

1947

Some substitution reactions of organosilicon compounds

Robert Anthony Benkeser
Iowa State College

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SOME SUBSTITUTION REACTIONS OF ORGANOSILICON COMPOUNDS

by

Robert Anthony Benkeser

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

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INTRODUCTION

Tetraethylsilane was synthesized by Friedel and Crafts in 1863 and it marked the beginning of a new field of organic chemistry. But until the advent of the twentieth century organosilicon compounds remained a laboratory oddity. They were difficult to prepare, certain structures were in doubt, and in general silicon chemistry was not clearly understood.

Two separate discoveries in the early years of the twentieth century changed all this; however. In 1900 Victor Grignard published details of his historic organomagnesium reactions, and in 1904 Frederick Stanley Kipping an English chemist was quick to apply this reaction to the synthesis of new silicon compounds. Under the guiding hand of the industrious Kipping, the list of organosilicon compounds steadily increased, and it became apparent even to the casual observer that this was a new field and one whose chemistry did not resemble that of carbon as it was originally supposed. From 1904 until the late thirties the organic chemistry of silicon was investigated chiefly in university laboratories. But shortly after Kipping's withdrawal from the field came a new discovery - the silicones! Industry was quick to recognize the possibilities of these amazing polymers and in the past few years the stimulus for research in this field has

shifted from the universities to the industrial laboratory. But many interesting and fundamental problems of silicon chemistry remain for the university laboratory to solve.

One of these problems involves a study of substitution into the organic silicon molecule. What little work has been done in this field was accomplished by Kipping in some meager nitration studies, but his results were sometimes inconclusive and occasionally resulted in failure.

Accordingly it is the primary purpose of this work to study substitution reactions on organosilicon compounds. An attempt is made to elucidate the stability of these compounds towards acids, halogens, and organometallic reagents. A secondary purpose of this work is to synthesize some silicon compounds containing reactive groups which will lend themselves to the formation of new compounds with specific and useful biological properties.

NOMENCLATURE

The nomenclature used throughout this work is in accord with that suggested by the Committee on Nomenclature, Spelling and Pronunciation of the American Chemical Society (1).

Naturally the literature references cited between 1927 and 1936 do not adhere to this new system, but for the sake of uniformity and simplicity it was adopted here. The more salient features of this new system include:

1. The name silane for the compound SiH_4 , and the term silyl for the radical SiH_3 -. The older system used silicane and silicyl.
2. The name disilane, trisilane etc. for compounds with the formula $\text{H}_3\text{Si}(\text{SiH}_2)_n\text{SiH}_3$ depending upon the number of silicon atoms present. The older system used disilicane, trisilicane, etc.
3. The name silanol and silanediol for compounds like H_3SiOH and $\text{H}_2\text{Si}(\text{OH})_2$. The older system used silicol and silicanediol.

1. Crane, Chem. Eng. News, 24, 1233 (1946).

HISTORICAL

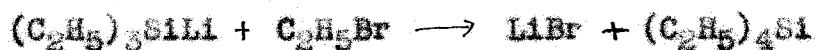
Organosilicon Chemistry from 1927 to 1936

This review has attempted to record all of the organosilicon compounds abstracted in Chemical Abstracts and Chemisches Zentralblatt from January 1, 1927 to January 1, 1937. The original and cross references were consulted whenever possible. Not only are the new organosilicon compounds listed with their physical constants, but any new method of preparation or new reaction has also been noted.

Organosilicon chemistry from 1937 to 1948 has been reviewed in the Doctoral Dissertation of Russell N. Clark.

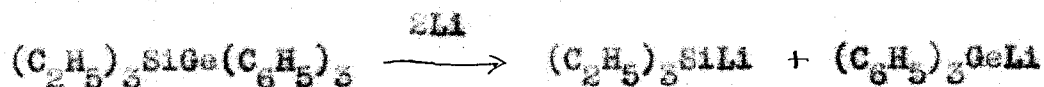
Alkyl Derivatives of the Type R₄Si

Tetraethylsilane, (C₂H₅)₄Si, is prepared by the action of ethylmagnesium bromide on silicon tetrafluoride where about 50% proceeds to triethylfluorosilane and the other half gives tetraethylsilane (2). It boils at 153° at atmospheric pressure; n_D^{25} 1.4255; d_4^{25} 0.7769. This compound can also be prepared by treating triethylsilyllithium with ethyl bromide (3):



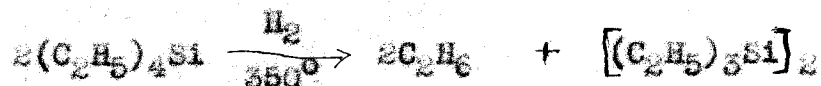
-
2. Gierut, Sowa, and Niewland, J. Am. Chem. Soc., **58**, 897 (1936).
 3. Kraus and Nelson, ibid., **56**, 195 (1934).

The triethylsilyllithium was prepared by the cleavage of triethylsilyltriphenylgermane (3):



Tetra-n-propylsilane, $(\text{n-C}_3\text{H}_7)_4\text{Si}$, can be prepared from n-propylmagnesium bromide and silicon tetrachloride (4). The compound boils at $213 - 215^\circ$ at 751 mm; $d_{40}^{24.5} = 0.7809$.

At 350° and under high hydrogen pressure, tetraethylsilane splits off ethane giving hexaethyldisilane and complicated condensation products (5). Thus:



The Raman spectrum (6) of tetraethylsilane has been measured as well as its solubilities in various solvents (7).

Alkyl Derivatives of the Type $\text{R}_3\text{SiR}'$

Trimethylethylsilane, $(\text{CH}_3)_3\text{SiC}_2\text{H}_5$, can be prepared from methylmagnesium bromide and ethyltrichlorosilane. It boils at $62.2^\circ - 63.4^\circ$ at 756 mm. (8,9). When heated thirty hours at 280°

4. Sugden and Wilkins, J. Chem. Soc., 126 (1931).
5. (a) Ipatiev and Dolgov, Ber., 62B, 1220 (1929) (b) See also Dolgov and Volnov, J. Gen. Chem., (U.S.S.R.) 1, 330 (1931). [C.A., 26, 2168 (1932)].
6. Anderson, J. Chem. Phys., 4, 161 (1936).
7. Bjerrum and Jozefowicz, Z. physik. Chem., A159, 194 (1932). [C.A., 26, 3169 (1932)].
8. Whitmore and co-workers, J. Am. Chem. Soc., 68, 475 (1946).
9. Bygden, Ber., 44, 2640 (1911).

under 100 atmospheres of hydrogen pressure, it decomposes to form tetramethylsilane, dimethyldiethylsilane, and hexamethyldisilane (10).

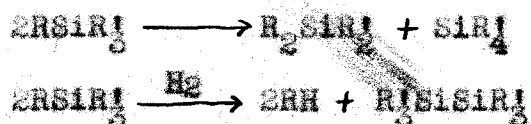
Triethyl-n-propylsilane, $(C_2H_5)_3SiC_3H_7-n$, can be obtained from n-propyltrichlorosilane and ethylmagnesium bromide (11). It boils at $171-5^\circ$. When heated forty-eight hours at 300° and under 100 atmospheres of hydrogen pressure it decomposes to form n-hexane, tetraethylsilane, diethyldipropylsilane and hexaethyldisilane (10).

Triethylisobutylsilane, $(C_2H_5)_3SiC_4H_9-i$, can be obtained from isobutyltrichlorosilane and ethylmagnesium bromide. It boils at $185-9^\circ$. When heated for forty-eight hours at 300° under 100 atmospheres of hydrogen pressure no clearly defined products can be isolated but tetraethylsilane and di-isobutyldiethylsilane are suspected to be present (10).

Triethylisoamylsilane, $(C_2H_5)_3SiC_5H_{11-i}$, boiling at $201-205.5^\circ$ can be obtained from isoamyltrichlorosilane and ethylmagnesium bromide. When heated for forty-eight hours at 300° under 100 atmospheres of hydrogen pressure there was obtained di-isoamyldiethylsilane, tetraethylsilane, and triethylisoamylsilane (10).

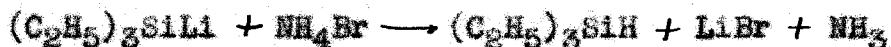
In all the cases shown above a decomposition and rearrangement took place according to the scheme:

10. Dolgov and Volnov, Zhur. Obshchei. Khim., 1, 91 (1931).
 [C.A., 25, 4535 (1931)].
 11. Bygden, Dissertation, Uppsala, 1916.



The generalization can be made that when there are three substituents of one kind present and one of another, the latter is more loosely bound and is displaced on heating (10).

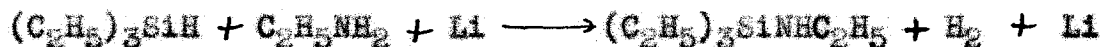
Triethylsilane, $(C_2H_5)_3SiH$, first prepared (12) in 1872 by the action of diethylzinc and sodium on tetraethoxysilane, was later prepared by Kraus (3) by treating triethylsilyllithium with ammonium bromide:



The compound boils at 107-110° at atmospheric pressure. If triethylsilane is treated with potassium amide in liquid ammonia, no ammonia is evolved as might be expected but rather the following occurs (3):

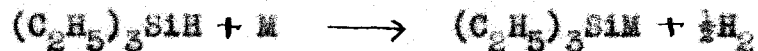


Likewise triethylsilane reacts with ethylamine in the presence of lithium to form triethylsilylethylamine (3):



12. Ladenburg, Ann., 164, 300 (1872).

This reaction does not follow the course of the analogous carbon compound, triphenylmethane, which reacts with the alkali metals in liquid ammonia according to the scheme:



Since triethylsilane is only slightly soluble in liquid ammonia, ethylamine was employed as the solvent. The lithium, however, seemed to take no part in the reaction but merely served as a catalyst. The rate of the reaction increased with increasing concentrations of lithium but despite varying amounts of the metal employed the reaction seemed to proceed in about the same yield as judged by the amount of hydrogen evolved.

Triethylbenzylsilane, $(\text{C}_2\text{H}_5)_3\text{SiCH}_2\text{C}_6\text{H}_5$, can be prepared either by the reaction of ethylmagnesium bromide on benzyltrichlorosilane (3), or by treating triethylbromosilane with benzylmagnesium chloride (3). The former procedure gives about a 40% yield, and the latter a 50% yield. The compound boils at 267-9° and is insoluble in liquid ammonia but is very soluble in ethylamine. It does not freeze at -35°C. The compound reacts with lithium in ethylamine but the products are uncertain (3).

Mixed Aryl-Alkyl Derivatives of the Type $\text{R}_2\text{R}'\text{R}''\text{Si}$

Dicyclohexylphenylsilane, $(\text{C}_6\text{H}_{11})_2\text{SiH}(\text{C}_6\text{H}_5)$, is produced by treating phenyltrichlorosilane with a large excess of cyclo-

hexylmagnesium bromide (13). It boils at $160-5^{\circ}$ at 4 mm. and melts at $52-3^{\circ}$ (13). It dissolves in all the common solvents with the exception of ethanol and acetic acid in the cold and can be distilled undecomposed at atmospheric pressure (b.p. $340-5^{\circ}$). The compound can be readily converted into the silanol by the action of oxidizing agents like ammoniacal silver nitrate, or potassium permanganate (13). It reacts readily with bromine so that it can be titrated with bromine in carbon tetrachloride to determine its purity. When warmed with iodine it forms a sticky product which is presumably dicyclohexylphenylosilane.

Dicyclohexylphenylethylsilane, $(C_6H_{11})_2Si^{C_2H_5}C_6H_5$, is prepared by treating dicyclohexylphenylbromosilane with ethylmagnesium bromide (13). It boils at 370° . When treated with bromine in glacial acetic acid, ethyl bromide, bromobenzene and an oil are formed. The latter apparently consists of a mixture of condensation products of dicyclohexylsilanediol (13).

Aryl Derivatives of the Type R_4Si

Tetraphenylsilane, $(C_6H_5)_4Si$, can be prepared from silicon tetrachloride, chlorobenzene, and sodium (14) or from bromobenzene, magnesium, and silicon tetrachloride (15) or from silicon tetrabromide and phenylmagnesium bromide (16) or from silicon tetra-

13. Cusa and Kipping, J. Chem. Soc., 1040 (1933).

14. Pollis, Ber., 18, 1540 (1885).

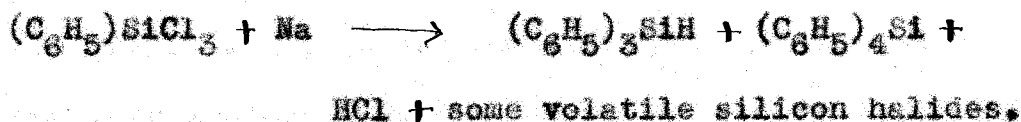
15. Manulkin and Yakubovs, J. Gen. Chem. (U.S.S.R.), 10, 1300 (1940). [C.A., 35, 3246 (1941)].

16. Schumb and Safer, J. Am. Chem. Soc., 61, 363 (1939).

fluoride, chlorobenzene, and sodium (17). It melts at 235° and has a density of 1.078 at 20° C. Kraus (18) succeeded in preparing the compound by a coupling reaction between triphenylsilyllithium and bromobenzene:

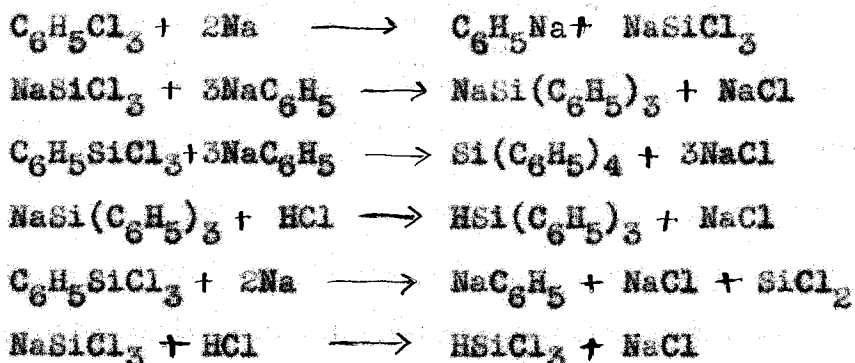


Actually tetraphenylsilane has often been isolated as a by-product in certain complex reactions. Thus when phenyltrichlorosilane is treated with sodium in boiling xylene or in the absence of a solvent a complex reaction occurs (19), but if it is heated with sodium in a stream of pure nitrogen, a mixture of tri- and tetraphenylsilane is obtained (20, 21):



The tetraphenylsilane is explained by postulating the prior production of phenylsodium which then reacts with the unchanged trichloride:

-
17. Wiley, U.S. Pat. 2,238,669, April 15, 1940. [C.A., 35, 4782 (1941)].
 18. Kraus and Eatough, J. Am. Chem. Soc., 55, 5008 (1933).
 19. Kipping, Murray, and Maltby, J. Chem. Soc., 1180 (1929).
 20. Kipping, Blackburn, and Short, ibid., 1290 (1931).
 21. Kipping and Short, ibid., 1029 (1930).



These equations would also indicate that the volatile silicon halides formed in the reaction are trichlorosilane and silicon dichloride although no absolute proof of their presence was obtained (20).

Tetraphenylsilane is an exceedingly stable compound which can be distilled undecomposed above 530°. At 490° and under high hydrogen pressure it remains unchanged (5a). Only at 490° do complicated condensations begin to occur. In the presence of aluminum chloride (22), however, at about 50°, it is decomposed about 80% into silicon tetrachloride and phenylaluminum dichloride.

Tetra-*m*-nitrotetraphenylsilane, (*m*-No₂C₆H₄)₄Si, is obtained in about a 10% yield by the nitration of tetraphenylsilane (23) in carbon tetrachloride at 0° C. using fuming nitric acid. From chloroform it is obtained as six-sided plates melting at 255-6°. The remainder of the crude nitration product is thought

22. Evison and Kipping, *ibid.*, 2774 (1931).

23. Kipping and Blackburn, *ibid.*, 2200 (1932).

to be a mixture of ortho, meta, and para isomers in the same molecule. The presence of the ortho isomer has not been demonstrated, but it is thought to be present. If the ortho isomer were present, it would lead to the possibility of fifteen isomers.

Tetra m-aminotetraphenylsilane, (m-NH₂C₆H₄)₄Si, is obtained by the reduction (24) of the tetra-m-nitro compound in boiling acetic acid with zinc and hydrochloric acid or by catalytic reduction in ethyl acetate at 2-3 atmospheres using platinum oxide. The compound sublimes at 350° and melts at 380°. It is insoluble in most of the organic solvents, but is sparingly soluble in boiling phenol, cyclonexanol, aniline, or pyridine. The free base is stable towards acids and alkalis.

Tetra-m-aminotetraphenylsilane tetrahydrochloride, (m-NH₂C₆H₄)₄Si·4HCl, crystallizes from a concentrated hydrochloric acid solution of the free amine in slender microscopic needles. It is very soluble in water, sparingly so in alcohol and in 40% hydrochloric acid (24). The oxalate, picrate, platinumchloride, and acetate all precipitate from a solution of the hydrochloride and the appropriate reagent but they are unstable in aqueous solution (24). The hydrochloride can be diazotized and coupled with β-naphthol in an alkaline solution giving a red precipitate (24). A solution of the hydrochloride when treated with bromine-water gives a colorless precipitate of a bromo derivative which

24. Kipping and Blackburn, ibid., 1085 (1935).

does not melt below 300° (24).

Tetraisopropyltetra-*m*-aminotetraphenylsilane,

$[(\text{CH}_3)_2\text{CHNHC}_6\text{H}_4]_4\text{Si}$, is produced by the reduction (24) of the tetra-*m*-nitro compound with tin and hydrochloric acid in boiling acetone. The melting point is 135° and the yield is 78%. It is soluble in acetone, ethyl acetate, chloroform, and less so in alcohol.

Tetraisopropyltetra-*m*-aminotetraphenylsilane tetrahydrochlor-

ide, $[(\text{CH}_3)_2\text{CHNHC}_6\text{H}_4]_4\text{Si}\cdot 4\text{HCl}$, is a crystalline solid melting above 300°. It is readily soluble in water and its acid solution gives with sodium nitrite a pale yellow precipitate, the filtrate from which gives no precipitate with an alkaline solution of β -naphthol (24).

Tetra-*m*-acetaminotetraphenylsilane, $(\text{CH}_3\text{CONHC}_6\text{H}_4)_4\text{Si}$, is produced (24) by refluxing the tetra-*m*-amine compound with acetic anhydride. The melting point is 300-1°. It is sparingly soluble in most of the organic solvents but dissolves readily in hot phenol and boiling acetic acid. When boiled with alcoholic potassium hydroxide it gives the tetra-*m*-base (24).

Tetrabenzylsilane, $(\text{C}_6\text{H}_5\text{CH}_2)_4\text{Si}$, can be prepared normally in a variety of ways (14, 15, 25, 26, 27) but has been obtained

25. Arzbruni, *Ber.*, **19**, 1023 (1886).

26. Soshestvenskaya, *J. Gen. Chem.*, (U.S.S.R.), **5**, 284 (1935). [C.A., **32**, 5392 (1935)].

27. Soshestvenskaya, *Ibid.*, **10**, 1689 (1940). [C.A., **35**, 3240 (1941)].

as a by-product in certain reactions studied by Kipping (28, 29). Thus when benzyldichlorosilane is treated with sodium, a mixture of tribenzylsilane and tetrabenzylsilane was isolated. The compound melts at $128-9^{\circ}$ and is stable (10) toward hydrogenation at 100 atmospheres. This proves that phenyl groups directly attached to silicon as in tetraphenylsilane and through intermediate atoms of carbon are incapable of hydrogenation because of the "anti-catalytic" action of silicon (10). This anticatalytic action is not apparent in hydrogenolysis reactions involving organosilanes.

Tetra- α -thienylsilane, $(\alpha\text{-C}_4\text{H}_3\text{S})_4\text{Si}$, is prepared by treating α -thienylmagnesium iodide with silicon tetrachloride (30). It melts at 135.5° (corr.) and is quite soluble in benzene, ether, and hot ethanol but is difficultly soluble in cold ethanol. (30).

Trimethylphenylsilane, $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$, can be prepared from phenyltrichlorosilane and methylmagnesium iodide. It boils at $168-172^{\circ}$. When heated for forty eight hours at 300° and under 100 atmospheres of hydrogen, methane, benzene, tetramethylsilane, hexamethyldisilane, and dimethyldiphenylsilane are formed (10).

Triethylphenylsilane, $(\text{C}_2\text{H}_5)_3\text{SiC}_6\text{H}_5$, can be prepared from phenyltrichlorosilane and ethylmagnesium bromide (31). It boils

28. Evison and Kipping, J. Chem. Soc., 2830 (1931).

29. Steele and Kipping, ibid., 1431 (1928).

30. Krause and Benwanz, Ber., 62, 1710 (1929).

31. Bygden, ibid., 45, 709 (1912).

at 237-240°; d_{15}^{15} 0.906. When heated for four days at 300-330° under high hydrogen pressure it is 60% decomposed into tetraethylsilane, diethyldiphenylsilane, benzene, hexaethyldisilane, and triethylsilanol (5a).

Metallic sodium does not react with triethylphenylsilane in liquid ammonia, probably because of the insolubility of the silicon compound. Lithium in ethylamine reacts readily with it, without the evolution of a gas and with the formation of a clear, orange colored solution. No evidence of benzene was found so that apparently the phenyl group was not split off by the lithium. Possibly hydrogenation occurred (3).

Diphenyldimethylsilane, $(C_6H_5)_2Si(CH_3)_2$, can be prepared by treating diphenyldichlorosilane with an excess of methylmagnesium iodide in an ethereal solution (32). It boils at 176-8° at 45 mm.

