberg, *Tetrahedron Lett.*, 1971, **12**, 3445; M. E. Scheller, G. Iwasaki, and B. Frei, *Helv. Chim. Acta*, 1986, **69**, 1378.

[54] A. G. Brook and H. W. Kucera, *J. Organomet. Chem.*, 1975, **87**, 263.

[55] H. J. Reich, J. J. Rusek, and R. E. Olson, *J. Am. Chem. Soc.*, 1979, **101**, 2225.

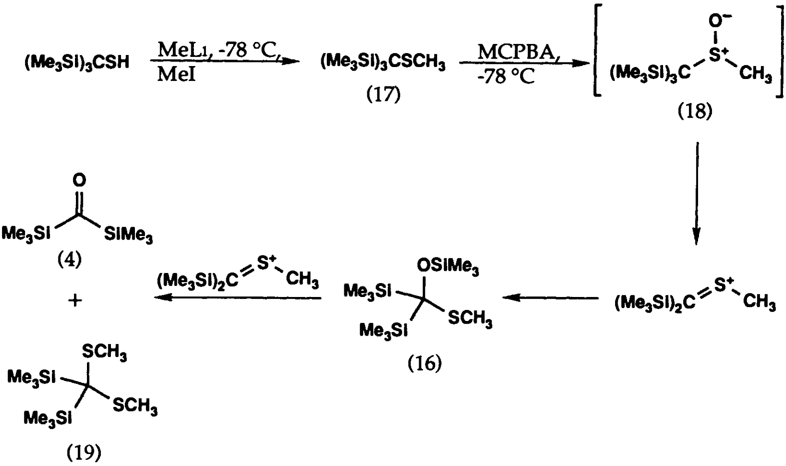
[56] R. L. Danheiser and D. M. Fink, *Tetrahedron Lett.*, 1985, **26**, 2509.

[57] R. Bürstinghaus and D. Seebach, *Chem. Ber.*, 1977, **110**, 841.

[58] A. Ricci, A. Degl'Innocenti, M. Ancillotti, G. Seconi, and P. Dembech, *Tetrahedron Lett.*, 1986, **27**, 5985.

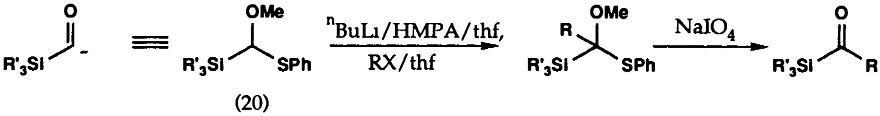
[59] D. J. Ager, *Chem. Rev.*, 1982, **11**, 493.

[60] H. J. Reich and S. K. Shah, *J. Org. Chem.*, 1977, **42**, 1773.



Scheme 3

(Scheme 4)[61] This synthesis is successful for a wide range of aliphatic R groups and provides an excellent overall yield However, the synthesis of aromatic acyl silanes by this method would clearly be difficult or impossible, requiring aromatic nucleophilic substitution



Scheme 4

(iii) *Silyl Metallic Species* One of the earliest syntheses of an acyl silane involved the reaction of triphenylsilyl potassium with benzoyl chloride[2] at low temperature (Scheme 5a)

Scheme 5a

The very low yield of benzoyl triphenylsilane (6%) and the similar yields obtained from the reactions of silyl lithium reagents with acetyl chloride[62] to give acetyl triphenylsilane demonstrate that this is not a very useful method for the synthesis of simple acyl silanes However, this method has proved successful

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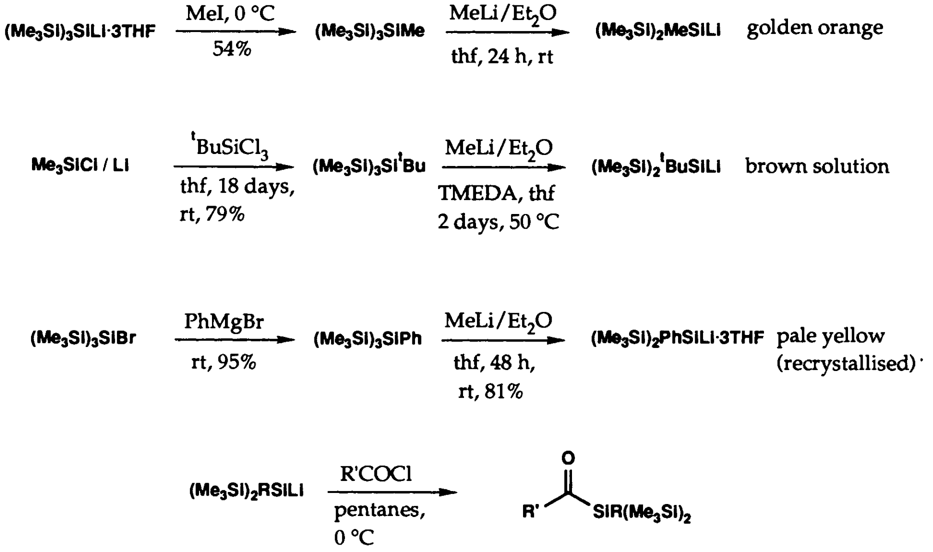
[61] T Mandai, M Yamaguchi, Y Nakayama, J Otera, and M Kawada, *Tetrahedron Lett*, 1985, **26**, 2675

[62] D Wittenberg and H Gilman, *J Am Chem Soc*, 1958, **80**, 4529

for the preparation of acyl tris-(trimethylsilyl) silanes and their derivatives.[27,34,63] The tris-(trimethylsilyl) silyl ('sisyl') lithium reagent is formed by deprotonation of tris-(trimethylsilyl) silane using an alkyl lithium reagent; alkyl bis-(trimethylsilyl) silyl lithium species have been prepared by a number of methods (Scheme 5b).[29] Some of these silyl lithium reagents, which are yellow to orange to brown in colour, are remarkably stable; for example phenyl bis-(trimethylsilyl) silyl lithium forms a pale yellow solid 'ate' complex $Ph(Me_3Si)_2SiLi.THF$ which could be recrystallized.



Scheme 5b

The tris-(trimethylsilyl)- and alkyl bis-(trimethylsilyl)- silyl lithium reagents react cleanly with acyl chlorides, typically at 0 °C, to give the corresponding acyl silanes in up to *ca.* 85% yields. Tris-(trimethylsilyl) silyl lithium, which also forms an 'ate' complex with three molecules of THF, has also been shown to react with carbon dioxide to give the interesting crystalline tris-(trimethylsilyl) silane carboxylic acid after acidic work-up in 85% yield.[26] The methyl ester and several silyl esters were prepared from this acid by conventional means (Scheme 5c).

A less reactive silyl metal species may be prepared by the addition of copper(I) salts to form a silyl cuprate. Lithium bis-(triphenylsilyl) cuprate reacts with a variety of acyl chlorides to give the corresponding acyl silanes in moderate to good yields (Scheme 6a).[64] Dilithium bis-(trimethylsilyl) cyano cuprate $Li_2(Me_3$-

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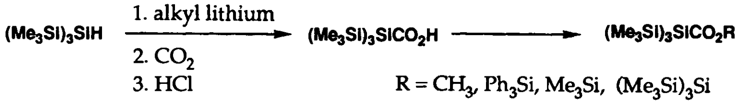
[63] A. G. Brook and K. M. Baines, *Adv. Organomet. Chem.*, 1986, **25**, 1; G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 419; 'The Chemistry of Organic Silicon Compounds', ed. S. Patai and Z. Rappoport, Wiley, 1989.

[64] N. Duffaut, J. Dunoguès, C. Biran, R. Calas, and J. Gerval, *J. Organomet. Chem.*, 1978, **161**, C23



$$(Me_3Si)_3SiH \xrightarrow[\text{2. } CO_2 \text{ 3. HCl}]{\text{1. alkyl lithium}} (Me_3Si)_3SiCO_2H \longrightarrow (Me_3Si)_3SiCO_2R$$

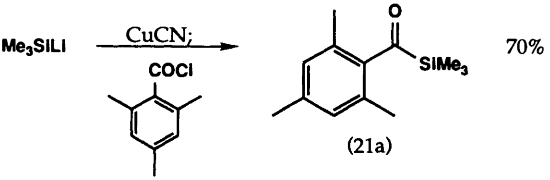
$R = CH_3, Ph_3Si, Me_3Si, (Me_3Si)_3Si$

Scheme 5c

Si)2CuCN was found to be particularly effective for the preparation of sterically hindered acyl silanes (Scheme 6b); this reaction appears to be a good general preparative method.[11]

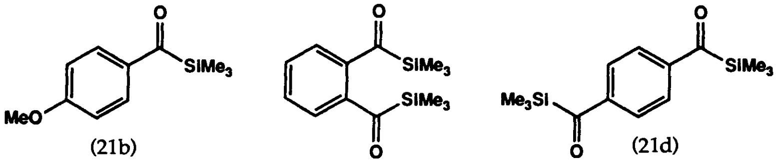
R	Yield
Me	>90%
Et	>90%
^{t}Bu	75%
Ph	<20%

Scheme 6a



(21a)

Scheme 6b



(21b) (21c) (21d)

Scheme 6c

Recent work by Kang utilizes the low ionic character of the aluminium–silicon bond to develop probably the most general and effective synthesis of simple acyl silanes that has been reported in the literature to date, successful for aliphatic, aromatic, heteroaromatic, and even cyclopropyl acyl silanes.[65] Acyl chlorides are treated with lithium tetrakis-(trimethylsilyl) aluminium or lithium methyl tris-(trimethylsilyl) aluminium in the presence of a cuprous cyanide catalyst to give the acyl silanes in truly excellent yields after work-up (Scheme 7).

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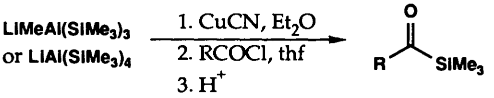
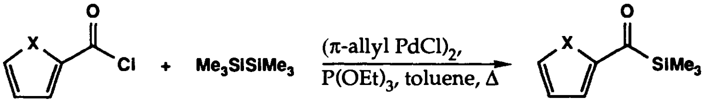
[65] J Kang, J H Lee, K S Kim, J U Jeong, and C Pyun, *Tetrahedron Lett*, 1987, **28**, 3261



typically up to *ca.* 90%

Scheme 7

(iv) *Palladium-catalysed Coupling.*—A wide range of aromatic and heteroaromatic acyl silanes has been synthesised *via* transition metal catalysed coupling (*e.g.* Scheme 8).[22,66] This synthesis is very successful for a variety of substrates, including furyl, thienyl, and pyrryl, and also for aryl acyl silanes containing electron-withdrawing groups, which are otherwise difficult to prepare. However the method cannot be employed for the synthesis of aliphatic acyl silanes[66] and is therefore complementary to some of the methods described above.

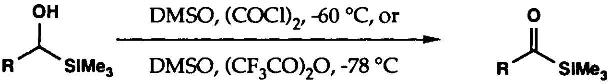


(21e), X=O, S, NMe

Scheme 8

(v) *Oxidation Reactions.* Among the most common routes for the synthesis of acyl silanes are those based on oxidation methodology. Since the oxidation of secondary alcohols to ketones by any of a wide variety of oxidizing agents is commonly a successful reaction, it might be expected that the corresponding oxidation of α-hydroxy silanes would be useful for acyl silane synthesis.[5] However, this method is often far from straightforward.

Several oxidizing systems have been examined,[67] but the most satisfactory method for oxidation of α-hydroxy silanes to acyl silanes is based on the Swern oxidation and is shown in Scheme 9.[46,47,50]



Scheme 9

If chromic acid oxidation reagents are used for this transformation the major products often arise from silicon–carbon bond cleavage, as illustrated in Scheme 10,[5] although such a reaction has been used successfully for the preparation of cyclopropyl acyl silanes (Section 3E).[68]

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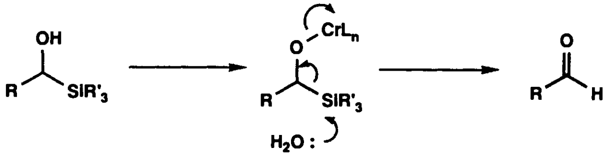
[66] K. Yamamoto, S. Suzuki, and J. Tsuji, *Tetrahedron Lett.*, 1980, **21**, 1653.

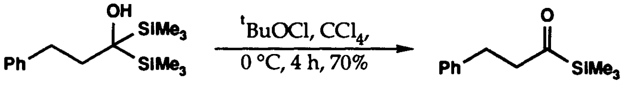
[67] A. G. Brook and J. Pierce, *J. Organomet. Chem.*, 1965, **30**, 2566.

[68] M. E. Scheller and B. Frei, *Helv. Chim. Acta*, 1986, **69**, 44; M. E. Scheller and B. Frei, *Helv. Chim. Acta*, 1985, **68**, 44.



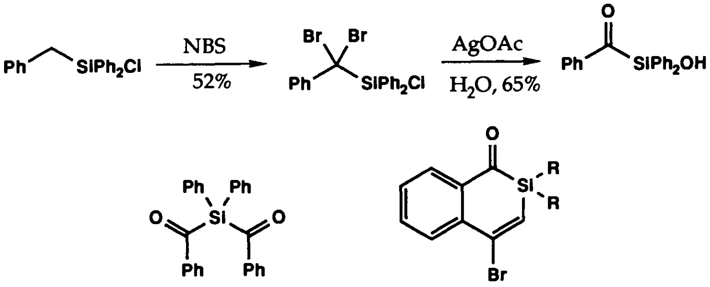
Scheme 10

However, this problem of silicon–carbon bond cleavage has been cleverly utilized in an acyl silane synthesis by incorporation of two silicon moieties (Scheme 11).



