ORGANOSILYLMETALLIC COMPOUNDS: THEIR FORMATION AND REACTIONS, AND COMPARISON WITH RELATED TYPES

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SOME aspects of the chemistry of organosilicon compounds have recently been the subject of several monographs and reviews.[1] The field of silylmetallic compounds, however, has been mentioned only briefly and in few of these articles.[1g,h]

Although the formation of triphenylsilyl-lithium as a reaction intermediate was first reported[2] in 1933, useful methods for the preparation of organosilylmetallic compounds were not published until 1951. Their chemistry and reactions have been intensively and extensively studied in subsequent years.

Compounds of the general formula RR′R″SiM where R, R′, and R″ are organic radicals or hydrogen, and M is a metal, fall into the category of this Review. Emphasis will be placed on the silyl-alkali-metal compounds. These highly active reagents—triphenylsilyl-lithium, for example—can be easily prepared in solution. Comparable in reactivity with corresponding organometallic compounds such as Grignard reagents, organolithium compounds, or triphenylmethyl-sodium, silylmetallic compounds often show dissimilarities in their mode of reaction. Their reaction with a variety of functional groups is potentially a source of new types of organosilicon compounds. Reactions are not necessarily restricted to the formation of silicon–carbon bonds: it is possible to form bonds between silicon and many other elements.

1. Preparation of silylmetallic compounds

(a) Early Unsuccessful Attempts.—"Even after a very short experience, it was evident that corresponding derivatives of the two elements in

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[1](*a*) H. W. Post, "Silicones and Other Organic Silicon Compounds," Rheinhold Publ. Corp., New York, N.Y., 1949; (*b*) E. G. Rochow, "An Introduction to the Chemistry of Silicones," 2nd edn., John Wiley & Sons, Inc., New York, N.Y., 1951; (*c*) A. Ya. Yakubovich and V. A. Ginsburg, *Uspekhi Khim.*, 1949, **18,** 46; (*d*) K. A. Andrianov, A. A. Zhdanov, S. A. Golubstsov, and M. V. Sobolevskii, *ibid.*, 1949, **18,** 145; (*e*) K. A. Andrianov and A. A. Zhdanov, *ibid.*, 1952, **21,** 207; (*f*) H. Gilman and G. E. Dunn, *Chem. Rev.*, 1953, **52,** 77; (*g*) A. G. Brook, *Chemistry in Canada*, Sept. 1955, 43; (*h*) A. G. MacDiarmid, *Quart. Rev.*, 1956, **10,** 208; (*i*) P. D. George, M. Prober, and J. R. Elliot, *Chem. Rev.*, 1956, **56,** 1065; (*j*) I. J. Wilk, *J. Chem. Educ.*, 1957, **34,** 463; (*k*) A. D. Petrov and V. F. Mironov, "Darstellung und Eigenschaften von Siliziumkohlenwasserstoffen," Akademie-Verlag, Berlin, 1955; (*l*) M. Kumada, *Yûki Gôsei Kagaku Kyokai Shi*, 1958, **16,** 379.

[2] C. A. Kraus and H. Eatough, *J. Amer. Chem. Soc.*, 1933, **55,** 5008.

question showed very considerable differences in their chemical properties." This viewpoint of Kipping[3] after forty years of research in silicon chemistry seemed to be confirmed by unsuccessful attempts to prepare silylmetallic compounds employing methods which are useful for organometallic compounds.

The reaction of metals with organic halides is perhaps the most fundamental one for the preparation of organometallic compounds.[4] Trialkyl- and triaryl-silyl halides have been allowed to react with alkali metals in non-polar solvents or without solvent. Although the process may involve the formation of a silylmetallic intermediate, the end products have been disilanes:[5]

$$2R_3SiCl + 2Na \rightarrow R_3Si{\cdot}SiR_3 + 2NaCl$$

Numerous examples of metallations of the type, $RH + R'Li \rightarrow RLi + R'H$, are known in carbon chemistry.[6] Corresponding reactions of Si–H types with organolithium compounds resulted in the displacement of a hydride ion and the formation of a new silicon–carbon bond:[7]

$$R_3SiH + R'Li \rightarrow R_3SiR' + LiH$$

Whereas triphenylmethylpotassium is formed from triphenylmethane and potassium amide,[8] related reactions of triphenylsilane give silylamines:[9]

$$\begin{aligned} Ph_3CH + KNH_2 &\rightarrow Ph_3CK + NH_3 \\ Ph_3SiH + LiNR_2 &\rightarrow Ph_3Si{\cdot}NR_2 + LiH \end{aligned}$$

Halogen–metal interconversion is another method of choice for the preparation of many organoalkali-metal compounds.[4,10]

Silyl halides generally yield coupling products when allowed to react with organoalkali-metal compounds:[11]

$$\begin{aligned} RX + R'Li &\rightarrow RLi + R'X \\ R_3SiX + R'Li &\rightarrow R_3SiR' + LiX \end{aligned}$$

In special cases where halogen–metal interconversion occurs in silicon

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[3] F. S. Kipping, *Proc. Roy. Soc.*, 1937, *A*, **159**, 139.

[4] R. G. Jones and H. Gilman, *Chem. Rev.*, 1954, **54**, 835.

[5] (*a*) W. Schlenk, J. Renning, and G. Racky, *Ber.*, 1911, **44**, 1178; (*b*) F. S. Kipping, *Proc. Chem. Soc.*, 1911, **27**, 143; (*c*) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, 1951, **73**, 5077; (*d*) M. G. Voronkov and Yu. I. Khubodin, *Zhur. obschchei Khim.*, 1956, **26**, 586; (*e*) M. P. Brown and G. W. A. Fowles, *J.*, 1958, 2811.

[6] See the reviews: (*a*) H. Gilman and A. Morton, "Organic Reactions," John Wiley & Sons, Inc., New York, N.Y., 1954, Vol. VIII, p. 258ff.; (*b*) R. A. Benkeser, D. S. Foster, D. M. Sauve, and J. F. Nobis, *Chem. Rev.*, 1957, **57**, 867.

[7] (*a*) H. Gilman and S. P. Massie, *J. Amer. Chem. Soc.*, 1946, **68**, 1128; (*b*) R. N. Meals, *ibid.*, p. 1880; (*c*) R. A. Benkeser and F. J. Riel, *ibid.*, 1951, **73**, 3472; (*d*) H. Gilman and E. Zuech, *ibid.*, 1957, **79**, 4560; and references cited therein.

[8] C. A. Kraus and R. Rosen, *J. Amer. Chem. Soc.*, 1925, **47**, 2739.

[9] H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *ibid.*, 1950; **72**, 5767.

[10] R. A. Jones and H. Gilman in "Organic Reactions," John Wiley & Sons, Inc., New York, N.Y., 1951, Vol. VI, p. 339ff.

[11] See ref. 1(*b*), sections 3 and 4.

chemistry, as in the reaction between silyl halides and the stilbene–dilithium adduct,[12] the Si–Li intermediate couples immediately with the silyl halide to give a disilane as the final product:

$$R_3SiCl + (CHPhLi)_2 \rightarrow PhCH{=}CHPh + LiCl + R_3SiLi \xrightarrow[R_3SiCl]{} R_3Si{\cdot}SiR_3$$

(b) **Metal Cleavage of Non-functional Silanes and Disilanes.**—In 1951 Benkeser and Severson[13] reported the cleavage of (αα-dimethylbenzyl)-triphenylsilane with sodium–potassium alloy in ether to give a mixture of triphenylsilylpotassium and (αα-dimethylbenzyl)phenylpotassium:

$$Ph_3Si{\cdot}CMe_2Ph + 2K \rightarrow Ph_3SiK + PhMe_2CK$$

Similarly, *αp*-bistriphenylsilylcumene was cleaved by the alloy.[13] In the same year it was found[14] that triphenylsilylpotassium could be prepared free from other products by the cleavage of hexaphenyldisilane with sodium–potassium alloy in ether. The yellow-brown silylpotassium reagent is obtained as a suspension:

$$Ph_3Si{\cdot}SiPh_3 + 2K \rightarrow 2Ph_3SiK$$

It was found advantageous to remove excess of alloy from the mixture by amalgamation.[15] Although cleavage occurred neither with sodium dispersion in xylene or dioxan,[14] nor with sodium amalgam or lithium in ethyl ether, hexaphenyldisilane was cleaved by sodium–potassium alloy in hot n-butyl ether[14] or, though very slowly, in benzene or light petroleum.[15b] Triphenylsilylrubidium and triphenylsilylcæsium have been prepared by cleavage of the disilane with rubidium and cæsium, respectively, in ethyl ether.[15b]

The first *solutions* of silylmetallic compounds were obtained in ethylene glycol dimethyl ether. It was found that in this solvent hexaphenyldisilane is cleaved, not only by sodium–potassium alloy, but also by sodium and lithium.[16] Unfortunately, these solutions are not stable and have to be used immediately after their preparation. Triphenylsilyl-lithium in ethylene glycol dimethyl ether gave a negative Colour Test I[17] after one hour's refluxing. The ether cleavage product was methyltriphenylsilane.[18]

Although only triaryl types were accessible before tetrahydrofuran came into use as solvent, the latter made possible the preparation of silylalkalimetal reagents containing aliphatic as well as aromatic groups. Triphenylsilyl-lithium,[19] methyldiphenylsilyl-lithium,[19] dimethylphenylsilyl-lithium,[19]

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[12] M. V. George, D. Wittenberg, and H. Gilman, *J. Amer. Chem. Soc.*, 1959, **81**, 361.

[13] R. A. Benkeser and R. G. Severson, *ibid.*, 1951, **73**, 1424.

[14] H. Gilman and T. C. Wu, *ibid.*, p. 4031.

[15] (*a*) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, *ibid.*, 1952, **74**, 561; (*b*) H. Gilman and T. C. Wu, *J. Org. Chem.*, 1953, **18**, 753.

[16] A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 1954, **76**, 278.

[17] H. Gilman and F. Schulze, *ibid.*, 1925, **47**, 2002; G. Wittig, *Angew. Chem.*, 1940, **53**, 243.

[18] D. Wittenberg, D. Akoi, and H. Gilman, *J. Amer. Chem. Soc.*, 1958, **80**, 5933.

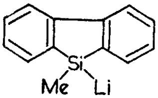
[19] H. Gilman and G. D. Lichtenwalter, *ibid.*, p. 608.

and 5-lithio-5-methyldibenzosilole,[20] prepared from the corresponding disilanes in tetrahydrofuran, are examples of this type. These solutions are fairly stable at room temperature for long times, providing a distinct advantage over the use of ethylene glycol dimethyl ether as solvent.

Although the cleavage of hexaphenyldisilane by lithium in tetrahydropyran is rather slow at room temperature,[18,21] this solvent may be advantageous in some cases because of its fair stability towards cleavage by triphenylsilyl-lithium, even at high temperatures.[18]

Other solvents in which hexaphenyldisilane has been cleaved include dioxan[18] and pyridine.[22] Cleavage was also accomplished by sodium in liquid ammonia.[23] In each of these cases, secondary reactions occurred between the Si-Li reagents and the solvent. [For a detailed discussion see sections 2(e) and 2(f) below.]

TABLE 1. *Silylalkali-metal compounds prepared by metal cleavage of symmetrical disilanes.*

Compound	Solvent*	Derivative made with	Yield (%)	Ref.
Ph_3SiK	Et_2O	PhBr	40—96	13, 14, 15†
Ph_3SiK	Et_2O	Me_3SiCl	45—75	13, 14, 15
Ph_3SiK	Bu_2O	Me_3SiCl	47	14
p-$TolPh_2SiK$	Et_2O	p-$Tol_2PhSiCl$	52	24
p-Tol_3SiK	Et_2O	Ph_3SiCl	26	24
p-Tol_3SiK	Et_2O	CO_2	56	25
Ph_3SiRb	Et_2O	Me_3SiCl	48	15*b*
Ph_3SiCs	Et_2O	Me_3SiCl	26	15*b*
Ph_3SiK	GDME	Me_3SiCl	77	16
Ph_3SiNa	GDME	Me_3SiCl	68	16
Ph_3SiLi	GDME	Me_3SiCl	72	16
Ph_3SiLi	THF	Me_3SiCl	79	19
$Ph_2MeSiLi$	THF	Me_3SiCl	74	19
$PhMe_2SiLi$	THF	Me_3SiCl	47	19
	THF	Me_2SO_4	54	20

* GDME = Ethylene glycol dimethyl ether; THF = tetrahydrofuran.

† Also H. Gilman, G. D. Lichtenwalter, and D. J. Peterson, unpublished studies.