Diphenyldiethylsilane, $(C_6H_5)_2Si(C_2H_5)_2$, can be prepared in 98% yield by the interaction of diphenyldichlorosilane (1 mole) and ethylmagnesium bromide (3 moles) at 150-160° (33). The compound boils at 295-8° at 760 mm.

Triphenylethylsilane, $(C_6H_5)_3SiC_2H_5$, can be obtained by refluxing triphenylchlorosilane with ethylmagnesium bromide.

32. Kipping, J. Chem. Soc., 104 (1927).

33. Kipping and Cusa, ibid., 1088 (1935).

It melts at 76°. When heated for twenty-five hours in benzene at 300-20° and under 100 atmospheres of hydrogen it rearranges to form diethylphenylsilane, diethyldiphenylsilane, and tetraphenylsilane (10).

Aryl Derivatives of the Type R₃R₂Si

Triphenylsilane, (C₆H₅)₃SiH, is prepared by the action of phenylmagnesium bromide on trichlorosilane (34):



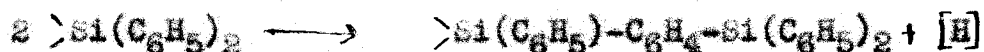
It boils at 152-167° at 2 mm. and melts at 36-7°. It can also be prepared by the action of triphenylsilyllithium on ammonium bromide (18):



Triphenylsilane is also produced in small amounts as a by-product in certain reactions. Thus Kipping and Murray (35) obtained a thick oil upon distillation of the "glue-like" substance formed by the action of sodium on diphenyldichlorosilane, and they identified this oil as triphenylsilane. Also Kipping and Short (21) obtained a mixture of tri- and tetraphenylsilane by heating phenyltrichlorosilane with sodium in a stream of pure nitrogen. The formation of the triphenylsilane is explained by assuming that it is produced from phenyl groups by changes such as:

34. Reynolds, Bigelow, and Kraus, J. Am. Chem. Soc., 51, 3067 (1929).

35. Kipping and Murray, J. Chem. Soc., 360 (1928).



Tribenzylsilane, $(\text{C}_6\text{H}_4\text{CH}_2)_3\text{SiH}$, is prepared (28) along with some tetrabenzylsilane by treating benzyldichlorosilane with sodium. It melts at 91° and is soluble in benzene, chloroform, acetone, and hot light petroleum ether.

Alkyl Derivatives of the Type RSiX_3

Cyclohexyltrichlorosilane, $\text{C}_6\text{H}_{11}\text{SiCl}_3$, is prepared by the interaction of silicon tetrachloride and cyclohexylmagnesium bromide (36). The compound is a fuming liquid boiling at $206\text{-}211^\circ$ at 760 mm. Distillation of the crude reaction product yields besides the desired material some dicyclohexyldichlorosilane. The yield of the dichloride thus obtained is very small, however, and the main portion of the product consists of derivatives of disilane which signifies that the silicon atoms had somehow become directly united during the reaction.

Aryl Derivatives of the Type RSiX_3

Phenyltrichlorosilane, $(\text{C}_6\text{H}_5)\text{SiCl}_3$, can be prepared ordinarily in a variety of ways (37, 38, 39, 40). It is produced in small amounts by the fission of tetraphenylsilane, octaphenyl-

36. Palmer and Kipping, *ibid.*, 1020 (1930).

37. Sommer and Whitmore, *J. Am. Chem. Soc.*, **68**, 485 (1946).

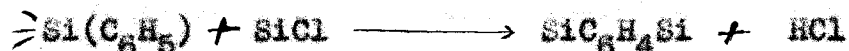
38. Schumb and Sutter, *ibid.*, **63**, 93 (1941).

39. Fleming, U.S. Pat. 2,386,485, Oct. 9, 1945. [*C.A.*, **40**, 206 (1946)].

40. Miller and Schreiber, U.S. Pat. 2,379,621, July 3, 1945. [*C.A.*, **39**, 4619 (1945)].

cyclotetrasilane, hexaphenylcyclotrisiloxane, and tetrabenzylsilane with aluminum chloride (22). It boils at 198° at 744 mm.

The chemical reactions of phenyltrichlorosilane are rather interesting. Kipping and co-workers (19) attempted the formation of a silicon to silicon triple bond (which is still unknown) by treating phenyltrichlorosilane with sodium. Three variations in reaction conditions were tried: 1) the two substances were heated at 180° in the absence of a solvent, 2) they were heated in boiling benzene or toluene, 3) they were heated in benzene in a sealed tube at about 150° . Under all these conditions the trichloride was converted into a complex mixture of products, the components of which contain not only $\text{>Si}(\text{C}_6\text{H}_5)$ and some $\text{>Si}(\text{C}_6\text{H}_5)_2$ groups but also some silicon atoms uncombined with carbon. Some of these silicon atoms seem to be unsaturated, and are probably tervalent, but most of them had become saturated by combination with oxygen. When phenyltrichlorosilane is heated with sodium in a stream of pure nitrogen, a mixture of tri- and tetraphenylsilane is obtained (21), besides some hydrogen chloride and some volatile silicon halides. If these volatile halides are collected in benzene or toluene, and the water is added, an inorganic solid is precipitated immediately (20). This solid has the composition $\text{H}_2\text{Si}_2\text{O}_3$, but its origin has not been ascertained. An attempt is made to explain the presence of the hydrogen chloride by the following reaction:



When phenyltrichlorosilane (13, 41) is treated with an excess of cyclohexylmagnesium bromide, and oxygen is excluded, there is produced a mixture of products including dicyclohexylphenylsilane (b.p. 182° at 4 mm.), cyclohexyloxydicyclohexylphenylsilane, dicyclohexylphenylsilanol and condensation products of cyclohexylphenylsilanediol. When oxygen is not excluded, the principal product is cyclohexyloxydicyclohexylphenylsilane. (m.p. $103-4^\circ$).

Alkyl Derivatives of the Type R_2SiX_2

Dicyclohexyldichlorosilane, $(\text{C}_6\text{H}_{11})_2\text{SiCl}_2$, is obtained (36) by the interaction of silicon tetrachloride and cyclohexylmagnesium bromide, besides some cyclohexyltrichlorosilane and probably some tricyclohexylchlorosilane. Constants for the compound are not given. Hydrolysis yields dicyclohexylsilanediol.

Aryl Derivatives of the Type R_2SiX_2

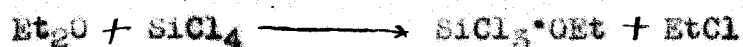
Diphenyldichlorosilane, $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$, can be made from silicon tetrachloride and either phenylmagnesium bromide (42, 43) or phenyllithium (39). It boils at 305° , and at 160° at 10-11 mm. The compound which Kipping and Murray (43) had

41. Cusa and Kipping, J. Chem. Soc., 2205 (1932).

42. Hyde and DeLong, J. Am. Chem. Soc., 63, 1194 (1941).

43. Kipping and Murray, J. Chem. Soc., 2734 (1927).

prepared and first thought to be diphenyldichlorosilane later was found to analyze about 4-5% low for chlorine. It was found to contain traces of phenol which was apparently caused by the oxidation of phenylmagnesium bromide but even when this was removed the diphenyldichlorosilane was not pure. No matter how thoroughly the Grignard ether was freed from alcohol, the purity of the dichloride could not be improved and all samples of it gave alcohol on hydrolysis. It was finally discovered that silicon tetrachloride cleaves ethyl ether even at ordinary temperatures according to the scheme:



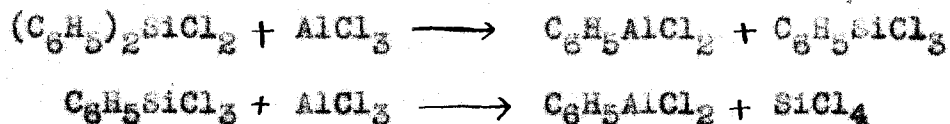
This ethoxytrichlorosilane reacts with the phenylmagnesium bromide to form diphenylethoxychlorosilane. This latter compound cannot be separated from diphenyldichlorosilane by distillation. This reaction may account for the difficulties in preparing various organic derivatives of silicon (43).

The action of sodium on diphenyldichlorosilane in toluene yields a glue-like readily soluble product (44) consisting mainly of an amorphous form of octaphenylcyclotetrasilane. The crystalline form of this compound does not melt up to 400° and is practically insoluble in cold acetone. Distillation of this glue-like substance (35) yields a thick oil which has been identified as triphenylsilane, although the constants for this product do not agree with those of Ladenburg (45).

44. Kipping ibid., 2719 (1927).

45. Ladenburg, Ber., 40, 2278 (1907).

If diphenyldichlorosilane is treated with aluminum chloride (22) and ethyl bromide, a mixture of silicon tetrachloride, phenyltrichlorosilane, and ethyl derivatives of benzene are obtained. The reaction can be formulated:



If diphenyldichlorosilane is treated with phenol (46) in benzene at 150° a mixture of phenoxydiphenylchlorosilane, diphenoxydiphenylsilane, and unchanged diphenyldichlorosilane results:



Dibenzoyldichlorosilane, $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SiCl}_2$, prepared from silicon tetrachloride and benzylmagnesium chloride forms colorless prisms which melt at 50-2° and boil at 241-5° at 100 mm. (47, 48).

When dibenzoyldichlorosilane in toluene is treated with sodium and potassium (29) in the absence of oxygen a very complex reaction occurs and a small amount of hexabenzoyldisiloxane, $[\text{Si}(\text{CH}_2\text{C}_6\text{H}_5)_3]_2\text{O}$, and 15% tetrabenzoylsilane are isolated. The rest of the product is a glue-like solid which is believed to be octabenzoyltetrasilane monoxide $[\text{Si}(\text{CH}_2\text{C}_6\text{H}_5)_2]_4\text{O}$ mixed possibly with analogous oxides.

46. Kipping, J. Chem. Soc., 2728 (1927).

47. Robison and Kipping, ibid., 93, 439 (1908).

48. Martin and Kipping, ibid., 95, 302 (1909).

Di-p-tolyldichlorosilane, $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{SiCl}_2$, is prepared by the action of p-tolylmagnesium bromide with silicon tetrachloride (49). It is a liquid boiling at $237\text{-}9^\circ$ at 50 mm.

If di-p-tolyldichlorosilane is treated with sodium, two crystalline products can be isolated, octa-p-tolyltetrasilane and octa-p-tolylcyclotetrasilane. The former melts at $290\text{-}3^\circ$ and its diiodide at 300° . The octa-p-tolylcyclotetrasilane melts at 310° . At least two other amorphous products can be isolated from this reaction but they are unidentified (49).

Mixed Alkyl-Aryl Derivatives of the Type R'R'SiX₂

Cyclohexylphenyldichlorosilane, $(\text{C}_6\text{H}_{11})_2\text{Si}\begin{matrix} \text{Cl}_2 \\ \diagdown \\ \text{C}_6\text{H}_5 \end{matrix}$, is produced besides dicyclohexylphenylchlorosilane by treating phenyltrichlorosilane with cyclohexylmagnesium bromide (41). It boils at $123\text{-}5^\circ$ at 0.5 mm. or at $163\text{-}5^\circ$ at 4 mm. It fumes only slightly in air and acquires a bluish hue on exposure to light (41).

Mixed Alkyl-Aryl Derivatives of the Type R₂R'SiX

Dicyclohexylphenylchlorosilane, $(\text{C}_6\text{H}_{11})_2\text{Si}\begin{matrix} \text{Cl} \\ \diagdown \\ \text{C}_6\text{H}_5 \end{matrix}$, is produced besides cyclohexylphenyldichlorosilane as described above (41). It boils at $188\text{-}192^\circ$ at 2 mm. and melts at $45\text{-}6^\circ$. It does not fume in moist air and is only slowly hydrolyzed by cold water.

49. Steel and Kipping, ibid., 2545 (1929).

Alkyl Derivatives of the Type R₃SiX

Triethylfluorosilane, (50, 51) $(C_2H_5)_3SiF$, is prepared by treating hexaethyldisiloxane with a mixture of concentrated sulfuric acid and the corresponding sodium or ammonium fluoride. The mixture is allowed to stand for some hours and the product is extracted with petroleum ether and finally distilled. It is a liquid with a camphor-like odor boiling at 109° at 745 mm.; d_4^{25} 0.8354; n_D^{25} 1.3900 (2). The yields are practically quantitative. Triethylfluorosilane is much more stable toward hydrolysis than is the corresponding bromide and may be distilled in air without decomposition.

This is a general method of preparation that can be applied to any trialkylsilyl halide. This compound can also be prepared by treating silicon tetrafluoride with ethylmagnesium chloride (2).

Tri-n-propylfluorosilane, $(n-C_3H_7)_3SiF$, is prepared in 62% yield by treating silicon tetrafluoride with n-propylmagnesium bromide (2). It boils at 175° at 745 mm.; d_4^{25} 0.8339; n_D^{25} 1.4107.

50. Flood, J. Am. Chem. Soc., 55, 1735 (1933).

51. Flood and Horvitz, ibid., 55, 2534 (1933).

Tri-n-butylfluorosilane, $(n-C_4H_9)_3SiF$, is prepared in 70% yield by treating silicon tetrafluoride with n-butylmagnesium chloride (2). It boils at 224° at 745 mm.; d_4^{25} 0.8372; n_D^{25} 1.4250.

Tri-n-amyfluorosilane, $(n-C_5H_{11})_3SiF$, is prepared in 58% yield by treating silicon tetrafluoride with n-amyilmagnesium chloride (2). It boils at 267° at 745 mm.; d_4^{25} 0.8389; n_D^{25} 1.4305.

It is interesting to note that the use of alkyl chlorides rather than bromides seemed to give better yields of the tri-alkylsilyl fluorides (2). Also the fluorine atom, in general, is very inactive toward hydrolysis and will not react with sodium in liquid ammonia. The fluorides are definitely less reactive than the corresponding bromide or chloride (2).

Tricyclohexylchlorosilane, $(C_6H_{11})_3SiCl$, although never isolated is thought to be formed along with cyclohexyltrichlorosilane, and dicyclohexyldichlorosilane when silicon tetrachloride is treated with cyclohexylmagnesium bromide (36).

Triethylbromosilane, $(C_2H_5)_3SiBr$, can be prepared in practically quantitative yields by treating a mixture of concentrated sulfuric acid and hexaethylidisiloxane with sodium or ammonium bromide (50). It boils at 161° and is slowly decomposed by water. The bromine is easily replaced by the hydroxyl through the use of aqueous potassium hydroxide or sodium carbonate.

Triethylchlorosilane, $(C_2H_5)_3SiCl$, can be prepared in practically quantitative yields by treating a mixture of concentrated sulfuric acid and hexaethyldisiloxane with sodium or ammonium chloride (50). It boils at $143-5^\circ$ and has a density at 0° of 0.9249. It is slowly decomposed by water to form triethylsilanol.

Aryl Derivatives of the Type R_3SiX

Triphenylbromosilane, $(C_6H_5)_3SiBr$, can be prepared by the bromination of triphenylsilane in carbon tetrachloride (54):



This reaction proceeds in almost quantitative yield. The compound melts at $118-120^\circ$ and is easily decomposed by water or alcohol. It is soluble in ether and hot benzene but is difficultly soluble in ligroin.

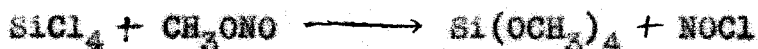
Tri-p-tolylchlorosilane, $(p-CH_3C_6H_4)_3SiCl$, is prepared by treating silicon tetrachloride with p-tolylmagnesium bromide (52). It is a solid melting at $115-6^\circ$. If it is refluxed with an aqueous solution of ammonium hydroxide it is converted to the silanol (m.p. $99-100^\circ$). The silanol in turn can be converted to the disiloxane by heating with alcoholic sodium hydroxide (m.p. $223-4^\circ$). The chloride itself is readily soluble in most of the

52. Steele and Kipping, J. Chem. Soc., 357 (1929).

common solvents; it does not fume appreciably on exposure to moist air, and is only slowly decomposed by cold water.

Alkyl Derivatives of the Type (RO)₄Si

Tetramethoxysilane, (CH₃O)₄Si, can be prepared by the addition of anhydrous methanol to silicon tetrachloride (53, 54, 55, 56, 57). It can also be prepared in 80% yield by the reaction of methyl nitrite on silicon tetrachloride (58).

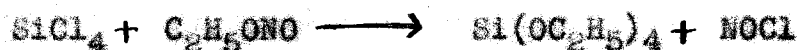


It boils at 120-5° at 760 mm.; d_4^{25} 1.032.

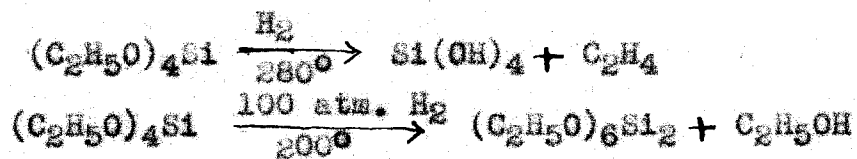
Tetraethoxysilane, (C₂H₅O)₄Si, can be prepared by the action of absolute ethanol (53, 54, 56, 59, 60) or sodium ethoxide (61) on silicon tetrachloride. It boils at 165-7° at 760 mm. or at 95.5° -97.5° at 70 mm.; d_4^{25} 0.9292. The difficulty involved in the preparation of alkyl orthosilicates in general is the evolution of hydrogen chloride gas which usually carries some

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53. Andrianov, Compt. rend. acad. sci. U.R.S.S., 28, 66 (1940). [C.A., 35, 2431 (1941)].
54. Kalinin, ibid., 18, 433 (1938). [C.A., 32, 6227 (1938)].
55. Peppard, Brown, and Johnson, J. Am. Chem. Soc., 68, 73 (1946).
56. Cunradi and Lechner, Ger. Pat. 512, 716, I.G. Farbinind. A.G., Jan. 19, 1927. [Chem. Zentr., I, 2932 (1931)].
57. Konrad, Bachle, and Signer, Ann., 474, 276 (1929).
58. Bolzani, Ger. Pat. 459, 738, I.G. Farbinind. A.G., May 15, 1928. [Chem. Zentr., II, 1716 (1928)].
59. Solana and Moles, Anales soc. espan. fis. quim., 28, 171 (1930). [Chem. Zentr., I, 2228 (1930)].
60. Solana and Moles, ibid., 30, 886 (1932). [Chem. Zentr., I, 3691 (1933)].
61. Backer and Klasens, Rec. trav. chim., 61, 500 (1942).

unreacted silicon tetrachloride over with it. The procedure as designed by Dearing and Reid (62) tends to obviate this difficulty by adding the silicon tetrachloride dropwise to the alcohol in a freezing mixture. The escaping hydrogen chloride is led through a small amount of cold alcohol to recover the silicon tetrachloride that is carried off. By this method tetraethoxysilane is prepared in 70% yield. Tetraethoxysilane can also be prepared by treating silicon tetrachloride with ethyl nitrite (58):



Tetraethoxysilane is cleaved by hydrogen (5b) under high temperature and pressure according to the scheme:



Tetraisopropoxysilane, $[(\text{CH}_3)_2\text{CHO}]_4\text{Si}$, can be prepared by the action of isopropyl nitrite on silicon tetrachloride (58). It boils at 78-80° at 50 mm.

Tetra-*n*-butoxysilane, $(\text{n-C}_4\text{H}_9\text{O})_4\text{Si}$, is prepared from silicon tetrachloride and *n*-butanol (53, 54, 62, 63). It can also be prepared from silicon tetrachloride and *n*-butyl nitrite (58).

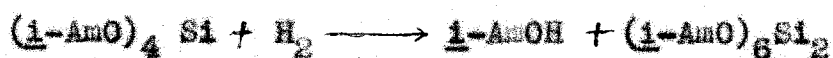
62. Dearing and Reid, J. Am. Chem. Soc., **50**, 3058 (1928).

63. Post and Hofrichter, J. Org. Chem., **5**, 572 (1940).

The compound boils at 150-2° at 18 mm. (56) or at 160-5° at 20 mm. (62); d_4^{25} 0.9194.

Tetra-n-amylloxysilane, $(n-C_4H_9O)_4Si$, is prepared by the action of n-amyl alcohol on silicon tetrachloride (62). The compound boils at 145-50° at 3 mm.; d_4^{25} 0.8933.

Tetra-isoamylloxysilane, is cleaved by hydrogen at high pressure (5b).

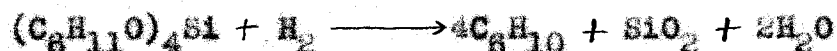


Tetra-n-heptoxysilane, $(n-C_7H_{15}O)_4Si$ is prepared by the action of n-heptyl alcohol on silicon tetrachloride (62). It boils at 200-15° at 3 mm.; d_4^{25} 0.8958.

Tetra-n-octoxysilane, $(n-C_8H_{17}O)_4Si$, is also prepared by the action of n-octyl alcohol on silicon tetrachloride (62). It boils at 240° at 3 mm.

Tetramenthoxysilane, is prepared by the reaction between menthol and silicon tetrachloride (64). The compound boils at 264° at 7 mm. and melts at 93°.

Tetracyclohexyloxysilane, $(C_6H_{11}O)_4Si$, is cleaved by hydrogen (5b) at 380°:



64. Uchida and Kondo, J. Soc. Chem. Ind. Japan, 36, Suppl. binding, 190 (1933). [C.A., 27, 3464 (1933)].

The products are cyclohexene, silicon dioxide and water.