Scheme11

Benzoyl silanes and substituted benzoyl silanes have been produced from the corresponding α,α-dibromobenzyl silanes by oxidation with silver acetate in acetone–ethanol–water mixture[4] or silica gel[69] in good yields (Scheme 12). The very first synthesis of an acyl silane was accomplished using this method,[4] but it is clearly restricted to benzyl and allyl silanes where geminal dihalides can easily be procured. Brook has been able to prepare the diacyl silane (20a)[4] and Corriu has prepared several interesting cyclic acyl silanes such as (21)[70] using this approach.



(20a) (21)

Scheme 12

Various acyl silanes have been synthesized by the photosensitized oxygenation of silyl diazo compounds using meso-tetraphenyl porphine as the sensitizer (Scheme 13).[24]

Although this synthesis is successful for aromatic acyl silanes and the

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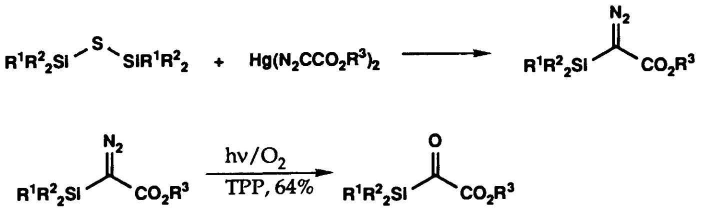
[69] A Degl'Innocenti, D R M Walton, G Seconi, G Pirazzini, and A Ricci, *Tetrahedron Lett*, 1980, **21**, 3927

[70] R Corriu and J Masse, *J Organomet Chem*, 1970, **22**, 321

Table 6 *Acyl silane preparation from silyl diazo compounds*[24]

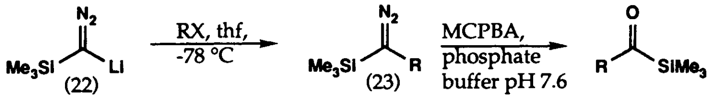
Entry	*Silyl diazo compound*	*Acyl silane*	*Yield/%*
1	$Me_3SiC(N_2)CO_2Et$	$Me_3SiCOCO_2Et$	40
2	$Me_3SiC(N_2)CO_2Me$	$Me_3SiCOCO_2Me$	42
3	$PhMe_2SiC(N_2)CO_2Me$	$PhMe_2SiCOCO_2Me$	43
4	$Me_3SiC(N_2)Ph$	$Me_3SiCOPh$	42
5	$PhMe_2SiC(N_2)Ph$	$PhMe_2SiCOPh$	51
6	$Ph_3SiC(N_2)Ph$	$Ph_3SiCOPh$	64



Scheme 13

interesting yellow-coloured α-carboxyacyl silanes, as shown in Table 6, it is not general, and purification difficulties are often encountered in the synthesis of aliphatic and other acyl silanes, resulting in low overall yields.

A successful alternative method for acyl silane synthesis involving silyl diazo intermediates utilizes trimethylsilyl diazomethane (Scheme 14).[71] The lithiated



Scheme 14

derivative (22) smoothly reacts with alkyl halides in THF solution in good yields to give α-trimethylsilyl diazoalkanes (23). Cleavage of the diazo moiety is effected in benzene solution using *meta*-chloroperbenzoic acid oxidation in the presence of a phosphate buffer (pH 7.6) to prevent side reactions. This gives access to a wide variety of acyl silanes in yields as high as 71%. Once again, however, aromatic acyl silanes cannot be readily prepared using this route since an aromatic nucleophilic substitution reaction would be required.

Aromatic acyl silanes and the unstable pink bis-(trimethylsilyl) ketone (4) have been prepared in good yields *via* the oxidation of phosphonium ylids (Scheme 15).[23]

(vi) *Hydroboration–Oxidation of Alkynyl Silanes.* Hydroboration–oxidation of alkynyl silanes is a superior method for producing a variety of substituted acyl silanes from readily available starting materials.[72,73] Although the

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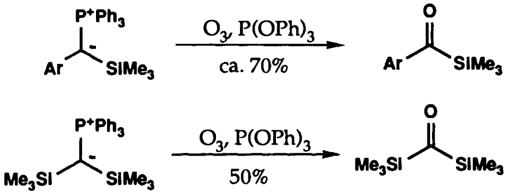
[71] T. Aoyama and T. Shioiri, *Tetrahedron Lett.*, 1986, **27**, 2005.

[72] A. Hassner and J. Soderquist, *J. Organomet. Chem.*, 1977, **131**, C1.

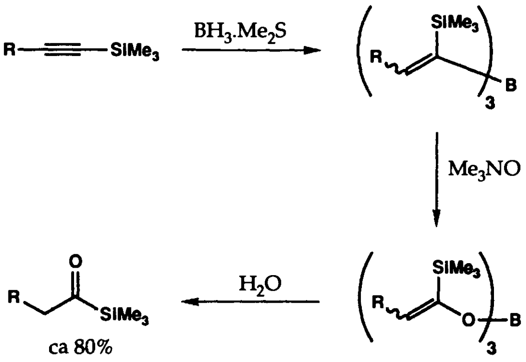
[73] G. Zweifel and S. J. Bäcklund, *J. Am. Chem. Soc.*, 1977, **99**, 3184.



Scheme 15

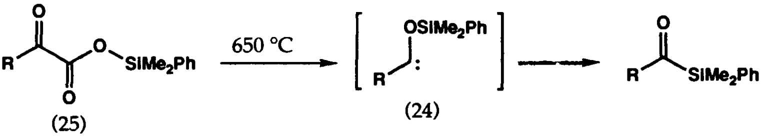
hydroboration–oxidation procedures initially studied gave only moderate yields of acyl silanes, the sequence was modified by Zweifel to produce an excellent and general one-pot synthesis of acyl silanes which proceeds in high yields (Scheme 16).[9] In the opinion of the present authors, this method is the best for the preparation of simple alkyl acyl silanes.

One limitation of this scheme is that the yield of acyl silane is reduced if the group R is very bulky; furthermore, aryl acyl silanes obviously cannot be prepared using this method. The use of alkaline peroxide in the oxidation step must be avoided as the acyl silane product is converted into silyl ester by this reagent.



Scheme 16

(vii) *Rearrangement of Silyloxycarbenes.* Certain acyl silanes may be obtained by the pyrolytic rearrangement of silyloxycarbenes (24) derived from α-ketoesters (25) (Scheme 17).[74]

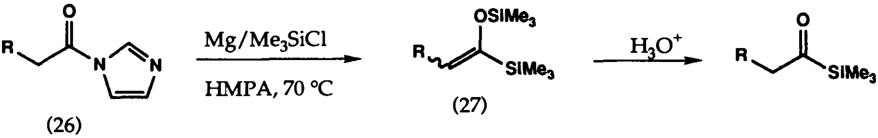


Scheme 17

The generality of this approach is restricted, for example by possible difficulty in the preparation of the requisite α-ketoesters (25), and by the fact that the pyrolysis only takes place in high yield when R = Ph.

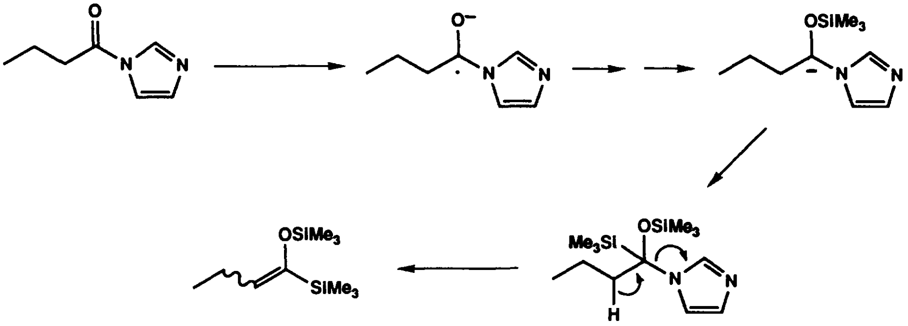
(viii) *Enolate Methodology*. The trimethylsilyl enol ethers of acyl silanes (27) have been prepared using a variety of routes and are obvious precursors to acyl silanes, since simple hydrolysis of the silyl enol ethers would be expected to liberate the corresponding acyl silanes in excellent yields.

Acyl imidazoles (26) react *via* a silyl acyloin reaction under somewhat unpleasant conditions to give the corresponding silyl enol ethers (27) in moderate yields (Scheme 18).[75]



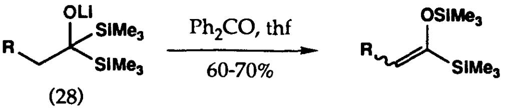
Scheme 18

A possible mechanism for this reaction is outlined in Scheme 19.



Scheme 19

The lithium alkoxides of bis-(trimethylsilyl) alkan-1-ols (28) react with benzophenone to produce the silyl enol ethers of acyl silanes in good yields (Scheme 20).[76]



Scheme 20

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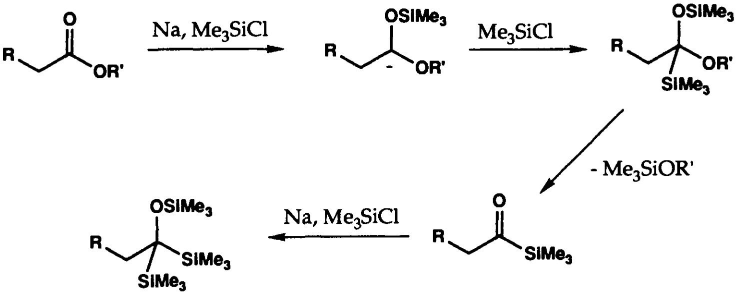
[74] A. G. Brook, J. W. Harris, and A. R. Bassindale, *J. Organomet. Chem.*, 1975, **99**, 379.

[75] P. Bourgeois, J. Dunoguès, N. Duffaut, and P. Lapouyade, *J. Organomet. Chem.*, 1974, **80**, C25.

[76] I. Kuwajima, M. Arai, and T. Sato, *J. Am. Chem. Soc.*, 1977, **99**, 4181.

The parent bis-(trimethylsilyl) alkan-1-ols were synthesized in reasonable yields by hydrolysis of the geminal disilane carbinol silyl ethers (29),[77,78] which in turn were synthesized from the corresponding esters using a silyl acyloin reaction which, ironically, proceeds *via* formation of an acyl silane intermediate (Scheme 21).[77]

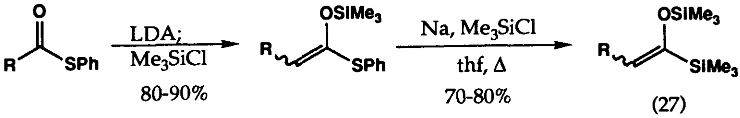


(29)

Scheme 21

Picard has reported alternative, rather more direct, approaches to acyl silanes and to silyl enol ethers (27) by similar reductive silylation of substituted benzoates and of α,β-dihalo-α,β-unsaturated acyl chlorides respectively using trimethyl chlorosilane–magnesium–HMPA.[79]

A much more general synthesis of silyl enol ethers (27) is based on the reductive cleavage of the carbon–sulphur bond of the silyl enol ether of a thioester using sodium metal and chlorotrimethylsilane, again in a silyl acyloin reaction (Scheme 22).[80,81]



(27)

Scheme 22

Another efficient synthesis of silyl enol ethers (27) utilizes an intramolecular 1,2-silicon shift in α-silyl acyl lithium species (29a), prepared from an α-lithiosilane

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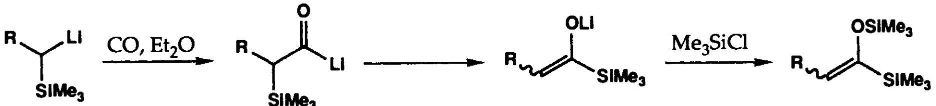
[77] I Kuwajima, N Minami, T Abe, and T Sato, *Bull Chem Soc Jpn*, 1978, **51**, 2391

[78] I Kuwajima, T Sato, N Minami, and T Abe, *Tetrahedron Lett*, 1976, **17**, 1591

[79] J-P Picard, R Calas, J Dunogues, and N Duffaut, *J Organomet Chem*, 1971, **26**, 183, J-P Picard, R Calas, J Dunogues, N Duffaut, J Gerval, and P Lapouyade, *J Org Chem*, 1979, **44**, 420, J-P Picard, A Ekouya, J Dunogues, N Duffaut, and R Calas, *J Organomet Chem*, 1975, **93**, 51, P Bourgeois, *J Organomet Chem*, 1972, **76**, C1

[80] I Kuwajima, M Kato, and T Sato, *J Chem Soc, Chem Commun*, 1978, 478

[81] T Cohen and J R Matz, *J Am Chem Soc*, 1980, **102**, 6900

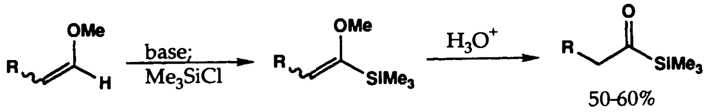


(27)

Scheme 23

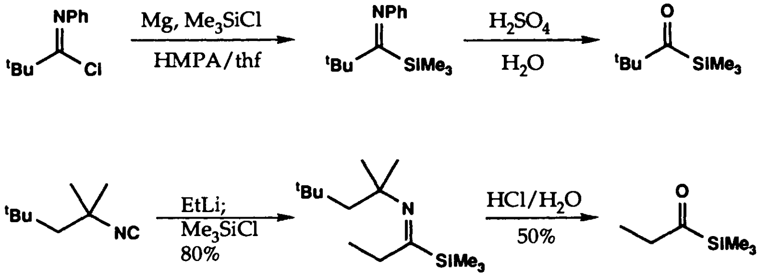
(Scheme 23).[82] This method is very simple to carry out in the laboratory and produces the silyl enol ethers in good yield with high isomeric purity (usually *E* isomer >90% of mixture).