The metal cleavage of a hexa-alkyldisilane has not been accomplished to date, and no stable solutions of trialkylsilylalkali-metal compounds useful for synthetic purposes have been prepared. Although hexa-alkyl compounds of tin and lead can be split by alkali metals to give the alkali-metal salts,[5e,26] the corresponding compounds of germanium and silicon

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[20] H. Gilman and R. D. Gorsich, *ibid.*, p. 3243.

[21] M. V. George, unpublished studies.

[22] D. Wittenberg and H. Gilman, *Chem and Ind.*, 1958, 390.

[23] T. C. Wu and H. Gilman, *J. Org. Chem.*, 1958, **23**, 913.

[24] H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.*, 1953, **75**, 3762.

[25] A. G. Brook and R. J. Mauris, *ibid.*, 1957, **79**, 971.

[26] C. A. Kraus and W. V. Sessions, *ibid.*, 1925, **47**, 2361.

seem to be truly resistant to cleavage by alkali metals. Thus hexaethyldisilane is not cleaved by lithium in ethylamine[27] or by sodium–potassium alloy (either alone or in a number of solvents),[5e,28,29] although the disilane is readily cleaved by halogens.[28] No reaction was observed between triethylphenylsilane and sodium in liquid ammonia.[27] Benkeser and Severson[13] reported no reaction between (αα-dimethylbenzyl)trimethylsilane and sodium–potassium alloy in ether. Trimethylphenylsilane has been cleaved at −50° by sodium–potassium alloy in tetrahydrofuran. Although it was possible to characterise phenylpotassium in the reaction mixture by preparation of derivatives, no evidence was found for the presence of trimethylsilylpotassium.[29]

Some of the reactions achieved by such methods are listed in Table 1.

Another possible route for the preparation of trialkylsilyl-metal compounds involved cleavage of unsymmetrical disilanes. Trimethylphenylsilane, in low yield, together with tetraphenylsilane were isolated from the cleavage of 1,1,1-trimethyl-2,2,2-triphenyldisilane by sodium–potassium alloy, after preparation of these derivatives with bromobenzene:[28]

$$\mathrm{Me_3Si{\cdot}SiPh_3 + 2K \rightarrow Ph_3SiK + Me_3SiK \xrightarrow[+PhBr]{} Ph_4Si + Me_3SiPh}$$

Cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane by lithium in tetrahydrofuran, followed by acid-hydrolysis, gave low yields of triethylsilane and hexaethyldisilane in addition to triphenylsilane,[30] indicating that triethylsilyl-lithium was one of the intermediates.

(c) **Metal Cleavage of Various Functional Silanes.**—While disilanes are usually prepared by reactions of the corresponding chlorosilanes with alkali metals,[5] and silylmetallic compounds by metal-cleavage of disilanes, methods have been investigated to combine these two steps by a proper choice of solvent and metal. Chlorotriphenylsilane was converted into triphenylsilylpotassium by the use of sodium–potassium alloy in ether,[14,15b] whereas in xylene the reaction stops at the disilane stage.[15b] Similarly, tri-*p*-tolylsilylpotassium was prepared from chlorotri-*p*-tolylsilane.[25] By using lithium in tetrahydrofuran, it is possible to prepare several silyl-lithium compounds directly from the corresponding chlorosilanes. Triphenylsilyl-lithium,[31] methyldiphenylsilyl-lithium,[18] and 1-phenyl-1-silacyclohexyl-lithium[32] were formed by this method. It is interesting that trialkylchlorosilanes are converted into the disilane by lithium in tetrahydrofuran;[33] no further cleavage has been observed.

Since it was found[33] that silyl-lithium compounds couple readily with

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[27] C. A. Kraus and W. K. Nelson, *ibid.*, 1934, **56**, 195.
[28] H. Gilman, R. K. Ingham, and A. G. Smith, *J. Org. Chem.*, 1953, **18**, 1743.
[29] M. B. Hughes, unpublished studies.
[30] G. D. Lichtenwalter and D. Wittenberg, unpublished studies.
[31] H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. and Ind.*, 1958, 1479.
[32] H. Gilman, G. D. Lichtenwalter, and D. J. Peterson, unpublished studies.
[33] D. Wittenberg and G. D. Lichtenwalter, unpublished studies.

chlorosilanes even at —70°, the reaction is thought to proceed in two steps; first, the formation of a disilane, and, secondly, its cleavage:

$$2Ph_3SiCl + 2Li \rightarrow 2LiCl + Ph_3Si{\cdot}SiPh_3 \xrightarrow[+\,2Li]{} 2Ph_3SiLi$$

TABLE 2. *Silylalkali-metal compounds prepared from various organosilicon compounds.*

Compound	Prepared from	Solvent*	Derivative prepared with	Yield (%)	Ref.
Ph_3SiK	Ph_3SiCl	Et_2O	Me_3SiCl	67	15*b*
p-Tol_3SiK	*p*-Tol_3SiCl	Et_2O	CO_2	69	25
Ph_3SiLi	Ph_3SiCl	THF	Me_3SiCl	83	31
$Ph_2MeSiLi$	$Ph_2MeSiCl$	THF	Furan	27	18
			Ph_3SiCl	36	31
$PhEt_2SiLi$	$PhEt_2SiCl$	THF	Ph_3SiCl	34	32
Ph_3SiK	$Ph_3Si{\cdot}OEt$	Et_2O	PhBr	24	15*b*
Ph_3SiK	$Ph_3Si{\cdot}OMe$	Et_2O	PhBr	79	34
Ph_3SiK	Ph_3SiH	Et_2O	PhBr	67	34
$(p\text{-}Ph{\cdot}C_6H_4)_3SiK$	$(p\text{-}Ph{\cdot}C_6H_4)_3SiH$	Et_2O	$p\text{-}Ph{\cdot}C_6H_4Br$	48	34
Ph_3SiLi	Ph_3SiH	THF	Me_2SO_4	63	†
$Ph_2MeSiLi$	$Ph_2MeSiCl$	THF	Ph_3SiCl	66	†
$(Ph_3Ge)_3SiLi$	$(Ph_3Ge)_3SiH$	NH_2Et	EtBr	63	‡
Et_3SiLi	$Et_3Si{\cdot}GePh_3$	NH_2Et	EtBr	—	27
Ph_3SiK	$Ph_3Si{\cdot}GePh_3$	Et_2O	CO_2	86	§
Ph_3SiK	$Ph_3Si{\cdot}CPh_3$	Et_2O	CO_2	70	¶
Ph_3SiK	$Ph_3Si{\cdot}CMe_2Ph$	Et_2O	PhBr	39	13
Ph_3SiK	Ph_4Si	Et_2O	Ph_3SiCl	70	15*b*
Ph_3SiLi	Ph_4Si	THF	Me_3SiCl	79	†
Ph_3SiK	$Ph_3Si{\cdot}SiMe_3$	Et_2O	PhBr	50	15*b*, 28
Ph_3SiK	$Ph_3Si{\cdot}SiEt_3$	Et_2O	PhBr	39	28

* THF = Tetrahydrofuran.

† R. D. Gorsich, unpublished studies.

‡ J. G. Milligan, Ph.D. Thesis, Brown University, Providence, R.I., 1934; J. G. Milligan and C. A. Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 5297.

§ H. Gilman and C. W. Gerow, *ibid.*, 1956, **78**, 5823.

¶ A. G. Brooke, H. Gilman and L. S. Miller, *ibid*, 1953, **75**, 4579.

The use of chlorosilanes may be advantageous in many cases (cf. Table 2); however, the yields of the silylmetallic reagents often appear to be slightly lower than from the corresponding disilanes. Furthermore, chlorosilanes, though commercially available, require special precautions owing to their ease of hydrolysis.

Alkoxysilanes such as ethoxytriphenylsilane[15b] and methoxytriphenylsilane[34] have also been used for the preparation of triphenylsilylpotassium with sodium–potassium alloy in ethyl ether as the cleaving agent. This reaction also may involve the intermediate formation of hexaphenyldisilane.

The reaction of *N*-ethyl(triphenylsilyl)amine with lithium in ethylamine had been reported to yield solutions of triphenylsilyl-lithium.[2] Later

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[34] R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Amer. Chem. Soc.*, 1952, **74**, 648.

workers[35] obtained the same "red solutions", but were able to show that reduction of phenyl groups occurs rather than formation of Si–Li bonds.

Various silicon hydrides on treatment with sodium–potassium alloy in ethyl ether or with lithium in tetrahydrofuran yielded the corresponding silylalkali-metal compounds. Tris-*p*-biphenylylsilylpotassium,[34] triphenylsilylpotassium,[34] triphenylsilyl-lithium,[36] and methyldiphenylsilyl-lithium[36] have been prepared by this method. The process actually appears to involve cleavage of aryl groups from the silicon atom; the arylalkali-metal compound then reacts with the silicon hydride to form a non-functional silane, which in turn is again cleaved by the metal:

$$\mathrm{R_3SiH} \xrightarrow[+\,2\mathrm{Li}]{} \mathrm{R_2SiHLi + RLi} \xrightarrow[+\,2\mathrm{Li}]{} \mathrm{RSiHLi_2 + 2RLi}$$

$$\begin{array}{lcl}
\mathrm{RLi + R_3SiH} & \rightarrow & \mathrm{R_4Si} \\
\mathrm{R_4Si + 2Li} & \rightarrow & \mathrm{R_3SiLi + RLi} \\
n\mathrm{R_2SiHLi} & \rightarrow & n\mathrm{LiH + (R_2Si)}_n \\
n\mathrm{RSiHLi_2} & \rightarrow & n\mathrm{LiH + (RSiLi)}_n
\end{array}$$

Gorsich[36] isolated tetraphenylsilane after reaction of triphenylsilane with lithium in tetrahydrofuran and showed that tetraphenylsilane in turn can be cleaved to a mixture of triphenylsilyl-lithium and phenyllithium. It was also demonstrated that lithium in tetrahydrofuran splits off two biphenyl groups from tri-*o*-biphenylylsilane.[36] By a similar mechanism tetraphenylsilane appears to be formed from phenylsilane as well as from diphenylsilane, and from triphenylsilane with sodium–potassium alloy in ether.[35,37]

Although in all of these reactions the silyl-metallic compounds containing SiH groups were expected as by-products, no evidence for their presence was found. Instead, a polymer and a metal hydride were isolated:

$$n\mathrm{R_2SiHLi} \rightarrow \mathrm{(R_2Si)}_n + n\mathrm{LiH}$$

The reaction of triphenylsilane with lithium in ether seems to take a different course, the main product being hexaphenyldisilane.[5c] Triethylsilane apparently does not react under similar conditions.[34] In liquid ammonia, bistriphenylsilylamine was formed from sodium and triphenylsilane.[38] Other reactions of alkali metals with various silicon hydrides and with chlorosilanes which may involve the formation of silylmetallic compounds as intermediates have been described by Kipping and his collaborators,[39] and by Benkeser and Foster.[40]

Triphenylgermyltriphenylsilane, on treatment with sodium–potassium

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[35] R. A. Benkeser, R. E. Robinson, and H. Landesman, *ibid.*, p. 5699.

[36] R. D. Gorsich, unpublished studies.

[37] R. A. Benkeser and D. J. Foster, *J. Amer. Chem. Soc.*, 1952, **74**, 4200.

[38] H. H. Reynolds, L. A. Bigelow, and C. H. Kraus, *ibid.*, 1929, **51**, 3067.

[39] A. R. Steele, and F. S. Kipping, *J.*, 1928, 1431; F. S. Kipping, *J.*, 1923, **123**, 2590; 1924, **125**, 2291; F. S. Kipping and J. E. Sands, *J.*, 1921, **119**, 830; F. S. Kipping and A. G. Murray, *J.*, 1929, 360; F. S. Kipping and J. F. Short, *J.*, 1930, 1029.