Tetra- β -chloroethoxysilane, $(\beta\text{-ClC}_2\text{H}_4\text{O})_4\text{Si}$, is prepared by the action of β -chloroethylnitrite on silicon tetrachloride (58). This compound can also be prepared in 73% yield by treating ethylene oxide with silicon tetrachloride (65, 66, 67) and from β -chloroethanol and silicon tetrachloride (67). It boils at 195-200° at 15 mm. or at 153-4° at 2 mm.: n_D^{20} 1.4641; d_4^{20} 1.344.

Aryl Derivatives of the Type $(\text{RO})_4\text{Si}$

Tetraphenoxysilane, $(\text{C}_6\text{H}_5\text{O})_4\text{Si}$, is prepared by the action of phenyl acetate on silicon tetrachloride (68) or by treatment of any one of the three possible phenoxychlorosilanes with sodium (69). It melts at 48° (69).



In all cases the products are the same: tetraphenoxysilane, sodium chloride, and silicon. The latter may be changed to silica or silicoformic acid by the action of water during its separation from the sodium and sodium chloride. The compound can also be prepared besides other products by the reaction of

65. Patnode and Sauer, U.S. Pat. 2,381,137, August 7, 1945. [C.A., 39, 4838 (1945)].
 66. Patnode and Sauer, U.S. Pat. 2,381,137, August 7, 1945. [C.A., 39, 4890 (1945)].
 67. Sauer and Patnode, J. Am. Chem. Soc., 67, 1548 (1945).
 68. Volnov, J. Gen. Chem., (U.S.S.R.), 9, 2269 (1939). [C.A., 34, 5048 (1940)].
 69. Thompson and Kipping, J. Chem. Soc., 1176 (1929).

phenol with silicon tetrachloride (69).

Tetra-*o*-anisylloxysilane, $(\text{o-CH}_3\text{OC}_6\text{H}_4\text{O})_4\text{Si}$, is prepared from silicon tetrachloride and guaiacol (70). The compound boils at $317\text{-}323^\circ$ at 12 mm.

Tetra-*p*-bromophenoxysilane, $(\text{p-BrC}_6\text{H}_4\text{O})_4\text{Si}$, can be prepared in "good" yield by heating one mole of silicon tetrachloride and four moles of *p*-bromophenol in an oil bath at 150° (70). The compound boils at 356° at 12 mm. In the reaction of one mole of silicon tetrachloride and two moles of *p*-bromophenol there was isolated pure only tri-*p*-bromophenoxychlorosilane and the tetra compound.

In general it might be said that under hydrogen pressure tetra-*p*-bromophenoxysilane or any tetra-aryloxysilane will decompose starting at about 280° , and the decomposition will be complete at about 380° (5b):



Tetrabenzylloxysilane, $(\text{C}_6\text{H}_5\text{CH}_2\text{O})_4\text{Si}$, can be prepared from benzyl alcohol and silicon tetrachloride (56). It is a water-clear substance boiling at $245.5\text{-}246^\circ$ at 0.5 mm.

Tetra-*o*-nitrophenoxysilane, $(\text{o-NO}_2\text{C}_6\text{H}_4\text{O})_4\text{Si}$, was prepared by treating silicon tetrachloride with *o*-nitrophenol (71). It is an unstable compound, and no constants are given.

70. Jerg and Stetter, J. prakt. Chem., **117**, 305 (1927).

71. Dolgov, Uspekhi Khim., **1**, 626 (1932). [Chem. Zentr. **II**, 2258 (1933)].

Tetra-*p*-nitrophenoxysilane, $(p\text{-NO}_2\text{C}_6\text{H}_4\text{O})_4\text{Si}$, was prepared by treating silicon tetrachloride with *p*-nitrophenol (71). It is unstable and no constants are given.

Tetra-*p*-cresoxysilane, $(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_4\text{Si}$, can be prepared from *p*-cresol and silicon tetrachloride. It melts at 69° and decomposes at 350° , and under fifty atmospheres of hydrogen, to *p*-cresol and silicon (5b).

Aryl Derivatives of the Type $(\text{RO})_3\text{SiR}$

Triphenoxyphenylsilane, $(\text{C}_6\text{H}_5\text{O})_3\text{Si}(\text{C}_6\text{H}_5)$, is prepared by treating triphenoxychlorosilane with phenylmagnesium bromide (70). It boils at 250° at 13 mm. and melts at 45° . It is very soluble in the ordinary inert organic solvents.

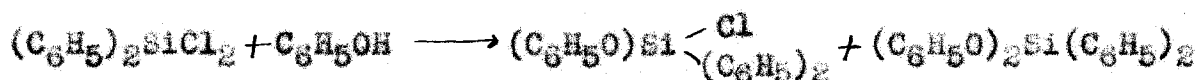
Alkyl Derivatives of the Type $(\text{R}'\text{O})_2\text{SiR}_2$

Dicyclohexylsilanediol, $(\text{C}_6\text{H}_{11})_2\text{Si}(\text{OH})_2$, is formed as an insoluble oil when redistilled cyclohexylphenyldichlorosilane is hydrolyzed with potassium hydroxide (41). (This is conclusive proof that cyclohexylmagnesium bromide may substitute a cyclohexyl group for a phenyl in phenyltrichlorosilane or cyclohexylphenyldichlorosilane). After solidification it is crystallized from ethyl acetate and melts at $164\text{--}5^\circ$. It decomposes a few degrees above its melting point giving glue-like condensation products. It is very soluble in ethanol, acetone, and ether.

Aryl Derivatives of the Type $\text{R}_2\text{Si}(\text{OR}')_2$

Diphenoxydiphenylsilane, $(\text{C}_6\text{H}_5\text{O})_2\text{Si}(\text{C}_6\text{H}_5)_2$, can be prepared (46) along with phenoxydiphenylchlorosilane by treating

diphenyldichlorosilane with phenol in benzene at 150°.



It is also formed along with other substances when phenoxydiphenylchlorosilane is boiled 2-3 hours with sodium in dry toluene (46) or by the reaction of two equivalents of phenylmagnesium bromide with one equivalent of diphenoxydichlorosilane (70). When boiled with water for a short time, the diphenoxy derivative is not appreciably hydrolyzed because of its insolubility. It is also relatively stable towards a 5% solution of sodium hydroxide, but it is very readily hydrolyzed in the presence of acetone or alcohol with the separation of hexaphenylcyclotrisiloxane while sodium phenoxide remains in solution (46). The compound melts at 70-1° and is very soluble in ether, chloroform, and benzene but only moderately so in cold ethanol.

Diphenylsilanediol, $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$, can be prepared from silicon tetrachloride and phenylmagnesium bromide (72) or by the action of dilute ammonium hydroxide or water on diphenyldichlorosilane (73). It is apparently also formed by the hydrolysis of diphenyldiphenoxysilane with hydrochloric acid. The compound melts at 116° with rapid heating (70).

When diphenylsilanediol is treated with hot alkali, two complex substances are produced (74). The one $[\text{Si}(\text{C}_6\text{H}_5)_2\text{O}]_A$ (A)

72. Diltney and Eduardoff, Ber., 37, 1139 (1904).

73. Martin, ibid., 45, 403 (1912).

74. Kipping and Murray, J. Chem. Soc., 1427 (1928).

is practically insoluble in all the ordinary solvents whereas the other $[\text{Si}(\text{C}_6\text{H}_5)_2\text{O}]_B$ (B) is sparingly soluble in benzene. Compound B gives a molecular weight of 3900 in camphor, and the other seems even more complex.

Di-p-tolylsilanediol, $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Si}(\text{OH})_2$, is easily produced by hydrolyzing the dichloride but its isolation is troublesome because like diphenylsilanediol it readily undergoes condensation in the presence of acids and alkalis to give both open and closed chain compounds (75). It melts at $113\text{-}6^\circ$ according to the rate of heating and is very soluble in acetone, ether, chloroform, and ethyl acetate, but is only slightly soluble in cold benzene, carbon disulfide, carbon tetrachloride, and cold petroleum ether. It dissolves readily and completely in 5% aqueous sodium hydroxide, but the solution soon becomes turbid and the condensation products begin to form (75).

When treated with hot alkali, the condensation products formed are the open and closed chain compounds formed from three molecules of the diol and a substance which is probably $[\text{Si}(\text{C}_7\text{H}_7)_2\text{O}]_4$. Two other substances were isolated which correspond with the two diphenyl analogues described above. The product insoluble in benzene $[\text{Si}(\text{C}_7\text{H}_7)_2\text{O}]_A$ gives a molecular weight in camphor of 3450, but these results are not trustworthy owing to the slight solubility of the substance. The more soluble compound gives a molecular weight of 4150 which is probably more nearly correct (74).

75. Pink and Kipping, ibid., 2830 (1923).

Mixed Aryl-Alkyl Derivatives of the Type $R_2R'SiOR''$

Dicyclohexylphenylsilanol, $(C_6H_{11})_2Si \begin{matrix} OH \\ \diagdown \\ C_6H_5 \end{matrix}$, is produced by the hydrolysis of dicyclohexylphenylchlorosilane (41) with aqueous alkali or by treatment of cyclohexyloxydicyclohexylphenylsilane with acetyl or benzoyl chloride (13) or by treating dicyclohexylphenylsilane with 80% potassium hydroxide in an organic solvent. It melts at $145-6^\circ$ and dissolves freely in the cold in all the common organic solvents except light petroleum. It is insoluble in alkali and cannot be converted to the disiloxane by treating it with alkalis, sodium ethoxide or ethanolic hydrogen chloride (41).

Cyclohexyloxydicyclohexylphenylsilane, $(C_6H_{11}O)Si \begin{matrix} C_6H_5 \\ \diagdown \\ (C_6H_{11})_2 \end{matrix}$, is produced in the reaction of phenyltrichlorosilane (13) with cyclohexylmagnesium bromide. It melts at $103-4^\circ$ and is readily soluble in all the common solvents with the exception of alcohol, acetone, and acetic acid in the cold. It is unchanged by heating with acetone and 5% potassium hydroxide.

Mixed Aryl-Alkyl Derivatives of the Type $RR'Si(OR'')_2$

Cyclohexylphenylsilanediol, $(C_6H_{11})Si \begin{matrix} C_6H_5 \\ \diagdown \\ (OH)_2 \end{matrix}$, is produced by the hydrolysis of cyclohexylphenyldichlorosilane with a 5% potassium hydroxide solution (41). It melts at $123-4^\circ$ and is soluble in petroleum ether, carbon disulfide, and hot water.

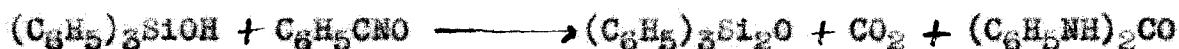
Alkyl Derivatives of the Type R_3SiOR'

Triethylsilanol, $(C_2H_5)_3SiOH$, can be prepared by the hydrolysis of triethylsilylethylamine (3). It boils at $153-5^\circ$.

Aryl Derivatives of the Type R_3SiOR'

Triphenylsilanol, $(C_6H_5)_3SiOH$, is formed by the hydrolysis of triphenylchlorosilane with boiling water or a little ammonium hydroxide (76, 77). It can also be produced from the bromide by hydrolysis with a potassium hydroxide solution at 120° . It is also formed by the hydrolysis of di-triphenylsilylamine with hydrochloric acid. It is readily soluble in alcohol, ether, chloroform, or benzene and may be crystallized from acetone. It melts at $148-150^\circ$.

It does not form a urethan when treated with phenylisocyanate but instead the following reaction occurs (10):



Tri-p-tolylsilanol, $(p-CH_3C_6H_4)_3SiOH$, is formed by refluxing tri-p-tolylchlorosilane (52) with dilute ammonium hydroxide. It melts at $99-100^\circ$ and is readily soluble in chloroform, benzene, and acetone, but much less so in cold, light petroleum ether (52).

Hexa-p-tolyldisiloxane, $[(p-CH_3C_6H_4)_3Si]_2O$, is formed by heating tri-p-tolylsilanol with a 10% solution of alcoholic sodium hydroxide. It melts at $223-4^\circ$. It dissolves freely in

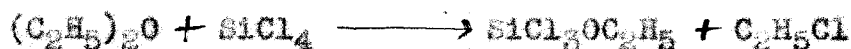
76. Polis, Ber., 19, 1012 (1886).

77. Ladenburg, ibid., 40, 2274 (1907).

chloroform, and fairly readily in benzene, but is only sparingly soluble in light petroleum and acetone.

Alkyl Derivatives of the Type ROSiX_3

Ethoxytrichlorosilane, $\text{C}_2\text{H}_5\text{OSiCl}_3$, is formed in small amounts at room temperatures by the cleavage of ethyl ether with silicon tetrachloride (43):



Menthoxytrichlorosilane, boiling at $112-3^\circ$ at 9 mm. is prepared by treating menthol with silicon tetrachloride (64);
 d_4^{21} 1.1439; n_D^{21} 1.4615.

Alkyl Derivatives of the Type $(\text{R}_3\text{Si})_2\text{O}$

Hexaethyldisiloxane, $[(\text{C}_2\text{H}_5)_3\text{Si}]_2\text{O}$, can be prepared by treating potassium di-triethylsilylamide, or the corresponding amine with water (3). It boils at 231° at atmospheric pressure.

Aryl Derivatives of the Type $(\text{R}_3\text{Si})_2\text{O}$

Tetraphenyldimethyldisiloxane, $[(\text{C}_6\text{H}_5)_2\text{CH}_3\text{Si}]_2\text{O}$, is isolated by decomposition of diphenylmethylsilanol at its boiling point (52). It melts at $51-2^\circ$ and is very soluble in the common organic solvents but is only sparingly soluble in cold ethanol.

Hexabenzylidisiloxane, $[(C_6H_5CH_2)_2Si]_2O$, can be isolated from the reaction of dibenzylchlorosilane and sodium in toluene (29). It melts at $205-6^{\circ}$. It is also formed by treating tribenzylsilane with acetone and potassium hydroxide (28).

Aryl Derivatives of the Type $ROSiX_3$

Phenoxytrichlorosilane, $(C_6H_5O)SiCl_3$, is produced besides other products by the reaction of phenol with silicon tetrachloride (69). It boils at $183-6^{\circ}$ at 60 mm. It is a viscous liquid of high density which fumes strongly in the air and is miscible with most anhydrous solvents. It is readily hydrolyzed by water.

Alkyl Derivatives of the Type $(RO)_2SiX_2$

Dimenthoxydichlorosilane, boiling at 188° at 5 mm. is formed by treating menthol with silicon tetrachloride (64);

$d_4^{16.5}$ 1.0580; $n_D^{16.5}$ 1.4709.

Aryl Derivatives of the Type $(RO)_2SiX_2$

Diphenoxydichlorosilane, $(C_6H_5O)_2SiCl_2$, boiling at $167-71^{\circ}$ at 13 mm. is formed along with other products by the reaction of phenol with silicon tetrachloride (69, 70). Other boiling points listed for the compound are: $199.5-202^{\circ}$ at 40 mm. and $215-8^{\circ}$ at 60 mm. (69). It is a viscous fuming liquid similar in properties to the monophenoxy derivative. It is easily soluble in absolute chloroform, ether, or benzene.

Alkyl Derivatives of the Type (RO)₃SiX

Trimenthoxychlorosilane, is prepared by the action of menthol on silicon tetrachloride (64). It boils at 244-5° at 10 mm.; d_4^{18} 0.9784; $n_D^{18.5}$ 1.4699.

Aryl Derivatives of the Type (RO)₃SiX

Triphenoxychlorosilane, (C₆H₅O)₃SiCl, is formed besides other products by the reaction of phenol on silicon tetrachloride (69, 70). The boiling points given for the compound are: 235-9° at 25 mm., 229-30° at 14 mm., 252-5° at 60 mm. It is very viscous, and miscible with most anhydrous solvents, and fumes only slightly in moist air.

Tri-p-bromophenoxychlorosilane, (p-BrC₆H₄O)₃SiCl, is produced besides tetra-p-bromophenoxychlorosilane by the reaction of p-bromophenol on silicon tetrachloride (70). It distills at 310-20° at 12 mm.

Aryl Derivatives of the Type RO₂SiRX

Phenoxydiphenylchlorosilane, (C₆H₅O)Si $\begin{matrix} \text{Cl} \\ \diagdown \\ (\text{C}_6\text{H}_5)_2 \end{matrix}$, is prepared (46) by the interaction of phenol and diphenyldichlorosilane in benzene. It boils at 252-4° at 40 mm. It is a thick oil which barely fumes in air and is miscible with light petroleum, and other anhydrous solvents. It is immediately and completely soluble in a 5% solution of potassium hydroxide, giving

the potassium derivatives of phenol and of diphenylsilanediol. When exposed to moist air it is converted to hexaphenylcyclotri-siloxane (46).

Alkyl Derivatives of the Type R_3SiSiR_3

Hexaethylidisilane, $(C_2H_5)_6Si_2$, boiling without decomposition at 255° is prepared in 54% yield by heating triethylbromosilane with sodium in a closed tube (3) at $140-5^\circ$ for ten hours. It is a colorless liquid, insoluble in liquid ammonia but very soluble in ethylamine. It does not react with sodium in liquid ammonia or with lithium in ethylamine (3).

Mixed Aliphatic-Aromatic Compounds Containing the $-NO_2$ Group

(see p. 11)

p-Nitrophenyltriethylsilane, $p-NO_2C_6H_4Si(C_2H_5)_3$, is produced along with some meta isomer by the nitration of triethylphenylsilane (33) with fuming nitric acid in acetic anhydride. The mixture of meta and para isomers distills with some decomposition at $140-60^\circ$ at 12 mm. The presence of the isomers is established by treating the mixture with water and bromine in a closed tube at 110° for three hours to yield the meta and para bromonitrobenzene. The actual amount of the para isomer thus detected was 82% of the theoretical amount and only 5% of the meta isomer was obtained. The conclusion was reached that the triethylsilyl group is strongly para orienting.

m-Nitrophenyltriethylsilane, $m\text{-NO}_2\text{C}_6\text{H}_4\text{Si}(\text{C}_2\text{H}_5)_3$, is produced in about a 5% yield as described above by the nitration of the triethylphenylsilane (33).

Bis-(p-nitrophenyl)diethylsilane, $(p\text{-NO}_2\text{C}_6\text{H}_4)_2\text{Si}(\text{C}_2\text{H}_5)_2$, is produced along with some meta isomer in about 76% yield by the nitration of diphenyldiethylsilane (33). The mixture of isomers boils at $295\text{-}8^\circ$ at 760 mm. and a bromine cleavage as described above indicates the presence of about 14% of the meta-isomer.

Bis-(m-nitrophenyl)diethylsilane, $(m\text{-NO}_2\text{C}_6\text{H}_4)_2\text{Si}(\text{C}_2\text{H}_5)_2$, is produced as described above in about 14% yield by the nitration of diphenyldiethylsilane (33). It separates slowly as a solid from the mixture of isomers and melts at $102\text{-}3^\circ$. The compound is slowly attacked by alkalis, fuming nitric acid, and hot, concentrated sulfuric acid giving nitrobenzene.

Tris-(p-nitrophenyl)ethylsilane, $(p\text{-NO}_2\text{C}_6\text{H}_4)_3\text{SiC}_2\text{H}_5$, is prepared in 36% yield by the nitration of triphenylethylsilane (33).

Tris-(m-nitrophenyl)ethylsilane, $(m\text{-NO}_2\text{C}_6\text{H}_4)_3\text{SiC}_2\text{H}_5$, is prepared in about 44% yield along with the para isomer (see above) by the nitration of triphenylethylsilane (33). The conclusion drawn is that the triphenylsilyl group is strongly meta orienting in contrast to the triphenylmethyl and the triethylsilyl which are para orienting. It was also noted that a

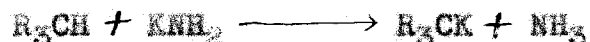
nitro group meta or para to a silicon atom was very stable toward acids, but much less so toward boiling alkalis (33).

Tri-Alkyl and Tri-Arylsilylamines

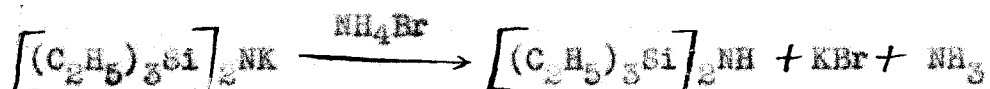
Potassium di-triethylsilylamide, $(C_2H_5)_3Si_2NK$, is formed by treating triethylsilane with potassium amide in liquid ammonia (3):



It was hoped that this reaction would lead to a Si-metal bond since it parallels similar carbon reactions:

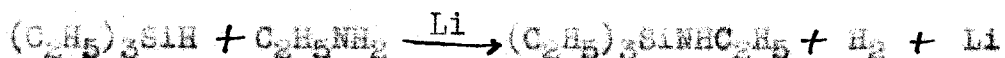


Di-(triethylsilyl)amine, $(C_2H_5)_3Si_2NH$, boiling at 100° at 1 mm. is synthesized by treating potassium di-triethylsilylamide with ammonium bromide (3):

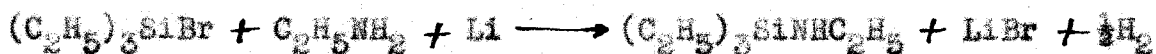


The compound is a clear colorless oil with a faint campher-like odor. It is insoluble in and heavier than liquid ammonia and distills at 100° at 1 mm.

Triethylsilylethylamine, $(C_2H_5)_3SiNEC_2H_5$, is prepared by treating triethylsilane with lithium in ethylamine. Apparently the lithium does not enter into the reaction (3) but merely serves as a catalyst:

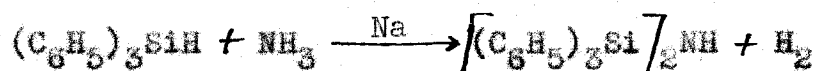


It is also formed by treating triethylbromosilane with ethylamine and lithium (3). It distills readily under reduced pressure and is soluble in ethylamine.



