

1946

# The introduction of functional groups into some organosilanes

Russell N. Clark  
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THE INTRODUCTION OF FUNCTIONAL GROUPS  
INTO SOME ORGANOSILANES

by

Russell N. Clark

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

Iowa State College  
1946

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T8096 ✓

## TABLE OF CONTENTS

	Page
INTRODUCTION . . . . .	1
NOMENCLATURE . . . . .	2
HISTORICAL . . . . .	3
A. A Brief Review of Organosilicon Chemistry from 1863 to 1927 . . . . .	3
B. Organosilicon Chemistry from 1937 to 1946	6
Introduction . . . . .	6
Alkyl Derivatives of the Type $R_4Si$ . . .	6
Alkyl Derivatives of the Type $R'R_3Si$ . .	10
Aryl Derivatives of the Type $R_4Si$ . . .	15
Aryl Derivatives of the Type $R'R_3Si$ . . .	18
Alkyl Derivatives of the Type $RSiX_3$ . . .	18
Aryl Derivatives of the Type $RSiX_3$ . . .	25
Alkyl Derivatives of the Type $R_2SiX_2$ . .	27
Aryl Derivatives of the Type $R_2SiX_2$ . . .	30
Alkyl Derivatives of the Type $RR'SiX_2$ . .	30
Mixed Aryl-Alkyl Derivatives of the Type $RR'SiX_2$ . . . . .	32
Alkyl Derivatives of the Type $R_3SiX$ . . .	32
Aryl Derivatives of the Type $R_3SiX$ . . .	34
Alkyl Derivatives of the Type $R_2R'SiX$ . .	34
Alkyl Derivatives of the Type $(RO)_4Si$ . .	35
Aryl Derivatives of the Type $(RO)_4Si$ . .	39

	Page
Alkyl Derivatives of the Type $(RO)_3SiOR'$ .	39
Mixed Aryl-Alkyl Derivatives of the Type $(RO)_3SiOR'$ . . . . .	45
Alkyl Derivatives of the Type $(RO)_2Si(OR')_2$ . . . . .	46
Mixed Aryl-Alkyl Derivatives of the Type $(RO)_2Si(OR')_2$ . . . . .	48
Alkyl Derivatives of the Type $RSi(OR')_3$ .	49
Aryl Derivatives of the Type $RSi(OR)_3$ . .	53
Alkyl Derivatives of the Type $R_2Si(OR')_2$ .	55
Aryl Derivatives of the Type $R_2Si(OR')_2$ .	57
Alkyl Derivatives of the Type $RR'Si(OR'')_2$	59
Mixed Aryl-Alkyl Derivatives of the Type $RR'Si(OR')_2$ . . . . .	59
Alkyl Derivatives of the Type $R_3SiOR'$ . .	59
Aryl Derivatives of the Type $R_3SiOR'$ . .	61
Alkyl Derivatives of the Type $RSiOR'$ . .	61
Alkyl Derivatives of the Type $ROSIX_3$ . .	62
Aryl Derivatives of the Type $ROSIX_3$ . . .	63
Alkyl Derivatives of the Type $(RO)_2SiX_2$ .	64
Aryl Derivatives of the Type $(RO)_2SiX_2$ .	66
Alkyl Derivatives of the Type $(RO)(R'O)SiX_2$ . . . . .	66
Alkyl Derivatives of the Type $(RO)_3SiX$ .	67
Aryl Derivatives of the Type $(RO)_3SiX$ . .	69
Alkyl Derivatives of the Type $(RO)(R'O)_2SiX$ . . . . .	70



Alkyl Derivatives of the Type	Page
$(R-\overset{O}{\underset{  }{C}}-O)_n SiY_{4-n}$ . . . . .	70
Alkyl Derivatives of the Type $R_3 SiNR_2$ . . . . .	72
Alkyl Derivatives of the Type $(RS)_4 Si$ . . . . .	73
Alkyl Derivatives of the Type $(RS)_2 Si(SR')_2$ . . . . .	75
Alkyl Derivatives of the Type $(RS)_3 Si(OR')$ . . . . .	75
Alkyl Derivatives of the Type $(RS)_3 SiX$ . . . . .	75
Alkyl Derivatives of the Type $(RS)_2 SiX_2$ . . . . .	76
Alkyl Derivatives of the Type $RSSiX_3$ . . . . .	76
Alkyl Derivatives of the Type $R_3 Si-O-SiR_3$ . . . . .	76
Aryl Derivatives of the Type $R_3 SiOSiR_3$ . . . . .	78
Alkyl Derivatives of the Type $\angle(RO)_3 Si \angle_2 O$ . . . . .	79
Alkyl Derivatives of the Type $\angle RO(R'O)_2 Si \angle_2 O$ . . . . .	80
Alkyl Derivatives of the Type $\angle R_2 R' OSi \angle_2 O$ . . . . .	81
Alkyl Derivatives of the Type $\angle(RS)_3 Si \angle_2 O$ . . . . .	81
Higher Linear Siloxane Derivatives . . . . .	81
Alkyl Derivatives of the Type $\angle R_3 Si \angle_2 NR'$ . . . . .	82
Alkyl Derivatives of the Type $R_3 Si-SiR_3$ . . . . .	83
Aryl Derivatives of the Type $R_3 Si-SiR_3$ . . . . .	84
Silicon Polymers . . . . .	85
EXPERIMENTAL . . . . .	93
A. Silicon Compounds . . . . .	93

	Page
✓ Tetraethylsilane . . . . .	93
✓ Tetra- <u>n</u> -butylsilane . . . . .	94
Tetraisopropylsilane (Attempted) . . . . .	95
Tetra- <u>t</u> -butylsilane (Attempted). . . . .	97
✓ Tetraphenylsilane . . . . .	98
✓ Triphenyl- <u>p</u> -tolylsilane . . . . .	99
✓ Tri- <u>p</u> -tolylphenylsilane . . . . .	100
$\Delta$ -Picolyltriphenylsilane (Attempted). . . . .	100
Diphenyldi- <u>p</u> -tolylsilane . . . . .	102
✓ Triphenylmethylsilane . . . . .	103
✓ Trimethylphenylsilane . . . . .	104
✓ Triphenylsilanol . . . . .	104
✓ Triphenylethoxysilane . . . . .	105
✓ Trimethyl- <u>p</u> -bromophenylsilane . . . . .	106
Trimethyl- <u>p</u> -lithiophenylsilane . . . . .	108
✓ Benzyltriethoxysilane . . . . .	108
✓ Trimethylbenzylsilane . . . . .	110
Attempted bromination of trimethyl- benzylsilane . . . . .	111
Attempted nitration of trimethylbenzyl- silane . . . . .	112
✓ Phenyltriethoxysilane . . . . .	113
Attempted nitration of phenyltriethoxy- silane . . . . .	114
✓ <u>p</u> -Aminophenyltriethoxysilane . . . . .	114
✓ Triethylchlorosilane . . . . .	116

	Page
Reformatsky reaction with triphenylchlorosilane . . . . .	116
Reformatsky reaction with triethylchlorosilane . . . . .	117
Ethyl triethylsilylacetate (Attempted). . . . .	117
Ethyl triphenylsilylacetate (Attempted) . . . . .	118
Reaction between triethylchlorosilane and ethyl sodioacetoacetate . . . . .	118
Reaction of triphenylchlorosilane and ethyl sodioacetoacetate . . . . .	122
Reaction between triphenylchlorosilane and diethyl sodiomalonate . . . . .	122
Reaction of triethylchlorosilane with diethyl sodiomalonate . . . . .	123
B.	
$\beta$ -Lactams of $\beta$ -Anilino- $\beta$ -phenylpropionic Acids . . . . .	123
$\beta$ -Lactam of $\beta$ -anilino- $\beta$ -phenylpropionic acid . . . . .	123
Basic hydrolysis of the $\beta$ -lactam of $\beta$ -anilino- $\beta$ -phenylpropionic acid. . . . .	124
Acid hydrolysis of the $\beta$ -lactam of $\beta$ -anilino- $\beta$ -phenylpropionic acid . . . . .	124
Ethyl $\beta$ -anilino- $\beta$ -phenylpropionate . . . . .	125
Ethyl $\beta$ -anilino- $\beta$ -phenylpropionate . . . . .	125
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with methylmagnesium iodide . . . . .	126
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with <i>n</i> -butyllithium . . . . .	127
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with lithium diethylamide . . . . .	127
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with diethylzinc . . . . .	127

	Page
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with phenyllithium . . . .	128
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with methyllithium . . . .	128
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with phenylethynylmagnesium iodide . . . . .	129
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with phenylethynyllithium.	129
Acetomesitylene . . . . .	130
Reaction of ethyl $\beta$ -anilino- $\beta$ -phenylpropionate with acetomesitylmagnesium bromide . . . . .	130
Variation of solvent in the preparation of the $\beta$ -lactam of $\beta$ -anilino- $\beta$ -phenylpropionic acid . . . . .	130
Variation of the zinc employed in the preparation of the $\beta$ -lactam of $\beta$ -anilino- $\beta$ -phenylpropionic acid . . . . .	131
<u>o</u> -Chlorobenzal- <u>p</u> -chloroaniline . . . . .	131
$\beta$ -Lactam of $\beta$ - <u>p</u> -chloroanilino- $\beta$ - <u>o</u> -chlorophenylpropionic acid . . . . .	132
<u>p</u> -Anisal- <u>p</u> -anisidine . . . . .	132
$\beta$ -Lactam of $\beta$ - <u>p</u> -anisidino- $\beta$ - <u>p</u> -anisylpropionic acid . . . . .	132
<u>p</u> -Anisal- <u>p</u> -chloroaniline . . . . .	133
$\beta$ -Lactam of $\beta$ - <u>p</u> -chloroanilino- $\beta$ - <u>p</u> -anisylpropionic acid . . . . .	133
<u>p</u> -Anisal- <u>m</u> -chloroaniline . . . . .	134
$\beta$ -Lactam of $\beta$ - <u>m</u> -chloroanilino- $\beta$ - <u>p</u> -anisylpropionic acid . . . . .	134
<u>p</u> -Anisal- <u>o</u> -chloroaniline . . . . .	134

	Page
Attempted preparation of the $\beta$ -lactam of $\beta$ - <u>o</u> -chloroanilino- $\beta$ - <u>p</u> -anisyl- propionic acid . . . . .	135
<u>o</u> -Chlorobenzal- <u>o</u> -chloroaniline . . . . .	135
Attempted preparation of the $\beta$ -lactam of $\beta$ - <u>o</u> -chloroanilino- $\beta$ - <u>o</u> -chloro- phenylpropionic acid . . . . .	135
Benzal- <u>p</u> -chloroaniline . . . . .	136
$\beta$ -Lactam of $\beta$ - <u>p</u> -chloroanilino- $\beta$ -phenyl- propionic acid . . . . .	136
Benzal- <u>p</u> -anisidine . . . . .	136
$\beta$ -Lactam of $\beta$ - <u>p</u> -anisidino- $\beta$ -phenyl- propionic acid . . . . .	137
<u>o</u> -Chlorobenzalaniline . . . . .	137
$\beta$ -Lactam of $\beta$ -anilino- $\beta$ - <u>o</u> -chloro- phenylpropionic acid . . . . .	137
N,N'-Benzal-bis- $\Delta$ -pyridylamine . . . . .	138
Benzal- $\Delta$ -pyridylamine . . . . .	138
Attempted preparation of the $\beta$ -lactam of $\beta$ - $\Delta$ -pyridylamino- $\beta$ -phenylpropionic acid . . . . .	138
Attempted preparation of benzal- <u>o</u> -chloro- aniline . . . . .	139
Benzal- <u>o</u> -chloroaniline . . . . .	139
Attempted preparation of the $\beta$ -lactam of $\beta$ - <u>o</u> -chloroanilino- $\beta$ -phenylpropionic acid . . . . .	140
C. Phenylpyridine Derivatives . . . . .	140
2-Phenylpyridine . . . . .	140
2-Nitrophenylpyridines . . . . .	140

	Page
2-(4'-Aminophenyl)pyridine . . . . .	141
2-(4'-Benzalaminophenyl)pyridine . . . . .	142
2-(4'-Salicylalaminophenyl)pyridine . . . . .	142
2- $\sqrt{4}$ '-(2'',5''-Dimethylpyrrol-1'')phenyl]-pyridine . . . . .	142
2-(4'-Formylaminophenyl)pyridine . . . . .	143
2-(4'-Acetaminophenyl)pyridine . . . . .	143
2-(3'-Nitro-4'-acetaminophenyl)pyridine . . . . .	144
2-(3'-Nitro-4'-aminophenyl)pyridine . . . . .	145
2-(3'-Nitro-4'-formylaminophenyl)pyridine . . . . .	145
<u>p</u> -Anisyllithium . . . . .	145
2-(4'-Methoxyphenyl)pyridine . . . . .	146
2-(4'-Hydroxyphenyl)pyridine . . . . .	147
2-(3'-Nitro-4'-hydroxyphenyl)pyridine . . . . .	148
<u>p</u> -Bromothiophenol . . . . .	149
<u>p</u> -Mercaptophenyllithium . . . . .	150
2-(4'-Mercaptophenyl)pyridine . . . . .	152
$\gamma$ -( <u>p</u> -Nitrophenyl)propyl chloride (262) . . . . .	152
Diethyl- $\sqrt{\gamma}$ -( <u>p</u> -nitrophenyl)propyl]-amine . . . . .	153
Diethyl- $\sqrt{\gamma}$ -( <u>p</u> -aminophenyl)propyl]-amine . . . . .	153
2-Nitrophenylpyridines . . . . .	154
2-(2'-Aminophenyl)pyridine . . . . .	156
2- $\sqrt{2}$ '-(2'',5''-Dimethylpyrrol-1'')phenyl]-pyridine . . . . .	156
3-(2'-Aminophenyl)pyridine . . . . .	157
2-(2'-Salicylalaminophenyl)pyridine . . . . .	157

	Page
3- $\sqrt{2'}$ -(2",5"-Dimethylpyrryl-1")phenyl]-pyridine . . . . .	157
3-Nitropyridines . . . . .	158
4-(3'-Aminophenyl)pyridine . . . . .	160
3-(3'-Aminophenyl)pyridine . . . . .	161
2-(3'-Aminophenyl)pyridine . . . . .	161
2- $\sqrt{3'}$ -(2",5"-Dimethylpyrryl-1")phenyl]-pyridine . . . . .	162
2-(3'-Salicylaminophenyl)pyridine . . . . .	162
4-Nitrophenylpyridines . . . . .	163
2,6-(4',4"-Diaminodiphenyl)pyridine . . . . .	164
3-(4'-Aminophenyl)pyridine . . . . .	164
3- $\sqrt{4'}$ -(2",5"-Dimethylpyrryl-1")phenyl]-pyridine . . . . .	164
3-Nitro-4-aminoanisole . . . . .	165
3-Nitro-4-bromoanisole . . . . .	165
3-Amino-4-bromoanisole . . . . .	166
2-Amino-4-methoxybenzoic acid . . . . .	167
Attempted preparation of 2-(2'-amino-4'-methoxyphenyl)pyridine . . . . .	167
2-Nitro-4-methoxyphenylpyridines . . . . .	168
2-(2'-Amino-4'-methoxyphenyl)pyridine . . . . .	170
Deamination of 2-(2'-amino-4'-methoxyphenyl)pyridine . . . . .	171
Attempted reduction of 3(?)-(2'-Nitro-4'-methoxyphenyl)pyridine . . . . .	172
2-(4'-Nitrophenyl)thiophene . . . . .	172

	Page
2-(4'-Aminophenyl)thiophene. . . . .	173
Deamination of 2-(4'-aminophenyl)- thiophene . . . . .	174
DISCUSSION . . . . .	177
A. Silicon Compounds . . . . .	177
B. $\beta$ -Lactams of $\beta$ -Anilino- $\beta$ -phenyl- propionic Acids . . . . .	187
C. The Phenylpyridines . . . . .	189
SUMMARY . . . . .	191



## INTRODUCTION

During the eighty years since its inception, the chemistry of organosilicon compounds has, to a very great extent, concerned itself with surrounding the silicon atom with completely saturated hydrocarbon radicals. Such work has given molecules that are an end within themselves.

It was the primary purpose of this thesis to prepare, directly or indirectly, organosilanes which contain functional groups and which lend themselves to more extensive and fundamental studies. In particular, one of the broader purposes of this thesis was to investigate the general relationships between the chemistry of similar silicon and carbon molecules. In view of this purpose an effort was made to synthesize some nitrogen-containing silicon compounds to compare their properties, and incidentally their biological activity, with various nitrogen-containing carbon compounds.

## NOMENCLATURE

The nomenclature employed for the organosilicon compounds appearing throughout this work is in accord with that suggested by the Committee on Nomenclature, Spelling, and Pronunciation of the American Chemical Society (1). For the convenience of the reader a list of the more common rules of nomenclature will be reproduced here.

1. The name of the compound  $\text{SiH}_4$  is silane, the radical derived from it,  $\text{H}_3\text{Si}-$ , is silyl.

2. Compounds having the general formula  $\text{H}_3\text{Si}(\text{SiH}_2)_n\text{SiH}_3$  are called disilane, trisilane, etc., according to the number of silicon atoms present. The radicals derived from these compounds are disilyl-, trisilyl-, etc.

3. Hydroxy derivatives in which OH is attached to silicon are named by adding the suffixes ol, diol, triol, etc., to the parent compound. Thus:  $\text{H}_3\text{SiOH}$ , silanol;  $\text{H}_2\text{Si}(\text{OH})_2$ , silanediol.

4. Compounds having the formula  $\text{H}_3\text{Si}(\text{OSiH}_2)_n\text{OSiH}_3$  are called disiloxane, trisiloxane, etc., according to the number of silicon atoms present.

5. Compounds having the formula  $\text{H}_3\text{Si}(\text{NHSiH}_2)_n\text{NHSiH}_3$  are called disilazane, trisilazane, etc., according to the number of silicon atoms present.

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

## HISTORICAL

A. A Brief Review of Organosilicon Chemistry  
from 1863 to 1927.

In 1863 Friedel and Crafts (2) synthesized tetraethylsilane by heating diethylzinc with silicon tetrachloride in a sealed tube. This was the beginning of organosilicon chemistry. Two decades later Polis (3) prepared the first arylsilicon compound by the action of sodium and an aryl halide on silicon tetrachloride. Until the twentieth century, all tetraaryl- and tetraalkyl-silanes were prepared by these two methods. However, in 1904 Kipping (4) indicated that Grignard reagents could be used in the synthesis of organosilanes. Chemists rapidly adopted this method of preparation, both because of its relative ease, and because it allowed the more or less stepwise introduction of organic radicals into silicon tetrachloride. It was through this stepwise process that Kipping (5) prepared his optically active silicon compounds.

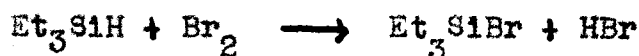
These same methods of preparation were applied (5, 6, 7) to the preparation of disilanes.

- 
2. Friedel and Crafts, Ann., 127, 28 (1863).
  3. Polis, Ber., 18, 1540 (1885).
  4. Kipping, Proc. Chem. Soc., 20, 15 (1904).
  5. Kipping, J. Chem. Soc., 92, 717 (1907).
  6. Bygdén, Ber., 45, 707 (1912).
  7. Friedel and Ladenburg, Ann., 203, 241 (1880).

The silicon to alkyl-carbon bond is relatively stable, since it resists cleavage by the halogens and the mineral acids. The silicon to aryl-carbon bond, on the other hand, is very easily broken. Thus, this bond is cleaved by the action of phosphorus pentachloride (8), bromine (9), sulfuric acid (10), nitric acid (11), and even slowly by hydrogen chloride (12).