[40] R. A. Benkeser and D. J. Foster, *J. Amer. Chem. Soc.*, 1952, **74**, 5314.

alloy, afforded a mixture of triphenylgermylpotassium and triphenylsilylpotassium:[41]

$$\mathrm{Ph_3Ge{\cdot}SiPh_3 + 2K \rightarrow Ph_3GeK + Ph_3SiK}$$

An analogous cleavage of triphenyl(triphenylmethyl)silane has been described.[42] Lithium in ethylamine has been used to split triethyl(triphenylgermyl)silane,[27] and tris(triphenylgermyl)silyl-lithium was obtained from tristriphenylgermylsilane and lithium in ethylamine; however, the latter silylmetallic compound was described as unstable in this solvent.[43,44]

(d) **Silylalkali-metal Compounds containing more than One Silicon Atom.**—An early attempt to obtain pentaphenyldisilanyl-lithium from chloropentaphenyldisilane and lithium in diethyl ether or di-n-butyl ether was unsuccessful,[45] while with sodium in refluxing xylene, decaphenyltetrasilane was formed.[45]

Cleavage of octaphenyltrisilane by lithium in tetrahydrofuran gave a mixture of pentaphenyldisilanyl-lithium and triphenylsilyl-lithium,[46] identified after acid-hydrolysis as pentaphenyldisilane and triphenylsilane. Cleavage of decaphenyltetrasilane by lithium in tetrahydrofuran gave a mixture of triphenylsilyl-lithium, pentaphenyldisilanyl-lithium, and heptaphenyltrisilanyl-lithium.[46] It is noteworthy that apparently no diphenylsilylenedilithium was formed in these cleavages, since diphenylsilane was not isolated after acid-hydrolysis.

$$\mathrm{Ph_3Si{\cdot}SiPh_2{\cdot}SiPh_3 + 2Li \rightarrow Ph_3Si{\cdot}SiPh_2Li + Ph_3SiLi}$$

$$\begin{array}{lll} \mathrm{Ph_3Si{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_3 + 2Li} & \rightarrow & \mathrm{2Ph_3Si{\cdot}SiPh_2Li} \\ & \searrow & \mathrm{Ph_3Si{\cdot}SiPh_2{\cdot}SiPh_2Li + Ph_3SiLi} \end{array}$$

(e) **Interconversions.**—Some coupling reactions of silyl-lithium compounds with chlorosilanes produced the desired unsymmetrical disilanes in very low yields. The symmetrical disilanes were formed as the main products.[19,47] Subsequent studies[30] have indicated that cleavages of disilanes by silyl-lithium compounds were involved. Hexaphenyldisilane, although very sparingly soluble, was readily cleaved by dimethylphenylsilyl-lithium in tetrahydrofuran to give triphenylsilyl-lithium and 1,1,2,2-tetramethyl-1, 2-diphenyldisilane:

$$\begin{array}{lll} \mathrm{PhMe_2SiLi + Ph_3Si{\cdot}SiPh_3} & \rightarrow & \mathrm{Ph_3Si{\cdot}SiPhMe_2 + Ph_3SiLi} \\ \mathrm{PhMe_2SiLi + Ph_3Si{\cdot}SiPhMe_2} & \rightarrow & \mathrm{PhMe_2Si{\cdot}SiPhMe_2 + Ph_3SiLi} \end{array}$$

Similarly, dimethylphenylsilyl-lithium cleaved 1,2-dimethyl-1,1,2,2-tetraphenyldisilane to yield methyldiphenylsilyl-lithium and 1,1,2,2-tetramethyl-1,2-diphenyldisilane. Triphenylsilyl-lithium and 1,2-dimethyl-1,1,2,2-tetra-

[41] H. Gilman and C. W. Gerow, *ibid.*, 1956, **78**, 5823.

[42] A. G. Brook, H. Gilman, and L. S. Miller, *ibid.*, 1953, **75**, 4579.

[43] J. G. Milligan, Ph.D. Thesis, Brown University, Providence, R.I., 1934.

[44] J. G. Milligan and C. A. Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 5279.

[45] T. C. Wu, unpublished studies.

[46] D. Wittenberg, M. V. George, and H. Gilman, *J. Amer. Chem. Soc.*, 1959, **91**, in the press.

[47] For a detailed discussion, see section 2(*h*) below.

phenyldisilane resulted from the reaction of methyldiphenylsilyl-lithium with hexaphenyldisilane:

$$2PhMe_2SiLi + Ph_2MeSi{\cdot}SiPh_2Me \rightarrow 2Ph_2MeSiLi + PhMe_2Si{\cdot}SiPhMe_2$$
$$2Ph_2MeSiLi + Ph_3Si{\cdot}SiPh_3 \rightarrow 2Ph_3SiLi + Ph_2MeSi{\cdot}SiPh_2Me$$

When 1,1,1-triethyl-2,2,2-triphenyldisilane was allowed to react with lithium in tetrahydrofuran, triethylsilane and triphenylsilane, in addition to a small amount of hexaethyldisilane, were isolated after acid-hydrolysis.[30] The isolation of the latter indicates the formation of triethylsilyl-lithium which, by cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane, gives triphenylsilyl-lithium and hexaethyldisilane:

$$Ph_3Si{\cdot}SiEt_3 + 2Li \rightarrow Ph_3SiLi + Et_3SiLi$$
$$Et_3SiLi + Ph_3Si{\cdot}SiEt_3 \rightarrow Ph_3SiLi + Et_3Si{\cdot}SiEt_3$$

A similar cleavage of pentaphenyldisilane by triphenylsilyl-lithium appeared to be an attractive route to the unknown species, diphenylsilyl-lithium. Although hexaphenyldisilane was actually found in this reaction,[46] diphenylsilyl-lithium seemed to decompose into lithium hydride and a diphenylsilylene polymer under the experimental conditions:

$$Ph_3SiLi + Ph_3Si{\cdot}SiPh_2H \rightarrow Ph_3Si{\cdot}SiPh_3 + Ph_2SiHLi$$
$$nPh_2SiHLi \rightarrow nLiH + (Ph_2Si)_n$$

On the assumption that the silicon–silicon bond strength remains nearly constant with varying numbers of alkyl and aryl substituents, the cleavage experiments suggest that the reactivity of silyl-lithium compounds increases with an increasing number of alkyl groups on the silicon atom:

$$Ph_3SiLi < Ph_2MeSiLi < PhMe_2SiLi < Et_3SiLi$$

2. Reactions of silylalkali-metal compounds

(a) With Hydrocarbons.—Shortly after the first successful preparation of triphenylsilylpotassium,[13,14] it was observed that this reagent adds to the olefinic linkage of *trans*-stilbene.[48] After hydrolysis, 1,2-diphenyl-1-triphenylsilylethane was isolated:

$$Ph_3SiK + PhCH{=}CHPh \xrightarrow[H_2O]{} Ph_3Si{\cdot}CHPh{\cdot}CH_2Ph$$

However, it was found that the reaction of triphenylsilyl-lithium with *trans*-stilbene in ethylene glycol dimethyl ether did not yield this product; instead, a number of more complex compounds including 1,2-diphenyl-1,2-bistriphenylsilylethane and 1,2,3,4-tetraphenyl-1-triphenylsilylbutane were formed.[49] The results suggest that the addition product, formed initially, behaved as an active organometallic reagent which could react with other stilbene molecules as has been observed in other cases.[50,51]

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[48] H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.*, 1953, **75**, 234.
[49] A. G. Brook, K. M. Tai, and H. Gilman, *ibid.*, 1955, **77**, 6219.
[50] K. Ziegler, H. Grimm, and R. Willer, *Annalen*, 1939, **542**, 90.
[51] K. Ziegler and H. Kleiner, *ibid.*, 1929, **473**, 57.

Treatment of tolane with triphenylsilyl-lithium yielded, in addition to polymeric material, some 1,2-diphenyl-1,2-bistriphenylsilylethane.[49] Formation of this product suggests that two moles of the Si–Li reagent added across the triple bond of tolane:

$$2Ph_3SiLi + PhC{\equiv}CPh \xrightarrow[H_2O]{} Ph_3Si{\cdot}CHPh{\cdot}CHPh{\cdot}SiPh_3$$

Triphenylsilyl-lithium in tetrahydrofuran and triphenylsilylpotassium in ethyl ether were also found to add to 1,1-diphenylethylene and to triphenylethylene.[52] Attempts to add the same reagents to tetraphenylethylene and to a variety of aliphatic and cycloalkenes were, however, unsuccessful.[52]

Recently it was found that triphenylsilyl-lithium adds smoothly to anthracene, to give 9,10-dihydro-9-lithio-10-triphenylsilylanthracene.[53]

Triphenylsilyl-potassium, -sodium, and -lithium were found to metallate triarylmethanes.[54] Whereas tetraphenylmethane was unaffected by triphenylsilyl-lithium,[33] fluorene was readily metallated to yield triphenylsilane and 9-fluorenyl-lithium.[33] If the silylmetallic reagent is present in excess in metallations, it slowly reacts further with the triarylsilane to yield a tetra-arylsilane.[47]

(b) **With Organic Halides.**—In reactions of silylalkali-metal compounds with organic halides, three different modes of interaction have been observed: direct coupling; halogen–metal interconversion; and dehydrohalogenation.

(*i*) *Alkyl and aralkyl halides.* Although no alkyl fluorides have yet been investigated, reactions of triphenylsilyl-lithium with butyl and allyl chloride give high yields of the coupling products, butyltriphenylsilane and allyltriphenylsilane, respectively.[55] With alkyl bromides, fair yields of

$$Ph_3SiLi + BuCl \rightarrow Ph_3SiBu + LiCl$$

coupling products have been obtained by using triphenylsilylpotassium in ether. On the other hand, alkyl bromides react with triphenylsilyl-lithium mainly by halogen–metal interconversion, to give hexaphenyldisilane.[55] On reaction of triphenylsilyl-lithium with 1,4-dibromobutane, only 3% of tetramethylenebistriphenylsilane was isolated, hexaphenyldisilane being the main product.[56] Methyl iodide and triphenylsilylpotassium afforded 33% of methyltriphenylsilane and 52% of hexaphenyldisilane.[34]

Low yields of isopropyltriphenylsilane were obtained from triphenylsilyl-lithium and isopropyl chloride;[55] none was isolated, however, when isopropyl bromide was used and no cyclohexyltriphenylsilane was formed from cyclohexyl bromide and triphenylsilylpotassium.[57] The hexaphenyldisilane is the result of a halogen–metal interconversion when t-butyl

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[52] T. C. Wu and D. Wittenberg, unpublished studies.

[53] O. L. Marrs, unpublished studies.

[54] A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 1954, **76**, 2338.

[55] H. Gilman and D. Aoki, *J. Org. Chem.*, 1959, **24**, 426.

[56] D. Wittenberg and H. Gilman, *J. Amer. Chem. Soc.*, 1958, **80**, 2677.

[57] A. G. Brook and S. Wolfe, *ibid.*, 1957, **79**, 1431.

bromide and triphenylsilyl-lithium are allowed to interact. In contrast, t-butyl chloride gives mainly triphenylsilane under the same conditions;[55] this process probably involves dehydrohalogenation:

$$Ph_3SiLi + Me_3CCl \rightarrow Ph_3SiH + Me_2C{=}CH_2 + LiCl$$

The reaction of benzyl chloride with triphenylsilylpotassium gave fair yields of benzyltriphenylsilane, in addition to bibenzyl and hexaphenyldisilane:[15,57]

$$Ph_3SiK + Ph{\cdot}CH_2Cl \rightarrow Ph_3SiCl + Ph{\cdot}CH_2K$$

$$Ph{\cdot}CH_2K + Ph_3SiK + Ph{\cdot}CH_2Cl \rightarrow Ph{\cdot}CH_2{\cdot}CH_2Ph + Ph_3Si{\cdot}CH_2Ph + Ph_3Si{\cdot}SiPh_3$$

Attempts to prepare triphenyltriphenylmethylsilane from triphenylmethyl chloride and triphenylsilylpotassium yielded hexaphenyldisilane and hexaphenylethane instead.[42] This again demonstrates the occurrence of halogen–metal interconversion.

The use of alkyl sulphates instead of alkyl halides in coupling reactions with silylalkali-metal compounds greatly diminishes or entirely eliminates any side halogen–metal interconversion-type reactions. For example, when 5-lithio-5-methyldibenzosilole[20] was treated with methyl sulphate, only 5,5-dimethyldibenzosilole was isolated

(*ii*) *Aryl halides.* Bromobenzene has been widely used for preparing derivatives from triphenylsilylpotassium;[13,14,15,34,55,57] however, tetraphenylsilane has rarely been obtained in yields exceeding 50%.

Slightly higher yields have been obtained by using chlorobenzene instead.[15,55] Fluorobenzene reacts extremely slowly,[15] possibly because of metallation in the *ortho*-position. Extensive and excellent studies by Brook and Wolfe[57] have demonstrated that, with aryl bromides and chlorides, halogen–metal interconversion can account for the side-products which were isolated. By adding triphenylsilylpotassium to a mixture of bromobenzene and benzophenone, they were able to capture phenylpotassium as triphenylmethanol:

$$Ph_3SiK + PhBr \rightarrow Ph_3SiBr + PhK \rightarrow Ph_3C{\cdot}OH$$

As a method of choice, 2-triphenylsilyldibenzothiophen and 9-ethyl-3-triphenylsilylcarbazole have been obtained from the corresponding bromides and triphenylsilylpotassium.[58] Similarly, tetra-*p*-biphenylylsilane was prepared from 4-bromobiphenyl and tri-*p*-biphenylylsilylpotassium,[34] while *p*-fluorophenyltriphenylsilane was obtained from *p*-bromofluorobenzene and triphenylsilyl-lithium.[55]

Brook and Wolfe[57] were able to show that the yields and nature of the products from silylmetallic compounds and organic halides are greatly influenced by the mode of addition. Addition of the silylmetallic compound to the halide, the reverse addition, and slow simultaneous addition of the reagents have been employed. It was found that simultaneous addition gave the highest yields of coupling products. The yields of interconversion products seem to increase, while the yields of coupling products decrease,

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[58] R. Meen and H. Gilman, *J. Org. Chem.*, 1955, **20**, 73.

when the silylpotassium reagent in ether is replaced by the corresponding silyl-lithium reagent in tetrahydrofuran.