The compound is a clear, colorless liquid with a camphor-like odor. It hydrolyzes to form triethylsilanol but does not react with lithium in ethylamine solution (3).

Di-triphenylsilylamine, $[(\text{C}_6\text{H}_5)_3\text{Si}]_2\text{NH}$, is formed by the reaction between triphenylsilane and sodium in liquid ammonia (34).



The compound melts at 175° and is not affected by air or even by boiling dilute sodium hydroxide. It can be hydrolyzed with hydrochloric acid to give ammonium chloride and triphenylsilanol.

Triphenylsilyl-ethylamine, $(\text{C}_6\text{H}_5)_3\text{Si}\cdot\text{C}_2\text{H}_5\text{NH}_2$, is prepared by treating triphenylbromosilane with one equivalent of lithium in ethylamine (18).



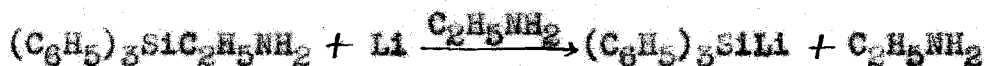
The compound melts at 45° and can be distilled at 150° in a high vacuum. It dissociates in boiling ether to form hexaphenyldisilane and ethylamine:



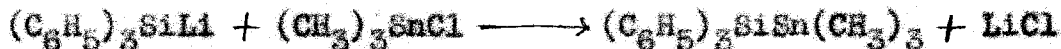
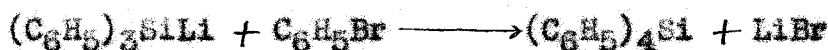
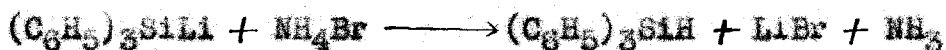
It is soluble in all the ordinary organic solvents except low boiling petroleum ether and ethanol.

Organometallic Derivatives Containing the Si-Metal Group

Triphenylsilyllithium, $(\text{C}_6\text{H}_5)_3\text{SiLi}$, is prepared by treating triphenylsilyl-ethylamine (see above) with one equivalent of lithium in ethylamine (18):

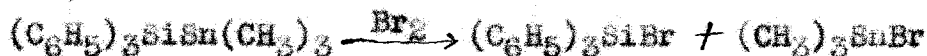


Triphenylsilyllithium reacts with ammonium bromide, bromobenzene, and trimethylchlorostannane (18):



Triphenylsilyltrimethylstannane, $(\text{C}_6\text{H}_5)_3\text{SiSn}(\text{CH}_3)_3$, is prepared as shown above by the reaction of triphenylsilyllithium and trimethylchlorostannane (18). It is an oil which analyzed well but gave a molecular weight by cryoscopic methods which was 50% too high with no obvious explanation. Its identity was

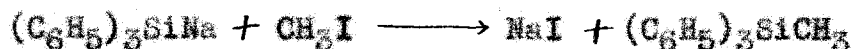
definitely established by cleavage with bromine:



Triphenylsilylsodium, $(\text{C}_6\text{H}_5)_3\text{SiNa}$, is prepared by treating triphenylsilyltrimethylstannane with sodium (18):



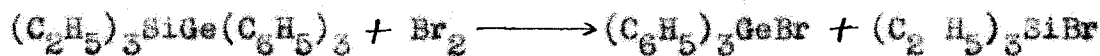
The compound reacts with methyl iodide to form triphenylmethylsilane:



Triethylsilyltriphenylgermane, $(\text{C}_2\text{H}_5)_3\text{SiGe}(\text{C}_6\text{H}_5)_3$, is formed by the reaction between triethylbromosilane and triphenylgermanylnsodium (3):



The compound crystallizes from ethanol and melts at 93.5° . It is readily cleaved by bromine:

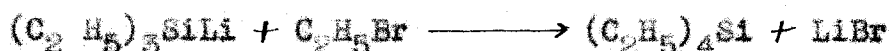
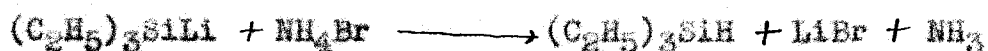


It is very soluble in benzene and petroleum ether and moderately soluble in hot methanol and ethanol.

Triethylsilyllithium, $(C_2H_5)_3SiLi$, is formed along with triphenylgermanyllithium by the reaction of triethylsilyltriphenylgermane with lithium and ethylamine (3):



The triethylsilyllithium reacts with ammonium bromide and ethyl bromide:



Derivatives Involving the Si-S Group (see p. 13)

Tetramethylmercaptosilane, $(CH_3S)_4Si$, can be prepared by the reaction of silicon tetrachloride with an excess of sodium methyl mercaptide in benzene (78). The yields are 35-40% of the theoretical. The compound boils at $144-6^\circ$ at 12 mm.; d_4^{35} 1.1888; n_D^{35} 1.5989. It melts at 31° .

Tetraethylmercaptosilane, $(C_2H_5S)_4Si$, can be prepared by the reaction of silicon tetrachloride with an excess of sodium ethyl mercaptide (78). The compound boils at $169 - 71^\circ$ at 12 mm.; d_4^{25} 1.0785; n_D^{25} 1.5638.

Tetra-n-propylmercaptosilane, $(n-C_3H_7S)_4Si$, can be prepared by the reaction of silicon tetrachloride with an excess of sodium n-propyl mercaptide (78). It boils at $204-6^\circ$ at 17 mm. Backer and Stienstra, Rec. trav. chim., 51, 1197 (1932).

Tetra-isopropylmercaptosilane, $(i-C_3H_7S)_4Si$, can be prepared by the reaction of silicon tetrachloride with an excess of sodium isopropyl mercaptide (78). It boils at $176-8^\circ$ at 13 mm.; d_4^{35} 1.0099; n_D^{35} 1.5350. It melts at 33.5° .

Tri-t-butylmercaptochlorosilane, $[(CH_3)_3CS]_3SiCl$, is prepared in 60% yield by treating sodium-t-butyl mercaptide with silicon tetrachloride (79). It boils at $161-3^\circ$ at 3-4 mm. and melts at 71° . It is not very soluble in alcohol or acetic acid, but it dissolves readily in acetone, chloroform, and benzene.

Tri-t-butylmercaptomethylmercaptosilane, $[(CH_3)_3CS]_3SiSCH_3$, is prepared in 66% yield by treating tri-t-butylmercaptochlorosilane with sodium methyl mercaptide (79). It boils at $159-60^\circ$ at 4 mm. and melts at $43-4^\circ$. It is not very soluble in alcohol, but is quite soluble in ether, acetone, chloroform, and benzene.

Tri-t-butylmercaptoethylmercaptosilane, $[(CH_3)_3CS]_3SiSC_2H_5$, is prepared in 75% yield by treating tri-t-butylmercaptochlorosilane with sodium ethyl mercaptide (79). It boils at $183-4^\circ$ at 4 mm. or at $189-91^\circ$ at 12 mm. and melts at $26-7^\circ$.

Tri-t-butylmercaptoisopropylmercaptosilane, $[(CH_3)_3CS]_3SiSCH(CH_3)_2$, is prepared in 25% yield by treating tri-t-butylmercaptochlorosilane with sodium isopropyl mercaptide (79). It boils at $161-3^\circ$ at 3-4 mm. and melts at 105° . The

79. Backer and Stienstra, ibid., 54, 38 (1935).

compound is only slightly soluble in alcohol and acetic acid, but dissolves readily in ether, acetone, and benzene.

Tetra-*t*-butylmercaptosilane, $[(\text{CH}_3)_3\text{CS}]_4\text{Si}$, is prepared in 48% yield by treating tri-*t*-butylmercaptosilane with sodium-*t*-butyl mercaptide (79). The compound melts at $160-1^\circ$ and is very soluble in benzene and chloroform.

Hexa-*t*-butylmercaptodisiloxane, $\left\{[(\text{CH}_3)_3\text{CS}]_3\text{Si}\right\}_2\text{O}$, is prepared by treating tri-*t*-butylmercaptosilane with sodium hydroxide (79). The compound melts at $248-9^\circ$ and is quite soluble in benzene and chloroform.

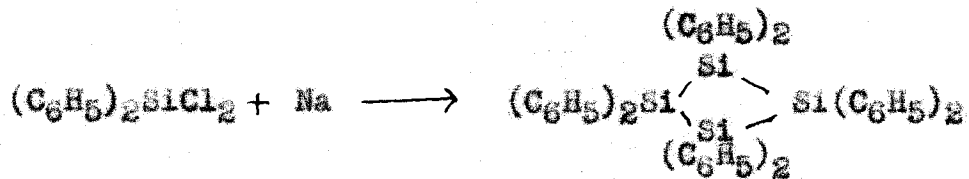
Tri-*t*-butylmercaptosilanol, $[(\text{CH}_3)_3\text{CS}]_3\text{SiOH}$, is prepared in 46% yield by treating tri-*t*-butylmercaptosilane with alcoholic potassium hydroxide (79). The compound melts at $90-1^\circ$.

Phenylmercaptotrichlorosilane, $\text{C}_6\text{H}_5\text{SSiCl}_3$, boiling at 110° at 12 mm. is prepared in low yields by the reaction of thiophenol with silicon tetrachloride (79). It is a clear, mobile liquid, which fumes strongly in the air and is easily decomposed.

Silicon Derivatives With a Cyclic Structure

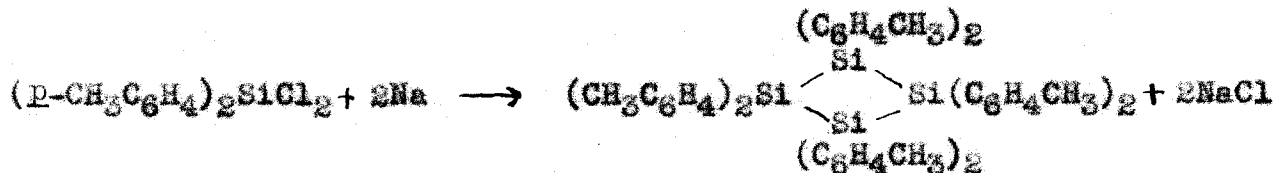
Octaphenylcyclotetrasilane, amorphous form, is produced by the action of sodium on diphenyldichlorosilane in toluene. The

crystalline form does not melt up to 400° and is practically insoluble in cold acetone, ether, and alcohol (44), but is very soluble in benzene, chloroform, and hot ethyl acetate.



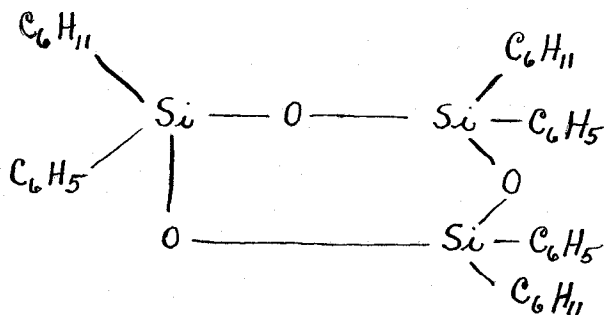
The amorphous form is probably caused by the molecules becoming entangled with one another and can be converted to the crystalline form by heating it rapidly in a test tube in an inert atmosphere. When partly melted, the cooled product is treated with cold acetone, leaving the crystalline form undissolved (44). Distillation of the "glue-like" or amorphous form gives a thick oil which has been identified as triphenylsilane (35). Some tetraphenylsilane has also been detected. The residue left after this distillation is a very complex mixture, some fractions of which seem to have a molecular weight exceeding 4000 (35). The compound seems to undergo fission under the influence of aluminum chloride (22).

Octa-p-tolylcyclotetrasilane, is formed by the reaction between di-p-tolyldichlorosilane and sodium (49). The rhomboidal prisms melt at 310° and are very soluble in benzene and chloroform. It can probably also exist in the amorphous form.



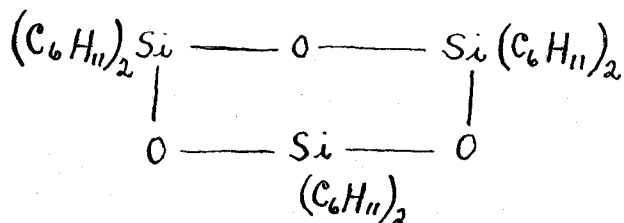
Its benzene solution does not absorb iodine and it is unchanged when boiled with tetrachloethane or nitrobenzene.

Tricyclohexyltriphenylcyclotrisiloxane is formed in 10% yield by the reaction of cyclohexylphenylsilanediol with acetyl chloride (41). The compound melts at 117-8° and the probable formula is:



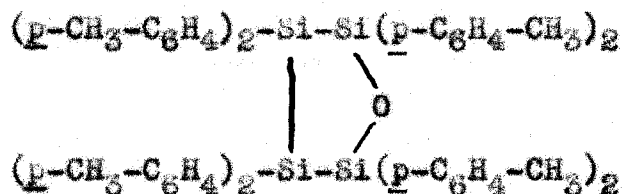
It can be crystallized from cold acetone and ethyl alcohol but all other solvents give "glue-like" solids.

Hexacyclohexylcyclotrisiloxane, is formed when dicyclohexylsilanediol (m.p. 164-5°) is treated with bromine (41) in an acetic acid solution at 80-90°. It is also formed by treating cyclohexyloxydicyclohexylphenylsilane with bromine or hydrogen bromide (13). The compound melts at 237-9°, and the probable formula is:



The compound is also formed by treating a solution of dicyclohexylphenylsilanol in acetic acid with a few drops of concentrated nitric acid or by boiling the silanol with a mixture of hydrochloric and acetic acids (41).

Octa-p-tolylcyclotetrasilane monoxide is formed from octa-p-tolyldiiodotetrasilane by hydrolysis with aqueous acetone (49). The compound melts at $228-9^{\circ}$. The probable formula is:



It is soluble in boiling acetone or chloroform, but only sparingly so in alcohol or acetic acid.

Compounds containing Tervalent Silicon Atoms and Their Derivatives

Octa-p-tolyltetrasilane is formed besides the cyclic compound in the reaction of di-p-tolyldichlorosilane with sodium. The formula assigned by Kipping (49) to this compound is:



Two other amorphous products are isolated in this reaction which have not been identified. The compound melts at $230-3^{\circ}$ and is difficultly soluble in ordinary solvents.

Octa-p-tolyldiodotetrasilane is formed from octa-p-tolyltetrasilane by reaction with iodine (49). It forms colorless plates which are soluble in benzene, but only slightly so in ether. The compound melts with decomposition at 300°. The probable formula is:



Diphenoxyoctaphenyltetrasilane is one of the compounds produced by treating phenoxydiphenylchlorosilane (46) with sodium in dry toluene. Upon crystallization from chloroform and benzene it melts at 215-6°. Its formula is:



The compound is decomposed when it is heated with piperidine and a concentrated solution of sodium hydroxide, giving the sodium derivatives of phenol and diphenylsilanediol with evolution of hydrogen. It is practically insoluble in ether, acetone, alcohol, and glacial acetic acid. It is unchanged by heating with a glacial acetic acid solution of nitric acid, and is only slowly hydrolyzed with alcoholic hydrochloric acid. Its stability may be attributed to steric hindrance.

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EXPERIMENTAL

A. Silicon Compounds

Triphenyl-p-anisylsilane.- Phenyllithium (80) was prepared in 91% yield from 17.3 g. (0.11 mole) of bromobenzene and 1.6 g. (0.23 g. atom) of lithium. To 4.18 g. (0.025 mole) of silicon tetrachloride dissolve in 50 ml. of ether was added 60 ml. of the phenyllithium solution containing 0.074 mole. p-Anisyllithium (81) was added to a positive Color Test I (82). After refluxing one-half hour the solution was hydrolyzed and filtered. A white precipitate was filtered off which was somewhat ether soluble. The ether layer was evaporated, and the solid thus obtained was combined with the first crop and crystallized from absolute ethanol. The yield was 5.5 g. (61%) melting at 156-7°.

Anal. Calcd. for $C_{25}H_{22}OSi$: Si, 7.64. Found: Si, 7.67.

p-(2,5-Dimethyl-1-pyrryl)-tetraphenylsilane.- To 0.315 g. (0.045 g. atom) of lithium (83) suspended in 10 ml. of ether was added 5 g. (0.02 mole) of p-(2,5-dimethylpyrryl-1)-phenyl

80. Gilman, Zoellner, and Selby, J. Am. Chem. Soc., 54, 1957 (1932)

81. The p-anisyllithium was prepared in essential accordance with directions of Dr. John T. Edward of this laboratory.

82. Gilman and Schulze, J. Am. Chem. Soc., 47, 2002 (1925)

83. Cf. Hazelwood, et al., J. Proc. Roy. Soc., N. S. Wales, 71, 92 (1937) C.A. 32, 1695 (1938); See also Gilman and O'Donnell, J. Am. Chem. Soc. 66, 840 (1944); Gilman, Stuckwisch and Nobis, ibid., 68, 326 (1946); Gilman and Toman, ibid., 68 1576 (1946).

bromide dissolved in 40 ml. of ether. After addition was complete, the mixture was refluxed another one-half hour. The yield by acid titration was 94%. To 27 ml. of this solution containing 0.01 mole of the lithium compound was added 3 g. (0.01 mole) of triphenylchlorosilane (prepared from silicon tetrachloride and three equivalents of phenyllithium) in 50 ml. of ether. After refluxing one and one-half hours, the solution was hydrolyzed and after separating the ether layer, the solvent was removed. Two crystallizations of the residue from dilute ethanol gave 1.5 g. (35%) of product melting at 187.5-188.5°.

Anal. Calcd. for $C_{30}H_{27}NSi$: Si, 6.53. Found: Si, 6.49.

Triethyl-p-tolylsilane.- To 50 g. (0.241 mole of triethylchlorosilane (84) dissolved in 80 ml. of ether was added an ethereal solution of p-tolylolithium until a positive Color Test I (82) was obtained. After refluxing one hour the solution was hydrolyzed, and the ether was separated and dried over calcium chloride. After removal of the solvent, the residue distilled at 87-90°/0.1 mm; n_D^{20} 1.5060. d_4^{20} 0.8958; MR, found 68.3; calcd. 68.5

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.6. Found: Si, 13.4.

Triethyl-p-anisylsilane.- p-Anisylolithium was prepared

84. Kindly supplied by the Dow Chemical Co., Midland, Michigan.

from 140 g. (0.75 mole) of p-bromoanisole in 500 ml. of ether and 16.8 g. (2.4 g. atom) of lithium metal suspended in 500 ml. of ether. The addition required twenty minutes. This solution was added to 50 g. (0.241 mole) of triethylchlorosilane (84) in 60 ml. of ether. When a positive Color Test I (82) was obtained, the solution was refluxed one hour and then hydrolyzed. After separating the ether layer, it was dried over sodium sulfate. After removal of the solvent, the residue distilled at 100-105°/0.2 mm. The yield of a colorless oil was 47 g. (64%)
 n_D^{20} 1.5130; d_4^{20} 0.9487; MR, found 70.3; calcd. 70.1.

Anal. Calcd. for $C_{13}H_{22}OSi$: 12.6. Found: Si, 12.4.

Metalation of Triethyl-p-anisylsilane.-- To 8 g. (0.036 mole) of triethyl-p-anisylsilane dissolved in 40 ml. of ether was added 70 ml. of ether containing 0.032 mole of butyllithium. The mixture was refluxed sixteen hours and then carbonated by jet-wise addition to crushed dry-ice. After warming to room temperature, dilute hydrochloric acid was added to dissolve some lithium hydroxide which had formed. The ether layer was separated, and was shaken with about 100 ml. of 10% sodium carbonate. The aqueous layer was acidified and an oil separated which solidified upon cooling and scratching. The yield of crude acid was 4.5 g. (47%). Purification was effected by redissolving the solid in aqueous sodium carbonate, extracting with ether and precipitating again with hydrochloric acid. The material thus obtained melted at 52-56° with some preliminary softening.

Calcd: neut. equiv., 266. Found: neut. equiv., 264.

Structure Proof of Metalation Product(Triethyl-3-carboxy-4-methoxyphenylsilane).- Two grams (0.0075 mole) of crude acid obtained by the procedure outlined above was dissolved in 30 ml. of glacial acetic acid, and 1.6 g. (0.01 g. atom) of bromine was added along with 0.25 g. of iodine. The solution was stirred at room temperature for twenty-two hours, and then was poured into water. Upon standing crystals separated which were filtered off and washed with a concentrated sodium bisulfite solution. Crystallization from hot water gave 1 g. (58%) of a white solid melting at 118-119°.

A mixed m. p. with an authentic sample of 2-methoxy-5-bromobenzoic acid showed no depression. Thus metalation of triethyl-*p*-anisylsilane occurs ortho to the ether linkage which is the conventional orientation (85).

Triphenyl-2-thienylsilane.- To 6 g. (0.071 mole) of freshly distilled thiophene was added 0.055 mole of butyllithium in 90 ml. of ether and the mixture was refluxed four hours when a Color Test II showed the absence of the butyllithium. This solution was then added to a triphenylchlorosilane solution which was prepared by adding 0.084 mole of phenyllithium in 74 ml. of ether to 4.8 g. (0.028 mole) of silicon tetrachloride.

85. See Gilman and Bebb, *J. Am. Chem. Soc.*, 61, 109 (1939); Gilman et al., *ibid.*, 56, 1412 (1934); Gilman and Webb, *ibid.*, 62, 987 (1940); Morton, Little, and Strong, *ibid.*, 65, 1339 (1943) for orientation studies in metalation reactions.

