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Aryloxy and related organosilicon chemistry

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ARYLOXY AND RELATED ORGANOSILICON CHEMISTRY

by

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I. INTRODUCTION

The thermal stability of silicone and organosilicon oils
is well known and has been utilized to solve many of the
lubrication problems arising in modern day aircraft. However,
silicones are not very effective in maintaining their unique
properties, such as foam suppression, after irradiation.[1]

In direct contrast to this is the high radiation resist-
ance exhibited by the polyaryl ethers, which have been herald-
ed as possible strong competitors for future markets in high
temperature lubricants.[2] These new materials are reported to
have a considerably larger useful temperature range than the
present materials and to be two to five times more stable
under nuclear radiation.[3,4] The logical extension of this
work was to incorporate these two moieties into a single mole-
cule, with the hope of producing a lubricant with still great-
er thermal and nuclear radiation stability.[4]

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[1] A. H. Matuszak. Nuclear radiation resistant turbine
engine lubrcants. Wright Air Development Center Technical
Report 57-255. September 1957.

[2] New ethers pace lubricants. Chem. Eng. News, 37, 64,
April 13, 1959.

[3] W. L. Rice. Nuclear radiation resistant lubricants.
Wright Air Development Center Technical Report 57-299, Part
II. May 1958.

[4] C. L. Mahoney, W. W. Kerlin, E. R. Barnum, K. J. Sax,
W. S. Saari and P. H. Williams. Engine oil development.
Wright Air Development Center Technical Report 57-177, Part
II. August 1958.

The general purpose of this investigation was to synthesize unique silicon derivatives of aryloxy compounds and to explore more fully the fundamental chemistry of such systems. In the course of the study, it was necessary at times to deviate from aryloxy systems to related areas in order to correlate their interesting chemistry with that of other organosilicon compounds.

The specific purposes of this investigation have been: (1) to improve the dimetalation of diphenyl ether, the intermediate in the preparation of oxygen containing cyclic silicon compounds; (2) to prepare unsymmetrical and other unique derivatives of phenoxasilin, the silicon analog of xanthene; (3) to prepare, for the first time, silicon derivatives of xanthene; (4) to continue the exploratory investigation of the reactions of silylmetallic compounds,[5] specifically with oxygen containing substrates, and to bring more clearly into focus the relative reactivities of these silylmetallic reagents; (5) to prepare and investigate the chemistry of some silanecarboxylic acids possessing greater stability than those presently known.

The historical section has been developed in such a manner that the information which is presented will be pertinent to the ensuing investigation and discussion.

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[5] For a summarizing review on organosilylmetallic chemistry, see D. Wittenberg and H. Gilman, Quart. Rev., 13, 116 (1959).

II. HISTORICAL

A. Organometallic Reactions with Diphenyl Ether

1. Organolithium reagents

The first report of the metalation of diphenyl ether by an organolithium reagent is credited to Gilman and Bebb.[6] By reacting n-butyllithium with diphenyl ether in petroleum ether for twenty hours, these workers were able to isolate o-phenoxybenzoic acid in a 7% yield. Using ethyl ether as the solvent, the yields were increased to 54 and 60% at the end of six hours and twenty hours, respectively. Diphenyl ether was also metalated by tert.-butyllithium to give a 14.0% yield of the acid on carbonation.[7]

The dimetalation of diphenyl ether was achieved by the use of n-butyllithium.[8] However, it was necessary to reflux two equivalents of n-butyllithium with diphenyl ether for a total of seventy-two hours before the metalation had proceeded to a satisfactory extent. In order to prove that dimetalation had occurred in the 2,2'-positions, the dilithium compound was carbonated and the product so formed was acidified to yield

[6]H. Gilman and R. L. Bebb, J. Am. Chem. Soc., 61, 109 (1939).

[7]H. Gilman, A. H. Haubein and H. Hartzfeld, J. Org. Chem., 19, 1034 (1954).

[8]K. Oita and H. Gilman, J. Am. Chem. Soc., 79, 339 (1957).

the known acid, 2,2'-dicarboxydiphenyl ether, in 23.4% yield.
Further proof was obtained by reaction of the 2,2'-dilithio-
diphenyl ether with R_2SiX_2 reagents to obtain the appropriate
cyclic silicon compounds.[8,9]

When the phenyl ether contained a halogen substituent,
an interesting side reaction was observed. If n-butyllithium
and p-bromophenyl phenyl ether were refluxed together for
twenty hours and then carbonated, a yield of 20% of 5-bromo-
2-phenoxybenzoic acid was obtained.[10] No o- or p-phenoxy-
benzoic acids were isolated. If the reaction was run for a
short time, a 70% yield of p-phenoxybenzoic acid was obtain-
ed.[11] This supported the suggestion that a halogen-metal
interconversion occurred, with subsequent metalation of
p-bromophenyl phenyl ether by the new organolithium reagent.[12]

The reaction was later studied in more detail,[13] and it
was found that when the halogen was iodine or bromine,

[9]H. Gilman and D. Miles, J. Org. Chem., 23, 1363 (1958).

[10]H. Gilman, W. Langham and A. L. Jacoby, J. Am. Chem. Soc., 61, 106 (1939).

[11]H. Gilman, W. Langham and F. W. Moore, ibid., 62, 2327 (1940).

[12]For a review on the halogen-metal interconversion reaction, see H. Gilman and J. W. Morton, Jr. The halogen-metal interconversion reaction with organolithium compounds. In R. Adams, ed. in chief. Organic reactions. Vol. 6, p. 339. New York, N. Y., John Wiley and Sons, Inc. 1951.

[13]W. Langham, R. Q. Brewster and H. Gilman, J. Am. Chem. Soc., 63, 545 (1941).

halogen-metal interconversion was the predominant reaction under mild conditions. Iodophenyl phenyl ethers underwent interconversions more readily than bromophenyl phenyl ethers, and chlorophenyl phenyl ethers were essentially not affected. Under more drastic conditions, however, the p-halogenophenyl phenyl ethers underwent appreciable metalation with methyllithium, n-butyllithium and phenyllithium. In all cases the metal entered the position ortho to the ether linkage in the halogenated nucleus. Halogen-metal interconversion was not observed between p-halogenophenyl phenyl ethers and methyllithium. The lack of halogen-metal interconversion with p-chlorophenyl phenyl ether was later utilized in the preparation of silicon derivatives of phenyl ether with the silicon ortho to the oxygen in the halogen-substituted ring.[14]

Several attempts were made to cleave diphenyl ether with organolithium reagents in a similar manner as is done with organosodium compounds. The latter cleavages will be discussed in more detail in the next section of this historical discussion. It will suffice at present to mention only several reactions along this line with organolithium compounds. Lüttinghaus and Sääf[15] could isolate no phenolic products after diphenyl ether had been reacted with phenyllithium at

[14]K. Oita and H. Gilman, J. Org. Chem., 21, 1009 (1956).

[15]A. Lüttringhaus and G. Sääf, Angew. Chem., 51, 915 (1938).

38° for four and one-half days. Wittig and Pohmer[16] treated diphenyl ether with phenyllithium for four weeks at room temperature and subsequently reacted the mixture with benzophenone. In addition to a small amount of recovered starting material, they isolated the metalation derivative, o-phenoxytritanol, which could be cyclized to 9,9-diphenylxanthene. Again there was no evidence indicating ether cleavage. However when the reaction was run at 20° for four days and at 60° for the same length of time, a 7% yield of o-phenoxybiphenyl was obtained. Obviously, metalation predominated over cleavage.

It should be noted in review that in every instance of metalation with organolithium reagents, the position of attack has been ortho to the oxygen.

2. Organosodium reagents

In 1939, Lüttringhaus and Sääf[17] found that the reaction of diphenyl ether with phenylsodium gave a large number of products, which included o-phenylphenol, biphenyl, 2-phenoxybiphenyl, and di-2-biphenyl ether. The results were rationalized by assuming that metalation ortho to the oxygen had occurred, followed by some unique rearrangement. A similar rearrangement was also observed with the higher homologs, such

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[16]G. Wittig and L. Pohmer, Ber., 89, 1334 (1956).

[17]A. Lüttringhaus and G. Sääf, Ann., 542, 241 (1939).

as the biphenyl ethers.[16,18] In a like manner, diphenyl ether
with triphenylmethylsodium was reported to have given tetra-
phenylmethane, phenol, and o-phenylphenol.[19]

In 1955, Lüttringhaus and Schubert[20] suggested that evi-
dence existed for the presence of the o-phenylene double rad-
ical, more commonly called "benzyne", in these reactions. The
benzyne intermediate had been proposed previously by Wittig[21]
in 1942 to explain some organometallic reactions with fluoro-
benzene, and by Roberts and co-workers[22] in 1953 to explain
the reactions of chlorobenzene with potassium amide. Lüttring-
haus and Schubert[20] reported, as evidence for this intermedi-
ate, that diphenyl ether could be metalated directly with
sodium-potassium alloy to obtain as products o- and p-phenyl-
phenolate salts, 2-phenoxybiphenyl, higher phenols, triphenyl-
ene and 4,5,9,10-dibenzopyrene. The o-potassiophenyl phenyl
ether (I) apparently dissociated into the potassium salt of
phenol and benzyne (II). Dimerization of the latter gave

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[18]A. Lüttringhaus and G. Sääf, ibid., 557, 25 (1945).

[19]A. Lüttringhaus, G. Sääf, E. Sucker and G. Borth,
ibid., 557, 46 (1945).

[20]A. Lüttringhaus and K. Schubert, Naturwiss., 42, 17
(1955).

[21]G. Wittig, ibid., 30, 699 (1942).

[22]J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and
C. W. Vaughan, J. Am. Chem. Soc., 75, 3290 (1953).

diphenylene; trimerization gave triphenylene (III); and addi-

tion of one more C_6H_4 gave the dihydro form of 4,5,9,10-

dibenzopyrene (IV), which easily lost its two hydrogen atoms.

Although the rearrangement was well known and a possible

mechanism had been proposed, there was still no real proof for

the benzyne intermediate. It was three years later before

Lüttringhaus and Schuster[23] obtained this proof through an

excellent investigation. They noted that triphenylmethyl-

sodium did not react under their conditions with diphenyl

ether. Accordingly, triphenylmethylsodium and isoamylsodium

were placed in the same reaction mixture with diphenyl ether,

and tetraphenylmethane was isolated as the reaction product.

This provided more proof for the existence of the benzyne (II)

intermediate, and incidentally provided an excellent method

for the synthesis of tetraphenylmethane.

As mentioned in the previous section, there was no re-

action when diphenyl ether was reacted with phenyllithium at

$38°$ for four and one-half days[15] or for four weeks at room

temperature.[16] However, when diphenyl ether and phenyllithium

were reacted for four days at $20°$ and four days at $60°$, a 7%

yield of o-phenoxybiphenyl, a benzyne product, was obtained.

The reaction of diphenyl ether with diphenyllithium-

sodium reagent for four days with subsequent derivatization

[23]A. Lüttringhaus and H. Schuster, <u>Angew. Chem.</u>, <u>70</u>, 438 (1958).

II $\xrightarrow{\text{Trimerization}}$

III   + II

IV

II + $(C_6H_5)_3CNa \longrightarrow (C_6H_5)_3C$
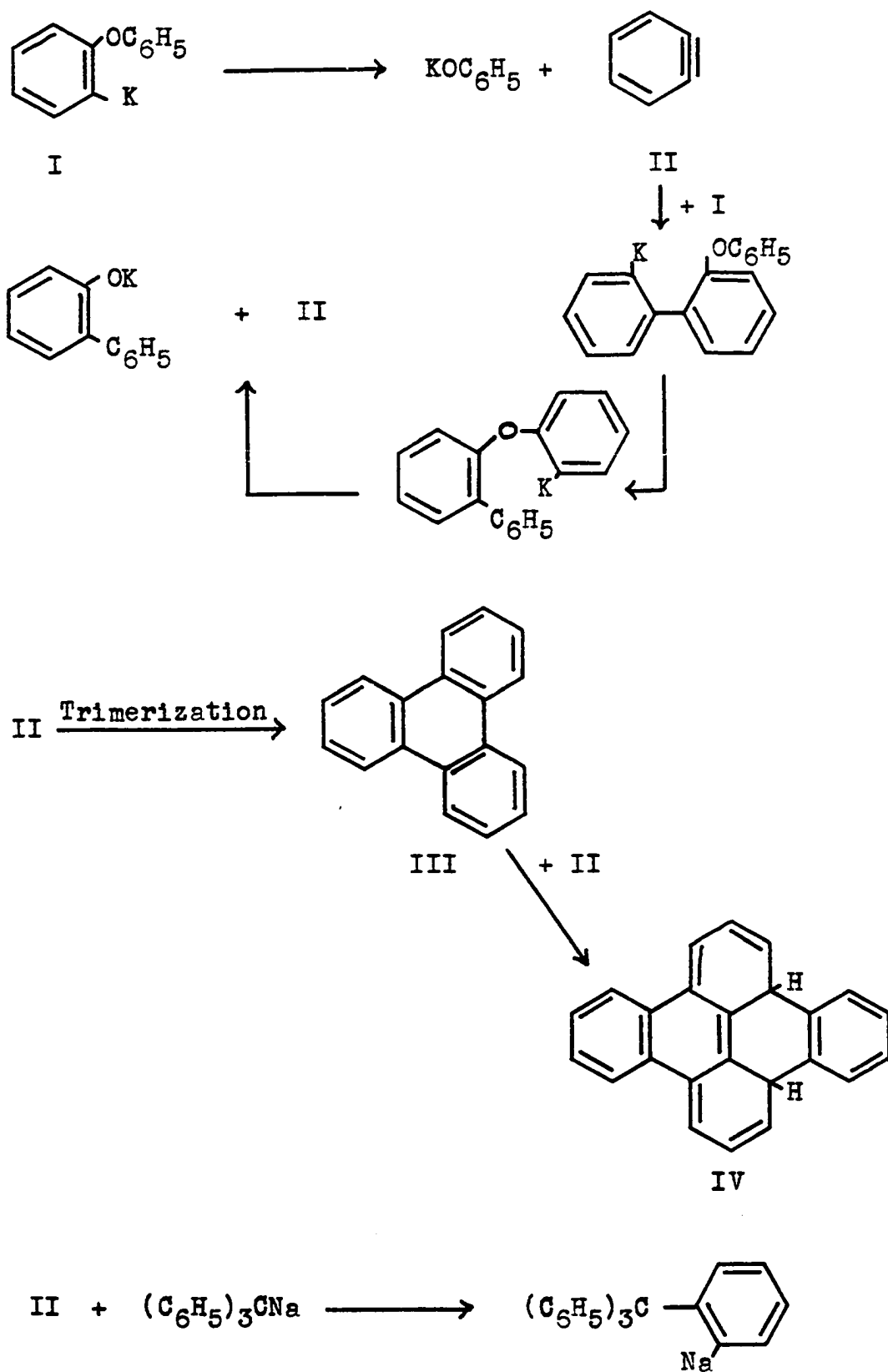
with benzophenone gave bis-(α-hydroxybenzhydryl)diphenyl ether, recovered diphenyl ether and o-phenoxytritanol, the normal ketone addition product.[16] Treating the ether with the same reagent for four days at 20° and four days at 60° gave 28% of phenol, 20% of o-phenylphenol and 19% of o-phenoxybiphenyl. It appears that the more strongly electropositive sodium, compared to lithium, facilitates cleavage in the ortho-position. Thus, the benzyne is observed in the reaction of organosodium reagents with diphenyl ether; while metalation is the predominant reaction with organolithium reagents.

3. Organomercury reagents

The mercuration of diphenyl ether by mercuric acetate in glacial acetic acid gave good results.[24,25] In all cases the 4-mercuri compound was isolated. This is in contrast to anisole which gave 14% ortho and 86% para substitution.[25] Considering the relative steric requirements of the methoxy group with that of phenoxy, it would be expected that the amount of ortho substitution in diphenyl ether would be quite small.

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[24]W. D. Schroeder and R. Q. Brewster, J. Am. Chem. Soc., 60, 751 (1938).

[25]H. C. Brown and M. Dubeck, ibid., 82, 1939 (1960).

4. Grignard reagents

An interesting rearrangement was noted by Späth[26] during the treatment of diphenyl ether with ethylmagnesium bromide at 170-190°, wherein o-phenylphenol was the product rather than the expected metalated compound. In the light of present knowledge, benzyne must have been the intermediate species.

Diphenyl ether is usually unaffected in a refluxing ether solution of alkyl Grignard reagents or in the presence of cobaltous chloride. However, when these were mixed together, diphenyl ether was cleaved at room temperature.[27] The cleavage was explained on the basis of a free radical mechanism. The Grignard reagents, in the presence of cobaltous chloride, differed considerably in their effectiveness as cleaving agents. tert.-Butylmagnesium halide was the most effective, ethyl- and methylmagnesium halides less effective, and the phenylmagnesium halides without effect.[27]

This cleavage reaction has recently been applied to several methoxydiphenyl ether derivatives and the conditions of the reaction examined with the object of using the cleavage

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[26]E. Späth, Monatsh., 35, 319 (1914).

[27]M. S. Kharasch and R. L. Huang, J. Org. Chem., 17, 669 (1952).

in future synthetic schemes.[28,29,30]

B. Silicon Derivatives of Diphenyl Ether

With the increased interest in the chemistry of poly-phenyl ether systems, it was deemed necessary to tabulate the known silicon derivatives of diphenyl ether. Accordingly, this section of the historical discussion is devoted to a brief enumeration of the various methods of preparing these derivatives and to Table 1, a complete listing of all known silicon derivatives of diphenyl ether along with their physical constants.

There are four general methods of preparing silicon substituted phenyl ethers:

(1) Metalation of the phenyl ether by an organolithium compound, followed by derivatization with an organosilicon halide or hydride.[9,14,31]

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[28]M. Tomita and Y. Watanabe, J. Pharm. Soc. (Japan), 73, 918 (1953). (Original available but not translated; abstracted in C. A., 48, 10652 (1954).)

[29]M. Tomita and Y. Watanabe, ibid., 73, 1283 (1953). (Original available but not translated; abstracted in C. A., 49, 213 (1955).)

[30]M. Tomita and Y. Watanabe, ibid., 74, 1363 (1954). (Original available but not translated; abstracted in C. A., 49, 15931 (1955).)

[31]O. Marrs, Iowa State University of Science and Technology, Ames, Iowa. Information concerning silicon derivatives of phenyl ether. Private communication. 1960.

$$xC_6H_5OC_6H_5 + \underline{n}\text{-}C_4H_9Li \xrightarrow{X_xSiR_{4-x}} (C_6H_5OC_6H_4)_xSiR_{4-x}$$
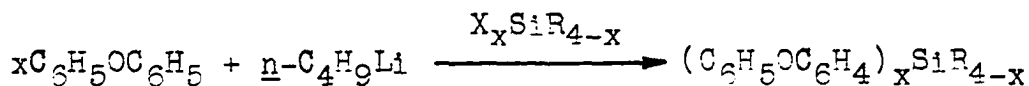
where X is halogen or hydrogen.

(2) A halogen-metal interconversion reaction involving a halogen-substituted phenyl ether, with subsequent derivatization with the appropriate silicon compound.[9,31,32]

$$xC_6H_5OC_6H_4X' + \underline{n}\text{-}C_4H_9Li \xrightarrow{X_xSiR_{4-x}} (C_6H_5OC_6H_4)_xSiR_{4-x}$$
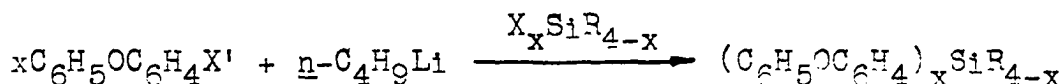
where X is halogen or hydrogen and X' is halogen.

(3) Preparation of a Grignard reagent from a halogen-substituted phenyl ether, with subsequent derivatization with either an organosilicon halide or hydride.[4,33,34]

$$xC_6H_5OC_6H_4X' + Mg \xrightarrow{X_xSiR_{4-x}} (C_6H_5OC_6H_4)_xSiR_{4-x}$$
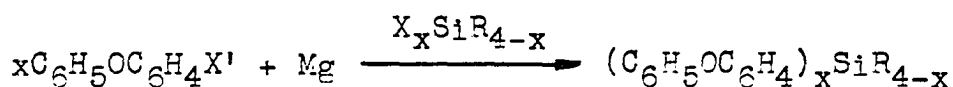
where X is halogen or hydrogen and X' is halogen.

(4) A Wurtz-Fittig coupling of a halogen-substituted phenyl ether with a halosilane by means of reaction with

[32]H. Gilman and J. J. Goodman, J. Org. Chem., 22, 45 (1957).

[33]H. Gilman and E. A. Zuech, J. Am. Chem. Soc., 81, 5925 (1959).

[34]H. Gilman, B. J. Gaj, J. W. Diehl, O. L. Marrs and W. J. Trepka. Organo-metallic and organo-metalloidal high temperature and related materials. Wright Air Development Center Technical Report 53-426, Part VI. December, 1958.

Table 1. Silicon derivatives of diphenyl ether

Formula	Name	M.p., °C	B.p., °C (mm.)	n_D^{20}	d_4^{20}	Ref.
$C_{18}H_{16}OSi$	p-Phenoxyphenylphenylsilane	--	145-147 (0.02)	1.6093	--	33
$C_{18}H_{26}OSi_2$	(Oxydi-o-phenylene)bis-(trimethylsilane)	--	117-120 (0.001)	1.5415	1.432	9
$C_{18}H_{26}OSi_2$	(Oxydi-p-phenylene)bis-(trimethylsilane)	--	124-130 (0.0?)	1.5372	0.993	9
$C_{19}H_{18}OSi$	Methyl-p-phenoxyphenylphenylsilane	--	139-141 (0.021)	1.610	1.0802[a]	34
$C_{22}H_{34}O_5Si_2$	(Oxydi-p-phenylene)bis-(diethoxymethylsilane	--	195 (0.1)	1.5013[b]	1.054[c]	36
$C_{24}H_{20}OSi$	p-Phenoxyphenyldiphenylsilane	53-54	190-193 (0.015)	1.6300	1.1251[a]	34
$C_{24}H_{24}O_2Si$	Dimethylbis-(p-phenoxyphenyl)silane	--	220-225 (0.5)	--	--	4

[a] d_{20}^{20}.

[b] n_D^{25}.

[c] d_4^{25}.

Table 1. (Continued)

Formula	Name	M.p., °C	B.p., °C (mm.)	n_D^{20}	d_4^{20}	Ref.
$C_{25}H_{22}OSi$	p-Phenoxyphenylphenyl-o-tolylsilane	--	205-207 (0.004)	--	--	33
$C_{25}H_{22}O_2Si$	p-Anisyl-p-phenoxyphenyl-phenylsilane	--	227-230 (0.005)	--	--	33
$C_{26}H_{24}OSi$	Methyl-p-phenoxyphenylphenyl-o-tolylsilane	72-75	210-213 (0.004)	--	--	33
$C_{26}H_{24}O_2Si$	p-Anisyl-p-phenoxyphenyl-phenylsilane	--	225-228 (0.003)	--	--	33
$C_{28}H_{30}OSi_2$	(Oxydi-p-phenylene)bis-(di-methylphenylsilane)	-8	249 (2.6)	--	--	35
$C_{30}H_{23}ClOSi$	(2-Phenoxy-5-chlorophenyl)-triphenylsilane	161-162.5	--	--	--	14
$C_{30}H_{24}OSi$	o-Phenoxyphenyltriphenyl-silane	145-146	--	--	--	14
$C_{30}H_{24}OSi$	m-Phenoxyphenyltriphenyl-silane	d	220-230 (0.075)	--	--	37
$C_{30}H_{24}O_2Si$	o-Phenoxyphenyl-p-phenoxy-phenylphenylsilane	--	234-236 (0.003)	--	--	33

[d]Amorphous solid.

Table 1. (Continued)

Formula	Name	M.p., °C	B.p., °C (mm.)	n_D^{20}	d_4^{20}	Ref.
$C_{31}H_{26}O_2Si$	Methyl-o-phenoxyphenyl-p-phenoxyphenylphenylsilane	--	225-227 (0.004)	--	--	33
$C_{32}H_{28}OSi$	p-Phenoxyphenylphenyl-o-tolyl-p-tolylsilane	--	249-251 (0.004)	--	--	33
$C_{32}H_{28}O_2Si$	p-Anisyl-p-phenoxyphenyl-phenyl-p-tolylsilane	--	260-264 (0.003)	--	--	33
$C_{33}H_{30}OSi$	Tribenzyl-o-phenoxyphenyl-silane	81-82.5	--	--	--	31
$C_{33}H_{30}OSi$	Tribenzyl-m-phenoxyphenyl-silane	--	240-243 (0.003)	--	--	31
$C_{33}H_{30}OSi$	Tribenzyl-p-phenoxyphenyl-phenylsilane	105-107	--	--	--	31
$C_{36}H_{26}Cl_2O_2Si$	Bis-(2-phenoxy-5-chloro-phenyl)diphenylsilane	151-152	--	--	--	14
$C_{36}H_{28}OSi$	o-Biphenylyl-m-phenoxyphenyl-diphenylsilane	--	238	--	--	37
$C_{36}H_{28}O_2Si$	Bis-(o-phenoxyphenyl)di-phenylsilane	162.5-164.5	--	--	--	14
$C_{36}H_{28}O_2Si$	Bis-(m-phenoxyphenyl)di-phenylsilane	d	256-257 (0.025)	--	--	37

Table 1. (Continued)

Formula	Name	M.p., °C	B.p., °C (mm.)	n_D^{20}	d_4^{20}	Ref.
$C_{36}H_{28}O_2Si$	Bis-(p-phenoxyphenyl)di-phenylsilane	162-163	--	--	--	32
$C_{36}H_{28}O_2Si$	m-(m-Phenoxy)phenoxyphenyl-triphenylsilane	--	278-280 (0.07)	--	--	37
$C_{42}H_{32}O_3Si$	Tris-(o-phenoxyphenyl)phenyl-silane	192-193	--	--	--	14
$C_{42}H_{32}O_3Si$	Tris-(m-phenoxyphenyl)phenyl-silane	--	272-304 (0.015-0.020)	--	--	37
$C_{42}H_{32}O_3Si$	Tris-(p-phenoxyphenyl)phenyl-silane	149-150	--	--	--	32
$C_{48}H_{36}O_4Si$	Tetrakis-(o-phenoxyphenyl)-silane	284-285	--	--	--	14
$C_{48}H_{36}O_4Si$	Tetrakis-(m-phenoxyphenyl)-silane	100-101.5	--	--	--	37
$C_{48}H_{36}O_4Si$	Tetrakis-(p-phenoxyphenyl)-silane	204	--	--	--	32
$C_{48}H_{38}OSi_2$	(Oxydi-p-phenylene)bis-(tri-phenylsilane)	306-307	--	--	--	38

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Table 1. (Continued)

Formula	Name	M.p., °C	B.p., °C (mm.)	n_D^{20}	d_4^{20}	Ref.
$C_{48}H_{52}O_3Si$	n-Dodecyltris-(p-phenoxy-phenyl)silane	--	315-320 (0.004)	--	--	32,39
$C_{48}H_{68}O_2Si$	Di-n-dodecylbis-(o-phenoxy-phenyl)silane	--	260-270 (0.001)	1.5290	0.9680	9
$C_{48}H_{68}O_2Si$	Di-n-dodecylbis-(p-phenoxy-phenyl)silane	--	275-280 (0.001)	1.5380	0.9776	9
$C_{54}H_{50}OSi_2$	(Oxydi-p-phenylene)bis-(tri-benzylsilane)	[d]	320-322 (0.001)	--	--	9
$C_{60}H_{108}OSi$	Tri-n-hexadecyl-p-phenoxy-phenylsilane	--	205-215 (0.005)	1.4960	0.8971	9

sodium.[35,36]

$$C_6H_5OC_6H_4X + R_3SiX \xrightarrow{\text{Na}} (C_6H_5OC_6H_4)SiR_3$$
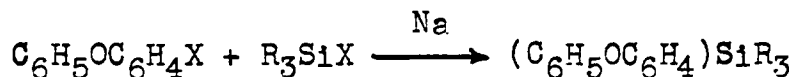
where X is halogen.

These preparative methods give the appropriate silicon compounds in good to excellent yields. The method of choice appears to depend upon the position of substitution desired, i.e., metalation for an _ortho_ derivative but halogen-metal interconversion or a Grignard reagent for the _meta_ or _para_ derivative. As mentioned previously, Table 1 lists all known silicon derivatives of diphenyl ether along with the physical constants and references to the preparations. Several compounds are reported for which there were no preparative procedures described.[37,38,39]

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[35]H. A. Clark, U. S. Patent 2,628,242. February, 1953. (Original not available for examination; abstracted in _C. A._, 47, 9346 (1953).) British Patent 671,553. May, 1952. (Original not available for examination; abstracted in _C. A._, 47, 4909 (1953).)

[36]L. W. Breed, F. Baiocchi and H. W. Clark. Development of thermally stable silicon containing resins. Wright Air Development Center Technical Report 54-143. May, 1957.

[37]S. Aftergut and G. P. Brown, _Chem. and Ind._ (_London_), 1479 (1958).

[38]H. Gilman and R. D. Gorsich. Organo-metallic and organo-metalloidal high temperature lubricants and related materials. Wright Air Development Center Technical Report 53-426, Part II. October, 1954.

[39]H. Gilman and R. D. Gorsich. Organo-metallic and organometalloidal high temperature lubricants and related materials. Wright Air Development Center Technical Report 53-426, Part IV. May, 1957.

C. Phenoxasilin Chemistry

Another type of silicon derivative of diphenyl ether is a cyclic compound incorporating both silicon and oxygen into the same cycle, namely, the phenoxasilin system.[40] As can be
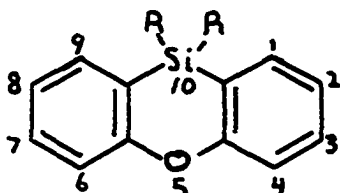
seen, this is the silicon analog of xanthene.

10,10-Diphenylphenoxasilin was prepared by Oita and Gilman[8] in 1957 by the dimetalation of diphenyl ether with n-butyllithium, and subsequent reaction of this intermediate with dichlorodiphenylsilane. In a similar manner, the
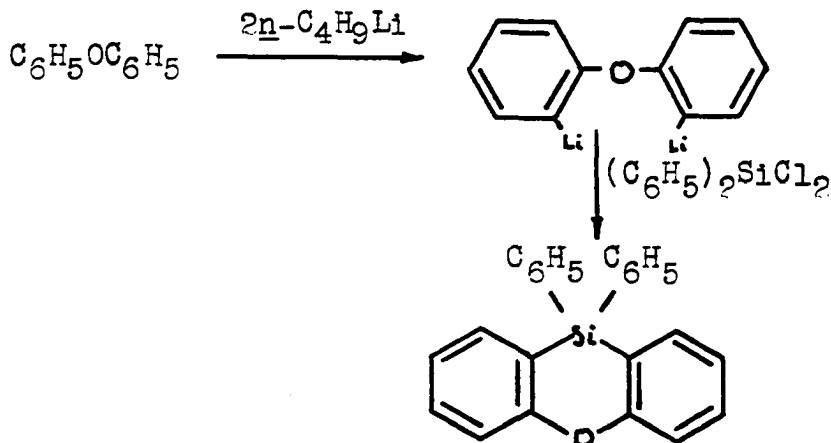
$$C_6H_5OC_6H_5 \xrightarrow{2\underline{n}-C_4H_9Li}$$

$$(C_6H_5)_2SiCl_2$$

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dimethyl and spiro analogs were prepared from dichlorodimethyl-
silane and silicon tetrachloride, respectively. Later in the
same year, Hitchcock and co-workers[41] prepared both the di-
phenyl and spiro compounds by reaction of the appropriate
chlorosilanes with the dilithium intermediate obtained by a
halogen-metal interconversion reaction with o,o'-dibromodi-
phenyl ether. They were also able to prepare several compounds
with nuclear substituents through the use of tolyl ethers.

T. Yu and co-workers[42] prepared 2,8-dimethyl-10,10-
diphenylphenoxasilin by means of a Wurtz coupling of o,o'-
dibromo-p,p'-dimethyldiphenyl ether and dichlorodiphenylsilane
with sodium in refluxing petroleum ether. However, when they
refluxed the same halogenated ether with silicon tetrachloride
in iso-amyl ether under Wurtz conditions, the product report-
edly obtained was 10-chloro-2,8-dimethyl-10-(5-methyl-2-p-
tolyloxy)phenoxasilin. This reaction supported some of their
other results in that the Wurtz reaction involving an aryl
bromide containing an ortho-substituent produces only the
chlorotriarylsilane, in low yield.

The most novel, but certainly not the most practicable,
method of obtaining the phenoxasilin system was reported by

[41]C. H. S. Hitchcock, F. G. Mann and A. Vanterpool, J.
Chem. Soc., 4537 (1957).

[42]T. Yu, L. Hsu and S. Wu, Hua Hsieh Hsieh Pao, 24, 170
(1958). (Original not available for examination; abstracted
in C. A., 53, 6233 (1959).)