It is interesting to note that as yet no silicon to carbon unsaturated linkage has been formed.

The halogen-organosilanes, as chlorotriethylsilane are normally formed by the action of the appropriate amount of Grignard reagent upon the silicon tetrachloride (10), or by the action of the halogen upon the corresponding organosilane (13), as:



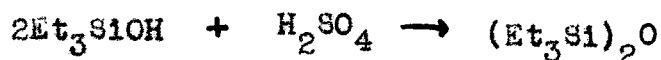
These halogen compounds readily hydrolyze in the presence of water or dilute base. In the case of the mono-halogen compounds, the corresponding silanols are obtained (14). In the instance of the dihalogen compounds, the corresponding diols are formed (15). These were then known to go very easily to

- 
8. Polis, Ber., 19, 1012 (1886).
  9. Ladenburg, ibid., 40, 2274 (1907).
  10. Kipping, J. Chem. Soc., 91, 209 (1907).
  11. Ladenburg, Ann., 173, 143 (1874).
  12. Kipping and Lloyd, J. Chem. Soc., 79, 449 (1901).
  13. Pape, Ann., 222, 354 (1884).
  14. Ladenburg, ibid., 164, 300 (1872).
  15. Robinson and Kipping, J. Chem. Soc., 93, 439 (1908).

the so-called "silicones." Now it is recognized that these "silicones" are really polymers. The trihalogen compounds also give polymeric materials on hydrolysis (16).

Alcohols react with these halogen compounds to give the corresponding ethoxy-derivatives (16). These same ethoxy-compounds were also synthesized by the action of diethylzinc and sodium on tetraethoxysilane (14).

The silanols are readily converted to the corresponding disiloxanes in the presence of common dehydrating agents (14), as:



This brief review merely highlights the salient points of organosilicon chemistry. For an extensive study of organosilicon chemistry one or more of the excellent general reference works on this subject (17, 18, 19, 20, 21, 22, 23, 24) may be consulted.

- 
16. Melzer, Ber., 41, 3390 (1908).
  17. Friend, "A Text-Book of Inorganic Chemistry", Volume XI, Part I, Charles Griffin and Company, Ltd., London, 1928, p. 246.
  18. Krause and Grosse, "Die Chemie der metall-organischen Verbindungen", Gebrüder Borntraeger, Berlin, 1937, p. 263.
  19. Grignard, DuPont, and Locquin, "Traité de chimie organique. T. XIV. Composés azotés de l'acide carbonique. Composés organoarsénies, organophosphorés ou organosilicés," Masson and Cie, Paris, 1939.
  20. Rochow, "Introduction to the Chemistry of the Silicones", John Wiley and Sons, New York, 1946.
  21. Robinson, Sci. J. Roy. Coll. Sct., 15, 24 (1945).
  22. Kipping, Proc. Roy. Soc. London, 159, 139 (1937).
  23. Hausman, J. Chem. Ed., 23, 16 (1946).
  24. Rochow and Norton, Colloid Chemistry, 6, 1092 (1946).

## B. Organosilicon Chemistry from 1937 to 1946

## Introduction

This review has attempted to record all of the organosilicon compounds abstracted in Chemical Abstracts from January 1, 1937 to September 20, 1946. The methods of preparation and the constants for the compounds reported during these years as well as their significant properties were noted.

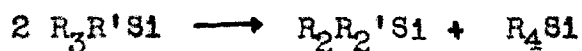
Organosilicon chemistry from 1927 to 1936 is to be reviewed in the Doctoral Dissertation of Mr. Robert A. Benkeser.

Alkyl Derivatives of the Type  $B_4Si$ 

Tetramethylsilane,  $Si(CH_3)_4$ , is prepared by the action of the methyl Grignard reagent on silicon tetrachloride for 22 hours both in ethyl ether (25), and in *n*-butyl ether (26). The pure product boils at  $26.64^\circ$  at 760 mm. (26), at  $26^\circ$  (25). Its constants are  $d^{20}$  1.0232,  $n_D^{20}$  1.3683, and  $MR_D$  33.48 ml (27). The solid compound exhibits two crystalline forms, the  $\alpha$ -form melting at  $-102$ , and the  $\beta$ -form melting at  $-99^\circ$  (26). The heat of vaporization of liquid tetramethylsilane at its normal boiling point is 5785 cal./mole (26). Other physical data are

- 
25. Whitmore and Sommer, J. Am. Chem. Soc., 68, 481 (1946).  
 26. Aston, Kennedy, and Messerly, ibid., 63, 2343 (1941).  
 27. Holzapfel, Z. Elektrochem., 47, 327 (1941) [C. A., 35, 5377 (1941)]/.

(37), 153-153.2° at 759 mm. (34), 153° at 760 mm., and 108° at 200 mm. (36). Its other constants are:  $d_4^{20}$  0.7674 (34),  $d^{20}$  0.7810,  $d^{20}$  0.7662,  $d^{60}$  0.7352 (36), and  $d^{20}$  0.7284 (27);  $n_D^{20}$  1.3832 (27), and  $n_D^{20}$  1.4268 (36); and  $MR_D$  52.14 (27). When equimolecular amounts of tetraethylsilane are allowed to react with tetra-n-propylsilane at 180° in the presence of aluminum chloride random redistribution occurs and all possible products are isolated in the theoretical, statistical proportions (38, 39). These results are somewhat in variance with those of Dolgov and Volnov (40) who found that alkyl compounds at 300° rearranged according to the scheme:



They only isolated the symmetrical compounds, ascribing this fact to their greater thermal stability. The thermal decomposition of tetraethylsilane has been studied (41) and found to be of the first order.

Tetra-n-propylsilane,  $(n-C_3H_7)_4Si$ . The thermal decomposition of this compound has also been studied (41) and found to be of the first order. It boils at 212°.

Tetra-n-butylsilane,  $(n-C_4H_9)_4Si$ , is synthesized by the 24

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38. Calingaert and Beatty, ibid., 61, 2748 (1939).  
 39. Calingaert, Soroos and Hnizda, ibid., 62, 1107 (1940).  
 40. Dolgov and Volnov, Zhur. Obshchel. Khim., 1, 91 (1931).  
C. A., 25, 4535 (1931).  
 41. Warring, Trans. Faraday Soc., 36, 1142 (1940). C. A.,  
35, 2400 (1941).

hour action of the n-butyl Grignard reagent upon an ether solution of silicon tetrachloride (34), or an ether solution of tetraethoxysilane (42). The product boils at 231° at 760 mm. (42) and at 150-153° at 17 mm. (34);  $d_4^{22}$  0.822 (42), and  $d_4^{25}$  0.8109 (34); and  $n_D^{22}$  1.4332 (42).

Sauer (30) casts ~~no~~ doubt upon the compound of Post and Hofrichter (42) by pointing out that its  $MR_D^{22}$  (obs.) is 81.12 as against a  $MR_D^{22}$  (calcd.) of 85.49. If this were the tri-n-butylethoxysilane, Sauer indicates, the molecular refractions would check within 0.2 unit.

Tetra-n-amylsilane (n-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>Si, is prepared in 80 per cent yield when n-amyl chloride and silicon tetrachloride are acted upon by sodium (37). It is also obtained (37) when sodium wire and n-amyl chloride are heated with hexachlorodisilane. The product is a colorless, odorless oil that is soluble in the common organic solvents. It boils at 313°;  $d_4^{32}$  0.8252; and  $n_D^{25}$  1.4510.

Tetra-i-amylsilane, (i-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>Si. These constants have been redetermined for this product (27);  $d^{20}$  0.8254;  $n_D^{20}$  1.4183; and  $MR_D$  107.53. No method of preparation is indicated for this compound.

Tetraallylsilane, (C<sub>3</sub>H<sub>5</sub>)<sub>4</sub>Si, is produced in 90 per cent

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



yield by the Barbier modification of the Grignard reaction from allyl chloride or bromide (43). The solvent is a mixture of benzene and ether. It boils at 102-103° at 15 mm.;  $n_D^{20}$  1.4864; and  $d_4^{20}$  0.8353. Tetraallylsilane polymerizes upon heating to 50-200° in the presence of an organic peroxide as a catalyst. It may be polymerized alone or in solvents such as toluene. It may also be co-polymerized with such compounds as vinyl acetate, styrene, etc.

#### Alkyl Derivatives of the Type R'R<sub>3</sub>Si

Trimethylsilane, (CH<sub>3</sub>)<sub>3</sub>SiH, is prepared in "poor" yield from silicochloroform and methylmagnesium bromide in ether (44). The compound boils at 9-11°.

Chloromethyltrimethylsilane, (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Cl, results from the chlorination of tetramethylsilane irradiated with ultraviolet light (25). It boils at 97.1° at 734 mm.;  $n_D^{20}$  1.4180. This preparation readily gives the Grignard reagent in 90 per cent yield.

Trimethylchloromercuriomethylsilane, (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>HgCl, is obtained by the action of mercuric chloride on the Grignard reagent of trimethylchloromethylsilane (25). It melts at 74-76°.

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43. Kropa, U. S. Pat. 2,388,161, October 30, 1945. C. A., 40, 592 (1946)<sup>7</sup>
44. Taylor and Waldon, J. Am. Chem. Soc., 66, 842 (1944).

Trimethyliodomethylsilane,  $(\text{CH}_3)_3\text{Si}(\text{CH}_2\text{I})$ , is synthesized by the action of sodium iodide on an acetone solution of trimethylchloromethylsilane (25). It boils at  $139.5^\circ$  at 744 mm.;  $n_D^{20}$  1.4917.

Trimethylethylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_2\text{H}_5)$ , is isolated from the reaction of methylmagnesium chloride on ethyltrichlorosilane first in the presence, then in the absence of ether (36). This product boils at  $25^\circ$  at 200 mm. and  $62^\circ$  at 760 mm.;  $d^{20}$  0.7040, and  $d^{20}$  0.6849; and  $n_D^{20}$  1.3820.

Trimethyl- $\alpha$ -chloroethylsilane,  $(\text{CH}_3)_3\text{SiCHClCH}_3$ . The preparation of this compound was effected through the action of methylmagnesium bromide upon  $\alpha$ -chloroethyltrichlorosilane for 14 hours (45). The compound boils at  $117.8^\circ$  at 735 mm.;  $n_D^{20}$  1.4242.

Trimethyl- $\alpha$ -chloromercurioethylsilane,  $(\text{CH}_3)_3\text{SiCH}(\text{HgCl})\text{CH}_3$ , is prepared by the action of mercuric chloride upon the corresponding Grignard reagent (45). It melts at  $97^\circ$ .

Trimethyl- $n$ -propylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_3\text{H}_7\text{-}n)$ , is synthesized from methylmagnesium bromide and  $n$ -propyltrichlorosilane in the absence of ether (36). It boils at  $49^\circ$  at 200 mm. and  $90^\circ$  at 760 mm.;  $d^{20}$  0.7197,  $d^{20}$  0.7020, and  $d^{60}$  0.6653; and  $n_D^{20}$  1.3929.

Trimethyl- $n$ -butylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_4\text{H}_9\text{-}n)$ . This synthesis is accomplished through the action of  $n$ -butyltrichlorosilane upon methylmagnesium bromide (36). The product boils at  $74^\circ$  at 200 mm.

45. Sommer and Whitmore, ibid., 68, 485 (1946).

and  $115^{\circ}$  at 760 mm.;  $d^0$  0.7352,  $d^{20}$  0.7181, and  $d^{60}$  0.6835; and  $n_D^{20}$  1.4030.

Trimethyl-n-amylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_5\text{H}_{11}\text{-n})$ , is prepared by the action of n-amyltrichlorosilane on methylmagnesium bromide in the absence of ether (36). It distills at  $95^{\circ}$  at 200 mm. and  $139^{\circ}$  at 760 mm.;  $d^0$  0.7477,  $d^{20}$  0.7313, and  $d^{60}$  0.6979; and  $n_D^{20}$  1.4030.

Trimethyl-n-hexylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_6\text{H}_{13}\text{-n})$ , is made from n-hexyltrichlorosilane and methylmagnesium bromide in the absence of ether (35). It boils at  $117^{\circ}$  at 200 mm. and  $163^{\circ}$  at 760 mm.;  $d^0$  0.7578,  $d^{20}$  0.7422, and  $d^{60}$  0.7100; and  $n_D^{20}$  1.4154.

Trimethyl-n-heptylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_7\text{H}_{15}\text{-n})$ , is synthesized through the action of methylmagnesium iodide upon n-heptyltrichlorosilane in the absence of ether (36). The compound distills at  $137^{\circ}$  at 200 mm. and  $184^{\circ}$  at 760 mm.;  $d^0$  0.7659,  $d^{20}$  0.7506, and  $d^{60}$  0.7196; and  $n_D^{20}$  1.4201.

Trimethyl-n-octylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_8\text{H}_{17}\text{-n})$  is made from methylmagnesium bromide and n-octyltrichlorosilane in the absence of ether (35). It boils at  $156^{\circ}$  at 200 mm. and  $202^{\circ}$  at 760 mm.;  $d^0$  0.7729,  $d^{20}$  0.7581, and  $d^{60}$  0.7277; and  $n_D^{20}$  1.4242.

Trimethyl-n-decylsilane,  $(\text{CH}_3)_3\text{Si}(\text{C}_{10}\text{H}_{21}\text{-n})$  is produced from methylmagnesium bromide and n-decyltrichlorosilane in the absence of ether (36). It distills at  $191^{\circ}$  at 200 mm. and  $240^{\circ}$

at 760 mm.;  $d^0$  0.7848,  $d^{20}$  0.7705, and  $d^{60}$  0.7413; and  $n_D^{20}$  1.4310.

Trimethylaurylsilane,  $(CH_3)_3Si(C_{12}H_{25}-n)$ , is synthesized by the action of trimethylchlorosilane upon laurylmagnesium bromide in the absence of ether (36). It boils at  $222^\circ$  at 200 mm. and  $273^\circ$  at 760 mm.;  $d^0$  0.7938,  $d^{20}$  0.7800, and  $d^{60}$  0.7515; and  $n_D^{20}$  1.4358.

Trimethylmyristylsilane,  $(CH_3)_3Si(C_{14}H_{29}-n)$  is produced by the action of methylmagnesium bromide upon myristyltrichlorosilane in the absence of ether (36). It distills at  $250^\circ$  at 200 mm. and  $300^\circ$  at 760 mm.;  $d^{20}$  0.7911 and  $d^{60}$  0.7634; and  $n_D^{20}$  1.4410.

Triethylmethylsilane,  $(C_2H_5)_3SiCH_3$ , is made from triethylchlorosilane and methylmagnesium bromide in the absence of ether (36), and from triethylsilane and methyllithium in ether solution (46). Methylmagnesium bromide is without action on triethylsilane (46). The compound distills at  $84^\circ$  at 200 mm.,  $127^\circ$  at 760 mm. (36), and  $127^\circ$  (46);  $d^0$  0.7600,  $d^{20}$  0.7437,  $d^{60}$  0.7107 (36), and  $d_{20}^{20}$  0.7420; and  $n_D^{20}$  1.4160 (36).

Triethyl- $\beta$ -chloroethylsilane,  $(C_2H_5)_3SiCH_2CH_2Cl$ , is prepared along with the  $\alpha$ -isomer by the action of chlorine on cooled tetraethylsilane (35). It distills at  $80-82^\circ$  at 9 mm.;  $d_{17}^{17}$  0.9158; and  $n_D^{17}$  1.4562. Triethyl- $\alpha$ -chloroethylsilane,  $(C_2H_5)_3SiCHClCH_3$ , is isolated together with the  $\beta$ -isomer when chlorine is allowed to react with tetraethylsilane (35). It boils at  $72-73^\circ$  at 9 mm.;  $d_{17}^{17}$  0.9143; and  $n_D^{17}$  1.4538.  
46. Gilman and Massie, ibid., 68, 1128 (1946).

Triethylvinylsilane,  $(C_2H_5)_3SiC_2H_3$ , is produced from the reaction of warm alkali on triethyl- $\beta$ -chloroethylsilane or by the reaction of alkali on the  $\alpha$ -isomer at  $145^\circ$  in a sealed tube (35). It boils at  $146^\circ$ ;  $d_{20}^{20}$  0.7767;  $n_D^{20}$  1.4330; and  $MR_D$  63.22. This product does not polymerize even in the presence of benzoyl peroxide or sulfuric acid.

Triethyl- $\beta$ -acetoxethylsilane,  $(C_2H_5)_3Si(CH_2)_2O_2CCH_3$ , is formed from an acetic acid solution of fused potassium acetate and triethyl- $\beta$ -chloroethylsilane (47). The compound distills at  $208-214^\circ$ .

Triethyl- $\beta$ -hydroxyethylsilane,  $(C_2H_5)_3Si(CH_2)_2OH$ , results when triethyl- $\beta$ -chloroethylsilane is refluxed with alcoholic potassium hydroxide (47). The product boils at  $190^\circ$ .

Triethyl- $i$ -propylsilane,  $(C_2H_5)_3SiC_3H_7-i$ , is synthesized from ethylmagnesium bromide and  $i$ -propyltrichlorosilane (36). It distills at  $127^\circ$  at 200 mm. and  $173^\circ$  at 760 mm.;  $d^0$  0.7868,  $d^{20}$  0.7860,  $d^{40}$  0.7724, and  $d^{60}$  0.7423; and  $n_D^{20}$  1.4308.

Triethyl- $n$ -amylsilane,  $(C_2H_5)_3SiC_5H_{11}-n$ , is prepared from the action of the  $n$ -amyl Grignard reagent upon triethylchlorosilane in the absence of ether (36). It boils at  $162^\circ$  at 200 mm. and  $211^\circ$  at 760 mm.;  $d^0$  0.7977,  $d^{20}$  0.7835, and  $d^{60}$  0.7545; and  $n_D^{20}$  1.4377.

Triethyl- $n$ -hexylsilane,  $(C_2H_5)_3SiC_6H_{13}-n$ , is produced from  
 47. Niedzielski, *ibid.*, 62, 3519 (1940).

triethylchlorosilane and n-hexylmagnesium bromide in the absence of ether (36). The product distills at 179° at 200 mm. and 230° at 760 mm.;  $d^0$  0.8018,  $d^{20}$  0.7880, and  $d^{60}$  0.7595; and  $n_D^{20}$  1.4400.

Triethyl-n-heptylsilane,  $(C_2H_5)_3SiC_7H_{15}-n$ , is made from triethylchlorosilane and n-heptylmagnesium bromide in the absence of ether (36). It distills at 196° at 200 mm. and 247° at 760 mm.;  $d^0$  0.8045,  $d^{20}$  0.7907, and  $d^{60}$  0.7627; and  $n_D^{20}$  1.4422.

Triethyl-n-octylsilane,  $(C_2H_5)_3SiC_8H_{17}-n$ , is synthesized by the action of n-octyltrichlorosilane upon ethylmagnesium bromide in the absence of ether (36). It boils at 208° at 200 mm. and at 262° at 760 mm.;  $d^0$  0.8108,  $d^{20}$  0.7971, and  $d^{60}$  0.7696; and  $n_D^{20}$  1.4438.

Triethyl-n-decylsilane,  $(C_2H_5)_3SiC_{10}H_{21}-n$ , is prepared from n-decyltrichlorosilane and ethylmagnesium bromide in the absence of ether (36). It distills at 241° at 200 mm. and 293° at 760 mm.;  $d^0$  0.8175,  $d^{20}$  0.8036, and  $d^{60}$  0.7771; and  $n_D^{20}$  1.4472.