Methyl enol ethers of acyl silanes have been prepared in good yield by the silylation of vinyl lithium reagents derived from methyl enol ethers (Scheme 24).[83] Reaction conditions were found to be critical; best results were obtained by the low temperature addition of an excess of t-butyllithium in THF solution followed by gradual temperature increase to 0 °C, followed in turn by addition of chlorotrimethylsilane at −78 °C.



Scheme 24

(ix) *Silylation of Metalloaldimines.* Several acyl silanes have been prepared by the silylation of metalloaldimines followed by hydrolysis (Scheme 25).[84,85]



Scheme 25

One limitation of this scheme is the ready decomposition of the aldimine (30) to give aldehyde in addition to acyl silane in approximately equal amounts (Scheme 26):[85]

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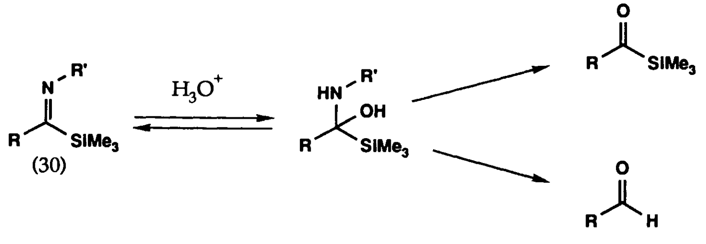
[82] S. Murai, I. Ryu, J. Iriguchi, and N. Sonoda, *J. Am. Chem. Soc.*, 1984, **106**, 2440.

[83] J. A. Soderquist and G. J.-H. Hsu, *Organometallics*, 1982, **1**, 830; E. M. Dexheimer and L. Spialter, *J. Organomet. Chem.*, 1976, **107**, 229.

[84] P. Bourgeois, *J. Organomet. Chem.*, 1974, **76**, C1.

[85] G. E. Niznik, W. H. Morrison, and H. M. Walborsky, *J. Org. Chem.*, 1974, **39**, 600.

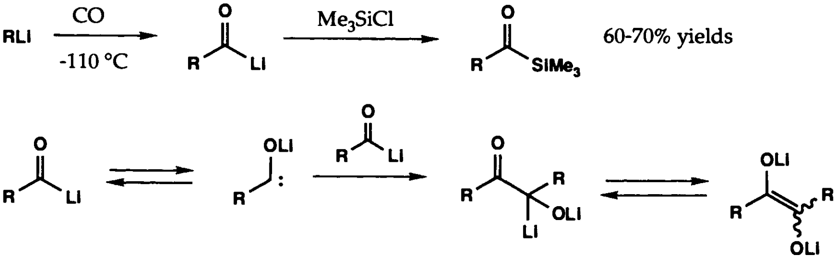


(30)

ca. 1:1

Scheme 26

(x) *Silylation of Acyl Metallic Species.* Perhaps the most direct method of synthesizing an acyl silane is by reaction of an acyl lithium with a silicon electrophile as shown in Scheme 27.[86,87] Although this method is successful for a variety of alkyl acyl silanes in moderate yields, low temperatures must be used in order to avoid destruction of the products as indicated, and the method is not suitable for aryl acyl silanes.



60-70% yields

Scheme 27

N,*N*-Diethyl carbamyl trimethylsilane (31) has been prepared by the reaction of bis-(trimethylsilyl) sulphide with bis-*N*,*N*-diethyl carbamyl mercury (Scheme 28).[25]

(31)

Scheme 28

B. α-Haloacyl Silanes.—The most obvious procedure for the synthesis of α-haloacyl silanes is direct bromination of silyl enol ethers (27) using bromine at low temperature (Scheme 29a).[14,88] While this route can be successful, it does

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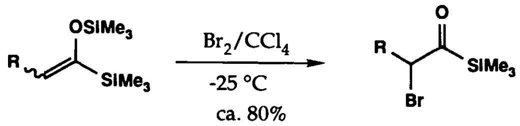
[86] D Seyferth and R M Weinstein, *J Am Chem Soc*, 1982, **104**, 5534

[87] D Seyferth and R C Hui, *Organometallics*, 1984, **3**, 327

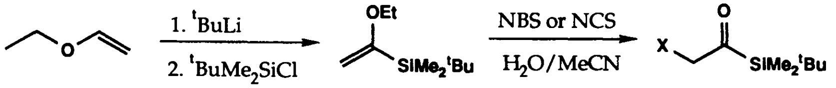
[88] I Kuwajima, T Abe, and N Minami, *Chem Lett*, 1976, 993



Scheme 29a

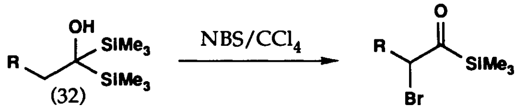
suffer from the general sensitivity of both the starting materials and the products.

Electrophilic halogenation of alkyl enol ethers of acyl t-butyldimethylsilanes, prepared by deprotonation and silylation of vinyl ethers,[83] has also been used (Scheme 29b).[89] α-Iodoacyl silanes were prepared by the same authors by treatment of α-bromoacyl silanes with sodium iodide in acetone.



Scheme 29b

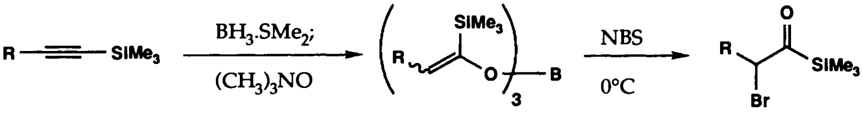
There is also one report in the literature that treatment of a series of bis-(trimethylsilyl) alkan-1-ols (32) with *N*-bromosuccinimide in carbon tetrachloride gives the corresponding α-haloacyl silanes in moderate yields (Scheme 30).[88]



(32)

Scheme 30

The best method to date for preparing α-haloacyl silanes is based on bromination of an enol borinate (33) at 0 °C, a route which proceeds in good yield and involves no sensitive intermediates. This method offers a convenient one-pot synthesis of α-haloacyl silanes from readily available starting materials as the intermediate enol borinates are very easily prepared from silyl acetylenes (Scheme 31a).[90,91]



(33)

50-60% overall

Scheme 31a

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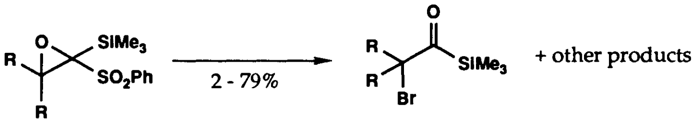
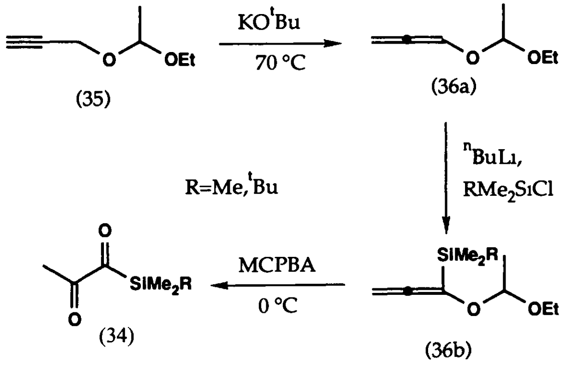
[89] J. S. Nowick and R. L. Danheiser, *J. Org. Chem.*, 1989, **54**, 2798.
[90] P. C. B. Page and S. Rosenthal, *Tetrahedron Lett.*, 1986, **27**, 5421.
[91] J. Hooz and J. N. Bridson, *Can. J. Chem.*, 1972, **50**, 2387.

Recent work has shown that α-bromoacyl silanes may be isolated in variable yields from the reaction of magnesium bromide etherate with 2-phenylsulphonyl-2-trimethylsilyl oxiranes (Scheme 31b) [92a]



Scheme 31b

C. α-Ketoacyl Silanes.—α-Ketoacyl silanes are a deep rich crimson colour and are particularly sensitive to light The α-ketoacyl silanes (34) were first synthesized in 1983 *via* allene methodology as shown in Scheme 32,[15] although the yellow-coloured α-carboxyacyl silanes were already known at that time[24] [Section 3A(v)] Thus, isomerization of the propargyl ether (35) with potassium t-butoxide at 70 °C gave the allene (36a) in excellent yield[92b] Lithiation of allene (36a) with butyl-lithium at −78 °C and subsequent reaction with a chlorosilane to give (36b), followed by oxidative work-up with *meta*-chloroperbenzoic acid (presumably proceeding *via* an epoxide) provided the unstable α-ketoacyl silanes (34) in moderate yields



Scheme 32

A much more general and very simple synthesis requiring a minimum of laboratory manipulation utilizes a Swern oxidation of the corresponding diols (37) to give the α-ketoacylsilanes directly in useful yields (Scheme 33)[93] Purification in this case was accomplished in the dark by chromatography at −78 °C or distillation

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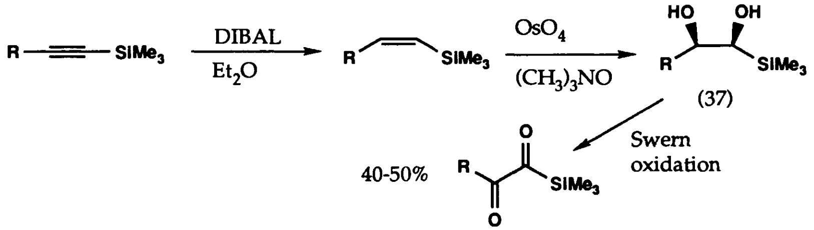
[92a] C T Hewkin and R F W Jackson, *Tetrahedron Lett*, 1990, **31**, 1877

[92b] S Hoff, L Brandsma, and J F Arens, *Recl Trav Chim Pays-Bas*, 1968, **87**, 916

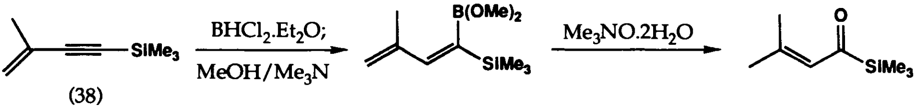
[93] P C B Page and S Rosenthal, *Tetrahedron Lett*, 1986, **27**, 2527



Scheme 33

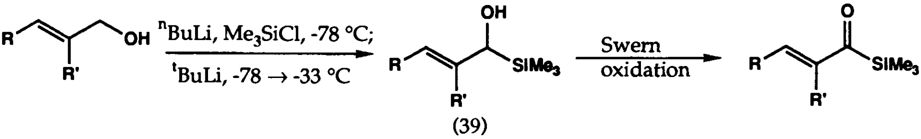
D. α,β-Unsaturated Acyl Silanes.—α,β-Unsaturated acyl silanes, which are yellow or yellow-green in colour, are less sensitive than the other types of acyl silane discussed above and have been synthesized by several different routes.

(i) *Hydroboration–Oxidation of Enynes.* α,β-Unsaturated acyl silanes have been prepared by hydroboration methodology, similar to that used in the synthesis of aliphatic acyl silanes (*vide supra*) (Scheme 34).[72] This synthesis is somewhat unsatisfactory due to the difficulty of synthesizing functionalized enynes such as (38).



Scheme 34

(ii) *Oxidation of Allylic Carbinols.* A superior synthesis of α,β-unsaturated acyl silanes is based on the Swern oxidation of α-hydroxy allyl silanes (39) (Scheme 35).[16]

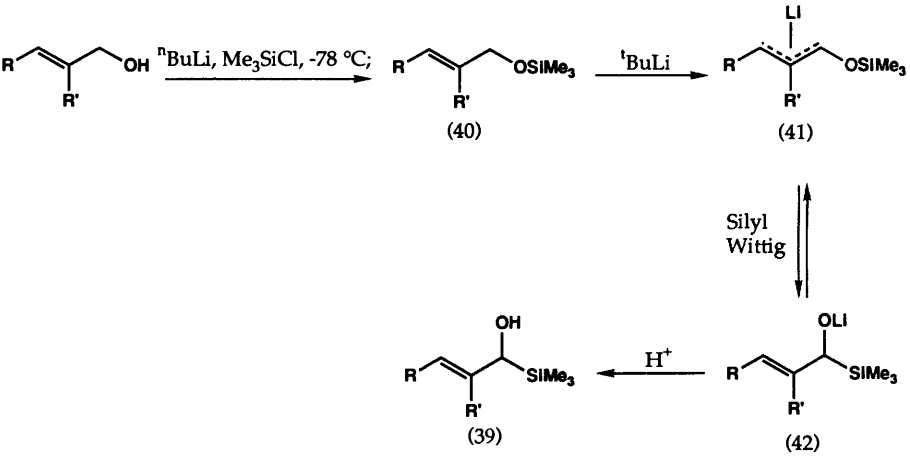


Scheme 35

This simple two-step synthesis hinges on the Wittig rearrangement [94,95] as illustrated in Scheme 36, and is successful on a large scale. The metallation of allyl silyl ethers (40) generates a rapidly interconverting mixture of two organometallic species (41) and (42). Although alkylation of this mixture of organometallic derivatives generally proceeds at the C-3 position [*via* (41)],

[94] W. C. Still and T. L. Macdonald, *J. Am. Chem. Soc.*, 1974, **96**, 5561.