(c) **With Aldehydes and Ketones.**—In general, silylmetallic compounds react with *aliphatic* aldehydes and ketones in the same manner as do organolithium and Grignard reagents, to give silyl-substituted alcohols. Triphenylsilylmethanol results from the reaction of triphenylsilylpotassium with formaldehyde;[59] 1-triphenylsilylethanol[60,61] and 1-triphenylsilylpropan-1-ol[62] were formed on reaction of the corresponding silyl-lithium reagent with acetaldehyde and propionaldehyde, respectively.

Similarly, triphenylsilyl-lithium was shown to add normally to acetone,[63,64] cyclohexanone,[64] nonadecan-2-one, octadecan-3-one, pentadecan-8-one, and tricosan-12-one,[64] *e.g.*:

$$Ph_3SiLi + COMe_2 \xrightarrow[H_2O]{} Ph_3Si{\cdot}CMe_2{\cdot}OH$$

An important side-reaction is the abstraction of an acidic hydrogen atom from the aldehyde or ketone by the silyl-lithium compound, to give the corresponding silicon hydride as by-product.[60,64]

In one case the yield of triphenylsilane from the reaction of triphenylsilyl-lithium with dibenzyl ketone was 78%. None of the α-silyl-alcohol was isolated.[64]

Rather surprising results were obtained from reactions involving silylalkali-metal compounds with aromatic ketones. Triphenylsilylpotassium was found to add to benzophenone, to give after hydrolysis diphenylmethoxytriphenylsilane rather than the expected diphenyltriphenylsilylmethanol.[65] Since silylmetallic compounds add normally to aliphatic ketones and, since the closely related triphenylgermylmetallic compounds give normal addition products with benzophenone,[66,67] it did not seem likely that inverse addition had taken place. It was postulated therefore that normal addition had occurred, followed by rearrangement. Triphenylsilyl-lithium, methyldiphenylsilyl-lithium, and dimethylphenylsilyl-lithium in tetrahydrofuran solution were also found to give the corresponding alkoxysilanes instead of alcohols.[68] The "rearrangement hypothesis" was supported by experiments by Brook,[63] who succeeded in preparing diphenyltriphenylsilylmethanol and showed that under mild basic conditions this compound rearranges to give diphenylmethoxytriphenyl silane:

$$Ph_3SiLi + Ph_2CO \rightarrow [Ph_3Si{\cdot}C(OLi)Ph_2] \rightarrow Ph_3Si{\cdot}O{\cdot}CPh_2Li \xrightarrow[H_2O]{} Ph_3Si{\cdot}O{\cdot}CHPh_2$$

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[59] H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.*, 1954, **76**, 2502.
[60] D. Wittenberg and H. Gilman, *ibid.*, 1958, **80**, 4529.
[61] A. G. Brook, C. M. Warner, and M. E. McGriskin, *ibid.*, 1959, **81**, 981.
[62] H. Gilman and D. J. Peterson, *J. Org. Chem.*, 1958, **23**, 1895.
[63] A. G. Brook, *J. Amer. Chem. Soc.*, 1958, **80**, 1886.
[64] H. Gilman and G. D. Lichtenwalter, *ibid.*, p. 2680.
[65] H. Gilman and T. C. Wu, *ibid.*, 1953, **75**, 2935.
[66] H. Gilman and C. W. Gerow, *ibid.*, 1955, **77**, 5740.
[67] A. G. Brook and N. V. Schwartz, unpublished studies.
[68] H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.*, 1958, **80**, 607.

It is noteworthy that in carbon chemistry the corresponding "Wittig rearrangement"[69–72] takes a completely different course; phenyl-substituted ethers rearrange upon metallation to the corresponding alcohols:

$$\mathrm{Ph{\cdot}CH_2{\cdot}OR} \xrightarrow[\mathrm{PhLi}]{} \mathrm{PhCHLi{\cdot}OR} \rightarrow \mathrm{PhCHR{\cdot}OLi} \xrightarrow[\mathrm{H_2O}]{} \mathrm{PhCHR{\cdot}OH}$$

Schlenk and Ochs reported[73] that the deeply coloured benzophenone ketyl is formed in the reaction between triphenylmethylsodium and benzophenone. The question, whether the deep blue colour of reaction mixtures of silylmetallic compounds with benzophenone is also due to a metal ketyl, or to the C–M type addition product, is still unanswered. Brook and his co-workers[74] recently showed, that under certain conditions, triphenylsilylalkali-metal reagents react with 2 mols. of benzophenone; after hydrolysis, tetraphenyl-2-triphenylsiloxyethanol is isolated. The reaction might possibly involve an equilibrium of the following type:

$$\mathrm{Ph_3Si{\cdot}O{\cdot}CLiPh_2 + Ph_2CO \rightleftharpoons Ph_3Si{\cdot}O{\cdot}CPh_2{\cdot}CPh_2{\cdot}OLi}$$

The formation of small amounts of benzpinacol from the reactions of benzophenone with methyldiphenylsilyl-lithium or dimethylphenylsilyl-lithium may involve a similar intermediate.[68]

Carboxylation of a reaction mixture from triphenylsilylpotassium and benzophenone gave benzilic acid and triphenylsilanol.[74] The reaction may possibly involve a cleavage similar to that observed in carboxylation of α-lithiobenzyltriphenylsilane:[75]

$$\mathrm{Ph_3Si{\cdot}O{\cdot}CPh_2K} \xrightarrow[\mathrm{CO_2,H_2O}]{} \mathrm{Ph_3Si{\cdot}OH + Ph_2C(OH){\cdot}CO_2H}$$

From the reaction of triphenylsilyl-lithium with benzaldehyde, similar "abnormal" addition products were found.[76] In addition to benzyloxytriphenylsilane, hexaphenyldisilane, 1,2-diphenylethane-1,2-diol, and 1,2-diphenyl-2-triphenylsiloxyethanol were isolated.

(d) With Derivatives of Carboxylic Acids.—Brook[77] found that triphenylsilylpotassium and benzoyl chloride give a low yield of benzoyltriphenylsilane, the first reported α-silyl-ketone, in addition to hexaphenyldisilane.

From the reaction of triphenylsilyl-lithium with acetyl chloride, acetyltriphenylsilane was isolated in a low yield, together with 1,1-bis(triphenylsilyl)ethanol, triphenylsilane, and triphenyl-(1-triphenylsiloxyethyl)silane, the rearrangement product of 1,1-bis(triphenylsilyl)ethanol:[60]

$$\mathrm{Ph_3SiLi + CH_3{\cdot}COCl \rightarrow Ph_3Si{\cdot}CO{\cdot}CH_3} \xrightarrow[\mathrm{+\ Ph_3SiLi}]{}$$

$$\mathrm{(Ph_3Si)_2C(OH){\cdot}CH_3} \xrightarrow[\mathrm{Rearr.}]{} \mathrm{Ph_3Si{\cdot}CH(CH_3){\cdot}OSiPh_3}$$

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[69] G. Wittig and L. Löhmann, *Annalen*, 1942, **550**, 260.

[70] G. Wittig and W. Happe, *ibid.*, 1947, **557**, 205.

[71] G. Wittig and R. Clausnizer, *ibid.*, 1954, **588**, 145.

[72] G. Wittig and E. Stahnecker, *ibid.*, 1957, **605**, 69.

[73] W. Schlenk and R. Ochs, *Ber.*, 1916, **49**, 612.

[74] A. G. Brook, N. V. Schwartz, M. E. McGriskin, N. Wolfish, and M. Gold, unpublished studies.

[75] H. Gilman and H. Hartzfeld, *ibid.*, 1951, **73**, 5878.

[76] D. Wittenberg and T. C. Wu, unpublished studies.

[77] A. G. Brook, *J. Amer. Chem. Soc.*, 1957, **79**, 4373.

In this connection it should be pointed out that triphenylmethylsodium does not add to aliphatic acid chlorides; enolisation occurs with the quantitative formation of triphenylmethane.[78]

Acetic anhydride and ethyl acetate, on treatment with triphenylsilyl-lithium, gave results[62] analogous to those observed in the acetyl chloride reaction. Triphenyl-(1-triphenylsiloxypropyl)silane was isolated when propionyl chloride was allowed to react with the same silyl-lithium reagent, while phenylacetyl chloride was predominantly enolised.[62] Acrylonitrile was polymerised by triphenylsilyl-lithium.[62]

Lithium cyanide and tetraphenylsilane were among the products obtained on reaction of benzonitrile with triphenylsilyl-lithium. The nitrile group in this reaction behaves as a pseudo-halide:[62]

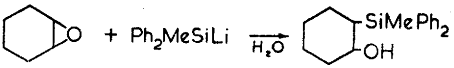
$$\mathrm{PhCN + Ph_3SiLi \rightarrow Ph_4Si + LiCN}$$

The reaction of methyl triphenylgermanecarboxylate with triphenylsilyl-lithium gave an excellent yield of triphenylgermyltriphenylsilane:[79]

$$\mathrm{Ph_3SiLi + Ph_3Ge{\cdot}CO_2Me \rightarrow Ph_3Si{\cdot}GePh_3 + LiOMe + CO}$$

(e) **With Epoxides and Ethers.**—Although the reactions of silyl-lithium reagents with aliphatic ketones, aldehydes, and acid chlorides [sections 2(c) and (d)] have proved useful methods for the preparation of certain α-silyl-alcohols, a variety of β-silyl-alcohols have been synthesised from the reactions of silyl-lithium reagents with epoxides.[80]

When triphenylsilyl-lithium was allowed to react with ethylene oxide, propylene oxide, styrene oxide, and cyclohexene oxide, good yields of 2-triphenylsilylethanol, 1-triphenylsilylpropan-2-ol, 1-phenyl-2-triphenylsilylethanol, and 2-triphenylsilylcyclohexanol, respectively, were obtained.[80] Similarly, methyldiphenylsilyl-lithium added to styrene oxide and cyclohexene oxide to give 2-(methyldiphenylsilyl)-1-phenylethanol and 2-(methyldiphenylsilyl)cyclohexanol, respectively:[80]



If these few experiments allow generalisation, silyl-lithium reagents seem to add to epoxides in the selective manner characteristic of organolithium

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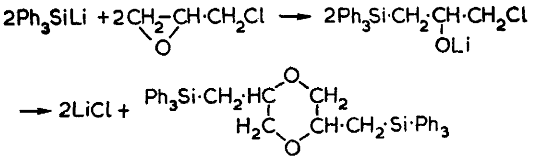
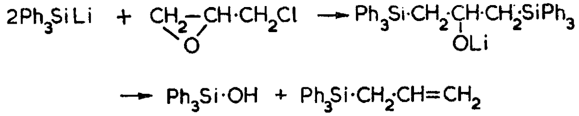
[78] W. Schlenk and E. Bergmann, *Annalen*, 1928, **464**, 1.
[79] H. Gilman and C. W. Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 4675.
[80] (*a*) H. Gilman, D. Aoki, and D. Wittenberg, *ibid.*, 1959, **81**, 1107; (*b*) D. Aoki, unpublished studies.

compounds.[81,82] Likewise, triphenylgermyl-lithium has recently been reported to add to certain epoxides.[83]

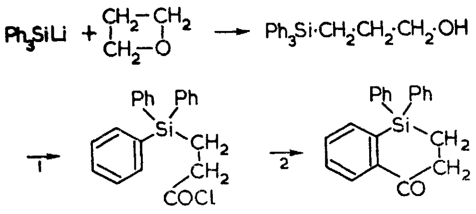
Though the reaction of aryl-lithium compounds with epichlorohydrin has been used as a convenient synthesis of arylpropylene chlorohydrins,[84] no corresponding compound has been isolated by utilising triphenylsilyllithium. Instead, there were found allyltriphenylsilane,[80] 1-chloro-3-triphenylsilylpropan-2-ol, 1,3-bistriphenylsilylpropan-2-ol, and triphenylsilanol, in addition to 2,5-bis(triphenylsilylmethyl)-1,4-dioxan:[80b]





A high yield of hexaphenyldisilane, together with some allyltriphenylsilane and triphenylsilanol, were obtained when triphenylsilyl-lithium was allowed to react with epibromohydrin;[80] the reaction apparently involved a halogen–metal interconversion.[85]

The reaction of Grignard reagents and organolithium compounds with trimethylene oxide has been shown to give good yields of 3-substituted alcohols.[86] Similarly, with triphenylgermyl-lithium, 3-triphenylgermyl-



Reagents: 1, CrO_3, then SO_2Cl_2. 2, $AlCl_3$.