#### Aryl Derivatives of the Type $R_4Si$

Tetraphenylsilane,  $(C_6H_5)_4Si$ , is prepared by the action of phenylmagnesium bromide upon silicon tetrachloride (48), silicon

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48. Manulkin and Yakubova, J. Gen. Chem. U.S.S.R., 10, 1300 (1940). C. A., 35, 3240 (1941)/.

tetrabromide (49), or sodium fluorosilicate (48). The Barbier modification of the Grignard reaction may also be used (49) if the resulting mixture is then heated in the absence of ether. Another mode of preparation is the action of sodium and chlorobenzene upon silicon tetrafluoride (50) or upon silicon tetrachloride in the presence of ethyl acetate as a catalyst (48). This compound is also isolated from the reaction of sodium and chlorobenzene on hexachlorodisilane and hexachlorodisiloxane (37). This product is reported to melt at  $233^{\circ}$  (37) and  $232^{\circ}$  (49). When tetraphenylsilane is acted upon by silver nitrate in absolute ethanol no cleavage is noted as there is in the case of tetraphenyltin, tetraphenyllead, and tetramethyllead (51). Nitrogen trioxide (52) and diethylbarium (53) also are without action on this compound, whereas both of these reagents cleave tetraphenyltin and tetraphenyllead. The crystalline and molecular structure of this compound have been investigated (54). The refraction of the silicon to phenyl bond and group (Si-C<sub>6</sub>H<sub>5</sub>) has been calculated as 27.43 (30). After irradiation with ultraviolet light, tetraphenylsilane displays luminescence (55). The

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49. Schumb and Saffer, J. Am. Chem. Soc., 61, 363 (1939).  
 50. Wiley, U. S. Pat. 2,238,669, April 15, 1940. C. A., 35, 4782 (1941)]  
 51. Gilman and Woods, J. Am. Chem. Soc., 65, 435 (1943).  
 52. Makarova and Nesmeyanov, J. Gen. Chem. U.S.S.R., 9, 771 (1939). C. A., 34, 391 (1940)]  
 53. Gilman, Haubein, O'Donnell, and Woods, J. Am. Chem. Soc., 67, 922 (1945).  
 54. Giacomello, Gazz. chim. ital., 68, 422 (1938). C. A., 32, 9046 (1938)]  
 55. Clapp, J. Am. Chem. Soc., 61, 523 (1939).

extinction coefficient of this molecule in a chloroform solution has been measured (56).

Tetrabenzylsilane,  $(C_6H_5CH_2)_4Si$ , may be synthesized from benzylmagnesium chloride and silicon tetrachloride (48), or sodium fluorosilicate (48, 57, 58) by use of the "forced" Grignard reaction, i. e. by the removal of the ether and heating the reactants at elevated temperatures. The compound is also isolated when silicon tetrafluoride is introduced into the stirred Grignard reagent at room temperature (59); sodium fluorosilicate will not give this product under these conditions (57). This compound melts at  $127.5^\circ$  (59),  $127^\circ$  (57), and  $125-6^\circ$  (48).

Tetra-p-tolylsilane,  $(p-CH_3C_6H_4)_4Si$ , is prepared from p-tolylmagnesium bromide and silicon tetrachloride in the absence of ether (49). The yield is only 35%. Its melting point is  $226^\circ$ . This compound luminesces after irradiation with ultra-violet light (55).

Tetra-m-tolylsilane,  $(m-CH_3C_6H_4)_4Si$ , is synthesized by the "forced" Grignard reaction between m-tolylmagnesium bromide and silicon tetrachloride in only 8% yield (49). It melts at  $148^\circ$ .

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56. Milazzo, Gazz. chim. ital., 71, 73 (1941). C.A., 37, 1928 (1943)✓
57. Soshestvenskaya, J. Gen. Chem. U.S.S.R., 8, 284 (1938). C. A., 32, 5392 (1938)✓.
58. Soshestvenskaya, ibid., 10, 1689 (1940). C. A., 35, 3240 (1941)✓
59. Medaks, ibid., 8, 291 (1938). C. A., 32, 5392 (1938)✓,



Tetra-*o*-tolylsilane,  $(\text{o-CH}_3\text{C}_6\text{H}_4)_4\text{Si}$ , could not be isolated from the "forced" Grignard reaction between *o*-tolylmagnesium bromide and silicon tetrachloride even when it was continued for three days (49). Neither could it be obtained when sodium, *o*-bromotoluene, and silicon tetrachloride were refluxed in benzene for three days (49).

Tetra-*p*-xenylsilane,  $(\text{p-C}_6\text{H}_5\text{C}_6\text{H}_4)_4\text{Si}$ , is produced from the action of sodium and *p*-chlorobiphenyl upon silicon tetrachloride or hexachlorodisilane (37) in ether. The compound melts at  $274^\circ$  and is soluble in benzene and toluene. It recrystallizes from benzene with two molecules of solvent. This product does not luminesce after irradiation with ultraviolet light (55).

#### Aryl Derivatives of the Type $\text{R}'\text{R}_3\text{Si}$

Triphenylsilane,  $(\text{C}_6\text{H}_5)_3\text{SiH}$ , reacts with  $\text{RLi}$  compounds to give *R*-substituted triphenylsilanes (46). It has a dipole moment of 0.1 D (32).

#### Alkyl Derivatives of the Type $\text{RSiX}_3$

Methyltrichlorosilane,  $\text{CH}_3\text{SiCl}_3$ , is prepared by the action of an excess of a methylmagnesium halide solution on an ether solution of silicon tetrachloride at room temperature or below (45, 60, 61). When *n*-butyl ether is employed as the solvent (60),

60. Gilliam, Liebafsky, and Winslow, J. Am. Chem. Soc., **63**, 801 (1941).

61. Rochow, U. S. Pat. 2,286,763, June 16, 1942 C. A., **36**, 7032 (1942)].

the yield falls off markedly. Methyllithium has been most recently used to prepare this product in ether solution (62). However, attempts to prepare this chlorosilane from dimethylzinc or dimethylmercury have been unsuccessful (60). Commercially, the favored preparation seems to be the one that uses the passage of methyl chloride over a silicon-catalyst alloy. The common catalysts are copper (63) and aluminum (64); the temperatures employed range from 285° to 400°. This alloy may contain as little as 50 per cent, (63, 65) and as much as 98 per cent silicon (63), but the most commonly used varieties contain 80-90 per cent silicon (66, 67). The alloy may be in the form of chips (63), porous solids (65, 66, 67, 68), or powder (58, 62). Very often the gaseous chloride is diluted with as much as 50 per cent nitrogen before beginning its passage through the reaction tube (66).

All of these preparations furnish mixtures of all the possible methylchlorosilanes which are difficult to separate both from one another and from starting material. This chlorosilane reportedly distills at 66-67° at 766 mm. (60), 66-67° at 754 mm. (60) and 64.9-65.1° (45). It melts at -90° (60),

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62. Fleming, U. S. Pat. 2,386,452, Oct. 9, 1945 [C. A., 40, 603 (1946)].
63. Rochow, J. Am. Chem. Soc., 67, 963 (1945).
64. Hurd, ibid., 67, 1545 (1945).
65. Rochow and Gilliam, U. S. Pat. 2,383,818, August 28, 1945. [C. A., 40, 348 (1946)].
66. Patnode and Schiessler, U. S. Pat. 2,381,000, August 7, 1945. [C. A., 39, 4889 (1945)].
67. Rochow, U. S. Pat. 2,380,995, August 7, 1945. [C. A., 39, 4889 (1945)].
68. Rochow and Patnode, U. S. Pat. 2,380,996, August 7, 1945. [C. A., 39, 4889 (1945)].

and has this density:  $d^{26.5}$  1.23. The silicon to chlorine bond is reported to have a length of  $2.02 \pm 0.03 \text{ \AA}$  (69) or  $2.01 \pm 0.02 \text{ \AA}$  (69), the chlorine to chlorine distance a length of  $3.27 \pm 0.03 \text{ \AA}$  (39), and the chlorine to silicon to chlorine angle a value of  $109 \pm 3^\circ$  (69). The refraction value for the silicon to chlorine bond is 7.18 mls. (30). Methyltrichlorosilane will not chlorinate under the conditions that ethyltrichlorosilane will (46).

Dichlorosilylmethyltrichlorosilane,  $\text{Cl}_2\text{HSiCH}_2\text{SiCl}_3$ , is obtained along with trichlorosilylmethyltrichlorosilane by the action of methylene dichloride upon a silicon-copper alloy heated to  $300\text{-}400^\circ$  (66). It distills at  $51\text{-}52.5^\circ$  at 10 mm.

Trichlorosilylmethyltrichlorosilane,  $\text{Cl}_3\text{SiCH}_2\text{SiCl}_3$ , is formed together with dichlorosilylmethyltrichlorosilane when methylene chloride is passed over a silicon-copper alloy at  $300\text{-}400^\circ$  (66). It boils at  $63.7\text{-}65^\circ$  at 10 mm.

Methyltribromosilane,  $\text{CH}_3\text{SiBr}_3$ , is synthesized by the passage of methyl bromide over a silicon-copper alloy at a temperature ranging from  $250\text{-}400^\circ$  (63, 67, 68). The compound distills at  $133.5^\circ$  (63).

69. Livingston and Brockway, J. Am. Chem. Soc., **68**, 719 (1946); ibid., **66**, 94 (1944).

Methyltriiodosilane,  $\text{CH}_3\text{SiI}_3$ . This and the other iodosilanes have apparently been prepared in low yield, but have not been isolated (63, 67, 68).

Methyltrifluorosilane,  $\text{CH}_3\text{SiF}_3$ , is formed catalytically from a copper-silicon alloy and silicon tetrafluoride at 250-400° (63, 67, 68), and from the action of hydrogen fluoride upon cooled methyltrichlorosilane (70). This product boils at -28° and is immediately hydrolyzed by water (70). It is thermally stable to 400°, and only decomposes slowly at 600°.

Thiocyanotrichlorosilane,  $\text{SiCl}_3\text{SCN}$ , is formed from silicon thiocyanate and silicon tetrachloride; a small quantity of silicon thiocyanate is present as an impurity (71). The compound boils at 129.5°, melts at  $75 \pm 2^\circ$ , has a heat of vaporization of 9420 cal./mol., and these constants:  $n^{20}$  1.5091, and  $d^{24}$  1.461.

Ethyltrichlorosilane,  $\text{C}_2\text{H}_5\text{SiCl}_3$ , is synthesized by the prolonged action of the Grignard reagent upon silicon tetrachloride (45), by the immediate action of ethyllithium on silicon tetrachloride (62), and directly by the action of ethyl chloride upon a silicon-copper alloy at elevated temperatures (63, 67, 68). The compound boils at 99-100° (45), and 100° (62).

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70. Pearson, Brice, and Simons, ibid., 67, 1769 (1945).  
 71. Anderson, ibid., 67, 223 (1945).

$\alpha$ -Chloroethyltrichlorosilane,  $\text{CH}_3\text{CHClSiCl}_3$ , is produced along with the  $\beta$ -isomer when ethyltrichlorosilane is treated with thionyl chloride in the presence of benzoyl peroxide (45). The compound distills at  $138^\circ$  at 734 mm. Only the silicon chlorine atoms can be titrated.

$\beta$ -Chloroethyltrichlorosilane,  $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ , is formed together with the  $\alpha$ -isomer when ethyltrichlorosilane is treated with thionyl chloride (45). It distills at  $152^\circ$  at 734 mm. All of the chlorine may be titrated in this compound.

$\beta$ -Trichlorosilylethyltrichlorosilane,  $\text{Cl}_3\text{Si}(\text{CH}_2)_2\text{SiCl}_3$ , is made when ethylene chloride is passed over a heated copper-silicon alloy (66). The product distills at  $92.5\text{--}93^\circ$  at 25 mm., and melts at  $27\text{--}29^\circ$ .

Ethyltribromosilane,  $\text{C}_2\text{H}_5\text{SiBr}_3$ , is apparently prepared by the passage of ethyl bromide through a heated tube containing a copper-silicon alloy (63, 67, 68). Actually, though, no compound has been isolated as such.

Ethyltrifluorosilane,  $\text{C}_2\text{H}_5\text{SiF}_3$ , is formed when ethyltrichlorosilane is added to zinc fluoride at  $55^\circ$  (72) or when "ethyl silicic acid" is heated with sulfuric acid and calcium fluoride (72). It melts at  $-105^\circ$  and distills at  $-4.4^\circ$  at 760 mm.

Vinyltrichlorosilane,  $\text{C}_2\text{H}_3\text{SiCl}_3$ , is prepared from the

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72. Emeléus and Wilkins, J. Chem. Soc., 454 (1944).

action of quinoline upon a mixture of  $\alpha$ - and  $\beta$ -chloroethyltrichlorosilanes (73). It occurs as a by-product of the action of quinoline on the chlorination product of diethyldichlorosilane (73). Another mode of preparation is through the action of vinyl chloride on a heated copper-silicon alloy (73). It boils at  $92^{\circ}$ ;  $d_{27}^{27}$  1.264. This compound, and others like it, hydrolyzes without loss of unsaturation.

n-Propyltrichlorosilane,  $n\text{-C}_3\text{H}_7\text{SiCl}_3$ , is furnished from the reaction between the Grignard reagent and silicon tetrachloride (74). It boils at  $122\text{-}124^{\circ}$  at 734 mm.

$\alpha$ -Chloro-n-propyltrichlorosilane,  $\text{CH}_3\text{CH}_2\text{CHClSiCl}_3$ , is formed together with the  $\beta$ - and  $\gamma$ -isomers when thionyl chloride is heated with n-propyltrichlorosilane (74). It distills at  $157^{\circ}$  at 739 mm.

$\beta$ -Chloro-n-propyltrichlorosilane,  $\text{CH}_3\text{CHClCH}_2\text{SiCl}_3$ , is produced along with the  $\alpha$ - and  $\gamma$ -isomers when thionyl chloride and n-propyltrichlorosilane react (74). It boils at  $162^{\circ}$  at 729 mm.

$\gamma$ -Chloro-n-propyltrichlorosilane,  $\text{Cl}(\text{CH}_2)_3\text{SiCl}_3$ , results from the action of thionyl chloride upon n-propyltrichlorosilane together with the  $\beta$ - and  $\gamma$ -isomers. It distills at  $178.5^{\circ}$  at 732 mm. (74).

73. Hurd, J. Am. Chem. Soc., 67, 1813 (1945).

74. Sommer, Dorfman, Goldberg, and Whitmore, ibid., 68, 488 (1946).

Allyltrichlorosilane,  $C_3H_5SiCl_3$ , is prepared when allyl chloride is passed over a heated copper-silicon alloy; the di- and triallylchlorosilanes are isolated also. It boils at  $117.5^\circ$ ;  $d_{27}^{27}$  1.211 (73).

n-Butyltrifluorosilane,  $n-C_4H_9SiF_3$ , is produced from the reaction of hydrogen fluoride with n-butyltrichlorosilane. It distills at  $50-52^\circ$ ;  $d_4^{26.5}$  1.006. (70).

n-Amyltrichlorosilane,  $n-C_5H_{11}SiCl_3$ , is made from the Grignard reagent and silicon tetrachloride in an ether solution (36). It boils at  $107^\circ$  at 120 mm.

n-Amyltrifluorosilane,  $n-C_5H_{11}SiF_3$ , is made from hydrogen fluoride and the corresponding trichloro-compound (70). It distills at  $77^\circ$ ;  $d_4^{26.5}$  0.9923.

n-Hexyltrichlorosilane,  $n-C_6H_{13}SiCl_3$ , is produced from n-hexylmagnesium bromide and silicon tetrachloride either in an ether solution (36), or in a toluene solution (75). It distills at  $127^\circ$  at 98 mm.

n-Octyltrichlorosilane,  $n-C_8H_{17}SiCl_3$ , is synthesized from the Grignard reagent and silicon tetrachloride in an ether solution (36). It boils at  $119^\circ$  at 28 mm.

n-Decyltrichlorosilane,  $n-C_{10}H_{21}SiCl_3$ , results from the reaction between n-decylmagnesium bromide and silicon tetrachloride in an ether solution. It distills at  $183^\circ$  at 84 mm. (36).

75. Andrianov and Gribanova, J. Gen. Chem. U.S.S.R., 8, 552 (1938). [C. A., 32, 7892 (1938)].

Lauryltrichlorosilane,  $n\text{-C}_{12}\text{H}_{25}\text{SiCl}_3$ , is prepared from laurylmagnesium bromide and silicon tetrachloride in an ether solution. It boils at  $120^\circ$  at 3 mm.

Myristyltrichlorosilane,  $n\text{-C}_{14}\text{H}_{29}\text{SiCl}_3$ , is formed from myristylmagnesium bromide and silicon tetrachloride in an ether solution. It distills at  $156^\circ$  at 3 mm. (36).

#### Aryl Derivatives of the Type $\text{RSiX}_3$

Phenyltrichlorosilane,  $\text{C}_6\text{H}_5\text{SiCl}_3$ , is formed by the action of phenylmagnesium bromide (45) or phenyllithium (62) upon an ether solution of silicon tetrachloride. It also results from the action of phenylsodium on silicon tetrachloride in petroleum ether (76), and from the action of benzene on silicon-chloroform or silicon tetrachloride at  $750^\circ$  in the presence of quartz (77). Industrially, the compound is synthesized by the "direct method", employing the action of chlorobenzene on a silicon-metal alloy heated at  $250^\circ$  to  $680^\circ$ . Although a copper-silicon alloy seems to be most commonly used in this reaction (63, 65, 67, 68), it has been discovered (78) that a 10 per cent silver-silicon alloy gives the highest yields of phenyltrichlorosilane. Moreover, if a trace of hydrogen chloride is employed in the reaction using a silicon-copper alloy, the yields are found to increase. The reaction

76. Schumb and Sutter, J. Am. Chem. Soc., 63, 93 (1941).

77. Miller and Schreiber, U. S. Pat. 2,379,821, July 3, 1945. C. A., 39, 4619 (1945).

78. Rochow and Gilliam, J. Am. Chem. Soc., 67, 1772 (1945).



temperature reported varies from 680° (78) to 570° (78) to 420° (63) to 400° (67) to 230° (63). This product distills at 201° (63), 201.5° (78), 198° at 744 mm. (45), 195-200° (62, 64), and 71-74° at 11 mm. (77). Phenyltrichlorosilane does not chlorinate under the conditions that ethyltrichlorosilane (45) does.

Phenyltribromosilane,  $C_6H_5SiBr_3$ , is prepared by the reaction of bromobenzene and a copper-silicon alloy at 250-400° (63, 67, 68). Its constants are unreported.

Phenyltrifluorosilane,  $C_6H_5SiF_3$ , results from the action of hydrogen fluoride (70) or zinc fluoride (72) on phenyltrichlorosilane, or from the reaction of calcium fluoride, sulfuric acid, and "phenylsiliconic acid" (72). It distills at 101-102° (70) and 101.8° at 760 mm.;  $d_4^{17}$  1.212 (65), and  $d_4^{26.5}$  1.201.

2-Methoxy-5-bromophenyltrichlorosilane, 2-CH<sub>3</sub>-5-Br- $C_6H_3SiCl_3$ , is prepared from the corresponding lithium compound and silicon tetrachloride (62). It distills at 130-140° at 13 mm.

Benzyltrichlorosilane,  $C_6H_5CH_2SiCl_3$ , is produced from the corresponding magnesium (45) or lithium compound (62) and silicon tetrachloride. It boils at 145-148° at 100 mm.

$\alpha$ -Chlorobenzyltrichlorosilane,  $C_6H_5CHClSiCl_3$ , is synthesized by heating thionyl chloride with benzyltrichlorosilane in the presence of a catalyst. It distills at 162° at

75 mm. (45).