[95] A. Wright and R. West, *J. Am. Chem. Soc.*, 1974, **96**, 3214.

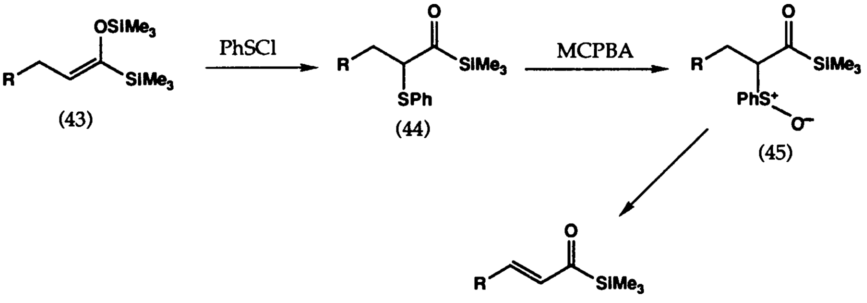


Scheme 36

'hard' electrophiles such as protons react predominantly at the oxygen atom of the alkoxide intermediates (42) leading to formation of the desired α-hydroxy allyl silanes.

(iii) *Enolate Methodology.* A number of α,β-unsaturated acyl silanes have been prepared *via* silyl enol ethers of acyl silanes as shown below (Scheme 37).[96] Addition of phenyl sulphenyl chloride to the silyl enol ether (43) with subsequent elimination of chlorotrimethyl silane gave the α-thioacyl silane (44). Oxidation of the sulphide (44) to the sulphoxide (45) with *meta*-chloroperbenzoic acid, followed by *in situ* elimination of benzenesulphenic acid produced the α,β-unsaturated acyl silane in good yield.

α,β-Unsaturated acylsilanes have also been prepared in a stereospecific manner



Scheme 37

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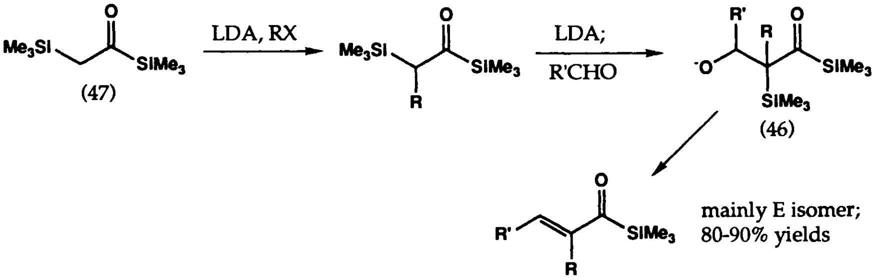
[96] N. Minami, T. Abe, and I. Kuwajima, *J. Organomet. Chem.*, 1978, **145**, C1.

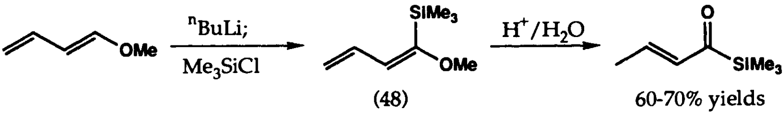
by an interesting aldol–Peterson reaction sequence *via* intermediate (46) (Scheme 38).[97,98]



Scheme 38

Although this synthesis is reasonably successful for a variety of acyl silanes, it is rather lengthy and requires initial preparation of the sensitive acyl silanes (47).

(iv) *Hydrolysis of Silyl Dienes and Silyl Allenes.* One of the simplest methods for preparation of an α,β-unsaturated acyl silane is by hydrolysis of a silyl diene (48) (Scheme 39).[12] However, preparation of more highly functionalized dienes would necessarily involve difficult and lengthy synthesis and this method is therefore most useful for simple substrates.



Scheme 39

Perhaps the most versatile synthesis of α,β-unsaturated acyl silanes involves the use of allene methodology as developed by a number of groups,[15,18–21] indeed the first example of an α,β-unsaturated acyl silane was prepared by such a route[18] as was the only example of an allenic acyl silane (from a 1-trimethylsilyl-1-trimethylsilyloxy-1,2,3-alkatriene).[19] Reich[15] uses ethoxyethyl allenyl ethers (35) as precursors to α,β-unsaturated acyl silanes, as the relatively large and polar protecting group gives them much better handling characteristics than simpler analogues (Scheme 40).

Allenes such as (49) are also excellent precursors to a variety of α-substituted α,β-unsaturated acyl silanes in good yields, as shown in Scheme 41.[15]

As a further development of this work the synthesis of acetylenic acyl silanes (50) has been achieved as shown in Scheme 42a.[15] Oxidation of the selenium substituted allenyl ethers (51) with *meta*-chloroperbenzoic acid at −78 °C gave

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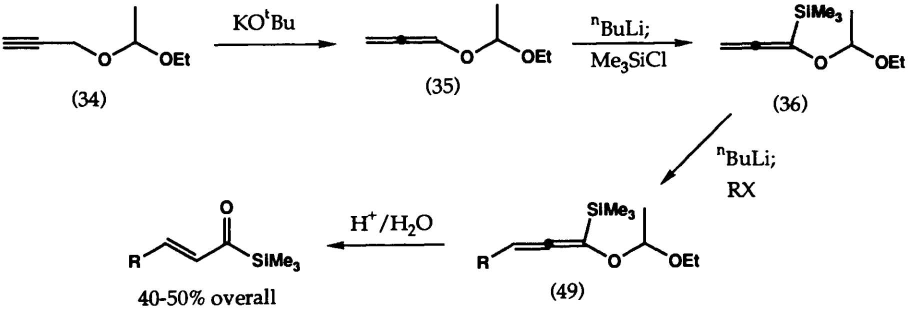
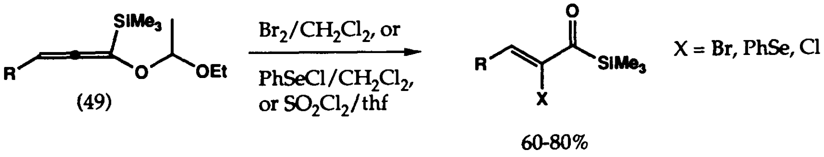
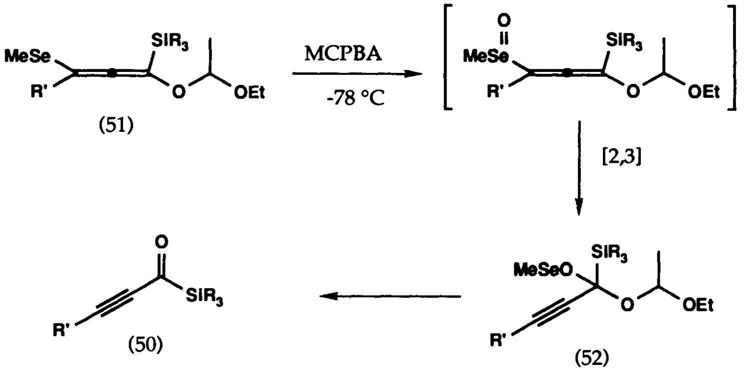
[97] J. A. Miller and G Zweifel, *J. Am. Chem. Soc.*, 1981, **103**, 6217.
[98] D. J. Ager, *Synthesis*, 1984, 384



Scheme 40



Scheme 41



Scheme 42a

the corresponding unstable selenoxides which underwent an *in situ* [2,3] sigmatropic shift to give acetals (52). Loss of seleneyl ester on work-up gave the acetylenic acyl silanes (50) in approximately 50% yields.

A limited number of functionalized acyl silanes have been prepared by the use of 1,3-dithianes as described above;[45,99] however, this route is unfavourable for the synthesis of α,β-unsaturated acyl silanes.[16] Analogous acetylenic 1,3-dioxanes

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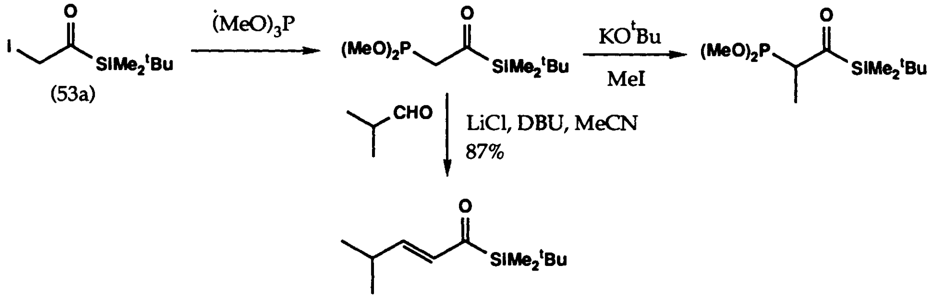
[99] R. L. Danheiser and D. M. Fink, *Tetrahedron Lett.*, 1985, **26**, 2513.

have however been used as precursors to α,β-acetylenic acyl silanes,[100] as have formyl silanes [Section 3A(i)].[50]

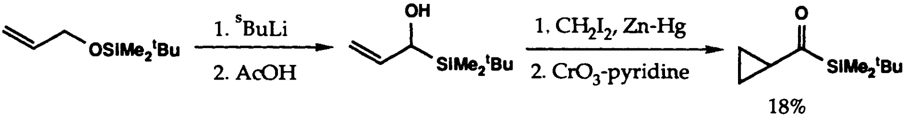
(v) *Horner–Emmons Reactions.* Danheiser has successfully employed the Horner–Emmons reaction of α-phosphonoacyl silanes to prepared α,β-unsaturated acyl silanes in 54—97% yields (Scheme 42b).[89] The α-phosphonoacyl silane intermediates, prepared from α-iodoacyl silane (53a) *via* the Arbuzov reaction, were shown to undergo enolate alkylation, for example using potassium t-butoxide and methyl iodide; the alkylated products also underwent Horner–Emmons reaction.



Scheme 42b

E. Cyclopropyl Acyl Silanes.—Cyclopropyl acyl silanes were first prepared from α,β-unsaturated acyl silanes by treatment with diazomethane followed by vapour-phase pyrolysis of the intermediate pyrazoline derivatives (Scheme 63, section 4D).[99] They are cleaved or rearranged by acid under more mild conditions than their carbon analogues.[101]

In one alternative route, Frei has successfully employed the Wittig rearrangement of allylic silyl ethers followed by Simmons–Smith cyclopropanation and Collins oxidation to produce cyclopropyl acyl silanes in 10—85% yields (Scheme 42c).[68] Particular success was achieved using geraniol as the substrate.



Scheme 42c

Nakajima has shown that cyclopropyl acyl silane (53b) may be prepared by reaction of 1-lithio-1-trimethylsilyl cyclopropanes with dichloromethyl methyl

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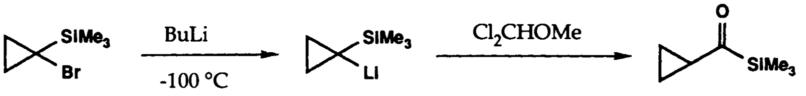
[100] K. J. H. Kruithof, R. F. Schmitz, and G. W. Klumpp, *J. Chem. Soc., Chem. Commun.*, 1983, 239; K. J. H. Kruithof, R. F. Schmitz, and G. W. Klumpp, *Tetrahedron*, 1983, **39**, 3073.

[101] T. Nakajima, H. Miyaji, M. Segi, and S. Suga, *Chem. Lett.*, 1986, 181.

ether at low temperature in THF solution, a reaction which is said to involve a carbene intermediate and a 1,2-silicon shift (Scheme 42d).[102]

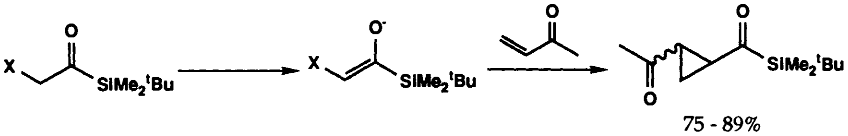


(53b)

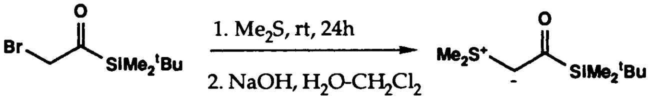
Scheme 42d

A much superior route, successful as a general synthetic method for acyl silanes, involves treatment of acid chlorides with lithium tetrakis-(trimethylsilyl) aluminium or lithium methyl tris-(trimethylsilyl) aluminium and cuprous cyanide [Scheme 7, Section 3A(ii)].[65] For example, cyclopropyl acyl silane (53b) was formed in 89% yield using this procedure.

Recent work by Danheiser[103] has explored cyclopropyl acyl silane generation from α-haloacyl silanes *via* McCoy reactions (Scheme 42e) and *via* sulphur ylids (Scheme 42f). Ylid species such as (53c) were found to be stable in aprotic solvents in the presence of lithium salts and were used effectively for the cyclopropanation of α,β-unsaturated aldehydes.