[81] S. J. Cristol, J. R. Douglas, and J. S. Meek, *J. Amer. Chem. Soc.*, 1951, **73**, 816.

[82] For a detailed discussion of reactions of Grignard reagents with epoxides, see the excellent reviews by N. G. Gaylord and E. I. Becker, *Chem. Rev.*, 1951, **49**, 413; S. Winstein and R. B. Henderson in Chapter I, Vol. I, of Elderfield's "Heterocyclic Compounds," John Wiley & Sons, Inc., New York, N.Y., 1950; and M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice Hall, Inc., New York, N.Y., 1954.

[83] H. Gilman, C. W. Gerow, and M. B. Hughes, unpublished studies.

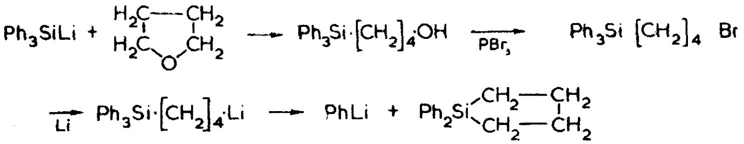
[84] H. Gilman, B. Hofferth, and J. Honeycutt, *J. Amer. Chem. Soc.*, 1952, **74**, 1594.

[85] See section 2(b).

[86] S. Searles, *J. Amer. Chem. Soc.*, 1951, **73**, 124.

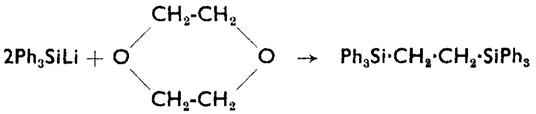
propanol was obtained.[83] Triphenylsilyl-lithium produced the corresponding 3-triphenylsilylpropanol in a 77% yield.[18] This alcohol on oxidation yielded β-triphenylsilyl propionic acid. The corresponding acid chloride, on treatment with aluminium chloride in nitrobenzene, underwent cyclisation to give 1,2,3,4-tetrahydro-4-oxo-1,1-diphenyl-1-silanaphthalene, the first reported derivative in the silanaphthalene series.[87]

Wittig and Rückert[88] reported that tetrahydrofuran is unaffected by triphenylmethylsodium, but is readily cleaved by the same reagent in the presence of triphenylboron. Normant[89] found that Grignard reagents cleave tetrahydrofuran at 200° to give primary alcohols of the type $R\cdot[CH_2]_4\cdot OH$. Triphenylsilyl-lithium, as well as methyldiphenylsilyl-lithium, cleaved this solvent slowly at the boiling point,[36] and more readily at 125°, to give 4-triphenylsilylbutan-1-ol and 4-(methyldiphenylsilyl)s butan-1-ol,[18] respectively. Conversion of these alcohols into the bromide- and subsequent treatment with lithium offers a new route to silacyclopentanes *via* an intramolecular cleavage-cyclisation:[58]



None of the expected 5-triphenylsilylpentanol was isolated when triphenylsilyl-lithium was prepared in tetrahydropyran and allowed to react with the solvent at elevated temperatures: instead, a high-melting polymer was obtained.[18]

Ethylene glycol dimethyl ether was cleaved by triphenylsilyl-lithium to give methyltriphenylsilane in high yield. The corresponding cleavage of dioxan gave ethylenebistriphenylsilane, in addition to ethyltriphenylsilane, tetraphenylsilane, and unidentified products:[18]



Only a small amount of benzyltriphenylsilane, the ether cleavage product, was obtained when triphenylsilyl-lithium was allowed to react with benzyl methyl ether. The main reaction involved a metallation of the ether.[18]

The reaction of phenyl-lithium with 1,4-epoxy-1,4-dihydronaphthalene, a highly strained cyclic ether, has been reported to yield 2-phenylnaphthalene.[90,91] The corresponding reaction with triphenylsilyl-lithium gave the expected silicon compound, 2-naphthyltriphenylsilane in low yield.

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[87] P. B. Talukdar and D. Wittenberg, unpublished studies.
[88] G. Wittig and A. Rückert, *Annalen*, 1950, **566**, 104.
[89] H. Normant, *Compt. rend.*, 1954, **239**, 1510.
[90] G. Wittig and L. Pohmer, *Chem. Ber.*, 1956, **89**, 1334.
[91] G. Wittig, *Angew. Chem.*, 1957, **69**, 245.

Naphthalene and triphenylsilanol were obtained as the main products. These were probably formed as a result of the aromatisation of an alcohol formed as an intermediate.

Cleavage of alkyl dialkylaminomethyl ethers with Grignard reagents[92,93] and organolithium compounds[94] has been described as a convenient synthesis of certain tertiary amines. Similarly, triphenylsilyl-lithium was found to cleave 1-(n-butoxymethyl)piperidine to give 1-(triphenylsilylmethyl)piperidine:[18]

$$C_4H_9{\cdot}O{\cdot}CH_2{\cdot}NC_5H_{10} + Ph_3SiLi \rightarrow Ph_3Si{\cdot}CH_2{\cdot}NC_5H_{10} + C_4H_9{\cdot}OLi$$

(f) **With Nitrogen Compounds.**—During early attempts to prepare silylmetallic compounds, Kraus and Eatough[2] treated bromotriphenylsilane with lithium in ethylamine, to obtain *N*-ethyltriphenylsilylamine. Trimethyltriphenylsilyltin[2] and hexaphenyldisilane[23] have been cleaved by sodium in liquid ammonia, and triethyltriphenylgermylsilane by lithium in ethylamine.[27] However, since all silylalkali-metal compounds seem to react readily with ammonia, ammonia and ethylamine are probably not suitable solvents for their preparation.

When silyl-lithium compounds prepared in tetrahydrofuran were allowed to react with several primary and secondary amines,[95] an instantaneous reaction occurred and a negative colour test[17] was obtained. Working up the reaction mixture gave lithium hydride and good yields of silylamines:

$$Ph_3SiLi + R_2NH \rightarrow Ph_3SiH + R_2NLi \rightarrow LiH + Ph_3Si{\cdot}NR_2$$

N-n-Butyl-1,1,1-triphenylsilylamine, 4-triphenylsilylmorpholine, and 1,4-bistriphenylsilylpiperazine are a few representative compounds prepared by this method. The reaction apparently proceeds in two steps, the first being a metallation of the amine, and the second a hydride displacement by the amide anion. Analogous reactions of triphenylsilane with lithium dialkylamides have been reported.[9] Diphenylamine[95] and *N*-(diphenylmethyl)aniline[96] were also metallated by triphenylsilyl-lithium. In these cases, however, no secondary coupling occurred.

Whereas alkyl- and aryl-lithium compounds attack pyridine in the 2-position,[97] and selective nucleophiles such as benzylmagnesium chloride[98,99] and allylmagnesium bromide[100] give very low yields of 4-substituted products, triphenylsilyl-lithium adds smoothly to pyridine, to give good yields of 4-triphenylsilyl-1,4-dihydropyridine, a compound

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[92] G. M. Robinson and R. Robinson, *J.*, 1923, **123**, 532.
[93] S. P. Massie, *Iowa State Coll. J. Sci.*, 1946, **21**, 41 (*Chem. Abs.*, 1947, **41**, 3044).
[94] A. H. Haubein, *ibid.*, 1943, **18**, 48 (*Chem. Abs.*, 1944, **38**, 716).
[95] H. Gilman and G. Lichtenwalter, unpublished studies.
[96] D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles, and H. Gilman, *ibid.*, p. 4532.
[97] K. Ziegler and A. Zeiser, *Ber.*, 1930, **63**, 1847; *Annalen*, 1931, **485**, 174.
[98] W. L. C. Veer and S. Goldsmidt, *Rec. Trav. chim.*, 1946, **65**, 793.
[99] R. A. Benkeser and D. S. Holton, *J. Amer. Chem. Soc.*, 1951, **73**, 5861.
[100] H. Gilman, J. Eisch, and T. S. Soddy, *ibid.*, 1957, **79**, 1245.

which is easily oxidised to 4-triphenylsilylpyridine.[22] None of the 2-substituted isomer was detected. In contrast, triphenylmethylsodium, and the even more reactive diphenylmethylsodium, do not react with pyridine.[101,102]

Triphenylsilyl-lithium has also been found to add to acridine in the 9,10-positions, to yield, after hydrolysis, 9-triphenylsilylacridan.[103]

One distinct chemical difference between Grignard reagents and organolithium compounds is demonstrated by their modes of addition to the azomethine linkage of benzophenone anil. It has been shown that phenylmagnesium bromide does not react in ether, but under forced conditions a lateral-nuclear 1,4-addition occurs to give *N*-(α-2-biphenylylbenzyl)aniline.[104,105] Phenyl-lithium, however, with benzophenone anil gives a 1,2-addition product, *N*-(triphenylmethyl)aniline.[106,107] The compound formed on the reaction of triphenylsilyl-lithium or -potassium with benzophenone anil was *N*-diphenylmethyl-*N*-phenyl-1,1,1-triphenylsilylamine, an "abnormal" addition product containing a Si–N bond:[96]

$$\mathrm{Ph_3SiK + Ph_2C{=}NPh \rightarrow (Ph_3Si)Ph_2C{\cdot}NKPh \xrightarrow[H_2O]{} Ph_2CH{\cdot}NPh{\cdot}SiPh_3}$$

The "abnormal" addition may be visualised to occur analogously to the related reactions of aromatic ketones with silylmetallic compounds by assuming that the initial step involves a "normal" addition and is followed by a rearrangement.

Although phenylmagnesium bromide, phenyl-lithium, and phenylsodium react with azobenzene at room temperature, yielding hydrazobenzene and biphenyl, reactions at low temperatures have been found to give mediocre yields of triphenylhydrazine, the addition product.[108-110] Triphenylsilyl-potassium and -lithium add smoothly to the azo-linkage to give *NN'*-diphenyl-*N*-triphenylsilylhydrazine in high yields.[96] The compound was synthesised unambiguously from *NN'*-dilithio-*NN'*-diphenylhydrazine and chlorotriphenylsilane in tetrahydrofuran:

$$\mathrm{Ph_3SiK + PhN{=}NPh \xrightarrow[H_2O]{} Ph_3Si{\cdot}PhN{\cdot}NHPh \xleftarrow[H_2O]{} Ph_3SiCl + PhNLi{\cdot}NLiPh}$$

The same compound was obtained in fair yield on reaction of triphenylsilyl-lithium with azoxybenzene.[111] In this reaction, in which triphenylsilanol was formed as a by-product, the mechanism possibly

[101] K. Ziegler and H. Wollschitt, *Annalen*, 1930, **479**, 123.

[102] E. Bergmann and W. Rosenthal, *J. prakt. Chem.*, 1932, **135**, 267.

[103] H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, 1958, **23**, 1586.

[104] H. Gilman, J. E. Kirby, and C. R. Kinney, *J. Amer. Chem. Soc.*, 1929, **51**, 2252.

[105] R. C. Fuson, R. J. Lokken, and R. L. Pedrotti, *ibid.*, 1956, **78**, 6064.

[106] H. Gilman and R. H. Kirby, *ibid.*, 1933, **55**, 1265.

[107] J. Eisch and H. Gilman, *Chem. Rev.*, 1957, **57**, 525.

[108] H. Gilman and J. C. Bailie, *J. Org. Chem.*, 1937, **2**, 84.

[109] F. M. Beringer, J. A. Farr, jun., and S. Sands, *J. Amer. Chem. Soc.*, 1953, **75**, 3984.

[110] P. F. Holt and B. P. Hughes, *J.*, 1954, 764; 1955, 1320.

[111] M. V. George, P. B. Talukder, C. W. Gerow, and H. Gilman, unpublished studies.

involves reduction of the N–O linkage and subsequent addition of a second molecule of the silyl-lithium reagent to the azobenzene:

$$\mathrm{Ph_3SiLi + PhN{=}NPh \rightarrow Ph_3Si{\cdot}OLi + PhN{=}NPh \xrightarrow[Ph_3SiLi]{} Ph_3Si{\cdot}PhN{\cdot}NLiPh}$$

Whereas phenyl isocyanate with triphenylsilylpotassium gave large amounts of hexaphenyldisilane in addition to some *sym*-diphenylurea, phenyl isothiocyanate reacted with two molecules of triphenylsilylpotassium, to give a compound which may be bis(triphenylsilyl) ketone anil:[112]

$$\mathrm{2Ph_3SiK + PhN{=}C{=}S \rightarrow K_2S + (Ph_3Si)_2C{=}NPh}$$

Reactions of silylmetallic compounds with nitriles have been discussed in section 2 (d).