The solution was refluxed three-quarters of an hour after the addition of the thienyllithium and was then hydrolyzed. A white precipitate was filtered off and was crystallized from dilute dioxane. The yield was 6 g. (63%) melting at 203-206° with softening at 200°. Subsequent experiments with this compound by Mr. Frederick Marshall seemed to indicate a trace of tetraphenylsilane was present.

Anal. Calcd. for $C_{22}H_{18}SSi$: Si, 8.19. Found: Si, 8.19

Metalation of Triphenyl-2-thienylsilane(Triphenyl-2-thienyl-5-carboxysilane).- To a warm 1:1 mixture of ether-benzene was added 2 g. (0.0058 mole) of triphenyl-2-thienylsilane and 0.0116 mole of butyllithium in 80 ml. of ether. After refluxing for three hours the mixture was carbonated by jet-wise addition to dry ice and then allowed to warm to room temperature. Water was added, and the aqueous layer was acidified with hydrochloric acid. After filtration there was obtained 1.5 g. of acidic material which was crystallized twice from dilute ethanol to give 1g. (45%) melting at 188-190° with some preliminary softening.

Calcd: neut. equiv., 386. Found: neut. equiv., 383.

Anal. Calcd. for $C_{23}H_{18}O_2SSi$: Si, 7.25. Found: Si, 7.29.

Trimethylphenylsilane.- An ethereal solution of phenyllithium containing 0.56 mole per liter was added dropwise to a solution of 50 g. (0.47 mole) of trimethylchlorosilane (86) in

86. Purchased from the General Electric Company, Schenectady, New York.

150 ml. of dry ether until a positive Color Test I (82) was obtained. After one-half hour of additional reflux, the solution was hydrolyzed; the ether layer was separated and dried over sodium sulfate. Upon removal of the solvent and distillation of the residue through a 10" Vigreux column there was obtained 40 g. of material (67%) boiling at 167-70° at atmospheric pressure. This material was redistilled through a glass-helices packed column of 15 theoretical plates and a small forerun of bromobenzene was obtained. The remainder boiled at 166.5-166.7° at 741 mm. n_D^{20} 1.4910; d_4^{20} 0.8634; MR, (87) found 50.3; calcd. 50.15.

Nitration of Trimethylphenylsilane.- To 24.4 g. (0.162 mole) of trimethylphenylsilane dissolved in 190 ml. of freshly distilled acetic anhydride, 22 ml. of fuming nitric acid was added dropwise. The mixture was stirred and cooled efficiently so as to keep the temperature below 5° C. When the addition of the acid was complete, the solution was stirred at 0-5° for eight hours. It was then poured into a concentrated ammonium hydroxide-ice mixture and the oily supernatant layer was extracted with ether and dried over sodium sulfate. Removal of the solvent and fractionation of the residue gave 17.4 g. (55%) of a pale yellow liquid boiling at 73-76° at 0.6 mm. n_D^{20} 1.5274; d_4^{20} 1.060; MR, (87) found 56.50; calcd. 56.349.

B7. See Sauer, J. Am. Chem. Soc., **68**, 954 (1946) for the values used in calculating these molecular refractions.

In another trial the identical directions as described above were followed. There was obtained 23 g. (73%) of a yellow liquid boiling at 82-3° at 0.7 mm. n_D^{20} 1.5279; d_4^{20} 1.061; NR, (87) found 56.55; calcd. 56.349.

Anal. Calcd. for $C_9H_{13}O_2NSi$: Si, 14.35. Found: Si, 14.04.

Structure Proof of the Nitration Product of Trimethylphenylsilane.- Six g. (0.03 mole) of the above nitro compound and 5.5 g. (0.034 g. atom) of bromine were mixed at room temperature. When the initial heat of the reaction had subsided, the mixture was refluxed for ten minutes, and then allowed to stand at room temperature for five days during which time crystals began to separate out. It was then poured into a concentrated sodium sulfite solution and was stirred until the bromine color had disappeared. The aqueous layer was decanted and the residue was crystallized twice from dilute ethanol. There was obtained 0.7 g. of pure *p*-nitro-bromobenzene (mixed m.p.). The yield of this cleavage product is only 11.5% based on the starting nitro compound.

This reaction was repeated using 2.5 g. (0.013 mole) of the nitro compound, 0.5 g. of iodine and 3.2 g. (0.02 g. atom) of bromine. Thirty ml. of glacial acetic acid was used as a solvent and the solution was refluxed for four hours. After pouring into a concentrated sodium sulfite solution, it was extracted with ether. The ether was dried over sodium

sulfate and was removed under reduced pressure leaving 1.1 g. of an oily solid (43%) which proved to be *p*-nitrobromobenzene (mixed m.p.).

Reduction of *p*-Nitrophenyltrimethylsilane.- To 60 ml. of absolute ethanol was added 11 g. (0.056 mole) of the nitro compound along with one level teaspoon of Raney nickel. It was reduced at sixty pounds hydrogen pressure and absorbed the theoretical thirteen pounds in one hour.

In the second reduction, 8.5 g. (0.043 mole) of the nitro compound was dissolved in 60 ml. of absolute ethanol with one level teaspoon of Raney nickel and at fifty eight pounds of hydrogen pressure it absorbed the theoretical ten and one-half pounds in forty-five minutes.

After combining the two runs and filtering to remove the catalyst the alcohol was removed under reduced pressure. Fractionation of the residue gave 12.8 g. (78%) of a yellow liquid boiling at 55-58° at 0.5 mm. n_D^{20} 1.5381; d_4^{20} 0.9396; MR, found 54.9; calcd, 54.46. This compound was redistilled through a glass spiral column and two fractions were collected; 6.3 g. boiling at 51.5 - 55.5° and the remainder boiling at 53.5 - 55.5°. The first fraction gave the following constants: n_D^{20} 1.5380; d_4^{20} 0.9521; MR, (87), found 54.34; calcd. 54.46.

In another reduction 8.6 g. (0.044 mole) of the nitro compound was dissolved in 50 ml. of absolute ethanol and one-fourth teaspoon of Raney nickel was added. With a starting

pressure of fifty-three pounds of hydrogen, it absorbed the theoretical nine and one-half pounds in ten minutes. Upon removal of the catalyst and ethanol, the residue was distilled and 5.8 g. (80%) of a colorless distillate boiling at 66 - 66.5° at 0.7 mm. was collected. n_D^{20} 1.5380; d_4^{20} 0.9477; MR, (87) found 54.57; calcd. 54.46.

Anal. Calcd. for $C_9H_{15}NSi$: Si, 16.97. Found: Si, 16.54 and 16.50.

Bromination of Trimethylphenylsilane. (Attempted).- A mixture of 8 g. (0.05 g. atom) of bromine, 6 g. (0.04 mole) of trimethylphenylsilane and 0.5 g. of iodine was stirred at room temperature for twenty hours and was then poured into an aqueous sodium bisulfite solution. After extraction with ether, drying with calcium chloride, and removal of the solvent the residue was distilled. There was obtained 4.5 g. of a liquid boiling at 36-39° at 3 mm. It was suspected that this was bromobenzene because the index of refraction checked closely. Accordingly, the 2,4-dinitro derivative was prepared and was shown by a mixed melting point to be identical with an authentic specimen of 2,4-dinitrobromobenzene. Based upon the bromobenzene recovered, 72% of the trimethylphenylsilane was cleaved.

Triethylphenylsilane.- An ethereal solution of 1.1 molar phenyllithium was added to 150 g. (1.0 mole) of crude triethylchlorosilane (88) dissolved in 300 ml. of ether until a positive

88. Supplied by the Dow Corning Company. Midland, Michigan.

Color Test I (82) was obtained. After refluxing one-half hour, the ether layer was separated and dried over calcium chloride. Removal of the solvent and distillation of the residue gave 110 g. (57%) of an amber liquid boiling at 236-240° at 742 mm. Redistillation gave a water-white product boiling at 81° at 0.7 mm.

Metalation of Triethylphenylsilane. (Attempted).- To 7 g. (0.036 mole) of triethylphenylsilane dissolved in 10 ml. of ether was added 50 ml. of an ethereal solution of butyllithium containing 0.04 mole. After refluxing for twenty-four hours the solution was carbonated but the only acidic material isolated was valeric acid.

Trimethyl-9-fluorylsilane.- To 17 g. (0.11 mole) of fluorene dissolved in 70 ml. of ether there was added 48 ml. of an ethereal solution of *n*-butyllithium containing 0.12 mole. Gas evolution was vigorous and after the spontaneous reflux had subsided, the yellowish-brown mixture was refluxed for sixteen hours. To this solution of 9-fluoryllithium was added dropwise 13 g. (0.12 mole) of trimethylchlorosilane in 50 ml. of ether. After the addition was complete, the mixture was refluxed for two hours. After hydrolysis and separation and drying of the ether layer, the solvent was removed leaving a yellow solid melting poorly at 83-91°. Three crystallizations from dilute ethanol gave 12.8 g. of a colorless solid (49%) melting at 97.5-99.5°.

Anal. Calcd. for $C_{16}H_{18}Si$; Si, 11.7. Found: Si, 11.4.

Metalation of Trimethyl-9-fluorylsilane.(Attempted).-

To 3 g. (0.0126 mole) of trimethyl-9-fluorylsilane dissolved in 25 ml. of ether was added 10 ml. of an ethereal solution of butyllithium containing 0.014 mole. The mixture was refluxed four and one-half hours and then carbonated by jet-wise addition to dry ice. After warming to room temperature the ether layer was shaken with 10% hydrochloric acid until all the solid was in solution. The ether layer was extracted three times with small portions of 10% potassium hydroxide and the combined basic extracts were neutralized with 10% hydrochloric acid. After filtering there was obtained 1.3 g. (37%) of an acid melting after two crystallizations from hot benzene at 221-2°. This acid did not contain silicon, and by a mixed melting point with an authentic specimen it was shown to be fluorene-9-carboxylic acid (89).

Calcd: neut. equiv., 210. Found: neut. equiv., 210.

B. Quinolinemethanols

Alkylation of Ethyl 6-Methoxy-2-phenylcinchonoylacetate with 3-Diethylaminopropyl Chloride.(Attempted).- To 100 ml. of absolute ethanol was added 1.15 g. of sodium (0.05 g. atom), and when the reaction was complete 17.5 g. (0.05 mole) of ethyl 6-methoxy-2-phenylcinchonoylacetate was added. The

89. Miller and Bachman, J. Am. Chem. Soc., 57, 766 (1935).

mixture was heated until complete solution occurred. Then 9.0 g. (0.06 mole) of 3-diethylaminopropyl chloride was added dropwise over a forty-five minute period. Sodium chloride began to precipitate after about five minutes of heating. After refluxing for three hours the mixture was cooled and filtered and 2.7 g. of sodium chloride was collected instead of the theoretical 2.9 g. The ethanol was removed under reduced pressure, and the oily residue was decarboxylated by heating with 1:1 hydrochloric acid. There was obtained 8 g. of a compound melting at 84-94°. Two crystallizations from ethanol gave 4 g. (30%) of pure 6-methoxy-2-phenyl-4-quinolyl methyl ketone (mixed m.p.). After making the aqueous hydrochloric acid solution basic with sodium hydroxide, a brown oil was obtained which later solidified and proved to be more 6-methoxy-2-phenyl-4-quinolyl methyl ketone. By working up some of the solid residues this material was again isolated, but no trace of the desired alkylated product was detected.

Alkylation of Ethyl 6-Methoxy-2-phenylquinolinoylacetate with *n*-Butyl Bromide (Attempted).- To 100 ml. of absolute ethanol was added 1.15 g. of sodium (0.05 g. atom), and when the reaction was complete, 17.5 g. (0.05 mole) of the ester was added. After refluxing for five minutes solution was complete and 8.22 g. (0.06 mole) of *n*-butyl bromide was added dropwise over a period of twenty minutes. After seven and one-half hours of refluxing, little sodium bromide had

precipitated. The solvent was evaporated, and the remaining sodium bromide was removed by dissolving the residue in ether and filtering. After removal of the ether the residual oil was decarboxylated with 1:1 hydrochloric acid. The only product isolated was 6-methoxy-2-phenyl-4-quinolyl methyl ketone, (mixed m.p.).

Alkylation of Ethyl 6-Methoxy-2-phenyleinchoninoylacetate with Propylene Chlorohydrin.(Attempted).- Directions identical with those described above were followed. The amount of propylene chlorohydrin used was 5.64 g. (0.059 mole) and the reaction time was seventeen hours. Only 6-methoxy-2-phenyl-4-quinolyl methyl ketone could be isolated from the reaction product.

Alkylation of Ethyl 6-Methoxy-2-phenyleinchoninoylacetate with n-Butyl Iodide.(Attempted).- Directions identical with those described above were followed. The amount of n-butyl iodide used was 11.05 g. (0.06 mole). The reaction time was nine hours and 5.8 g. of sodium iodide was obtained instead of the theoretical 7.5 g. Only 6-methoxy-2-phenyl-4-quinolyl methyl ketone could be identified in the reaction product.

Alkylation of Ethyl 6-Methoxy-2-phenyleinchoninoylacetate with Ethyl Iodide.(Attempted).- To 50 ml. of dry ethanol was added 0.6 g. of sodium (0.026 g. atom) and when the reaction was complete, 8.8 g. (0.026 mole) of the keto ester was added

all at once. After the dropwise addition of 7.8 g. (0.05 mole) of ethyl iodide, the mixture was refluxed twenty-four hours and then worked up as described previously. None of the desired alkylation product could be obtained by decarboxylation with hydrochloric acid, but again the methyl ketone was isolated.

6-Methoxy-2-phenyl-4-quinolyl (β,β -bis-cyanoethyl) Methyl

Ketone.-- To a mixture of 10 g. (0.037 mole) of 6-methoxy-2-phenyl-4-quinolyl methyl ketone and 1 g. of sodium methoxide in 100 ml. of dioxane was added 1.8 g. (0.034 mole) of redistilled acrylonitrile. The solution was heated without stirring between 40-50° for one hour and then stirred at room temperature for twenty four hours. The solution was filtered and the dioxane was removed under reduced pressure leaving a dark brown oil which solidified with scratching. After shaking the solid twice with anhydrous ether to dissolve out the residual 4-methyl ketone, the suspended material was filtered off and crystallized twice from 95% ethanol. Pale yellow needles were obtained in very poor yield (3%) melting at 189-190.5° (corr.).

Anal. Calcd. for $C_{24}H_{21}O_2N_2$: M, 10.96. Found: M, 11.21.

Reaction between Benzaldehyde and 3-Diethylaminopropyl

thium. (Attempted).-- To 1.1 g. (0.16 g. atom) of lithium cut in thin pieces and suspended in 20 ml. of dry ether was added gradually 14.9 g. (0.1 mole) of freshly distilled 3-diethylamino-propyl chloride in 25 ml. of ether. Ten drops of methyl iodide was added and after refluxing five minutes Color Test I was

negative. Five more drops of methyl iodide were added and then 9 g. (0.05 mole) of benzaldehyde in 40 ml. ether was added dropwise over a period of one and one-quarter hours. After stirring and refluxing for sixteen hours only traces of lithium remained. After pouring onto ice, the ether layer was separated and was shaken with 25 ml. of 2N. hydrochloric acid. The acid layer was neutralized with 10% potassium hydroxide and was again extracted with ether. Ethanolic hydrogen chloride precipitated an oil which could not be solidified.

Tetramethylene Chlorohydrin.- Using 114 g. (1.58 moles) of tetrahydrofuran (90), and following the directions of Organic Syntheses (91) there was obtained 107 g. (79%) of tetramethylene chlorohydrin boiling at 60-63° at 3 mm.

Tetramethylene Chlorobromide.- Using 105 g. (1.0 mole) of trimethylene chlorohydrin and following the directions of Cloke (92) there was obtained 117 g. (72%) of tetramethylene chlorobromide boiling at 35° at 1.5 mm.

4-Di-n-butylaminobutyl Chloride.(Attempted).- A mixture of 50 g. (0.292 mole) of tetramethylene chlorobromide, 50 ml. of dry ether, and 75.4 g. (0.584 mole) of di-n-butylamine was heated with stirring in an oil bath for twenty-four hours

90. Kindly supplied by the E.I. duPont De Nemours and Company, Wilmington, Delaware.

91. ORG. SYN., Coll. Vol. II, p. 571. 1943.

92. Cloke, Anderson, Loebmann, and Smith, J. Am. Chem. Soc., 53, 2791 (1931).

between 40-50°. The solution was filtered and the precipitate was washed with ether. The filtrate was extracted with three - 100 ml. portions of 2 N hydrochloric acid. The acid layer was made basic with 20% potassium hydroxide and was again extracted with ether. After drying and removing the solvent, the residue was distilled. There was obtained 25 g. of a liquid boiling at 82-4° at 55 mm. n_D^{20} 1.4185; d_4^{20} 0.7607.

This same experiment was repeated exactly as described above except that the temperature was kept at about 40° for twelve hours. There was obtained 32.5 g. of a liquid boiling at 78-9° at 50 mm. n_D^{20} 1.4188; d_4^{20} 0.7638. Both this material and that above proved to be unchanged di-n-butylamine.

α -(3-Diethylaminopropylmercaptomethyl)-6-methoxy-2-phenyl-4-quinolinemethanol Dihydrochloride.- To 150 ml. of absolute ethanol was added 0.69 g. (0.03 g. atom) of sodium and after solution was complete, 5.9 g. (0.04 mole) of 3-diethylaminopropylmercaptan (93) (n_D^{20} = 1.4668) was added all at once. To the clear solution was added rapidly 7.8 g. (0.022 mole) of α -bromomethyl-6-methoxy-2-phenyl-4-quinolinemethanol (94). The reddish solution was refluxed thirty minutes, when solution was complete and sodium bromide had made its appearance. The ethanol was partially removed under reduced pressure and after adding ethanolic hydrogen chloride, it was removed completely. Water was added; the

93. Gilman, Plunkett, Tolman, Fullhart, and Broadbent, ibid., 67, 1845 (1945). See, also, Gilman and Woods, ibid., 67, 1843 (1945); and Albertson and Clinton, ibid., 67, 1222 (1945).

94. Lutz, et al., ibid., 68, 1813 (1946).

mixture was filtered, and then made alkaline with ammonium hydroxide. After extracting the basic solution with ether, ethanolic hydrogen chloride was added to the ether layer. The oil which separated solidified upon scratching. The yellow solid was crystallized twice from absolute ethanol. The first crystallization yielded a hygroscopic solid, but the second gave a stable product which was dried in a vacuum desiccator over phosphorous pentoxide. The yield was 8 g. (73%). The m.p. was 182-5° with preliminary softening.

Anal. Calcd. for $C_{26}H_{32}O_2N_2 \cdot 2HCl$: S, 6.45; Cl, 14.28.
Found: S, 6.69; Cl, 13.95.

4-Methyl-*4*'-phenyl-6-methoxy-2-phenyl-4-quinolinemethanol.

Phenylmagnesium bromide was prepared by adding dropwise 8.3 g. (0.053 mole) of bromobenzene in 15 ml. of ether to 1.3 g. (0.053 mole) of magnesium in 20 ml. of ether. After all the magnesium had dissolved, 5. g. (0.018 mole) of 6-methoxy-2-phenyl-4-quinolyl methyl ketone (94) in 25 ml. of benzene was added gradually over a forty-five minute period. It was then refluxed three hours; poured into a saturated ammonium chloride-ice mixture and filtered. The benzene layer was separated and the solvent was evaporated leaving a white solid. After two crystallizations from benzene it melted at 188-188.5°. The yield was 4.5 g. or 71%.

Anal. Calcd. for $C_{24}H_{21}O_2N$: N, 3.94. Found: N, 4.27.

l,l-Dimethyl-6-methoxy-2-phenyl-4-quinolinemethanol.-

Methylmagnesium iodide was prepared by adding 7.5 g. (0.053 mole) of methyl iodide in 15 ml. of ether to 1.3 g. (0.053 g. atom) of magnesium turnings suspended in 20 ml. of ether. When practically all the magnesium had dissolved, 4.5 g. (0.016 mole) of 6-methoxy-2-phenyl-4-quinolyl methyl ketone (94) in 75 ml. of benzene was added gradually over a thirty minute period. After refluxing the solution for three hours, it was poured into a saturated ammonium chloride-ice mixture. The organic layer was separated, and the solvent was evaporated. The crude yield of white solid was 4 g. (84%). Two crystallizations from benzene gave a constant melting point of 153.5-155.5°. The final yield was 3 g. or 63%.

Anal. Calcd. for $C_{19}H_{19}O_2N$: N, 4.78. Found: N, 5.06.

l-Methyl-*l*-(*p*-dimethylaminophenyl)-6-methoxy-2-phenyl-4-quinolinemethanol.- *p*-Dimethylaminophenyllithium was prepared

by adding 14 g. (0.07 mole) of *p*-bromodimethylaniline in 75 ml. of ether to 0.8 g. (0.11 g. atom) of lithium suspended in 25 ml. of ether. When practically all the lithium had dissolved, 4.5 g. (0.016 mole) of 6-methoxy-2-phenyl-4-quinolyl methyl ketone (94) in 50 ml. of benzene was added dropwise. The solution turned dark red and heat was evolved. After refluxing for three hours it was permitted to stand overnight and then hydrolyzed with ice water. The organic layer was

separated and dried over sodium sulfate. After evaporation of the solvent under reduced pressure, there remained 2 g. of a white solid which was washed with ether and then crystallized once from benzene - petroleum ether. The m.p. was 184-6°.

Anal. Calcd. for $C_{26}H_{26}O_2N_2$: N, 7.03. Found: N, 7.29.