Scheme 42e



(53c)

Scheme 42f

4 Reactions of Acylsilanes

A. Simple Acylsilanes.—Acyl silanes, although sensitive to light and to basic media, frequently behave as typical ketones when treated with a wide variety of reagents (Scheme 43).[5,104–107]

However, they also exhibit abnormal behaviour involving rearrangements leading to silicon–oxygen bond formation, especially when treated with nucleophilic reagents.[5,55,104,105]

Acyl silanes are extremely sensitive to basic conditions;[1,5] for example, alcoholic solutions of benzoyl triphenyl silane containing a trace of aqueous base

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[102] T Nakajima, H Miyaji, M Segi, and S Suga, *Chem Lett*, 1986, 177

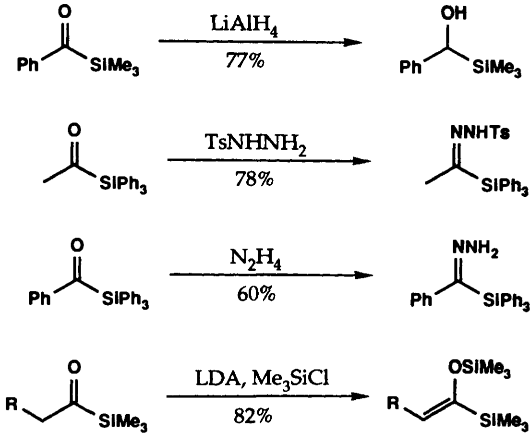
[103] J S Nowick and R L Danheiser, *Tetrahedron*, 1988, **44**, 4113

[104] I Fleming, in 'Comprehensive Organic Chemistry', Vol 3, ed N Jones, Pergamon Press, Oxford, 1979, 647

[105] P D Magnus, T Sarkar, and S Djuric, in 'Comprehensive Organometallic Chemistry', Vol 7, Pergamon Press, Oxford, 1982, 631

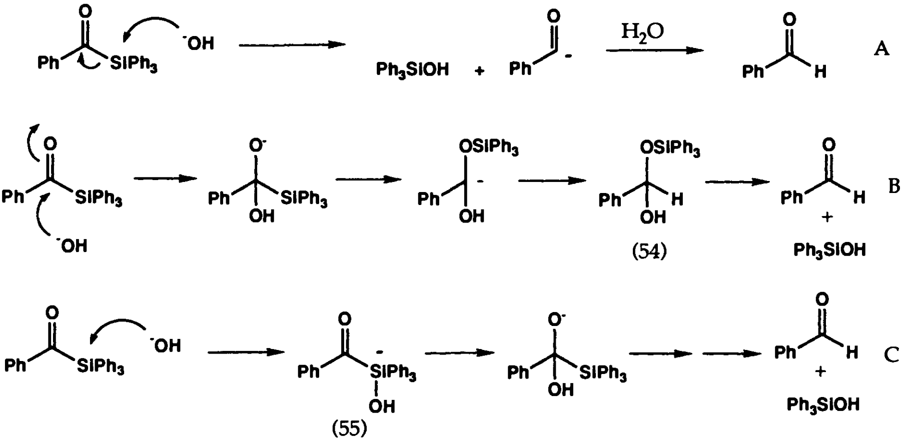
[106] E W Colvin, in 'Silicon in Organic Synthesis', Butterworths, London, 1981

[107] E W Colvin, in 'Silicon Reagents in Organic Synthesis', Academic Press, London, 1988



Scheme 43

rapidly produce triphenylsilanol and benzaldehyde.[1,5] At least three mechanisms are conceivable for this reaction: *S*$_N$2 displacement at the silicon atom [Path A]; nucleophilic attack at the carbonyl carbon atom followed by Brook rearrangement [Path B], initially to give a hemiacetal (54); or alternatively, nucleophilic attack at the silicon atom to form a pentacoordinate silicon anionic intermediate (55), followed by migration of the nucleophile to the carbonyl group [Path C] and subsequent Brook rearrangement as described for [Path B] (Scheme 44).



Scheme 44

The 1,2-migration of silicon to an oxygen anion formed by nucleophilic addition to a carbonyl group[1,5,108] (Brook rearrangement) is a very common

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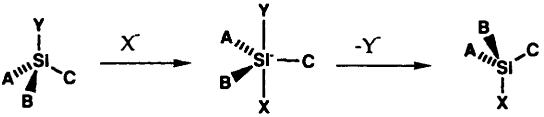
[108] A. G. Brook, *Acc. Chem. Res.*, 1974, 7 77.

pathway by which acyl silanes react when treated with nucleophiles, the major driving force probably being formation of the strong Si–O bond. Brook has shown by using various optically active acyl silanes that this rearrangement usually occurs with retention of configuration at the silicon atom (*vide infra*).[108] The stereochemical course of the Brook rearrangement and that of a multitude of other nucleophilic additions to silicon atoms can be accounted for if a pentacovalent trigonal bipyramidal intermediate is involved in the substitution process.[109,110] An intermediate is of course possible in the silicon series, where it is not in the carbon series, because the empty *d*-orbitals on silicon are just about low enough in energy for bonding to be profitable. In the simplest case, inversion of configuration is observed when the intermediate is formed (56) ⟶ (57) and decomposes (57) ⟶ (58) without pseudorotation taking place (Scheme 45).

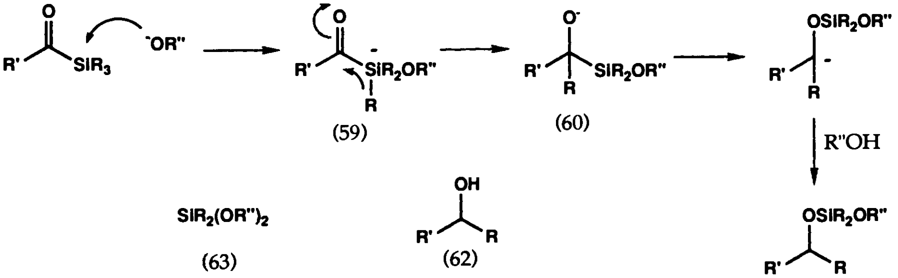


(56) (57) (58)

Scheme 45

The base-catalysed solvolysis of acyl silanes has been studied in detail by Ricci, who, following various kinetic measurements, has suggested that the probable reaction pathway involves direct attack of hydroxide ion at the carbonyl group (Scheme 44, Path B), the rate determining step being the migration of the trialkylsilyl group from carbon to oxygen.[111]

The reaction of acyl silanes with alkoxide ions has been studied in great detail (Scheme 46).[112,113] Again, the reaction pathway was rationalized by invoking a



Scheme 46

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[109] I Fleming, in 'Comprehensive Organic Chemistry', Vol 3, ed N Jones, Pergamon Press, Oxford, 1979, 554

[110] R J P Corriu and C Guerin, *Adv Organomet Chem*, 1982, **20**, 265

[111] D Rietropaolo, A Ricci, M Taddei, and M Fiorenza, *J Organomet Chem*, 1980, **197**, 7

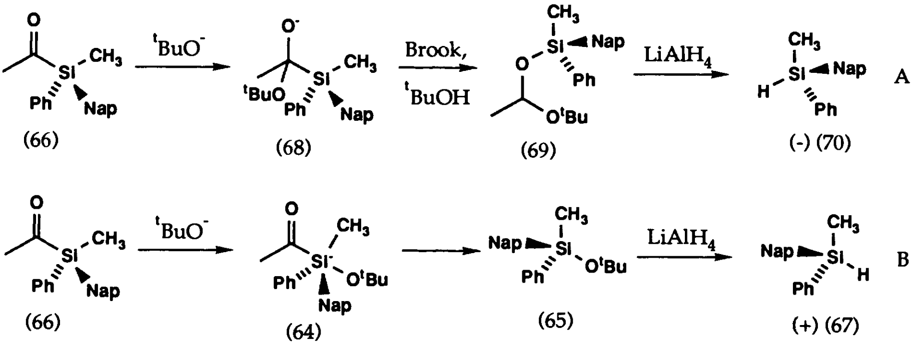
[112] A G Brook and N V Schwartz, *J Org Chem*, 1962, **27**, 2311

[113] A G Brook, W Limburg, and T S D Vandersar, *Can J Chem*, 1978, **56**, 2758

nucleophilic attack by alkoxide ion at the silicon atom of the ketone giving a pentacoordinate silicon anionic species (59), which can then suffer 1,2-migration of an alkyl group from the silicon atom to the carbonyl carbon atom to give the alkoxide ion (60). The intermediate (60) then undergoes a Brook rearrangement to yield the unsymmetrical dialkoxy silane (61), usually the major product. Other reaction products such as alcohol (62) and dialkoxy silane (63), arise from a transetherification reaction between the alkoxide ion and the unsymmetrical dialkoxy silane. A competing reaction, corresponding to nucleophilic displacement of the acyl group from the silicon atom, is also observed. This displacement reaction becomes favoured over rearrangement as the polarity of the solvent system increases (Scheme 47).[5,114]

Scheme 47

Later elegant work by Brook[113] using t-butoxide ion and optically active acyl silanes led him to suggest that the cleavage products arise from direct attack of the butoxide ion at the carbonyl group followed by Brook rearrangement. Evidence for this proposal is outlined in Scheme 48. Should cleavage arise from (64) *via* attack at silicon, then the t-butoxy silane (65) would be formed with overall inversion of configuration at silicon relative to (66). Reduction of (65) would lead, with retention of configuration, to the (+)-silane (67) (Path B), although experiments have shown that under the reaction conditions employed by Brook this reduction is at best very slow. Similar rearrangements of alkyl acyl silanes have been observed upon treatment with fluoride ion.[115]



Nap = 1-naphthyl

Scheme 48

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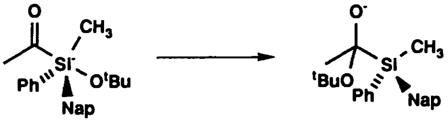
[114] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1935, 244.

[115] P. C. B. Page, S. Rosenthal, and R. V. Williams, *Tetrahedron Lett.*, 1987, **28**, 4455.

Conversely, were nucleophilic attack of the alkoxide ion at the carbonyl group of (66) occurring, then the ion formed, (68), should rearrange to (69) with retention of configuration at silicon. Reduction of (69) with lithium aluminium hydride would then produce (−)-naphthyl phenyl methyl silane (70).

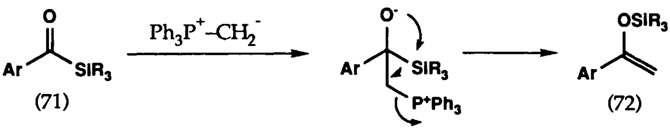
When the reaction was carried out only the (−)-silane (70) was isolated from the cleavage products of the reaction mixture, suggesting that cleavage occurred *via* nucleophilic attack of the alkoxide ion at the carbonyl group (Path A). No t-butoxysilane was detected among the products of reduction. Brook does not discuss the possibility of pseudorotation of (64), which could lead to the ether (65) being formed with overall retention of configuration at the silicon atom (see Scheme 45). However, the fact that no t-butoxysilane could be isolated from the reduction products suggests that cleavage probably does arise *via* path A. There is also the possibility of a migration of the t-butoxide group from the silicon atom to the carbonyl carbon atom as shown in Scheme 49, a sequence which cannot be disproved by these experiments. However, such a migration of the butoxide moiety in (64) seems unlikely as it requires the strong silicon–oxygen bond to be broken.



(64) (68)

Scheme 49

Acyl silanes display a range of behaviour when treated with carbon nucleophiles.[5,55,104] For example, on the one hand, when a variety of aryl acyl silanes (71) were reacted with an alkylidene phosphorane, none of the expected alkenes were obtained, and the only reaction products found were silyl enol ether (72) and triphenylphosphine (Scheme 50).[116,117]



(71) (72)

Scheme 50

On the other hand, when alkyl acyl silanes (73a) were reacted with Wittig reagents only the normal olefinated vinyl silane products were isolated (Schemes 51a,b).[116,117] Under soluble lithium salt conditions *Z*-vinyl silanes were produced

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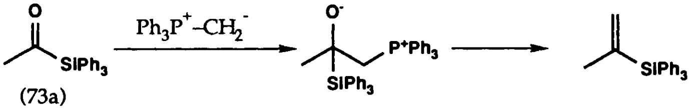
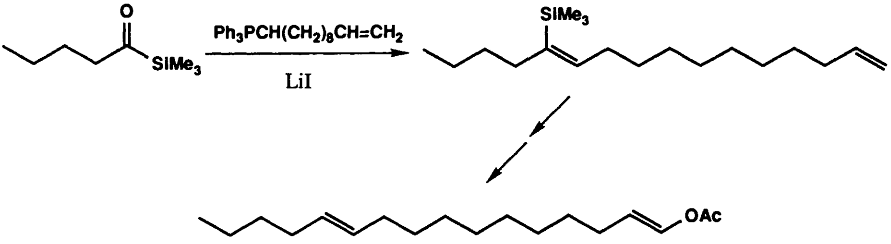
[116] A. G. Brook and S. A. Fieldhouse, *J. Organomet. Chem.*, 1967, **10**, 235.

[117] J. A. Soderquist and C. L. Anderson, *Tetrahedron Lett.*, 1988, **29**, 2425; J. A. Soderquist and C. L. Anderson, *Tetrahedron Lett.*, 1988, **29**, 2777.



(73a)

Scheme 51a



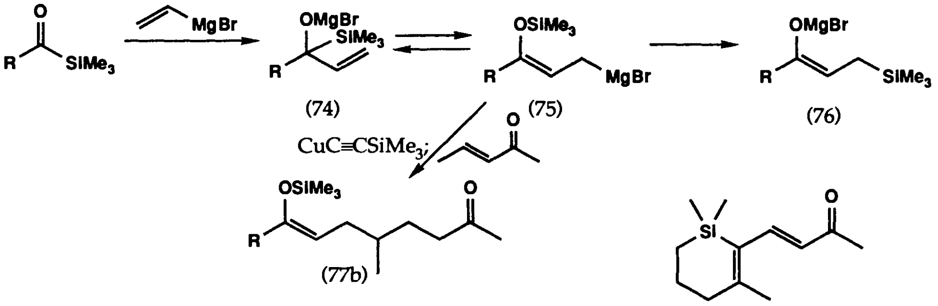
(73b)

Scheme 51b

with very high selectivity; this route was used to prepare a true pheromone component of the sweet potato leaf folder moth (73b) (Scheme 51b).[117]

Diazomethane reacts in a similar manner to Wittig reagents,[5] suggesting that if the substituent at the acyl group is alkyl, and hence carbanion-destabilizing, the rearrangement is inhibited and generally does not occur at all, or at best is very slow relative to the alternative 'normal' reaction pathway; however, when the substituent is aromatic, and therefore capable of stabilizing incipient carbanion formation as the silicon–carbon bond cleaves, rearrangement occurs readily, and silyl ether product is predominant or exclusive.