Gilman et al.[43,44] After an equimolar mixture of diphenyl-
silane and phenoxathiin had been refluxed for 6 days, 10,10-
diphenylphenoxasilin was obtained in a ?% yield. This reac-
tion was typical of a number of sulfur-containing heterocycles
in which the sulfur atom was replaced by the diphenylsilylene
group simply by heating with diphenylsilane.

All of the reported phenoxasilin compounds are tabulated
in Table 2, along with their physical properties and refer-
ences to their preparation. In a few instances, there is
some question as to the physical property, since a more stable
derivative may have been prepared for identification. How-
ever, these are included to make the table as complete as
possible.

Through a study of molecular models,[8] it has been shown
that the presence of the oxygen atom in the six-membered
cyclic system greatly alleviated the silicon-carbon bond
strain which had been shown to be present in the five membered
cyclic silicon system, 5,5-dibenzosilole.[45] 10,10-Diphenyl-
phenoxasilin and its 2,7-dimethyl derivative have dipole
moments of 0.97 ± 0.03 and 1.01 ± 0.3 D in benzene, respec-

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[43]H. Gilman and D. Wittenberg, J. Am. Chem. Soc., 79,
6339 (1957).

[44]D. Wittenberg, H. A. McNinch and H. Gilman, ibid.,
80, 5418 (1958).

[45]H. Gilman and R. D. Gorsich, ibid., 77, 6380 (1955).

Table 2. Phenoxasilin compounds

Formula	Name	M.p.,°C	Ref.
$C_{14}H_{14}OSi$	10,10-Dimethylphenoxasilin	78.5-79.0[a] 74.5-77.0[b]	8 41
$C_{24}H_{16}O_2Si$	10,10'-Spirobiphenoxasilin	280-282 284-285	41 8
$C_{24}H_{18}OSi$	10,10-Diphenylphenoxasilin	178-179 176-179 175-176	43,44 8 41
$C_{25}H_{19}OBrSi$	2-Aldehydo-10,10-diphenylphenoxasilin	[c,d]	41
$C_{25}H_{19}OBrSi$	2-Bromomethyl-10,10-diphenylphenoxasilin	131.5-132 dec.	41
$C_{25}H_{20}OSi$	2-Methyl-10,10-diphenylphenoxasilin	153-155	41
$C_{25}H_{20}OSi$	3-Methyl-10,10-diphenylphenoxasilin	161-162	41
$C_{26}H_{18}O_5Si$	2-Aldehydo-10-hydroxy-10-(5-aldehydo-2-phenoxyphenyl)phenoxasilin[d]	230-231	41

[a]B.p. 292-297°/atmospheric pressure.

[b]B.p. 159-161°/9 mm.

[c]Identified as the 2,4-dinitrophenylhydrozone, m.p. 286-288° dec.

[d]Structure not rigorously established.

Table 2. (Continued)

Formula	Name	M.p., $^{\circ}$C	Ref.
$C_{26}H_{20}O_3Br_2Si$	2-Bromomethyl-10-hydroxy-10-(5-bromo-methyl-2-phenoxyphenyl)phenoxasilin[d]	168-171 dec.	41
$C_{26}H_{22}OSi$	10,10-Dibenzylphenoxasilin	[e]	9
$C_{26}H_{22}OSi$	2,7-Dimethyl-10,10-diphenylphenoxasilin	166-168	41
$C_{26}H_{22}OSi$	2,8-Dimethyl-10,10-diphenylphenoxasilin	174	42
$C_{26}H_{22}O_3Si$	10-Hydroxy-4-methyl-10-(4-methyl-2-phenoxyphenyl)phenoxasilin[d]	215-217	41
$C_{26}H_{22}O_3Si$	10-Hydroxy-2-methyl-10-(5-methyl-2-phenoxyphenyl)phenoxasilin	198-200	41
$C_{28}H_{25}ClO_2Si$	10-Chloro-2,8-dimethyl-10-(5-methyl-2-p-tolyloxy)phenoxasilin	220-222	42
$C_{36}H_{58}OSi$	10,10-Di-n-dodecylphenoxasilin	[f]	9

[e]B.p. 194-195°/0.003 mm., n_D^{20} 1.6322.

[f]B.p. 247-255°/0.009 mm., n_D^{20} 1.5135, d_4^{20} 0.9359.

24

tively.[41] Using this information, a "rough" calculation of 158-165° and 154-158° for the interplanar angles has been made.[41]

There have been only limited studies made of the chemical properties of the phenoxasilin system. 10,10-Diphenylphenoxasilin and 10,10'-spirobiphenoxasilin have been cleaved by lithium in dioxane to yield o-hydroxyphenyltriphenylsilane and bis-(o-hydroxyphenyl)diphenylsilane, respectively.[8] A methyl substituent on the ring can be brominated using N-bromosuccinimide with benzoyl peroxide as catalyst. For example, 2-methyl-10,10-diphenylphenoxasilin was converted to the 2-bromomethyl derivative by interaction with N-bromosuccinimide.[41] Attempts to convert the bromomethyl group into an acidic or basic group failed. The 2-dibromomethyl derivative, formed in the same manner, resisted normal hydrolysis. However, with silver nitrate in aqueous 2-ethoxyethanol, it was converted to the 2-aldehyde, which was identified only as its 2,4-dinitrophenylhydrazone.

10,10'-Spirobiphenoxasilin was found to possess considerable stability.[41] This was shown by the fact that 2,2'-dilithiodiphenyl ether, when treated with one molecular equivalent of silicon tetrachloride, formed only the spirocyclic derivative, apparently to the exclusion of 10,10-dichlorophenoxasilin. Further, the spiro compound was recovered unchanged after it had been treated with fuming nitric acid in

hot acetic anhydride solution, with bromine in boiling chloroform solution, and with N-bromosuccinimide and benzoyl peroxide in boiling carbon tetrachloride solution. The use of more vigorous conditions appeared to cause extensive rupture of the cyclic system.

The presence of methyl groups on the phenyl ether appear to cause certain problems of ring closure. For example, only the silanol, 10-hydroxy-2-methyl-10-(5-methyl-2-phenoxyphenyl)phenoxasilin could be formed from 2,2'-dilithio-5-methyldiphenyl ether and silicon tetrachloride.[41] The presence of the methyl group inhibited the formation of the spirocyclic system, while apparently not affecting that of the initial phenoxasilin ring system. The mechanistic rationale considers the inductive effects of the methyl group as causing a much increased negative contribution to silicon, making the cyclization reaction more difficult.

D. Reactions of Organosilylmetallic Reagents

The field of organosilylmetallic chemistry has been expanding rapidly both in scope and in importance. Since this field has become so broad and since a very excellent review[5] concerning organosilylmetallic chemistry has appeared recently, this section of the historical review will be limited to a discussion of the three areas most closely related to the research problems encountered in this thesis.

1. With ethers

Organosilylmetallic reagents cleave epoxides with the subsequent formation of β-silylcarbinols. For example,

$$R_3SiLi + \underset{\underset{O}{\diagdown\diagup}}{CH_2CHR'} \longrightarrow R_3SiCH_2\underset{\underset{OH}{|}}{CHR'}$$
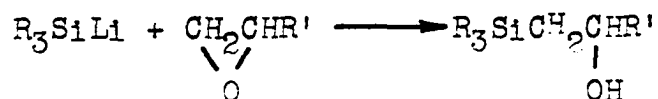
triphenylsilyllithium was found to react with ethylene oxide and with propylene oxide to form 2-triphenylsilylethanol and 1-triphenylsilylpropan-2-ol, respectively.[46] The reaction of triphenylsilyllithium and of methyldiphenylsilyllithium with styrene oxide gave good yields of 1-phenyl-2-triphenylsilyl-ethanol and of 1-phenyl-2-methyldiphenylsilylethanol. Triphenylgermyllithium also has been reported to react with certain epoxides.[47]

When triphenylsilyllithium was reacted with the poly-functional ether, 1,2-epoxy-3-allyloxypropane, 1,2-dihydroxy-3-triphenylsilylpropane and allyltriphenylsilane were isolated.[48] Evidently, both eopxy ring opening and ether cleavage

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[46]H. Gilman, D. Aoki and D. Wittenberg, ibid., 81, 1107 (1959).

[47]H. Gilman, C. W. Gerow and M. B. Hughes, Iowa State University of Science and Technology, Ames, Iowa. Information concerning germylmetallic reactions. Private communication. 1958.

[48]D. Aoki, Iowa State University of Science and Technology, Ames, Iowa. Information concerning epoxides. Private communication. 1960.

occurred.

The reaction of organosilylmetallic reagents with the epihalohydrins depended largely on the halogen.[46] The predominant product from the reaction of triphenylsilyllithium with epibromohydrin was hexaphenyldisilane, apparently involving a halogen-metal interconversion reaction, with subsequent interaction of the resulting bromosilane with an excess of the silylmetallic reagent. In contrast, the reaction with epichlorohydrin did not involve halogen-metal interconversion, as evidenced by the absence of hexaphenyldisilane.[46] When the reaction was carried out at low temperatures, the first step involved an opening of the epoxide ring to give the β-silyl alcohol, however, if a second equivalent of triphenylsilyllithium was present, a halogen-metal interconversion reaction did take place to give the observed product, 2-hydroxy-1,3-bis-(triphenylsilyl)propane.[48] Thus, a relative reactivity series of bromo⟩epoxy⟩chloro seems to exist in reaction with triphenylsilyllithium.

Cyclic ethers involving larger ring systems are also cleaved by silylmetallic reagents. 4-Hydroxybutyltriphenylsilane was obtained in 18% yield after triphenylsilyllithium had been refluxed with tetrahydrofuran for several days.[49]

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[49]H. Gilman and R. D. Gorsich, Iowa State University of Science and Technology, Ames, Iowa. Information concerning reaction of triphenylsilyllithium with tetrahydrofuran. Private communication. 1957.

However, larger yields of the respective carbinols were

$$(C_6H_5)_3SiLi + \underline{CH_2CH_2CH_2CH_2O} \longrightarrow (C_6H_5)_3Si(CH_2)_4OH$$
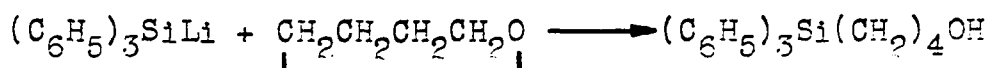
obtained when triphenylsilyllithium or methyldiphenylsilyllithium were reacted with tetrahydrofuran in sealed tubes at elevated temperatures.[50,51] It should be noted that triphenylgermyllithium has been reported to give only a polymer when heated with tetrahydrofuran.[47] However, E. A. Zuech, Ames, Iowa, in a recent private communication (1960) reported the isolation of 4-hydroxybutyltriphenylgermane as the result of the reaction of triphenylgermyllithium with tetrahydrofuran. Trimethylene oxide was cleaved by both triphenylsilyllithium[51] and by triphenylgermyllithium[47] to form 3-substituted propanols in good yields. The highly strained cyclic ether, 1,4-dihydronaphthalene-1,4-endoxide, gave a low yield of 2-naphthyltriphenylsilane, in addition to naphthalene and triphenylsilanol, upon reaction with triphenylsilyllithium.[51]

When triphenylsilyllithium was prepared in tetrahydropyran and subsequently reacted at elevated temperatures with the solvent, a high melting polymer was obtained, rather than the expected 5-triphenylsilylpentanol.[51] The same reaction with dioxane gave a low yield of ethylenebis-(triphenylsi-

[50]D. Wittenberg and H. Gilman, _J. Am. Chem. Soc._, **80**, 2677 (1958).

[51]D. Wittenberg, D. Aoki and H. Hilman, _ibid._, **80**, 5933 (1958).

lane).[51] S-Trioxane did not give any of the expected ether

cleavage products subsequent to reaction with triphenylsilyl-

lithium at reflux temperature.[51]

The methyl ether, 1,2-dimethoxyethane, has been used as

a solvent in the preparation of certain organosilylmetallic

compounds.[52] This ether, however, is also cleaved when warmed

with organosilylmetallic reagents.[51,52] In the case of tri-

phenylsilyllithium, the product of the cleavage has been es-

tablished as methyltriphenylsilane.[51] A similar methyl ether

cleavage was not observed in reaction with benzyl methyl

$$(C_6H_5)_3SiLi + CH_3OCH_2CH_2OCH_3 \longrightarrow (C_6H_5)_3SiCH_3$$
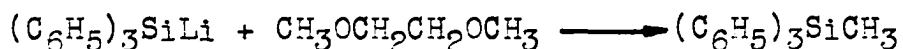
ether. Instead, the major products were 1-phenylethanol and

tetraphenylsilane.[51] The products were explained as having

occurred via a Wittig rearrangement[53] of the α-metalated

benzyl methyl ether.

Certain dialkylaminomethyl ethers were cleaved by tri-

phenylsilyllithium. For example, N-(n-butyoxymethyl)piperi-

dine reacted with the silylmetallic reagent to give N-(tri-

phenylsilylmethyl)piperidine.[51]

Diphenyl ether is one of the few ethers which is not

cleaved by triphenylsilyllithium. A trace of o,o'-dicarboxy-

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[52]A. G. Brook and H. Gilman, ibid., 76, 278 (1954).

[53]G. Wittig and L. Löhmann, Ann., 550, 260 (1942).

diphenyl ether was obtained upon carbonation of the reaction mixture, indicating that a small amount of dimetalation had occurred.[51]

In summary, the reaction of organosilylmetallic reagents with ethers is one of cleavage, except with diphenyl ether which is a metalation reaction.

2. In metalations

A metalation reaction is one which involves the replacement of an acidic hydrogen by a metal to give a true organometallic compound.[54,55] This reaction also occurs with

$$RH + RM' \longrightarrow RM + R'H$$

silylmetallic reagents, but to a much more limited extent than with organolithium reagents.

Triphenylsilyllithium, -potassium and -sodium were found to metalate triarylmethanes rapidly and practically quantitatively.[56] When an excess of the silylpotassium or -sodium

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[54]H. Gilman. Organometallic compounds. In H. Gilman, ed. in chief. Organic chemistry. Vol. 1, p. 533. New York, N. Y., John Wiley and Sons, Inc. 1953.

[55]H. Gilman. The metalation reaction with organolithium compounds. In R. Adams, ed. in chief. Organic reactions. Vol. 8, p. 260. New York, N. Y., John Wiley and Sons, Inc. 1954.

[56]A. G. Brook and H. Gilman, J. Am. Chem. Soc., 76, 2338 (1954).

$$R_3SiM + R'_3CH \longrightarrow R_3SiH + R_3'CM$$
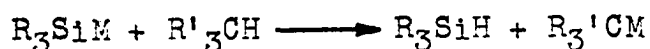
reagent was used, a large quantity of tetraphenylsilane was isolated as the result of a secondary reaction involving the triphenylsilane formed during the metalation. The same secondary reaction did not take place with triphenylsilyllithium. It should also be noted that triphenylsilylpotassium and -sodium reacted at room temperature with some triaryl-silanes to give high yields of the corresponding tetraaryl-silanes.[57] This was in contrast to triphenylsilyllithium which gave only a low yield of tetraarylsilane, with a predominant coupling to the hexaaryldisilane.

Compounds containing the more acidic hydrogens are metalated rapidly by silylmetallic reagents. Phenylacetylene[58] was metalated by triphenylsilylpotassium, although the major product isolated through the aforementioned reaction was tetraphenylsilane. Diphenylmethane,[59] phenyl acetylene,[59] fluorene,[59] 9,10-dihydroanthracene[59] and thiaxanthene[60] were metalated by triphenylsilyllithium, the corresponding acids

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[57]A. G. Brook and H. Gilman, ibid., 76, 2333 (1954).

[58]H. Gilman and T. C. Wu, ibid., 75, 2509 (1953).

[59]O. L. Marrs, Iowa State University of Science and Technology, Ames, Iowa. Information concerning metalations. Private communication. 1960.

[60]J. W. Diehl. Some organometallic reactions with heterocyclic compounds. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1959.

being isolated subsequent to carbonation.

With less acidic systems, the metalation reaction proceeded only to a limited extent. 10-Ethylphenothiazine was metalated by triphenylsilyllithium to give only a trace of acid upon carbonation.[60] A trace of benzyltriphenylsilane was isolated after triphenylsilyllithium had reacted with toluene in the presence of hexaphenyldisilane. It is believed that benzyllithium, formed by the metalation of toluene by triphenylsilyllithium, cleaved the disilane to give the observed product.[61] Triphenylsilyllithium was reported to react with diphenyl ether to give, following carbonation, a trace of 2,2'-dicarboxydiphenyl ether.[51] However, diphenyl sulfide, diphenyl sulfone and di-p-tolyl sulfone were cleaved by triphenylsilyllithium, as were diphenyl sulfone, diphenyl sulfide and diphenyl sulfoxide by triphenylsilylpotassium.[62]

Systems containing still less acidic hydrogens are not affected by reaction with triphenylsilyllithium, although they may be metalated by organolithium reagents.[55] The specific compounds found unreactive were sym.-tetraphenylethane,[59] dibenzofuran,[59] dibenzothiophene,[62] dibenzothiophene-5,5-

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[61]H. Gilman, B. J. Gaj and G. Schwebke, Iowa State University of Science and Technology, Ames, Iowa. Information concerning metalation of toluene. Private communication. 1960.

[62]D. Wittenberg, T. C. Wu and H. Gilman, _J. Org. Chem._, 23, 1898 (1958).

dioxide[62] and 10-ethylphenothiazine-5,5-dioxide.[60] Triphenyl-silyllithium with 10-ethylphenothiazine-5-oxide reduced the sulfoxide linkage.[60]

Triphenylgermyllithium reacted in a manner quite similar to that of the silylmetallic compounds. Fluorene was metalated by triphenylgermyllithium to give a high yield of fluorene-9-carboxylic acid on carbonation, but metalation of the much less acidic system, dibenzofuran, was unsuccessful.[63] Triphenyltin-lithium metalated fluorene only in a very low yield, while triphenyllead-lithium did not react with it.[59] It should also be mentioned that triphenylgermane was metalated by triphenylsilyllithium to give a good yield of tri-phenylgermanecarboxylic acid following carbonation.[64]

If we are allowed to extend the definition of metalation somewhat, the preparation of a number of silylamines through the reaction of triphenylsilyllithium with primary and second-ary alkyl amines might also be an example of this reaction.[65] The procedure involves an initial "metalation" of the amine

[63]H. Gilman and C. W. Gerow, ibid., 23, 1582 (1958).

[64]E. A. Zuech, Iowa State University of Science and Technology, Ames, Iowa. Information concerning metalation of triphenylgermane. Private communication. 1960.

[65]G. D. Lichtenwalter. Organosilylmetallic compounds and derivatives. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

followed by coupling with triphenylsilane. Although metala-
tion also apparently occurred with diphenylamine[65] and with

$$R_3SiLi + R_2'NH \longrightarrow R_3SiH + R_2'NLi \longrightarrow R_3SiNR'_2 + LiH$$
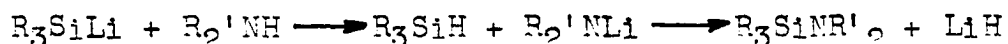
N-(diphenylmethyl)aniline,[66] since triphenylsilane was iso-
lated following a negative Color Test I,[67] no secondary
coupling reaction occurred. The presence of a phenyl group
on the nitrogen atom probably reduced the nucleophilicity of
the lithium amide to such an extent that it was no longer
capable of displacing the hydride ion from triphenylsilane.[65]

Extending the definition of metalation still further,
triphenylsilylpotassium reacted with certain phenylcarbinols
to give, in all cases, high yields of tetraphenylsilane.[58]
Triphenylsilanol also gave a high yield of tetraphenylsilane.

3. Relative reactivities

There are two classical reactions which have been used
to determine the relative reactivities of organometallic com-
pounds in general terms: (1) addition to an olefinic linkage
and; (2) addition to a carbonyl group.[54] Highly reactive
compounds add to both the olefinic linkage and the carbonyl
group; the moderately reactive compounds add only to the

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[66]D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles
and H. Gilman, _J. Am. Chem. Soc._, _80_, 4532 (1958).

[67]H. Gilman and F. Schulze, _ibid._, _47_, 2002 (1925).

carbonyl group; and the relatively unreactive compounds do not add to either linkage in a reasonable time.[54] Naturally, other methods are necessary for more specific relations within these three major divisions. Included in these methods are competitive reactions with a functional group, the halogen-metal interconversion reaction,[12] use of color tests[67,68] and metalation reactions.[55]

The relative reactivities of organosilylmetallic compounds will be discussed in relation to several basic reactions that they undergo. These reactions have been discussed in detail in a previous review;[5] accordingly, although leading references will be given, no attempt will be made to discuss the reactions other than in the manner in which they help to determine the relative reactivities of silylmetallic reagents.

a. **Addition to olefins**   Triphenylsilyllithium[69] and -potassium[69] add to 1,1-diphenylethylene, as does triphenyl-germylpotassium[70] and -lithium.[70] Triphenylsilyllithium also was found to add smoothly to triphenylethylene,[69] and both the potassium[71] and lithium[72] reagent added to trans-stilbene.

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[68]H. Gilman and J. Swiss, ibid., 60, 1847 (1940).

[69]T. C. Wu, D. Wittenberg and H. Gilman, J. Org. Chem., 25, 596 (1960).

[70]H. Gilman and C. W. Gerow, J. Am. Chem. Soc., 79, 342 (1957).

[71]H. Gilman and T. C. Wu, ibid., 75, 234 (1953).

[72]A. G. Brook, K. M. Tai and H. Gilman, ibid., 77, 6219 (1955).

However, neither triphenylgermylpotassium nor -lithium added to the latter linkage.[70] This particular difference in reactivity may be attributed to steric factors arising from the larger size of the germanium atom rather than to a greater reactivity of the silyl compounds, since triphenylgermyllithium added to octadecene-1,[70] while triphenylsilylpotassium did not add under the same conditions.[69]

The aforementioned addition reactions tend to place germyl- and silylmetallic compounds among the "highly reactive" organometallic reagents. However, great care must be taken in this interpretation as these addition reactions are somewhat limited. No addition product was isolated from the reaction of the silylmetallic reagents-with tetraphenylethylene; also, triphenylsilylpotassium did not add to a variety of aliphatic and alicyclic olefins.[69] Triphenylgermyllithium was apparently unreactive toward both cyclohexene and octene-1.[70] It should be mentioned that triphenyltinlithium was unreactive in all of the addition reactions mentioned above, placing it in a category of lesser reactivity.[73]

b. <u>Addition to carbonyl groups</u>   Silylmetallic reagents have been found to add across the carbonyl linkage

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[73]H. Gilman and S. D. Rosenberg, <u>J</u>. <u>Org</u>. <u>Chem</u>., <u>18</u>, 1554 (1953).

in aliphatic[74,75] and aromatic[76,77] ketones (apparently a
normal addition to the aromatic carbonyl occurred, followed
by a rearrangement), aromatic and aliphatic aldehydes,[78,79,80,
81,82] and to derivatives of carboxylic acids.[80,81,83] Tri-
phenylgermylmetallic compounds[84] also added to the carbonyl
functions of several aldehydes and ketones. These reactions
clearly indicate that both silyl- and germylmetallic reagents
are at least "moderately reactive" on the basis of the pre-
vious definition and, coupled with their additions to olefins,
give further evidence for their right to be classified as
"highly reactive".

The reaction of a silylmetallic reagent with benzal-

[74]A. G. Brook, J. Am. Chem. Soc., 80, 1886 (1958).

[75]H. Gilman and G. D. Lichtenwalter, ibid., 80, 2680
(1958).

[76]H. Gilman and T. C. Wu, ibid., 75, 2935 (1953).

[77]H. Gilman and G. D. Lichtenwalter, ibid., 80, 607
(1958).

[78]H. Gilman and T. C. Wu, ibid., 76, 2502 (1954).

[79]A. G. Brook, C. M. Werner and M. E. McGriskin, ibid.,
81, 981 (1959).

[80]D. Wittenberg and H. Gilman, ibid., 80, 4529 (1958).

[81]H. Gilman and D. J. Peterson, J. Org. Chem., 23, 1895
(1958).

[82]D. Wittenberg, T. C. Wu and H. Gilman, ibid., 24, 1349
(1959).

[83]A. G. Brook, J. Am. Chem. Soc., 79, 4373 (1957).

[84]H. Gilman and C. W. Gerow, ibid., 77, 5740 (1955).

acetophenone, a reaction which might have allowed a more defi-
nite classification, has been found to be unsatisfactory.
When an organometallic reagent is allowed to react with
benzalacetophenone, two possible reactions may occur depend-
ing upon the reactivity of the organometallic compound: (1)
1,4-addition by moderately reactive compounds or; (2) 1,2-
addition by highly reactive compounds.[54] Triphenylgermyl-
lithium apparently added predominantly in the 1,4-position
indicating moderate reactivity,[70] however, triphenylsilyl-
lithium did not give identifiable products.[85] Anticipating
the discussion to follow under metalations, triphenylsilyl-
lithium is probably more reactive than triphenylgermyllithium
and very likely gave considerable 1,2-addition product, which
was not isolated.

In further support of the high reactivity of silylmetal-
lic reagents in this type of reaction, triphenylsilyllithium
and -potassium have been found to add to the azomethine link-
age of benzophenone anil and to azobenzene.[66] Triphenylsilyl-
lithium added to pyridine in the 4-position,[86] and to acridine

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[85]H. Gilman and G. D. Lichtenwalter, Iowa State Univer-
sity of Science and Technology, Ames, Iowa. Information con-
cerning reaction of triphenylsilyllithium with benzalaceto-
phenone. Private communication. 1958.

[86]D. Wittenberg and H. Gilman, Chem. and Ind. (London),
390 (1958).

across the 9,10-linkage.[87] These reactions are all typical

of highly reactive and selective reagents.

c. Halogen-metal interconversion reactions   Another

reaction which gives an indication of the general class of

organometallic reactivity is that of halogen-metal intercon-

version, a reaction which is successful only for highly reac-

tive organometallic reagents.[12] Silylmetallic reagents react

with both alkyl and aryl halides to give either coupling or

halogen-metal interconversion products depending upon the

halide used and the mode of addition.[50,60,88,89,90,91,92,93,

94,95] In most of the reactions, there was some degree of

[87]H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 23, 1586 (1958).

[88]H. Gilman and D. Aoki, ibid., 24, 426 (1959).

[89]A. G. Brook and S. Wolfe, J. Am. Chem. Soc., 79, 1431 (1957).

[90]R. A. Benkeser, H. Landesman and D. J. Foster, ibid., 74, 648 (1952).

[91]A. G. Brook, H. Gilman and L. S. Miller, ibid., 75, 4759 (1953).

[92]R. A. Benkeser and R. G. Severson, ibid., 73, 1424 (1951).

[93]H. Gilman and T. C. Wu, ibid., 73, 4031 (1951).

[94]H. Gilman and T. C. Wu, J. Org. Chem., 18, 753 (1953).

[95]G. D. Dappen, Iowa State University of Science and Technology, Ames, Iowa. Information regarding the reaction of triphenylsilyllithium with aryl halides. Private communication. 1960.

halogen-metal interconversion noted. Germylmetallic reagents have been reported to react with organic halides to give very small amounts, if any, of hexaphenyldigermane,[96] but stannylmetallic compounds[97] have been reported to give interconversion products. These results indicate again that silylmetallic reagents are highly reactive, but the results tend to confuse the previous conclusions concerning germylmetallic reagents.

Along these same lines of consideration, silylmetallic reagents[98] give a negative Color Test II A,[68] a test for highly reactive organometallic reagents which is dependent upon a halogen-metal interconversion reaction. A positive test may be obtained if the reagents involved are added quite rapidly. It is believed that the failure to give this test in a normal fashion is not due to the lesser reactivity of the silylmetallic reagents, but is due to a rapid coupling of bromotriphenylsilane and p-dimethylaminophenyllithium. These two compounds would have been formed by the halogen-metal

[96]C. W. Gerow. The preparation and cleavage of some organogermanium compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1956.

[97]H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, *18*, 680 (1953).

[98]H. J. S. Winkler, Iowa State University of Science and Technology, Ames, Iowa. Information concerning Color Test II A with silylmetallics. Private communication. 1960.

interconversion reaction of the silylmetallic compound with the first reagent of the color test, p-bromodimethylaniline.

d. <u>Metalation reactions</u>   One of the more elegant studies which has shown great usefulness in relating reactivities of organometallic compounds is that attributed to Conant and Wheland,[99] and later to studies of McEwen.[100] The technique involved was to allow the anion of a weak acid to react with another weak acid. Determination of the relative amounts of different substances present at the point of

$$R_1H + R_2^- \longrightarrow R_2H + R_1^-$$

equilibrium was taken as a measure of the relative strengths of the two acids. The results were determined by carbonation or by colorimetric measurements. The order of acid strength as determined by these several studies can be shown as:

$$\underline{n}\text{-}C_4H_{10} \ \langle \ C_6H_6 \ \langle \ C_6H_5CH(CH_3)_2 \ \langle \ C_6H_5CH_3 \ \langle \ (C_6H_5)_2CHCH_3$$

$$\langle \ (C_6H_5)_2CH_2 \ \langle \ (C_6H_5)_3CH \ \langle \ (C_6H_5)_2(\underline{\alpha}\text{-}C_{10}H_7)CH \ \langle \ \text{xanthene}$$

$$\langle \ \text{fluorene} \ \langle \ \text{9-phenylfluorene} \ \langle \ \text{indene} \ \langle \ C_6H_5C{\equiv}CH$$
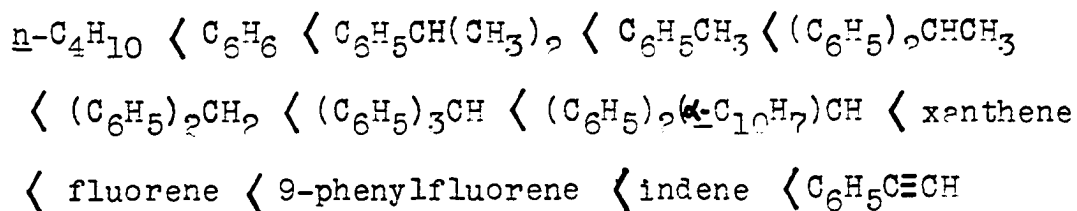
As mentioned in a previous section of the historical discussion, silylmetallic reagents have metalated diphenylmethane,[59] triphenylmethane,[56] fluorene[59] and phenylacetylene[58] in good yields, but toluene only in poor yield.[61]

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[99] J. B. Conant and G. W. Wheland, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>54</u>, 1212 (1932).

[100] W. K. McEwen, <u>ibid</u>., <u>58</u>, 1124 (1936).

Triphenylgermyllithium metalated fluorene[63] in good yield. Triphenylgermane has in turn been metalated by n-butyllithium and by phenyllithium in good yield.[101] However, triphenyl-silane gave only coupling products with organolithium reagents,[102] a result attributed to the differences in electronegativity between silicon and germanium in reference to hydrogen.

On the basis of these results, silyl- and germylmetallic anions probably should be considered as possessing greater nucleophilic activity than the diphenylmethyl anion and less than the benzyl anion, but further studies are necessary for a more accurate placement in the series. There has been no report of a successful relationship of the various silyl-metallic reagents themselves through metalation reactions.

At this point, the relative anion strength of the metallic members of Group IV A can be related unambiguously. Triphenyllead-lithium did not metalate fluorene;[59] triphenyl-tin-lithium metalated fluorene in an 11 percent yield;[59] and both triphenylgermyllithium[63] and -silyllithium[59] metalated the compound in good yield. Triphenylsilyllithium in turn metalated triphenylgermane.[64] Thus, the order of proton

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[101]H. Gilman and C. W. Gerow, ibid., 78, 5435 (1956).

[102]H. Gilman and H. W. Melvin, ibid., 71, 4050 (1949).

affinity is as follows:

$$(C_6H_5)_3Pb^- \langle (C_6H_5)_3Sn^- \langle (C_6H_5)_3Ge^- \langle (C_6H_5)_3Si^-$$
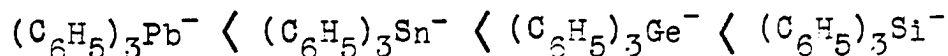
e. <u>Cleavage reactions</u>   It is in this area that some differentiation can be made between the various silyllithium compounds. As the number of alkyl substituents increases on a disilane, the cleavage of this disilane by lithium in tetrahydrofuran becomes slower. Hexaphenyldisilane, despite its low solubility, is cleaved more readily by lithium than is <u>sym</u>.-dimethyltetraphenyldisilane, which in turn is cleaved more readily than is <u>sym</u>.-tetramethyldiphenyldisilane.[103] <u>sym</u>.-Tetraphenyldisilane is cleaved only to a small extent,[104] while hexaalkyldisilanes have entirely resisted cleavage by metals.[105,106] The resonance stabilization of the anions formed may be the driving force for these reactions. It would be logical also to assume that the greater the resonance stabilization, the lesser would be the nucleophilic character of the anion and the following order should then hold:

[103]H. Gilman and G. D. Lichtenwalter, <u>ibid</u>., <u>80</u>, 608 (1958).

[104]H. Gilman and W. Steudel, <u>Chem</u>. <u>and</u> <u>Ind</u>. (<u>London</u>), 1094 (1959).