Δ -Methyl- Δ -ethyl-6-methoxy-2-phenyl-4-quinolinemethanol.-

Methylmagnesium iodide was prepared by adding 7.1 g. (0.05 mole) of methyl iodide in 25 ml. of ether to 1.2 g. (0.05 g. atom) of magnesium suspended in 25 ml. of ether. Then 5 g. (0.017 mole) of 6-methoxy-2-phenyl-4-quinoly ethyl ketone (95) dissolved in 50 ml. of benzene was added gradually over a forty-five minute period. After refluxing three hours, the solution was hydrolyzed with a saturated ammonium chloride solution. After separating and drying the organic layer over sodium sulfate, the solvent was evaporated leaving 4.4 g. of a white solid melting at 105-112°. The yield was 84%. This material was found to be very soluble in ethanol, acetone, ethyl acetate, benzene, dioxane, and ether, but only slightly soluble in petroleum ether. It was finally crystallized from a mixture of 10 vol. of benzene: 15 vol. of petroleum ether. After two such crystallizations it melted at 117-118°.

Anal. Calcd. for $C_{20}H_{21}O_2N$: N, 4.56. Found: N, 4.89.

95. Kindly supplied by Dr. Leo Tolman.

4-Methyl-6-methoxy-2-phenyl-4-quinolinemethanol.— Methylmagnesium iodide was prepared by adding 8.1 g. (0.057 mole) of methyl iodide in 20 ml. of ether to 1.4 g. (0.057 g. atom) of magnesium suspended in 20 ml. of ether. Five grams (0.019 mole) of 6-methoxy-2-phenylquinoline-4-aldehyde (96) dissolved in 75 ml. of benzene was added dropwise over a forty-minute period with no external heat being applied. After the addition was complete, the clear solution was refluxed for three hours, and then hydrolyzed by pouring into an ice-ammonium chloride solution. After extracting the aqueous layer twice more with ether, the combined organic layers were dried over sodium sulfate. After removal of the solvent the residual yellow oil solidified to give 5.3 g. or a quantitative yield of a white solid. Crystallization from a mixture of 10 vol. of benzene: 15 vol. of petroleum ether gave 4.7 g. (89%) melting at 119-120°.

Anal. Calcd. for $C_{18}H_{17}O_2N$: N, 5.02, Found: N, 5.01.

4-(2-Methyl-2'-hydroxypropyl)-6-methoxy-2-phenyl-4-quinolinemethanol.— Methylmagnesium iodide was prepared using 7.8 g. (0.055 mole) of methyl iodide and 1.3 g. (0.055 g. atom) of magnesium. Four grams (0.011 mole) of α -carbethoxymethyl-6-methoxy-2-phenyl-4-quinolinemethanol (94) in 50 ml. of benzene was added dropwise to the stirred solution. After refluxing for

96. Kindly supplied by Mr. Frederick J. Marshall. See Gilman, Marshall, and Benkeser, J. Am. Chem. Soc. **68**, 1649 (1946) for a preparation of this aldehyde.

seven hours, the solution was hydrolyzed and worked up as described previously. Crystallization from benzene raised the melting point to 157-158.5°. The yield was 60%.

Anal. Calcd. for $C_{21}H_{23}O_3N$: N, 4.15. Found: N, 3.92.

Δ -Carbethoxymethyl-6-methoxy-2-phenyl-4-quinolinemethanol.-

Five grams (0.013 mole) of ethyl-6-methoxy-2-phenylcinchoniny-lacetate (94) in 50 ml. of absolute ethanol was reduced for one and three-quarter hours at sixty pounds hydrogen pressure with a level teaspoon of Raney nickel as catalyst. After crystallization from 5 vol. of benzene; 20 vol. of petroleum ether (b.p. = 60-68°) there was obtained 4 g. (80%) of a white solid melting at 123-124°.

Anal. Calcd. for $C_{21}H_{21}O_4N$: N, 3.99. Found: N, 4.10.

Δ -(3-Diethylaminopropyl)-6-methoxy-2-phenyl-4-quinoline-methanol Dihydrochloride.- The procedure employed was essentially that of Marxer (97). To a suspension of 1 g. of pure magnesium and 1 g. of activated copper-magnesium alloy (98) in 15 ml. of dry ether was added ten drops of dry ethyl bromide. Then 8.5 g. (0.057 mole) of freshly distilled 3-diethylamino-propyl chloride (99) was added over a three minute period. A white precipitate formed and an exothermic reaction set in.

97. Marxer, Helv. Chim. Acta., 24, 209E (1941).

98. Gilman, Peterson, and Schulze, Rec. trav. chim., 47, 19 (1928).

99. Gilman and Shirley, J. Am. Chem. Soc., 66, 888 (1944).

Ten more drops of ethyl bromide was added, and the mixture was heated at reflux for five minutes. Then 5 g. (0.019 mole) of 6-methoxy-2-phenylquinoline-4-aldehyde (96) in 85 ml. of dry thiphen-free benzene was added portionwise over a seventy-five minute period. There was little evidence of reaction, but the precipitate appeared to dissolve. After refluxing for twenty hours, the mixture was hydrolyzed by an iced saturated ammonium chloride solution. Subsequent to filtration to remove the alloy and a trace of magnesium, the organic layer was separated and the aqueous layer was extracted once with ether. The combined organic layers were dried over sodium sulfate; the solvent was removed under reduced pressure on a water bath, and the heavy brown oily residue which remained was dissolved in a small volume of ether. The dropwise addition of ethanolic hydrogen chloride precipitated the dihydrochloride which was obtained in a yield of 8.3 g. (97%). After two crystallizations from a warm mixture of 95% ethanol and ether, the compound melted with decomposition in a rapidly heated bath at 238-244°. The yield of purified compound was 65%.

Anal. Calcd. for $C_{24}H_{30}O_2N_2 \cdot 2HCl$: N, 6.22; Cl, 15.74.
Found: N, 6.12; Cl, 15.80.

λ -(3-Di-n-butylaminopropyl)-6-methoxy-2-phenyl-4-quinolinemethanol Dihydrochloride. The procedure used for this synthesis was like that described for the preceding preparation. The reactants were 5 g. (0.019 mole) of the aldehyde (96),

1 g. of magnesium, 1 g. of the activated copper-magnesium alloy, and 11.7 g. (0.057 mole) of 3-di-p-butylaminopropyl chloride, prepared in accordance with the method of Marxer (97). After refluxing the mixture for twenty four hours, 8 g. of a gummy hydrochloride was obtained. This was crystallized three times from a mixture of 95% ethanol and ether to give 5 g. (52%) of a light yellow product melting at 200-203°.

Anal. Calcd. for $C_{28}H_{38}O_2N_2 \cdot 2HCl$: N, 5.54; Cl, 14.0.

Found: N, 5.80; Cl, 13.83.

L-(p-Dimethylaminophenyl)-6-methoxy-2-phenyl-4-quinoline-methanol Dihydrochloride.- To 0.53 g. (0.076 g. atom) of lithium suspended in 10 ml. of dry ether was added 7.6 g. (0.038 mole) of redistilled "practical" p-bromodimethylaniline dissolved in 25 ml. of ether. The addition required about one-half hour, and when half completed heat was applied to the flask. When the lithium had disappeared (15 min. after addition was completed), 5 g. (0.019 mole) of 6-methoxy-2-phenyl-4-quinoline-aldehyde (96) in 85 ml. of anhydrous "thio-free" benzene was added dropwise over a thirty-minute period. After an additional 15 minute reflux, it was hydrolyzed with an ammonium chloride solution; filtered; and the organic layer dried over sodium sulfate. Removal of the solvent left a thick, dark oily residue which was dissolved in 95% ethanol, and precipitated as the dihydrochloride with ethanolic hydrogen

chloride. Two crystallizations from an ether-ethanol mixture (once with the use of Norit) gave a pale yellow amorphous solid darkening at 170° and decomposing at 180-190°.

Anal. Calcd. for $C_{25}H_{24}O_2N_2 \cdot 2HCl$: Cl, 15.5. Found: Cl, 15.1.

Δ -(*o*-Anisyl)-6-methoxy-2-phenyl-4-quinolinemethanol Hydrochloride.- To 0.6 g. (0.025 g. atom) of magnesium suspended in 15 ml. of dry ether was added 4.7 g. (0.025 mole) of *o*-bromoanisole in 30 ml. of ether. The mixture was refluxed gently throughout the formation of the Grignard reagent which required forty-five minutes. Then 5 g. (0.019 mole) of 6-methoxy-2-phenylquinoline-4-aldehyde (96) dissolved in 85 ml. of benzene was added dropwise. The mixture was refluxed an additional one-half hour before hydrolyzing with an ammonium chloride solution. After filtering, the organic layer was dried over sodium sulfate. After removal of the solvent under vacuum, the residue set up as an amber glass which did not crystallize with scratching. Accordingly it was dissolved in a small amount of absolute ethanol and the hydrochloride was precipitated with ethanolic hydrogen chloride. The yield was 6.5 g. (84%) of a yellow crystalline solid; m.p. 217-220°.

Anal. Calcd. for $C_{24}H_{21}O_3N \cdot HCl$: Cl, 8.73. Found: Cl, 8.89.

Δ -(2-Quinolylmethyl)-6-methoxy-2-phenyl-4-quinolinemethanol Dihydrochloride (100).- A mixture of 3 g. (0.011 mole) of 6-methoxy-2-phenylquinoline-4-aldehyde (96) 6 ml. of freshly 100. See Kaplan and Lindwall, *ibid.*, 65, 927 (1943) for similar condensations.

distilled quinaldine and seven drops of diethylamine was refluxed for twenty hours in 10 ml. of n-propanol. The mixture was cooled; ether was added; and then the yellow dihydrochloride was precipitated with ethanolic hydrogen chloride. After two crystallizations from hot absolute ethanol it melted at 220-224°. The yield of pure material was 2 g. or 38%. A mixed melting point with quinaldine hydrochloride was 185-195°.

Anal. Calcd. for $C_{27}H_{22}O_2N_2 \cdot 2HCl$: Cl, 14.71. Found: Cl, 14.81.

6-Methoxy-2-phenyl-4-quinolyl-p-dimethylaminostyryl Ketone

(101).-- A mixture of 5 g. (0.018 mole) of 6-methoxy 2-phenyl-4-quinolyl methyl ketone and 2.7 g. (0.018 mole) of p-dimethylaminobenzaldehyde was heated in 100 ml. of absolute ethanol until complete solution was effected. Then 0.5 g. of sodium methoxide was added, and the solution was cooled somewhat in an ice-bath. It was placed in a refrigerator for four hours, and then allowed to stand at room temperature overnight. A red oil separated which later solidified. The yellow-red precipitate was filtered to yield about 7 g. (95%) of crude product. After several crystallizations from ethyl acetate which were attended with rather heavy losses it melted at 149.5-150.5° (corr.) with some preliminary softening at 144°.

Anal. Calcd. for $C_{27}H_{24}O_2N_2$: N, 6.86. Found: N, 7.18.

101. See Gilman and Karmas, Ibid., 67, 342 (1945) for other examples of styrylquinolines.

6-Methoxy-2-phenyl-4-quinolyl Styryl Ketone (101).- To 10 g. (0.036 mole of 6-methoxy-2-phenyl-4-quinolyl methyl ketone (94) suspended in 10 ml. of absolute ethanol was added 1.8 g. (0.046 mole) of sodium hydroxide in 16 ml. of water. The mixture was cooled to 15° and 3.8 g. (0.036 mole) of benzaldehyde (previously shaken with aqueous sodium carbonate) was added all at once. The ice-bath was removed, and the mixture was allowed to reach room temperature. The mixture was stirred for four hours, and the yellow solid which had separated was filtered off and crystallized twice from 95% ethanol and once from warm ethyl acetate. A faint yellow granular solid was obtained melting sharply at 134.5-135.5° (corr.)

Anal. Calcd. for $C_{25}H_{19}O_2N$: N, 3.84. Found: N, 4.09.

C. Quinoline Sulfides

8-(3-Diethylaminopropylamino)-6-quinolyl Methyl Sulfide

Dihydrochloride.- Four grams (0.029 mole) of 8-amino-6-quinolyl methyl sulfide (102), 3.75 g. (0.025 mole) of freshly distilled 3-diethylaminopropyl chloride (99) and 5.4 g. (0.02 mole) of sodium citrate were added to 25 ml. of commercial absolute ethanol, and the mixture was refluxed for forty-eight hours. It was then cooled, poured into 250 ml. of water, and made

102. Kindly supplied by Drs. S. Massie and L. Tolman. See Gilman et al., ibid., 68, 1577 (1946) for the preparation of this compound.

strongly basic with solid sodium hydroxide. The solution was extracted with ether, and after drying the ether layer over sodium sulfate it was filtered. Ethanolic hydrogen chloride was added to precipitate a yellow dihydrochloride. After several crystallizations from a 95% ethanol - ether mixture, 3.0 g. (38%) of yellow needles were obtained melting at 214-218° in a rapidly heated bath, but with some preliminary softening. The analytical sample melted at 217-220°.

Anal. Calcd. for $C_{17}H_{25}N_3S \cdot 2HCl$: Cl, 18.9; S, 8.5.
Found: Cl, 18.8; S, 8.3.

8-(2,5-Dimethyl-1-pyrryl)-6-quinolyl Methyl Sulfide (83).-

Two grams (0.01 mole) of 8-amino-6-quinolyl methyl sulfide, 1.2 g. (0.01 mole) of acetylacetone, 10 ml. of 95% ethanol and 1 ml. of glacial acetic acid were refluxed together with stirring for four hours. After cooling and standing overnight, a tan crystalline solid separated, which was filtered, washed with water, and dried. The yield was 2.5 g. (93%) of a compound melting at 145-146° with no further purification.

Anal. Calcd. for $C_{16}H_{16}N_2S$: N, 10.4. Found: N, 10.7.

8-Nitro-7-quinolyl Methyl Sulfide.- Four grams (0.019 mole) of 7-chloro-8-nitroquinoline (103) was dissolved in 35 ml. of hot methyl cellosolve, and while the solution was

103. Kindly supplied by Prof. C. D. Hurd of Northwestern University.

refluxing, 9 ml. of 3 molar sodium methyl mercaptide (in methyl cellosolve) was added dropwise over a two-minute period. After addition was complete, the solution was refluxed an additional one-half hour, then cooled and the solvent was removed under reduced pressure, leaving 4 g. of crude material. One crystallization from 95% ethanol gave 2.5 g. (60%) melting at 157-159.5°.

Anal. Calcd. for $C_{10}H_8O_2N_2S$: S, 14.5 Found: S, 14.0.

8-Amino-7-quinolyl Methyl Sulfide.- Three grams (0.0136 mole) of 8-nitro-7-quinolyl methyl sulfide was suspended in 40 ml. of commercial absolute ethanol along with one level teaspoonful of Raney nickel. The reduction was run at sixty pounds hydrogen pressure for three hours. The ethanol was partially removed under reduced pressure, and the amine was precipitated by the addition of ethanolic hydrogen chloride. The melting point of the crude material was 195-205°. Crystallization from an absolute ethanol - ether mixture gave 1.4 g. (47%) of a red crystalline hydrochloride melting at 205-210°.

Anal. Calcd. for $C_{10}H_9N_2S \cdot HCl$: Cl, 15.8. Found: Cl, 16.1.

7-Chloro-4-quinolyl Methyl Sulfide.- To 5 g. (0.025 mole) of 4,7-dichloroquinoline (104) dissolved in 50 ml. of hot methyl cellosolve was added 0.035 mole of sodium methyl

104. Kindly supplied by National Aniline Co. See Surrey and Hamner, J. Am. Chem. Soc., 68, 113 (1946) for the preparation of this compound.

mercaptide in 12 ml. of methyl cellosolve dropwise over a five-minute period. After refluxing for sixteen hours, during which time sodium chloride had precipitated, the solvent was removed under reduced pressure, and the resultant oil solidified with scratching. Two crystallizations from dilute ethanol raised the melting point to $124-5^{\circ}$. The yield of pure compound was quantitative.

Anal. Calcd. for $C_{10}H_8NSCl$: Cl, 17.0. Found: Cl, 16.9.

6-Nitro-2-quinolyl Methyl Sulfide.- To 5 g. (0.024 mole) of 2-chloro-6-nitroquinoline (105) (m.p. $222-4^{\circ}$) in 40 ml. of methyl cellosolve was added 0.024 mole of sodium methyl mercaptide in 8 ml. of the same solvent. After refluxing for three hours the solution was filtered while still hot, and from the filtrate 3 g. of tan needles separated, melting at $142-144^{\circ}$. Crystallization from methyl cellosolve raised the melting point to $148-9^{\circ}$. The yield was 57%.

Anal. Calcd. for $C_{10}H_8O_2N_2S$: S, 14.5. Found: S, 14.3.

6-Amino-2-quinolyl Methyl Sulfide.- Fourteen grams (0.064 mole) of 6-nitro-2-quinolyl methyl sulfide in 250 ml. of absolute ethanol was reduced at fifty-eight pounds of hydrogen pressure with one level teaspoon of Raney nickel catalyst for five hours. The solution had to be heated to boiling before reduction began. After filtering off the

105. Fischer and Guthmann, J. Prakt. Chem., 93, 381 (1916).

catalyst and removing the solvent under reduced pressure, there remained 11 grams (91%) of a greenish oil which solidified only slowly with cooling and scratching. The melting point of 68-72° was unchanged by distillation. The free base was converted to the hydrochloride with ethanolic hydrogen chloride and after two crystallizations from an ethanol-ether mixture it melted at 208-210°.

Anal. Calcd. for $C_{10}H_{10}N_2S \cdot HCl$: Cl, 15.7. Found: Cl, 15.9.

6-(5-Isopropylaminoamylamino)-2-quinolyl Methyl Sulfide.-

A mixture of 3 g. (0.016 mole) of 6-amino-2-quinolyl methyl sulfide, 4 g. (0.024 mole) of 1-chloro-5-isopropylaminopentane hydrochloride and 3.5 g. (0.016 mole) of sodium citrate in 20 ml. of absolute ethanol was refluxed twenty-four hours. It was then poured into 300 ml. of water; made strongly basic with sodium hydroxide and then extracted with ether. After drying the ether layer over sodium sulfate, a solid hydrochloride was precipitated by the addition of ethanolic hydrogen chloride. Four grams (68%) of a crude yellow solid was obtained which was crystallized from a 95% ethanol-ether mixture to yield 2 g. (34%) of pure material melting at 219-221°.

Anal. Calcd. for $C_{18}H_{27}N_3S \cdot 3HCl$: Cl, 25.9. Found: Cl, 25.9.

D. 7-Chloroquinolines (106)

2-Phenyl-4,7-dichloroquinoline.-- Phenyllithium was prepared in 91% yield from 11 g. (0.07 mole) of bromobenzene and 1 g. (0.14 g. atom) of lithium. Thirty-two ml. of this solution (0.034 mole) was cooled to 0° and 60 ml. of ether containing 5 g. (0.026 mole) of 4,7-dichloroquinoline (107) was added in three and one-half minutes, and the mixture was stirred an additional two and one-half minutes. After hydrolyzing with 30 ml. of water, the ether layer was separated, and the solvent was removed immediately under reduced pressure. The reddish oily residue was dissolved in a small amount of 95% ethanol and then added to a hot solution of 7 g. of picric acid in 40 ml. of ethanol. The solution turned a deep red and a solid red picrate precipitated immediately. After drying and decomposing with a 1:1 ammonium hydroxide solution, a dark brown solid resulted which after one crystallization from 95% ethanol with Norit yielded 2.5 g. (35%) of a white solid melting at 99-100°.

Anal. Calcd. for $C_{15}H_9NCl_2$: Cl, 25.9. Found: Cl, 25.4.

2-p-Methoxyphenyl-4,7-dichloroquinoline.-- To 3.8 g. (0.46 g. atom) of finely cut lithium metal suspended in 160 ml.

106. See Gilman and Benkeser, *J. Am. Chem. Soc.*, **69**, 123 (1947).
See also Gilman and Spatz, *ibid.*, **66**, 621 (1944); Gilman, Christian, and Spatz, *ibid.*, **68**, 979 (1946); Gilman, Towle, and Spatz, *ibid.*, **68**, 2017 (1946).
107. Surrey and Hammer, *ibid.*, **69**, 123 (1947).

of ether was added 37.4 g. (0.2 mole) of p-bromoanisole in 150 ml. of ether. The addition required twelve minutes and cooling by an ice bath was necessary. After addition was complete, the dark solution was stirred at room temperature for an additional eight minutes when all spontaneous reflux ceased (81).

To 200 ml. of this solution cooled to 0° was added 10 g. (0.052 mole) of 4,7-dichloroquinoline in 140 ml. of ether also cooled in ice. The addition was complete in five and one-half minutes, and the mixture was stirred another three minutes before hydrolysis with 60 ml. of water. The ether layer was separated, and the solvent was removed. The residue was dissolved in a small amount of hot 95% ethanol and was added to 14 g. of picric acid dissolved in 80 ml. of 95% ethanol. A red picrate precipitated almost immediately and was filtered off and dried. Decomposition was effected by refluxing the picrate for fifteen minutes with a 1:1 ammonium hydroxide solution. The dark brown free-base was dissolved in 500 ml. of ether and the solution was filtered to remove some insoluble material. After removal of the ether, the greenish residue melted at 117-119°. Crystallization from dilute ethanol gave 9.2 g. (58%) of a light green solid melting at 119-121°. The analytical sample was crystallized again from hot dilute ethanol and Norit and a white amorphous solid melting at 121-121.5° was obtained.

Anal. Calcd. for $C_{16}H_{11}ONCl_2$: Cl, 23.3. Found: Cl, 23.0.