Kuwajima has used the Brook rearrangement to great effect by using acyl silanes as homoenolate equivalents (Scheme 52).[8,118] Vinyl Grignard reagents react with acyl silanes to give intermediates (74) which subsequently undergo Brook rearrangement to give the homoenolates (75). One important side-reaction is that (75) can undergo a



Scheme 52

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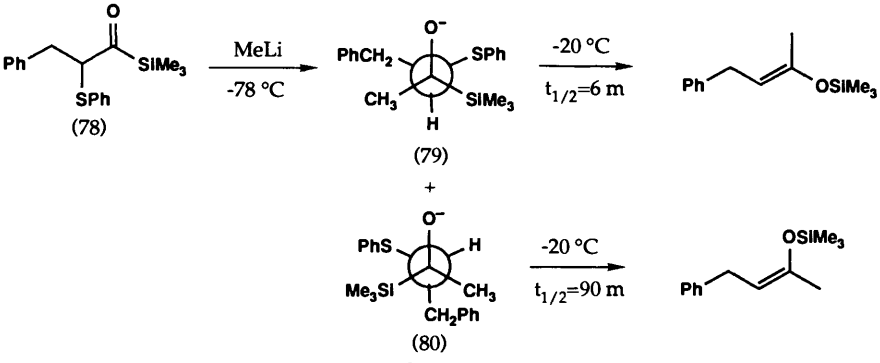
[118] I. Kuwajima, T. Matsutani, and J. Enda, *Tetrahedron Lett.*, 1984, **25**, 5307.



Scheme 53a

further, irreversible, 1,4-silyl group shift to produce the enolate of a β-trimethylsilyl ketone (76). This side-reaction can be partially suppressed by keeping the temperature low, by using larger alkyl groups attached to the silicon atom, and by using magnesium instead of lithium enolates. The difference observed between lithium and magnesium homoenolates may be due to the less ionic character of the carbon–magnesium bond reducing the propensity for attack at the silicon atom to form (76). Sila-β-ionone (77a), an intermediate for sila-vitamin A synthesis, has been prepared *via* addition of an acetylenic Grignard reagent to a cyclic acyl silane.[119]

Kuwajima was able to form cuprate reagents from (75) by using copper trimethylsilyl acetylide. These reagents perform various conjugate addition reactions with enones to provide 1,6-dicarbonyl compounds (77b) in good overall yields.

α-Phenylthioacyl silanes (78) give silyl enol ethers with very high stereoselectivity when reacted with organolithium reagents (Scheme 53a).[120] The major diastereoisomer formed in the addition reaction is the *erythro* isomer (79); this is perhaps best rationalized by invoking a Felkin–Anh transition state (PhS group *anti* to attacking nucleophile).[121] The alcohols rearrange *via* a Brook migration with concerted expulsion of the phenylthiolate leaving group; because of the stereoelectronic demands of the reaction, the silyl group must be eclipsed with a hydrogen atom during the carbon to oxygen migration in the major diastereoisomer (79) and with a benzyl moiety in the minor, less reactive diastereoisomer (80).

Recently acyl silanes containing chiral centres at the α-carbon atom have been shown to undergo highly stereoselective addition of organolithium and Grignard reagents; the resulting α-hydroxy silanes, which could be protiodesilylated with >99% retention of configuration, being formed in 39—89% yield and with diastereoselectivity up to >100:1.[122]

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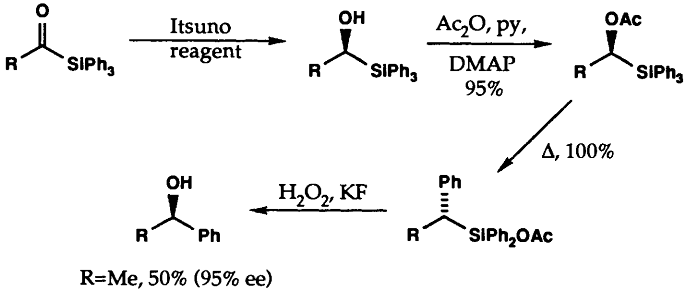
[119] R. Münsted and U. Wannagat, *J. Organomet. Chem.*, 1987, **322**, 11; R. Münsted and U. Wannagat, *Monatsh. Chem.*, 1985, **116**, 693.

[120] H. J. Reich, R. C. Holtan, and S. L. Borkowsky, *J. Org. Chem.*, 1987, **52**, 312.

[121] M. Cherest, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, 1968, 2199; N. T. Anh and O. Eisenstein, *Nouv. J. Chim.*, 1977, **1**, 61; A. S. Cieplak, *J. Am. Chem. Soc.*, 1981, **103**, 4540.

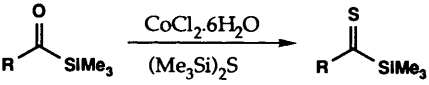
[122] M. Nakada, Y. Urano, K. Susumu, and M. Ohno, *J. Am. Chem. Soc.*, 1988, **110**, 4826.

Buynak has successfully exploited the steric bulk of the silyl group in some acyl silanes to effect asymmetric reduction of the carbonyl group using the Itsuno reagent[123] [a 2:1 complex of borane and (*S*)-C-1-2-amino-3-methyl-1,1-diphenylbutan-1-ol] (Scheme 53b).[124] Transformation of the resultant alcohols into the products *via* a thermal silicon-to-carbon migration of a phenyl group was found to occur stereospecifically to give products of high enantiomeric purity.[125]



Scheme 53b

Acyl silanes react with bis-(trimethylsilyl) sulphide in the presence of a $CoCl_2.6H_2O$ catalyst to afford the corresponding thiocarbonyl derivatives (Scheme 53c).[126] The reaction is mild and proceeds in good yields and, interestingly, is also applicable to aldehydes.



Scheme 53c

Acyl silanes have very recently been used by Schinzer as reagents for diastereoselective aldol condensations.[13] The acyl silanes, prepared using the method of Soderquist,[12] were treated with LDA followed by aldehydes to give aldol products in up to >20:1 selectivity in favour of the *syn* products. Product mixtures were analysed as the carboxylic acids (Scheme 53d). For R^1 = methyl no selectivity was observed. However, increasing steric bulk at the silicon atom gave superior results.

Kuwajima has used acyl silanes as aldehyde equivalents in Lewis acid-catalysed aldol reactions between silyl enol ethers of acyl silanes and acetals. The resulting β-alkoxy acyl silanes were treated with tetrabutyl ammonium hydroxide or tetrabutyl ammonium fluoride to give the corresponding α,β-unsaturated aldehydes.[127]

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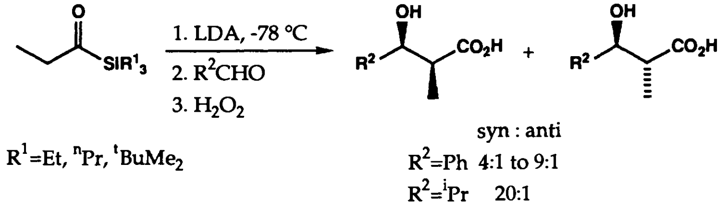
[123] S. Itsuno, M. Nakano, K. Miyazaki, H. Masuda, K. Ito, A. Hirao, and S. Nakahama, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2039.

[124] J. D. Buynak, J. B. Strickland, T. Hurd, and A. Phan, *J. Chem. Soc., Chem. Commun.*, 1989, 89.

[125] A. R. Bassindale, A. G. Brook, P. F. Jones, and J. M. Lennon, *Can. J. Chem.*, 1975, **53**, 332.

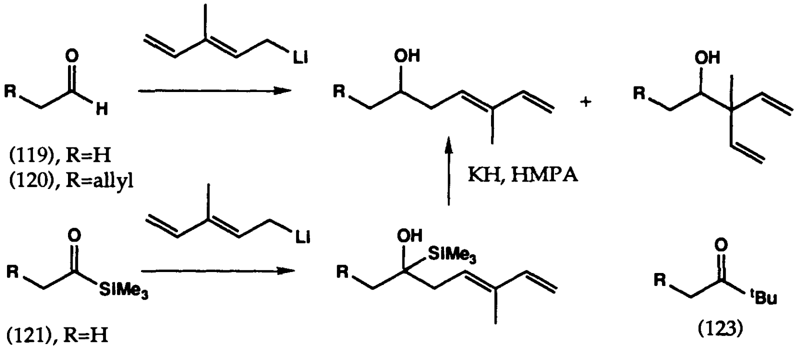
[126] A. Ricci, A. Degl'Innocenti, A. Capperucci, and G. Reginato, *J. Org. Chem.*, 1989, **54**, 19.

[127] T. Sato, M. Arai, and I. Kuwajima, *J. Am. Chem. Soc.*, 1977, **99**, 5827.



Scheme 53d

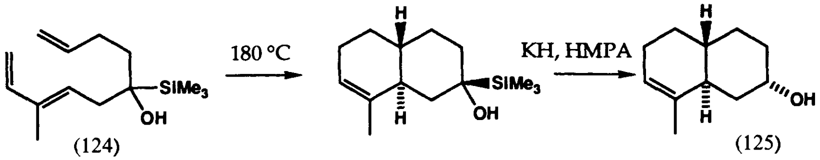
Wilson has found that acyl silanes may be used as synthetic equivalents of sterically-hindered aldehydes.[128] Coupling of aldehydes such as (119) and (120) with 3-methylpentadienyl lithium gave rise to a mixture of regioisomers. However, when analogous acyl silanes (121) and (122) were used, only the conjugated isomers were formed (Scheme 53e). This selectivity is similar to that found in the reaction of sterically-hindered ketone (123). The silyl carbinol adducts are easily desilylated *via* a Brook rearrangement to give the corresponding alcohols.



(119), R=H
(120), R=allyl
(121), R=H
(122), R=allyl
(123)

Scheme 53e

Adduct (124) underwent a highly diastereoselective intramolecular Diels–Alder reaction to give alcohol (125) after stereospecific desilylation (Scheme 53f). The authors comment that acyl silanes provide higher overall yields than aldehydes in these reactions as they are less prone to self-condensation and are also



(124)
(125)

Scheme 53f

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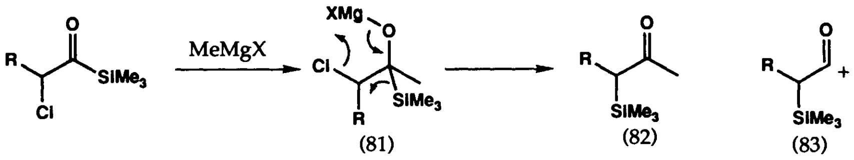
[128] S. R. Wilson, M. S. Hague, and R. N. Misra, *J. Org. Chem.*, 1982, **47**, 747.

superior substrates in that the bulky silyl group may be used for stereocontrol of subsequent reactions.

B. α-Haloacyl Silanes.—α-Haloacyl silanes react with Grignard reagents in a rather unusual manner (Scheme 54).[14,106,107] The expected alkoxide (81) is generated initially, and the reaction then proceeds through loss of chloride ion from the alkoxide and concomitant 1,2-rearrangement of the trimethylsilyl group to afford the product (82). α-Haloacyl silanes therefore behave as α-trimethylsilyl acylium ion (83) equivalents in this reaction. Initial nucleophilic attack at the carbonyl group of the acyl silane may be facilitated compared with α-chloroketones by σ–π interaction with the neighbouring silyl group, while the 1,2-rearrangement may be accelerated compared with the lithium analogue by the more polar character of the oxygen–magnesium bond.[129,130]

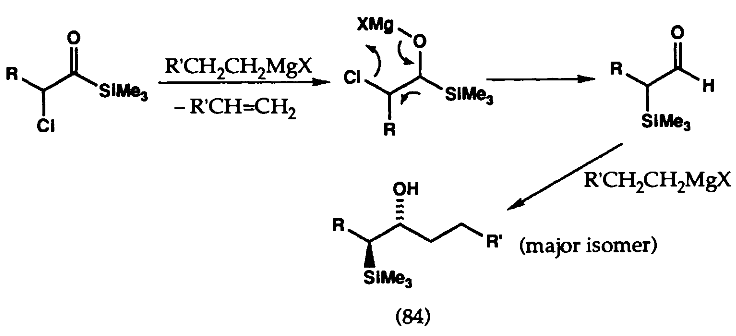


Scheme 54

If the Grignard reagents possess β-hydrogen atoms, then β-hydroxyalkyl trimethylsilanes (84), rather than β-ketoalkyl trimethylsilanes, are formed with high diastereoselectivity (Scheme 55).[14,128]

The hydroxy silanes can then undergo stereocontrolled elimination of trimethylsilanol to give alkenes (Scheme 56).