[105]H. Gilman, R. K. Ingham and A. G. Smith, <u>J</u>. <u>Org</u>. <u>Chem</u>., <u>18</u>, 1743 (1953).

[106]M. B. Hughes. Some correlations between organosilicon compounds and organogermanium compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

$$(C_6H_5)_3Si^- \ \langle \ (C_6H_5)_2CH_3Si^- \ \langle \ C_6H_5(CH_3)_2Si^- \langle \ (CH_3)_3Si^-$$
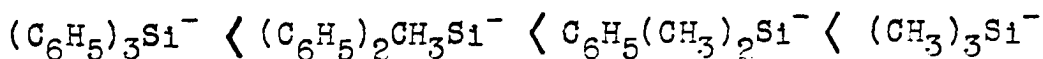
This order of anion strength received considerable experimental support as the result of some cleavage studies of disilanes by silyllithium compounds.[107] In this series of reactions a disilane was reacted with a silylmetallic reagent to give as products a new disilane, incorporating the more reactive silyl moiety; and the lesser reactive silyl-metallic compound, appearing as the corresponding silanol upon hydrolysis. The series developed was in agreement with the order of reactivity mentioned above. On the basis of some preliminary studies,[98] the same order appears to hold in the rate of cleavage of the reaction solvent, tetrahydrofuran.

In summary, it may be stated: (1) in addition reactions to olefins and carbonyl systems, and in halogen-metal interconversion reactions, silylmetallic reagents should be classified as "highly reactive" when based upon the definitions of reactivity devised for organometallic systems; (2) in metalation reactions silylmetallic compounds are, at best, moderately reactive; (3) based upon cleavage reactions, it appears that the reactivity of silylmetallic compounds decreases as the number of aryl substituents on the silicon increases; and (4) in the Group IV A series, Si, Ge, Sn and Pb, there is a decrease in reactivity with increasing atomic weight.

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[107]H. Gilman, G. D. Lichtenwalter and D. Wittenberg, _J. Am. Chem. Soc._, _81_, 5320 (1959).

E. Silanecarboxylic Acids

1. Preparation of acids

Benkeser and Severson,[92] in their initial investigation of the preparation and properties of triphenylsilylpotassium, found that the compound reacted with carbon dioxide to produce a white crystalline solid. This material was stable at room temperature, but when heated, decomposed to form carbon monoxide and a mixture of triphenylsilanol and hexaphenyldisilane. On the basis of its analysis and general behavior, they concluded that this carbonation product was triphenylsilanecarboxylic acid. Brook and Gilman[108] also prepared the acid in good yield by the carbonation of triphenylsilylpotassium. Further proof of structure for the acid was given by the preparation of the methyl ester and its reduction with lithium aluminum hydride to the carbinol, triphenylhydroxymethylsilane.[108]

Triphenylsilanecarboxylic acid has also been prepared by the carbonation of triphenylsilyllithium.[109] The only other silanecarboxylic acid that has been prepared is tri-p-tolylsilanecarboxylic acid by carbonation of the silylpotassium

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[108] A. G. Brook and H. Gilman, ibid., 77, 2322 (1955).

[109] M. V. George and H. Gilman, ibid., 81, 3288 (1959).

reagent.[110] Triphenylgermanecarboxylic acid, a similar acid, was prepared by the carbonation of triphenylgermylpotassium.[111]

2. Chemistry of acids

The chemistry of the silanecarboxylic acids is much different than that of other carboxylic acid systems. Benkeser and Severson[99] found that their crude acid decomposed upon heating with the evolution of carbon monoxide. This decomposition could also be effected by treatment with acid, and to some extent by merely dissolving the solid in solvents like acetone and ethanol. In all of these reactions only carbon monoxide was evolved. Later studies[112] have shown that all known organosilicon compounds, in which the silicon is attached directly to a carboxylic acid or ester group, undergo thermal rearrangement accompanied by the elimination of the carbonyl group as carbon monoxide. Careful work-up of the reaction mixture from the thermal decomposition of triphenylsilanecarboxylic acid (V) at its melting point (180°) has shown that the products formed are carbon monoxide, formic acid, triphenylsilylformate (VI), triphenylsilanol (VII) and

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

[111]A. G. Brook and H. Gilman, *ibid.*, **76**, 77 (1954).

[112]A. G. Brook, *ibid.*, **77**, 4827 (1955).

hexaphenyldisiloxane (IX).[112] Elucidation of the reaction

path as occurring through the intermediate formation of tri-

phenylsilyl triphenylsilanecarboxylate (VIII) was accomplish-

ed by Brook,[112] who was able to synthesize the compound.

$$(C_6H_5)_3SiOCH \longleftarrow (C_6H_5)_3SiCOH \longrightarrow CO + (C_6H_5)_3SiOH$$

$$\begin{matrix} O \\ \parallel \end{matrix}$$

VI   V   VII

$$HCOH + (C_6H_5)_3SiCOSi(C_6H_5)_3 \longrightarrow CO +$$

VIII $(C_6H_5)_3SiOSi(C_6H_5)_3$

                  IX

$$C_5H_5N$$

$$(C_6H_5)_3SiCOH + (C_6H_5)_3SiCl$$
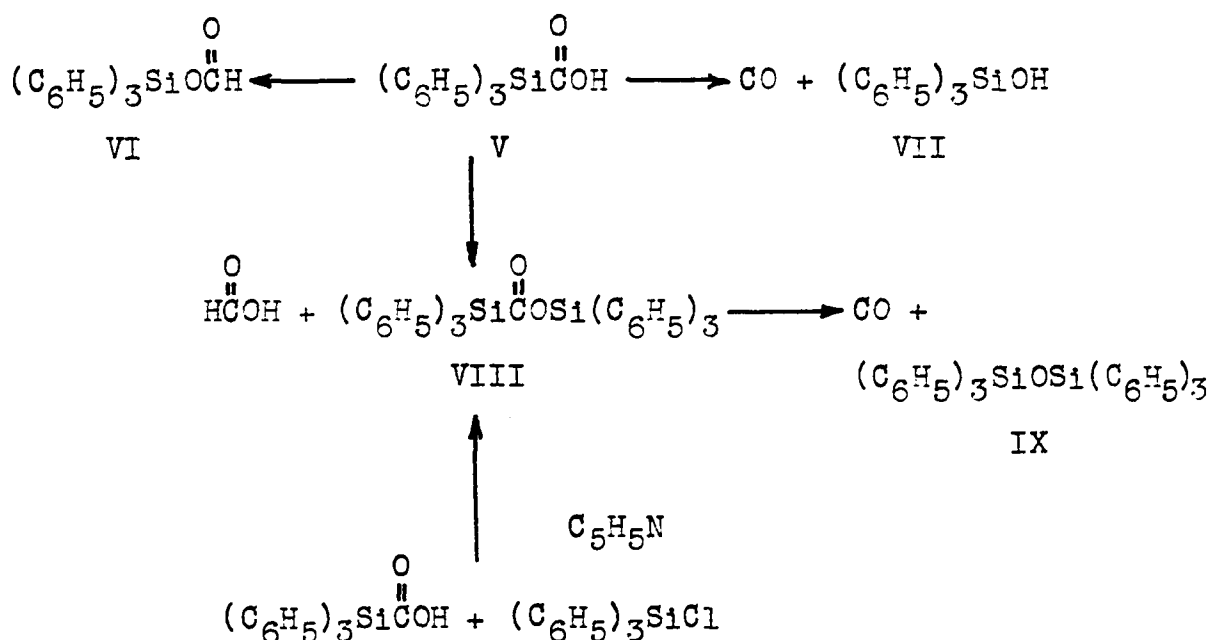
A close analogy exists between the behavior of triphenyl-

silanecarboxylic acid and triphenylgermanecarboxylic acid in-

sofar as their thermal decompositions are concerned.[111,112]

Like its silicon analog, triphenylgermanecarboxylic acid will

liberate carbon monoxide on melting. However, water and a

high yield of triphenylgermyl triphenylgermanecarboxylate,

$(C_6H_5)_3GeCOOGe(C_6H_5)_3$, are obtained rather than the expected

digermoxane and germol. Heating at elevated temperatures

(190°) will give triphenylgermol and hexaphenyldigermoxane.

It is interesting to observe, despite the fact that bonds to

germanium are generally somewhat weaker than the corresponding

bonds to silicon,[113] that triphenylgermanecarboxylic acid and
its derivatives are somewhat more stable towards thermal re-
arrangements than are its silicon analogs. This may be due
to decreased steric strain in the germanium compounds.

It was also found that, while crude triphenylsilane-
carboxylic acid was relatively unstable decomposing in warm
absolute ethanol with the evolution of carbon monoxide,[92]
purified samples were relatively stable and failed to decom-
pose in absolute ethanol or in ethanol-pyridine solutions.[108]
Complete decomposition of the pure acid, with evolution of
carbon monoxide, occurred rapidly by treatment with only
catalytic amounts of sodium hydroxide or sodium ethoxide in
absolute ethanol, and more slowly with sodium methoxide in
absolute methanol, or with aqueous pyridine. It was demon-
strated[108] that a nucleophilic attack by base on silicon
occurs with evolution of carbon monoxide, and, if the base is
alkoxide, the resulting alkoxytriphenylsilane is hydrolyzed
so that only triphenylsilanol is isolated.

The decomposition of triphenylsilanecarboxylic acid
appeared not to be acid catalyzed.[108] The acid was stable to
brief refluxing in ethanol containing a trace of aqueous
hydrochloric acid, but partial elimination of carbon monoxide
did occur upon prolonged refluxing with 6N sulfuric acid, or
in solution with ethanol and 6N sulfuric acid. However, an

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[113]M. L. Huggins, _ibid._, 75, 4123 (1953).

equivalent amount of decomposition occurred when the sulfuric
acid was replaced by distilled water.

3. Chemistry of esters

Treatment of triphenylsilanecarboxylic acid with excess
diazomethane gave excellent yields of the ester, methyl tri-
phenylsilanecarboxylate.[108,110] The ethyl ester was prepared
similarly from diazoethane. The methyl and ethyl esters of
tri-p-tolylsilanecarboxylic acid were prepared in a like man-
ner. The very interesting ester triphenylsilyl triphenyl-
silanecarboxylate (VIII) was prepared by reacting the acid
with chlorotriphenylsilane.[112] The corresponding germanium
compound could be prepared simply by heating the acid.[111]

Methyl triphenylsilanecarboxylate is a reasonably stable
solid which does not decompose on melting, but like the acid,
is very sensitive to alkaline reagents.[108] Treatment of the
compound at room temperature with catalytic amounts of sodium
hydroxide, sodium methoxide or sodium ethoxide yielded tri-
phenylsilanol, triphenylmethoxysilane, triphenylethoxysilane,
and carbon monoxide. However, treatment of methyl triphenyl-
silanecarboxylate with lithium aluminum hydride led to a
smooth reduction of the compound to triphenylhydroxymethyl-
silane.

Brook and Mauris[110] carried out a very careful investi-
gation of the base catalyzed rearrangement of these esters

to determine whether the process was intra- or intermolecular.
When a mixture of two different esters was subjected to the
conditions of the rearrangement, these workers found that it
had involved the migration of the alkoxyl group from the
carbonyl group to the silicon atom in the same molecule. The
isolation of two, rather than four, products proved the
process to be intramolecular. These workers[110] proposed a
three-membered cyclic intermediate formed by attack of the
most electronegative atom, oxygen, on the least electro-
negative atom, silicon. Subsequent release of electrons to
the carbonyl group results in its evolution as carbon mon-

$$R_3Si:C::O \longrightarrow R_3Si:C::O \longrightarrow R_3Si:OR' + :C::O$$
$$\begin{array}{c} | \\ :O: \\ | \\ R' \end{array} \qquad \begin{array}{c} O: \\ | \\ R' \end{array}$$
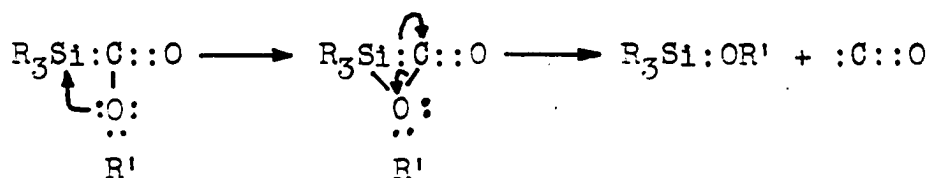
oxide. No exact analogy to this type of rearrangement is
known in carbon chemistry.

III. EXPERIMENTAL

A. General

Reactions involving silylmetallic or organometallic compounds were carried out in oven-dried glassware under an atmosphere of dried, oxygen-freed nitrogen.[114] Diethyl ether, when employed as a reaction solvent, was dried over sodium wire before usage. When tetrahydrofuran was employed as a reaction medium, drying was accomplished by refluxing over sodium for at least 24 hours and distilling, immediately before use, from lithium aluminum hydride. Melting and boiling points are reported in degrees Centigrade and are uncorrected. Infrared spectra were obtained either on a Baird, Model B, or Perkin-Elmer, Model 21, recording spectrophotometer.

n-Butyllithium,[115] phenyllithium[116] and methyllithium were prepared as diethyl ether solutions by reported procedures in average yields of 80.4%, 96.1% and 91.5%, respectively. Other organometallic reagents, not used so extensive-

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[114]K. Oita. Direct preparation of some organolithium compounds from lithium and RX compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1955.

[115]H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949).

[116]H. Gilman, E. A. Zoellner and W. M. Selby, ibid., 55, 1252 (1933).

ly, are mentioned in the text of the experimental presenta-
tion. All silylmetallic compounds were prepared by the
lithium cleavage of the respective symmetrical disilanes in
tetrahydrofuran.[103]

B. Development of an Improved Procedure for the Dimetalation of Diphenyl Ether

1. n-Butyllithium in tetrahydrofuran-ether mixed solvent (1:1) at room temperature

To a solution of 25.5 g. (0.15 mole) of diphenyl ether
and 250 ml. of tetrahydrofuran was added slowly 0.35 mole of
n-butyllithium in 290 ml. of ether solution. The reaction
flask was cooled at ice-bath temperature throughout the addi-
tion, which was completed in 25 minutes. The ice-bath was
then removed and stirring was continued. The dark green re-
action mixture gave a strongly positive Color Test II.[68]
Six hours later, Color Test II gave an initial negative test,
but a dark reddish-brown color developed upon standing.
Eight hours later the same results were obtained, and it was
concluded that this was a negative test. Color Test I[67] was
strongly positive. The reaction mixture was poured jet-wise
through a glass wool plug into a dried, nitrogen swept, addi-
tion funnel prior to derivatization.

A two-liter, four-necked flask was equipped with con-
denser, nitrogen inlets, true-bore stirrer, and two addition
funnels; one containing about 0.15 mole of 2,2'-dilithiodi-

phenyl ether in 500 ml. of ether-tetrahydrofuran solution, and
the other containing 19.4 g. (0.15 mole) of dichlorodimethyl-
silane dissolved in 250 ml. of tetrahydrofuran. One hundred
milliliters of the 2,2'-dilithiodiphenyl ether solution was
added to the flask and stirring was begun. The remainder was
added simultaneously with the dropwise addition of the di-
chlorodimethylsilane solution. For the first 15 minutes of
the addition, spontaneous refluxing occurred, but, when it
stopped, heat was applied to maintain a gentle reflux. Upon
completion of addition, Color Test I was negative, and hydrol-
ysis was effected with dilute hydrochloric acid. The layers
were separated, the aqueous layer was extracted several times
with ether, and the combined extracts and organic layer was
dried over anhydrous sodium sulfate.

The solvent was stripped off to leave a dark brown oil,
which was distilled at atmospheric pressure to give a light
brown oil boiling over the range 296-301°. The oil solidified
when seeded with a crystal of 10,10-dimethylphenoxasilin. The
crude material weighed 17.8 g. (52.5%), melting range 60-74°.
Two recrystallizations from methanol raised the melting point
to 74-79° (lit. value,[8] 78.5-79.0°), 10.8 g. (32.0%). The
material was not obtained in an optimum degree of purity since
the relative amounts obtained were of major importance. The
melting point of a mixture with an authentic sample was unde-
pressed, and the infrared spectra were superimposable.

The reaction was repeated under identical conditions but using larger quantities (2.5 times greater). The large bulk of the solutions proved difficult to handle and a lower yield of derivative was obtained (33.5%).

2. n-Butyllithium in tetrahydrofuran-ether mixed solvent at mild reflux

a. 1:1.1 Tetrahydrofuran-ether ratio   A 440 ml. ether solution containing 0.575 mole of n-butyllithium was added rapidly to a solution of 42.5 g. (0.25 mole) of diphenyl ether and 350 ml. of tetrahydrofuran cooled to ice-bath temperature. The ice-bath was removed, and the reaction mixture was warmed to a mild reflux temperature. Color Test II remained positive for 3 hours, but became negative after 4 hours. Color Test I was positive.

Derivatization was effected with 32.2 g. (0.25 mole) of dichlorodimethylsilane dissolved in 350 ml. of tetrahydrofuran as described in the previous experiment. Recrystallization of the crude solid from methanol gave 25.8 g. (45.5%) of 10,10-dimethylphenoxasilin, m.p. 75-79°.

b. 1:1.3 Tetrahydrofuran-ether ratio   The above procedure was followed in the reaction of 46.8 g. (0.275 mole) of diphenyl ether dissolved in 400 ml. of tetrahydrofuran with 0.605 mole of n-butyllithium in 590 ml. of ether solution. A total of 5 hours of mild reflux was necessary before Color Test II became negative. Derivatization with dichlorodimethyl-

silane gave 28.5 g. (50.5%) of 10,10-dimethylphenoxasilin, m. p. 74-79°.

3. <u>n-Butyllithium in tetrahydrofuran</u>

A tetrahydrofuran solution of 0.0895 mole of <u>n</u>-butyl-lithium,[117] cooled to -25 ± 5° by means of a Dry Ice-acetone cooled addition funnel, was added slowly to a solution of 6.80 g. (0.04 mole) of diphenyl ether and 80 ml. of tetra-hydrofuran, also cooled to -25 ± 5°. Addition was completed in 20 minutes. The dark green solution gave a positive Color Test II. After the reaction mixture had stirred at this temperature for 5 hours, the color test remained positive. Accordingly, the solution was allowed to warm to ice-bath temperature and stirred overnight. The next morning, Color Test II was negative.

Derivatization was carried out with a solution of 5.16 g. (0.04 mole) of dichlorodimethylsilane and 75 ml. of tetra-hydrofuran using the same procedure as discussed previously. Subsequent to distillation, there was obtained 1.80 g. (20.0%) of crude 10,10-dimethylphenoxasilin melting over the range 65-75°. A recrystallization from methanol gave 1.50 g. (16.6%) of purer product, m. p. 74-78°.

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[117]H. Gilman and B. J. Gaj, <u>J</u>. <u>Org</u>. <u>Chem</u>., <u>22</u>, 1165 (1957).

4. Phenyllithium in tetrahydrofuran-
   ether mixed solvent (1:1)

A solution of 0.605 mole of phenyllithium in 480 ml. of
ether was added rapidly to a solution of 46.8 g. (0.275 mole)
of diphenyl ether and 400 ml. of tetrahydrofuran. The reac-
tion mixture was kept at ice-bath temperature during the addi-
tion. The ice-bath was removed and the reaction mixture was
warmed at a gentle reflux overnight. The next morning Color
Test I was dark blue. The reaction mixture was reacted with
32.2 g. (0.25 mole) of dichlorodimethylsilane dissolved in
400 ml. of tetrahydrofuran as described previously. Work-up
in the usual manner gave 18.9 g. (33.4%) of crude product,
m. p. 74-78°. A recrystallization from methanol gave 13.4
g. (23.7%) of 10,10-dimethylphenoxasilin, m. p. 78-80.5°.

5. Methyllithium (attempted)

To a solution of 46.8 g. (0.275 mole) of diphenyl ether
dissolved in 400 ml. of tetrahydrofuran, cooled to ice-bath
temperature, was added rapidly 0.605 mole of methyllithium
in 615 ml. of ether solution. Upon completion of addition,
the ice-bath was removed, and the reaction mixture was warmed
at mild reflux temperature overnight. The next morning,
derivatization was carried out in the usual manner with a
solution of 32.2 g. (0.25 mole) of dichlorodimethylsilane
dissolved in 400 ml. of tetrahydrofuran.

The dark oil, obtained upon removal of the solvent, was distilled at atmospheric pressure. A dark oil was collected boiling over the range 270-309°, but this could not be induced to crystallize, even when the oil was cooled in a Dry Ice-acetone bath and seeded with an authentic sample. None of the desired product was isolated and the oil is believed to be polymeric in nature.

C. Preparation of Phenoxasilin Compounds

1. 10,10-Diphenylphenoxasilin from diphenylsilane

2,2'-Dilithiodiphenyl ether was prepared by reacting 6.80 g. (0.04 mole) of diphenyl ether dissolved in 60 ml. of tetrahydrofuran with 0.092 mole of n-butyllithium in 138 ml. of ether solution at mild reflux temperature for 5 hours. This solution was added to a flask with the simultaneous addition of 7.37 g. (0.04 mole) of diphenylsilane dissolved in 60 ml. of tetrahydrofuran as described in the preceding section. Slight spontaneous refluxing occurred. To aid the reaction, mild warming was applied. The addition was completed in 10 minutes. Color Test I[67] was positive, accordingly, the reaction mixture was heated at reflux overnight. Color Test I was still positive and remained slightly positive after another 6 hours of refluxing. Hydrolysis was effected with 200 ml. of water and the usual work-up was carried out. The ether extracts were evaporated under an air-jet to leave an

oily solid. This was washed with petroleum ether (b. p. 60-70°) to give 5.65 g. (40.3%) of 10,10-diphenylphenoxasilin, melting range 165-173°. A recrystallization from petroleum ether (b. p. 80-110°) raised the melting point to 172-176.5°, 3.90 g. (27.8%); and a recrystallization from ethyl acetate gave 2.80 g. (20.0%) of pure product, m.p. 176-178°. A melting point of a mixture with an authentic sample was un-depressed.[8]

2. 10-Phenylphenoxasilin

2,2'-Dilithiodiphenyl ether, approximately 0.12 mole prepared by the dimetalation of diphenyl ether by n-butyllithium as described in the first section, was added to a flask with the simultaneous addition of a solution of 16.2 g. (0.15 mole) of phenylsilane[118] and 200 ml. of tetrahydrofuran. The rate of addition was adjusted in such a manner that there was always a slight excess of phenylsilane. Slight spontaneous refluxing occurred during the addition. Color Test I was deep violet. The reaction mixture was stirred overnight at room temperature; Color Test I was then a light violet. The light colored solution was poured onto crushed ice acidified with sulfuric acid. The layers were separated, and the aqueous layer extracted several times with ether.

118A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).

After drying the ether extracts over anhydrous sodium sulfate, the solvent was stripped off to leave a yellow oil, which was distilled under reduced pressure to give 2.30 g. (11.3%) of recovered diphenyl ether, b. p. $46\text{-}47^{\circ}$ (0.08 mm.), n_D^{20} 1.5838, and another oil boiling over the range $119\text{-}127^{\circ}$ (0.05 mm.). This oil solidified upon cooling in an ice-bath. The solid was washed with methanol to give 10.9 g. (33.0%) of white solid, melting range $51\text{-}72^{\circ}$. A recrystallization from methanol gave 8.50 g. (25.8%) of pure 10-phenylphenoxasilin, m. p. $81\text{-}83^{\circ}$.

Anal.[119] Calcd. for $C_{18}H_{14}OSi$: Si, 10.25. Found: Si, 10.14, 10.21.

The infrared spectrum as a carbon tetrachloride solution showed the characteristic Si-H band at 4.65μ in addition to the bands for Si-phenyl and diphenyl ether.

In order to obtain sufficient quantities of the silane for starting material, the reaction was repeated several times to give the cyclic silane in pure yields of 15.4 and 23.7%.

3. **10,10-Diphenylphenoxasilin from phenyllithium and 10-phenylphenoxasilin**

An ether solution of 0.0073 mole of phenyllithium was added over a period of 10 minutes to 2.00 g. (0.0073 mole)

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[119]Silicon analyses were performed by the procedure of H. Gilman, H. W. Melvin and G. E. Dunn, ibid., 72, 5767 (1950).

of 10-phenylphenoxasilin dissolved in 50 ml. of ether. Color

Test I was slightly positive upon completion of addition, and

after the solution had been stirred at room temperature for

4 hours; however, after 1 hour of refluxing the reaction mix-

ture, the color test was negative. Hydrolysis was effected

with water. The usual work-up gave 1.30 g. (50.6%) of 10,10-

diphenylphenoxasilin melting over the range 164-178$^{\mathrm{o}}$. A re-

crystallization from petroleum ether (b. p. 80-110$^{\mathrm{o}}$) raised

the melting point to 176-178$^{\mathrm{o}}$, 1.00 g. (39.0%) (mixture melt-

ing point identification).

4. 10-Methyl-10-phenylphenoxasilin

Methyllithium, 0.0182 mole in ether solution, was added

slowly to 5.00 g. (0.0182 mole) of 10-phenylphenoxasilin dis-

solved in 75 ml. of ether. There was no evident evolution of

heat during the addition, but the solution turned white.

Color Test I was positive at the completion of addition but

was negative after the solution had stirred at room tempera-

ture for 2 hours. The solution was hydrolyzed with aqueous

ammonium chloride solution and the usual separation and ex-

traction employed. Evaporation of the ether solvent left

a colorless oil. This crystallized after being taken up in

ethanol and the ethanol solution evaporated under an air-jet.

Several recrystallizations of the solid from the same solvent

gave 3.15 g. (60.0%) of 10-methyl-10-phenylphenoxasilin as

white crystals, m. p. 56.5-58.0°.

Anal. Calcd. for $C_{19}H_{16}OSi$: Si, 9.75. Found: Si, 9.53, 9.77, 9.88.

The infrared spectrum as a carbon disulfide solution was quite similar to those of the following 10-phenyl-10-tolyl-phenoxasilins except for a small peak at 8.14μ which is characteristic of Si-methyl absorption.

5. 10-Phenyl-10-o-tolylphenoxasilin

An ether solution containing 0.00726 mole of o-tolyl-lithium[116] was added slowly to 2.00 g. (0.00726 mole) of 10-phenylphenoxasilin dissolved in 50 ml. of ether. The white solution gave a mildly positive Color Test I. After the reaction mixture had stirred at room temperature for 2 hours, Color Test I was still faintly positive. The reaction mixture was hydrolyzed with aqueous ammonium chloride solution and worked up in the usual manner to give a white solid. This was recrystallized from ethanol to give 1.25 g. (47.2%) of 10-phenyl-10-o-tolylphenoxasilin as white crystals, m. p. 116-117.5°.

Anal. Calcd. for $C_{25}H_{20}OSi$: Si, 7.72. Found: Si, 7.58, 7.82.

The infrared spectrum as a carbon disulfide solution showed the characteristic absorption bands for C-H aromatic and aliphatic, ether linkage, and Si-phenyl.

6. 10-Phenyl-10-p-tolylphenoxasilin

An ether solution of 0.00726 mole of p-tolyllithium[116] was added slowly to 2.00 g. (0.00726 mole) of 10-phenyl-phenoxasilin dissolved in 50 ml. of ether. Slight spontaneous refluxing occurred during the addition, and the solution turned white. Color Test I was moderately positive, but after the solution had been refluxed for 2 hours it was only slightly positive. The reaction mixture was hydrolyzed with water and worked up in the same manner as described previously to give 2.10 g. (79.3%) of crude material melting over the range 141°-to a turbid liquid. Several recrystallizations from petroleum ether (b. p. 80-110°) gave 1.25 g. (47.2%) of pure 10-phenyl-10-p-tolylphenoxasilin, m. p. 155-157°.

Anal. Calcd. for $C_{25}H_{20}OSi$: Si, 7.72. Found: Si, 7.73, 7.77.

The infrared spectrum as a carbon disulfide solution was similar to that of 10-phenyl-10-o-tolylphenoxasilin.

7. 10-(o-Biphenylyl)-10-phenylphenoxasilin

An ethereal solution of 0.011 mole of 2-biphenylyl-lithium[114] was added slowly to 3.00 g. (0.011 mole) of 10-phenylphenoxasilin dissolved in 100 ml. of ether. Color Test I was strongly positive at the completion of addition, but was negative after the reaction mixture had stirred at room temperature for 2.5 hours. Hydrolysis was effected with

dilute aqueous ammonium chloride, and the usual work-up was carried out to give a white, oily solid. Several recrystallizations from petroleum ether gave 2.20 g. (47.2%) of 10-(o-biphenylyl)-10-phenylphenoxasilin as a white crystalline solid, m. p. 150-151°.

Anal. Calcd. for $C_{30}H_{22}OSi$: Si, 6.59. Found: Si, 6.47, 6.57.

The infrared spectrum was in good agreement with those of similar phenoxasilin compounds.

8. 10-(p-phenoxyphenyl)-10-phenylphenoxasilin

To 0.0182 mole of n-butyllithium as an ethereal solution cooled to -20° was added slowly 4.53 g. (0.0182 mole) of p-bromophenyl phenyl ether dissolved in 100 ml. of ether. The addition was adjusted at a rate to maintain the temperature at -20°. Upon completion of addition, the clear solution gave a negative Color Test II,[68] but a positive Color Test I. Five grams (0.0182 mole) of 10-phenylphenoxasilin dissolved in 100 ml. of ether was added rapidly to the cooled solution. The reaction mixture was allowed to warm to room temperature. Since Color Test I was mildly positive, the reaction mixture was stirred at room temperature overnight. The color test was then negative. The solution was hydrolyzed with dilute aqueous ammonium chloride solution and the usual separation and ether extraction employed. Evaporation of the solvent

left a colorless oil which solidified after standing for several days. The solid was washed with petroleum ether (b. p. 60-70°) and recrystallized several times from the same solvent to give 1.55 g. (19.3%) of 10-(p-phenoxyphenyl)-10-phenylphenoxasilin, m. p. 136-137°.

Anal. Calcd. for $C_{30}H_{22}O_2Si$: Si, 6.3?. Found: Si, 6.11, 6.21.

9. 10-Hydroxy-10-phenylphenoxasilin

To 2.00 g. (0.0073 mole) of 10-phenylphenoxasilin suspended in 20 ml. of absolute ethanol was added slowly a solution of 1.51 g. (0.027 mole) of potassium hydroxide dissolved in 5 ml. of water and 15 ml. of absolute ethanol. A gas was given off rapidly during the addition, which was completed in 10 minutes. The reaction mixture was diluted with aqueous ammonium chloride solution. A white oil separated out which was extracted with ether and the usual work-up effected. Evaporation of the ether solvent left a white solid which was recrystallized several times from petroleum ether (b. p. 60-70°) to give 1.64 g. (77.4%) of 10-hydroxy-10-phenylphenoxasilin as a white crystalline solid, m. p. 124-125°.

Anal. Calcd. for $C_{18}H_{14}O_2Si$: Si, 9.66. Found: Si, 9.38, 9.47, 9.53, 9.61.

The infrared spectrum as a carbon disulfide solution was quite similar to that of other phenoxasilin compounds except

for an unassociated hydroxyl absorption peak at 2.70 μ.

10. 10,10'-Oxybis-(10-phenylphenoxasilin)

One gram (0.0034 mole) of 10-hydroxy-10-phenylphenoxa-
silin was suspended in 20 ml. of 98% formic acid and the mix-
ture was refluxed for 1 hour. Upon cooling to room tempera-
ture, the reaction mixture was filtered to leave a white
solid. This was washed free of formic acid and dried to give
0.80 g. (85.1%) of crude 10,10'-oxybis-(10-phenylphenoxasilin)
melting over the range 167-183°. After trituration with
ethanol and recrystallization from petroleum ether (b. p. 80-
110°), the white solid melted 189.5-191°, 0.35 g. (37.3%).
The melting point of a mixture with a sample of solid isolated
and analyzed previously in this Laboratory[120] was undepressed.
The infrared spectra were also superimposable.

11. 10-Benzyl-10-phenylphenoxasilin

A tetrahydrofuran solution containing 0.0117 mole of
benzyllithium[121] was added to 3.20 g. (0.0117 mole) of 10-
phenylphenoxasilin dissolved in 50 ml. of ether. There was

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[120]G. Schwebke, Iowa State University of Science and
Technology, Ames, Iowa. Information on 10,10'-oxybis-(10-
phenylphenoxasilin). Private communication. 1960.

[121]H. A. McNinch. Preparation and some reactions of
organolithium reagents of the benzyl type. Unpublished M. S.
Thesis. Ames, Iowa, Library, Iowa State University of Science
and Technology. 1959.

no spontaneous evolution of heat. At first the color of the benzyllithium solution was rapidly lost,- but at the end of the addition the color of the solution was orange. Color Test I was mildly positive, but after the reaction mixture had stirred overnight at room temperature the color test was negative. Following hydrolysis with dilute aqueous ammonium chloride and the usual work-up, evaporation of the ether solvent left a colorless oil which solidifed upon standing for a day. The oily solid was washed with petroleum ether (b. p. 60-70°) and recrystallized from the same solvent to give 0.95 g. (28.0%) of 10-hydroxy-10-phenylphenoxasilin, m. p. 124-125.5^{o}. The melting point of a mixture with an authentic specimen was not depressed, and the infrared spectrum was superimposable with that of an authentic sample.