(g) **With Organosulphur Compounds.**—Only a few reactions between silylmetallic compounds and organosulphur compounds have been investigated and rather unexpected results have been obtained.

Butyl-lithium has been reported to metallate diphenyl sulphide in the *ortho*-position.[113] With phenylsodium,[114] as well as with diphenyl-lithium-sodium,[115] dibenzothiophen was obtained as a secondary product. The reaction of diphenyl sulphide with triphenylsilyl-lithium, followed by carboxylation, gave benzoic acid and thiophenol, in addition to hexaphenyldisilane:[116]

$$\mathrm{Ph_2S + Ph_3SiLi \rightarrow PhLi + Ph_3Si{\cdot}SPh}$$
$$\mathrm{Ph_3Si{\cdot}SPh + Ph_3SiLi \rightarrow PhSLi + Ph_3Si{\cdot}SiPh_3}$$

The formation of these products is best explained by a cleavage of the phenyl–sulphur bond to give phenyl-lithium and triphenyl(phenylthio)-silane; the latter then couples with triphenylsilyl-lithium to form hexaphenyldisilane and lithium phenyl sulphide. The last step is analogous to the reported cleavage of triphenyl-(*p*-tolylthio)silane by triphenylsilyl-lithium to give hexaphenyldisilane and lithium *p*-tolyl sulphide.[117,118]

Hexaphenyldisilane and tetraphenylsilane were isolated after reaction of diphenyl sulphone with triphenylsilylpotassium. With triphenylsilyl-lithium, *m*-phenylenebistriphenylsilane, triphenylsilanol, hexaphenyldisiloxane, benzenesulphinic acid, thiophenol, and hydrogen sulphide in addition to hexaphenyldisilane and tetraphenylsilane were isolated from the reaction mixtures. Benzoic acid and *p*-triphenylsilylbenzoic acid were identified in carboxylated reaction mixtures.[116] The mode of formation of these compounds is still unknown. As the initial step, a cleavage of the phenyl–sulphur bond has been postulated, since only benzoic acid,

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[112] T. C. Wu, unpublished studies.

[113] H. Gilman and R. L. Bebb, *J. Amer. Chem. Soc.*, 1939, **61**, 109.

[114] V. A. Lüttringhaus, G. Wagner-v. Säaf, E. Sucker, and G. Borth, *Annalen*, 1945, **557**, 54.

[115] G. Wittig and E. Benz, *Chem. Ber.*, 1958, **91**, 873.

[116] D. Wittenberg, T. C. Wu, and H. Gilman, *J. Org. Chem.*, 1959, **23**, 1898.

[117] H. Gilman and D. Wittenberg, *J. Amer. Chem. Soc.*, 1957, **79**, 6339.

[118] D. Wittenberg, H. A. McNinch, and H. Gilman, *ibid.*, 1958, **80**, 5418.

triphenylsilanol, and benzenesulphinic acid are formed at low temperatures:

$$\begin{aligned} &Ph{\cdot}SO_2{\cdot}Ph + Ph_3SiLi \rightarrow PhLi + Ph_3Si{\cdot}SO_2{\cdot}Ph \\ &\xrightarrow[CO_2,\ H_2O]{} Ph{\cdot}CO_2H + Ph{\cdot}SO_2H + Ph_3Si{\cdot}OH \end{aligned}$$

An attempt to synthesise triphenyl(phenylsulphonyl)silane from triphenylsilyl-lithium and benzenesulphonyl chloride resulted in the formation of hexaphenyldisilane and lithium benzenesulphinate:

$$2Ph_3SiLi + Ph{\cdot}SO_2Cl \rightarrow Ph_6Si_2 + Ph{\cdot}SO_2Li + LiCl$$

(h) With Organosilicon Compounds.—(*i*) *Silicon halides.* The reaction of silylmetallic compounds with a variety of chlorosilanes has been used in syntheses of disilanes, especially unsymmetrical ones which are inaccessible by other methods. 1,1,1-Trimethyl-2,2,2-triphenyldisilane has been prepared by reaction of triphenylsilyl-potassium,[13,14,15,16] -lithium,[16,19,36] -rubidium[15b] and -cæsium[15b] with chlorotrimethylsilane. Similarly, 1,1,1-triethyl-2,2,2-triphenyldisilane has been prepared from triphenylsilylpotassium and chlorotriethylsilane,[13,15,28,34] 1,1,1-trihexadecyl-2,2,2-triphenyldisilane from triphenylsilyl-lithium and chlorotrihexadecylsilane,[119] and 1,1-dimethyl-1,2,2,2-tetraphenyldisilane from triphenylsilylpotassium and methyldiphenylsilyl chloride.[28]

A number of hexa-aryldisilanes containing phenyl and *p*-tolyl groups was obtained by coupling a triarylsilylpotassium with a triarylchlorosilane.[24] Partially chlorinated disilanes have been synthesised by reactions involving triphenylsilylpotassium with one equivalent of silicon tetrachloride, trichlorophenylsilane, and dichlorodiphenylsilane. The products were 1,1,1-trichloro-2,2,2-triphenyldisilane,[24] 1,1-dichloro-1,2,2,2-tetraphenyldisilane,[24] and chloropentaphenyldisilane,[15] respectively.

When two equivalents of triphenylsilylpotassium were allowed to react with dichlorodiphenylsilane, octaphenyltrisilane was formed:[15,120]

$$Ph_3SiK + Ph_2SiCl_2 \rightarrow Ph_3Si{\cdot}SiPh_2Cl \xrightarrow[Ph_3SiK]{} Ph_3Si{\cdot}SiPh_2{\cdot}SiPh_3$$

Reaction of triphenylsilyl-lithium with trichlorosilane gave a small amount of tristriphenylsilylsilane, the first reported branched-chain polysilane.[46]

Although coupling reactions of triarylsilyl-lithium compounds with aryl- and alkyl-substituted chlorosilanes seem to proceed without complications, reactions of silyl-lithium reagents containing alkyl as well as aryl groups with chlorotriphenylsilane yielded mixtures of several disilanes.[19] Further, the nature of the products was dependent upon the mode of addition. Slow addition of dimethylphenylsilyl-lithium to chlorotriphenylsilane gave 1,1-dimethyl-1,2,2,2-tetraphenyldisilane. When the

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[119] D. H. Miles, unpublished studies.

[120] H. Gilman and J. J. Goodman, *J. Amer. Chem. Soc.*, 1953, **75**, 1250.

reverse addition was employed, hexaphenyldisilane and 1,1,2,2-tetramethyl-1,2-diphenyldisilane were formed.[19] The products appear to indicate that halogen–metal interconversion occurred between the Si–Li and Si–Cl compounds, but subsequent studies have confirmed that cleavages of disilanes by silyl-lithium reagents are involved. In the presence of excess of the silyl-lithium reagent, the initial coupling product is cleaved by the silylmetallic compound, to give a symmetrical disilane and a less reactive silyl-lithium compound[30] [see section 1(e)]:

$$\begin{aligned}
\mathrm{PhMe_2SiLi + Ph_3SiCl} &\rightarrow \mathrm{PhMe_2Si{\cdot}SiPh_3 + LiCl} \\
\mathrm{PhMe_2SiLi + PhMe_2Si{\cdot}SiPh_3} &\rightarrow \mathrm{PhMe_2Si{\cdot}SiPhMe_2 + Ph_3SiLi} \\
\mathrm{Ph_3SiLi + Ph_3SiCl} &\rightarrow \mathrm{Ph_3Si{\cdot}SiPh_3 + LiCl}
\end{aligned}$$

Large amounts of hexaphenyldisilane have been isolated after reactions of triphenylsilyl-lithium with silicon tetrachloride, trichlorosilane, ethyl silicate, dichlorodiphenylsilane, and chloropentaphenyldisilane.[46] This effect is much more pronounced with silyl-lithium reagents in tetrahydrofuran than with silylpotassium reagents in ethyl ether. A mechanism involving the cleavage of a disilane by the silylmetallic compound has been proposed:

$$\begin{aligned}
\mathrm{Ph_3SiLi + SiCl_4} &\rightarrow \mathrm{Ph_3Si{\cdot}SiCl_3} \xrightarrow[+\ \mathrm{Ph_3SiLi}]{} \mathrm{Ph_3Si{\cdot}SiPh_3 + LiSiCl_3} \\
n\mathrm{LiSiCl_3} &\rightarrow n\mathrm{LiCl + (SiCl_2)}_n \\
\mathrm{Ph_3Si{\cdot}SiPh_2Cl + Ph_3SiLi} &\rightarrow \mathrm{Ph_3Si{\cdot}SiPh_3 + Ph_2SiClLi} \\
n\mathrm{Ph_2SiClLi} &\rightarrow n\mathrm{LiCl + (Ph_2Si)}_n
\end{aligned}$$

When (diphenylmethoxy)diphenylsilane, obtained from diphenylsilane and benzophenone,[121] was allowed to react with triphenylsilyl-lithium, diphenylmethanol was formed in high yield, in addition to some pentaphenyl disilane. Some hexaphenyldisilane was formed owing to further attack of pentaphenyldisilane by the silyl-lithium reagent [see section 1(e)].

Related cleavages of disilanes by organometallic compounds have been known since 1869 when Friedel and Ladenburg[122] investigated the reaction of diethylzinc with hexaiododisilane and obtained the expected hexaethyldisilane in addition to some tetraethylsilane. Similarly, tetraphenylsilane was the only product from hexachlorodisilane, chlorobenzene, and sodium.[123] When octachlorotrisilane was treated with phenylmagnesium bromide, the products were hexaphenyldisilane and tetraphenylsilane.[124]

(*ii*) *Silicon hydrides.* Reactions of excess of triphenylsilylpotassium with phenylacetylene as well as with several phenyl-substituted alcohols gave high yields of tetraphenylsilane.[125] Similarly, triarylmethanes when treated with an excess of a triarylsilylpotassium compound gave tetra-arylsilanes.[54] A subsequent investigation showed that in all of these experiments, the

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[121] H. Gilman and D. Wittenberg, *J. Org. Chem.*, 1958, **23**, 501.

[122] C. Friedel and A. Ladenburg, *Compt. rend.*, 1869, **68**, 923; *Annalen*, 1880, **203**, 251.

[123] L. Gattermann and K. Weinlig, *Ber.*, 1894, **27**, 1946.

[124] W. C. Schumb and C. M. Saffer, *J. Amer. Chem. Soc.*, 1939, **61**, 363.

[125] H. Gilman and T. C. Wu, *ibid.*, 1953, **75**, 2509.

tetra-arylsilane is formed by reaction of a triarylsilylmetal with a triarylsilane:[126]

$$R_3SiK + R_3SiH \rightarrow R_4Si + \text{"other products"}$$

Examination of a number of reactions proved that it is possible to cleave more than one aryl group from a triarylsilane.[126] The reaction is even more complex when the silylmetallic compound and the silane have different aryl groups:

$$R_3SiK + R'_3SiH \rightarrow R_4Si + R_3SiR' + R'_3SiR + R'_4Si + \text{"other products"}$$

Thus, tetraphenylsilane, tetra-*p*-tolylsilane, and phenyltri-*p*-tolylsilane were isolated from the products of reaction of triphenylsilylpotassium with tri-*p*-tolylsilane in ethyl ether. Tetraphenylsilane and phenyltri-*p*-tolylsilane were formed from tri-*p*-tolylsilylpotassium and triphenylsilane.[126]

The reaction of triphenylsilyl-lithium with triphenylsilane is slower and gives a high yield of tetraphenylsilane in tetrahydrofuran at elevated temperatures.[36] The same reaction in ethylene glycol dimethyl ether seems to take a different course: hexaphenyldisilane as well as tetraphenylsilane were isolated.[126] The coupling of triphenylsilyl-lithium with triphenylsilane to form hexaphenyldisilane is not unexpected, since treatment of triphenylsilane with organolithium compounds is a well-recognised method for preparing tetrasubstituted silanes:[7]

$$Ph_3SiLi + Ph_3SiH \rightarrow Ph_3Si{\cdot}SiPh_3 + LiH$$

The formation of tetra-arylsilanes in these reactions, however, is surprising and is still not completely understood.

(i) **With Inorganic Compounds.**—(*i*) *Hydrolysis.* The products formed by hydrolysis of silylmetallic compounds depend on the conditions employed. Benkeser and Severson[13] have shown that decomposition of triphenylsilylpotassium with hydrochloric acid yields triphenylsilane. In the presence of sodium–potassium alloy, treatment with dry hydrogen chloride, diluted with oxygen-free nitrogen, has been recommended.[13] Only triphenylsilanol was obtained on reaction of triphenylsilylpotassium with water.[15] It seems certain that under these conditions the silicon hydride, formed initially, is attacked by the strong base formed during hydrolysis, to yield the silanol and gaseous hydrogen:[127]

$$Ph_3SiK + H_2O \rightarrow Ph_3SiH + KOH$$

$$Ph_3SiH + H_2O \xrightarrow[(KOH)]{} Ph_3Si{\cdot}OH + H_2$$

If water, an alcohol, or other acidic compound is employed, in an amount insufficient for complete hydrolysis of the silylmetallic reagent, interaction may take place between the silicon hydride formed and the silylmetallic compound [see section 2(h)].