Alkyl Derivatives of the Type R<sub>2</sub>SiX<sub>2</sub>

Dimethyldichlorosilane, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, is commonly prepared by the action of a methylmagnesium halide on silicon tetrachloride in ethyl ether (60, 61, 79) or in n-butyl ether (60). Methyl lithium and silicon tetrachloride also give this product (62), as does methyltrichlorosilane and a methylmagnesium halide (80). It is also produced by the action of hydrogen (64) or methyl chloride (64) on methyltrichlorosilane at about 500°. For the direct production of this methylchlorosilane catalytically see methyltrichlorosilane; the methods are identical. Dilution with nitrogen is particularly effective in this case giving yields as high as 86 per cent (81). A special modification of the general silicon-alloy procedure for the preparation of methylchlorosilanes which gives excellent yields of dimethyldichlorosilane is that which involves the mingling of the gaseous halide and powdered alloy dust before entrance into a heating chamber kept at 1000° (82). Dimethyldichlorosilane boils at 70° (64), 70° at 757 mm. (79), 69.0 - 70.2° at 744 mm. (60), and 70° at 740 mm. (79), and melts at -86° (60); density: d<sup>25</sup> 1.06 (60). This

79. Hyde and DeLong, ibid., 63, 1194 (1941).

80. Gilliam and Sauer, ibid., 66, 1793 (1944).

81. Sprung and Gilliam, U. S. Pat. 2,380,999, August 7, 1945. [C. A., 39, 4889 (1945)].

82. Reed and Coe, U. S. Pat. 2,389,931, November 27, 1945. [C. A., 40, 1536 (1946)].

compound gives no reaction with hydrogen (60) and is used to reclaim silicone elastomers (83). The silicon to chlorine bond measures  $1.99 \pm 0.03 \text{ \AA}$ , the silicon to carbon bond  $1.83 \pm 0.06 \text{ \AA}$ , the chlorine to chlorine distance  $3.25 \pm 0.04 \text{ \AA}$ , and the carbon to chlorine distance  $3.12 \pm 0.06 \text{ \AA}$  (69).

Dimethyldibromosilane,  $(\text{CH}_3)_2\text{SiBr}_2$ , is prepared in the same way as methyltribromosilane (63, 67, 68). It distills at  $112.3^\circ$ .

Dimethyldifluorosilane,  $(\text{CH}_3)_2\text{SiF}_2$ , is formed from dimethyldichlorosilane and hydrogen fluoride (70). It is synthesized catalytically from methyl fluoride in the same way as methyltrifluorosilane. It boils at  $2^\circ$ .

Diethyldichlorosilane,  $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$ , is produced from the reaction of silicon tetrachloride with ethylmagnesium bromide (79, 84) or with ethyllithium (62). It may also be formed directly from ethyl chloride and a silicon alloy (63, 67, 68). It distills at  $130^\circ$  (62), and  $131^\circ$  at 740 mm. (79).

Diethyldifluorosilane,  $(\text{C}_2\text{H}_5)_2\text{SiF}_2$ , results from the reaction of diethyldichlorosilane with zinc fluoride (72) or "diethyl silicone" with calcium fluoride and sulfuric acid (72). It melts at  $-78.7^\circ$  and distills at  $60.9^\circ$  at 760 mm. and  $59.7^\circ$  at 726 mm. The compound is only very slowly hydrolyzed by water and has the odor of wintergreen.

83. Wright and Oliver, U. S. Pat. 2,392,713, January 8, 1946.  
J. C. A., 40, 4556 (1946).
84. Alfrey, Honn, and Mark, J. Polymer Sci., 1, 102 (1946).  
J. C. A., 40, 3396 (1946).

Divinyldichlorosilane,  $(C_2H_3)_2SiCl_2$ , is synthesized from the chlorination product of diethyldichlorosilane by the action of quinoline (73), or by the action of vinyl chloride on a heated copper-silicon alloy (73). It distills at 118-119°, or 124°;  $d_{27}^{27}$  1.088.

Diallyldichlorosilane,  $(C_3H_5)_2SiCl_2$ , results from the action of allyl chloride on a copper-silicon alloy (73). It boils at 165 ± 2° at 760 mm. and 82-84° at 50 mm. The compound is stable on storage.

Di-n-butyl difluorosilane,  $(n-C_4H_9)_2SiF_2$ , is made from hydrogen fluoride and the corresponding chloro-compound. It boils at 154°;  $d_4^{26.5}$  0.9048 (70).

Di-n-amyl difluorosilane,  $(n-C_5H_{11})_2SiF_2$ , is formed from the action of hydrogen fluoride upon the corresponding dichloro-compound (70). It distills at 193°;  $d_4^{26.5}$  0.8972.

Tri(dichlorosilylmethylene),  $(Cl_2SiCH_2)_3$ , is produced when a mixture of methylene chloride and dry nitrogen are passed over a silicon-copper alloy (68, 85). It boils at 120-137° at 10 mm. and melts at 81-82.5°.

n(Dichlorosilylmethylene),  $(Cl_2SiCH_2)_n$ , is isolated in the preparation of the previous compound. It distills at 200° at 10 mm. (68, 85).

85. Patnode and Schiessler, U. S. Pat. 2,381,002, August 7, 1945. [C. A., 39, 4888 (1945)].

Aryl Derivatives of the Type  $R_2SiX_2$

Diphenyldichlorosilane,  $(C_6H_5)_2SiCl_2$ , is made from silicon tetrachloride and either phenylmagnesium bromide (79) or phenyllithium (62). For the catalytic preparation of this compound see phenyltrichlorosilane since these compounds are prepared at the same time by the same method. Diphenyldichlorosilane boils at  $305^\circ$  (63, 78) and  $160^\circ$  at 10-11 mm. (79).

Diphenyldibromosilane,  $(C_6H_5)_2SiBr_2$ , is prepared catalytically from bromobenzene and a copper-silicon alloy (63, 67, 68). It distills at  $170-180^\circ$  at 12 mm. (63).

Diphenyldifluorosilane,  $(C_6H_5)_2SiF_2$ , is synthesized from the corresponding dichloro-compound and either zinc fluoride (72), or hydrogen fluoride (70). It distills at  $246-247^\circ$  (70),  $252^\circ$  at 760 mm., and  $158^\circ$  at 50 mm. (72);  $d_4^{24}$  1.145 (72), and  $d_4^{26.5}$  1.155 (70).

Dibenzoyldichlorosilane,  $(C_6H_5CH_2)_2SiCl_2$ , boils at  $172-173^\circ$  at 8 mm. and forms a thick oil when heated with diphenylolpropane (86).

Alkyl Derivatives of the Type  $RR'SiX_2$

Methyldichlorosilane,  $CH_3(H)SiCl_2$ , is formed from the

86. Hanford, U. S. Pat. 2,386,793, October 16, 1945.  
 [C. A., 40, 604 (1946)].

action of hydrogen and methyl chloride on a heated copper-silicon alloy (87), or from the action of hydrogen on methyltrichlorosilane in the presence of an aluminum catalyst (64). It distills at  $41^{\circ}$  (64).

(Chloromethyl)methyldichlorosilane,  $(\text{ClCH}_2)\text{CH}_3\text{SiCl}_2$ , results from the chlorination of dimethyldichlorosilane. It distills at  $121.3^{\circ}$  (88).

(Dichloromethyl)methyldichlorosilane,  $(\text{Cl}_2\text{CH})\text{CH}_3\text{SiCl}_2$ , is formed when chlorine acts upon dimethyldichlorosilane. It boils at  $107\text{--}108^{\circ}$  at 225 mm. (88).

(Trichloromethyl)methyldichlorosilane,  $(\text{CCl}_3)\text{CH}_3\text{SiCl}_2$ , is prepared from chlorine and dimethyldichlorosilane. It distills at  $109^{\circ}$  at 150 mm. and melts at  $99^{\circ}$  (88).

$\alpha$ -Chloroethylmethyldichlorosilane,  $(\text{CH}_3\text{CHCl})\text{CH}_3\text{SiCl}_2$ , is produced from thionyl chloride and ethylmethyldichlorosilane (73). It boils at  $135\text{--}136^{\circ}$ .

$\beta$ -Chloroethylmethyldichlorosilane,  $(\text{CH}_2\text{ClCH}_2)\text{CH}_3\text{SiCl}_2$ , is formed from thionyl chloride and ethylmethyldichlorosilane (73). It distills at  $156\text{--}157^{\circ}$ .

Vinylmethyldichlorosilane,  $(\text{C}_2\text{H}_3)\text{CH}_3\text{SiCl}_2$ , is made either from the action of quinoline on a mixture of  $\alpha$ - and  $\beta$ -chloroethylmethyldichlorosilanes (73), or from the action

87. Sprung and Gilliam, U. S. Pat. 2,380,998, August 7, 1945  
 [C. A., 39, 4889 (1945)].

88. Krieble and Elliot, J. Am. Chem. Soc., 67, 1810 (1945).

of methylmagnesium bromide on vinyltrichlorosilane (73). It distills at  $92-93^{\circ}$ ;  $d_{27}^{27}$  1.085.

Allyldichlorosilane,  $(C_3H_5)HSiCl_2$ , is synthesized from allyl chloride and a copper-silicon alloy (73). It distills at  $97^{\circ}$ ;  $d_{27}^{27}$  1.086.

Allylmethyldichlorosilane,  $(C_3H_5)CH_3SiCl_2$ , is formed from methylmagnesium bromide and allyltrichlorosilane (73). It boils at  $119-120^{\circ}$ ;  $d_{27}^{27}$  0.922.

#### Mixed Aryl-Alkyl Derivatives of the Type $RR'SiX_2$

Phenylmethyldichlorosilane,  $(C_6H_5)CH_3SiCl_2$ , is formed from methyltrichlorosilane and a phenylmagnesium halide ether solution (79). It boils at  $82.5^{\circ}$  at 83 mm.;  $d_{25}^{25}$  1.1875.

Phenylethyldichlorosilane,  $(C_6H_5)C_2H_5SiCl_2$ , results from the action of phenyllithium (62) or phenylmagnesium bromide (79) on ethyltrichlorosilane. It distills at  $100^{\circ}$  at 13 mm. (79) and at  $225-235^{\circ}$  (62).

#### Alkyl Derivatives of the Type $R_3SiX$

Monocyanosilane,  $H_3SiCN$ , is prepared by passing moniodosilane over silver cyanide at room temperature under a pressure of 25 mm. (89). It melts at  $34^{\circ}$ .

89. Emeléus, Maddock, and Reid, J. Chem. Soc., 353 (1941).

Trimethylchlorosilane,  $(\text{CH}_3)_3\text{SiCl}$ , is manufactured commercially from methyl chloride and a silicon-copper alloy (see methyltrichlorosilane). It is also produced from the action of methylmagnesium chloride on a mixture of dimethyldichlorosilane and methyltrichlorosilane (80), and from the action of hydrogen or methyl chloride on dimethyldichlorosilane or methyltrichlorosilane in the presence of aluminum (64).

Chlorine with trimethylsilane (44), or phosphorus pentachloride with trimethylethoxysilane (90) also gives this product. It boils at  $57-59^\circ$  at 747 mm.,  $59^\circ$  at 760 mm. (44),  $58^\circ$  at 743 mm. (90)  $57.7^\circ$  at 760 mm. (80), and  $57^\circ$  (64). It melts at  $-40^\circ$  (44);  $d_{27}^{27}$  0.8536 (80) and  $d_4^{25}$  0.846.

Trimethylbromosilane,  $(\text{CH}_3)_3\text{SiBr}$ , is produced from methyl bromide and dimethyldibromosilane in the presence of aluminum (64). It boils at  $80-81^\circ$ .

Triethylchlorosilane,  $(\text{C}_2\text{H}_5)_3\text{SiCl}$ , is made from ethyl chloride and heated copper-silicon alloy (63). It has a dipole moment of 2.07 D (91).

Tri-n-butylfluorosilane,  $(\text{n-C}_4\text{H}_9)_3\text{SiF}$ , is formed from hydrogen fluoride and the corresponding chlorosilane. It distills at  $212-224^\circ$ ;  $d_4^{26.5}$  0.8465. This compound hydrolyzes only with difficulty (70).

90. McGregor and Warrick, U. S. Pat. 2,386,488, October 9, 1945. [*C. A.*, 40, 592 (1946)].

91. Malatesta and Pizzoti, *Gazz. chim. ital.*, 73, 143 (1943). [*C. A.*, 38, 3885 (1944)].



Tri-n-amyfluorosilane,  $(n-C_5H_{11})_3SiF$ , is obtained from hydrogen fluoride and tri-n-amychlorosilane. It boils at  $263-266^\circ$ ;  $d_4^{26.4}$  0.8415 (70).

Aryl Derivatives of the Type  $R_3SiX$

Triphenylchlorosilane,  $(C_6H_5)_3SiCl$ , is obtained in small yield along with the other phenylchlorosilanes when phenyllithium reacts with silicon tetrachloride (62) and when chlorobenzene reacts with a heated copper-silicon alloy (78). It distills at  $378^\circ$  (73).

Triphenylfluorosilane,  $(C_6H_5)_3SiF$ , is made from the action of phenylmagnesium bromide upon silicon tetrafluoride (92). It boils at  $200-210^\circ$  at 10 mm. and melts at  $64^\circ$ . The product does not react readily with water.

Tribenzylfluorosilane,  $(C_6H_5CH_2)_3SiF$ , is produced from the Grignard reagent and silicon tetrafluoride (59). It melts at  $79^\circ$  and boils at  $235.5^\circ$  at 7.5 mm.

Alkyl Derivatives of the Type  $B_2R'SiX$

Chloromethyldimethylchlorosilane,  $(CH_2Cl)(CH_3)_2SiCl$ , is synthesized from chlorine and trimethylchlorosilane. It boils at  $115^\circ$  (88).

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92. Medoks and Kotelkov, J. Gen. Chem. U.S.S.R., 7, 2007 (1937). [C. A., 32, 531 (1938)].

Dichloromethyldimethylchlorosilane,  $(\text{CHCl}_2)(\text{CH}_3)_2\text{SiCl}$ , is obtained from chlorine and trimethylchlorosilane besides the above compound. It distils at  $149^\circ$  (88).

Di-(chloromethyl)methylchlorosilane,  $(\text{CH}_2\text{Cl})_2\text{CH}_3\text{SiCl}$ , is formed from chlorine and trimethylchlorosilane besides the above compounds. It boils at  $172^\circ$  (88).

Vinyldimethylchlorosilane,  $(\text{C}_2\text{H}_3)(\text{CH}_3)_2\text{SiCl}$ , results from the action of methylmagnesium bromide on vinyltrichlorosilane. It distils at  $111-113^\circ$ ;  $d_{27}^{27}$  0.922 (73).

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

Tetramethoxysilane,  $(\text{CH}_3\text{O})_4\text{Si}$ , is formed by the rapid addition of anhydrous methanol to silicon tetrachloride (93, 94, 95). Silver isocyanate is without action on this ester (96) even at  $450^\circ$ . The ester is stabilized by such compounds as triamylamine (97), and it is used to apply protective coatings to iron (98), and to make mixed glyceride esters which are

93. Andrianov, Compt rend. acad. sci. U.R.S.S., 28, 66 (1940). [C. A., 35, 2431 (1941)].
94. Peppard, Brown, and Johnson, J. Am. Chem. Soc., 68, 73 (1946).
95. Kalinin, Compt. rend. acad. sci. U.R.S.S., 18, 433 (1938). [C. A., 32, 6227 (1938)].
96. Forbes and Anderson, J. Am. Chem. Soc., 66, 1703 (1944).
97. Vaughn, U. S. Pat. 2,114,866, April 19, 1938. [C. A., 32, 4606 (1938)].
98. Yudin, Compt. rend. acad. sci. U.R.S.S., 25, 614 (1939). [C. A., 34, 4044 (1940)].

used in pharmacy (99). The other lower alkyl-esters of silicic acid may also be used for this purpose. The vapors of tetramethoxysilane have a particularly insidious effect on the eye. Exposure to these vapors under certain conditions causes a necrosis of the corneal cells which progresses long after exposure and which is resistant to treatment. In some instances even blindness has resulted (100). This compound boils at  $42.5-43.0^{\circ}$  at 34 mm. (94). The refraction value for the silicon to oxygen bond is 1.751 mls. (30).

Tetraethoxysilane,  $(C_2H_5O)_4Si$ , results from the action of absolute ethanol (93, 95), or sodium ethoxide (101) on a solution of silicon tetrachloride in an inert solvent. It distills at  $95.5-97.5^{\circ}$  at 70 mm. (101). When this ester is heated with acetyl chloride (102), benzoyl chloride (102), or ethylene glycol (94) a polymeric product results. Acetyl bromide or benzoyl bromide gives ethyl bromide and the corresponding acetates in this reaction (102). The hydrogen halides cleave this ester furnishing the corresponding ethyl halides (102).

Tetra-( $\beta$ -chloroethoxy)silane,  $(ClCH_2CH_2O)_4Si$ , is synthesized from the reaction of ethylene oxide with refluxing

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99. I. G. Farb. -ind.-A. G., British Pat. 450,875, July 27, 1936. [C. A., 32, 217 (1937)].  
 100. Cogan and Setterstrom, Chem. Eng. News, 24, 2499 (1946).  
 101. Backer and Klasens, Rec. trav. chim., 61, 500 (1942).  
 102. Post and Norton, J. Org. Chem., 6, 528 (1942).

silicon tetrachloride (103, 104, 105), and from  $\beta$ -chloroethanol and silicon tetrachloride (105). It reportedly boils at 153-154<sup>o</sup> at 2 mm. (105), 159-162<sup>o</sup> at 2 mm. (104), and 184<sup>o</sup> at 7 mm. (105);  $d_4^{20}$  1.444 (105), and  $n_D^{20}$  1.4641 (105). This compound indicates a greater reactivity towards hydrolysis than the corresponding unsubstituted ester (103).

Tetra-( $\beta$ -aminoethoxy)silane,  $(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_4\text{Si}$ , has been recorded in the literature; however, all that is indicated is that it is used in pharmacy (106).

Tetra-(1,3-dichloropropoxy-2-)silane,  $\overline{\overline{(\text{ClCH}_2)_2\text{CHO}}}_4\text{Si}$ , results from the action of the corresponding alcohol on silicon tetrachloride (107). It distils at 213-214<sup>o</sup> at 0.2 mm.;  $d_{17}^{17}$  1.4610; and  $n_D^{17}$  1.4964.

Tetraalloxysilane,  $(\text{C}_3\text{H}_5\text{O})_4\text{Si}$ , is made from the reaction of allyl alcohol with tetraethoxy- or tetramethoxy-silane (94). It boils at 134-134.5<sup>o</sup> at 34 mm.;  $n_D^{20}$  1.4329.

Tetra-n-butoxysilane,  $(\text{n-C}_4\text{H}_9\text{O})_4\text{Si}$ , is prepared from n-butanol and silicon tetrachloride (42, 93, 95); the highest yields are obtained when the hydrogen chloride produced is

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103. Patnode and Sauer, U. S. Pat. 2,381,137, August 7, 1945. C. A., 39, 4888 (1945)7.
104. Patnode and Sauer, U. S. Pat. 2,381,138, August 7, 1945. C. A., 39, 4890 (1945)7.
105. Sauer and Patnode, J. Am. Chem. Soc., 67, 1548 (1945).
106. I. G. Farbin. -ind. A. G., Ger. Pat. 637,532, October 20, 1936. C. A., 31, 2752 (1937)7.
107. Volnov, J. Gen. Chem. U.S.S.R., 10, 1717 (1940). C. A. 35, 3962 (1941)7.

swept away by dry air (42). The compound boils at 142-144° at 3 mm. (42);  $d_4^{20}$  0.899; and  $n_D^{20}$  1.4128. With hydrogen chloride this ester gives an ill-defined reaction; whereas, with hydrogen iodide and hydrogen bromide it yields the corresponding butyl halides (102).