Evaporation of the mother liquor left a small amount of oil, which crystallized upon standing. The solid was recrystallized from ethanol to give a trace of white crystals believed to be 10-benzyl-10-phenylphenoxasilin, m. p. 89-90°.

<u>Anal</u>. Calcd. for $C_{25}H_{20}OSi$: C, 82.30; H, 5.53. Found: C, 82.50, 82.60; H, 5.86, 6.01.

12. <u>10-Bromo-10-phenylphenoxasilin</u>

To a solution of 5.00 g. (0.018 mole) of 10-phenylphenoxasilin dissolved in 100 ml. of carbon tetrachloride was added, in small portions, 3.20 g. (0.018 mole) of N-bromosuccinimide.

The solution became yellow in color and quite warm, a water bath being used to control the temperature. The reaction mixture was stirred for 3 hours at room temperature. At the end of that period, the mixture was filtered under nitrogen to give 1.50 g. (84.2%) of succinimide, m. p. 121-125° (mixture melting point). The red filtrate was distilled, using the reduced pressure of a water aspirator, to leave a brown residue. This was recrystallized from petroleum ether (b. p. 80-110°) to give 3.35 g. (52.6%) of 10-bromo-10-phenylphenoxasilin as a light yellow solid, m. p. 96-99°.

Anal. Calcd. for $C_{18}H_{13}BrOSi$: Si, 7.96. Found: Si, 8.18, 8.18.

The infrared spectrum as a carbon tetrachloride solution was identical to that of the starting material except for the absence of the Si-H absorption peak.

The recrystallization solvent was hydrolyzed with water and worked up in the usual manner to give, after recrystallization from petroleum ether (b. p. 80-110°), 0.35 g. (6.68%) of 10-hydroxy-10-phenylphenoxasilin, m. p. 123-124° (mixture melting point).

The reaction was repeated to give a yield of 63.?% of 10-bromo-10-phenylphenoxasilin, m. p. 96.5-99.0^o, and 24.9% of 10-hydroxy-10-phenylphenoxasilin.

To provide added proof for the structure of the bromo compound, 2.00 g. (0.0057 mole) was reacted with an ethereal

solution of 0.0057 mole of phenyllithium. The reaction was carried out and worked up in the same manner as described for the reaction of 10-phenylphenoxasilin with phenyllithium. There was obtained 0.70 g. (35.3%) of crude 10,10-diphenyl-phenoxasilin melting over the range 149°-to a turbid liquid. Two recrystallizations from petroleum ether (b. p. 80-110°) raised the melting point to 177-179° (mixture melting point). 10-Hydroxy-10-phenylphenoxasilin, 0.55 g. (33.5%), was also isolated.

13.   10,10'-Diphenyl-10,10'-bi-(phenoxasilin)

To a solution of 5.00 g. (0.0142 mole) of 10-bromo-10-phenylphenoxasilin and 75 ml. of xylene was added 0.345 g. (0.015 g. atom) of sodium cut into several small pieces. The mixture was heated at reflux for 24 hours. After the brown solution had cooled, it was poured into ethanol. The ethanol was diluted with an equal volume of water. A small amount of insoluble material was filtered off, but, since it partially dissolved upon washing with benzene, it was added to the organic layer. The layers were separated and the aqueous layer was extracted several times with benzene. Evaporation of the solvent left a yellow solid which was slurried with ethanol to give 3.55 g. (91.2%) of crude 10,10'-diphenyl-10,10'-bi-(phenoxasilin), melting range 206-225°. Recrystallization from benzene-petroleum ether (b. p. 60-70°) and from petroleum

ether (b. p. 80-110°) gave 2.20 g. (56.5%) of pure product,
m. p. 231-233°.

Anal. Calcd. for $C_{36}H_{26}O_2Si_2$: Si, 10.28. Found: Si,
10.15, 10.22.

The infrared spectrum as a carbon disulfide solution was
superimposable with that of 10,10-diphenylphenoxasilin except
for the band at 14.45 μ, which is smaller and not split into
a doublet.

14. 2-Trimethylsilyl-10,10-diphenylphenoxasilin

To 10.0 g. (0.0412 mole) of 4-trimethylsilylphenyl phenyl
ether dissolved in 60 ml. of tetrahydrofuran and cooled to
ice-bath temperature was added slowly an ether solution con-
taining 0.092 mole of n-butyllithium. The light yellow solu-
tion gave a positive Color Test II. The ice-bath was removed,
and, after the solution had stirred at room temperature for
one hour, mild warming was applied for 15 hours. Color Test
II was then negative, but Color Test I was strongly positive.
The reaction mixture, after it had been poured jet-wise through
a glass wool plug into a dried, nitrogen swept addition funnel,
was added dropwise to a flask with the simultaneous addition
of 10.4 g. (0.0412 mole) of dichlorodiphenylsilane dissolved
in 50 ml. of tetrahydrofuran. Spontaneous refluxing occur-
red. Color Test I was negative upon completion of addition.
Following hydrolysis with dilute aqueous ammonium chloride

solution, the usual work-up was carried out to yield a brown
oil. This was distilled at reduced pressure to give 8.05 g.
of oil boiling over the range 185-198° (0.05 mm.). Treatment
of the oil with methanol gave 3.15 g. (18.2%) of a white
solid, melting range 114-120°. After several recrystalliza-
tions from methanol, the melting point of the 2-trimethyl-
silyl-10,10-diphenylphenoxasilin was raised to 123-124°, 2.95
g. (16.9%).

Anal. Calcd. for $C_{27}H_{26}OSi_2$: C, 76.70; H, 6.20. Found:
C, 76.85, 77.00; H, 5.75, 5.83.

15. Bromination of 10,10-dimethyl-
phenoxasilin (attempted)

a. With bromide-bromate mixture   Five grams (0.022
mole) of 10,10-dimethylphenoxasilin dissolved in glacial
acetic acid was allowed to react with a mixture of 4.17 g.
(0.035 mole) of potassium bromide and 1.17 g. (0.007 mole) of
potassium bromate dissolved in 12 ml. of water. A red color
appeared immediately, however, this color disappeared in
about 2 minutes. The reaction mixture was refluxed for 1.5
hours. Aqueous sodium bisulfite was then added, and a yellow
oil settled out after the solution was cooled in an ice-bath.
The aqueous layer was decanted off, and the oil washed with
2% sodium hydroxide, followed by washing with dilute hydro-
chloric acid. Attempts to crystallize the oil failed. The
infrared spectrum showed bands for OH and Si-O-Si indicating

that rupture of the ring had occurred.

b. **With N-bromosuccinimide**

i. **In refluxing carbon tetrachloride with zinc chloride catalyst**   N-Bromosuccinimide, 4.43 g. (0.025 mole), was added to a solution of 5.00 g. (0.022 mole) of 10,10-dimethylphenoxasilin and 150 ml. of carbon tetrachloride. The solution was stirred overnight at room temperature, but there was no visible reaction. The reaction mixture was heated to reflux temperature, also without any visible reaction occurring. The flask and contents were cooled to room temperature and 3.40 g. (0.025 mole) of anhydrous zinc chloride was added. The reaction mixture was warmed at reflux temperature for 1.5 hours, at which time the solution was dark orange in color. The reaction mixture was cooled and filtered. The orange filtrate was evaporated under an air-jet to give a crystalline solid. This was recrystallized from methanol to give 4.75 g. (95.0%) of recovered starting material. No bromo derivative of 10,10-dimethylphenoxasilin was isolated.

ii. **In refluxing benzene**   Five grams (0.022 mole) of 10,10-dimethylphenoxasilin dissolved in 150 ml. of benzene was mixed with 4.43 g. (0.025 mole) of N-bromosuccinimide, and the reaction mixture was heated at reflux temperature for several hours. Upon cooling, a white solid settled out of the solution. This was filtered off, and the

filtrate was evaporated under an air-jet to leave an orange, crystalline material. This was chromatographed on an alumina column and eluted with petroleum ether (b. p. 60-70°) to give 3.45 g. (69.0%) of recovered starting material. A small amount of succinimide, m. p. 122-125° (mixture melting point), was also isolated, indicating that some bromine had been released. However, a bromo derivative of 10,10-dimethyl-phenoxasilin was not isolated.

iii. **In refluxing glacial acetic acid** - The previous reaction was repeated using glacial acetic acid as the solvent. A dark color developed upon refluxing; there being no observable reaction at room temperature. After refluxing for 24 hours, the reaction mixture was diluted with water and extracted with ether. The oil resulting from evaporation of the ether solvent was chromatographed on alumina, but only resinous material was eluted. Identifiable materials could not be isolated.

D. Preparation of Some Silicon Derivatives of Xanthene

1. **9-Triphenylsilylxanthene**

a. **From 9-lithioxanthene and chlorotriphenylsilane** Chlorotriphenylsilane, 16.95 g. (0.0575 mole) dissolved in 200 ml. of ether, was added slowly to an ethereal solution of

0.0548 mole of 9-lithioxanthene,[122] prepared from 10.0 g.

(0.0548 mole) of xanthene[123] dissolved in 100 ml. of ether

and an ethereal solution of 0.057 mole of n-butyllithium.

The light orange solution gave a negative Color Test I[67] upon

completion of addition. The reaction mixture was hydrolyzed

with water, the layers separated, the aqueous layer extracted

twice with 200 ml. portions of ether, and the combined organic

layer and extractions dried over anhydrous sodium sulfate.

The ether was decanted from the drying agent and evaporated

under an air-jet to leave a yellow solid. This was recrystal-

lized several times from ethanol to give 12.7 g. (52.6%) of

9-triphenylsilylxanthene, m. p. 164.5-166°.

Anal. Calcd. for $C_{31}H_{24}OSi$: Si, 6.38. Found: Si, 6.35,

6.36.

The infrared spectrum showed prominent absorption peaks

at 3.35, 8.02, 9.10, and 13.50μ, characteristic of C-H

aromatic, aromatic ether, Si-phenyl, and ortho disubstitu-

tion, respectively.

b. **From 9-lithioxanthene and triphenylsilane (attempted)**
To an ethereal solution of 0.0548 mole of 9-lithioxanthene,

prepared as described in the previous reaction, was added 14.5

g. (0.0548 mole) of triphenylsilane dissolved in 150 ml. of

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[122]R. R. Burtner and J. W. Cusic, J. Am. Chem. Soc., 65,
1582 (1943).

[123]Generously donated by Mallinkrodt Chemical Works,
St. Louis, Missouri.

ether. The addition, which proceeded without visible reaction, was completed in 10 minutes. Color Test I was strongly positive, and the reaction mixture was heated at reflux temperature for 16 hours. However, Color Test I was still positive. The reaction mixture was carbonated by pouring jetwise into a Dry Ice-ether slurry. After the solution had warmed to room temperature, it was extracted several times with 2.5% sodium hydroxide solution; the remaining organic layer was dried over anhydrous sodium sulfate. The basic extract was acidified with 10% hydrochloric acid solution to precipitate a yellow solid which was filtered, washed with water, and dried to give 8.65 g. (69.7%) of crude acid, m. p. 218-221°. A recrystallization from glacial acetic acid gave 5.40 g. (43.5%) of xanthene-9-carboxylic acid, m. p. 222.5-225° (mixture melting point). The literature value[122] is 222°.

Evaporation of the solvent from the original organic layer left a yellow oil which was chromatographed on alumina. Elution with petroleum ether (b. p. 60-70°) gave 13.9 g. (95.8%) of crude triphenylsilane melting over the range 37-43°. This was recrystallized from methanol to yield 11.1 g. (76.5%) of pure material, m. p. 43-46° (mixture melting point). Elution of the column with benzene gave 0.15 g. (1.53%) of dixanthene,[124] m. p. 205-206° (mixture melting point). Fur-

ther elution of the column with ethanol gave 0.15 g. (0.98%) of triphenylsilanol, m. p. 153-154° (mixture melting point).

2. 9-Trimethylsilylxanthene

An ethereal solution of 0.0548 mole of 9-lithioxanthene, prepared as described in the preceding experiment, was added to 6.20 g. (0.057 mole) of chlorotrimethylsilane dissolved in 100 ml. of ether. The addition proceeded with slight spontaneous refluxing and was completed in 15 minutes. The yellow solution gave a negative Color Test I. The reaction mixture was hydrolyzed and worked up in the same manner as described in the preceding section to yield a light brown solid. The solid was recrystallized from ethanol to give 9.40 g. (67.3%) of 9-trimethylsilylxanthene, m. p. 119.5-121°.

Anal. Calcd. for $C_{16}H_{18}OSi$: C, 75.50; H, 7.13. Found: C, 75.75, 75.79; H, 7.22, 7.23.

The infrared spectrum showed, in addition to the bands for C-H aromatic and aliphatic and aryl ether, a doublet at 13.2 and 13.4 μ which is characteristic of $SiMe_3$.

3. Diphenylbis-(9-xanthyl)silane

To an ethereal solution of 0.0548 mole of 9-lithioxanthene was added slowly 6.94 g. (0.0274 mole) of dichlorodiphenylsilane dissolved in 50 ml. of ether. The reaction mixture was then refluxed for 5 hours, at which time Color Test

I was negative. Following aqueous hydrolysis, the solid which separated out at the interface of the liquids was removed by filtration. The organic layer was worked up in the usual manner to yield a small amount of solid which was identical with the insoluble material which had been filtered off. These solids were combined and recrystallized from benzene to give 7.55 g. (50.6%) of diphenylbis-(9-xanthyl)silane, m. p. 214-216°.

Anal. Calcd. for $C_{38}H_{28}O_2Si$: Si, 5.16. Found: Si, 5.13, 5.20.

The material was insoluble in carbon disulfide, but the infrared spectrum as a potassium bromide pellet showed absorption peaks for Si-phenyl and an aromatic ether.

4. Dimethylbis-(9-xanthyl)silane

To 0.0548 mole of 9-lithioxanthene in ether solution was added dropwise 3.53 g. (0.0274 mole) of dichlorodimethyl-silane dissolved in 50 ml. of ether. After the reaction mixture had stirred at room temperature for one hour and had been heated at reflux temperature for 5 hours, Color Test I was negative. Following aqueous hydrolysis, the usual work-up was employed. Evaporation of the solvent left a red solid which was recrystallized from ethanol several times to give 4.50 g. (39.1%) of dimethylbis-(9-xanthyl)-silane, m. p. 173-174°.

Anal. Calcd. for $C_{27}H_{24}O_2Si$: C, 80.00; H, 5.74. Found: C, 80.34, 80.49; H, 5.49, 5.58.

The infrared spectrum was quite similar to that of 9-trimethylsilylxanthene except for the intensities of the absorption peaks for C–H.

5. 9,9-Diphenyl-4-triphenylsilylxanthene

Ten grams (0.030 mole) of 9,9-diphenylxanthene[125] was suspended in 100 ml. of ether and an ethereal solution of 0.0306 mole of n-butyllithium added. The yellow solution was refluxed for 5 hours. The resulting orange solution gave a negative Color Test II[68] but a positive Color Test I. To this solution was added 9.14 g. (0.0306 mole) of chlorotriphenylsilane dissolved in 100 ml. of ether. Color Test I was positive at the completion of the addition, and was still moderately positive after the reaction mixture had been heated at reflux temperature for 18 hours. Two hundred milliliters of benzene was added and the ether was distilled until the temperature reached 60°. The reaction mixture was then refluxed for 4 hours, at which time Color Test I was negative. Hydrolysis was carried out by the addition of water, and a suspended white solid was filtered off. The organic layer was worked up in the usual manner to give a yellow solid

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[125]F. Ullman and G. Enge, Ber., 37, 2367 (1904).

which proved to be the same as the insoluble material previously filtered from the solution. The solids were combined and recrystallized from benzene-petroleum ether (b. p. 60-70°) to give 3.95 g. (21.6%) of 9,9-diphenyl-4-triphenylsilyl-xanthene, m. p. 269-271.5° dec.

Anal. Calcd. for $C_{43}H_{32}OSi$: Si, 4.6?. Found: Si, 4.64, 4.65.

The position of substitution is assigned as _ortho_ to the hetero atom by analogy to all other metalations of aryl ethers by organolithium compounds.[55] The infrared spectrum showed absorptions bands at 3.30, 8.05 and 9.05 μ, indicative of C-H aromatic, aryl ether and Si-phenyl, respectively, and substitution bands for 1,?,3-trisubstitution and/or 1,?-disubstitution.

6. 2-Trimethylsilyl-9,9-diphenylxanthene

An ethereal solution of 0.065? mole of _n_-butyllithium was added to 15.0 g. (0.062 mole) of 4-trimethylsilylphenyl phenyl ether, and the reaction mixture was refluxed for 24 hours. Color Test II was negative but Color Test I was positive. To the solution was added 11.9 g. (0.065? mole) of benzophenone dissolved in 100 ml. of ether. Color Test I was negative at the completion of addition. Hydrolysis was effected with aqueous ammonium chloride and the usual work-up carried out. Evaporation of the solvent left a yellow oil.

The oil was chromatographed on alumina, using petroleum ether (b. p. 60-70°) as the eluent, to give a white, oily solid. This was recrystallized several times from petroleum ether (b. p. 60-70°) to yield 4.00 g. (15.5%) of product, m. p. 134.5-136°. The infrared spectrum had absorption bands for OH, C-H aromatic and aliphatic, aromatic ether, SiMe, SiMe$_3$, and Si-phenyl, in good agreement with the expected carbinol. There was also a band at 13.3 μ indicative of ortho-disubstitution, but a band between 12.3 and 12.5 μ characteristic of 1,2,4-trisubstitution was absent. Although definite proof is lacking, it appears that substitution occurred on the ring without the silicon substituent.

One gram (0.00235 mole) of carbinol was dissolved in 25 ml. of warm glacial acetic acid, and two drops of concentrated sulfuric acid were added. The solution immediately turned dark red and a white solid separated out. The reaction mixture was poured into ice water, and the white solid was filtered off and recrystallized several times from petroleum ether (b. p. 80-110°) to give 0.80 g. (83.5%) of 2-trimethylsilyl-9,9-diphenylxanthene, m. p. 200-201.5°. A mixture melting point with 9,9-diphenylxanthene, which also melts at 200-202°[125] and could have arisen if desilylation had occurred, was depressed.

 <u>Anal</u>. Calcd. for C$_{28}$H$_{26}$OSi: C, 82.80; H, 6.46. Found: C, 83.48, 83.66; H, 6.58, 6.78.

The infrared spectrum showed absorption bands for C-H aromatic and aliphatic, SiMe, SiMe$_3$, ether linkage, and Si-phenyl. The remaining absorption bands of the spectrum were in good agreement with the expected product.

7. Reaction of triphenylsilyllithium with xanthone

To a suspension of 9.81 g. (0.05 mole) of xanthone and 100 ml. of tetrahydrofuran was added 0.05 mole of triphenyl-silyllithium in tetrahydrofuran solution. The color of the solution changed from red to green to dark brown. Color Test I was slightly positive upon completion of addition, but was negative after the reaction mixture had stirred at room temperature for 5 hours. The reaction mixture was hydrolyzed with ammonium chloride solution. The white solid which formed at the interface of the liquids was filtered off and the organic layer was worked up in the usual manner. The insoluble material was later added to the red oily solid resulting from the evaporation of the organic layer, and the combined solids were dissolved in hot benzene and chromatographed on alumina using benzene as the eluent. A yellow solid decomposing over the range 246-284° was isolated. Several recrystallizations from benzene and from petroleum ether (b. p. 80-110°) gave 2.90 g. (12.7%) of xanthhydryloxytriphenylsilane, decomposition range 246-282°.

<u>Anal</u>. Calcd. for C$_{31}$H$_{24}$O$_2$Si: Si, 6.14. Found: Si,

6.07, 6.08.

The infrared spectrum is in good agreement with the expected rearranged product with an absence of OH and carbonyl bands, the presence of diaryl ether and Si-phenyl bands, and a band at 9.35μ which is characteristic of the Si-O-C linkage.

The only other material from the chromatography was a brown tar which was not investigated further.

8. Metalation of xanthene by triphenylsilyllithium

a. **Derivatization by carbonation**   Ten grams (0.055 mole) of xanthene was dissolved in 50 ml. of tetrahydrofuran, and the reaction mixture was cooled to ice-bath temperature. To the solution was added 0.055 mole of triphenylsilyllithium in tetrahydrofuran solution over a period of 45 minutes. The dark-red solution was stirred at ice-bath temperature for 0.5 hour and at room temperature for 4 hours. Color Test I was mildly positive. A 50 ml. aliquot (about 1/3 of the total reaction mixture) was carbonated by pouring into a Dry Ice-ether slurry. The remaining solution was allowed to stir overnight at room temperature. The next morning, it was carbonated in a similar manner.

1. **4 Hour aliquot**   After the solution had warmed to room temperature, it was extracted with 2.5% sodium hydroxide solution. The basic extracts were acidified with 10%

hydrochloric acid solution to give 3.70 g. (90.2% based upon 1/3 total volume aliquot) of crude acid, melting range 215-222°. This was recrystallized from ethanol-water to give 1.50 g. (36.5%) of xanthene-9-carboxylic acid, m. p. 216-220° (mixture melting point). The literature value[122] is 222°. The infrared spectrum was identical with that of an authentic sample.

 ii. <u>16 Hour aliquot</u> The same isolation procedure was carried out as described above to give 4.30 g. (53.2%) of crude acid, m. p. 205-210° dec. A recrystallization from petroleum ether (b. p. 60-70°) gave 2.10 g. (25.9%) of relatively pure acid, m. p. 217-220° (mixture melting point).

The combined crude acid represents a 64.0% yield; while the pure acid represents a yield of only 29.2%. No attempt was made to work up the mother liquors.

The original organic layers from the basic extractions were combined, and the solvent evaporated to leave a yellow oil. The oil was chromatographed on alumina to recover 0.60 g. (6.00%) of recovered xanthene, m. p. 97-99° (mixture melting point).

 b. <u>Derivatization with chlorotriphenylsilane</u> Ten grams (0.055 mole) of xanthene was metalated by 0.055 mole of triphenylsilyllithium as described in the previous reaction and was subsequently reacted with 16.5 g. (0.056 mole) of

chlorotriphenylsilane dissolved in 50 ml. of tetrahydrofuran.
There was no spontaneous refluxing, but the color of the solu-
tion changed to black. Color Test I was negative. Aqueous
hydrolysis was followed by the usual work-up. Evaporation of
the solvent left a dark brown solid which was chromatographed
on alumina. Elution of the column with petroleum ether
(b. p. 60-70°) gave, after several recrystallizations from
ethanol, 0.90 g. (9.00%) of recovered xanthene, m. p. 100-102°
(mixture melting point). Elution of the column with benzene
gave, subsequent to several recrystallizations from ethanol,
3.50 g. (14.4%) of 9-triphenylsilylxanthene, m. p. 164.5-166°
(mixture melting point). Elution of the column with ethanol
gave a solid which was recrystallized from petroleum ether
(b. p. 80-110°) to give 7.55 g. (48.7%) of triphenylsilanol,
m. p. 151-153.5° (mixture melting point).

<div align="center">

E. Reaction of Triphenylsilyllithium with
Some Alkyl-Aryl Ethers

</div>

1. Anisole

A tetrahydrofuran solution of 0.059 mole of triphenyl-
silyllithium was added slowly to 6.40 g. (0.059 mole) of
anisole dissolved in 120 ml. of tetrahydrofuran. There was
no apparent reaction during the addition, which was completed
in 45 minutes. The color of the solution was dark brown.
The reaction mixture was warmed at 50° for 24 hours, at which

time Color Test I[67] was slightly positive. Hydrolysis was effected with concentrated aqueous ammonium chloride solution, and the organic layer separated.

The organic layer was extracted several times with a total of 400 ml. of 2 1/2% aqueous sodium hydroxide. The basic extract was acidified with 10% aqueous hydrochloric acid, and the acidified solution was extracted with ether. The ether extracts were dried over sodium sulfate and later evaporated under an air-jet to leave an oil with a strong phenolic odor. This was brominated following a published procedure,[126] and the resulting solid was recrystallized from ethanol-water to give 7.75 g. (31.5%) of 2,4,6-tribromophenol, m. p. 93.5-94° (mixture melting point).

The original organic layer was evaporated to leave a white solid which was chromatographed on alumina. Elution of the column with petroleum ether (b. p. 60-70°) gave a white solid which was recrystallized from ethanol to yield 10.4 g. (64.2%) of methyltriphenylsilane, m. p. 67-69° (mixture melting point, infrared spectrum). Elution of the column with benzene gave a trace of impure tetraphenylsilane, melting range 172-220°, identified by comparison of the infrared spectrum with that of an authentic sample. Further elution of the column with ethyl acetate and with ethanol gave a

[126]R. L. Shriner, R. C. Fuson and D. Y. Curtin. The systematic identification of organic compounds. 4th ed., p. 264. New York, N. Y., John Wiley and Sons, Inc. 1956.

mixture of triphenylsilanol and 4-hydroxybutyltriphenylsilane which could not be separated, 0.60 g. ($\sim$ 3.70%), 120-145° melting range (infrared spectrum).

2. **Phenetole (attempted)**

To 2.71 g. (0.059 mole) of freshly distilled phenetole dissolved in 25 ml. of tetrahydrofuran was added a tetrahydrofuran solution of 0.059 mole of triphenylsilyllithium. The reaction mixture was warmed at 50° for 24 hours. Color Test I was strongly positive. The reaction mixture was then stirred at 60° for 72 hours, at which time Color Test I was only moderately positive. The dark red solution was hydrolyzed with ammonium chloride solution and worked up in the same manner as described in the previous reaction. The basic extraction gave a small amount of an oily residue with a strong phenolic odor. This was derivatized with bromine as in the previous experiment to give a small amount of light brown solid melting over the range 75-95°. A recrystallization from ethanol-water raised the melting point to 83-90°; however, there was not enough material for a second recrystallization.

Evaporation of the ether from the original organic layer left a white, oily solid which was chromatographed on alumina as in the previous reaction. The first fraction was an oil which was distilled at reduced pressure to give 6.45 g.

(9.46%) of triphenylsilane, b. p. 140-145° (0.5 mm.) (infrared spectrum comparison). From the vacuum pump trap was removed 0.60 g. (8.33%) of recovered phenetole (infrared spectrum). The second fraction from the chromatography was 0.65 g. (3.28%) of tetraphenylsilane melting over the range 217-230° (infrared spectrum). The third fraction, eluted by ethyl acetate, was 6.00 g. (30.6%) of 4-hydroxybutyltriphenyl-silane, m. p. 109-111° (mixture melting point). The last fraction, eluted by ethanol, was 0.25 g. (1.53%) of triphenyl-silanol (mixture melting point identification). The remaining material was a tarry residue which was not investigated further.

3. Phenyl n-propyl ether (attempted)

To 6.81 g. (0.05 mole) of phenyl n-propyl ether dissolved in 50 ml. of tetrahydrofuran was added 0.05 mole of triphenyl-silyllithium in tetrahydrofuran solution. Color Test I was strongly positive upon the completion of addition. The reaction mixture was warmed at 50° for 72 hours, but Color Test I was still positive. Hydrolysis was effected with concentrated ammonium chloride solution, and the same basic extraction work-up employed.

Evaporation of the organic layer left a yellow oil which was chromatographed on alumina in the usual manner. The first fraction was an oil which was distilled at reduced pressure

to give 6.10 g. (33.9%) of triphenylsilane, b. p. 141-145°
(0.5 mm.) (infrared spectrum). The oil crystallized when
cooled in an ice-bath. The solid was recrystallized from
methanol to give triphenylsilane as white crystals, m. p. 45-
46.5° (mixture melting point). The other materials from the
chromatography were 0.30 g. (1.78%) of tetraphenylsilane,
3.40 g. ($\sim$24.6%) of a mixture of triphenylsilanol and
4-hydroxybutyltriphenylsilane, and 0.10 g. (0.73%) of pure
triphenylsilanol. All of the compounds were identified by
mixture melting points and/or infrared spectra comparisons.

Evaporation of the solvent from the basic extraction
failed to leave a trace of phenolic material.

4. p-Dimethoxybenzene

a. 1:1 Ratio   A tetrahydrofuran solution of 0.059
mole of triphenylsilyllithium was added to 8.15 g. (0.059
mole) of p-dimethoxybenzene dissolved in 30 ml. of tetra-
hydrofuran. The solution was heated at 50°. Color Test I
was green after 6 hours, but was negative after 12 hours.
However, the reaction was allowed to stir at 50° for 12
hours more to insure completeness of reaction. The solution
was hydrolyzed with concentrated ammonium chloride solution
and the usual basic extraction work-up employed.

Evaporation of the solvent from the original organic
layer left a white solid. This was chromatographed on

alumina using the same procedure as described in the first reaction. There was obtained 9.80 g. (60.5%) of methyltriphenylsilane, m. p. 67-69° (mixture melting point) and 0.70 g. (~4.60%) of a mixture of triphenylsilanol and 4-hydroxybutyltriphenylsilane (infrared spectrum), melting range 128-138°. The only other material from the chromatography was a brown tar which was not investigated.

Evaporation of the ether from the basic extract fraction left 4.30 g. of a very dark red-brown solid. This was extracted with hot petroleum ether (b. p. 80-110°) to give, upon cooling, 2.20 g. (30.2%) of hydroquinone monomethyl ether, m. p. 55-57° (mixture melting point, infrared spectrum).

b. 2:1 Ratio   To 5.00 g. (0.036 mole) of p-dimethoxybenzene dissolved in 50 ml. of tetrahydrofuran was added 0.072 mole of triphenylsilyllithium in tetrahydrofuran solution. The reaction mixture was warmed at 50°. After 24 hours, Color Test I was moderately positive. Hydrolysis was effected with concentrated ammonium chloride solution, and the usual work-up with basic extraction was employed.

Evaporation of the ether from the original organic layer left a white solid which was chromatographed on alumina in the usual manner. Methyltriphenylsilane, 11.45 g. (115.8% based on the availability of one methoxyl or 57.8% on two available methoxyl groups), m. p. 67-69° (mixture melting point); tetraphenylsilane, 0.10 g. (0.40%) (infrared spectrum); and the

usual mixture of triphenylsilanol and 4-hydroxybutyltriphenyl-silane, 0.45 g. ($\sim$2.27%) (infrared spectrum), were isolated.

The ether from the basic extracts was evaporated to leave 4.20 g. of a dark-brown solid. The solid was extracted several times with hot petroleum ether (b. p. 60-70°) which upon cooling gave 1.65 g. (37.0%) of hydroquinone monomethyl ether, m. p. 56-58° (mixture melting point, infrared spectrum). The remaining residue was extracted several times with hot benzene. Upon cooling, 0.60 g. (15.2%) of hydroquinone, m. p. 170-172° (mixture melting point), crystallized. A small amount of black residue remained which was not investigated further.

5. 1-Methoxynaphthalene

To 7.91 g. (0.05 mole) of 1-methoxynaphthalene dissolved in 50 ml. of tetrahydrofuran was added 0.05 mole of triphenyl-silyllithium in tetrahydrofuran solution. After warming at 50° for 3 hours, the solution gave a moderate Color Test I; after 8 hours, faintly positive; and after 10 hours, negative. The deep red solution was allowed to stir at 50° for a total of 24 hours to insure completeness of reaction. The reaction mixture was hydrolyzed with concentrated ammonium chloride solution, and the usual basic extraction work-up was carried out.

The yellow solid resulting from evaporation of the sol-

vent from the original organic layer was chromatographed on alumina. The products obtained were 6.65 g. (48.5%) of methyltriphenylsilane, 0.90 g. (11.4%) of recovered 1-methoxynaphthalene, 0.25 g. (∿1.81%) of a mixture of triphenylsilanol and 4-hydroxybutyltriphenylsilane, and a small amount of an unidentified brown oil. All products were identified by mixture melting points or comparison of the infrared spectra.

Evaporation of the ether from the basic extraction left 4.40 g. (60.8%) of crude 1-naphthol as a red solid, m. p. 92-96°. This was recrystallized from petroleum ether (b. p. 80-110°) to give 4.20 g. (58.2%) of white flakes, m. p. 93-95° (mixture melting point, infrared spectrum).

6. 2-Methoxynaphthalene

2-Methoxynaphthalene, 7.91 g. (0.05 mole) was dissolved in 50 ml. of tetrahydrofuran, and a tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added rapidly. The reaction mixture was warmed at 50°. Color Test I was positive after 6 hours, but after 16 hours, it was negative. The reaction mixture was hydrolyzed with concentrated ammonium chloride solution, and the hydrolyzed mixture was worked up with the usual basic extraction.

The yellow solid resulting from evaporation of the solvent from the original organic layer was chromatographed on

alumina. From the chromatography were isolated 7.25 g. (52.5%) of methyltriphenylsilane, m. p. 67-69°; 0.30 g. (3.78%) of recovered 2-methoxynaphthalene, m. p. 71.5-75° from petroleum ether (b. p. 60-70°); 0.10 g. (0.59%) of tetraphenylsilane; and the usual tars and mixture of silanol and hydroxy compound. The products were identified by the method of mixture melting points.