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[126] A. G. Brook and H. Gilman, *ibid.*, 1954, **76**, 2333.

[127] For a theoretical discussion of the conversion of silicon hydrides into silanols under conditions of aqueous hydrolysis see H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, 1951, **73**, 3404.

(*ii*) *Carboxylation*. Carboxylation of triphenylsilylpotassium was found to yield an unstable acid which decomposed at its melting point to give carbon monoxide and, together with other products, triphenylsilanol.[13] Later studies described experimental conditions for the preparation of pure triphenylsilanecarboxylic acid in good yields.[15,21,128] In a basic medium the acid is readily decomposed to carbon monoxide and triphenylsilanol. It is possible to convert triphenylsilyl-lithium into triphenylsilanol in excellent yields by this method.[128] Base-catalysed eliminations and thermal rearrangements of triphenylsilanecarboxylic acid, its derivatives, and related compounds have been published recently.[25,129]

$$\mathrm{Ph_3SiK + CO_2 \rightarrow Ph_3Si{\cdot}CO_2K \rightarrow Ph_3Si{\cdot}CO_2H \rightarrow Ph_3Si{\cdot}OH + CO}$$

(*iii*) *Oxygen*. Reactions of triphenylsilyl-lithium with oxygen have been studied[21] for tetrahydrofuran and tetrahydropyran solutions at temperatures of 25°, 0° and −25°. The products were triphenylsilanol, triphenylsilane, and hexaphenyldisilane. Higher temperatures resulted in an increased amount of hexaphenyldisilane and a decreased amount of triphenylsilanol. The mechanism of the reaction is not clear, but may involve a free-radical path:

$$\begin{array}{lll}
\mathrm{Ph_3SiLi + O_2} & \rightarrow & \mathrm{Ph_3Si{\cdot}O{\cdot}OLi \xrightarrow[\mathrm{Ph_3SiLi}]{} 2Ph_3Si{\cdot}OLi} \\
\mathrm{Ph_3Si{\cdot}O{\cdot}OLi} & \rightarrow & \mathrm{Ph_3Si{\cdot}O{\cdot} + {\cdot}OLi} \\
\mathrm{Ph_3Si{\cdot}O{\cdot} + Ph_3SiLi} & \rightarrow & \mathrm{Ph_3Si{\cdot}OLi + Ph_3Si{\cdot}} \\
\mathrm{Ph_3Si{\cdot} + Solvent} & \rightarrow & \mathrm{Ph_3SiH} \\
\mathrm{2Ph_3Si{\cdot}} & \rightarrow & \mathrm{Ph_3Si{\cdot}SiPh_3}
\end{array}$$

(*iv*) *Sulphur*. Triphenylsilyl-lithium in tetrahydrofuran reacts smoothly with sulphur to give the lithium salt of triphenylsilanethiol. Subsequent reactions of this intermediate with methyl iodide, benzyl chloride, and benzoyl chloride have afforded methylthio-, benzylthio-, and benzoylthiotriphenylsilane, respectively, in good yields,[130] *e.g.*:

$$\mathrm{Ph_3SiLi + S \rightarrow Ph_3Si{\cdot}SLi \xrightarrow[\mathrm{MeI}]{} Ph_3Si{\cdot}SMe + LiI}$$

3. Compounds containing silicon bonded to non-alkali metals

(a) **Magnesium.**—Cusa and Kipping[131] in 1933 obtained dicyclohexylphenylsilane by reaction of trichlorophenylsilane with cyclohexylmagnesium bromide. This unexpected result was explained by postulating the intermediate formation of a silyl-Grignard reagent from chlorodicyclohexylphenylsilane and cyclohexylmagnesium bromide by means of a halogen–metal interconversion. A corresponding reaction between

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[128] A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 1955, **77**, 2322.
[129] A. G. Brook, *ibid.*, p. 4827.
[130] G. D. Lichtenwalter, unpublished studies.
[131] N. W. Cusa and F. S. Kipping, *J.*, 1933, 1040.

chlorotriphenylmethane and phenylmagnesium bromide has been reported by Gomberg and Cone:[132]

$$\mathrm{Ph_3CCl + PhMgX \rightarrow Ph_3C{\cdot}MgX \xrightarrow[H_2O]{} Ph_3CH}$$

$$\mathrm{Ph(C_6H_{11})_2SiCl + C_6H_{11}MgBr \rightarrow Ph(C_6H_{11})_2Si{\cdot}MgX}$$

A recent re-investigation[133] of Kipping's results showed that several sterically hindered Grignard reagents, such as those containing the cyclohexyl, cyclopentyl, isopropyl, or isobutyl group, react with trichlorophenylsilane to give compounds of the PhR_2SiH type, and further that the silicon hydride is formed before hydrolysis of the reaction mixture. The corresponding unsaturated hydrocarbons, cyclohexene, cyclopentene, propene, and isobutene were also identified as reaction products:

$$\mathrm{PhR_2SiCl + C_6H_{11}MgBr \rightarrow PhR_2SiH + C_6H_{10} + MgBrCl}$$

Similarly, triphenylsilane and cyclohexene were isolated after reaction of chlorotriphenylsilane with cyclohexylmagnesium bromide.[57] No silylmagnesium compound could be detected in these reactions. However, when tetrahydrofuran was employed as the solvent, a different course of reaction was observed. Hexaphenyldisilane was isolated in high yield when chlorotriphenylsilane was refluxed in this solvent with cyclohexyl-, 2-methylcyclohexyl- or phenyl-magnesium bromide.[133b] Chlorotrimethylsilane under corresponding conditions remained unchanged. The formation of triphenylsilylmagnesium bromide as an intermediate was confirmed by employing a mixture of chlorotriphenylsilane and chlorotrimethylsilane, which yielded 1,1,1-trimethyl-2,2,2-triphenyldisilane, the unsymmetrical coupling product.

$$\mathrm{Ph_3SiCl + 2C_6H_{11}MgBr \rightarrow Ph_3SiMgBr + C_6H_{12} + C_6H_{10} + MgClBr}$$

$$\mathrm{Ph_3SiMgBr + Ph_3SiCl \rightarrow Ph_3Si{\cdot}SiPh_3 + MgClBr}$$

$$\mathrm{Ph_3SiMgBr + Me_3SiCl \rightarrow Ph_3Si{\cdot}SiMe_3 + MgClBr}$$

It has been observed that magnesium dissolves in a solution of silyl iodide in isopentyl ether. The formation of silane, hydrogen, and silicon as the hydrolysis products was interpreted as meaning that an unstable silylmagnesium iodide was formed.[134] Silyl bromide, however, was found[135] not to react with magnesium in butyl ether. Neither triethyliodosilane[136] nor chlorotriphenylsilane[15b] reacts with magnesium in ether.

Preliminary experiments, however, indicate that formation of silylmagnesium reagents is also possible from the corresponding silyl-lithium compound and anhydrous magnesium bromide in tetrahydrofuran.[130]

(b) **Mercury.**—An unstable, volatile compound, possibly $SiH_3{\cdot}HgI$, has been reported from the reaction products of silyl iodide with mercury,

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[132] M. Gomberg and L. H. Cone, *Ber.*, 1906, **39**, 1461.

[133] (*a*) M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Amer. Chem. Soc.*, 1957, **79**, 2762; (*b*) T. G. Selin and R. West, *Tetrahedron*, 1959, **5**, 97.

[134] H. J. Emeléus, A. G. Maddock, and C. Reid, *Nature*, 1939, **144**, 328; *J.*, 1941, 353.

[135] E. R. Van Artsdalen and J. Gavis, *J. Amer. Chem. Soc.*, 1952, **74**, 3196.

[136] C. Eaborn, *J.*, 1949, 2755.

but no details of its properties were given.[134] Results obtained from reactions of silylmetallic compounds with organomercury compounds and mercury halides[137] also indicate the existence of unstable silicon–mercury compounds.

The reaction of triphenylsilyl-lithium with diphenylmercury in a 1:1 ratio yielded, after carboxylation, benzoic acid, tetraphenylsilane, and mercury. In an analogous reaction with di-*p*-tolylmercury, the products isolated were *p*-toluic acid, triphenyl-*p*-tolysilane, and mercury:

$$\mathrm{Ph_3SiLi + R_2Hg \rightarrow RLi + Ph_3Si{\cdot}HgPh \xrightarrow[CO_2,H_2O]{} R{\cdot}CO_2H + Ph_3SiR + Hg}$$

Similarly, tetraphenylsilane and metallic mercury were obtained from triphenylsilyl-lithium and phenylmercuric chloride. The formation of chlorotriphenylsilane and hexaphenyldisilane from mercury(II) chloride and triphenylsilyl-lithium was explained by a similar mechanism:

$$\mathrm{Ph_3SiLi + HgCl_2 \rightarrow LiCl + Ph_3Si{\cdot}HgCl \rightarrow Ph_3SiCl + Hg}$$

(c) **Germanium and Tin.**—Two different methods have been employed for the preparation of silicon–germanium and silicon–tin bonds: the reaction of a silylmetallic compound with a germanium or tin halide, and the reaction of a silicon halide with a germyl- or tin-metallic compound.

Triphenyltriphenylsilylgermane was obtained from the reaction of triphenylsilylpotassium with bromo- or chloro-triphenylgermane.[41] This compound was isolated also after reaction of triphenylsilyl-lithium with methyl triphenylgermanecarboxylate.[79] Reactions of triphenylgermylpotassium, -sodium, and -lithium with chloro- or bromo-triethylsilane gave triphenyltriethylsilylgermane.[27,138]

A quantitative yield of tristriphenylgermylsilane was obtained from triphenylgermylsodium and trichlorosilane.[43,44] Lithium in ethylamine converted the compound into the corresponding silyl-lithium derivative which, on subsequent coupling with ethyl bromide, gave ethyltristriphenylgermylsilane:

$$\mathrm{3Ph_3GeNa + SiHCl_3 \rightarrow (Ph_3Ge)_3SiH \rightarrow (Ph_3Ge)_3SiEt}$$

The same silyl-lithium reagent, when allowed to react with chlorotriphenyltin, yielded triphenyltris(triphenylgermyl)silyltin, the first reported compound containing a Ge–Si–Sn linkage:[139]

$$\mathrm{(Ph_3Ge)_3SiLi + ClSnPh_3 \rightarrow (Ph_3Ge)_3Si{\cdot}SnPh_3}$$

Trimethyltriphenylsilyltin was formed from triphenylsilyl-lithium and chlorotrimethyltin.[2] Triphenyltriphenylsilyltin has been obtained both

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[137] M. V. George, G. D. Lichtenwalter, and H. Gilman, *J. Amer. Chem. Soc.*, 1959, **81**, 978.

[138] H. Gilman and C. W. Gerow, *ibid.*, 1955, **77**, 5509.

[139] J. J. Goodman, unpublished studies.

from triphenylsilylpotassium with chlorotriphenyltin,[15b] and from chlorotriphenylsilane with triphenylstannyl-lithium.[140]

Various stable silylmetallic compounds are listed in Table 3.