Tetra-sec.-butoxysilane, (sec.-C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub>Si, is made from silicon tetrachloride and sec.-butanol (93, 95), or the sodium salt of sec.-butanol (101). It distils at 128-129° at 17 mm.;  $n_D^{18.5}$  1.410 (101).

Tetramethalloxysilane, (C<sub>4</sub>H<sub>7</sub>O)<sub>4</sub>Si, is produced when methallyl alcohol is refluxed with tetramethoxy- or tetraethoxysilane (94). It boils at 148-148.5° at 18 mm. and 126-128° at 4 mm.;  $n_D^{20}$  1.4430.

Tetracyclohexoxysilane, (cycle-C<sub>6</sub>H<sub>11</sub>O)<sub>4</sub>Si, is obtained from cyclohexanol and silicon tetrachloride (94). It distils at 218-257°. With ethanol little or no interaction is obtained even in the presence of a catalyst.

Tetra-n-heptoxysilane, (n-C<sub>7</sub>H<sub>15</sub>O)<sub>4</sub>Si, results from refluxing silicon tetrachloride with n-heptanol. It boils at 213.5° at 4 mm.;  $d_4^{29}$  0.876, and  $n_D^{29}$  1.4300 (108).

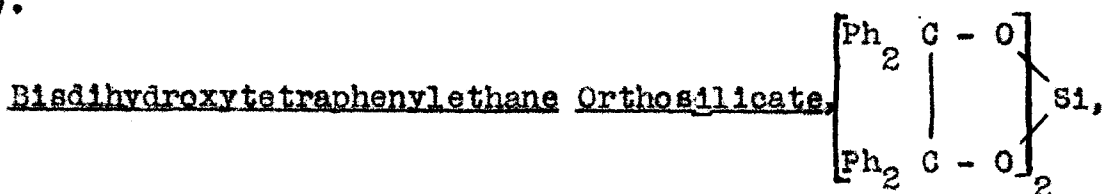
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108. Post and Hofrichter, J. Org. Chem., 4, 363 (1939).

Arvl Derivatives of the Type (RO)<sub>4</sub>Si

Tetraphenoxysilane, (C<sub>6</sub>H<sub>5</sub>O)<sub>4</sub>Si, is prepared by the action of phenyl acetate on silicon tetrachloride (109). This reaction proceeds much more rapidly than in the case of the alkyl esters. This product melts at 47-48°.

Tetra-p-cresoxysilane, (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>4</sub>Si, is made from p-acetoxytoluene and silicon tetrachloride. It melts at 69° (109).



is isolated from the reaction of silicon tetrachloride and magnesium upon benzophenone for 40-60 hours in the absence of ether (110). It melts at 240-245° and is soluble in the common organic solvents.

Alkyl Derivatives of the Type (EO)<sub>3</sub>SiOR'

Trimethoxyvalloxysilane, (CH<sub>3</sub>O)<sub>3</sub>SiOC<sub>3</sub>H<sub>5</sub>, is synthesized from allyl alcohol and either tetramethoxysilane (94) or trimethoxychlorosilane (111). This latter reagent alone gives a pure product. The compound boils at 70.5-70.8° at 34 mm.;  
 $n_D^{20}$  1.3919.

109. Volnov, J. Gen. Chem. U. S. S. R., 9, 2269 (1940).  
C. A., 34, 5048 (1940).  
 110. Kipping and Abrams, J. Chem. Soc., 81, (1944).  
 111. Peppard, Brown, and Johnson, J. Am. Chem. Soc., 68,  
70 (1946).

Trimethoxymethalloxysilane,  $(\text{CH}_3\text{O})_3\text{SiOC}_4\text{H}_7$ , results from the reaction of methallyl alcohol with either tetramethoxysilane (94) or trimethoxychlorosilane. It distills at  $83\text{-}83.5^\circ$  at 34 mm.;  $n_D^{20}$  1.4003.

Triethoxyvalloxy-silane,  $(\text{C}_2\text{H}_5\text{O})_3\text{SiOC}_3\text{H}_5$ , is obtained when allyl alcohol is refluxed with tetraethoxysilane (94) or with triethoxychlorosilane (111). It also may be isolated when tetraethoxysilane is heated with the corresponding alkoxy-compound (42, 112) for a prolonged period. It boils at  $93.5\text{-}94^\circ$  at 34 mm.;  $n_D^{20}$  1.3973.

Triethoxy-n-butoxysilane,  $(\text{C}_2\text{H}_5\text{O})_3\text{SiOC}_4\text{H}_9\text{-n}$ , is prepared from n-butanol and either tetraethoxysilane or triethoxychlorosilane (102). It also may be obtained when tetraethoxysilane and tetra-n-butoxysilane are heated together (112). It distills at  $88\text{-}90^\circ$  at 16 mm., and at  $82.5^\circ$  at 15 mm. (42);  $n_D^{20}$  1.3945 (105),  $n_D^{20}$  1.3935; and  $d_4^{20}$  0.920 (42).

Triethoxymethalloxysilane,  $(\text{C}_2\text{H}_5\text{O})_3\text{SiOC}_4\text{H}_7$ , is synthesized from methallyl alcohol and either tetraethoxysilane (94) or triethoxychlorosilane (111). It boils at  $92.5\text{-}93^\circ$  at 18 mm.;  $n_D^{20}$  1.4051.

Triethoxycyclohexoxysilane,  $(\text{C}_2\text{H}_5\text{O})_3\text{SiOC}_6\text{H}_{11}\text{-cyclo}$ , is

112. Peppard, Brown, and Johnson, ibid., 68, 77 (1946).

made from cyclohexanol and tetraethoxysilane (94); in this reaction the ethanol must be removed as it is formed. The product distills at 124-124.2° at 22 mm.

Triethoxyhexadecoxysilane,  $(C_2H_5O)_3SiOC_{16}H_{33}$ , is produced from hexadecyl alcohol and tetraethoxysilane (113). It has a boiling point of 312-16° at 15 mm.

Ethyl O-Triethoxysilylacetoacetate,  $CH_3CH(COOC_2H_5)OSi(OC_2H_5)_3$ , is made from the action of tetraethoxysilane upon ethyl acetoacetate (113). It has a boiling point of 115-120° at 14 mm.

Tri-n-propoxyhexadecoxysilane,  $(n-C_3H_7O)_3SiOC_{16}H_{33}$ , is produced from tri-n-propoxychlorosilane and hexadecyl alcohol (114). It boils at 235-240°.

Tri-n-propoxymenthoxysilane,  $(n-C_3H_7O)_3SiOC_{10}H_{19}$ , is isolated when tetra-n-propoxysilane is refluxed with menthol (113). It distills at 160-165° at 4 mm.

Triallyloxymethoxysilane,  $(C_3H_5O)_3SiOCH_3$ , is formed from allyl alcohol and either tetramethoxysilane (94) or methoxytrichlorosilane (111). It has a boiling point of 116.0-116.3°, at 34 mm.;  $n_D^{20}$  1.4252.

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113. ByK.-Guldenwerke chem. Fab. A.-G., Ger. Pat. 662,732, July 30, 1938. [C. A., 32, 9403 (1938)].
114. ByK.-Guldenwerke chem. Fab. A.-G., Ger. Pat. 625,077, May 24, 1938. [C. A., 32, 7678 (1938)].



Triallyloxyethoxysilane,  $(C_3H_5O)_3SiOC_2H_5$ , is prepared from the action of tetraethoxysilane upon either allyl alcohol (94) or tetraallyloxysilane (112). It also results from the interaction of ethoxytrichlorosilane and allyl alcohol (111). It distills at  $121-121.5^\circ$  at 34 mm.;  $n_D^{20}$  1.4230 (111).

Di-(trialloxyloxy)ethane,  $(C_3H_5O)_3Si-O(CH_2)_2-OSi-(OC_3H_5)_3$ , is synthesized from ethylene glycol and triallyloxychlorosilane (111). Its refractive index is  $n_D^{20}$  1.4442.

$\beta,\beta'$ -Di-(trialloxyloxy)diethyl ether,  $\Delta(C_3H_5O)_3Si-OC_2H_4/2O$ , is also produced from ethylene glycol and triallyloxychlorosilane (111). Its refractive index is  $n_D^{20}$  1.4391.

Triallyloxy-1-propoxysilane,  $(C_3H_5O)_3SiOC_3H_7-1$ , results from the reaction between isopropyl alcohol and triallyloxychlorosilane (111). It has a boiling point of  $74.5-75^\circ$  at 2 mm.;  $n_D^{20}$  1.4204.

Triallyloxy-1-butoxysilane,  $(C_3H_5O)_3SiOC_4H_9-1$ , is obtained from triallyloxychlorosilane and isobutanol (111). It boils at  $85.5-86.5^\circ$  at 3 mm.

Triallyloxy-s-butoxysilane,  $(C_3H_5O)_3SiOC_4H_9-s$ , is synthesized in the reaction between sec.-butanol and triallyloxychlorosilane. It distills at  $74.5-75.0^\circ$ ;  $n_D^{20}$  1.4242 (111).

Triallyloxy-t-butoxysilane,  $(C_3H_5O)_3SiOC_4H_9-t$ , is prepared from t-butanol and triallyloxychlorosilane. It has a boiling point of 73.0-73.5° at 2 mm.;  $n_D^{20}$  1.4214 (111).

Triallyloxy-n-amoxysilane,  $(C_3H_5O)_3SiOC_5H_{11}-n$ , is obtained from refluxing allyl alcohol with triethoxy-n-amoxysilane (94). It boils at 153.5° at 32 mm.;  $n_D^{20}$  1.4383.

Tri-t-butoxysilanol,  $(t-C_4H_9O)_3SiOH$ , is obtained as its sodium salt when sodium t-butoxide is permitted to react with tri-t-butoxychlorosilane (101). It melts at 65.5° and boils at 20 mm. at 103-105°.

Tri-t-butoxyethoxysilane,  $(t-C_4H_9O)_3SiOC_2H_5$ , is isolated after tri-t-butoxychlorosilane is heated with an ethanolic solution of sodium ethoxide for two days (101). It distills at 99-100°;  $n_D^{20}$  1.396.

Tri-t-butoxy-i-propoxysilane,  $(t-C_4H_9O)_3SiOC_3H_7-i$ , is synthesized by refluxing an alcoholic solution of tri-t-butoxychlorosilane and sodium isopropoxide. It has a boiling point of 104-105° (101).

Triallyloxycyclohexoxysilane,  $(C_3H_5O)_3SiOC_6H_{11}-cyclo$ , is prepared from cyclohexanol and triallyloxychlorosilane. It distills at 104.5-105.5° at 3 mm. (111).

Triallyloxy-n-hexadecoxysilane,  $(C_3H_5O)_3SiOC_{16}H_{33}$ , is

produced in a similar manner from n-hexadecanol and trialkoxychlorosilane. It boils at 225-228° at 2 mm.;  $n_D^{20}$  1.4440 (111).

Tri-n-butoxyethoxysilane,  $(n-C_4H_9O)_3SiOC_2H_5$ , is made from the prolonged action of tetraethoxysilane upon tetra-n-butoxysilane. It distils at 150.0-150.5° at 32 mm.;  $n_D^{20}$  1.4075 (112).

Tri-i-butoxymethalloxysilane,  $(i-C_4H_9O)_3SiOC_4H_7$ , is synthesized from i-butanol and methalloxytrichlorosilane. It boils at 106.5-107.5° at 3 mm.;  $n_D^{20}$  1.4135 (111).

Trimethalloxymethoxysilane,  $(C_4H_7O)_3SiOCH_3$ , is formed from the action of methallyl alcohol on either tetramethoxysilane (94) or methoxytrichlorosilane (111). It has a boiling point of 128.0-128.5° at 18 mm.;  $n_D^{20}$  1.4320.

Trimethalloxyethoxysilane,  $(C_4H_7O)_3SiOC_2H_5$ , is prepared from the reaction of methallyl alcohol with either tetraethoxysilane (94) or ethoxytrichlorosilane (111). It distils at 133-133.5° at 18 mm.;  $n_D^{20}$  1.4275.

Di-(trimethalloxysiloxy)ethane,  $(C_4H_7O)_3SiOC_2H_4OSi(OC_4H_7)_3$ , results when ethylene glycol is heated with trimethalloxychlorosilane. Its refractive index is  $n_D^{20}$  1.4487 (111).

$\beta,\beta'$ -Di-(trimethalloxysiloxy)diethyl ether,  $\Delta(C_4H_7O)_3SiOC_2H_4=7_2O$ , also results when ethylene glycol is warmed with trimethalloxychlorosilane. Its refractive index is  $n_D^{20}$  1.4510 (111).

Trimethalloxy-*i*-butoxysilane,  $(C_3H_5O)_3SiOC_4H_9-i$ , is isolated from the interaction of *i*-butanol and trimethalloxychlorosilane. It has a boiling point of 117-118° at 3 mm.;  $n_D^{20}$  1.4306 (111).

Tri-*n*-amoxvalloxysilane,  $(n-C_5H_{11}O)_3SiOC_3H_5$ , is prepared by refluxing triethoxyalloxysilane with *n*-amyl alcohol. It distills at 180.5-181° at 23 mm.;  $n_D^{20}$  1.4421 (94).

Mixed Aryl-Alkyl Derivatives of the Type  $(RO)_3SiOR'$

*p*-Di-(trimethoxysiloxy)benzene,  $(CH_3O)_3SiOC_6H_4/OSi-(OCH_3)_3-p$ , is produced from the corresponding chloro-compound and methanol (115). It has these constants:  $d_{20}^{20}$  1.21; and  $n_D^{15}$  1.4731.

*m*-Di-(trimethoxysiloxy)benzene,  $(CH_3O)_3SiOC_6H_4/OSi-(OCH_3)_3-m$ , is synthesized from the corresponding chloro-compound and methanol. It has these constants:  $d_{20}^{20}$  1.259; and  $n_D^{15}$  1.4916. It cannot be distilled because it decomposes into polymeric substances upon heating (115).

Triethoxyfurfuroxysilane,  $(C_2H_5O)_3SiOC_5H_5O$ , results from the reaction between furfuryl alcohol and triethoxychlorosilane (111). It boils at 85.5-86.5°.

115. Volnov and Dolgov, J. Gen. Chem. U.S.S.R., 10, 550 (1940). [C. A., 34, 7874 (1940)].

Alkyl Derivatives of the Type  $(RO)_2Si(OR^1)_2$

Dimethoxydialloxysilane,  $(CH_3O)_2Si(OC_3H_5)_2$ , is isolated from the reaction of allyl alcohol with either tetramethoxysilane (88) or dimethoxydichlorosilane (111). It has a boiling point of  $94.7-95^\circ$  at 34 mm.;  $n_D^{20}$  1.4110 (111).

Dimethoxydimethalloxysilane,  $(CH_3O)_2Si(OC_4H_7)_2$ , is produced from methallyl alcohol and either tetramethoxysilane (94) or dimethoxydichlorosilane (111). It distills at  $114.5-115^\circ$  at 34 mm.;  $n_D^{20}$  1.4156.

Diethoxydialloxysilane,  $(C_2H_5O)_2Si(OC_3H_5)_2$ , is made from allyl alcohol and either diethoxydichlorosilane (111) or tetraethoxysilane (94). It is also obtained when tetraethoxy- and tetraalloxysilane are refluxed for a prolonged period (102). It boils at  $107.5-108^\circ$  at 34 mm.;  $n_D^{20}$  1.4098 (111).

Diethoxydi-n-butoxysilane,  $(C_2H_5O)_2Si(OC_4H_9-n)_2$ , is prepared from n-butanol and tetraethoxysilane (102), or from the interaction of tetraethoxysilane and tetra-n-butoxysilane (112). It distills at  $105-107^\circ$  at 14 mm. (102),  $128-128.5^\circ$  at 32 mm. (102), and at  $100^\circ$  at 15 mm. (42);  $n_D^{20}$  1.4010 (102, 112),  $n_D^{20}$  1.4008; and  $d_4^{20}$  0.909 (42).

Diethoxydimethalloxysilane,  $(C_2H_5O)_2Si(OC_4H_7)_2$ , is isolated from the action of methallyl alcohol either upon

tetraethoxysilane (94) or upon diethoxydichlorosilane (111). It has a boiling point of 115.5-116° at 18 mm.;  $n_D^{20}$  1.4200.

Diethoxydi-n-hexadecoxysilane,  $(C_2H_5O)_2Si(OC_{16}H_{33}-n)_2$ , results from refluxing n-hexadecyl alcohol with tetraethoxysilane (113). It boils at 312-316° at 15 mm.

Di- $\sqrt$ Ethyl O-diethoxysilylacetoacetate,  $\sqrt{CH_3CH(COOC_2H_5)-O}_2Si(OC_2H_5)_2$ , is formed from ethyl acetoacetate and tetraethoxysilane. It distils at 155-160° at 14 mm. (113).

Di-i-propoxydialloxyasilane,  $(i-C_3H_7O)_2Si(OC_3H_5)_2$ , is made from i-propyl alcohol and dialloxydichlorosilane (111). It has a boiling point of 57.5-58° at 2 mm.;  $n_D^{20}$  1.4075.

Di-n-propoxydimenthoxyasilane,  $(n-C_3H_7O)_2Si(OC_{10}H_{19})_2$ , is obtained from tetra-n-propoxysilane and menthol (113). It boils at 223-230° at 5 mm.

Dialloxydi-i-butoxysilane,  $(C_3H_5O)_2Si(OC_4H_9-i)_2$ , is produced by the action of i-butanol upon dialloxydichlorosilane. It distils at 91.0-91.5° at 3 mm. (111).

Dialloxydi-t-butoxysilane,  $(C_3H_5O)_2Si(OC_4H_9-t)_2$ , is prepared from t-butanol and dialloxydichlorosilane. It has a boiling point of 61.5-62° at 2 mm.;  $n_D^{20}$  1.4121 (111).

Dialloxydicyclohexoxysilane,  $(C_3H_5O)_2Si(OC_6H_{11-cyclo})_2$ , is formed when cyclohexanol and dialloxydichlorosilane are added together in the presence of pyridine (111). It boils at 128-129° at 3 mm.

Dialloxydi-n-amoxysilane,  $(C_3H_5O)_2Si(OC_5H_{11-n})_2$ , is isolated from the prolonged reaction between diethoxydi-n-amoxysilane and allyl alcohol (94). It has the boiling point of 163-163.5° at 23 mm.;  $n_D^{20}$  1.4415.

Dimethalloxydi-i-butoxysilane,  $(C_4H_7O)_2Si(OC_4H_9-i)_2$ , is produced from the action of i-butanol upon dimethalloxydichlorosilane in the presence of pyridine (111). It distills at 114-115° at 3 mm.;  $n_D^{20}$  1.4216.

Dimethalloxydi-t-butoxysilane,  $(C_3H_5O)_2Si(OC_4H_9-t)_2$ , is prepared in the reaction between t-butanol and dimethalloxydichlorosilane. It boils at 82-83° at 2 mm.;  $n_D^{20}$  1.4219 (111).

Mixed Aryl-Alkyl Derivatives of the Type  $(RO)_2Si(OR')$

Diethoxydifurfuroxysilane,  $(C_2H_5O)_2Si(OC_5H_5O)_2$ , is made from furfuryl alcohol and diethoxydichlorosilane in the presence of pyridine which serves to remove the hydrogen chloride formed (111). It distills at 112.5-125.5° at 3 mm.

Alkyl Derivatives of the Type  $\text{RSi}(\text{OR}')_3$

Tri- $\beta$ -chloroethoxysilane,  $\text{HSi}(\text{OCH}_2\text{CH}_2\text{Cl})_3$ , is formed from the action of ethylene oxide on silicochloroform at  $60^\circ$  (104, 105). It distills at  $117\text{--}118^\circ$  at 2 mm.;  $n_D^{20}$  1.4577; and  $d_4^{20}$  (vac.) 1.2886 (105). The boiling point of  $70\text{--}73^\circ$  at 4.5 mm. is also recorded (104).