Evaporation of the solvent from the basic extraction left a brown solid which was recrystallized several times from petroleum ether (b. p. 80-110°) to give 4.25 g. (58.8%) of 2-naphthol, m. p. 119-122° (mixture melting point, infrared spectrum).

7. p-Chloroanisole

A tetrahydrofuran solution of triphenylsilyllithium (0.05 mole) was added slowly to 7.13 g. (0.05 mole) of p-chloroanisole dissolved in 50 ml. of tetrahydrofuran. Color Test I was positive at the completion of addition, but was negative after the reaction mixture had been warmed at 50° for 2 hours. The brown reaction mixture was hydrolyzed with concentrated ammonium chloride solution. A suspended white solid was filtered off, washed with ether, and dried to give 5.30 g. (40.7%) of hexaphenyldisilane, m. p. 363-364° (mixture melting point). The organic layer was worked up in the same manner as described previously.

Evaporation of the original organic solution left a white solid which was chromatographed on alumina to give 0.90 g. (12.6%) of recovered p-chloroanisole (infrared spectrum); 1.08 g. (5.73%) of p-anisyltriphenylsilane,[127] m. p. 157-159° after recrystallization from petroleum ether (b. p. 60-70°) (mixture melting point, infrared spectrum); and the usual impure triphenylsilanol, 0.90 g. ($\sim$ 6.5%) (infrared spectrum).

Evaporation of the basic extraction left only a trace of a dark oil with a phenolic odor, which could not be identified.

8. p-Fluoroanisole

To 6.30 g. (0.05 mole) of p-fluoroanisole dissolved in 50 ml. of tetrahydrofuran was added 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. The reaction mixture was warmed at 50°. After one hour, Color Test I was strongly positive; after 8 hours, it was only faintly positive. After 24 hours the color test was negative, and the gray solution was hydrolyzed and worked up following the usual procedure.

Evaporation of the ether from the original organic layer left a yellow solid which was chromatographed on alumina.

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[127]R. A. Benkeser. Some substitution reactions of organosilicon compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1947.

There were obtained 6.75 g. (49.2%) of methyltriphenylsilane, m. p. 67-69° (mixture melting point); 0.20 g. (1.09%) of p-anisyltriphenylsilane, m. p. 160-161.5° (mixture melting point); and a small amount of tarry residue which was not investigated further.

Evaporation of the ether from the basic extraction left a brown oil with a strong phenolic odor. This was distilled at reduced pressure to give 1.90 g. (30.5%) of p-fluorophenol, b. p. 76-77° (15 mm.), n_D^{20} 1.5055, m. p. 24.5° (lit. value,[128] b. p. 87°/23 mm., m. p. 26.5-27.0°). The infrared spectrum showed an associated OH, $-C-F$ split at 8.20 and 8.35μ, p-disubstitution at 12.10μ, and an aromatic substitution band at 13.40μ.

9. Dimethylphenylsilyllithium with 2-methoxynaphthalene

To 15.8 g. (0.10 mole) of 2-methoxynaphthalene dissolved in 50 ml. of tetrahydrofuran was added a tetrahydrofuran solution of dimethylphenylsilyllithium prepared by the lithium cleavage of 13.5 g. (0.05 mole) of sym.-tetramethyldiphenyl-disilane in tetrahydrofuran solution. The reaction mixture gave a positive Color Test I after it had been warmed at 50° for 24 hours. The solution was hydrolyzed with aqueous ammonium chloride and the usual basic extraction work-up

[128]C. M. Suter, E. J. Lawson and P. G. Smith, J. Am. Chem. Soc., 61, 161 (1939).

effected.

The original organic solution was distilled to remove the solvents, and the resulting yellow oil was distilled at atmospheric pressure to give 5.40 g. (35.9%) of impure tri-methylphenylsilane, boiling range 140-170°, n_D^{20} 1.4948 (lit. value,[105] b. p. 166-167°/735 mm., n_D^{20} 1.4896). The oil was redistilled at atmospheric pressure to give 3.70 g. (24.6%) of relatively pure material, boiling range 157-161°, n_D^{20} 1.4928. The infrared spectrum of the oil as a capillary cell was superimposable with that of an authentic sample.

Evaporation of the ether from the original basic ex-tracts left 6.90 g. (47.8%) of crude 2-naphthol, m. p. 115-120°. Several recrystallizations from petroleum ether, (b. p. 80-110°) gave 4.95 g. (34.4%) of pure 2-naphthol, m. p. 121-122° (mixture melting point, infrared spectrum).

10. Dimethylphenylsilyllithium with phenetole (attempted)

A tetrahydrofuran solution of dimethylphenylsilyllithium, prepared by the lithium cleavage of 10.0 g. (0.037 mole) of sym.-tetramethyldiphenyldisilane, was added to 9.17 g. (0.075 mole) of phenetole dissolved in 50 ml. of tetrahydrofuran. The reaction mixture was warmed at 50°, Color Test I being taken at various intervals. After 72 hours, the color test was still strongly positive. The usual basic extraction work-up was carried out following aqueous ammonium chloride

hydrolysis of the reaction mixture.

The original organic layer was distilled at atmospheric pressure to give, subsequent to removal of the solvent, 10.2 g. of impure phenetole boiling over the range 151-160° (740 mm.), n_D^{20} 1.5062. This was redistilled to give 7.70 g. (84.0%) of recovered phenetole, b. p. 167-170° (760 mm.), n_D^{20} 1.5066 (starting material, b. p. 172°, n_D^{20} 1.5076). The infrared spectrum was superimposable with that of the starting material. Ethyldimethylphenylsilane, the cleavage product, could not be detected.

Evaporation of the ether from the original basic extraction left a small amount of a brown oil with a strong phenolic odor. This was brominated to give 0.88 g. (3.57%) of crude 2,4,6-tribromophenol, m. p. 87-91°. Several recrystallizations from ethanol-water raised the melting point to 93-94° (mixture melting point).

11. Thioanisole

Triphenylsilyllithium, 0.05 mole in tetrahydrofuran solution, was added to 6.20 g. (0.05 mole) of thioanisole dissolved in 50 ml. of tetrahydrofuran. The addition was completed in 40 minutes, and the resulting dark solution gave a positive Color Test I. The reaction mixture was warmed at 50° for 24 hours, at which time the color test was negative. The solution was hydrolyzed with concentrated ammonium

chloride solution. A suspended white solid was filtered off to give 2.60 g. of white solid, 224-304° melting range. The solid was extracted with hot ethyl acetate to leave 0.80 g. (6.17%) of hexaphenyldisilane, m. p. 364-368° (mixture melting point). From the chilled ethyl acetate crystallized 1.40 g. (8.33%) of tetraphenylsilane, m. p. 232-234° (mixture melting point). The organic layer from the hydrolysis was subjected to the usual basic extraction work-up.

Subsequent to evaporation of the solvent, the resulting yellow solid was chromatographed on alumina to give 1.80 g. (13.1%) of methyltriphenylsilane, m. p. 65.5-67° (mixture melting point, infrared spectrum); 0.90 g. (5.35%) of tetraphenylsilane, m. p. 231-233° (mixture melting point); and some yellow tar which could not be crystallized.

Evaporation of the ether from the basic extract failed to leave any material which might be taken for thiophenol.

F. Reactions of Triphenylsilyllithium
with Symmetrical Acetals

1. Methylal

A tetrahydrofuran solution of 0.05 mole of triphenyl-silyllithium was added slowly to a solution of 3.80 g. (0.05 mole) of methylal[129] and 50 ml. of tetrahydrofuran. Slight

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[129]The acetals used in the study were Eastman White Label Grade Chemicals in which the infrared spectrum did not indicate the presence of carbonyl containing impurities.

warming occurred during the addition, which was completed in 30 minutes. The dark solution gave a positive Color Test I.[67] The reaction mixture was warmed with stirring. After 24 hours, Color Test I was slightly positive and after 36 hours it was negative. Hydrolysis was carried out with concentrated ammonium chloride solution. The layers were separated, and the organic layer dried over anhydrous sodium sulfate. Evaporation of the solvent left a yellow tarry residue which was chromatographed on alumina.

Elution with petroleum ether (b. p. 60-70°) gave 1.45 g. (10.6%) of crude methyltriphenylsilane melting over the range 53-64°. Several recrystallizations from ethanol gave 0.65 g. (4.73%) of pure material, m. p. 65-67°, which showed no depression when admixed with an authentic sample. The infrared spectrum also was identical with that of an authentic sample. Further elution of the column with the same solvent gave 0.30 g. (2.17%) of crude tetraphenylsilane, 182-210° melting range. Several recrystallizations from ethyl acetate gave 0.13 g. (0.94%) of pure tetraphenylsilane, m. p. 230-233° (mixture melting point, infrared spectra comparison). Still further elution with the same solvent gave 1.30 g. (8.96%) of crude triphenylhydroxymethylsilane,[78] melting over the range 108-115°. Recrystallization from petroleum ether (b. p. 80-110°) gave 0.90 g. (6.20%) of pure product, m. p. 116-117.5° (mixture melting point, infrared spectrum com-

parison).

Elution of the column with benzene gave 2.30 g. of a tarry residue, melting range 65°-to a cloudy liquid. Several recrystallizations from petroleum ether (b. p. 80-110°) gave 1.90 g. (11.5%) of crude 4-hydroxybutyltriphenylsilane, m. p. 107-109° (mixture melting point, infrared spectra comparison). Further elution with benzene gave 1.10 g. (7.97%) of crude triphenylsilanol, m. p. 142-146°. Several recrystallizations from petroleum ether (b. p. 80-110°) gave 0.40 g. of pure silanol (2.90%), m. p. 150.5-152° (mixture melting point). Elution with ethyl acetate gave a yellow tar from which no crystalline material could be extracted.

2. Dimethyl acetal

A tetrahydrofuran solution containing 0.05 mole of triphenylsilyllithium was added slowly to a solution of 4.50 g. (0.05 mole) of dimethyl acetal and 50 ml. of tetrahydrofuran. There was no apparent reaction during the addition, which was completed in 30 minutes. Color Test I was strongly positive. The reaction mixture was warmed at 50° with stirring for 24 hours. Color Test I remained strongly positive. Warming was increased to 60°. After 48 hours, Color Test I was negative. The reaction mixture was hydrolyzed with concentrated ammonium chloride solution, and the organic layer separated and dried over anhydrous sodium sulfate. Evaporation of the solvent

left an oily solid which was chromatographed on alumina.

Elution of the column with petroleum ether (b. p. 60-70°) gave 0.95 g. (6.94%) of crude methyltriphenylsilane, identified by comparison of the infrared spectrum with that of an authentic sample. Further elution with the same solvent gave a white solid melting over the range 168-200°. Several recrystallizations from ethyl acetate gave 0.20 g. (1.19%) of tetraphenylsilane, m. p. 230-232° (mixture melting point). Still further elution with the same solvent gave a white solid melting 97-101°. Recrystallization from petroleum ether (b. p. 80-110°) gave 0.60 g. (3.95%) of 1-triphenylsilylethanol,[80] m. p. 100-101° (mixture melting point, infrared spectra comparison).

Other products isolated from the chromatography were 4-hydroxybutyltriphenylsilane, 2.20 g. (13.25%); and triphenylsilanol, 0.30 g. (2.18%). These were identified by mixture melting points with authentic samples.

3. Diethyl formal

Triphenylsilyllithium, 0.05 mole in tetrahydrofuran solution, was added slowly to a solution of 5.90 g. (0.05 mole) of diethyl formal and 50 ml. of tetrahydrofuran. The addition was completed in 30 minutes. The dark solution, which gave a positive Color Test I, was heated at 60° with stirring. After 48 hours Color Test I was still quite posi-

tive, and the temperature was raised to mild reflux. After 48 hours Color Test I was negative. The reaction mixture was hydrolyzed with concentrated ammonium chloride solution, and the solution filtered to give 0.60 g. (4.26%) of hexaphenyldisilane, m. p. 364-368° (mixture melting point). The filtrate was extracted and the resulting oil, subsequent to evaporation of the solvent, was chromatographed on alumina using the technique described previously. Tetraphenylsilane, 0.25 g. (1.40%); 4-hydroxybutyltriphenylsilane, 6.25 g. (37.6%); and 0.20 g. (1.45%) of triphenylsilanol were isolated. All products were identified by mixture melting points with authentic samples. Neither ethyltriphenylsilane nor triphenylhydroxymethylsilane was found.

4. Acetal

A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added slowly to a solution of 5.40 g. (0.05 mole) of acetal and 50 ml. of tetrahydrofuran. There was no visible reaction during the addition, which took 25 minutes. Color Test I was strongly positive. The reaction mixture was warmed with stirring at 60° for 48 hours, at which time Color Test I was still strongly positive. The temperature was increased to mild refluxing. After 48 hours Color Test I was negative. Hydrolysis was carried out with concentrated ammonium chloride solution, and the same chromatographic work-

up as described previously was employed. Tetraphenylsilane, 0.30 g. (1.80%); and 4-hydroxybutyltriphenylsilane, 6.65 g. (40.1%), were isolated. The compounds were identified by mixture melting points. Again, neither ethyltriphenylsilane nor 1-triphenylsilylethanol were found.

5. 2,2-Dimethoxypropane

To a solution of 5.20 g. (0.05 mole) of 2,2-dimethoxypropane and 50 ml. of tetrahydrofuran was added 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. The reaction mixture was warmed at 50° for 24 hours, at which time Color Test I was still positive. Warming was increased to 60° for 24 hours, but Color Test I remained positive. It was necessary to reflux the reaction mixture for 48 hours before the color test went negative. The usual hydrolysis and chromatographic work-up were carried out. The first fractions of the chromatography were 1.40 g. of a colorless oil, the infrared spectrum of which was identical with triphenylsilane, and 0.30 g. (1.78%) of tetraphenylsilane, m. p. 231-235° (mixture melting point). The last petroleum ether elutions gave a very small amount of white solid, melting over the range 127-141°. A recrystallization from petroleum ether raised the melting range to 136-144°. The infrared spectrum of this material was identical to that of 2-triphenylsilyl-propan-2-ol.[75] Also obtained from the chromatography were

5.40 g. (32.4%) of 4-hydroxybutyltriphenylsilane, m. p. 106.5-109.5° (mixture melting point); and 0.30 g. (2.17%) of triphenylsilanol, m. p. 151-153° (mixture melting point).

6. **Preparation of triphenylsilyllithium in acetal (attempted)**

    a. **From hexaphenyldisilane and lithium**   To a rapidly stirred mixture of 5.00 g. (0.0097 mole) of hexaphenyldisilane and 1.01 g. (0.145 g. atom) of lithium was added sufficient acetal to make a paste. The paste was stirred for several hours at room temperature but there was no observable reaction, even after the paste had been warmed. The remainder of the acetal (a total of 50 ml.) was added and the mixture was refluxed for 84 hours. The solvent was light brown in color, but Color Test I was negative. The suspended white solid was filtered off, washed with ether and water, and dried to give 4.75 g. (95.0%) of recovered hexaphenyldisilane, m. p. 365-367° (mixture melting point). The organic layer was worked up in the usual manner. After distillation of the solvent and the acetal, a small amount of viscous oil remained. The infrared spectrum indicated only the bands expected for a hydrocarbon. The oil could not be identified.

    b. **From chlorotriphenylsilane and lithium**   About 10 ml. of acetal was added to a mixture of 10.0 g. (0.034 mole) of chlorotriphenylsilane and 0.94 g. (0.135 g. atom) of

lithium, and rapid stirring was started. There was no reaction after stirring at room temperature, even subsequent to warming. The remainder of the acetal (70 ml.) was added and the solution was heated at reflux for 24 hours. Color Test I was negative even though the solution was gray in color. After 72 hours the solution was brown in color, but Color Test I still remained negative. Upon cooling, a brown solid settled to the bottom of the flask with the supernatant liquid being orange. The reaction mixture was poured onto crushed ice, and the brown solid was filtered off, washed with ether and dried to give 2.55 g. (28.8%) of crude hexaphenyldisilane melting over the range 340-354°. A recrystallization from benzene raised the melting point to 358-363° (mixture melting point).

The organic layer was worked up as usual and the resulting brown solid chromatographed on alumina to give, in addition to some resinous materials, 0.80 g. (8.80%) of hexaphenyldisiloxane and 0.70 g. (7.76%) of triphenylsilanol.

G. Relative Reactivities of Silylmetallic Reagents

1. Competitive reaction of triphenylsilyllithium with functional group containing compounds

a. **Chlorobenzene and anisole**   To a stirred solution of 5.63 g. (0.05 mole) of chlorobenzene, 5.41 g. (0.05 mole) of anisole and 50 ml. of tetrahydrofuran was added 0.05 mole

of triphenylsilyllithium in tetrahydrofuran solution over a period of 10 minutes. The reaction mixture became warm during the addition, and a small amount of white solid appeared suspended in the dark solution. Color Test I[67] was positive. The reaction mixture was warmed at 50° for 1.5 hours, at which time Color Test I was negative. After the reaction mixture was hydrolyzed with concentrated ammonium chloride solution, the suspended white solid was filtered off, washed, and dried to give 6.60 g. (51.0%) of hexaphenyldisilane, m. p. 358-366°. The melting point of a mixture with an authentic sample was not depressed.

The original organic layer was separated, dried over anhydrous sodium sulfate, and then evaporated to leave a yellow oily solid. This was chromatographed on alumina. Elution with petroleum ether (b. p. $60-70^\circ$) gave 1.75 g. (30.6%) of recovered anisole, n_D^{20} 1.5181. The infrared spectrum was identical with that of an authentic specimen. Elution of the column with benzene gave a white solid melting over the range $205-228^\circ$. Several recrystallizations from ethyl acetate gave 1.95 g. (11.6%) of tetraphenylsilane, m. p. $230-232.5^\circ$ (mixture melting point, infrared spectra comparison). Elution of the column with ethyl acetate gave a white solid melting over the range $140-150^\circ$. Recrystallization from petroleum ether (b. p. $60-70^\circ$) gave 0.20 g. (1.45%) of triphenylsilanol, m. p. $155-156^\circ$ (mixture melting point).

Further elution of the column with ethyl acetate and with ethanol gave an orange tarry residue which was not investigated further.

b. <u>Chlorobenzene and n-octyl fluoride</u>   A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added to a solution of 6.61 g. (0.05 mole) of n-octyl fluoride, 5.63 g. (0.05 mole) of chlorobenzene, and 50 ml. of tetrahydrofuran over a 50 minute period. A white solid appeared suspended in the flask. Color Test I was positive at the completion of addition but was negative after the reaction mixture had stirred at room temperature overnight. Hydrolysis was carried out with concentrated ammonium chloride solution, and the resulting mixture was filtered and subjected to the chromatographic work-up described in the previous reaction. The insoluble material was 3.25 g. (25.0%) of hexaphenyldisilane, m. p. 365-369° (mixture melting point).

The chromatography yielded n-octyltriphenylsilane[95] (33.5% crude, 27.4% pure), m. p. 72-73°; and tetraphenylsilane (17.9% crude, 11.0% pure). The products were identified by mixture melting points and infrared spectra comparisons.

c. <u>Benzonitrile and chlorobenzene</u>   A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added slowly over a 45 minute period to a solution of 5.16 g. (0.05 mole) of benzonitrile, 5.63 g. (0.05 mole) of chlorobenzene

50 ml. of tetrahydrofuran. Slight warming occurred during the addition. The dark solution gave a positive Color Test I, and some white solid appeared to be suspended in it. After stirring at room temperature for 24 hours, Color Test I was slightly positive, but was negative after 36 hours of stirring. After hydrolysis of the reaction mixture with concentrated ammonium chloride solution, the white solid was filtered off, washed with ether, and dried to give 3.00 g. (23.0%) of hexaphenyldisilane. The filtrate was worked up in the usual manner to give tetraphenylsilane (2.68%) and a considerable amount of yellow tar. Nothing, however, was extracted from the tar.

d. <u>Chlorobenzene and benzophenone</u>   To a solution of 9.11 g. (0.05 mole) of benzophenone, 5.63 g. (0.05 mole) of chlorobenzene and 50 ml. of tetrahydrofuran was added slowly 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. As the addition proceeded the color of the solution changed from yellow to green to a final dark brown. No white solid was observed suspended in the solution. The addition was completed in 20 minutes. Color Test I was positive, but, after the reaction mixture had been stirred at room temperature for one hour, the color test was negative. A small amount of white solid was then observable. Hydrolysis was effected with dilute ammonium chloride solution, and the work-up was carried out as described previously.   − ·

The suspended white solid was 1.85 g. (14.3%) of hexa-phenyldisilane, m. p. 363-366° (mixture melting point). The colorless oil obtained from evaporation of the organic layer was chromatographed on alumina as described previously. There was obtained 6.00 g. (27.2%) of benzhydryloxytriphenylsi-lane,[77] m. p. 83-84.5°; 0.45 g. (2.68%) of tetraphenylsilane, melting range 227-234°; and 0.30 g. (2.17%) of triphenyl-silanol. The products were identified by the method of mixture melting points. No attempt was made to work-up the remaining yellow tar.

   e. **Chlorobenzene and styrene oxide**   To a solution of 5.63 g. (0.05 mole) of chlorobenzene, 6.01 g. (0.05 mole) of styrene oxide and 50 ml. of tetrahydrofuran chilled to ice-bath temperature was added slowly a tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium. Addition was completed in 30 minutes, at which time Color Test I was slightly posi-tive. The ice-bath was removed, and after the reaction mix-ture had stirred at room temperature for one hour, Color Test I was negative. No suspended solid was noted. Hydrolysis was effected with concentrated ammonium chloride solution, and the work-up with subsequent chromatography was carried out as described previously.

   The product isolated was 8.25 g. (43.3%) of 2-triphenyl-silyl-1-phenylethanol,[46] m. p. 135-137° (mixture melting point, infrared spectrum). The only other material present

was some dark brown tar which was not investigated further.

f. **Chlorobenzene and trimethyl phosphate**   A tetra-
hydrofuran solution of 0.05 mole of triphenylsilyllithium was
added to a solution of 7.00 g. (0.05 mole) of trimethyl phos-
phate, 5.63 g. (0.05 mole) of chlorobenzene, and 50 ml. of
tetrahydrofuran over a period of one hour. Warming of the
solution occurred and Color Test I was negative upon comple-
tion of the addition. Hydrolysis and chromatographic work-up
were effected as described previously.

The product was methyltriphenylsilane (71.1% crude,
65.3% pure), m. p. 67-69° (mixture melting point) together
with some tarry residues from which no pure materials were
isolated.

g. **Chlorobenzene and ethyl benzoate**   A tetrahydro-
furan solution of 0.05 mole of triphenylsilyllithium was added
slowly to a solution of 7.50 g. (0.05 mole) of ethyl benzoate,
5.63 g. (0.05 mole) of chlorobenzene and 50 ml. of tetra-
hydrofuran. The addition was completed in one hour, at which
time Color Test I was negative. There was no suspended solid
in the solution. Ammonium chloride solution hydrolysis and
the usual chromatographic work-up were effected.

Elution with petroleum ether (b. p. 60-70°) gave 1.15
g. (7.56%) of crude ethoxytriphenylsilane (infrared spectra
comparison), however, this could not be purified, probably
due to instability of the compound. Further elution with

petroleum ether (b. p. 60-70°) gave an intractable yellow tar.
Elution with benzene also gave a yellow tarry residue. How-
ever, when this was slurried with ethanol, 0.20 g. (3.77%) of
benzoin, m. p. 133-135° (mixture melting point, infrared
spectrum), was obtained. Evaporation of the ethanol extract
gave 0.90 g. (6.52%) of crude triphenylsilanol melting over
the range 131-148°. Recrystallization from petroleum ether
(b. p. 80-110°) raised the melting point to 152-153° (mixture
melting point).

h. <u>Trimethyl phosphate and styrene oxide</u>   To a solu-
tion of 7.00 g. (0.05 mole) of trimethyl phosphate, 6.01 g.
(0.05 mole) of styrene oxide and 50 ml. of tetrahydrofuran
was added slowly 0.05 mole of triphenylsilyllithium in tetra-
hydrofuran solution. The solution turned yellow, then orange,
and became warm during the addition, which was completed in
one hour. Color Test I was negative. The reaction mixture
was hydrolyzed with concentrated ammonium chloride solution
and the usual chromatographic work-up employed.

The products isolated were methyltriphenylsilane (46.0%
crude, 38.3% pure) and 2-triphenylsilyl-1-phenylethanol
(15.8% crude, 13.7% pure), both identified by mixture melt-
ing points. There was also some yellow tar from which no
crystalline solid could be extracted.

i. <u>Trimethyl phosphate and ethyl benzoate</u>   To a solu-
tion of 7.00 g. (0.05 mole) of trimethyl phosphate, 7.50 g.

(0.05 mole) of ethyl benzoate and 50 ml. of tetrahydrofuran
was added slowly 0.05 mole of triphenylsilyllithium in tetra-
hydrofuran solution. The solution became warm during the
addition, which was completed in 1.25 hours. Color Test I
was negative. Aqueous hydrolysis followed by the usual
chromatographic work-up gave methyltriphenylsilane (crude
40.1%, pure 28.8%), 0.30 g. of an unidentified solid, m. p.
183-185°, and triphenylsilanol (2.17%).

The infrared spectrum of the unknown solid showed bands
to be expected for the addition-rearrangement product,
phenyl-(triphenylsilyl)triphenylsiloxymethane, (C_6H_5)
$[(C_6H_5)_3Si][(C_6H_5)_3SiO]CH$. The silicon analysis also agrees
with the structure.

<u>Anal</u>. Calcd. for $C_{43}H_{36}OSi_2$: Si, 8.99. Found: Si,
9.04, 8.83.

However, other supporting evidence for the structure
could not be obtained.

2. Triphenylsilyllithium <u>versus</u> organometallic
   <u>compounds in coupling with chlorotriphenylsilane</u>

   a. <u>Triphenylsilyllithium and phenyllithium</u>   Tetra-
hydrofuran solutions of 0.05 mole of phenyllithium[117] and
0.05 mole of triphenylsilyllithium were each cooled to -50°
and mixed. While maintaining stirring, a solution containing
14.7 g. (0.05 mole) of chlorotriphenylsilane dissolved in
30 ml. of tetrahydrofuran was added over a period of 8 minutes

at the same temperature. A white solid was suspended in the
dark solution. Stirring was continued at -50° for 10 minutes
after the addition was complete. One hundred milliliters of
water was added and the hydrolyzed reaction mixture allowed
to warm to room temperature. Ether was added, and the sus-
pended white solid was filtered, washed with ether, and dried
to give 19.2 g. (73.8%) of hexaphenyldisilane, m. p. $360-366^o$
(mixture melting point).

The organic layer was worked up in the usual manner.
Evaporation of the solvent left a yellow solid which was
slurried with ethanol and filtered. The solid was dried to
give 3.00 g. (17.8%) of crude tetraphenylsilane melting over
the range $218-229^o$. Several recrystallizations from ethyl
acetate gave 2.02 g. (12.0%) of pure product, m. p. $231-234.5^o$
(mixture melting point).

    b. Triphenylsilyllithium and n-butyllithium   Tri-
phenylsilyllithium (0.05 mole) and n-butyllithium[117] (0.05
mole) in tetrahydrofuran were competitively reacted with 14.7
g. (0.05 mole) of chlorotriphenylsilane dissolved in 50 ml. of
tetrahydrofuran under the identical conditions of the previous
reaction. The insoluble material isolated was 15.8 g. (61.0%)
of hexaphenyldisilane, m. p. $366-368^o$ (mixture melting point).
The organic layer was worked up in the usual manner and the
resulting white solid chromatographed on alumina to give 3.65

g. (23.0%) of crude n-butyltriphenylsilane,[130] melting range
81-87°. A recrystallization from ethanol gave 3.40 g. (21.5%)
of pure product, m. p. 88-89° (mixture melting point).

c. Triphenylsilyllithium and benzyllithium   The com-
petitive reaction between 0.025 mole of triphenylsilyllithium
and 0.025 mole of benzyllithium[121] in tetrahydrofuran with
7.38 g. (0.025 mole) of chlorotriphenylsilane was carried
out exactly as described for the first reaction. The insolu-
ble material isolated was 7.00 g. (54.0%) of hexaphenyldisi-
lane, m. p. 364-366° (mixture melting point). The solid ob-
tained from evaporation of the solvent from the organic layer
was chromatographed on alumina. The products obtained were
0.75 g. (16.5%) of bibenzyl, m. p. 50-53° from methanol (mix-
ture melting point, infrared spectrum); 2.02 g. (23.0%) of
benzyltriphenylsilane,[130] m. p. 97.5-99° from ethanol (mixture
melting point, infrared spectrum); and some tarry residues
which were not investigated.

d. Triphenylsilyllithium and phenyllithium in mixed
tetrahydrofuran-ether solvent   Triphenylsilyllithium (0.05
mole in 115 ml. of tetrahydrofuran) and phenyllithium (0.05
mole in 51 ml. of ether) were reacted competitively with a
solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane and
30 ml. of tetrahydrofuran at -50° and for the same period of

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[130]H. Gilman and H. Hartzfeld, J. Am. Chem. Soc., 73,
5878 (1951).

time as described previously. Subsequent to aqueous hydrolysis, there was isolated 21.2 g. (81.7%) of insoluble hexaphenyldisilane, m. p. 363-367° (mixture melting point). The organic layer was worked up in the usual manner to give, following evaporation of the solvent, a yellow solid. This was slurried with ethanol to give 2.00 g. (11.9%) of crude tetraphenylsilane melting over the range 118-230°. Two recrystallizations from ethyl acetate gave 1.30 g. (7.72%) of pure tetraphenylsilane, m. p. 231-234° (mixture melting point).

e. **Triphenylsilyllithium and n-butyllithium in mixed tetrahydrofuran-ether solvent** The competitive reaction involving 14.7 g. (0.05 mole) of chlorotriphenylsilane dissolved in 30 ml. of tetrahydrofuran was carried out under the usual conditions with 0.05 mole of triphenylsilyllithium in 115 ml. of tetrahydrofuran solution and 0.05 mole of n-butyllithium in 74 ml. of ether solution. The hexaphenyldisilane isolated after hydrolysis of the reaction mixture was 20.2 g. (77.2%), m. p. 361-365° (mixture melting point). Chromatography of the colorless solid isolated from the organic layer gave 2.20 g. (13.9%) of crude n-butyltriphenylsilane melting over the range 82-88°. Several recrystallizations from ethanol gave 1.75 g. (11.0%) of pure material, m. p. 88-89° (mixture melting point). The remaining material was a tarry residue which was not investigated further.

f. <u>n-Butyllithium in tetrahydrofuran with hexaphenyl-</u>
<u>disilane at -50°</u>   A tetrahydrofuran solution of 0.05 mole
of n-butyllithium, previously cooled to -50°, was added rapid-
ly to a suspension of 26.0 g. (0.05 mole) of hexaphenyl-
disilane in 100 ml. of tetrahydrofuran at the same tempera-
ture. The reaction mixture was stirred at this temperature
for 18 minutes. Hydrolysis was then effected with water and
the suspension allowed to warm to room temperature. The sus-
pended solid was filtered, washed with ether, and dried to
give 25.2 g. (96.7%) of recovered hexaphenyldisilane, m. p.
365-368° (mixture melting point). The organic layer was
worked up in the usual manner. However, n-butyltriphenyl-
silane could not be detected in the trace of white solid
left upon evaporation of the solvent.

g. <u>Triphenylsilyllithium and phenyllithium with chloro-</u>
<u>trimethylsilane</u>   Tetrahydrofuran solutions of triphenyl-
silyllithium (0.05 mole) and phenyllithium (0.05 mole) were
separately cooled to -50° and then mixed. A solution of 5.43
g. (0.05 mole) of chlorotrimethylsilane dissolved in 30 ml.
of tetrahydrofuran was added dropwise at the same temperature
over an 8 minute period. The resulting solution appeared
homogeneous throughout the addition and for the subsequent
10 minute period of stirring. Hydrolysis was effected with
100 ml. of water. After warming to room temperature, the
solution was clear. Following the usual work-up, the solvent

was removed by distillation and the resulting oil was distilled at reduced pressure to give 1.50 g. (19.95%) of trimethylphenylsilane, b. p. 53-55° (10 mm.), n_D^{20} 1.4898 (lit. value,[105] b. p. 166-167°/735 mm., n_D^{20} 1.4880). The infrared spectrum was superimposable with that of an authentic specimen. The distillation residue solidified upon cooling to give, subsequent to slurrying with ethanol, 9.70 g. (58.3%) of crude 1,1,1-trimethyl-2,2,2-triphenyldisilane melting over the range 96-109°. Several recrystallizations from ethanol gave 8.20 g. (49.2%) of pure product, m. p. 107-109°[52] (mixture melting point, infrared spectrum). Evaporation of the ethanol extract gave only a yellow tarry residue which was not investigated further.