(d) Other Metals.—π-Cyclopentadienyldicarbonyl(trimethylsilyl)iron, a compound which is thought to contain a true silicon–iron bond, has been prepared from the corresponding sodium derivative and chlorotrimethylsilane.[141] The compound decomposes at 200° and reacts readily with oxygen:

$$(C_5H_5)(CO)_2FeNa + Me_3SiCl \rightarrow NaCl + (C_5H_5)(CO)_2Fe{\cdot}SiMe_3$$

TABLE 3. *Stable silylmetallic compounds*

Compound	Prepared from	M.p.	Yield (%)	Ref.
$Ph_3Si{\cdot}GePh_3$	$Ph_3SiK + Ph_3GeCl$	354—355°	43—63	41
	$Ph_3SiLi + Ph_3Ge{\cdot}CO_2Me$	357—359	84	79
$Et_3Si{\cdot}GePh_3$	$Ph_3GeNa + Et_3SiBr$	93·5	—	27
	$Ph_3GeK(Li) + Et_3SiCl$	97—98	40—63	138
$(Ph_3Ge)_3SiH$	$Ph_3GeNa + SiHCl_3$	170—171 187—188	100	44
$(Ph_3Ge)_3SiEt$	$(Ph_3Ge)_3SiLi + EtBr$	283	63	44
$(Ph_3Ge)_3SiBr$	$(Ph_3Ge)_3SiH + Br_2$	242	—	44
$(Ph_3Ge)_3SiCl$	$(Ph_3Ge)_3SiNH_2 + HCl$	230—231	—	44
$(Ph_3Ge)_3SiOH$	$(Ph_3Ge)_3SiBr + NH_4OH$	197	—	44
$(Ph_3Ge)_3Si{\cdot}NH_2$	$(Ph_3Ge)_3SiBr + NH_3$	206	—	44
$(Ph_3Ge)_3Si{\cdot}SnPh_3$	$(Ph_3Ge)_3SiLi + Ph_3SnCl$	340—342	15·5	139
$Ph_3Si{\cdot}SnMe_3$	$Ph_3SiLi + Me_3SnCl$	Liquid	—	2
$Ph_3Si{\cdot}SnPh_3$	$Ph_3SiK + Ph_3SnCl$	296—298	76	15*b*
	$Ph_3SiCl + Ph_3SnLi$	289—291	71	140
$(C_5H_5)(CO)_2Fe{\cdot}SiMe_3$	$(C_5H_5)(CO)_2FeNa$ $+ Me_3SiCl$	70	42	141

When silyl iodide was allowed to react with metallic zinc for a year in a sealed tube, a non-volatile liquid was obtained which showed the properties expected for silylzinc iodide.[134]

Preliminary experiments[33,130] indicate that several compounds containing silicon bonded to non-alkali metals are formed in reactions of silyllithium compounds with anhydrous metal halides in tetrahydrofuran. Many of these new silylmetallic compounds, however, are unstable and only their decomposition products have been isolated so far. Research in this field is still in progress.

4. Analytical procedures

(a) Colour Tests.—The most widely applied colour test for reactive organometallic compounds involves their reaction with Michler's ketone[17] which gives, after hydrolysis and oxidation with iodine in acetic acid, a

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[140] H. Gilman and S. D. Rosenberg, *J. Amer. Chem. Soc.*, 1952, **74**, 531.

[141] T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwiss.*, 1956, **43**, 129.

blue or blue-green colour. When triphenylsilylpotassium in ether was tested,[15] the supernatant liquid gave a Negative Colour Test I, whereas the precipitate gave an intense blue-violet colour in both the organic and the aqueous layer. Similarly, solutions of silyl-potassium, -sodium, and -lithium reagents in ethylene glycol dimethyl ether[16] and tetrahydrofuran[19] have been found to give a positive colour test I.

Colour Test IIA, the reaction of an organometallic compound with *p*-bromodimethylaniline followed by treatment with benzophenone and concentrated hydrochloric acid with production of a red colour, has been used to distinguish between highly reactive alkyl-lithium and less reactive aryl-lithium compounds.[142] Silyl-lithium compounds[33] gave a slightly positive test only under special conditions. This phenomenon, however, is not due to a lower reactivity on the part of the Si–Li reagents, but on the contrary is a reflection of their higher reactivity which immediately gives rise to coupling products.

(b) Quantitative Methods.—In some cases yields of silylalkali-metal compounds have been determined by titration of aliquot parts of a solution of reagent with acid.[19,31] In order to determine the alkoxide which may be formed by interaction of the silylmetallic compound and the solvent, the double-titration method[143] was employed.[16,19] In this method, the total alkali is determined by the usual titration, and a second aliquot portion is added to benzyl chloride and subsequently titrated with acid to determine the alkoxide content.

As a method which is thought to give the most reliable values, the procedure of Ziegler and his co-workers[144] is recommended. An aliquot part of the solution is allowed to react with n-butyl bromide: after hydrolysis the bromide content of the aqueous layer is determined by Volhard's method.

5. Relative reactivity of silylmetallic compounds and other comparisons with related types

(a) Cleavage Reactions.—Owing to their dissociation into free radicals, hexa-arylethanes are cleaved even under mild conditions, for instance by sodium amalgam. Symmetrical tetraphenylethane required sodium–potassium alloy for its conversion into diphenylmethylpotassium, while 1,2-diphenylethane and related diarylethanes are resistant toward cleavage by metals.[145] Similarly, it was found that the rate of cleavage of symmetrical disilanes by lithium increases as the number of phenyl groups attached to the silicon atoms increases.[19] Despite the extremely low solubility of hexaphenyldisilane in organic solvents, only a few hours are required for its

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[142] H. Gilman and J. Swiss, *J. Amer Chem. Soc.*, 1940, **62**, 1847.

[143] H. Gilman and A. H. Haubein, *ibid.*, 1944, **66**, 1515.

[144] K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Annalen*, 1929, **473**, 21.

[145] F. Runge, "Organometallverbindungen", Wissenschaftl. Verlags-GmbH., Stuttgart, 1944, p. 45.

complete cleavage. Lithium in tetrahydrofuran splits *sym*-dimethyltetraphenyldisilane in less than one hour, while the corresponding cleavage of *sym*-tetramethyldiphenyldisilane requires several hours. Hexa-alkyldisilanes are not cleaved by metals. Hexa-alkyldigermanes also seem to resist cleavage by metals, whereas alkali metals readily split hexamethylditin.[5e]

Increasing atomic weight and atomic radius should be factors leading to weakening of the M–M bond in R_6M_2 compounds. Moreover, replacement of alkyl by aryl groups should aid in weakening the M–M bond because of the greater electron-withdrawing power of the aryl groups. The aforementioned cleavage studies verify these theoretical aspects. Since delocalisation of the negative charge on the aryl groups will appreciably stabilise the anion, the compounds may be arranged in the following order of stability:

$$\mathrm{Ar_3M^-} > \mathrm{Ar_2AlkM^-} > \mathrm{ArAlk_2M^-} > \mathrm{Alk_3M^-}$$

Decreasing stability is equivalent to increasing reactivity. A corresponding reactivity series of silylmetallic compounds has been deduced from cleavage of disilanes by silyl-lithium compounds [see section 1(e)].

(b) **Metallation.**—At present it seems impossible to draw general conclusions concerning the reactivity of silylmetallic in comparison with organometallic compounds, since no kinetic studies have yet been performed. Moreover, comparison of corresponding reactions indicates that a silylmetallic can be more reactive than a given organometallic compound toward one substrate and less reactive toward another.

The anions of organoalkali-metal compounds, if compared under similar conditions, can be arranged in a series of increasing proton affinity:[146,147]

$$\mathrm{Bu^-} > \mathrm{Ph^-} > \mathrm{Ph{\cdot}CH_2^-} > \mathrm{Ph_2CH^-} > \mathrm{Ph_3C^-} > \mathrm{Ph{\cdot}NH^-} > \mathrm{RO^-}$$

Thus alkylsodium compounds have been found to metallate benzene; phenylpotassium metallates toluene to give benzylpotassium; and benzylpotassium will metallate diphenylmethane. Future studies may determine the exact position which triphenyl-silyl, -germyl and -tin anions would hold in such an expanded series: at present little information is available. Phenyl-lithium and butyl-lithium have been found to metallate triphenylgermane,[148] while triphenylgermyl-lithium has been found to metallate compounds such as fluorene.[149] Related metallations involving triphenyltin and triphenylstannyl-lithium have been described.[150] A metallation of

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[146] J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1212.

[147] W. K. McEwen, *ibid.*, 1936, **58**, 1124.

[148] H. Gilman and C. W. Gerow, *ibid.*, 1956, **78**, 5435.

[149] H. Gilman and C. W. Gerow, *J. Org. Chem.*, 1958, **23**, 1582.

[150] J. d'Ans, H. Zimmer, E. Endrulat, and K. Lübke, *Naturwiss.*, 1952, **39**, 450; G. Wittig, F. J. Meyer and C. Lange, *Annalen*, 1951, **571**, 167; H. Gilman and S. D. Rosenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 3592; H. Gilman and L. A. Gist, jun., *J. Org., Chem.*, 1957, **22**, 689.

triphenylsilane has not yet been accomplished since silicon hydrides, on treatment with various anions, displace a hydride anion rather than abstract a proton.[7,9] Although alkylpotassium compounds, such as phenylpotassium and even benzylpotassium are known to metallate ethyl ether readily, triphenylsilylpotassium is stable in this solvent, indicating its lower reactivity. On the other hand, triarylmethanes are readily metallated by silylalkali-metal compounds,[54] *e.g.*, fluorene by triphenylsilyl-lithium.[33] One might estimate that the proton affinity of the triphenylsilyl anion is between that of the benzyl and the triphenylmethyl anion and perhaps comparable with the corresponding diphenylmethyl anion.

(c) **Addition.**—Various organometallic compounds have been found to add to olefins. For example, αα-dimethylbenzylpotassium adds to anthracene, stilbene and 1,1-diphenylethylene, but not to triphenylethylene.[144,151] Triphenylsilyl-lithium adds to anthracene,[53] stilbene,[48] and 1,1-diphenylethylene,[52] as well as to triphenylethylene.[52] Triphenylgermyl-lithium adds to octadec-1-ene and 1,1-diphenylethylene, but not to stilbene.[152] Triphenyltinlithium is unreactive in all similar addition reactions.[153]

Compounds containing C–Li, Si–Li, and Ge–Li linkages add to the carbonyl group of aldehydes and ketones, add to the azo- and the azomethine linkage, and cleave organic oxides such as ethylene oxide and trimethylene oxide. Corresponding Sn–Li reagents are rather unreactive and only their addition to ethylene oxide has been accomplished.[153]

In the series of the triphenyl derivatives, Ph_3C–M, Ph_3Si–M, Ph_3Ge–M, Ph_3Sn–M, the silyl- and germyl-metallic compounds seem to be the most reactive in addition. Their reactivity seems to be comparable with that of αα-dimethylbenzylpotassium. Steric effects, as well as differences in electron-distribution in the carbon–metal and metal–metal bonds in these compounds, seem to be responsible for the specific differences observed in some of their additive reactions.

(d) **Coupling and Interconversion Reactions.**—Reactions of halides with organometallic compounds are known to proceed mainly by two routes: coupling and halogen–metal interconversion. Coupling of C–M, Si–M, Ge–M, Sn–M, and Pb–M types with alkyl and aryl halides have been widely applied for synthetic purposes. Interconversion has been used for the preparation of certain organolithium compounds[4,10] which are inaccessible by other methods.

Alkyl-lithium reagents convert aryl bromides and iodides into aryl-lithium compounds. Aryl-lithium reagents show interconversion with benzyl-type halides, as well as with aryl iodides. Germylmetallic compounds have not been fully investigated: only coupling, and no interconversion, products have been reported from their reactions with halides. Some stannyl-lithium compounds have been found to undergo halogen–metal

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[151] K. Ziegler and K. Bähr, *Ber.*, 1928, **61**, 253.
[152] H. Gilman and C. W. Gerow, *J. Amer. Chem. Soc.*, 1957, **79**, 342.
[153] H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, 1953, **18**, 1554.

interconversion with certain aryl iodides.[154] Silylmetallic compounds, as described in section 2(b), exhibit an extremely high order of reactivity in interconversion. Silylpotassium and, especially, silyl-lithium reagents give interconversion products not only when allowed to react with aryl bromides and iodides, but also when they react with aryl chlorides, alkyl bromides, and alkyl iodides. The phenylthio- and the phenylsulphonyl radical seem to act as pseudo-halogens since phenyl-lithium is formed in the reactions of triphenylsilyl-lithium with diphenyl sulphide and with diphenyl sulphone.[116]

Silylmetallic compounds also show a high order of reactivity in coupling reactions. When triphenylsilyl-lithium and phenyl-lithium were allowed to compete for chlorotriphenylsilane at −50°, hexaphenyldisilane was isolated in 85% yield and tetraphenylsilane in only 1·5% yield.

Reasons for the increased reactivity of silylmetallic compounds become clearer on comparison of bond energies of corresponding carbon and silicon compounds. Despite the fact that Si–H and Si–C bonds are slightly weaker than C–H and C–C bonds, silicon forms stronger bonds than carbon with electronegative elements such as O, N, F, Cl, Br, and I.[1f] Recent studies have shown that the triphenylsilyl radical readily abstracts a chlorine radical from chlorobenzene, a reaction not observed with hydrocarbon radicals.[155] The same tendency of silicon to combine with electronegative elements gives rise to interconversion when silylmetallic compounds are allowed to react with organic halides.

(e) **Conclusion.**—Organosilylmetallic compounds are a relatively new development in chemistry. Fortunately, they can now be prepared directly and with ease. The uncommon diversity of their chemical behaviour is striking. They promise to open broad avenues for the synthesis of organosilicon types which are either novel or have been inaccessible hitherto.

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[154] H. Gilman and S. D. Rosenberg, *ibid.*, p. 680.
[155] J. Curtice, H. Gilman, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1957, **79**, 4754.