Methyltriethoxysilane,  $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ , is made from ethanol and methyltrichlorosilane (62), and from methyl chloride, tetraethoxysilane, and magnesium in the absence of ether (116). This compound also results from the action of methylmagnesium iodide on tetraethoxysilane for three hours at  $150^\circ$  in the absence of ether (42). Another compound separated in this reaction is one that boils at  $73^\circ$  at 760 mm.;  $d_4^{20}$  0.891; and  $n_D^{20}$  1.3696. It is thought to be ethyl silicoacetate,  $\text{CH}_3\text{SiOOC}_2\text{H}_5$ . Methyltriethoxysilane boils at  $114^\circ$  at 740 mm. (116), and  $150\text{--}151^\circ$  at 760 mm. (42);  $d$  0.830 (116),  $d_4^{20}$  0.938, and  $n_D^{20}$  1.3869.

Methyltri- $\beta$ -chloroethoxysilane,  $\text{CH}_3\text{Si}(\text{OCH}_2\text{CH}_2\text{Cl})_3$ , results when ethylene oxide is reacted with methyltrichlorosilane under pressure (104, 105). It boils at  $137^\circ$  at 6 mm.;  $d_4^{20}$  (vac.) 1.257 and  $n_D^{20}$  1.4562 (105).

116. McGregor and Warrick, U. S. Pat. 2,380,057, July 10, 1945. [C. A., 40, 88(1946)].



Methyltri- $\beta$ -bromoethoxysilane,  $\text{CH}_3\text{Si}(\text{OCH}_2\text{CH}_2\text{Br})_3$ , is formed from methyltribromosilane and ethylene oxide when they are heated together under pressure (104). It distills at  $131^\circ$  at 1 mm.

Ethyltriethoxysilane,  $\text{C}_2\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$ , is produced when tetraethoxysilane is acted upon by the Grignard reagent in the absence of ether (108, 117, 118), or by methyl chloride and magnesium in the absence of ether (116). It is also formed from the Grignard reagent and triethoxychlorosilane in the presence of ether (119). This product distills at  $158\text{--}160^\circ$  (108, 117, 118), and  $159\text{--}162^\circ$  at 760 mm. (115);  $d_4^{20}$  0.8954 (119) and  $d_4^{20}$  0.9281 (118);  $n_D^{22}$  1.3853 (108, 117, 118);  $M_R^D$  49.93; and  $\gamma^{20}$  22.42 (119).

Ethyl-diethoxy-acetoxy-silane,  $\text{C}_2\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_2(\text{OOCCH}_3)$ , is synthesized by the action of acetic anhydride on ethyltriethoxysilane. It boils at  $191.5^\circ$  at 760 mm. with decomposition, and at  $94^\circ$  at 15 mm.;  $d_4^{20}$  1.020; and  $n_D^{20}$  1.4048 (117).

Ethyltri-n-propoxysilane,  $\text{C}_2\text{H}_5\text{Si}(\text{OC}_3\text{H}_7\text{-n})_3$ , results from heating the Grignard reagent with tetra-n-propoxysilane in the absence of ether (117), or from heating ethyltriethoxysilane with n-propanol for 96 hours (108). It has a boiling point of  $202\text{--}204^\circ$  at 760 mm. (108, 117);  $n_D^{24}$  1.4017 (108, 117),

117. Post and Hofrichter, J. Org. Chem., 5, 443 (1940).  
 118. Andrianov and Gribanova, J. Gen. Chem. U.S.S.R., 8, 558, (1938). [C. A., 32, 7892 (1938)].  
 119. Kalinin, Compt. rend. acad. sci. U.R.S.S., 26, 365 (1940). [C. A., 35, 2470 (1941)].

and  $n_D^{10}$  1.4060; and  $d_4^{23}$  0.986 (108).

Ethyltri-n-butoxysilane,  $C_2H_5Si(OC_4H_9-n)_3$ , is produced either from the reaction of the Grignard reagent with tetra-n-butoxysilane in the absence of ether (117), or from the prolonged treatment of n-butanol upon ethyltriethoxysilane (108). It boils at  $235-238^\circ$  at 760 mm.;  $n_D^{24}$  1.4128, and  $n_D^{10}$  1.4174; and  $d_4^{24}$  0.878 (108).

Ethyltri-i-butoxysilane,  $C_2H_5Si(OC_4H_9-i)_3$ , is prepared from ethylmagnesium bromide and tri-i-butoxychlorosilane in an ether solution (119). It distils at  $101-103^\circ$  at 8 mm.;  $d_4^{20}$  0.8679;  $n_D^{20}$  1.4100;  $MR_D$  78.75; and  $\gamma^{20}$  22.97.

Ethyltri-n-amoxysilane,  $C_2H_5Si(OC_5H_{11}-n)_3$ , is made from the prolonged action of n-amyl alcohol on ethyltriethoxysilane (108). It has a boiling point of  $285^\circ$  at 760 mm.;  $d_4$  0.891; and  $n_D^{23}$  1.4210, and  $n_D^{10}$  1.462.

Ethyltri-i-amoxysilane,  $C_2H_5Si(OC_5H_{11}-i)_3$ , is obtained when ethylmagnesium bromide in ether is added to a solution of tri-i-amoxychlorosilane in ether (119), or when isoamyl alcohol is heated with ethyltriethoxysilane for 96 hours (108). It boils at  $143-146^\circ$  at 12 mm.,  $151-154^\circ$  at 17 mm. (109), and  $266-269^\circ$  at 760 mm. (108);  $d_4$  0.891 (108), and  $d_4^{20}$  0.8625 (119); and  $n_D^{24}$  1.4170 (108),  $n_D^{20}$  1.4196 (119), and  $n_D^{10}$  1.4222 (108);  $MR_D$  92.79; and  $\gamma^{20}$  23.49 (119).

n-Propyltriethoxysilane,  $n\text{-C}_3\text{H}_7\text{Si}(\text{OC}_2\text{H}_5)_3$ , is prepared when the Grignard reagent is refluxed with tetraethoxysilane (42, 108, 118), or when the halide, magnesium, and tetraethoxysilane are digested together for an hour (118). It distills at  $177\text{-}179^\circ$  (118) and at  $179\text{-}180^\circ$  at 760 mm. (42, 108);  $d_4^{20}$  0.9194 (118), and  $d_4^{26}$  0.852 (108); and  $n_D^{26}$  1.4076 (42, 108).

Allyltrimethoxysilane,  $\text{C}_3\text{H}_5\text{Si}(\text{OCH}_3)_3$ , is formed when allyl bromide, magnesium, and tetramethoxysilane are heated together for an hour at  $90^\circ$  in the presence of iodine (120). It distills at  $167\text{-}178^\circ$ .

Allyltriethoxysilane,  $\text{C}_3\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$ , is obtained from refluxing tetraethoxysilane either with allylmagnesium bromide or with a mixture of allyl bromide and magnesium (121). It boils at  $172\text{-}178^\circ$ ;  $d_4^{20}$  0.9229;  $n_D^{20}$  1.3952; and  $M_R^D$  51.67.

n-Butyltriethoxysilane,  $n\text{-C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3$ , is synthesized from the Grignard reagent and tetraethoxysilane in the absence of ether (42). It boils at  $190\text{-}193^\circ$  at 740 mm.;  $d_4^{27}$  0.895; and  $n_D^{29}$  1.3976. This compound will not react with n-butanol to give alcohol interchange (108).

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120. Andrianov, Gribanova, and Kamenskaya, *Russ. Pat.* 53,544, July 31, 1938. [*C. A.*, 34, 5091 (1940)].
121. Andrianov and Kamenskaya, *J. Gen. Chem. U.S.S.R.*, 8, 969 (1938). [*C. A.*, 33, 1266 (1939)].

1-Butyltriethoxysilane,  $\text{1-C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3$ , results from heating either the Grignard reagent or 1-butyl halide and magnesium with tetraethoxysilane in the absence of ether (118). It has a boiling point of  $180\text{-}192^\circ$ ;  $d_4^{20}$  0.9104;  $n_D^{20}$  1.3908; and  $\text{MR}_D$  56.73.

1-Amyltriethoxysilane,  $\text{1-C}_5\text{H}_{11}\text{Si}(\text{OC}_2\text{H}_5)_3$ , is made in exactly the same manner as the corresponding isobutyl-compound (118). It distills at  $195\text{-}200^\circ$ ;  $d_4^{20}$  0.8955;  $n_D^{20}$  1.3982; and  $\text{MR}_D$  60.81.

n-Hexyltriethoxysilane,  $\text{n-C}_6\text{H}_{13}\text{Si}(\text{OC}_2\text{H}_5)_3$ , is produced according to the method described for the isobutyl-compound given above (118). It boils at  $200\text{-}220^\circ$ ;  $d_4^{20}$  0.8938;  $n_D^{20}$  1.4167; and  $\text{MR}_D$  68.4.

#### Aryl Derivatives of the Type $\text{RSi}(\text{OR}')_3$

Phenyltriethoxysilane,  $\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$ , is prepared in the absence of ether from phenylmagnesium bromide and tetraethoxysilane (108), and in the presence of ether both from phenyllithium (62) and tetraethoxysilane, and from the Grignard reagent and triethoxychlorosilane (108). It distills at  $120^\circ$  at 15 mm. (62),  $235\text{-}238^\circ$  at 760 mm. (108), and  $235\text{-}237^\circ$  (119);  $d_4^{20}$  0.9961 (112), and  $d^{10}$  1.0055 (108);  $n_D^{20}$  1.4718;  $\text{MR}_D$  65.90; and  $\gamma^{20}$  27.93 (119).

Phenyltri- $\beta$ -chloroethoxysilane,  $C_6H_5Si(OC_2H_4Cl)_3$ , is isolated from the action of ethylene oxide on phenyltrichlorosilane under pressure (104, 105). It has the boiling point of  $158^\circ$  at 1 mm.;  $n_D^{20}$  1.5077; and  $d_4^{20}$  1.268

Phenyltri- $n$ -propoxysilane,  $C_6H_5Si(OC_3H_7-n)_3$ , results from refluxing the corresponding trichloro-compound with  $n$ -propanol. It boils at  $192^\circ$  at 7 mm.;  $d_4^{20}$  1.036; and  $n_D^{20}$  1.5025 (108).

Phenyltri- $i$ -butoxysilane,  $C_6H_5Si(OC_4H_9-i)_3$ , reportedly distills at  $154-157^\circ$  at 10 mm.;  $d_4^{20}$  0.9380;  $n_D^{20}$  1.4600;  $MR_D$  93.14; and  $\gamma_4^{20}$  25.77 (119). The method of preparation of this compound is not given.

Phenyltri- $i$ -amoxysilane,  $C_6H_5Si(OC_5H_{11-i})_3$ , is formed from phenylmagnesium bromide and tri- $i$ -amoxychlorosilane in an ether solution. It has a boiling point of  $194-197^\circ$  at 18 mm.;  $d_4^{20}$  0.9095;  $n_D^{20}$  1.4432;  $MR_D$  106.40; and  $\gamma^{20}$  25.20 (119).

$p$ -Tolyltriethoxysilane,  $p-CH_3C_6H_4Si(OC_2H_5)_3$ , is prepared from the corresponding lithium compound and tetraethoxysilane. It boils at  $137^\circ$  at 14 mm. (62).

$p$ -Aminophenyltriethoxysilane,  $p-NH_2C_6H_4Si(OC_2H_5)_3$ , is formed in an ether solution apparently from lithium,  $p$ -bromoaniline, and tetraethoxysilane (62). It has a boiling point

of 145-150° at 14 mm.

p-Xenyltriethoxysilane,  $C_6H_5C_6H_4Si(OC_2H_5)_3$ , is produced in an ether solution from p-xenyllithium and tetraethoxysilane (62). It distills at 210-215° at 13 mm.

2,5-Dimethylphenyltriethoxysilane,  $2,5-(CH_3)_2C_6H_3Si(OC_2H_5)_3$ , results from the action of the appropriate lithium compound and tetraethoxysilane (62). It boils at 150° at 23 mm.

p-Dimethylaminophenyltriethoxysilane,  $(CH_3)_2NC_6H_4Si(OC_2H_5)_3$ , is obtained from p-dimethylaminophenyllithium and tetraethoxysilane in an ether solution (62). It has a boiling point of 180-182° at 14 mm.

Phenylethynyltriethoxysilane,  $C_6H_5C\equiv CSi(OC_2H_5)_3$ , is made in toluene from phenylethynylmagnesium bromide and tetraethoxysilane (122). It distills at 141-2°;  $d_{21}^{21}$  0.986, and  $d_{10}^{10}$  1.004;  $n_D^{21}$  1.4898, and  $n_D^{10}$  1.4939; and  $MR_D$  76.5.

#### Alkyl Derivatives of the Type $R_2Si(OR')_2$

Dimethyldiethoxysilane,  $(CH_3)_2Si(OC_2H_5)_2$ , is formed from heating a mixture of tetraethoxysilane and, either methylmagnesium iodide (42), or magnesium and methyl chloride (116, 123).

122. Volnov and Reutt, ibid., 10, 1600 (1940). C. A., 35, 2853 (1941)7.

123. McGregor and Warrick, U. S. Pat. 2,384,384, September 4, 1945. C. A., 40, 730 (1946)7.

It also results after ethanol is refluxed with dimethyldichlorosilane (62). It boils at  $112^{\circ}$  (123),  $114^{\circ}$  at 740 mm. (116), and  $110-111^{\circ}$  at 760 mm.;  $d$  0.830 (116), and  $d_4^{20}$  0.890; and  $n_D^{20}$  1.3839 (42).

Dimethyldi- $\beta$ -chloroethoxysilane,  $(CH_3)_2Si(OCH_2CH_2Cl)_2$ , results from the action of dimethyldichlorosilane upon ethylene oxide under pressure (104, 105). It has a boiling point of  $213^{\circ}$  at 758 mm.;  $n_D^{20}$  1.4420; and  $d_4^{20}$  1.135.

Dimethyldi- $\beta$ -bromoethoxysilane,  $(CH_3)_2Si(OCH_2CH_2Br)_2$ , is prepared in the same manner as the  $\beta$ -chloro-compound (104, 105). It distils at  $92^{\circ}$  at 2.5 mm.

Dimethyldi- $n$ -butoxysilane,  $(CH_3)_2Si(OC_4H_9-n)_2$ , is obtained by refluxing  $n$ -butanol with dimethyldichlorosilane (124). It boils at  $186-188^{\circ}$  at 760 mm. and  $75^{\circ}$  at 10 mm.;  $n_D^{25}$  1.4035, and  $n_D^{20}$  1.4058; and  $d_4^{20}$  0.8434.

Diethylsilanediol,  $(C_2H_5)_2Si(OH)_2$ , results from the careful hydrolysis of diethyldichlorosilane in an ether solution with dilute alkali (125). It boils at  $140^{\circ}$  and melts at  $96^{\circ}$ . It can be stored for long periods without condensation, and is very soluble in hydroxyl-containing organic solvents. This product may be reconverted to the dichloride by use of thionyl

124. Sauer, J. Am. Chem. Soc., 68, 138 (1946).

125. DiGiorgio, Sommer, and Whitmore, ibid., 68, 344 (1946).

chloride, and may be polymerized by use of phosphorus pentoxide (84).

Diethyldiethoxysilane,  $(C_2H_5)_2Si(OC_2H_5)_2$ , is prepared by refluxing a mixture of magnesium, tetraethoxysilane, and ethyl chloride (115). The other possible ethylethoxysilanes are also formed in the process. No constants are given for this product.

Diethyldiphenoxysilane,  $(C_2H_5)_2Si(OC_6H_5)_2$ , has a boiling point of 150-152° at 4.5 mm.;  $n_D^{25}$  1.5243 (86). It polymerizes with diphenylolpropane in the presence of sodium as a catalyst. Its method of preparation is not described.

#### Aryl Derivatives of the Type $B_2Si(OR')_2$

Diphenyldisilanediol,  $(C_6H_5)_2Si(OH)_2$ , is obtained from diphenyldichlorosilane by very careful hydrolysis in a toluene-t-amyl alcohol mixture maintained at 25°. It melts at 148° with decomposition (126), and at 155° (79). The melting point varies with the rate of heating (79).

Diphenyldi- $\beta$ -chloroethoxysilane,  $(C_6H_5)_2Si(OCH_2CH_2Cl)_2$ , is made from diphenyldichlorosilane and ethylene oxide under pressure and at a temperature below 60° (105). It distills at 142-146° at 0.1 mm.;  $n_D^{20}$  1.5510; and  $d_4^{20}$  1.2027.

126. Burkhard, ibid., 67, 2173 (1945).



Diphenyldi- $\beta$ -bromoethoxysilane,  $(C_6H_5)_2Si(OCH_2CH_2Br)_2$ , is made in the same manner described for the above  $\beta$ -chloro-compound. It boils at 142-146 $^{\circ}$  at 0.1 mm. (105).

Di-(p- $\omega$ -hydroxytolyl)diethoxysilane,  $(p-HOCH_2C_6H_4)_2Si(OC_2H_5)_2$ , is produced from the appropriate lithium compound and an ether solution of tetraethoxysilane (62). It distills at 200-210 $^{\circ}$  at 15 mm.

Diphenylethynyldiethoxysilane,  $(C_6H_5C\equiv C)_2Si(OC_2H_5)_2$ , is obtained along with the triethoxy-product when phenylethynylmagnesium bromide is heated in toluene with tetraethoxysilane (122). The product has a boiling point of 150-160 $^{\circ}$  at 5-6 mm.

Dibenzyl dibutoxysilane,  $(C_6H_5CH_2)_2Si(O-C_4H_9)_2$ , is formed when butanol is refluxed with dibenzyl dichlorosilane until hydrogen chloride evolution ceases (86). It boils at 206-207 $^{\circ}$  at 10 mm.

Dibenzyl diphenoxysilane,  $(C_6H_5CH_2)_2Si(OC_6H_5)_2$ , is synthesized in the same manner as the dibutoxy-compound described above (86). It has a boiling point of 230-231 $^{\circ}$  at 1 mm.;  $n_D^{25}$  1.5922; and  $d_4^{25}$  1.1164. When heated with such compounds as diphenylolpropane, hexamethylene glycol, decamethylene glycol, 4,4'-dihydroxybiphenyl, etc. (86) this product forms polymers. Dibenzyl diethoxysilane exhibits this same property.

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

Methyldi- $\beta$ -chloroethoxysilane,  $(CH_3)HSi(OCH_2CH_2Cl)_2$ , is prepared by heating a mixture of ethylene oxide and methyldichlorosilane (104, 105). It has a boiling point of  $95-7^\circ$  at 18 mm. (98) and  $93.5-94.5^\circ$  at 15 mm. (104);  $n_D^{20}$  1.4431; and  $d_4^{20}$  1.1643. This product seems to decompose if distilled at atmospheric pressure.

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

Phenylmethyldiethoxysilane,  $C_6H_5(CH_3)Si(OC_2H_5)_2$ , is apparently formed from the corresponding dichloro-compound and ethanol (62). It distills at  $105-110^\circ$  at 13 mm.

Alkyl Derivatives of the Type  $R_3SiOR'$

Trimethylsilanol,  $(CH_3)_3SiOH$ , is obtained by the reaction of methylmagnesium iodide with dimethyl silicone in *n*-butyl ether (127), by the reaction of hydrochloric acid with hexamethyldisilazane,  $\llbracket(CH_3)_3Si\rrbracket_2NH$ , (127), and by the reaction of water with trimethylchlorosilane (127). It distills at  $97-100^\circ$ ;  $n_D^{20}$  1.3800. It forms an azeotropic mixture with hexamethyldisiloxane that boils at  $89.8-90.2^\circ$  at 752 mm.;  $n_D^{20}$  1.3798. Upon two days' action with lead oxide,  $PbO$ , it

127. Sauer, ibid., 66, 1707 (1944).

gives a white crystalline derivative which is thought to be  $\text{[(CH}_3\text{)}_3\text{SiO}]_2\text{Pb}$ , di-(trimethylsiloxy)lead (128).