3. Competitive reaction of halosilanes with triphenylsilyllithium

a. Chlorotriphenylsilane and chlorotrimethylsilane

A solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane, 5.43 g. (0.05 mole) of chlorotrimethylsilane, and 75 ml. of tetrahydrofuran was cooled to -50°. To the solution was added 0.05 mole of triphenylsilyllithium in tetrahydrofuran, also cooled to -50°, over a 15 minute period. The reaction mixture was dark brown, and a white solid appeared suspended. The mixture was stirred at -50° for 10 minutes, at which time Color Test I[67] was negative. Hydrolysis was effected with water and the hydrolyzed mixture allowed to warm to room

temperature. The suspended white solid was filtered, washed with ether, and dried to give 7.05 g. (27.2%) of hexaphenyldisilane, m. p. 363-366° (mixture melting point).

Work-up of the organic layer left a yellow solid which was chromatographed on alumina. The products isolated were 7.55 g. (45.3%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m. p. 105-107.5° (mixture melting point); and 6.40 g. (46.2%) of triphenylsilanol, m. p. 150-151° (mixture melting point).

b. Chlorotriphenylsilane and chlorodimethylphenylsilane

A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was reacted with a solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane, 8.54 g. (0.05 mole) of chlorodimethylphenylsilane, and 75 ml. of tetrahydrofuran under the same conditions and reaction time described previously. The suspended white solid was filtered, washed with ether, and dried to give 7.85 g. (30.0%) of hexaphenyldisilane, m. p. 362-366° (mixture melting point). Work-up of the organic layer left a yellow solid which was chromatographed on alumina. Elution of the column with petroleum ether (b. p. 60-70°) gave 8.95 g. (44.8%) of crude 1,1-dimethyl-1,2,2,2-tetraphenyldisilane,[103] melting range 79-84°. Several recrystallizations from ethanol gave 8.00 g. (40.5%) of pure material, m. p. 83-85° (mixture melting point, infrared spectrum). Elution with benzene and the first ethyl acetate eluates gave 4.60 g. (33.3%) of crude triphenylsilanol melting over the range

146-153°. Two recrystallizations from petroleum ether (b. p. 80-110°) gave 3.45 g. (24.5%) of pure silanol, m. p. 150.5-152° (mixture melting point).

c. **Chlorotriphenylsilane and methyldiphenylchlorosilane**

The competitive coupling reaction between 14.7 g. (0.05 mole) of chlorotriphenylsilane and 11.6 g. (0.05 mole) of methyldiphenylchlorosilane dissolved in 50 ml. of tetrahydrofuran with 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution was carried out under the identical conditions used in the preceding reaction. The hexaphenyldisilane isolated was 8.95 g. (34.4%), m. p. 358-365° (mixture melting point). The organic layer was worked up in the usual manner and chromatographed on alumina. Elution with petroleum ether (b. p. 60-70°) gave 8.20 g. (35.9%) of crude methylpentaphenyldisilane, 130-139° melting range. Several recrystallizations from n-propanol gave 6.90 g. (30.4%) of pure methylpentaphenyldisilane,[103] m. p. 146-147° (mixture melting point, infrared spectrum). Elution of the column with benzene gave 7.00 g. (50.6%) of crude triphenylsilanol melting over the range 145-152°. A recrystallization from petroleum ether (b. p. 80-110°) raised the melting point to 152-154° (mixture melting point), 5.60 g. (40.5%).

d. **Bromotriphenylsilane and chlorotrimethylsilane**

A solution containing 5.43 g. (0.05 mole) of chlorotrimethylsilane, 16.5 g. (0.05 mole) of bromotriphenylsilane[91] and 75

ml. of tetrahydrofuran was reacted with 0.05 mole of triphenylsilyllithium in tetrahydrofuran exactly as described in the previous reaction. The products isolated through the usual work-up were hexaphenyldisilane, 6.80 g. (26.1%); 1,1,1-trimethyl-2,2,2-triphenyldisilane, 9.15 g. (55.0%) crude, 8.05 g. (48.5%) pure; and triphenylsilanol, 5.80 g. (42.0%) crude, 3.90 g. (28.3%) pure. All of the above products were identified by the method of mixture melting points.

e. Ethoxytriphenylsilane and chlorotrimethylsilane

A solution of 15.3 g. (0.05 mole) of ethoxytriphenylsilane,[131] 5.43 g. (0.05 mole) of chlorotrimethylsilane and 75 ml. of tetrahydrofuran was reacted with a tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium in the usual manner. There was no insoluble material resulting from the reaction. The usual chromatographic work-up was employed. The first fraction eluted with petroleum ether (b. p. 60-70°) was 21.4 g. of a white solid melting over the range 53-97°. The infrared spectrum indicated it to be a mixture of ethoxytriphenylsilane and 1,1,1-trimethyl-2,2,2-triphenyldisilane. The white solid was mixed with 50 ml. of absolute ethanol and 50 ml. of 10% hydrochloric acid and stirred at room temperature for one

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[131]B. J. Gaj. Reactions of triphenylsilyllithium with compounds containing group VB elements. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

hour. The suspension was extracted with ether and the ether extracts dried over anhydrous sodium sulfate. Evaporation of the solvent left a white solid which was slurried with ethanol and filtered. The insoluble material was recrystallized from ethanol several times to give 10.1 g. (60.3%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m. p. 107-110° (mixture melting point). The ethanol soluble portion proved to be 5.20 g. (37.6%) of triphenylsilanol, m. p. 152-154° (mixture melting point). Further elution of the chromatographic column with ethyl acetate gave an additional 2.50 g. (18.1%) of triphenylsilanol.

f. <u>Chlorotriphenylsilane and chlorotriethylsilane</u>
A solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane, 7.54 g. (0.05 mole) of chlorotriethylsilane and 75 ml. of tetrahydrofuran was reacted with a tetrahydrofuran solution of 0.02 mole of triphenylsilyllithium in the usual manner. The products isolated were 6.80 g. (26.1%) of hexaphenyldisilane, m. p. 359-364°; 8.40 g. (44.8%) of 1,1,1-triethyl-2,2,2-triphenyldisilane,[94] m. p. 95-97°; and 7.85 g. (56.8%) of triphenylsilanol, m. p. 150-151.5°. All products were identified by mixture melting points and/or infrared spectra comparisons.

g. <u>Reaction of chlorotriphenylsilane and chlorotrimethylsilane with sodium in refluxing xylene</u> A mixture of 29.5 g. (0.10 mole) of chlorotriphenylsilane, 10.9 g.

(0.10 mole) of chlorotrimethylsilane, 2.30 g. (0.10 g. atom) of sodium and 150 ml. of xylene was heated at reflux temperature for 5 hours. As the refluxing started, the sodium melted and the solution became dark blue in color. After the solution had cooled, it was poured into ethanol. There did not appear to be any unreacted sodium. The suspended white solid was filtered, washed with water and ether, and dried to give 3.30 g. (12.7%) of hexaphenyldisilane, m. p. 360-365° (mixture melting point). The organic layer from the filtrate was subjected to the usual chromatographic work-up. From the petroleum ether (b. p. 60-70°) eluates was obtained 15.2 g. (45.4%) of crude 1,1,1-trimethyl-2,2,2-triphenyldisilane melting over the range 101.5-107°. Recrystallization from ethanol gave 14.4 g. (43.2%) of pure disilane, m. p. 106.5-109° (mixture melting point, infrared spectrum). Elution of the column with benzene, ethyl acetate and with ethanol gave a total of 8.15 g. (29.5%) of triphenylsilanol, m. p. 150-151.5° (mixture melting point).

4. **Relative reactivities of silylmetallic reagents in the metalation of triphenylgermane**

   a. **Triphenylsilyllithium** A tetrahydrofuran solution of 0.02 mole of triphenylsilyllithium was added, over a 15 minute period, to 6.10 g. (0.02 mole) of triphenylgermane[132]

   [132]E. A. Zuech, Iowa State University of Science and Technology, Ames, Iowa. Information concerning the preparation of triphenylgermane. Private communication. 1960.

dissolved in 50 ml. of tetrahydrofuran. The solution turned dark green, but became lighter in color during 8 hours of stirring at room temperature. Carbonation was effected by pouring the reaction mixture jet-wise into a Dry Ice-ether slurry. After the carbonation mixture had warmed to slightly above 0° (one hour and 15 minutes), it was extracted with 200 ml. of chilled 2% aqueous sodium hydroxide and discarded. The basic extract was extracted once with ether and then acidified with chilled 10% hydrochloric acid. The acidified solution, which was cloudy, was extracted with ether, and the ether extracts were dried over anhydrous sodium sulfate. Subsequent to evaporation of the solvent, a yellow solid was obtained. This was slurried with ethanol to give 3.65 g. (52.3%) of crude triphenylgermanecarboxylic acid, m. p. 190-193° dec. This was recrystallized from ethanol to give 3.26 g. (46.7%) of pure acid, m. p. 186-188° dec. (lit. value,[111] 189-190° dec.) (mixture melting point, infrared spectrum).

The procedure was repeated with the reaction time being 5 hours to give 3.15 g. (45.1%) of crude acid, or 2.61 g. (37.3%) of pure acid after recrystallization from ethanol.

b. **Methyldiphenylsilyllithium** A solution of 6.10 g. (0.02 mole) of triphenylgermane and 50 ml. of tetrahydrofuran was reacted with 0.02 mole of methyldiphenylsilyllithium in tetrahydrofuran solution for 8 hours at room temperature. The reaction mixture was carbonated and worked up exactly as

described in the previous reaction. The crude acid was 4.30 g. (61.6%) decomposing over the range 157-190°. A recrystallization from ethanol gave 3.95 g. (56.6%) of pure acid, m. p. 187-191° dec. (mixture melting point).

The reaction was also run for 5 hours to give 3.60 g. (51.6%) of crude acid, or 3.10 g. (44.4%) of pure acid.

c. __Dimethylphenylsilyllithium__ A tetrahydrofuran solution of 0.02 mole of dimethylphenylsilyllithium was added, over a period of 15 minutes, to 6.10 g. (0.02 mole) of triphenylgermane dissolved in 50 ml. of tetrahydrofuran. The solution became warm during the addition, and was reddish brown in color. The reaction mixture was stirred at room temperature for 8 hours, at which time it was carbonated and worked up in the usual manner. The amount of crude acid was 4.00 g. (57.4%), m. p. 187-190° dec. This was recrystallized from ethanol to give 3.65 g. (52.3%) of pure triphenylgermanecarboxylic acid, m. p. 185-189° dec. (mixture melting point).

The reaction was repeated for the 5 hour period to give 3.10 g. (44.4%) of crude acid, or 2.98 g. (42.7%) of pure acid.

H. Preparation of Some Alkyl-Aryl Silanecarboxylic Acids and Their Esters

1. Dimethylphenylsilanecarboxylic acid

Dimethylphenylsilyllithium (0.074 mole in tetrahydrofuran solution) was carbonated by pouring into a Dry Ice-ether

slurry. The solution was allowed to warm to slightly above
0°. This was extracted as rapidly as possible with 200 ml. of
chilled 2% sodium hydroxide. The chilled extract was imme-
diately acidified to a pH of 5-6 with dilute hydrochloric
acid. Ether extraction was employed, and the extracts dried
over anhydrous sodium sulfate. The ether was decanted from
the sodium sulfate and evaporated under an air-jet to leave
7.35 g. (55.2%) of crude dimethylphenylsilanecarboxylic acid,
m. p. 51-56°. Several recrystallizations from petroleum ether
(b. p. 40-50°), cooled to ice-bath temperature, gave 4.65 g.
(34.9%) of white crystals, m. p. 56-58°. It was necessary to
cool the petroleum ether to ice-bath temperature and filter
while chilled due to the high solubility of the acid, even at
room temperature, in the solvent.

<u>Anal</u>. Calcd. for $C_9H_{12}O_2Si$: C, 59.95; H, 6.71; neut.
equiv., 180.28. Found: C, 59.90, 59.95; H, 6.60, 6.62;
neut. equiv., 181.63, 181.71.

The infrared spectrum of the compound in carbon disulfide
showed absorption bands at 6.04, 8.00, and 8.99μ, character-
istic of COOH, Si-methyl, and Si-phenyl groups, respectively.
There was also a broad band starting at 2.95 and ending at
3.95μ, with peaks at 3.30, 3.55, 3.70 and 3.95μ. This is
an associated O-H running into the C-H region.

The reaction was repeated twice to give the acid in crude
yields of 71.0 and 47.0% (pure yields of 50.2 and 30.0%),

respectively.

2. Methyldiphenylsilanecarboxylic acid

A tetrahydrofuran solution of 0.05 mole of methyldi-
phenylsilyllithium was carbonated by pouring jet-wise into a
Dry Ice-ether slurry. The same rapid work-up at low tempera-
tures as described previously for dimethylphenylsilanecar-
boxylic acid was employed to obtain 9.80 g. (67.5%) of crude
methyldiphenylsilanecarboxylic acid decomposing over the
range 124-132°. Several recrystallizations from petroleum
ether (b. p. 80-110°) gave 4.80 g. (33.1%) of white crystals,
m. p. 133.5-136° dec.

Anal. Calcd. for $C_{14}H_{14}O_2Si$: C, 69.50; H, 5.83; neut.
equiv., 242.34. Found: C, 69.45, 69.55; H, 5.66, 5.72;
neut. equiv., 247.3, 250.0, 257.4.

The infrared spectrum of the acid in carbon disulfide is
almost identical to that of dimethylphenylsilanecarboxylic
acid except for an intensification of the C-H aromatic peak
and a decrease of the C-H aliphatic and Si-methyl peaks.

A repeat of the reaction gave the acid in 84.0% crude
yield (66.5% pure yield).

3. Stability of acids towards heat and base

Dimethylphenylsilanecarboxylic acid melted at 56-58°
without decomposition. However, upon raising the temperature

to 125°, decomposition with gas evolution occurred. Methyl-diphenylsilanecarboxylic acid decomposed with gas evolution at its melting point, 133.5-136°. The gas which was evolved was carbon monoxide as evidenced by a black deposit on paper saturated with 5% palladium chloride.[133]

Methyldiphenylsilanecarboxylic acid was stable when treated with 10% sodium hydroxide. However, when an absolute ethanol solution was treated with a few drops of 10% sodium hydroxide, a slow evolution of carbon monoxide was detected by the palladium chloride test. The reaction in ethanol solution and not in the aqueous system was due to the increased solubility of the acid in ethanol. Dimethylphenylsilane-carboxylic acid dissolved in absolute ethanol also reacted with aqueous sodium hydroxide, but the black stain was not as dark as with the other acid and formed very slowly. It appears that dimethylphenylsilanecarboxylic acid is not so sensitive to base attack as is methyldiphenylsilanecarboxylic acid. In contrast, triphenylsilanecarboxylic acid gave a positive test very rapidly.

4. **Methyl dimethylphenylsilanecarboxylate**

Five grams (0.0278 mole) of dimethylphenylsilanecarboxylic acid was dissolved in 50 ml. of ether and agitated by

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[133]R. Nowicki, _Chem. Ztg._, _35_, 1120 (1911).

means of a magnetic stirrer. The diazomethane in ether solu-
tion was added slowly at room temperature. The addition was
completed in 5 minutes. The solution was yellow, but the
color was lost after a minute of stirring. The ether was
allowed to evaporate in a hood overnight. The resulting
colorless oil was distilled at reduced pressure to give 3.15
g. (57.9%) of methyl dimethylphenylsilanecarboxylate, b. p.
46-48° (0.03 mm.), n_D^{20} 1.5068, d_{20}^{20} 1.0226.

Anal. Calcd. for $C_{10}H_{14}O_2Si$: C, 61.82; H, 7.26; MR_D
56.48. Found: C, 61.69, 61.66; H, 7.45, 7.45; MR_D 56.53.

Molar refractions were calculated using the values of
Vogel _et_ _al_.[134,135]

The infrared spectrum in carbon disulfide showed absorp-
tion bands at 3.25, 3.40, 5.95, 8.00 and 8.79μ, character-
istic of C-H aryl, C-H aliphatic, ester carbonyl, Si-methyl,
and Si-phenyl, respectively.

A repeat of this reaction gave the ester in 90.2% yield,
b. p. 79-81° (1.2 mm.), n_D^{20} 1.5069.

5. **Methyl methyldiphenylsilanecarboxylate**

Nine grams (0.0373 mole) of methyldiphenylsilanecar-
boxylic acid was esterified by diazomethane in ether solution

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[134]A. I. Vogel, W. T. Creswell, G. H. Jeffrey and J.
Leicester, _J_. _Chem_. _Soc_., 514 (1952).

[135]A. I. Vogel, W. T. Creswell and J. Leicester, _J_.
Phys. _Chem_., _58_, 174 (1954).

and worked up as described in the previous experiment. Distillation of the resulting oil at reduced pressure gave 6.60 g. (69.3%) of methyl methyldiphenylsilanecarboxylate, b. p. 115-116° (0.02 mm.), n_D^{20} 1.5645, d_{20}^{20} 1.0926.

Anal. Calcd. for $C_{15}H_{16}O_2Si$: C, 70.28; H, 6.29; Si, 10.92; MR_D 76.37. Found: C, 70.64, 70.81; H, 6.48, 6.52; Si, 10.82, 10.90; MR_D 76.38.

The spectrum is similar to that of methyl dimethylphenylsilanecarboxylate, with the same change in intensities associated with the replacement of a methyl by a phenyl group.

6. Dimethylphenylhydroxymethylsilane

a. **From lithium aluminum hydride reduction of methyl dimethylphenylsilanecarboxylate**   Lithium aluminum hydride, 3.26 g. (0.086 mole), was added in small portions to 20.0 g. (0.103 mole) of methyl dimethylphenylsilanecarboxylate dissolved in 200 ml. of ether and cooled to ice-bath temperature. Vigorous refluxing occurred as each portion was added. The ice-bath was removed upon completion of addition, and the reaction mixture was allowed to stir at room temperature for 4.5 hours. The solution was then poured jet-wise onto crushed ice acidified with sulfuric acid. The usual work-up was employed. Distillation of the solvent left a colorless oil which was distilled at reduced pressure to give 13.6 g. (79.3%) of a colorless oil later shown to be dimethylphenyl-

hydroxymethylsilane, b. p. 130-135° (30 mm.), n_D^{20} 1.5220.

This was redistilled to give 12.1 g. (70.4%) of product,

b. p. 132-135° (27 mm.), n_D^{20} 1.5225, d_{20}^{20} 0.9899.

<u>Anal</u>. Calcd. for $C_9H_{14}OSi$: C, 65.00; H, 8.48; MR_D 51.65.
Found: C, 64.39, 64.56; H, 7.57, 7.74; MR_D 51.24.

The infrared spectrum in carbon disulfide showed the

absorption bands mentioned previously for C-H aromatic and

aliphatic, Si-methyl, and Si-phenyl; and, in addition, bands

at 2.97 and 10.00 μ indicative of an associated OH and

hydroxymethyl, respectively.

     b. <u>From reaction of dimethylphenylsilyllithium with</u>

<u>formaldehyde</u>   Formaldehyde gas, prepared by heating 20.0 g.

of paraformaldehyde, was passed over a rapidly stirred solu-

tion of 0.148 mole of dimethylphenylsilyllithium in tetra-

hydrofuran solution. The reaction mixture became quite warm

and mild refluxing occurred. A water bath was applied to

avoid overheating. The solution became lighter in color,

until after one hour it was light orange-brown. Color Test

I[67] was then negative. Stirring at room temperature was con-

tinued for 2 hours. Hydrolysis was effected with water and

the usual work-up employed. Evaporation of the solvent left

a colorless oil which was distilled at reduced pressure to

give 11.2 g. (45.3%) of dimethylphenylhydroxymethylsilane,

boiling over the range 111-117° (11 mm.), n_D^{20} 1.5256. The

oil was redistilled to give 8.80 g. (35.8%), b. p. 113-117°

(11 mm.), n_D^{20} 1.5251.

<u>Anal</u>. Calcd. for $C_9H_{14}OSi$: C, 65.0; H, 8.48; MR_D 51.66. Found: C, 64.43, 64.57; H, 8.02, 8.19; MR_D 50.35.

The infrared spectrum is superimposable with that of the oil obtained in the lithium aluminum hydride reduction of methyl dimethylphenylsilanecarboxylate.

IV. DISCUSSION

A. Development of an Improved Procedure for the Dimetalation of Diphenyl Ether

At the outset of the thesis problem, a large quantity of 10,10-dimethylphenoxasilin was needed in order that it might be used as a starting material in subsequent reactions. However, the long reaction time (72 hours) and the low yields (25.1%) indicated in the published directions[8] evidenced the necessity of developing a more facile procedure.

The published directions involved the dimetalation of diphenyl ether with n-butyllithium in diethyl ether, with subsequent reaction of the dilithiodiphenyl ether with dichlorodimethylsilane. The procedure was reinvestigated both in regard to the organometallic reagent and in regard to the solvent system. Derivatization was carried out through the use of dichlorodimethylsilane, rather than carbonation as is the usual procedure in such investigations, in order to obtain the desired starting material. The results of this investigation are summarized in Table 3.

Gilman and Gray,[136] in addition to other investigators, [137,138,139] had shown that in almost every metalation reaction

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[136]H. Gilman and S. Gray, *J. Org. Chem.*, *23*, 1476 (1958).

[137]H. Gilman and R. D. Gorsich, *ibid.*, *22*, 687 (1957).

[138]P. Tomboulian, *ibid.*, *24*, 229 (1959).

[139]D. W. Mayo, P. D. Shaw and M. Rausch, *Chem. and Ind.* (London), 1388 (1957).

Table 3. Dimetalation of diphenyl ether

Organometallic reagent	Solvent	Solvent ratio	Reaction conditions		Yield of cyclic derivative, %
			temp.	hrs.	
n-Butyllithium	THF[a] – ether	1:1	Room temp.	14	32.0
n-Butyllithium	THF – ether	1:1.1	Mild reflux	4	45.5
n-Butyllithium	THF – ether	1:1.3	Mild reflux	5	50.5
n-Butyllithium	THF	––	$-25 \pm 5^{\circ}$ $+$ 0°	5 $+$ 12	16.6
Phenyllithium	THF – ether	1:1	Mild reflux	12	23.7
Methyllithium	THF	––	Mild reflux	12	0

[a]THF is an abbreviation for tetrahydrofuran.

the use of tetrahydrofuran as the solvent gave significantly higher yields of the metalated product as compared to those obtained in diethyl ether. The use of tetrahydrofuran-ether mixed solvent systems did not appear to give as good yields of metalated products as were obtained when the reactions were run in tetrahydrofuran.

The present investigation also indicated the much greater activating effect of tetrahydrofuran in metalation reactions. Diphenyl ether was dimetalated quite rapidly by n-butyllithium in this solvent, and also in the mixed solvent system. However, the reaction in the mixed solvent system gave a greater yield of derivative (50.5%) than when carried out in tetrahydrofuran alone (16.6%). Phenyllithium in the mixed solvent system was also sufficiently reactive to give dimetalation, but to a lesser extent (27.7%). Methyllithium in tetrahydrofuran did not give a derivative indicative of dimetalation.

Why the mixed solvent system was more satisfactory in these metalations can best be explained by considering that two competing reactions are taking place. The organometallic reagent can either metalate diphenyl ether, or it can react with tetrahydrofuran. The latter reaction has been shown to occur quite rapidly, even at room temperature.[117] By employing a mixed solvent system, the rate of reaction with tetrahydrofuran decreased, and metalation became the predominant reaction. Whether this was due to a decreased solvation by

tetrahydrofuran or to dilution effects is not clear.

The stability of the organometallic reagent increased in the mixed solvent system without a significant decrease in metalating ability. In fact, a mild reflux could be employed for five hours before an n-butyllithium system would give a negative color test for highly reactive organometallic reagents.[68] As the ratio of ether to tetrahydrofuran was increased to much greater than one, the rate of metalation decreased to an extent that the mixed solvent system lost its attractiveness.

The optimum conditions for the dimetalation of diphenyl ether finally developed involved the preparation of n-butyllithium (1N) in diethyl ether, followed by addition to a tetrahydrofuran solution of diphenyl ether. The final solvent ratio of ether to tetrahydrofuran was about 1.3:1 for a maximum yield at a reasonable reaction time. The reaction mixture may be warmed mildly for 5 hours before use to obtain a maximum yield (50.5%), or it may be stirred at room temperature for 14 hours. The latter choice gave a lower yield of derivative (32.0%), but proved convenient in that the reaction mixture could be stirred overnight before subsequent reaction. The former choice required more attention. The only limiting factor appears to be a lower yield due to handling difficulties when large quantities of reagents are employed. Regardless, the procedure appears to improve greatly over the 72

hours of refluxing used previously to obtain a 25.1% yield of product.[8]

B. Preparation of Phenoxasilin Compounds

Most of the phenoxasilin compounds prepared previously were rather high melting solids.[8,9,41,42,43,44] The lowest melting was 10,10-dimethylphenoxasilin at $78.5-79^{\circ}$; however, alkyl-substituted silicon compounds are not noted for outstanding radiation stability. It was reasoned that if unsymmetrical phenoxasilin compounds could be prepared by attaching different aryl groups to the silicon atom, such dissymmetry would lower the melting points to a degree that the compounds might be practicable as lubricants.

The inaccessibility of unsymmetrical diorganosilicon halides negated the usual route to these compounds. The alternative approach was to prepare a phenoxasilin ring system containing either Si-X or Si-H at the bridge-position which could then be coupled with an RLi compound.

Such an approach was not new. Gilman and Gorsich[140] coupled 2,2'-dilithiobiphenyl with several monoorganosilicon halides, such as methyltrichlorosilane, to obtain 5-chloro-5-organodibenzosilole compounds. The halides were reacted with organolithium reagents to obtain unsymmetrical molecules.

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[140]H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 80, 1883 (1958).

Since many difficulties were experienced in the handling and storing of these halo silicon compounds, Zuech[141] substituted an $RSiH_3$ for the $RSiX_3$ compounds in reaction with N-ethyl-2,2'-dilithiodiphenylamine. The resulting cyclic Si-H compound could be handled with little fear of atmospheric hydrolysis, but still coupled readily with RLi compounds to give unsymmetrical phenazasilin compounds. The latter reaction was chosen as the method for preparing the proposed unsymmetrical phenoxasilin compounds.

The dilithium intermediate employed by Zuech[141] had been prepared through the use of a halogen-metal interconversion reaction and was known to be of relatively high quality. The 2,2'-dilithiodiphenyl ether (X) for the following reactions was prepared by the dimetalation of diphenyl ether in mixed solvent as described in the preceding section, and some doubt still remained as to the ease of its reaction with silicon hydrides. However, this uncertainty was readily removed with the isolation of the known compound, 10,10-diphenylphenoxasilin[8] (XI), from reaction of the dilithium intermediate with diphenylsilane.

2,2'-Dilithiodiphenyl ether was reacted with phenylsilane to give the functional Si-H compound, 10-phenylphenoxasilin

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[141]E. A. Zuech. Cyclic organosilicon and related compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

(XII). This was coupled with phenyllithium to give again the known 10,10-diphenylphenoxasilin (XI) as proof of structure. Subsequent reactions of 10-phenylphenoxasilin with methyl-, o-tolyl-, p-tolyl-, o-biphenylyl-, p-phenoxyphenyl- and benzyllithium gave the respective unsymmetrical phenoxasilin compounds XIII, XIV, XV, XVI, XVII and XVIII.

There is still some question concerning 10-benzyl-10-phenylphenoxasilin (XVIII). Only a trace of material which gave a marginal analysis was isolated. The result seems to be in line with the very low reactivity of benzyl type lithium reagents with Si-H compounds. More will be said concerning this in the next section. The major product isolated from the reaction was 10-hydroxy-10-phenylphenoxasilin (XIX) arising from hydrolysis of the Si-H bond. The silanol could also be prepared by direct reaction of the Si-H compound (XII) with alcoholic potassium hydroxide. Proof of structure for compound XIX was obtained by warming in 98% formic acid to give the disiloxane, 10,10'-oxybis-(10-phenylphenoxasilin) (XX).

10-Phenylphenoxasilin (XII) reacted spontaneously with N-bromosuccinimide at room temperature to give 10-bromo-10-phenylphenoxasilin (XXI) in good yield. The bromo compound did not fume in the atmosphere as does bromotriphenylsilane, possibly an indication of some steric interference in the cyclic system. However, the bromo compound was readily

XIII Methyl
XIV o-Tolyl
XV p-Tolyl
XVI o-Biphenyl
XVII p-Phenoxy-
        phenyl
XVIII Benzyl
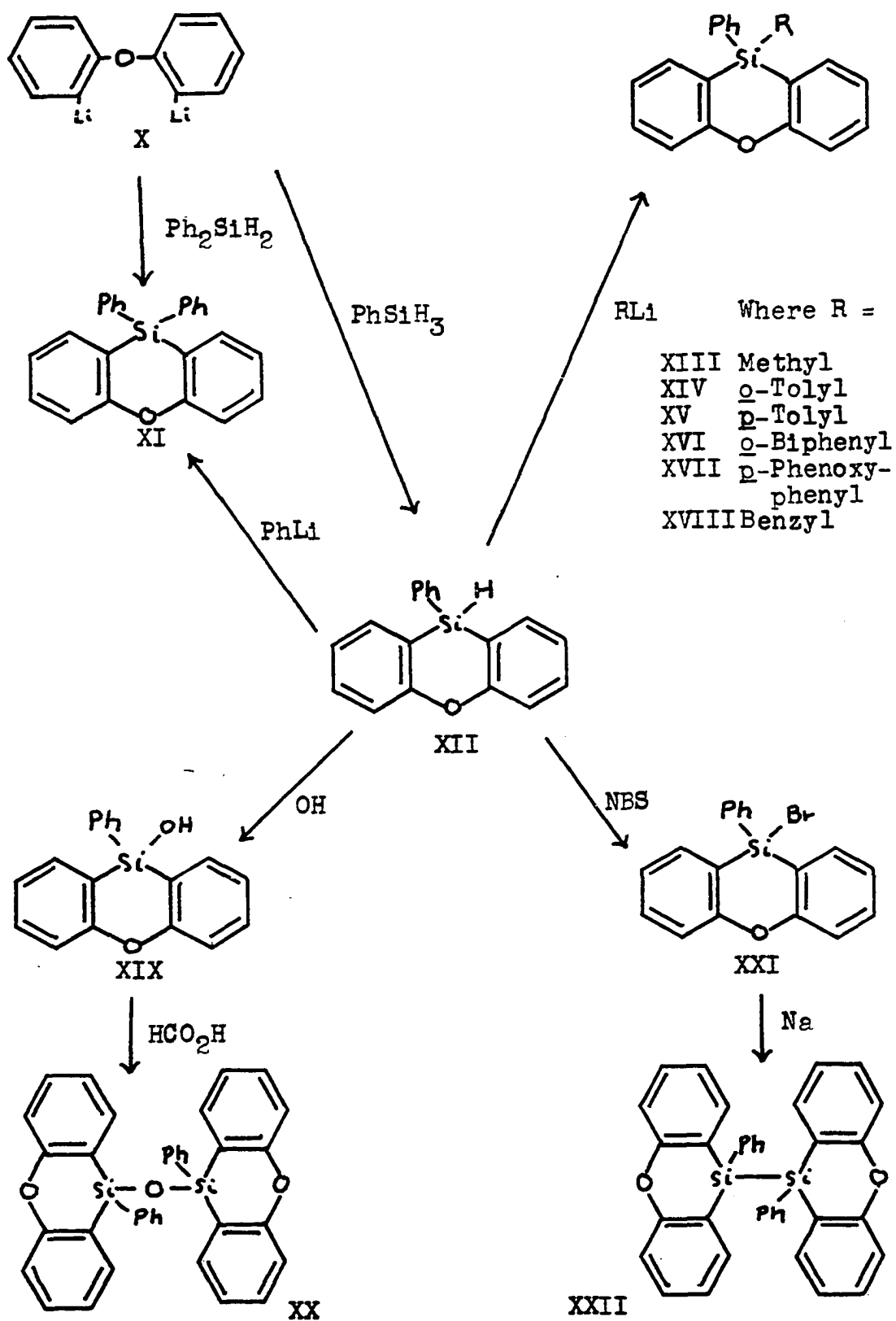
converted to the disilane (XXII) by refluxing with sodium in xylene.

The unsymmetrical cyclic silicon compound, 2-trimethyl-silyl-10,10-diphenylphenoxasilin (XXIV), was prepared by the dimetalation of 4-trimethylsilylphenyl phenyl ether (XXIII), followed by reaction with dichlorodiphenylsilane. As can be seen, the product was a silicon-substituted cyclic silicon compound.