2-p-Chlorophenyl-4,7-dichloroquinoline.- To 85 ml. of ether cooled to 0° and containing 0.066 mole of n-butyllithium was added 13.4 g. (0.07 mole) of p-chlorobromobenzene dissolved in 60 ml. of ether. The addition required four minutes and the solution was stirred an additional four minutes (108). To this solution was added 10 g. (0.052 mole) of 4,7-dichloroquinoline in 140 ml. of ether in a thin stream over a five and three-quarter minute period. The mixture was stirred an additional three minutes, and then hydrolyzed by the dropwise addition of 60 ml. of water. The picrate was formed as described above, and after decomposition with ammonium hydroxide, a light brown solid was obtained melting at 163-165°. Crystallization from methyl cellosolve raised the melting point to 166-167°. The yield of pure material was 12 g. or 57%.

Anal. Calcd. for $C_{15}H_8NCl_3$: Cl, 34.5. Found: Cl, 33.6.

2-p-Tolyl-4,7-dichloroquinoline. p-Tolyllithium was prepared in 80% yield from 1.4 g. lithium (0.2 g. atom) and 17.1 g. (0.1 mole) of p-bromotoluene. To 42 ml. of ether containing 0.034 mole of p-tolyllithium and cooled to 0°, was added 75 ml. of ether containing 5 g. (0.026 mole) of 4,7-dichloroquinoline and also cooled somewhat in ice. The addition required three minutes before hydrolysis with 30 ml. of water. Purification

108. Gilman, Langham, and Moore, ibid., 62, 2327 (1940); Langham, Brewster, and Gilman, ibid., 63, 545 (1941); Gilman, Langham, and Jacoby, ibid., 61, 106 (1939); Gilman and Jacoby, J. Org. Chem., 3, 108 (1938).

was effected through the picrate as described above and two crystallizations from 95% ethanol (once with Norit) gave 3.2 g. (43%) melting sharply at 124-125°.

Anal. Calcd. for $C_{16}H_{11}NCl_2$: Cl, 24.6. Found: Cl, 24.5.

2-p-Anisyl-7-chloro-4-(3-diethylaminopropylamino)quinoline.-

A mixture of 9 g. (0.029 mole) of 2-p-anisyl-4,7-dichloroquinoline, 8 g. (0.062 mole) of 3-diethylaminopropylamine (109), 18 g. of phenol and a trace of sodium iodide were heated at 160° for twenty-one hours. After cooling and pouring into 130 ml. of 35% sodium hydroxide, the solution was extracted three times with 100 ml. portions of ether. After drying the combined ether layers over sodium sulfate, the solvent was removed, leaving 7 g. of the free base. One crystallization from hot, dilute ethanol gave 6 g. (52%) melting at 118-119°.

Anal. Calcd. for $C_{23}H_{28}ON_3Cl$: Cl, 8.95. Found: Cl, 8.55.

2-p-Chlorophenyl-7-chloro-4-(3-diethylaminopropylamino)quinoline.- A mixture of 12 g. (0.039 mole) of 2-p-chlorophenyl-4,7-dichloroquinoline, 10.2 g. (0.078 mole) of 3-diethylaminopropylamine, 24 g. of phenol and a trace of sodium iodide were heated at 160° for twenty-three hours. After working up the mixture in exactly the same fashion as described above, there was obtained 9 g. (57%) of pure material melting at 127-128°.

Anal. Calcd. for $C_{22}H_{25}N_3Cl_2$: Cl, 17.6. Found: Cl, 17.2.

109. Kindly supplied by the Parke Davis Co. of Detroit, Michigan.

2-p-Tolyl-7-chloro-4-(3-diethylaminopropylamino)quinoline.-

A mixture of 4.2 g. (0.145 mole) of 2-p-tolyl-4,7-dichloroquinoline, 4.2 g. (0.0324 mole) of 3-diethylaminopropylamine, 10 g. of phenol and a trace of sodium iodide were heated at 160° for twenty-three hours. After working up as described above, there was obtained after crystallization from dilute ethanol, 2.2 g. (42%) of a white solid melting at 119.5-120.5°.

Anal. Calcd. for $C_{25}H_{28}N_3Cl$: Cl, 9.3. Found: Cl, 9.2.

2-Phenyl-7-chloro-4-quinoly-2-diethylaminoethyl Sulfide

Dihydrochloride.- In 40 ml. of absolute ethanol was added 0.23 g. (0.01 g. atom) of sodium metal, and to this solution was added 1.33 g. (0.01 mole) of 2-diethylaminoethyl mercaptan (110) in 10 ml. of absolute ethanol. Then 2 g. (0.007 mole) of 2-phenyl-4,7-dichloroquinoline was added, and the mixture was refluxed three hours. After cooling and filtering off the precipitated sodium chloride, the ethanol was removed under reduced pressure and the oily residue was dissolved in ether and again filtered. Ethanolic hydrogen chloride was added and an oil separated which solidified upon cooling. Crystallization from an ethanol-ether mixture gave 2.5 g. (81%) of a white solid melting at 165-175°.

Anal. Calcd. for $C_{21}H_{23}N_2Cl_2 \cdot 2HCl$: Cl, 24.0. Found: Cl, 23.5.

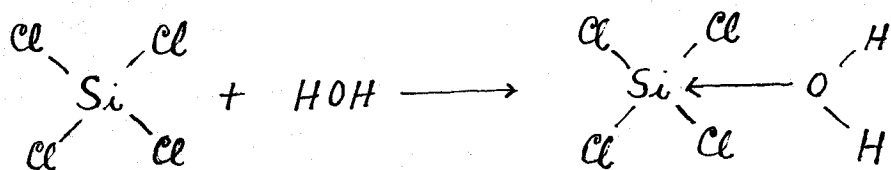
110. Gilman and Woods, J. Am. Chem. Soc., 67, 1843 (1945); Albertson and Clinton, ibid., 67, 1222 (1945); Gilman, Plunkett, Tolman, Fullhart, and Broadbent, ibid., 67, 1845 (1945).

DISCUSSION

A. Silicon Compounds

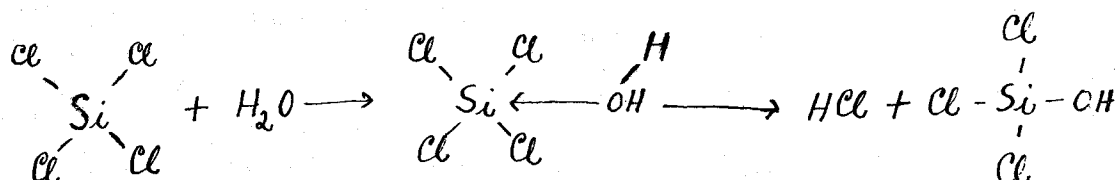
From a consideration of the position of silicon in the Periodic Table one would conclude that it should resemble carbon rather closely in most of its reactions. While this is true to some extent it soon becomes apparent even to the casual experimenter that actually this element resembles germanium and tin even more closely.

Silicon like carbon is tetravalent but unlike carbon it can expand its outer energy level to a maximum covalency of six rather than four (111). In fact it is this capacity for a covalency of six which explains the rapid hydrolysis of most silicon halides in contrast to the carbon halides which are usually much more stable. Thus it is very likely that the first step involved in the hydrolysis of silicon tetrachloride is the coordination of one molecule of water (112):

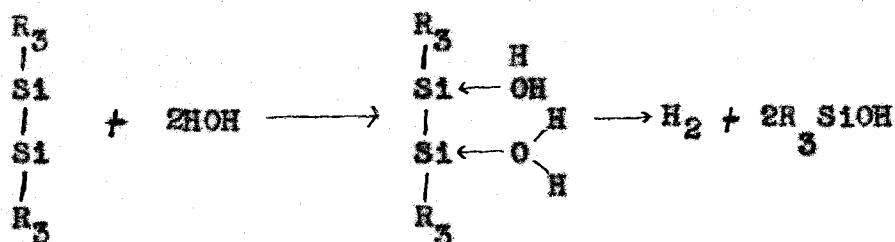


111. Sidgwick, *The Electronic Theory of Valency*, Chap. 9.
Oxford University Press, London, 1927.
112. Sidgwick, *loc. cit.*, p. 157

This coordination complex then decomposes by splitting out a molecule of the hydrogen chloride:



This process is repeated until all of the halogens have been replaced. Carbon tetrachloride, on the other hand, is completely inert toward hydrolysis because the carbon octet is complete and totally incapable of further expansion. Carbon cannot in any way attach itself to water and hence no reaction occurs. The same explanation can be offered for the rupture of silicon-silicon chains by water and hydroxyl ions while carbon chains are completely stable in the presence of these reagents. Again this is due to the power of silicon (but not carbon) to expand its valency shell: (111)



If one considers certain aspects of the organic chemistry of carbon, silicon, and germanium it becomes apparent that there is a gradation in regard to the type of reaction each will undergo. This is admirably illustrated by a consideration of substitution reactions in the three series of compounds.

Carbon compounds usually undergo substitution reactions like nitration, halogenation, Friedel Crafts, metalation etc. quite readily. Organosilicon compounds on the other hand undergo such reactions to only a very limited extent chiefly because of the instability of the carbon-silicon bond in the presence of halogens or acidic reagents. Substitution in the germanium series occurs even less readily because here the cleavage of the germanium-carbon bond becomes the principal reaction.

t-Butylbenzene (analogous to trimethylphenylsilane) if allowed to stand two hours at room temperature with a mixture of concentrated nitric and sulfuric acids yields a mixture (113) of the ortho (23%) and para (77%) isomers despite rather conflicting reports (114, 115, 116, 117, 118). No meta isomer has been detected. If this same compound is heated at 55-60° with a mixture of nitric and sulfuric acids, the 2,4-dinitro derivative is formed (117). But if the compound is refluxed 18 hours with 60 ml. of nitric acid (density 1.2) or is heated in a sealed tube with this acid, cleavage and oxidation occurs to form p-nitrobenzoic acid (117).

113. Craig, J. Am. Chem. Soc., 57, 195 (1935).

114. Senkowski, Ber., 23, 2412 (1890).

115. Baur, ibid., 27, 1610 (1894).

116. Henderson and Boyd, J. Chem. Soc., 97, 1665 (1910).

117. Malherbe, Ber., 52, 319 (1919).

118. Shoesmith and Mackie, J. Chem. Soc. 2334 (1928).

t-Butylbenzene can be brominated to form p-bromo-t-butylbenzene (119). If it is treated with iron powder and bromine at 0°, the t-butyl group is cleaved and all six ring positions are substituted to form hexabromobenzene (120). The compound can be chlorinated with sulfuryl chloride to yield B-chloro-t-butylbenzene in 70% yield (121). If it is heated with aluminum chloride and decahydronaphthalene the alkyl side chain is split off as isobutane (122).

It is interesting to contrast these reactions with those of the corresponding compounds in the silicon and germanium series. As is indicated in the experimental section, trimethylphenylsilane can be nitrated successfully at very low temperatures to yield p-nitrophenyltrimethylsilane. No meta isomer was isolated although the bromine cleavage used for structure proof did not proceed with the completeness that was desired. There was no evidence for any extensive cleavage of the silicon-phenyl bond. It is interesting to note here that Kipping was able to nitrate triethylphenylsilane and reports that 82% of the para derivative and only 5% of the meta could be isolated by fractional crystallization. Our results would seem to indicate that the trimethylsilyl-group is almost an exclusive para director. Unlike Kipping, we experienced no difficulty in

119. Chichibabin, Elgazine, and Lengold, J. Russ. Phys.-Chem. Soc., 60, 347; Bull. soc. Chim., 43, 238 (1928).

120. Hannon and Anderson, J. Am. Chem. Soc., 66, 1801 (1945).

121. Kharasch and Brown, ibid., 61, 2142 (1939).

122. Ipatieff and Pines, ibid., 59, 56 (1937).

reducing the nitro group to the amine using Raney nickel.

Attempted bromination of trimethylphenylsilane failed completely when, even under mild conditions, almost complete cleavage of the phenyl group occurred. Since no *p*-dibromobenzene was detected it must be concluded that the conditions employed were too mild to effect bromination but were vigorous enough to cause cleavage. Even with *t*-butylbenzene, however, the branched side chain can be cleaved with bromine. The instability of *t*-butylbenzene in the presence of aluminum chloride is reflected even more so in the silicon series where a symmetrical and otherwise stable compound like tetraphenylsilane is cleaved to silicon tetrachloride in 80% yields by this reagent.

Reports of successful substitution reactions in the germanium series are very meager because the principal reaction is the cleavage of the carbon-germanium bond. Thus if tetraphenylgermanium is treated with bromine in boiling carbon tetrachloride (123) or in ethylene dibromide (124) a quantitative yield of triphenylbromogermane is obtained. Also if triphenylchlorogermane is brominated an 80% yield of bromobenzene results from a cleavage of one of the phenyl groups (125).

123. Kraus and Foster, *ibid.*, 55, 3705 (1933).

124. Orndorff, Tabern, and Dennis, *ibid.*, 49, 2512 (1927).

125. Flood and Horvitz, *ibid.*, 55, 2534, (1933).

If tetraphenylgermane is warmed with concentrated sulfuric acid it sulfonates destructively with the elimination of phenyl groups (126). On the other hand tetrabenzylgermanium tetrasulfonic acid is prepared by sulfonating tetrabenzylgermane with fuming sulfuric acid below 35° (124). Shelton (127) reported that phenyltrichlorogermane could be nitrated at low temperatures to give 58% meta and 42% para substitution. But in general substitution reactions in the germanium series are not successful because of the electropositive nature of germanium and its ability to increase its valence shell to twelve electrons.

Our experimental results would seem to indicate that if the cleavage of the carbon-silicon bond can be suppressed, substitution reactions will proceed quite normally. This cleavage becomes more pronounced in mixed alkyl-aryl silicon types like trimethylphenylsilane and becomes less apparent in symmetrical compounds like tetraphenylsilane. Acidic reagents seem to facilitate the cleavage probably because they afford the electropositive silicon atom an opportunity to combine with a more electronegative element than carbon:



Halogenation might cause cleavage by a similar mechanism:



126. Morgan and Drew, J. Chem. Soc., 1760 (1925).

127. Shelton, Washington Meeting, Am. Chem. Soc. (1933).

On the other hand it might be conjectured that the organosilanes would be stable in the presence of compounds of a covalent character like butyllithium and this actually seems to be the case.

Since metalation is a type of substitution reaction, and since there are no literature reports on metalations of silicon compounds, this reaction was investigated. Triethyl-*p*-anisylsilane was metalated successfully and in the position ortho to the ether linkage. Although this is the conventional orientation it was not certain whether the triethylsilyl-group would influence the orientation, but apparently it did not. Also the triethylsilyl-group does not activate the phenyl nucleus in triethylphenylsilane sufficiently to permit metalation with butyllithium. It might be expected that more vigorous metalating agents like ethylsodium or ethylpotassium would react. Triphenyl- δ -thienylsilane was metalated successfully with butyllithium presumably in the free δ -position since thiophene itself can be dimetalated in the two δ -positions (128).

When trimethyl-9-fluorenylsilane was treated with butyllithium apparently a cleavage occurred because upon carbonation only fluorene-9-carboxylic acid was isolated.

In some cleavage studies of organosilanes by Mr. Frederick Marshall, triphenyl-2-thienylsilane was prepared by the directions

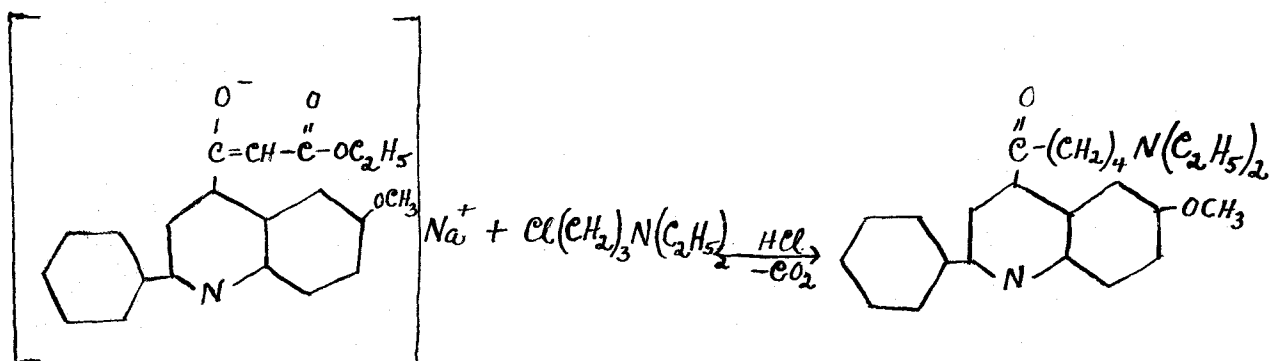
128. Unpublished Studies. David Shirley, Iowa State College.

given here and the compound melted at $195-8^{\circ}$ instead of $203-206^{\circ}$. An admixture of tetraphenylsilane raised this melting point rather than depressing it as might be expected. But upon cleavage of both samples with hydrogen chloride almost an identical amount of tetraphenylsilane was isolated. If the compound reported does contain some tetraphenylsilane it would seem impossible to remove it by crystallization.

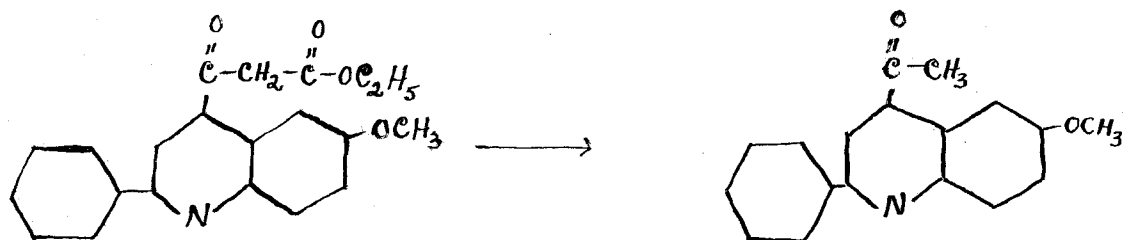
B. Quinolinemethanols

In search for a malaria cure it was discovered by Lutz (94) that compounds like α -(di-alkylaminomethyl)-6-methoxy-2-phenyl-4-quinolinemethanol were highly effective in the treatment of avian malaria and often showed activities up to thirty two times that of quinine. It was thought very appropriate to synthesize a series of these compounds with variations only in the constitution and length of the carbon chain in the 4-position. The first and most obvious approach to compounds of this sort involved an attempted alkylation of ethyl 6-methoxy-2-phenylcinchoninoylacetate (112) with 3-diethylamino-propyl chloride patterned after the method of Marvel (129):

129. Marvel, Zartman, and Bluthardt, J. Am. Chem. Soc., **49**, 2301 (1927).

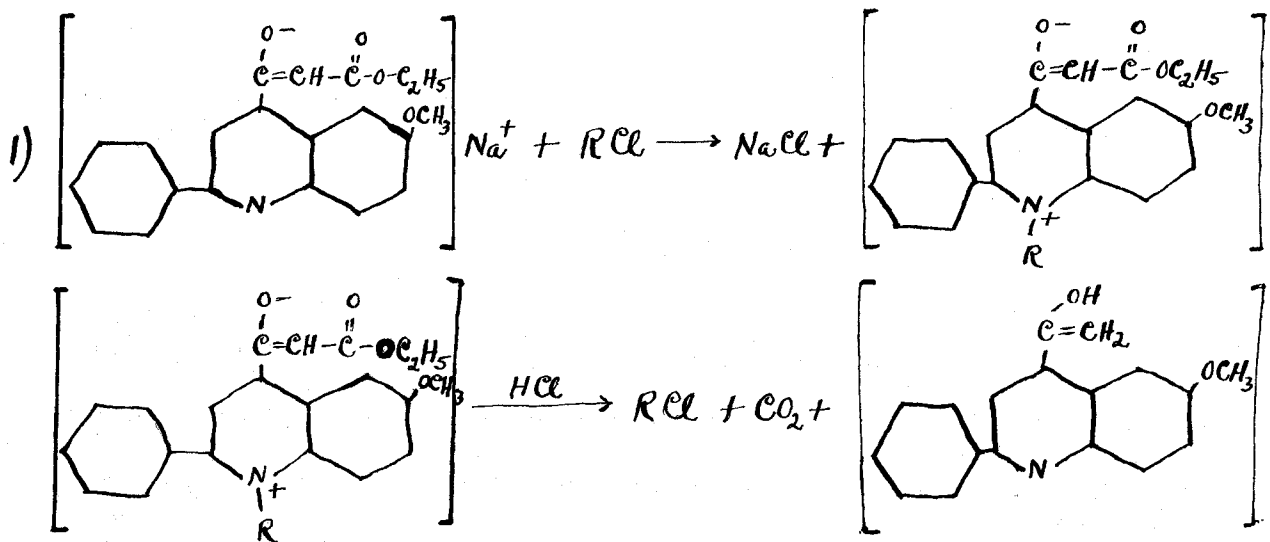


This was to be followed by a reduction of the ketone group to the carbinol. Despite several attempts to effect this alkylation none of the desired product could be isolated. Attempted alkylations using *n*-butyl iodide, ethyl iodide, *n*-butyl bromide, and propylene chlorohydrin all failed although it had been previously shown that the keto ester could be alkylated with methyl iodide (130). It is significant that in every alkylation attempt sodium halide was split out and often in theoretical amounts, but only the 4-methyl ketone was ever isolated. This latter product could have resulted only from a decarboxylation of the keto ester:

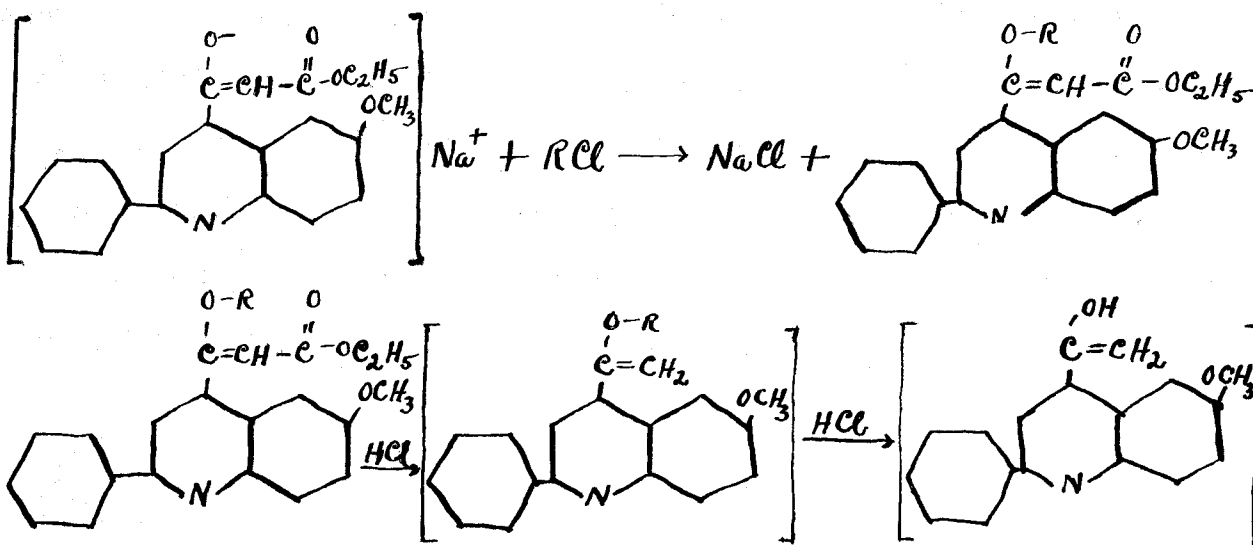


130. Unpublished Studies. Leo Tolman, Iowa State College (1945).

The presence of the sodium halide can be explained in at least one of two ways:



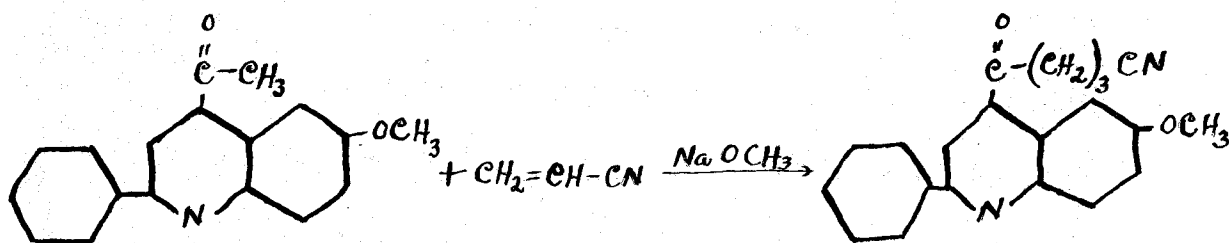
or perhaps oxygen alkylation occurred and the product thus formed was unstable:



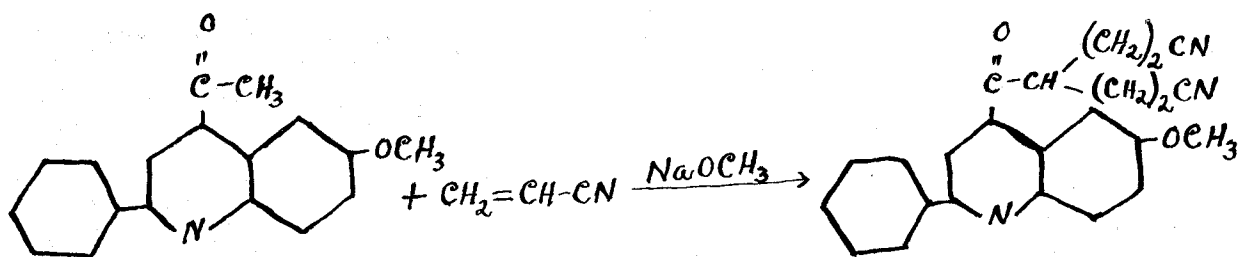
While there is no experimental evidence to support either mechanism, the first seems the more likely. The sodium halide made its appearance during the first few minutes of reaction which might be expected if the quaternary compound shown

above were formed. It is doubtful that oxygen alkylation would occur so rapidly. It is remarkable that while alkylation with methyl iodide occurs in good yield, ethyl iodide does not seem to react.

The second unsuccessful attempt involved a cyanoethylation reaction on the 6-methoxy-2-phenyl-4-quinolyl methyl ketone according to the procedure of Bruson (131). The hope was that mono-cyanoethylation would occur according to the scheme:

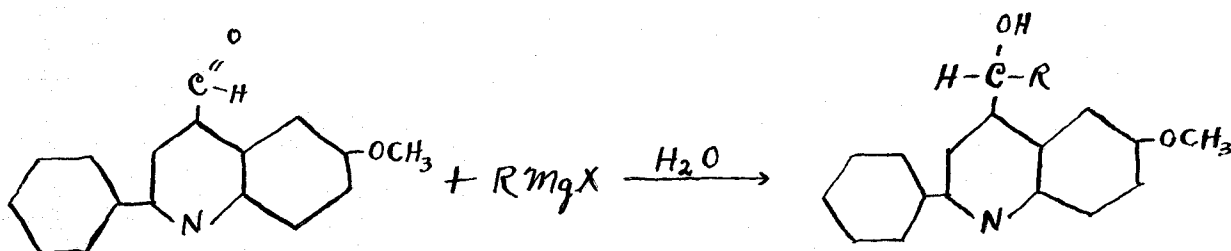


The resulting keto cyanide could then be reduced to an amino-carbinol and dialkylated. Unfortunately the method failed because di-cyanoethylation occurred:



The third attempt, and the one which proved successful, involved the Grignard reaction on 6-methoxy-2-phenyl-quinoline-4-aldehyde.

131. Bruson, J. Am. Chem. Soc., 64, 2457 (1942); (b) Bruson Riener, ibid., 64, 2850 (1942).

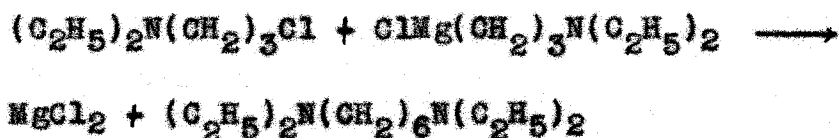


It was not known just how smoothly the above aldehyde would undergo the Grignard reaction, since occasionally in the quinoline series quaternary salt formation seems to occur with the Grignard reagent. The resulting complex is usually rather insoluble and the yields are noticeably lower. Thus Johnson and Hamilton (132) obtained a 55% yield in the reaction between quinoline-4-aldehyde and methylmagnesium iodide. But apparently the basicity of the nitrogen in 6-methoxy-2-phenylquinoline-4-aldehyde is much lower than in the unsubstituted quinoline-4-aldehyde, since it reacts with methylmagnesium iodide in an 89% yield. In fact the yields were excellent in every Grignard reaction in which this aldehyde was involved.

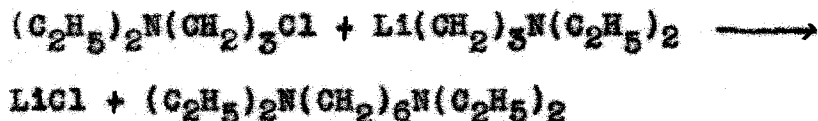
The preparation of the Grignard reagent of 3-diethylamino-propyl chloride proved rather troublesome since the mesh of the activated alloy used to initiate the reaction was found to be quite critical. In some orienting experiments alloy of 40-80 mesh was used, but the reactions failed completely. Next a block of the magnesium alloy (containing 12 3/4% copper) was obtained from the Dow Chemical Company and shavings were

132. Johnson and Hamilton, ibid., 63, 2864 (1941).

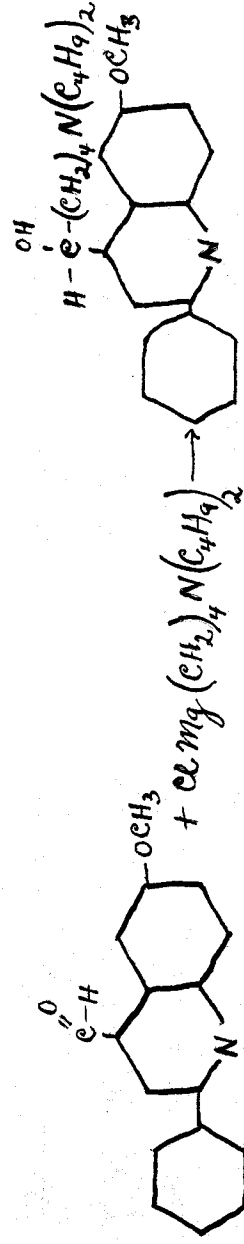
obtained from it by turning it on a lathe. In order to avoid contamination, these shavings were ground in a mortar until they were reduced to 100 mesh as measured by a standard sieve. After activation with iodine this alloy was found to be highly effective. It is to be noted that the Barbier technique was employed in this reaction to avoid as much as possible the coupling of the Grignard reagent with some unreacted chloride:



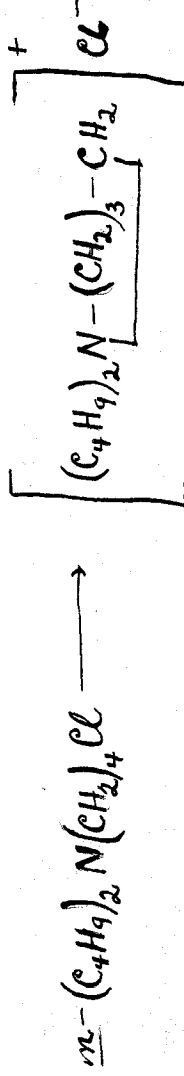
An attempt was made to employ lithium rather than magnesium in this reaction, and while a positive Color Test I was obtained occasionally, no product could be isolated. Since lithium chloride was in evidence it must be assumed that the lithium compound which formed coupled almost immediately:



In order to study more fully the effect of chain length on malarial activity it was thought desirable to synthesize a compound like α -(4-dibutylaminobutyl)-6-methoxy-2-phenyl-4-quinolinemethanol and compare its activity with its lower homolog. Again the most logical approach to this compound was the Grignard reaction using di-n-butylaminobutylmagnesium chloride:



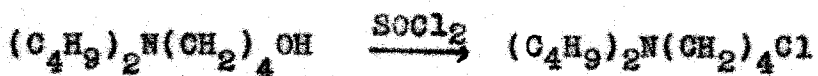
It was considered significant, however, that this chloride was not reported in the literature. It might be predicted that such a compound would be unstable due to a pronounced tendency for quaternization:



The resulting quaternary salt would contain a five-membered ring which according to the Baeyer theory is quite stable. Notwithstanding, a synthesis of the compound was attempted using the procedure employed by Marier for the propyl homolog:

$Cl-(CH_2)_3-Br + HN(C_4H_9)_2 \longrightarrow Cl-(CH_2)_3N(C_4H_9)_2$

Accordingly tetramethylene chlorobromide was treated with di-*n*-butylamine but rather surprisingly no product was isolated and only some unreacted di-*n*-butylamine was recovered. Perhaps some of the desired product was formed, but quaternized and thus separated from the reaction mixture. Another, and perhaps more positive approach to this compound would be through the carbamol:



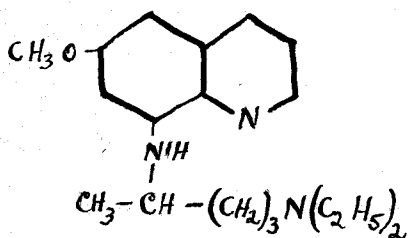
While this alcohol is at present unreported it would seem that it could be prepared by the method of Rohrmann and Schonle (133):



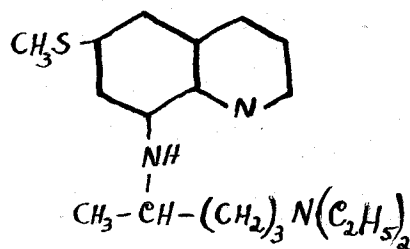
Nonetheless it is highly doubtful that the chloride would be sufficiently stable to permit it to undergo any prolonged reaction.

C. Quinoline Sulfides

Plasmochin [I] has long been known to be effective in the treatment of malaria and therefore it was thought desirable to prepare a sulfur analog of plasmochin [II] where the methoxy group is replaced by a 6-methylmercapto group.



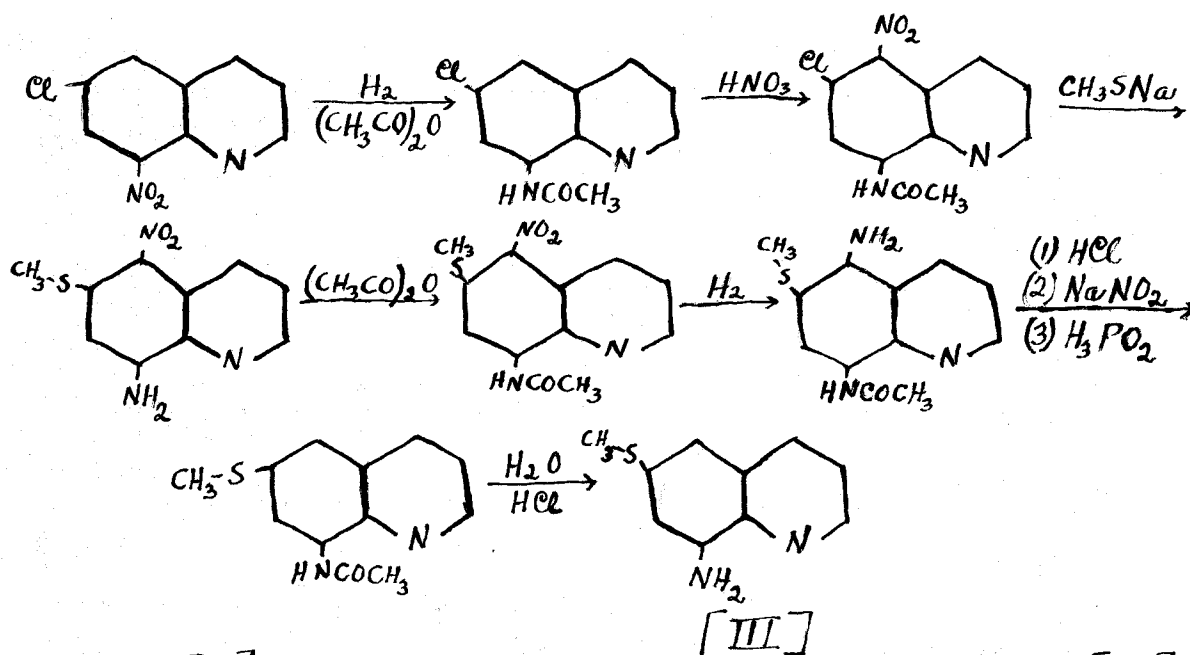
[I]



[II]

The following sequence of reactions was used in the synthesis of the sulfur analog (120):

133. Rohrmann and Schonle, *ibid.*, 66, 1640 (1944).



Compound [II] was obtained from the unsubstituted amine [III] by treating it with 3-diethylaminopropyl chloride in the presence of a sodium citrate buffer. The pH of the reaction mixture is an important factor in side-chain alkylations and the optimum value varies with the particular heterocycle and side-chain involved. Three common buffers are normally used in such reactions (134); namely, (1) sodium acetate, (2) sodium citrate, (3) an excess of the basic heterocycle itself.

Although an excess of the heterocycle often gives the best yields of the three methods mentioned, it was dismissed here as impractical because of the cost and scarcity of the amine [III]. The relative merits of sodium acetate and sodium citrate were not investigated when it was found that use of the

134. Ederfield et al., *ibid.*, 68, 1524 (1946).

latter substance produced the desired compound. The final product was very difficult to purify and the melting point was useless as a criterion of purity since the compound decomposed slightly on heating. Accordingly it was analyzed after each crystallization until the chlorine analysis was within 0.1% of the theoretical value.

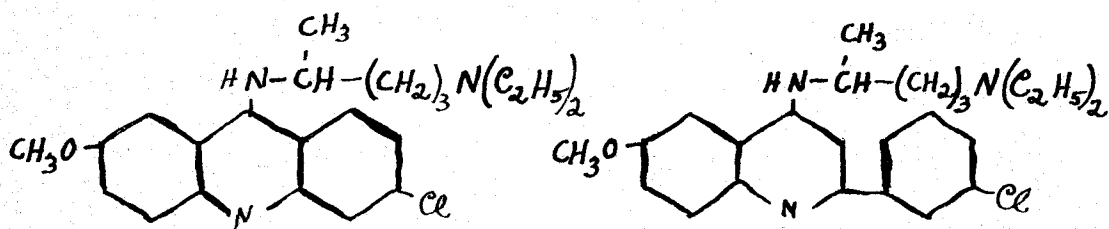
The compound 6-(5-isopropylaminoamylamino)-2-quinolyl methyl sulfide was considered of interest because compounds like 8-(5-isopropylaminoamylamino)-6-methoxyquinoline were recognized as promising antimalarials (135). Therefore it was thought desirable not only to substitute a methylmercapto group for the methoxy, but also to investigate the favorable positions in the quinoline nucleus with regard to antimalarial activity.

D. 7-Chloroquinolines

Prior to and during most of World War II atebirin I was one of the most widely used antimalarial drugs. But despite this wide usage it was recognized as having some definite disadvantages, the chief one of which was the skin bronzing which often accompanied its use. Hence several attempts were made in this laboratory to modify the structure of atebirin so as to retain its schizonticidal activity but destroy its undesirable

135. Drake et al., ibid., 68, 1529 (1946).

properties. The first step in this direction was by Gilman and Spatz (136) who prepared 6-methoxy-2-(3'-chlorophenyl)-4-[(α -methyl-4-diethylaminobutyl)-amino]-quinoline [II] and some related compounds.

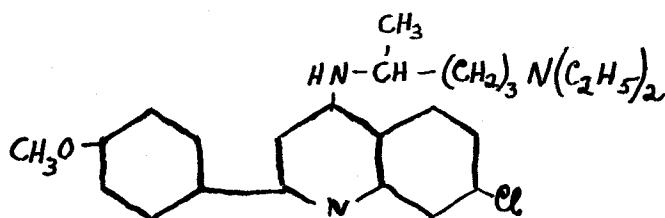


[I]

[II]

It is to be noted that the only difference between formulas [I] and [II] is that atebirin [I] contains a fused chlorobenzene group instead of the *m*-chlorophenyl group in [II]. Impetus was added to this investigation when compounds of this sort were found effective in the treatment of avian malaria. It is apparent from a study of the atebirin molecule that it is possible to "open" the other side of the molecule in the form of a *p*-methoxyphenyl group:

136. Gilman and Spatz, ibid., 66, 621 (1944).



[III]

Such a compound had been relatively inaccessible up to this time because of the difficulties in preparing 7-chloroquinoline derivatives. But since the recent availability of 4,7-dichloroquinoline (107), compounds of this type can be synthesized by an addition to the anil linkage of the appropriate RLi.

There are several points of interest connected with the preparation of the 7-chloroquinoline compounds. First of all it is to be noted that picric acid was used to oxidize the intermediate dihydro compounds produced by the anil additions. Air oxidation which is sometimes employed was found to be unsatisfactory here, and since the use of nitrobenzene entailed a troublesome steam distillation to effect its removal, another oxidizing agent was sought. Picric acid was found to be very satisfactory and no trace of the dihydro compound was ever isolated although no attempt was made to purify the crude picrate.

It is particularly striking that although the 4-chlorine in the quinoline nucleus is sufficiently reactive to undergo

condensation with 3-diethylaminopropylamine it is unreactive toward the RLi compound and there is no evidence of any coupling. On the other hand the 4-chlorine is far enough removed from the anil linkage so as to show no deactivating effect (137). A compound like 2-chloroquinoline shows no evidence for addition to the N=C group although this halogen is active enough to undergo hydrolysis or ammonolysis with ease.

137. Gilman and Spatz, ibid., 63, 1553 (1941).

SUMMARY

A thorough survey of organosilicon chemistry from 1927 to 1936 was presented.

Some general substitution reactions were investigated as to their applicability in introducing functional groups into the organosilicon molecule. Trimethylphenylsilane was successfully nitrated to yield *p*-nitrophenyltrimethylsilane. Perhaps some ortho or meta isomers were also formed, but none was isolated. The nitro group was successfully reduced to the amine.

Metalation of triethylphenylsilane with *n*-butyllithium could not be achieved, but triethyl-*p*-anisylsilane was metalated ortho to the ether linkage. Triphenyl- \mathcal{L} -thienylsilane was also metalated presumably in the free \mathcal{L} -position.

Bromination of trimethylphenylsilane could not be accomplished since the phenyl group was cleaved off as bromobenzene.

A series of di-alkylaminoalkyl-6-methoxy-2-phenyl-4-quinolinemethanols was prepared by the Grignard reaction between 6-methoxy-2-phenyl-4-quinoline aldehyde and the appropriate alkyl or aryl halides. It was hoped that these compounds would prove to be effective antimalarial agents.

A series of quinoline sulfides was prepared as well as a series of 7-chloroquinolines. The latter were patterned as "open models" of atebirin and complete the series begun by

Gilman and Spatz.

A consideration of substitution in the carbon, silicon, and germanium series is made and some theoretical aspects are discussed.