α-Haloacyl silanes have also been used as α-trimethylsilyl acylium ion equivalents in their reactions with enolates (Scheme 57).[131]



Scheme 55

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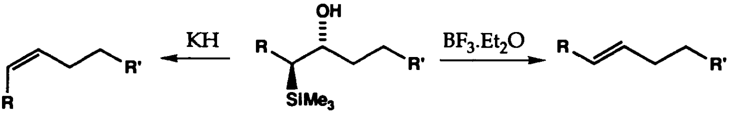
[129] N. de Kimpe, P. Sulmon, and N. Schamp, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 881.

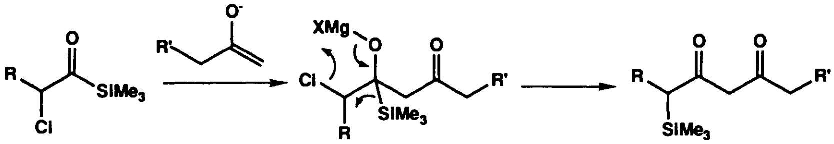
[130] D. J. Cram and F. A. Ald Elhafez, *J. Am. Chem. Soc.*, 1952, **74**, 5828.

[131] I. Kuwajima and K. Matsumoto, *Tetrahedron Lett.*, 1979, 4095.



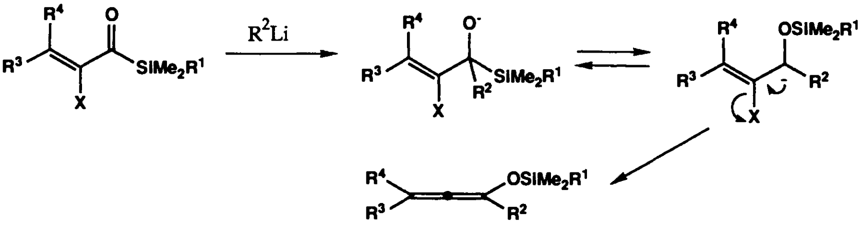
(84)

Scheme 56



Scheme 57

Reich has utilized the Brook rearrangement in α-halo-α,β-unsaturated acyl silanes to synthesize a series of silyloxyallenes (85), from which were synthesized a number of sesquiterpenes (Scheme 58).[17]



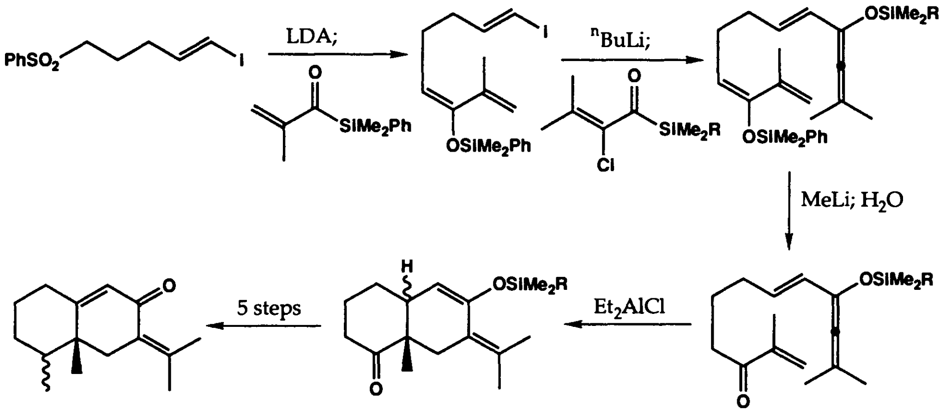
(85)

Scheme 58

Although Reich has also prepared silyloxyallenes by the alkylation of silyloxyallenyl lithium reagents, he favours the above scheme as it is less sensitive to solvent effects and other experimental parameters. An outline of the synthesis of dehydrofukinone (86) which elegantly exemplifies this methodology is shown in Scheme 59.[17]

α-Iodoacyl silanes have been used as precursors of α-phosphonoacyl silanes, which underwent successful enolate alkylation, and from which were prepared α,β-unsaturated acyl silanes *via* Horner–Emmons reaction [Section 3D(v)];[89] α-haloacyl silanes have also been used as precursors of cyclopropyl acyl silanes *via* McCoy reactions and *via* conversion into sulphur ylids (Section 3.5).[103]

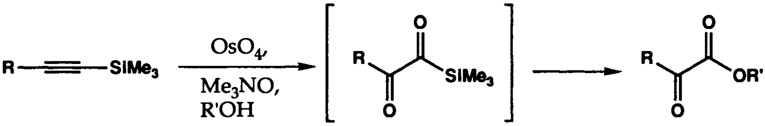
C. α-Ketoacyl Silanes.—α-Ketoacyl silanes are a deep rich red in colour and are especially sensitive, necessitating that purification and handling be carried out in the dark. Little chemistry of these interesting and very sensitive materials has been reported, although they have been implicated as intermediates in the



(86)

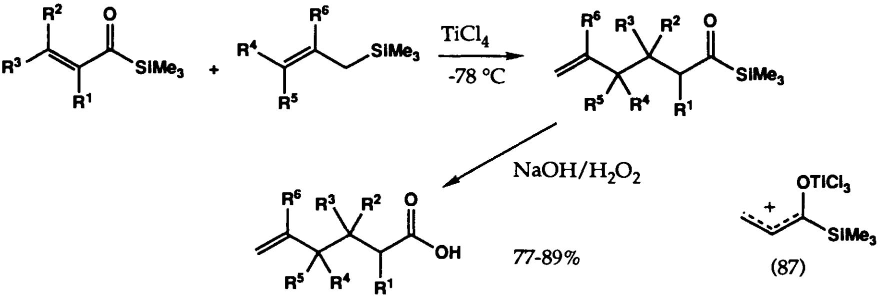
Scheme 59

oxidation of trimethylsilyl acetylenes with osmium tetroxide to give α-ketoesters (Scheme 60).[132]



Scheme 60

D. α,β-Unsaturated Acylsilanes.—α,β-Unsaturated acyl silanes, yellow or yellow-green in colour, serve as highly reactive carboxylic acid equivalents in conjugate



(87)

Scheme 61

allylation reactions with allyl silane derivatives (Scheme 61). α,β-Unsaturated acyl silanes are much more electrophilic than the corresponding carboxylic acids

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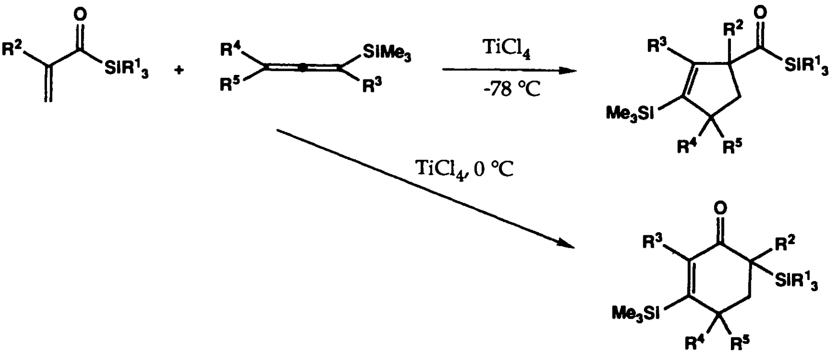
[132] P C. B. Page and S. Rosenthal, *Tetrahedron Lett.*, 1986, **27**, 1947.

and esters due to the net destabilizing effect of trialkylsilyl groups on α-carbocationic centres in intermediates such as (87).[32] They are oxidized to carboxylic acids by alkaline peroxide.[97]

α,β-Unsaturated acyl silanes combine with allenyl silanes in [3 + 2] and [3 + 3] annelation reactions to give five and six-membered carbocycles (Scheme 62a).[68,89,99,101–103]



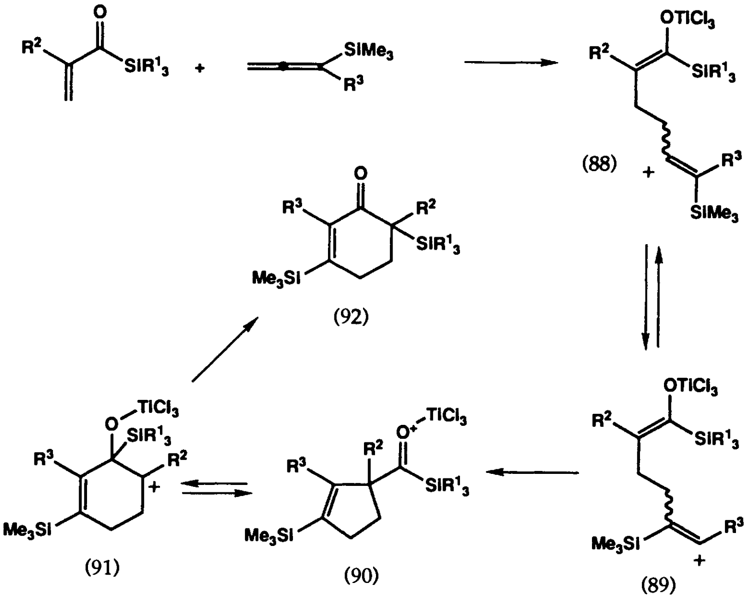
Scheme 62a

By manipulating the acyl silane trialkylsilyl group, the reaction temperature, and the nature of the acyl group, the course of these reactions may be controlled to produce either five or six-membered rings as desired. The reaction pathway is outlined in Scheme 62b.

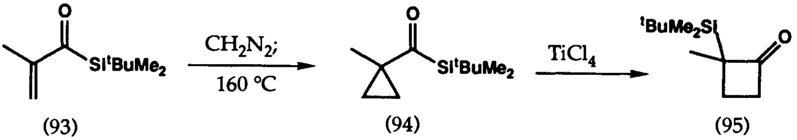
Regiospecific electrophilic substitution at C-3 of the allenyl silane provides a vinyl cation (88) which undergoes a 1,2-cationic trimethylsilyl shift to afford an isomeric vinyl cation (89). Cyclization then provides the cyclopentene (90). If R^1 is alkyl, R_3Si is trimethylsilyl, and the reaction is carried out at elevated temperature, (90) can undergo a further ring expansion to give the six-membered carbocycle (91), which undergoes a second 1,2-cationic shift of the trimethylsilyl moiety to produce the cyclohexenone (92). If desired, this further transformation can be prevented simply by employing the less mobile t-butyldimethylsilyl acyl silanes, minimizing the reaction time, and maintaining the reaction temperature below −78 °C.

1,3-Dipolar cycloaddition of diazomethane to acyl silane (93) afforded a pyrazoline derivative which was subjected to vapour phase pyrolysis to produce the first recorded cyclopropyl acyl silane (94) in 44% yield (Section 3E).[99] Exposure of (94) to one equivalent of titanium tetrachloride in dichloromethane (−78 °C ⟶ 0 °C, 1 h) provided the cyclobutanone (95) in 75% yield (Scheme 63).

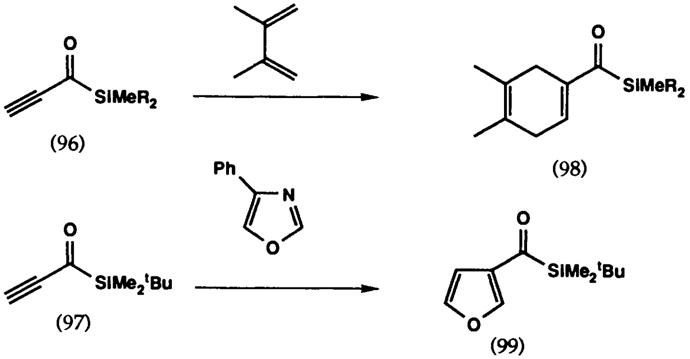
The Diels–Alder reactivity of α,β-acetylenic and ethylenic acyl silanes is comparable to that of the related methyl ketones, and these reactions can be used to prepare other useful α,β-unsaturated acyl silanes. The acetylenic acyl silanes (96) and(97) react with 2,3-dimethylbuta-1,3-diene and 4-phenyloxazole to give



Scheme 62b



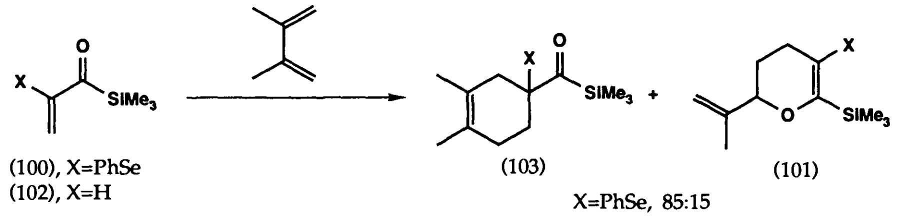
Scheme 63



Scheme 64

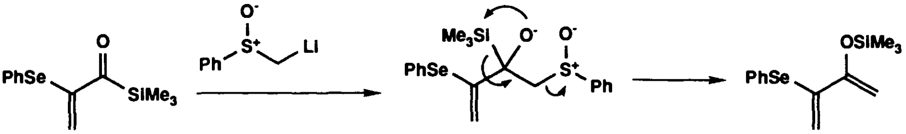
(98) and (99) respectively, under conditions similar to those required for more conventional acetylenic dienophiles (Scheme 64).[15]

The cycloaddition of selenium-substituted α,β-unsaturated acyl silane (100) with 2,3-dimethylbuta-1,3-diene shows an unusual effect in that a significant portion of the hetero-Diels–Alder adduct (101) is formed. It seems that the phenyl selenide substituent is responsible for this unusual reactivity, since the vinyl acyl silane (102) gives only the expected regioisomer (103) (Scheme 65).[15]