$(CH_3)_3 Si$—⬡—O—⬡   1) $\underline{n}-C_4H_9Li$ ⟶

2) Ph_2SiCl_2

XXIII

Ph Ph

Si

Si$(CH_3)_3$

O

XXIV
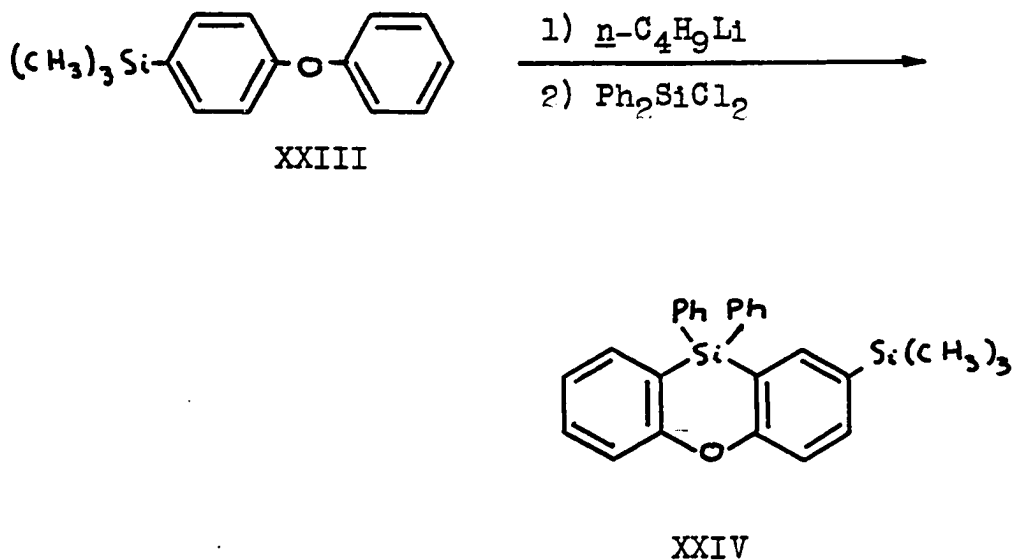
Table 4 summarizes the physical properties and thermal stabilities of the compounds prepared during this phase of the thesis investigation. The phenoxasilin compounds are note-worthy in the small amount, if any, of decomposition at their volatilization temperatures. However, only a few of the com-pounds volatilized at temperatures high enough to be of value.

Four compounds may be of interest, 10-o-biphenylyl-10-

Table 4. Phenoxasilin compounds

Compound	Yield, %	M.p., °C	Thermal stability, °C
10-Phenylphenoxasilin	25.8	81-83	Volatilizes 370-380, colorless condensate
10-Methyl-10-phenylphenoxasilin	60.0	56.5-58	Volatilizes 360-370, colorless condensate
10-Phenyl-10-o-tolylphenoxasilin	47.2	116-117.5	Microbubbles 320, volatilizes 438-444, clear distillate
10-Phenyl-10-p-tolylphenoxasilin	47.2	155-157	Microbubbles 402, volatilizes 444-446, light yellow condensate
10-o-Biphenylyl-10-phenylphenoxasilin	47.2	150-151	Volatilizes 480-492, light brown distillate
10-p-Phenoxyphenyl-10-phenylphenoxasilin	19.3	136-137	Volatilizes 526, light yellow distillate
10-Benzyl-10-phenylphenoxasilin	Trace	89-90	Microbubbles 328, volatilizes 446-450, colorless distillate
10-Hydroxy-10-phenylphenoxasilin	77.4	124-125	Occasional bubbles 270, rapid 310, apparent volatilization 416-418, light yellow condensate

Table 4. (Continued)

Compound	Yield, %	M.p., °C	Thermal stability, °C
10,10'-Oxybis-(10-phenylphenoxasilin)[120]	37.3	189.5-191	Volatilizes 554-556, light brown distillate
10-Bromo-10-phenylphenoxasilin	63.2	96-99	---
10,10'-Diphenyl-10,10'-bi-(phenoxasilin)	56.5	231-233	Microbubbles 370, volatilizes 512-524, light yellow distillate, darkens 550
2-Trimethylsilyl-10,10-diphenyl-phenoxasilin	16.9	123-124	Volatilizes 440-442, clear distillate

phenylphenoxasilin (XVI), 10-p-phenoxyphenyl-10-phenylphenoxa-
silin (XVII), 10,10'-oxybis-(10-phenylphenoxasilin) (XX) and
10,10'-diphenyl-10,10'-bi-(phenoxasilin) (XXII). These all
volatilize above 500° without significant decomposition. The
disiloxane (XX) and disilane (XXII) are relatively high melt-
ing and would only be of limited value. Of the other two,
10-p-phenoxyphenyl-10-phenylphenoxasilin is of greatest in-
terest. Although it is a solid melting at 136-137°, it
possesses good thermal stability. More important, it incor-
porates two phenoxyphenyl systems, noted for high radiation
resistance, into one compound. This particular material may
add desired stability when blended with other lubricants.

Several attempts were made to brominate 10,10-dimethyl-
phenoxasilin, either to introduce the halogen onto the methyl
group or onto the ring. N-Bromosuccinimide failed under a
variety of conditions to effect any reaction. A bromide-
bromate mixture was employed as one of the milder brominating
agents. However, extensive cleavage of the ring system
occurred, and the reaction was not pursued further.

C. Preparation of Some Silicon Derivatives of Xanthene

There are no reported silicon derivatives of xanthene
(XXV), the carbon analog of the phenoxasilin system. Although
such materials would not be expected to possess desirable
lubrication properties, compounds of this type might be of

academic interest.

The majority of compounds now being reported were substituted in the 9-, or bridge, position. The 9-position, being a benzylic carbon, is very reactive and is metalated quite readily by n-butyllithium.[122] Reaction of 9-lithioxanthene (XXVI) with several chlorosilanes gave the respective 9-substituted xanthenes (XXVII). Thus, 9-trimethylsilylxanthene, 9-triphenylsilylxanthene, dimethylbis-(9-xanthyl)-silane and diphenylbis-(9-xanthyl)silane were prepared from

XXV   XXVI

XXVII
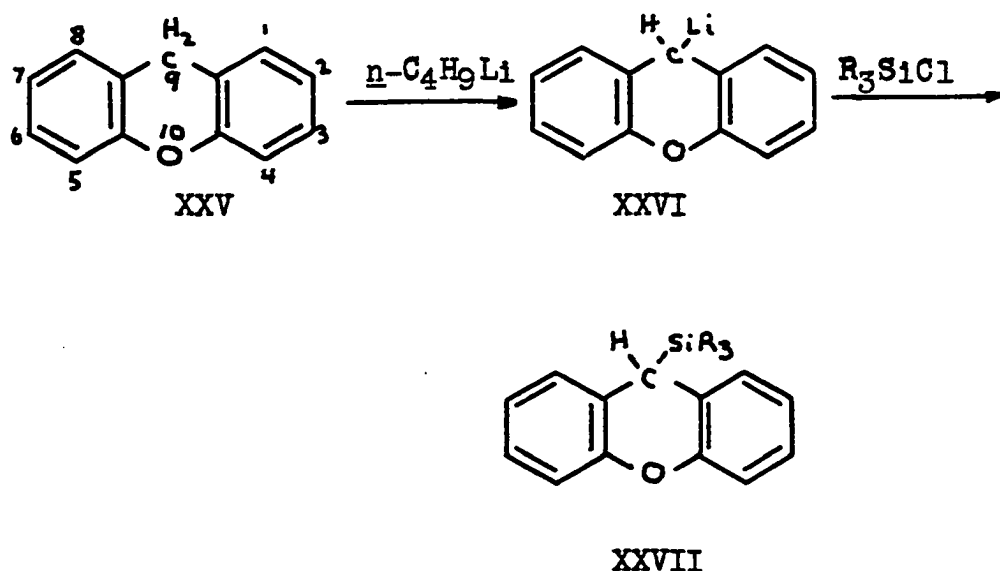
chlorotrimethyl-, chlorotriphenyl-, dichlorodimethyl- and dichlorodiphenylsilane, respectively. Triphenylsilane, an Si-H compound, did not react with 9-lithioxanthene. As indicated in Table 5, the compounds mentioned above either volatilize at quite low temperatures or decompose before volatil-

Table 5. Silicon derivatives of xanthene

Compound	Yield, %	M.p., °C	Thermal stability, °C
9-Trimethylsilylxanthene	67.3	119.5-121	Volatilizes 300-302, colorless condensate
9-Triphenylsilylxanthene	52.6	164.5-166	Microbubbles 252, darkens 370, volatilizes 420-430, dark brown distillate
Dimethylbis-(9-xanthyl)silane	39.1	173-174	Darkens 290, volatilizes 390-396, dark brown distillate
Diphenylbis-(9-xanthyl)silane	50.6	214-216	Darkens 320, volatilizes 398-400, dark brown condensate
2-Trimethylsilyl-9,9-diphenyl-xanthene	83.5	200-202	Volatilizes 410-420, light yellow distillate
9,9-Diphenyl-4-triphenylsilyl-xanthene	21.6	269-271.5 dec.	--
Xanthydryloxytriphenylsilane	12.7	246-282 dec.	--

144

ization.

Two silicon derivatives of 9,9-diphenylxanthene[125] were also prepared. 9,9-Diphenylxanthene was metalated with one equivalent of n-butyllithium and the intermediate lithium compound reacted with chlorotriphenylsilane. Since the 9-position was blocked, metalation should occur on the nucleus. Spectral evidence and analogy to other metalations of aryl ethers indicated that the substituent was in the 4-position, or ortho to the oxygen. Thus the resulting compound was considered to be 9,9-diphenyl-4-triphenylsilyl-xanthene.

The other silicon derivative of 9,9-diphenylxanthene prepared was 2-trimethylsilyl-9,9-diphenylxanthene (XXX). The
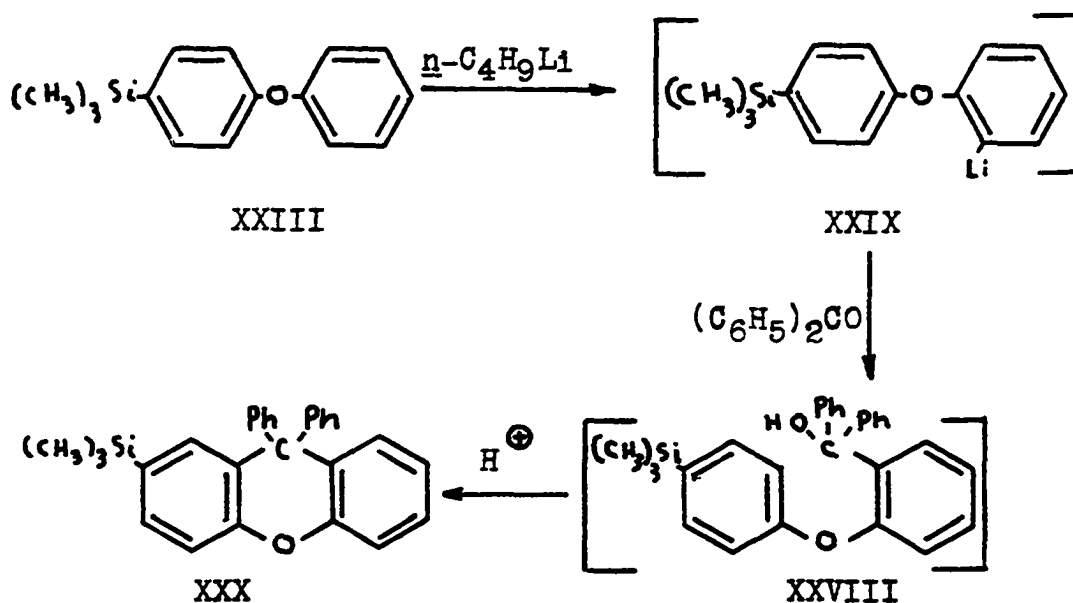
compound was prepared by cyclization of the carbinol (XXVIII)
obtained through reaction of 4-(4-trimethylsilyl)phenoxy-
phenyllithium (XXIX) with benzophenone. As mentioned in the
experimental presentation, spectral evidence indicated that
the metalation had taken place on the non-substituted ring.
An effort to determine the exact position of the substituent
was not made because, regardless of which ring possessed the
carbinol group, the same product would be obtained upon
cyclization.

It should be noted that this cyclic compound is the car-
bon analog of 2-trimethylsilyl-10,10-diphenylphenoxasilin pre-
pared in the previous section. It is interesting that the
carbon cycle, although it is of lower molecular weight, melts
over 70 degrees higher than the silicon compound and has less
satisfactory thermal characteristics.

The reaction of triphenylsilyllithium with xanthone gave
a small amount of a compound decomposing over a broad range
(246-282° dec.). The material could not be purified further,
and its analysis was in good agreement with that of xanthy-
dryloxytriphenylsilane. The structure as an addition-
rearrangement product was assigned on the basis of the infra-
red data which indicated the absence of the hydroxyl group and
the presence of the silicon-oxygen bond.

Triphenylsilyllithium metalated xanthene very rapidly at
room temperature. The resulting 9-lithioxanthene was

derivatized by carbonation and by reaction with chlorotri-
phenylsilane to give 9-xanthenecarboxylic acid[122] and 9-
triphenylsilylxanthene, respectively.

It is interesting that 9-triphenylsilylxanthene was not
isolated from the carbonation mixture. Such a product was
a distinct possibility since RLi compounds are known to couple
readily with an Si-H bond,[102,142,143,144,145] arising in this
reaction from the metalation step. The failure of 9-lithio-
xanthene to react with triphenylsilane and the very low yield
of 10-benzyl-10-phenylphenoxasilin from reaction of benzyl-
lithium with 10-phenylphenoxasilin may be recalled in this
connection. Thus, it appears that benzyl type lithium re-
agents will not couple readily with Si-H compounds, probably
due to charge‾delocalization.

D. Reaction of Triphenylsilyllithium with Some Alkyl-Aryl Ethers

While attempting to metalate anisole with triphenyl-
silyllithium, alkylation of the silylmetallic was observed.
The products isolated after the reaction mixture had been

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[142]H. Gilman and S. P. Massie, Jr., J. Am. Chem. Soc.,
68, 1128 (1946).

[143]R. N. Meals, ibid., 68, 1880 (1946).

[144]W. H. Nebergall, ibid., 72, 4702 (1950).

[145]J. S. Peake, W. H. Nebergall and Y. T. Chen, ibid.,
74, 1526 (1952).

warmed at 50° for 24 hours were methyltriphenylsilane and phenol. Apparently a facile ether cleavage had occurred. Ether cleavages by organometallic reagents are well known,[146] however, this particular cleavage occurred under quite mild conditions and gave well defined products. A similar cleavage involving 1,2-dimethoxyethane with the resultant formation of methyltriphenylsilane had been observed previously.[51]

The discovery evoked immediate interest and the reaction was applied to the next higher homologs, phenetole and phenyl n-propyl ether. However, even after extended reaction periods at higher temperatures, only a trace of cleavage was observed with the former ether and none with the latter.

The great difference in reactivity may involve several factors. The cleavage probably occurs through an S_N2 displacement mechanism with phenoxide ion being the leaving group. Such a reaction is very sensitive to steric factors

$$(C_6H_5)_3Si \ominus + R \overset{+}{O}-C_6H_5 \longrightarrow (C_6H_5)_3SiR + C_6H_5O\ominus$$
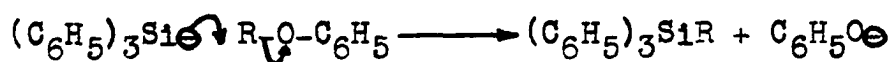
both around the carbon being attacked and of the anion, i.e., the rate of displacement is decreased significantly by small increases in steric hindrance.[147] Triphenylsilyllithium represents a very bulky grouping. In addition, it is probably

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[146]For a summarizing review on the cleavage of ethers, see R. L. Burwell, Jr., Chem. Rev., 54, 615 (1954).

[147]J. Hine. Physical organic chemistry. New York, N. Y., McGraw-Hill Book Co., Inc. 1956. pp. 138-167.

highly solvated with tetrahydrofuran molecules increasing its bulk still more. The large size of triphenylsilyllithium would amplify the increased steric hindrance arising from the change of methyl to ethyl or n-propyl ethers, and the cleavage reactions could not take place.

The cleavage reaction was carried out successfully with a large number of aryl methyl ethers, and the results are summarized in Table 6. In every instance, methyltriphenylsilane and the corresponding phenol were formed.

Triphenylsilyllithium cleaved one methyl group from p-dimethoxybenzene when the ratio of silyllithium reagent to ether was 1:1. When the ratio was increased to 2:1, one methyl group was cleaved to the extent of 37.0% and the second to the extent of 15.2%.

The reaction of triphenylsilyllithium with 1-methoxy-naphthalene and 2-methoxynaphthalene gave the corresponding cleavage products quite readily. Apparently the cleavage is not affected noticeably by steric conditions of the aryl group. The reactions with the naphthyl ethers appeared to proceed more rapidly than with anisole.

Triphenylsilyllithium reacted exclusively with the chloro group of p-chloroanisole to give hexaphenyldisilane and p-anisyltriphenylsilane. Reaction with p-fluoroanisole occurred at both groups, but cleavage was the predominant reaction. The result is in line with the lesser reactivity

Table 6.   Reaction of triphenylsilyllithium with some alkyl-aryl ethers

Ether	R₃SiLi	Ratio of R₃SiLi to ether	Conditions temp. °C	hrs.	Yield Alkyl-SiPh₃	Yield (%) phenol
Anisole	Triphenylsilyllithium	1:1	50	24	64.2	31.5[a]
Phenetole	Triphenylsilyllithium	1:1	50 + 60	24 + 72	0	trace
Phenyl n-propyl ether	Triphenylsilyllithium	1:1	50	72	0	0
p-Dimethoxybenzene	Triphenylsilyllithium	1:1	50	12	60.5	30.2
p-Dimethoxybenzene	Triphenylsilyllithium	2:1	50	24	57.8	37.0 mono[b] 15.2 di[c]
1-Methoxynaphthalene	Triphenylsilyllithium	1:1	50	10	48.5	58.2
2-Methoxynaphthalene	Triphenylsilyllithium	1:1	50	16	52.5	58.8
p-Chloroanisole	Triphenylsilyllithium	1:1	50	2	0[d]	trace

[a]Identified as 2,4,6-tribromophenol.

[b]Hydroquinone monomethyl ether.

[c]Hydroquinone.

[d]The primary products of the reaction were hexaphenyldisilane (40.7%) and p-anisyltriphenylsilane (5.73%).

Table 6. (Continued)

Ether	R₃SiLi	Ratio of R₃SiLi to ether	Conditions temp. °C	hrs.	Yield Alkyl- SiPh₃	Yield (%) phenol
p-Fluoroanisole	Triphenylsilyllithium	1:1	50	24	49.2[e]	30.5
2-Methoxynaphthalene	Dimethylphenylsilyl-lithium	1:1	50	24	35.9	34.4
Phenetole	Dimethylphenylsilyl-lithium	1:1	50	72	0	3.57[e]
Thioanisole	Triphenylsilyllithium	1:1	50	24	8.33[f]	0

[e]There was also obtained p-anisyltriphenylsilane (1.09%). No hexaphenyl-disilane was isolated.

[f]Tetraphenylsilane (13.7%) and hexaphenyldisilane (6.17%) were also isolated.

of fluoro- as compared to chlorobenzene.

Since steric requirements appeared to play such an important role in the reaction, it was thought that the use of a less bulky silylmetallic reagent might effect cleavage more readily. This was partially confirmed by a 3.57% yield of phenol obtained from the reaction of dimethylphenylsilyl-lithium with phenetole, a reaction which did not take place with triphenylsilyllithium. However, the reaction of dimethyl-phenylsilyllithium with 2-methoxynaphthalene did not proceed any more readily than when triphenylsilyllithium was employed. In fact, a lower yield of trimethylphenylsilane was obtained, probably due to the increased difficulty in the isolation procedure.

The reaction of triphenylsilyllithium with thioanisole, the sulfur analog of anisole, gave methyltriphenylsilane, tetraphenylsilane and hexaphenyldisilane. It would seem that, in addition to the usual displacement, another reaction mechanism must be considered. The mechanism is probably similar to one proposed for the reaction of triphenylsilyl-lithium with diphenyl sulfide.[62] Such a mechanism would in-volve the initial formation of triphenyl-(phenylthio)silane. The thiosilane would subsequently be cleaved by excess tri-phenylsilyllithium present with formation of the observed hexaphenyldisilane.

E. Reaction of Triphenylsilyllithium with Some Symmetrical Acetals

The reaction of triphenylsilyllithium with acetals was investigated as another phase in the comparison of the reactions of silylmetallic and organometallic reagents.[148,149] The acetals which were reacted with triphenylsilyllithium were methylal, diethyl formal, dimethyl acetal and acetal. One ketal, 2,2-dimethoxypropane, was also studied. The reactions were carried out in tetrahydrofuran at mild reflux temperature.

After sixty hours, the reaction mixture containing triphenylsilyllithium and methylal gave a negative Color Test I.[67] The major products isolated were methyltriphenylsilane (10.6% crude), triphenylhydroxymethylsilane (8.96% crude) and 4-hydroxybutyltriphenylsilane (11.5%). When dimethyl acetal was reacted with triphenylsilyllithium under similar conditions, the major products isolated were methyltriphenylsilane (6.94% crude), 1-triphenylsilylethanol (3.95%) and 4-hydroxybutyltriphenylsilane (13.3%).

Acetal and diethylformal did not appear to react with

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[148]For general references concerning the reaction of Grignard reagents with acetals, see M. S. Kharasch and O. Reinmuth. Grignard reactions of nonmetallic substances. New York, N. Y., Prentice-Hall, Inc. 1954. p. 1041.

[149]For leading references involving organolithium reagents with acetals, see G. Jones and H. D. Law, J. Chem. Soc., 3631 (1958).

triphenylsilyllithium. Color Test I became negative after ninety and one hundred twenty hours, respectively. The major product isolated was 4-hydroxybutyltriphenylsilane. 2,2-Dimethoxypropane gave a trace of 2-triphenylsilylpropan-2-ol and a large yield of 4-hydroxybutyltriphenylsilane (32.4%).

In all of the reactions, 4-hydroxybutyltriphenylsilane arose through cleavage of the tetrahydrofuran solvent at elevated temperatures.[50] Methyltriphenylsilane (XXXII) from methylal and from dimethyl acetal was formed by a cleavage of the carbon-oxygen bond in the same manner as it was in the formation from 1,2-dimethoxyethane.[51] Once the methyl group had been removed, the resulting anion probably collapsed immediately to form the aldehyde (or ketone) (XXXIII). Triphenylsilyllithium (XXXI) then reacted rapidly with the aldehyde to give the hydroxy compound (XXXIV).

$$
\begin{array}{c}
\text{OCH}_3 \\
|\\
\text{R-C-H} \\
|\\
\text{OCH}_3
\end{array}
+ (\text{C}_6\text{H}_5)_3\text{SiLi} \longrightarrow (\text{C}_6\text{H}_5)_3\text{SiCH}_3 + \left[\begin{array}{c} \ominus \\ | \\ \text{R-C-H} \\ | \\ \text{OCH}_3 \end{array} \right] \text{Li}^+
$$

XXXI   XXXII

$$
\begin{array}{c}
\text{OH} \\
|\\
\text{R-C-H} \\
|\\
\text{Si(C}_6\text{H}_5)_3
\end{array}
\xleftarrow{\quad\text{XXXI}\quad}
\left[\begin{array}{c} \text{O} \\ \| \\ \text{R-C-H} \end{array} \right] + \text{LiOCH}_3
$$

XXXIV   XXXIII
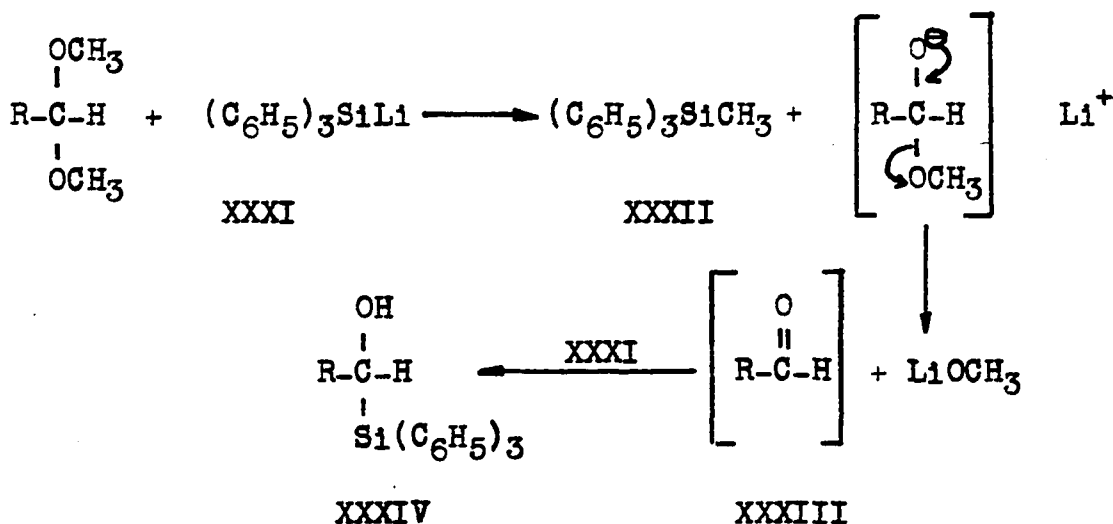
On the basis of the discussion in the previous section, triphenylsilyllithium does not react readily with groups much bulkier than methyl, except with highly reactive systems such as the phosphate esters.[150] Removal of the more bulky ethyl groups from the ethyl acetals did not occur, and the hydroxy compounds also could not form. Very little reaction occurred with the methyl ketal as indicated by isolation of only a trace of the hydroxy compound, again pointing up the extreme steric sensitivity of reactions involving triphenylsilyl-lithium.

An attempt was made to prepare triphenylsilyllithium using acetal as the solvent. Hexaphenyldisilane was not cleaved by lithium at room temperature or at elevated temperatures. Reaction of chlorotriphenylsilane with lithium did not occur at room temperature, but at elevated temperature a small amount (28.8%) of crude hexaphenyldisilane was isolated. It appears that the acetals will not be suitable as solvents for the preparation of silylmetallic reagents.

F. Relative Reactivities of Silylmetallic Reagents

As the chemistry of a new organometallic reagent is developed, one of the outstanding areas of interest is the relation of its reactivity with other systems. The reactions

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[150]M. V. George, B. J. Gaj and H. Gilman, *J. Org. Chem.*, 24, 624 (1959).

to be discussed were run to develop four areas of relative reactivities involving silylmetallic reagents: (1) relative reactivities of some functional groups with triphenylsilyl-lithium; (2) relative reactivity of triphenylsilyllithium compared to organometallic reagents in coupling with chloro-silanes; (3) relative reactivities of chlorosilanes coupling with triphenylsilyllithium; and (4) relative reactivities of silylmetallic reagents in metalation reactions.

As can be seen from the historical discussion and in the excellent review concerning silylmetallic chemistry,[5] some of the reactions of triphenylsilyllithium with various functional groups do not follow the reactions of their counterparts, i.e., Grignard reagents and organolithium reagents. The question arose as to whether or not the reactivities of the various functional groups with triphenylsilyllithium are in the same order as that generally observed with organometallic reagents.

This problem involving the reaction of organometallic reagents with functional groups had been the subject of several elegant investigations.[151,152] These were culminated by the well thought out and executed studies of Entemann and

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[151]H. Hibbert, J. Chem. Soc., 101, 341 (1912).

[152]H. Gilman, L. L. Heck and N. B. St. John, Rec. trav. chim., 49, 212 (1930).

Johnson.[153] These investigators carried out a series of competitive reactions in which one equivalent of phenylmagnesium bromide was added to a solution containing one equivalent of each of two reactants. An examination of the products revealed the extent of each reaction. On this basis, the relative reactivities of some functional groups are:

$$-CHO \rangle -COCH_3 \rangle -NCO \rangle -COF \rangle -COC_6H_5,$$
$$-COCl, -COBr \rangle -CO_2C_2H_5 \rangle -C\equiv N$$
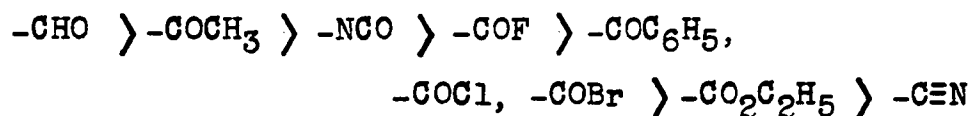
As mentioned previously, the reaction of triphenylsilyllithium with RX compounds produces hexaphenyldisilane in a secondary coupling reaction.[88] Since hexaphenyldisilane is insoluble in most organic solvents and, as a result, is very easy to isolate with excellent reproducibility of yield, the extent of its formation from a competitive reaction involving triphenylsilyllithium with a functional compound and an organic halide could be used as an indication of the relative reactivity of that functional grouping. The particular halide chosen as the standard for this study was chlorobenzene, which reacts with triphenylsilyllithium at a moderate rate to give a reproducible yield of 51-53% of hexaphenyldisilane.[95] Chlorobenzene is not known to interact with the functional groups under study, and would not be expected to catalyze

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[153]C. E. Entemann and J. R. Johnson, _J. Am. Chem. Soc._, **55**, 2900 (1933).

their reaction with triphenylsilyllithium.

A typical example of a competitive reaction involving chlorobenzene and its interpretation is shown below:

$$(C_6H_5)_3SiLi + C_6H_5Cl + C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5 \longrightarrow (C_6H_5)_4Si +$$

2.68%

$$(C_6H_5)_3SiSi(C_6H_5)_3 + (C_6H_5)_2HCOSi(C_6H_5)_3$$

14.3%   27.2%

As can be seen, a yield of only 14.3% of hexaphenyldisilane was obtained as compared to 51% when chlorobenzene is reacted alone with triphenylsilyllithium. This is approximately one-third as great, indicating that the ketone grouping must be more reactive than the halobenzene.

Two assumptions were made. The first assumption was that the same products would be obtained from the mixture as when each substrate was reacted with triphenylsilyllithium sep-arately. This assumption was justified since the same prod-ucts were always isolated in the competitive reactions. The second assumption was that a secondary reaction did not take place due to a shift in the point of equilibrium as the result of the insolubility of hexaphenyldisilane. It seems unlikely that these are equilibrium reactions since each goes rapidly to completion, there was always an insufficient amount of triphenylsilyllithium, and the reaction was usually inter-

rupted as soon as the silylmetallic compound was used up as evidenced by a negative Color Test I.[67] It should be noted in favor of this argument, that hexaphenyldisilane was not isolated in reactions involving the more reactive functional groups.

Unfortunately, the Entemann and Johnson series could not be studied in its entirety. A requirement of the functional group under study was that it must not give hexaphenyldisilane through its own reaction with triphenylsilyllithium. This eliminated the aldehyde grouping, which gives some hexaphenyldisilane following reaction with triphenylsilyllithium.[82] It would have been possible to include reactions in which low reproducible yields of hexaphenyldisilane are obtained, if the constant value was subtracted from the total amount of disilane obtained. Such reactions were not included to avoid further complications. Also, it would have been better if identifiable products could always have been obtained; however, this requirement was not so essential. The change in yield of hexaphenyldisilane compared to the standard still reflects the relative reactivity of the functional group. Identifiable products were not isolated from the reactions of triphenylsilyllithium with ethyl benzoate or with benzonitrile. Conclusions from these reactions were based on such a decrease in yield of hexaphenyldisilane.

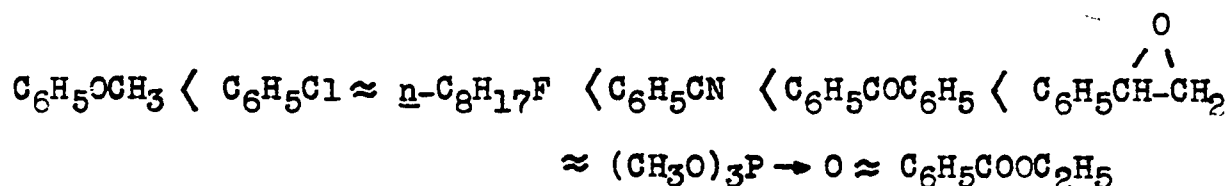The particular compounds which were brought into competi-

tion with chlorobenzene for triphenylsilyllithium were anisole, n-octyl fluoride,[95] benzonitrile,[81] benzophenone,[77] styrene oxide,[46] trimethyl phosphate,[131] and ethyl benzoate. The yields of hexaphenyldisilane from the competitive reactions are presented in Table 7.

Table 7. Yields of hexaphenyldisilane from competitive reactions of triphenylsilyllithium with chlorobenzene and various functional groups

Compounds	% Hexaphenyldisilane
Chlorobenzene[a]	53.0
Anisole	51.0
n-Octyl fluoride	25.0
Benzonitrile	23.0
Benzophenone	14.3
Styrene oxide	0
Trimethyl phosphate	0
Ethyl benzoate	0

[a]Yield of hexaphenyldisilane when chlorobenzene is reacted alone with triphenylsilyllithium.

From the results shown in Table 7, the following tentative series of relative reactivites was established:

$$C_6H_5OCH_3 \langle C_6H_5Cl \approx n\text{-}C_8H_{17}F \langle C_6H_5CN \langle C_6H_5COC_6H_5 \langle C_6H_5\overset{O}{\overset{/\backslash}{CH\text{-}CH_2}}$$

$$\approx (CH_3O)_3P \rightarrow O \approx C_6H_5COOC_2H_5$$

As can be seen, the results were not entirely satisfactory. A clear cut differentiation can not be made between chlorobenzene/n-octyl fluoride and styrene oxide/trimethyl phosphate/ethyl benzoate. The logical recourse was to employ the method of Entemann and Johnson, i.e., a careful product analysis of competitive reactions involving those functional groups not yet clearly placed.