Trimethylmethoxysilane,  $(\text{CH}_3)_3\text{SiOCH}_3$ , is produced from the reaction of methanol and trimethylchlorosilane in the presence of toluene or ether using pyridine as a catalyst (127). It has a boiling point of  $56.5\text{--}56.7^\circ$  at 747 mm. and  $57.0^\circ$  at 758-760 mm.;  $n_D^{20}$  1.3678. It also forms an azeotropic mixture with methanol distilling at  $49.6\text{--}50^\circ$  at 760 mm.;  $n_D^{20}$  1.3636.

Trimethylethoxysilane,  $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ , is made in xylene from ethanol and trimethylchlorosilane (127), and from bubbling methyl chloride into an ether mixture of dimethyldimethoxysilane and magnesium until all of the magnesium has disappeared (129). It boils at  $75\text{--}76^\circ$  (128) and  $74.9\text{--}75.0^\circ$  at 745 mm.;  $n_D^{20}$  1.3741; and  $d_4^{20}$  0.7573.

Trimethyl- $\beta$ -chloroethoxysilane,  $(\text{CH}_3)_3\text{SiOCH}_2\text{CH}_2\text{Cl}$ , is prepared from the reaction of a mixture of ethylene oxide and trimethylchlorosilane. This mixture may be placed under pressure or heated (104, 105). The product boils at  $131\text{--}132^\circ$  at 748 mm. and at  $134.3^\circ$  at 760 mm.;  $n_D^{20}$  1.4140; and  $d_4^{20}$  0.9443. This compound forms an azeotropic mixture with ethylene chlorohydrin boiling at  $120\text{--}122^\circ$ ;  $n_D^{20}$  1.426. With benzoyl chloride at  $130\text{--}140^\circ$  it regenerates trimethylchlorosilane (105).

128. Patnode and Schmidt, ibid., 67, 2272 (1945).

129. Daudt, U. S. Pat. 2,390,518, December 11, 1945. C. A., 40, 866 (1946)7.

Trimethyl-n-butoxysilane,  $(\text{CH}_3)_3\text{SiOC}_4\text{H}_9\text{-n}$ , results from the interaction of n-butanol and trimethylchlorosilane in the absence of solvent (127). It distills at  $124.5\text{-}124.7^\circ$  at 761 mm.;  $n_D^{20}$  1.3925; and  $d_4^{20}$  0.7774. It forms an azeotropic mixture with n-butanol boiling at  $111.0\text{-}111.5^\circ$  at 754 mm.;  $n_D^{20}$  1.3962.

Arvl Derivatives of the Type  $\text{R}_3\text{SiOR}'$

Triphenylsilanol,  $(\text{C}_6\text{H}_5)_3\text{OH}$ , is isolated from the reaction of octabromotrisiloxane or hexabromodisiloxane with an excess of phenylmagnesium bromide in the absence of ether. It melts at  $150^\circ$  (49).

Tri-(p-dimethylaminophenyl)silanol,  $(\text{p}-(\text{CH}_3)_2\text{N C}_6\text{H}_4)_3\text{Si-OH}$ , is reported as boiling at  $275\text{-}280^\circ$  (62).

Alkyl Derivatives of the Type  $\text{RSi}^{\text{O}}\text{OR}'$

Ethyl Silicoacetate,  $\text{CH}_3\text{SiOOC}_2\text{H}_5$ , is isolated as one of the products from the reaction of methylmagnesium iodide with tetraethoxysilane for three hours at  $150^\circ$  in the absence of ether (42). It distills at  $73^\circ$  at 760 mm.;  $d_4^{20}$  0.891; and  $n_D^{20}$  1.3696. Positive proof for the proposed formula for this compound is still lacking.

Alkyl Derivatives of the Type ROSiX<sub>3</sub>

Methoxytrichlorosilane, CH<sub>3</sub>OSiCl<sub>3</sub>, is obtained along with the other methoxychlorosilanes when methanol is added to silicon tetrachloride with cooling (111). It has a boiling point of 79-79.5°.

Methoxysilyltriisocyanate, CH<sub>3</sub>OSi(NCO)<sub>3</sub>, is made from methanol and silicon isocyanate. It boils at 168.4° at 760 mm.;  $d_4^{20}$  1.313;  $n^{20}$  1.4287; and MR<sub>D</sub> 36.3 (96).

Ethoxytrichlorosilane, C<sub>2</sub>H<sub>5</sub>OSiCl<sub>3</sub>, is prepared either from ethanol and silicon tetrachloride (111) or from the sealed tube reaction of acetyl chloride with tetraethoxysilane at 185° (102). This latter method gives poor yields. The product distills at 101.5-102°.

β,γ-Dibromo-η-propoxytrichlorosilane, CH<sub>2</sub>BrCHBrCH<sub>2</sub>OSiCl<sub>3</sub>, is isolated after a solution of β, γ-dibromo-η-propanol, and silicon tetrachloride, formed under cooling, is heated at reflux for two hours (107). It boils at 128-129° at 28 mm.;  $d_{15}^{15}$  1.911.

(1,3-Dichloropropoxy-2)-trichlorosilane, (ClCH<sub>2</sub>)<sub>2</sub>CHOSiCl<sub>3</sub>, is produced from 1,3-dichloropropanol-2 and silicon tetrachloride (107). The reactants are mixed at 0° and then heated at reflux for an hour. The product distills at 210° at 760 mm. and 92-3° at 12 mm.;  $d_{15}^{15}$  1.471.

Alloxytrichlorosilane,  $C_3H_5OSiCl_3$ , is prepared by adding allyl alcohol to cooled silicon tetrachloride (111). Another procedure (130) suggests then heating this mixture for an hour at reflux. The product has a boiling point of 122-122.5° (?) at atmospheric pressure (111), and 35.5-36° at 32 mm. (111, 130).

Methalloxytrichlorosilane,  $C_4H_7OSiCl_3$ , is produced upon the addition of methallyl alcohol to cooled silicon tetrachloride (111). This compound boils at 141-141.5° at atmospheric pressure, and at 53-53.5° at 32 mm.

Aryl Derivatives of the Type  $ROSiX_3$

Guaiacoxytrichlorosilane,  $o\text{-HO-C}_6\text{H}_4\text{OSiCl}_3$ , is made in a refluxing ether solution from guaiacol and silicon tetrachloride (131). It boils at 134-136° at 30 mm.;  $d_{18}^{18}$  1.3677.

p-Di-(trichlorosiloxy)benzene,  $p\text{-(Cl}_3\text{SiO)C}_6\text{H}_4\text{(OSiCl}_3\text{)}$ , is made in 75 per cent yield from reaction of hydroquinone with silicon tetrachloride in refluxing petroleum ether (115). The yield is very critically affected by the purity of the phenol used. The product boils at 276°;  $d_{18}^{18}$  1.22; and  $n_D^{15}$  1.4952.

m-Di-(trichlorosiloxy)benzene,  $m\text{-(Cl}_3\text{SiO)C}_6\text{H}_4\text{(OSiCl}_3\text{)}$ , is prepared in petroleum ether from resorcinol and silicon

131. Volnov and Mischelevich, J. Gen. Chem. U.S.S.R., 13, 213 (1943). [C. A., 38, 1484 (1944)].

tetrachloride (115). It boils at  $261^{\circ}$ ;  $d_{18}^{18}$  1.49; and  $n_D^{15}$  1.4961.

Thymoxytrichlorosilane,  $2-(1-C_3H_7)-5-CH_3-C_6H_3OSiCl_3$ , is synthesized when a solution of thymol and silicon tetrachloride in ether, formed under cooling, is refluxed for 30 minutes (131). It has a boiling point of  $122-124.5^{\circ}$  at 23 mm.;  $d_{18}^{18}$  1.3462.

Carvacroxytrichlorosilane,  $2-CH_3-5-(1-C_3H_7)C_6H_3OSiCl_3$ , is produced in the same manner as the thymol derivative (131). It distills at  $108-111^{\circ}$  at 4 mm.;  $d_{20}^{20}$  1.1798.

#### Alkyl Derivatives of the Type $(RO)_2SiX_2$

Dimethoxydichlorosilane,  $(CH_3O)_2SiCl_2$ , is obtained when methanol is added dropwise to cooled silicon tetrachloride. It distills at  $100-100.5^{\circ}$  (111).

Dimethoxysilyldiisocyanate,  $(CH_3O)_2Si(NCO)_2$ , is synthesized when silicon isocyanate and methanol are heated on a steam bath for an hour (96). It boils at  $152.1^{\circ}$ ;  $d_4^{20}$  1.208;  $n_D^{20}$  1.4028; and  $MR_D$  35.07.

Diethoxydichlorosilane,  $(C_2H_5O)_2SiCl_2$ , is prepared either from ethanol and silicon tetrachloride (111) or from equivalent amounts of tetraethoxysilane and acetyl chloride (102). The latter reaction must be conducted in a sealed tube at  $185^{\circ}$ . This compound is also one of the products ob-

tained from the prolonged action of ethyl acetate upon silicon tetrachloride (109). *n*-Butyl acetate will not give this type of reaction. This preparation distills at 135-137° at 748 mm. (109) and 51.5° at 32 mm. (102).

Diethoxydifluorosilane,  $(C_2H_5O)_2SiF_2$ , is synthesized by heating antimony trifluoride with tetraethoxysilane for 15 minutes (132). It has a boiling point of 83-83.5°.

Di-( $\beta, \gamma$ -dibromo-*n*-propoxy)dichlorosilane,  $(CH_2BrCH_2O)_2SiCl_2$ , is also obtained in the preparation of the mono-derivative (107). It distills at 115-120° at 1 mm. and decomposes most easily.

Di-(1,3-dichloropropoxy-2)-dichlorosilane,  $[(ClCH_2)_2CHO]_2SiCl_2$ , is produced from 1,3-dichloropropanol-2 and silicon tetrachloride (107). The reactants are mixed at 0° and then refluxed for two hours. The product distills at 140-1° at 0.28 mm.;  $d_{15}^{15}$  1.498.

Dialloxydichlorosilane,  $(C_3H_5O)_2SiCl_2$ , is prepared when a solution of allyl alcohol and silicon tetrachloride is heated together for an hour (111, 130). It has a boiling point of 80.5-81° at 32 mm.

Di-*i*-amoxydichlorosilane,  $(i-C_5H_{11}O)_2SiCl_2$ , results

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132. Peppard, Brown, and Johnson, J. Am. Chem. Soc., 68, 76 (1946).



when isoamyl acetate and silicon tetrachloride are heated for 30 hours at 180-200°. It boils at 108-110° at 8 mm. (109).

Dimethalloxydichlorosilane,  $(C_4H_7O)_2SiCl_2$ , is isolated along with all the other possible products from the interaction of methallyl alcohol and silicon tetrachloride (111). It has a boiling point of 88.5-89° at 20 mm.

#### Aryl Derivatives of the Type $(RO)_2SiX_2$

Diphenoxydichlorosilane,  $(C_6H_5O)_2SiCl_2$ , is one of the products isolated from the reaction of phenyl acetate with silicon tetrachloride (109). It distills at 208-213° at 5 mm. Benzyl acetate in this type of reaction gives acetyl chloride, benzyl chloride and silicon dioxide (109).

Dithymoxydichlorosilane,  $(2-(1-C_3H_7)-5-CH_3C_6H_3O)_2SiCl_2$ , is obtained upon heating an ether solution of thymol and silicon tetrachloride (131). It boils at 198-200° at 3 mm.;  $d_{18}^{18}$  1.1250. When guaiacol is reacted with silicon tetrachloride under conditions to give the di-ester, there is obtained a resinous mass that is considered to be guaia-dioxydichlorosilane (115) or diguaia-dioxysilane (131).

#### Alkyl Derivatives of the Type $(RO)(R'O)SiX_2$

Ethoxyalloyoxydichlorosilane,  $(C_2H_5O)C_3H_5OSiCl_2$ , is prepared from allyl alcohol and ethoxytrichlorosilane (111);

benzene is used as the solvent and isoquinoline to remove the hydrogen chloride formed. It distills at 66-66.5° at 32 mm.

Alloxy-cyclohexoxydichlorosilane,  $(C_3H_5O)_{cyclo-C_6H_{11}}OSiCl_2$ , is produced in the same way as the previously prepared compound. It boils at 127-127.5° at 32 mm. (111). It reacts with water to give a product thought to be alloxy-cyclohexoxysilicone,  $C_3H_5OSiOC_6H_{11-cyclo}$ .

#### Alkyl Derivatives of the Type $(RO)_3SiX$

Trimethoxychlorosilane,  $(CH_3O)_3SiCl$ , is isolated from the reaction products of methanol and silicon tetrachloride (111). It distills at 112-112.5°.

Trimethoxysilylisocyanate,  $(CH_3O)_3SiNCO$ , is obtained from the action of methanol on silicon isocyanate (96). It has a boiling point of 137.6° at 760 mm.;  $d_4^{20}$  1.233;  $n_D^{20}$  1.3839; and  $MR_D$  33.95.

Triethoxychlorosilane,  $(C_2H_5O)_3SiCl$ , is prepared from ethanol and silicon tetrachloride either in the absence of a solvent (111) or employing benzene as a solvent (95, 119). It also results when tetraethoxysilane is heated at 135° and above with benzoyl chloride or acetyl chloride (102). It has a boiling point of 156-157° at 744 mm. (102), 68.5-69° at 32 mm. (111), and 51-54° at 12 mm. It reacts with ethyl ricinoleate or guaiacol to give, as yet, nondefined products (114).

Triethoxyfluorosilane,  $(C_2H_5O)_3SiF$ , results from the 15 minute interaction of tetraethoxysilane and antimony trifluoride in the presence of antimony pentafluoride as a catalyst. It boils at  $133-133.5^\circ$  (132).

Tri-(1,3-dichloropropoxy-2-)chlorosilane,  $[(ClCH_2)_2CHO]_3SiCl$ , is made from the appropriate alcohol and silicon tetrachloride (107). It distills at  $196-197^\circ$  at 0.36 mm.;  $d_{15}^{15}$  1.482.

Triallyloxychlorosilane,  $(C_3H_5O)_3SiCl$ , is synthesized from allyl alcohol and silicon tetrachloride after heating them together for an hour (111,130). It boils at  $114.2-114.8^\circ$ .

Triallyloxyfluorosilane,  $(C_3H_5O)_3SiF$ , is prepared by heating allyl alcohol with triethoxyfluorosilane for an hour while distilling off the ethanol produced (132). It has a boiling point of  $99.0-99.5^\circ$ .

Tri-n-butoxychlorosilane,  $(n-C_4H_9O)_3SiCl$ , is synthesized from the reaction of acetyl chloride and tetra-n-butoxysilane in a sealed tube (102). It distills at  $84-85^\circ$  at 1 mm.

Tri-n-butoxybromosilane,  $(n-C_4H_9O)_3SiBr$ , is obtained from acetyl bromide and tetraethoxysilane in the same manner that the chloro-compound is prepared (102). The yield is very small.

Tri-sec-butoxychlorosilane,  $(sec-C_4H_9O)_3SiCl$ , is prepared

from the action of sec-butanol upon a benzene solution of silicon tetrachloride; dry air is blown through the reaction mixture to remove the hydrogen chloride formed (119). It has a boiling point of 106-109° at 10 mm.;  $d_4^{20}$  0.9392;  $n_D^{20}$  1.4103;  $MR_D$  74.60; and  $\gamma^{20}$  23.57.

Tri-tert.-butoxychlorosilane, (tert.-C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>SiCl, is produced by heating the sodium salt of tert.-butanol with silicon tetrachloride in petroleum ether (101). It distills at 86-87° at 12 mm.;  $n_D^{16}$  1.405.

Tri-n-butoxyfluorosilane, (n-C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>SiF, is synthesized from triethoxyfluorosilane and n-butanol (132). The solution is heated for an hour during which time the ethanol is distilled away as it is formed. It boils at 134-134.5°.

Trimethalloxychlorosilane, (C<sub>4</sub>H<sub>7</sub>O)<sub>3</sub>SiCl, is isolated from the mixture of methalloxysilanes obtained when silicon tetrachloride and methallyl alcohol are heated together. It has a boiling point of 122-123° at 20 mm. (111).

Tri-i-amoxychlorosilane, (i-C<sub>5</sub>H<sub>11</sub>O)<sub>3</sub>SiCl, is prepared from isoamyl alcohol and silicon tetrachloride. It distills at 143-146° at 12 mm. and 273-275°;  $d_4^{20}$  0.9362;  $n_D^{20}$  1.4209;  $MR_D$  88.35; and  $\gamma^{20}$  24.73 (119).

#### Arvl Derivatives of the Type (RO)<sub>3</sub>SiX

Triphenoxychlorosilane, (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>SiCl, is one of the

products that results from the action of phenyl acetate upon silicon tetrachloride (109). It boils at 215-218° at 4-5 mm.

Trithymoxychlorosilane,  $\sqrt[2]{(1-C_3H_7)-5-CH_3-C_6H_3O}_3SiCl$ , is made from silicon tetrachloride and thymol in an ether solution (131). It has a boiling point of 251-255° at 8 mm.;  $d_{20}^{20}$  1.1867.

Alkyl Derivatives of the Type RO(R'O)<sub>2</sub>SiX

Diethoxyvalloxychlorosilane,  $(C_2H_5O)_2C_3H_5OSiCl$ , is synthesized by heating diethoxydichlorosilane with allyl alcohol (111). It distils at 85.5-86° at 32 mm.

Dialloxyethoxychlorosilane,  $(C_3H_5O)_2C_2H_5OSiCl$ , is made in the same way as the previous compound from allyl alcohol and ethoxytrichlorosilane (111). It boils at 98-99° at 32 mm.

Dialloxycyclohexoxychlorosilane,  $(C_3H_5O)_2\text{cyclo}C_6H_{11}OSiCl$ , results from the interaction of dialloxydichlorosilane and cyclohexyl alcohol. It has a boiling point of 143-144° (111).

Dicyclohexoxyvalloxychlorosilane,  $(\text{cyclo}-C_6H_{11}O)_2C_3H_5OSiCl$ , is prepared from alloxytrichlorosilane and cyclohexyl alcohol (111). It distils at 148-148.5° at 2 mm.

Alkyl Derivatives of the Type  $\begin{matrix} O \\ || \\ R-C-O \end{matrix} SiX_{4-n}$

Tetraacetoxysilane,  $(CH_3COO)_4Si$ , is formed in small

yield when ethyl acetate, *n*-propyl acetate, or *i*-butylacetate is heated for four to five days with silicon tetrachloride (109). It melts at 110° and decomposes at 160°.

Triethoxyacetoxysilane,  $\text{CH}_3\text{COOSi}(\text{OC}_2\text{H}_5)_3$ , is produced from the interaction of acetic anhydride and tetraethoxysilane (117); the reaction time is 4-5 days. It boils at 81° at 19 mm.;  $d_4^{20}$  1.020; and  $n_D^{20}$  1.3910. Benzoic anhydride does not display this type of reaction. Triethoxyacetoxysilane when heated with acetyl chloride in a sealed tube in varying proportions and at various temperatures, furnishes only polymeric materials (102).

Diethoxydiacetoxysilane,  $(\text{CH}_3\text{COO})_2\text{Si}(\text{OC}_2\text{H}_5)_2$ , is also isolated from the reaction described in the previous preparation (102). It has a boiling point of 100° at 19 mm.;  $d_4^{20}$  1.075; and  $n_D^{20}$  1.3960.