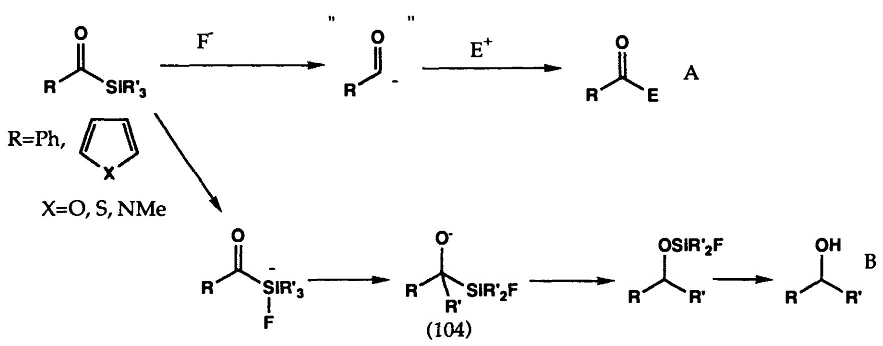
Scheme 65

α-Substituted α,β-unsaturated acyl silanes such as (100) have also been used to synthesize a series of substituted dienes in excellent yield (Scheme 66).[15]



Scheme 66

E. Acyl Silanes as Acyl Anion Precursors.—Various aromatic and heterocyclic acyl trimethylsilanes have been used as acyl anion equivalents by treatment with fluoride ion (Scheme 67, path A).[22,97,115,133,134]



Scheme 67

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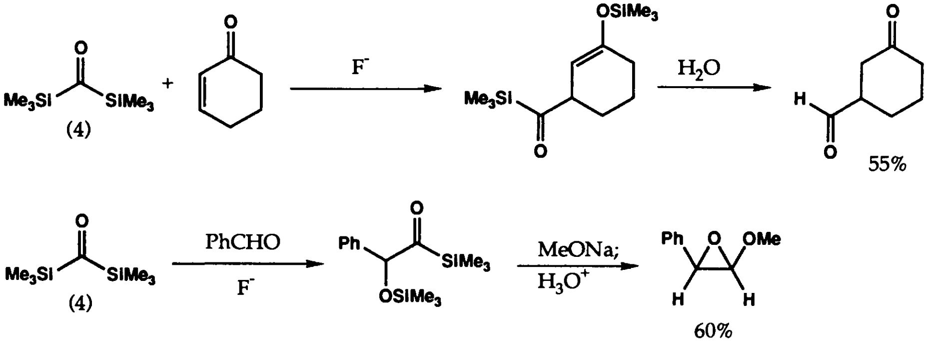
[133] C. H. Heathcock and D. Schinzer, *Tetrahedron Lett.*, 1981, **22**, 1881.

[134] A. Degl'Innocenti, S. Pike, D. R. M. Walton, G. Seconi, A. Ricci, and M. Fiorenza, *J. Chem. Soc., Chem. Commun.*, 1980, 1201.

Provided that the acyl substitutent is electron-withdrawing and there are no aryl substituents on the silicon atom, the acyl anion can be trapped by a variety of electrophiles in good to moderate yield, indeed pentacoordinate silicon anionic species and acyl anions have both been detected in gas-phase reactions of acyl silanes with fluoride ion.[135] One interesting variation is that the bis-(trimethylsilyl) ketone (4) may act as a source of the dianion CO^{2-} in the presence of fluoride ion (Scheme 68).[23]



Scheme 68

An alternative rearrangement pathway may be observed when simple alkyl acyl silanes are used or when the silicon atom bears aryl substituents. This pathway is similar to that suggested, but not observed, by Brook for reaction of acyl silanes with alkoxide ions.[112,113] Addition of fluoride ion induces a migration of one of the alkyl or aryl groups attached to the silicon atom to the carbonyl carbon atom to give (104) followed by a Brook rearrangement giving a rearranged alcohol after protic work-up (Scheme 67, path B).[115] The acyl anion reaction pathway may only be observed for these substrates at higher temperatures in the presence of acid. Both pathways may proceed *via* a pentacoordinate silicon anionic species as a common intermediate.

F. Photochemistry.—The interesting cyclic acyl silane 1,1-diphenyl silacyclohexanone (105) has been found to be unstable towards light, especially in the presence of oxygen. Subsequently (105) was shown to undergo photooxidation promoted by ambient light to produce the silicon-containing lactone (106). The lactone was subsequently hydrolysed to give a δ-(hydroxysilyl) carboxylic acid (107) (Scheme 69).[5,54]

Compound (105) was stable in the presence of oxygen in the absence of light over long periods.

The interesting photochemistry displayed by acyl silanes has been attributed to

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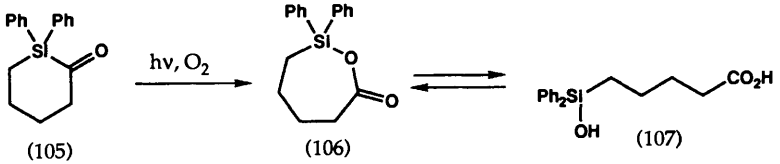
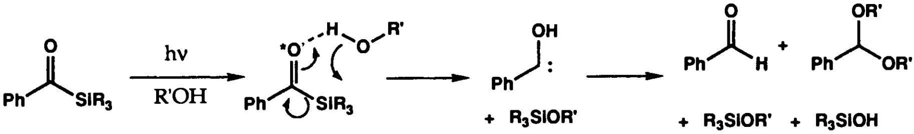
[135] C. H. de Puy, V. M. Bierbaum, R. Damrauer, and J. A. Soderquist, *J. Am. Chem. Soc.*, 1985, **107**, 3385.

the low-energy $n \longrightarrow \pi^*$ carbonyl group transition; subsequent work has shown that this photochemical oxidation is typical of other alkyl acyl silanes, but that aryl acyl silanes are inert.[5]

Acyl silanes also react with remarkable facility in alcoholic solution in the presence of near-visible radiation.[136] In the absence of base the reaction process involves cleavage of the acyl–silicon bond to give a silyl ether and an acetal. Silanol and aldehyde may also be isolated. The probable mechanism, which was suggested following experiments involving an optically active acyl silane, is shown in Scheme 70.[5]

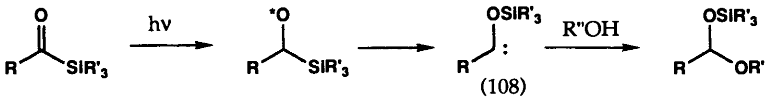


Scheme 69



Scheme 70

Quite apart from the above process is the near-quantitative formation of mixed acetal which occurs on photolysis of an alcoholic solution of an acyl silane containing trace amounts of base (typically pyridine).[5] This acetal is formed by the photochemical generation of a silyloxycarbene (108) from the acyl silane which inserts into the OH bond of a solvent molecule (Scheme 71).



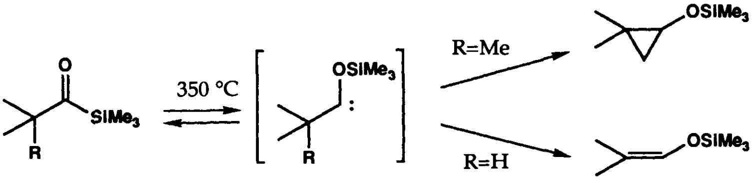
Scheme 71

Dalton has examined the above reaction in detail and has indeed found from various kinetic measurements that acetal formation occurs exclusively *via* reaction of the alcohol with an intermediate presumed to be the silyloxycarbene (108), formed from the acyl silane T_1 state.[137] Silyloxycarbenes are also formed on heating arylsilanes and have been trapped in an intramolecular fashion as shown in Scheme 72.[138]

[136] A G Brook and J M Duff, *J Am Chem Soc*, 1967, **89**, 454

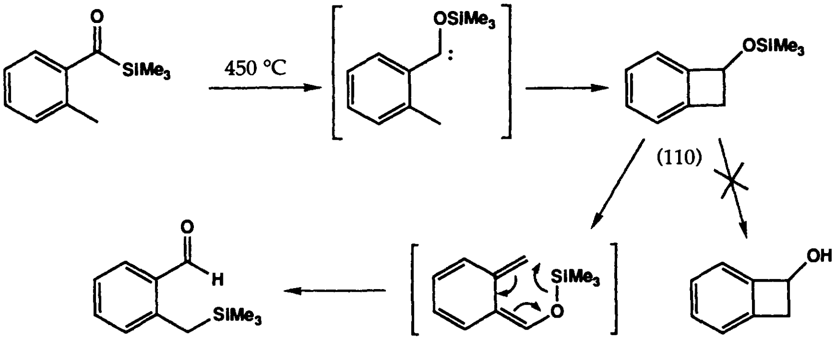
[137] R A Bourque, P D Davis, and J C Dalton, *J Am Chem Soc*, 1981, **103**, 697

[138] A R Bassindale, A G Brook, and J Harris, *J Organomet Chem*, 1975, **90**, C6



Scheme 72

Swenton attempted to utilize an intramolecular insertion reaction of silyloxycarbene generated from an acyl silane as a route to benzocyclobutenols (109) (Scheme 73).[139] However, the unstable compound (110) underwent ring opening



(110)

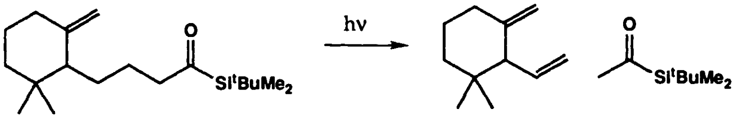
(111)

(109)

Scheme 73

and further rearrangement as shown above to give the aldehyde (111) in good yield.

Upon $n \longrightarrow \pi^*$ excitation, the acyl silane (112) undergoes a Norrish type II reaction as the major pathway, involving hydrogen abstraction and fragmentation to give the acyl silane (113) and the diene (114) as the major products (Scheme 74).[102] The ketone (115) was shown to behave in an analogous manner.



(112)

(114)

(113)

Scheme 74

Additionally, acyl silane (112) showed more typical photochemical behaviour, undergoing rearrangement to the silyloxycarbene intermediate (116). Insertion of (116) into the OH bond of the enol (117) led to compound (118) (Scheme 75).

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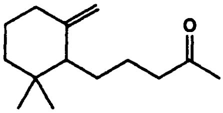
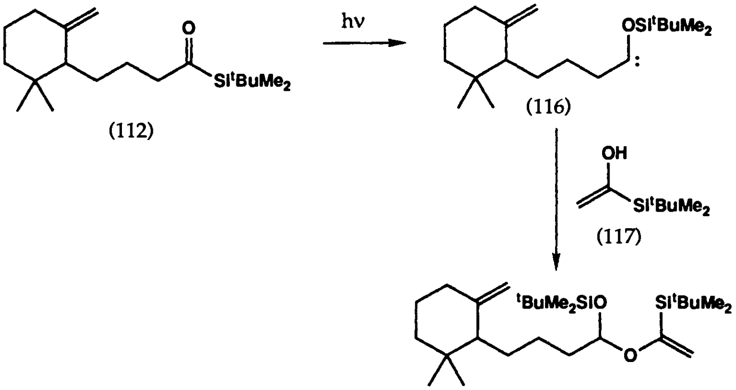
[139] C Shih and J. S. Swenton, *J Org Chem.*, 1982, **47**, 2668.

These findings demonstrate that the silyloxycarbene (116) reacts preferentially by an intermolecular insertion into an OH bond rather than by an intramolecular addition to a carbon–carbon double bond, or by an insertion into a neighbouring carbon–hydrogen bond.

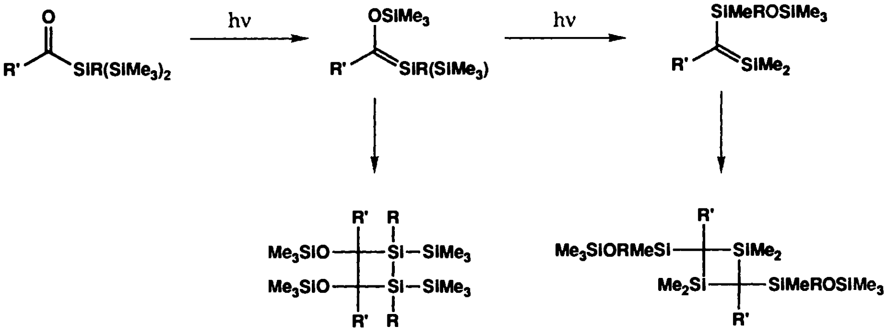


(115)



Scheme 75

Brook has shown that upon irradiation a wide variety of acyl tris-(trimethylsilyl) silanes and acyl alkyl bis-(trimethylsilyl) silanes undergo clean 1,3-rearrangements of silyl groups from silicon to oxygen to give silenes, many of which are remarkably stable and even recrystallizable (Scheme 76).[26,27,29,63] These silenes



Scheme 76

may undergo head-to-head or head-to-tail [2 + 2] dimerization to give 1,2- or 1,3-disilacyclobutanes dependent upon the nature of the alkyl groups present.[29] The structures of several 1,3-disilacyclobutanes have been determined by *X*-ray crystallography.[140]

5 Conclusion

We hope that we have shown in the above discussion that early difficulties encountered in synthesizing acyl silanes have been surmounted to a large extent by the multitude of synthetic methods now available for their preparation. In recent years several reactions of acyl silanes, for example the Brook rearrangement, have been utilized to great effect in forming a variety of useful synthetic intermediates. As the synthesis of acyl silanes becomes more sophisticated, and as functionalized acylsilanes become more accessible, it seems likely that these interesting materials will find increasing use in organic chemistry.

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[140] K. M. Baines, A. G. Brook, P. D. Lickiss, and J. F. Sawyer, *Organometallics*, 1989, **8**, 709.