Three such reactions were investigated and the results are presented in Table 8.

When triphenylsilyllithium was reacted with a mixture of chlorobenzene and n-octylfluoride, less than 50% of the yield of n-octyltriphenylsilane, compared to the yield obtained when n-octylfluoride alone is reacted with triphenylsilyl-lithium, was obtained (33.5 vs. 86.5%). The amount of tetraphenylsilane was decreased slightly compared to that obtained from the reaction of chlorobenzene alone with triphenylsilyl-lithium. The results indicated that n-octyl fluoride was reacting at a slower rate than was chlorobenzene.

From the competitive reaction involving trimethyl phosphate and styrene oxide, the products indicated that trimethyl phosphate had reacted approximately 60% as much as previously, and that styrene oxide had reacted only to an extent of 31.5%. Thus, trimethyl phosphate reacted more rapidly than styrene oxide.

The final competitive reaction was the least satisfactory

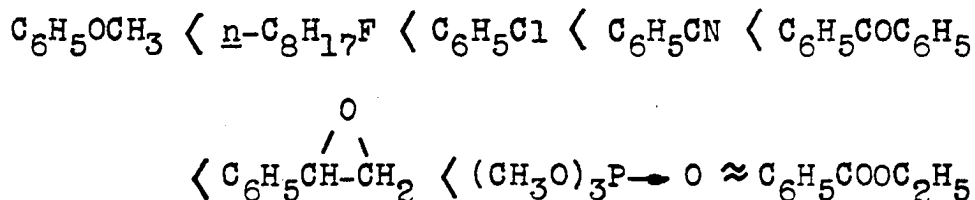Table 8. Products isolated from competitive reactions

Competing species	Products					
	Product	% obtained	% in previous reaction[a]	Product	% obtained	% in previous reaction
Chlorobenzene/ n-octyl fluoride	$(C_6H_5)_4Si$	11.0	12.0	$(C_6H_5)_3Si-C_8H_{17}-\underline{n}$	33.5	86.5
Trimethyl phosphate/styrene oxide	$(C_6H_5)_3SiCH_3$	46.0[b]	71.1[b]	$(C_6H_5)_3SiCH_2\underset{\underset{C_6H_5}{\vert}}{CHOH}$	15.8	43.3
Trimethyl phosphate/ethyl benzoate	$(C_6H_5)_3SiCH_3$	40.1[b]	71.1[b]	No definite product	--	--

[a]The percent reported here is based upon the yield of product obtained when the compound containing the functional group was reacted with triphenylsilyllithium.

[b]Crude yields are reported for methyltriphenylsilane because of its high solubility in the recrystallization solvent. This does not alter the basic conclusions since the yields are compared only with their own previous yields of similar purity.

of all, in that no definite product has thus far been iso-
lated from ethyl benzoate. The conclusions are based upon a
decrease in the yield of products obtained from trimethyl
phosphate. This would seem to be quite satisfactory except
that the amount of methyltriphenylsilane obtained was 57.8%
of the amount obtained when the reaction appeared to be ex-
clusive with the phosphate ester. Since conclusions are based
on the decrease in yield of methyltriphenylsilane, and evi-
dence can not be offered in the way of products for the re-
action with ethyl benzoate, a difference of only 7.8% under
the conditions of the reaction would not be large enough to
warrant a definite statement as to a difference in reactivity.

In summary, the results obtained in the competitive re-
actions indicate the following series of reactivities:

$$C_6H_5OCH_3 \; \langle \; \underline{n}\text{-}C_8H_{17}F \; \langle \; C_6H_5Cl \; \langle \; C_6H_5CN \; \langle \; C_6H_5COOC_6H_5$$

$$\langle \; C_6H_5\overset{O}{\overset{/ \backslash}{CH\text{-}CH_2}} \; \langle \; (CH_3O)_3P \rightarrow O \; \approx \; C_6H_5COOC_2H_5$$

The only functional group included in the Entemann-
Johnson series which appears to react at a different rate is
ethyl benzoate. With triphenylsilyllithium it appears to be
among the most reactive.

When comparisons are to be made with organometallic
systems the particular reaction involved must be discussed.
For example, organolithium compounds react readily with

tetrahydrofuran,[117] however triphenylsilyllithium cleaved this solvent only after prolonged refluxing.[50] These reactions indicate the higher degree of reactivity of organolithium reagents toward tetrahydrofuran. However, when the two classes of reagents were tested in a coupling reaction with a chlorosilane, rather surprising results were obtained.

Organometallic[154] and silylmetallic[5] reagents both couple readily with chlorosilanes. One molar equivalent of a chloro-

$$R'Li + R_3SiX \longrightarrow R_3SiR'$$
$$R'_3SiLi + R_3SiX \longrightarrow R_3SiSiR'_3$$
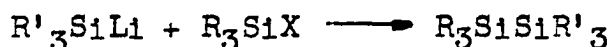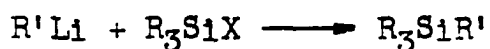
silane was added to a mixture of one molar equivalent each of an organometallic reagent and triphenylsilyllithium. In the majority of reactions the halosilane involved was chlorotriphenylsilane. Thus, the insoluble hexaphenyldisilane formed was easily separated from the tetrasubstituted silane, resulting in an accurate product analysis.

The reactions were run at a low temperature (-50°) to avoid secondary cleavages. Both tetrahydrofuran and tetrahydrofuran-ether mixed solvents were employed. The results of the study are given in Table 9.

Aryl-, alkyl- and aralkyllithium reagents were investigated in the reaction. Phenyllithium, n-butyllithium and

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[154] For an excellent coverage of the chemistry of organosilicon compounds, see C. Eaborn. Organosilicon compounds. London, England, Butterworths Scientific Publications. 1960.

Table 9. Triphenylsilyllithium versus organometallic compounds towards coupling with chlorosilanes

Organometallic	Solvent	Solvent ratio	Chlorosilane	Yield (%) disilane	Yield (%) Ph₃SiR
Phenyllithium	THF[a]	--	Triphenyl-	73.8	12.0
n-Butyllithium	THF	--	Triphenyl-	61.0	21.5
Benzyllithium	THF	--	Triphenyl-	54.0	23.0
Phenyllithium	THF/ether	~2:1	Triphenyl-	81.7	7.72
n-Butyllithium	THF/ether	~2:1	Triphenyl-	77.2	13.9
Phenyllithium	THF	--	Trimethyl-	49.2	20.0

[a]THF is an abbreviation for tetrahydrofuran.

benzyllithium were brought into competition with triphenyl-
silyllithium for an insufficient amount of chlorotriphenyl-
silane in tetrahydrofuran. In every instance, the quantity
of hexaphenyldisilane far outweighed that of the tetrasub-
stituted silane (73.8 vs. 12.0, 61.0 vs. 21.5 and 54.0 vs.
23.0%, respectively), indicating the much greater reactivity
of triphenylsilyllithium in coupling reactions. The differ-
ence was less with n-butyllithium than it was with phenyl-
lithium as would be expected on the basis of the generally
observed greater reactivity of the former reagent.

The reaction involving benzyllithium seems to be
anomolous. On the basis of hexaphenyldisilane it appears
more reactive than n-butyllithium, but on the basis of the
tetrasubstituted silane it would be of about equal reactiv-
ity. The discrepancy may be due to interference by the equal
quantity of alkoxide ion produced in the preparation of
benzyllithium.[121]

When the aforementioned reactions were carried out in a
tetrahydrofuran-ether mixed solvent system, the yield of
hexaphenyldisilane was increased significantly with a corre-
sponding decrease in yield of tetrasubstituted silane. The
results support arguments presented in the section involving
the dimetalation of diphenyl ether. Although the stabilities
of organometallic reagents are increased, there is a corre-
sponding decrease in their reactivity. At the lower tempera-

ture employed in these reactions, the decrease may be ampli-
fied. However, the mixed solvent system did not appear to
affect the reactivity of triphenylsilyllithium.

Gaj and Gilman[155] have shown recently that organolithium
reagents cleave hexaphenyldisilane in tetrahydrofuran under
moderate conditions. Such a cleavage would seriously affect
the results of the coupling reactions. However, when n-butyl-
lithium was allowed to react with hexaphenyldisilane under
the conditions of the competition reactions, hexaphenyldi-
silane was recovered almost quantitatively, and n-butyltri-
phenylsilane was not isolated, indicating the absence of
detectable cleavage.

The possibility of upsetting an equilibrium due to the
presence of insoluble hexaphenyldisilane can also be raised
in this series of reactions. In addition to the arguments
used in the previous section, the following reaction was run
which seems to negate such a possibility. Phenyllithium and
triphenylsilyllithium were brought into competition for
chlorotrimethylsilane under the same conditions used before.
All of the products were soluble in tetrahydrofuran, thus the
system remained homogeneous. Again, triphenylsilyllithium was
definitely more reactive than the organometallic compound.
The difference was not so large, but this may be due to the

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[155]B. J. Gaj and H. Gilman, Chem. and Ind. (London),
493 (1960).

greater reactivity of chlorotrimethylsilane versus chlorotri-
phenylsilane, resulting in a less selective reaction.

The previous reactions suggested another problem along
these lines, i.e., the relative reactivities of halosilanes
in coupling reactions with triphenylsilyllithium. According-
ly, a number of competitive reactions were run involving the
addition of triphenylsilyllithium to a mixture of two halo-
silanes cooled to -50°. In every instance, one of the halo-
silanes involved contained the triphenylsilyl- group. Thus,
hexaphenyldisilane was produced and was isolated readily. The
results of the investigation are shown in Table 10.

Table 10. Triphenylsilyllithium coupling with halosilanes

Mixture of halosilanes	Yield (%) $Ph_3SiSiPh_3$	Yield (%) unsymmetrical disilane
Chlorotrimethylsilane and chlorotriphenylsilane	27.2	45.3
Chlorodimethylphenylsilane and chlorotriphenylsilane	30.0	40.5
Methyldiphenylchlorosilane and chlorotriphenylsilane	34.4	35.9
Chlorotriethylsilane and chlorotriphenylsilane	26.1	44.8
Chlorotrimethylsilane and bromotriphenylsilane	26.1	48.5
Chlorotrimethylsilane and ethoxytriphenylsilane	0	60.3

On the basis of the amounts of hexaphenyldisilane and unsymmetrical disilane obtained, a clear cut distinction can be made involving the chlorosilanes: trimethyl, dimethylphenyl, methyldiphenyl and triphenyl. This decreasing order of coupling with triphenylsilyllithium appears to be dependent upon steric factors, and agrees with previous concepts concerning the steric sensitivity of silylmetallic reagents.
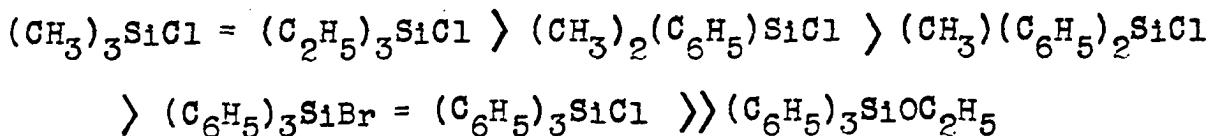
There does not seem to be any distinction between chlorotrimethylsilane and chlorotriethylsilane in their competition reactions with chlorotriphenylsilane for triphenylsilyllithium. The result was rather surprising since Sommers et al.[156] had shown that chlorotrimethylsilane reacted approximately twice as fast as chlorotriethylsilane in competitive reactions with ethylmagnesium bromide. Bromotriphenylsilane and chlorotriphenylsilane also gave almost identical results in their competitive reactions with chlorotrimethylsilane for triphenylsilyllithium. Upon closer inspection, the results become more meaningful. The reaction of triphenylsilyllithium with halosilanes is very rapid, in fact, Color Test I[67] is negative immediately upon completion of addition. The reaction must be almost instantaneous. The steric differences between chlorotrimethyl- and chlorotriethylsilane and the electronic differences between chloro-

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156L. H. Sommers, G. T. Kerr and F. C. Whitmore, *J*. *Am*. Chem. Soc., 70, 434 (1948).

triphenyl- and bromotriphenylsilane would become insignificant in a reaction occurring so rapidly.

The competitive reaction involving ethoxytriphenylsilane with chlorotrimethylsilane for triphenylsilyllithium did not give hexaphenyldisilane. The reaction of ethoxytriphenyl-silane with triphenylsilylpotassium had been reported to procede slowly,[157] thus it was not surprising that the only reaction observed took place between triphenylsilyllithium and chlorotrimethylsilane.

The competitive reactions allow establishment of the following order of reactivity of halosilanes in coupling re-actions with triphenylsilyllithium:

$$(CH_3)_3SiCl = (C_2H_5)_3SiCl \rangle (CH_3)_2(C_6H_5)SiCl \rangle (CH_3)(C_6H_5)_2SiCl$$

$$\rangle (C_6H_5)_3SiBr = (C_6H_5)_3SiCl \rangle\rangle (C_6H_5)_3SiOC_2H_5$$
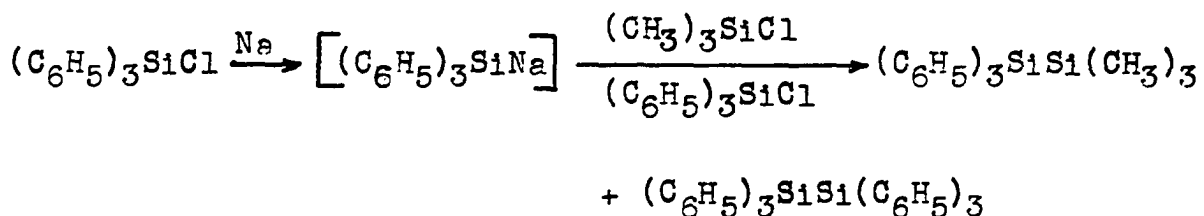
In a somewhat related reaction, a mixture of chlorotri-methylsilane and chlorotriphenylsilane was reacted with sodium. The mechanism of the coupling of chlorosilanes by sodium in xylene to give a disilane is not thoroughly under-stood. It has been suggested that it may involve a silyl-sodium intermediate. George et al.[158] reported a positive

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[157]H. Gilman and T. C. Wu, Iowa State University of Science and Technology, Ames, Iowa. Information concerning reactions of ethoxytriphenylsilane. Private communication. 1960.

[158]M. V. George, D. J. Peterson and H. Gilman, J. Am. Chem. Soc., 82, 403 (1960).

Color Test I[67] during the reaction of chlorotriphenylsilane
with sodium in tetrahydrofuran. However, it is possible that
the color was due to ketyl formation through reaction of sus-
pended sodium with Michler's ketone.

Brown and Fowles[159] reported that hexamethyldisilane
could not be prepared by the reaction of chlorotrimethylsilane
with sodium in refluxing xylene, a fact which was later con-
firmed in this Laboratory. It was suggested that the isola-
tion of 1,1,1-trimethyl-2,2,2-triphenyldisilane from a mixture
of chlorotrimethylsilane and chlorotriphenylsilane with sodium
in refluxing xylene would be proof of the intermediate forma-
tion of triphenylsilylsodium. Selin and West,[160] and Gilman

$$(C_6H_5)_3SiCl \xrightarrow{Na} \left[(C_6H_5)_3SiNa\right] \xrightarrow[\;(C_6H_5)_3SiCl\;]{(CH_3)_3SiCl} (C_6H_5)_3SiSi(CH_3)_3$$

$$+ \; (C_6H_5)_3SiSi(C_6H_5)_3$$

and Steudel[161] had used a similar system involving the same
chlorosilanes in tetrahydrofuran with magnesium to obtain sup-
port for an intermediate "silyl Grignard reagent".

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[159]M. P. Brown and G. W. A. Fowles, _J. Chem. Soc._,
2811 (1958).

[160]T. G. Selin and R. West, _Tetrahedron_, **5**, 97 (1959).

[161]H. Gilman and W. Steudel, Iowa State University of
Science and Technology, Ames, Iowa. Information involving
coupling reactions of chlorosilanes by magnesium in tetra-
hydrofuran. Private communication. 1960.

The coupling reaction involving a mixture of chlorotri-
methyl- and chlorotriphenylsilane with sodium in refluxing
xylene gave 12.7% of hexaphenyldisilane and 43.2% of 1,1,1-
trimethyl-2,2,2-triphenyldisilane. Isolation of the unsym-
metrical disilane offers strong support for the intermediate
formation of triphenylsilylsodium. The larger amount of
unsymmetrical compared to symmetrical disilane is in line
with the greater reactivity of chlorotrimethylsilane in
coupling reactions with silylmetallic reagents.

An attempt was made to relate the various silyllithium
reagents in metalation reactions. The main drawback of such
a study is that there has been only one type of system
metalated previously, compounds which contain relatively
acidic hydrogens. Such systems are metalated very rapidly,
and are not amenable to a study of this nature. After due
consideration of the compounds metalated by triphenylsilyl-
lithium, the metalation of triphenylgermane as described by
Zuech[64] was chosen for further study.

Triphenylgermane was reacted with triphenyl-, methyl-
diphenyl- and dimethylphenylsilyllithium for five and eight
hours, respectively. The yield of triphenylgermanecarboxylic
acid obtained following carbonation was taken as the extent
of metalation. The results are shown in Table 11.

Although the differences are not large, the alkyl sub-
stituted silylmetallic reagents gave a larger amount of

Table 11. Yields (%) of triphenylgermanecarboxylic acid

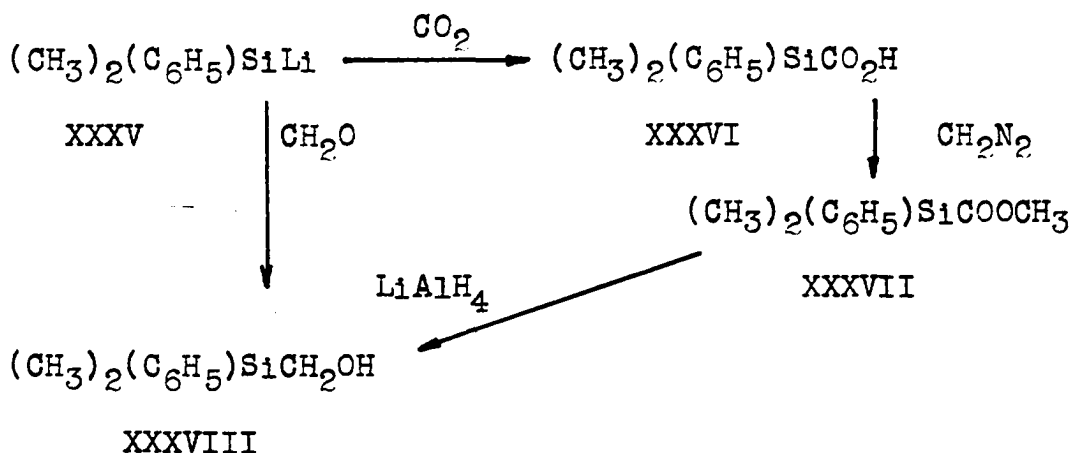| Silyllithium reagent	Length of reaction 8 hrs.	5 hrs.
Triphenyl-	46.7	57.3
Methyldiphenyl-	56.6	44.4
Dimethylphenyl-	5?.3	4?.7

metalation product than did triphenylsilyllithium. However, methyldiphenylsilyllithium gave the largest amount. It is believed that this is due to difficulties encountered in the work-up rather than an anomolous reactivity of methyldiphenylsilyllithium.

G. Preparation of Some Alkyl-Aryl Silanecarboxylic Acids and Their Esters

Incidental to a metalation study involving the use of some alkyl-substituted silylmetallic reagents, several new silanecarboxylic acids were prepared. The carbonation of dimethylphenylsilyllithium (XXXV), extraction of the reaction mixture with chilled 2% sodium hydroxide solution, acidification with dilute hydrochloric acid, and immediate extraction with ether gave dimethylphenylsilanecarboxylic acid (XXXVI) in 47% yield.

Confirmatory evidence for the structure of the acid was obtained by following the procedure for the structural proof

of triphenylsilanecarboxylic acid.[108] Dimethylphenylsilane-
carboxylic acid was converted to its methyl ester, methyl
dimethylphenylsilanecarboxylate (XXXVII), by reaction with
diazomethane. Reduction of the ester with lithium aluminum
hydride gave an hydroxy compound (XXXVIII) which was identical
with the compound obtained from dimethylphenylsilyllithium
and formaldehyde gas.

$$(CH_3)_2(C_6H_5)SiLi \xrightarrow{\quad CO_2 \quad} (CH_3)_2(C_6H_5)SiCO_2H$$

XXXV $\qquad$ $\downarrow CH_2O$ $\qquad\qquad$ XXXVI $\qquad$ $\downarrow CH_2N_2$

$$(CH_3)_2(C_6H_5)SiCOOCH_3$$

$$LiAlH_4 \qquad\qquad XXXVII$$

$$(CH_3)_2(C_6H_5)SiCH_2OH$$

XXXVIII

The carbonation of methyldiphenylsilyllithium gave methyl-
diphenylsilanecarboxylic acid, which also could be extracted
with chilled aqueous base. Reaction of the acid with diazo-
methane gave the expected methyl methyldiphenylsilanecarboxy-
late.

It was important to carry out the basic extraction of
the acids at low temperature and as rapidly as possible. When
the extraction of dimethylphenylsilanecarboxylic acid was
carried out slowly at room temperature, the yield was reduced
to 12.0%.

Dimethylphenylsilanecarboxylic acid melts at 56-58° without decomposition; however, when heated to 125°, it decomposes with the evolution of carbon monoxide. Methyldiphenylsilanecarboxylic acid will decarbonylate at its melting point (133.5-136°).

It was found that an ethanol solution of methyldiphenylsilanecarboxylic acid will decarbonylate slowly when treated with a few drops of aqueous sodium hydroxide. Dimethylphenylsilanecarboxylic acid will also decarbonylate under the same conditions, but the reaction is slower. This is in contrast to triphenylsilanecarboxylic acid which reacts quite rapidly.

Based upon the stabilities at their melting points and the rates at which ethanol solutions of the acids react with base, the following appears to be the order of stability:

$$(CH_3)_2(C_6H_5)SiCOOH \rangle (CH_3)(C_6H_5)_2SiCOOH \rangle (C_6H_5)_3SiCOOH$$
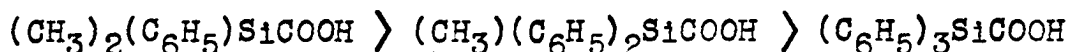
The decarbonylation of silanecarboxylic acids has been proposed to occur by means of attack of a nucleophilic species upon silicon.[108,110] If one considers the inductive effects of alkyl _versus_ aryl, the replacement of a phenyl by a methyl group would increase the electron density around silicon. This in turn would decrease the ease of nucleophilic attack, in agreement with the order of acid stability observed.

H. Suggestions for Further Research

10,10-Diphenylphenothiasilin was prepared by the extended heating of thianthrene and diphenylsilane.[43,44] A yield of only 4.05% was realized, and, since this compound holds high promise as an antioxidant, a better method for its preparation is desirable. The suggested synthesis would start with the preparation of 2,2'-dibromodiphenyl sulfide following a similar reaction path as that of Leandri et al.[162] for the preparation of 2,2'-dichlorodiphenyl sulfide. This would involve the reaction of the sodium salt of o-bromothiophenol with the diazotized form of o-bromoaniline. o-Bromothiophenol does not appear to be commercially available, but its preparation has been reported.[163] The 2,2'-dibromodiphenyl sulfide could be brought into reaction with n-butyllithium to effect a halogen-metal interconversion. Subsequent reaction with dichlorodiphenylsilane would give the desired compound. Proof of structure, in addition to a mixture melting point and an infrared spectra comparison with an authentic sample, could be obtained by oxidation to the known sulfone.[164]

Failing in this attempt, the di-Grignard reagent from the

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[162]G. Leandri, A. Mangini and R. Passerin, Gazz. Chim. ital., 84, 3 (1954). (Original available but not translated; abstracted in C. A., 50, 222 (1956)).

[163]H. F. Wilson, J. Am. Chem. Soc., 72, 5200 (1950).

[164]K. Oita and H. Gilman, J. Org. Chem., 22, 336 (1957).

known dichloro compound might be prepared in tetrahydrofuran
with subsequent reaction with dichlorodiphenylsilane, or the
dichloro compound might be brought into a Wurtz coupling re-
action with dichlorodiphenylsilane and sodium in a variety of
solvents.

Another approach to the same cyclic system would involve
the lithium aluminum hydride reduction of the sulfone, which
can be readily prepared.[164] Reports of the successful reduc-
tion of sulfones by this reagent have appeared.[165]

Brook[83] prepared triphenylsilyl phenyl ketone, the first
silyl-ketone, by the reaction of N-bromosuccinimide with
benzyltriphenylsilane, and subsequent reaction of the α,α-
dibromide with silver acetate. Since then, he has succeeded
in preparing the alkyl substituted silyl ketones by the same
reaction. The reaction of a silylmetallic reagent with
benzoyl chloride gave the ketone in low yield. The results
reported herein have indicated that dimethylphenyl- and
methyldiphenylsilanecarboxylic acids are more stable towards
base than is triphenylsilanecarboxylic acid. It would follow
that the corresponding silyl-ketones would also be more stable
and might be prepared by reaction of the silylmetallic reagent
with an acid halide.

However, other methods should also be explored for the
preparation of the ketones. It has been suggested that the

165F. G. Bordwell and W. H. McKellin, J. Am. Chem. Soc.,
73, 2251 (1951).

reaction of a silyllithium compound with cadmium chloride, followed by reaction with an acid chloride, might give the desired ketones. Lichtenwalter[65] has shown some evidence for the presence of the intermediate, bis-(triphenylsilyl)-cadmium. Reaction of the intermediate with benzoyl chloride failed to give the desired ketone. However, if the alkyl substituted silyl-ketones are more stable as proposed, the possibility of isolating such compounds from the reaction may be very good.

Another plan of attack would involve utilization of a derivative of a silanecarboxylic acid. One of the better methods for the preparation of a ketone is the reaction of an acid halide with an organocadmium reagent. This was first pointed out by Gilman and Nelson in 1936.[166] Subsequently many investigators have employed organocadmium reagents in the synthesis of ketones.[167,168] The preparation of the acid halides of dimethylphenyl- and methyldiphenylsilanecarboxylic acid has not been attempted. The esters of the acids are stable to acid conditions, thus the preparation of the corre-

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[166]H. Gilman and J. F. Nelson, **Rec. trav. chim.**, **55**, 518 (1936).

[167]J. Cason, **Chem. Revs.**, **40**, 15 (1947).

[168]D. A. Shirley. The synthesis of ketones from acid halides and organometallic compounds of magnesium, zinc and cadmium. In R. Adams, ed. in chief. Organic reactions. Vol. 8, pp. 28-58. New York, N. Y., John Wiley and Sons, Inc. 1954.

sponding acid halides seems reasonable.

The esters of the silanecarboxylic acids should be reacted with organometallic reagents to increase our knowledge of silanecarboxylic acid systems.

In this connection, it would be interesting to see if amides or azides of the silanecarboxylic acids can be prepared. These could be subjected to conditions of some of the well known carboxylic acid rearrangements, a phenomenon rarely encountered in silicon chemistry.

A different approach to relating the relative reactivities of silyllithium reagents would involve the reaction of dimethylphenylsilyllithium with triphenylsilane, with subsequent derivatization by trimethyl phosphate. Isolation of methyltriphenylsilane would provide evidence for the formation of triphenylsilyllithium during the reaction and would indicate clearly the greater proton affinity of dimethylphenylsilyllithium.

Finally, the alkoxysilanes have not been reacted extensively with silylmetallic reagents. It is known that the reaction of ethoxytriphenylsilane with triphenylsilylpotassium is very slow.[157] Since the preparation of alkoxysilanes is now convenient,[131] the reaction of a number of such compounds may give some surprising results and would extent our knowledge of silylmetallic chemistry.

V. SUMMARY

An historical review of the dimetalation of diphenyl ether, a tabulation of the silicon derivatives of diphenyl ether, and a discussion of phenoxasilin chemistry have been presented. In addition, a brief survey of the reactions of organosilylmetallic reagents with ethers, in metalations, and in relative reactivities was included. The chemistry of the silanecarboxylic acid systems was also discussed.

The procedure for the dimetalation of diphenyl ether was improved both in time of reaction and in yield of product. This was accomplished by employing n-butyllithium in a tetrahydrofuran-ether mixed solvent system.
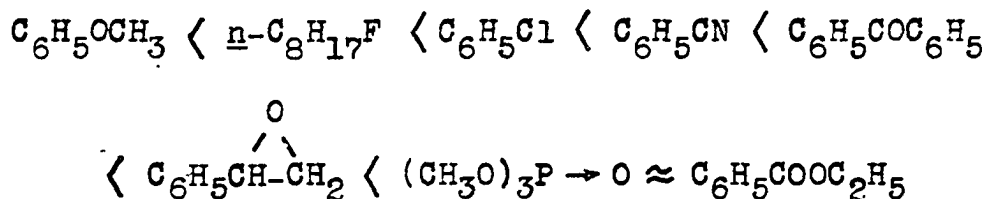
A number of unsymmetrical phenoxasilin compounds was prepared. The procedure involved the preparation of the functional Si-H compound, 10-phenylphenoxasilin, from 2,2'-dilithiodiphenyl ether and phenylsilane. Reaction of the Si-H compound with a number of RLi reagents produced the desired unsymmetrical phenoxasilin compounds. The chemistry of the phenoxasilin system was explored briefly.

Some silicon derivatives of xanthene were prepared. The xanthene molecule was substituted in the 9-, or bridge-position, in all of the molecules except two. These two were ring-substituted 9,9-diphenylxanthene derivatives. It was also found that xanthene is metalated readily by triphenylsilyllithium.

The reaction of triphenylsilyllithium with some methyl aryl ethers gave methyltriphenylsilane and the corresponding phenolic compound. The mild cleavage could not be extended to the ethyl or n-propyl phenyl ethers. The extreme steric sensitivity of triphenylsilyllithium is considered to be the major factor contributing to the lack of cleavage. Steric requirements of the aryl group did not appear to affect the reaction. The cleavage was not facilitated by the use of less bulky silylmetallic reagents.
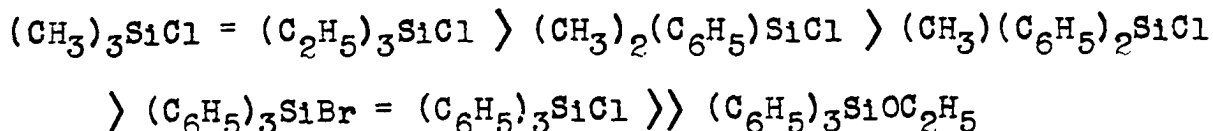
Triphenylsilyllithium cleaved the methyl groups from several symmetrical methyl acetals, however, the reaction again failed when the more bulky ethyl acetals were employed. Acetal was found not to be a suitable solvent for the preparation of silylmetallic reagents.

Through the use of competitive reactions, a series of relative reactivities involving silylmetallic reagents was developed. The relative reactivities of several functional groups with triphenylsilyllithium is in the following order:

$$C_6H_5OCH_3 < \text{n-}C_8H_{17}F < C_6H_5Cl < C_6H_5CN < C_6H_5COC_6H_5$$

$$< C_6H_5\overset{O}{\overset{/\backslash}{CH\text{-}CH_2}} < (CH_3O)_3P \rightarrow O \approx C_6H_5COOC_2H_5$$

Triphenylsilyllithium was found to couple with monochlorosilanes in tetrahydrofuran more readily than did n-butyllithium or phenyllithium. The difference was found to be

still greater in a mixed ether-tetrahydrofuran solvent system. The relative reactivities of monohalosilanes in coupling reactions with triphenylsilyllithium was found to be in the following order:

$$(CH_3)_3SiCl = (C_2H_5)_3SiCl \rangle (CH_3)_2(C_6H_5)SiCl \rangle (CH_3)(C_6H_5)_2SiCl$$
$$\rangle (C_6H_5)_3SiBr = (C_6H_5)_3SiCl \rangle\rangle (C_6H_5)_3SiOC_2H_5$$

Dimethylphenyl- and methyldiphenylsilyllithium have been found to be more reactive in the metalation of triphenylgermane than was triphenylsilyllithium.

Evidence has been obtained in support of the intermediate formation of triphenylsilylsodium in the coupling of chlorosilanes by sodium in xylene.

Dimethylphenyl- and phenyldimethylsilanecarboxylic acids have been prepared and adequately characterized. The acids were found to be more stable to base as the number of alkyl substituents on silicon increased.

$$(CH_3)_2(C_6H_5)SiCO_2H \rangle (CH_3)(C_6H_5)_2SiCO_2H \rangle (C_6H_5)_3SiCO_2H$$
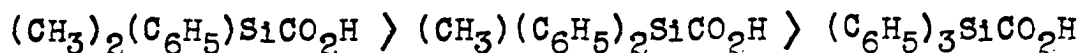
VI. ACKNOWLEDGMENT

Although it has been the combined aid of many people that has made the thesis work possible, the author wishes to express his sincerest appreciation as follows:

To Dr. Henry Gilman for helpful advice, constructive criticism and encouragement given throughout the course of the investigation.