Triethoxypropionoxysilane,  $\text{C}_2\text{H}_5\text{COOSi}(\text{OC}_2\text{H}_5)_3$ , is produced from the prolonged treatment of tetraethoxysilane with propionic anhydride (117). It boils at 101° at 15 mm.;  $d_4^{20}$  0.999; and  $n_D^{20}$  1.3946.

Diethoxydipropionoxysilane,  $(\text{C}_2\text{H}_5\text{COO})_2\text{Si}(\text{OC}_2\text{H}_5)_2$ , is also isolated from the preparation described above (117). It distills at 125° at 15 mm.;  $d_4^{20}$  1.025; and  $n_D^{20}$  1.3998.

Trimethylacetoxysilane,  $(\text{CH}_3)_3\text{SiO}_2\text{CCH}_3$ , is produced by the action of trimethyl- $\beta$ -chloroethoxysilane upon acetic anhydride. None of its constants is reported (105).

Alkyl Derivatives of the Type  $\text{R}_3\text{SiNR}_2$

Silyldimethylamine,  $(\text{CH}_3)_2\text{NSiH}_3$ , results when dimethylamine and monochlorosilane are merely added together (133, 134). No constants are given for this product. With trimethylamine, monochlorosilane merely forms an addition salt with a dissociation temperature of  $91^\circ$  at 760 mm.

Trimethylsilylmethylamine,  $(\text{CH}_3)_3\text{SiNHCH}_3$ , is made by the action of liquid methylamine or an ether solution of methylamine on trimethylchlorosilane (135). It distills at  $71^\circ$  at 755 mm.;  $n_D^{20}$  1.3905; and  $d_4^{20}$  0.7395.

Trimethylsilylethylamine,  $(\text{CH}_3)_3\text{SiNHC}_2\text{H}_5$ , is formed from the addition of trimethylchlorosilane to an ether solution of ethylamine (135). It has a boiling point of  $90.1$ - $90.8^\circ$ ;  $n_D^{20}$  1.3912.

Trimethylsilyldiethylamine,  $(\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2$ , results from the mere addition of trimethylchlorosilane to an ether solution of diethylamine (135). It boils at  $126.1$ - $126.4^\circ$  at 750 mm.;  $n_D^{20}$  1.4112 (135).

133. Emel us and Miller, Nature, 142, 996 (1938).

134. Emel us and Miller, J. Chem. Soc., 819 (1939).

135. Sauer and Hasek, J. Am. Chem. Soc., 68, 241 (1946).

Triethylsilylamine,  $(C_2H_5)_3SiNH_2$ , is made from the addition of triethylsilyl chloride to liquid ammonia (135). It distils at  $136.8-137.8^\circ$  at 753 mm.;  $n_D^{20}$  1.4259.

Alkyl Derivatives of the Type  $(RS)_4Si$

Tetra-t-thiobutoxysilane,  $(t-C_4H_9S)_4Si$ , is made by heating sodium t-butyl mercaptide with tri-t-thiobutoxychlorosilane in petroleum ether at  $170-175^\circ$  in a sealed tube (101). It melts at  $160-161^\circ$ .

Tri-i-thiopropoxy-t-thiobutoxysilane,  $(i-C_3H_7S)_3SiSC_4H_9-t$ , results from heating t-thiobutoxytrichlorosilane and sodium isopropyl mercaptide in ether for an hour (101, 136). It melts at  $23-23.5^\circ$  and boils at  $160-162^\circ$  at 3 mm.

Tri-t-thiobutoxy-n-thiopropoxysilane,  $(t-C_4H_9S)_3SiSC_3H_7-n$ , is produced from heating an ether solution of tri-t-thiobutoxychlorosilane with sodium n-propyl mercaptide (101, 136). It gives rhombic crystals that melt at  $62-62.5^\circ$ .

Tri-t-thiobutoxy-i-thiopropoxysilane,  $(t-C_4H_9S)_3SiSC_3H_7-i$ , is reported in the literature (137) as having tetragonal crystals isomorphic with tetra-t-thiobutoxysilane. Its method of preparation is not given.

Tri-t-thiobutoxy-n-thiobutoxysilane,  $(t-C_4H_9S)_3SiSC_4H_9-n$ ,  
 136. Klasens and Backer, Rec. trav. chim., 61, 513 (1942).  
 137. Klasens and Backer, Ibid., 58, 941 (1939).



is synthesized from sodium n-butyl mercaptide and tri-t-thiobutoxychlorosilane in an ether-benzene solution; the reactants are heated together for an hour. It boils at 153-153.5° at 1 mm. (101, 136).

Tri-t-thiobutoxy-i-thiobutoxysilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{SiSC}_4\text{H}_9\text{-i}$ , is prepared when sodium i-butyl mercaptide and tri-t-thiobutoxychlorosilane are heated in a sealed tube at 80° (101, 136). It distills at 146-148° and melts at 77-77.5°.

Tri-t-thiobutoxy-sec.-thiobutoxysilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{SiSC}_4\text{H}_9\text{-sec.}$ , is made from tri-t-thiobutoxysilane and sodium sec.-butyl mercaptide; these reactants are heated in petroleum ether for 12 hours (101, 136). It melts at 79-80° and boils at 145-147° at 1 mm.

Tri-t-thiobutoxy-t-thioamoxysilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{SiSC}_5\text{H}_{11}\text{-t}$ , melts at 111.5-114° and gives tetragonal crystals (101, 136). Conditions for its preparation are not given.

Tri-t-thiobutoxy-sec.-thiopentoxysilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{-SiSC}_5\text{H}_{11}\text{-sec.}$ , results from refluxing sodium sec.-pentyl mercaptide with tri-t-thiobutoxychlorosilane for 12 hours in petroleum ether (101, 136). It melts at 27-29° and boils at 169-170° at 2 mm.

Tri-t-thiobutoxycyclopentoxysilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{SiSC}_5\text{H}_9\text{-cyclo}$ , is formed when sodium cyclopentyl mercaptide is heated

to  $110^{\circ}$  with tri-t-thiobutoxychlorosilane for 12 hours (101, 136). It melts at  $104-105^{\circ}$  and gives tetragonal crystals.

Tri-t-thiobutoxycyclohexoxysilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{SiSC}_6\text{H}_{11}\text{-}$   
cyclo, is made in petroleum ether from sodium cyclohexyl mercaptide and tri-t-thiobutoxychlorosilane (101, 136). It melts at  $64-65^{\circ}$ .

Alkyl Derivatives of the Type  $(\text{RS})_2\text{Si}(\text{SR}')_2$

Di-i-thiopropoxydi-t-thiobutoxysilane,  $(\underline{i}\text{-C}_3\text{H}_7\text{S})_2\text{Si-}$   
 $(\text{SC}_4\text{H}_9\text{-}\underline{t})_2$ , results from heating sodium isopropyl mercaptide with di-t-thiobutoxydichlorosilane for five hours in petroleum ether. It melts at  $61.5-62.5^{\circ}$  and boils at  $147-8^{\circ}$  at 2 mm. (101).

Alkyl Derivatives of the Type  $(\text{RS})_3\text{Si}(\text{OR}')_1$

Tri-t-thiobutoxy-i-propoxysilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{SiOC}_3\text{H}_7\text{-}\underline{i}$ , is prepared in a sealed tube from sodium isopropoxide and tri-t-thiobutoxychlorosilane. It melts at  $55-56^{\circ}$  and distills at  $183-186^{\circ}$  at 5 mm. (101).

Alkyl Derivatives of the Type  $(\text{RS})_3\text{SiX}$

Tri-t-thiobutoxy chlorosilane,  $(\underline{t}\text{-C}_4\text{H}_9\text{S})_3\text{SiCl}$ , is produced from silicon tetrachloride and sodium t-butyl mercaptide; the reaction is conducted in benzene (101). It melts at  $71^{\circ}$ .

Alkyl Derivatives of the Type  $(RS)_2SiX_2$

Di-t-thiobutoxydichlorosilane,  $(t-C_4H_9S)_2SiCl_2$ , is prepared from silicon tetrachloride and sodium t-butyl mercaptide; the preparation is carried out in ether (101). It boils at  $133.5-135^\circ$  at 13 mm.;  $n_D^{16}$  1.522. The compound is stable and does not fume in the air (101).

Alkyl Derivatives of the Type  $RSSiX_3$

t-Thiobutoxytrichlorosilane,  $t-C_4H_9SSiCl_3$ , is also isolated from the previous preparation (101). It boils at  $174-7^\circ$ ; it readily fumes and decomposes in air.

Alkyl Derivatives of the Type  $R_3Si-O-SiR_3$

(The groups, R, may or may not be the same)

Hexamethyldisiloxane,  $(CH_3)_3SiOSi(CH_3)_3$ , is prepared from the hydrolysis of trimethylchlorosilane (127). Care must be taken to insure complete conversion of the intermediate silanol to the siloxane since these products form an azeotropic solution which is difficult to resolve. Distillation of the reaction product from phosphorus pentoxide seems to give this insurance. Hydrolysis of hexamethyldisilazane also furnishes this compound. It likewise occurs as an impurity in the preparation of trimethylsilyldiethylamine and trimethylsilylmethylamine (135). Another method of

preparation is furnished by the reaction of trimethyl-ethoxysilane with sulfuric or hydrochloric acid (138). If acetic anhydride is reacted with dimethylchloromethylchlorosilane (88) or trimethyl- $\beta$ -chloroethoxysilane (105) hexamethyldisiloxane is one of the products isolated. It has a boiling point of  $99^{\circ}$  (138) and  $100-100.9^{\circ}$  (127);  $n_D^{20}$  1.3774; and  $d_4^{20}$  0.7619. This compound gives a product identified as tri-(trimethylsiloxy)phosphate when it is slowly distilled from phosphorus pentoxide (127). It distills at  $85-87^{\circ}$  at 4 mm.;  $n_D^{20}$  1.4090. If hexamethyldisiloxane is mixed with fuming sulfuric acid di[trimethylsilyl]sulfate is formed (128). This latter product also results from the interaction of trimethylchlorosilane with sulfuric acid (139). It melts at  $56-58^{\circ}$  (139) or reportedly at  $45-46^{\circ}$  (128).

1,3-Di-(chloromethyl)-tetramethyldisiloxane,  $\text{[(ClCH}_2\text{)-(CH}_3\text{)}_2\text{Si}]_2\text{O}$ , is prepared by the hydrolysis of chloromethylchlorosilane (88). It distills at  $204.5^{\circ}$ ;  $n_D^{20}$  1.4390; and  $d_4^{20}$  1.045.

Chloromethylpentamethyldisiloxane,  $\text{CH}_2\text{Cl(CH}_3\text{)}_2\text{SiOSi(CH}_3\text{)}_3$ , is obtained when a mixture of chloromethyldimethylchlorosilane and trimethylchlorosilane are hydrolyzed and then heated together (88). It has a boiling point of  $204-204.5^{\circ}$ ;  $n_D^{20}$  1.4106; and  $d_4^{20}$  0.9105.

138. Daudt, U. S. Pat. 2,386,441, October 9, 1945. C. A., 40, 348 (1946).

139. Sommer, Pietriozza, Kerr, and Whitmore, J. Am. Chem. Soc., 68, 156 (1946).

1,1,1,-Trimethyl-3,3,3,-triethylidisiloxane,

$(\text{CH}_3)_3\text{SiOSi}(\text{C}_2\text{H}_5)_3$ , results from heating a solution of hexamethyl- and hexaethylidisiloxane in the presence of sulfuric acid (30). It boils at  $173.6-173.9^\circ$ ;  $n_D^{20}$  1.4098; and  $d_4^{20}$  0.8110.

Hexaethylidisiloxane,  $\Delta(\text{C}_2\text{H}_5)_3\text{Si}/_2\text{O}$ , mixed with fuming sulfuric acid gives di-(triethylsilyl)sulfate boiling at  $170^\circ$  at 12 mm.;  $n_D^{20}$  1.4442 (139).

Hexaethynylidisiloxane,  $\Delta(\text{CH}_3\text{C})_3\text{Si}/_2\text{O}$ , is produced from the addition of silicon tetrachloride to an ether solution of ethynylmagnesium bromide (122). After addition the solution is allowed to stand over night. This compound immediately decolorizes bromine water and forms a silver salt that explodes on heating.

Aryl Derivatives of the Type  $\text{R}_3\text{SiOSiR}_3$ 

Hexaphenyldisiloxane,  $\Delta(\text{C}_6\text{H}_5)_3\text{Si}/_2\text{O}$ , is prepared by the action of phenylmagnesium bromide on either hexabromo- or hexachloro-disiloxane. The Grignard reagent is added in ether and then the ether is removed and heating is continued (49). This product also results from the action of phenylsodium on hexabromodisiloxane (76). It melts at  $221^\circ$ .

Alkyl Derivatives of the Type  $\left[ \left( \text{RO} \right)_3 \text{Si} \right]_2 \text{O}$

Hexaethoxydisiloxane,  $\left[ \left( \text{C}_2\text{H}_5\text{O} \right)_3 \text{Si} \right]_2 \text{O}$ , is synthesized through the action of ethanol upon hexachlorodisiloxane; the hydrogen chloride must be removed by sweeping the solution with dry nitrogen (140). Hexabromodisiloxane will not give this product because the hydrogen bromide formed reacts with the ethanol to produce water which in turn causes hydrolysis of this starting material (140). If sodium ethoxide is warmed with hexabromodisilane this ethoxy derivative will form. Another method of preparation consists in adding water to a cooled solution of triethoxychlorosilane in the presence of pyridine (111). The compound boils at  $235^\circ$  (140) and  $95.5\text{--}96.5^\circ$  at 3 mm. It is a colorless, oily liquid that is practically incombustible in air; it is miscible with the common organic solvents and only very slowly hydrolyzed by water.

Hexaalloxydisiloxane,  $\left[ \left( \text{C}_3\text{H}_5\text{O} \right)_3 \text{Si} \right]_2 \text{O}$ , is produced from the addition of water to a solution of trialloxychlorosilane; pyridine must be present to remove the hydrogen chloride as it is formed (111). It has a boiling point of  $160\text{--}161^\circ$  at 10 mm.;  $n_D^{20}$  1.4394.

Hexamethalloxydisiloxane,  $\left[ \left( \text{C}_4\text{H}_7\text{O} \right)_3 \text{Si} \right]_2 \text{O}$ , is synthesized from water and trimethalloxychlorosilane (111) and from the 140. Schumb and Holloway, ibid., 65, 2753 (1941).

prolonged action of methallyl alcohol on hexaethoxydisiloxane (94). It boils at 176-178° at 4 mm.;  $n_D^{20}$  1.4414.

Hexa-*t*-butoxydisiloxane,  $\Delta(t-C_4H_9O)_3Si_2O$ , results when sodium *t*-butoxide and tri-*t*-butoxychlorosilane are heated together in a sealed tube for 15 hours at 170° (101). It gives hexagonal plates that melt at 260°.

Hexacyclohexoxydisiloxane,  $\Delta(cyclo-C_6H_{11}O)_3Si_2O$ , is produced from cyclohexanol and hexachlorodisiloxane; these reactants are merely heated together for eight hours (141). It melts at 217.1-217.6° and is soluble in the common organic solvents.

Alkyl Derivatives of the Type  $\Delta RO(R'O)_2Si_2O$

sym.-Tetraethoxydialloxydisiloxane,  $\Delta C_2H_5O(C_2H_5O)_2Si_2O$ , is synthesized by the slow addition of water to a solution of diethoxyalloychlorosilane; the reaction is conducted in the presence of pyridine. It boils at 149-151° at 18 mm.;  $n_D^{20}$  1.4080 (111).

sym.-Tetrahexoxydialloxydisiloxane,  $\Delta C_6H_{11}O(cyclo-C_6H_{11}O)_2Si_2O$ , is made from water and dicyclohexoxyalloychlorosilane in the presence of pyridine. Its constants are not reported (111).

141. Schumb and Holloway, Ibid., 63, 2852 (1941).

Alkyl Derivatives of the Type  $\overline{R_2R'OSi}_2O$

sym.-Tetramethyldi-n-butoxydisiloxane,

$\overline{[(CH_3)_2O(n-C_4H_9O)Si]}_2O$ , is prepared by treating a mixture of dimethyldichlorosilane and methyltrichlorosilane with n-butanol; the alcohol is added over an eight hour period to the reaction mixture maintained at  $90^\circ$  (124). This product also results from the two day action of n-butanol and water on dimethyldi-n-butoxysilane (124). It boils at  $224.5-225.5^\circ$  at 741 mm. and  $99-100^\circ$  at 10 mm.;  $n_D^{20}$  1.4051; and  $d_4^{20}$  0.8733.

Alkyl Derivatives of the Type  $\overline{(RS)_3Si}_2O$

Hexa-t-thiobutoxydisiloxane,  $\overline{[(t-C_4H_9S)_3Si]}_2O$ , is prepared from a solution of sodium hydroxide in dioxane and tri-t-thiobutoxychlorosilane (101). It melts at  $248-249^\circ$  with decomposition.

Higher Linear Siloxane Derivatives

Octaethoxytrisiloxane,  $(C_2H_5O)_8Si_3O_2$ , is produced from ethanol and octachlorotrisiloxane; the temperature is maintained at  $125^\circ$  and the hydrogen chloride produced is removed as it is formed (140).

sym.-Hexamethyldi-n-butoxytrisiloxane,

$\overline{[(n-C_4H_9O)(CH_3)_2SiO]}_2Si(CH_3)_2$ , is isolated from the reaction



mixture obtained either when n-butanol, water, and dimethyldi-n-butoxysilane, or when dimethyldichlorosilane, methyltrichlorosilane, and n-butanol are allowed to react for a prolonged period of time (124). This compound distills at  $125^{\circ}$  at 10 mm.;  $n_D^{20}$  1.4053.

Decaethoxytetrasiloxane,  $(C_2H_5O)_{10}Si_4O_3$ , is prepared from ethanol and decachlorotetrasiloxane at a temperature of  $150^{\circ}$ . It boils at  $290-295^{\circ}$  (140).

Tetradecaethoxyhexasiloxane,  $(C_2H_5O)_{14}Si_6O_5$ , results from the interaction of ethanol and tetradecachlorohexasiloxane when they are heated together at  $160^{\circ}$ ; the hydrogen chloride evolved must be removed. It distills at  $300-310^{\circ}$  (140).

Alkyl Derivatives of the Type  $\sqrt{B_3Si}_2NR'$

N-Methyldisilazane,  $(H_3Si)_2NCH_3$ , is made in quantitative yield by adding chlorosilane to an excess of methylamine (133, 134). It melts at  $32-3^{\circ}$  and is stable in air but is hydrolyzed by water.

N-Ethyldisilazane,  $(H_3Si)_2NC_2H_5$ , is prepared in quantitative yield in the same way as the previous compound (133, 134). It melts at  $65.9^{\circ}$  and is also stable to air.

Hexamethyldisilazane,  $\sqrt{(CH_3)_3Si}_2NH$ , is synthesized either by adding trimethylchlorosilane to liquid ammonia (127) or by adding ammonia to a refluxing ether solution of

trimethylchlorosilane (135). This latter reaction requires six hours. It boils at 125.2-125.7°;  $n_D^{20}$  1.4081. It is decomposed by methanol, water, and hydrochloric acid; but it gives no action with sodium (135).

Heptamethyldisilazane,  $[(CH_3)_2Si]_2NCH_3$ , results from heating a solution of trimethylsilylmethylamine and trimethylchlorosilane over night (135). It boils at 143-147°.

#### Alkyl Derivatives of the Type $R_3Si-SiR_3$

Hexamethyldisilane,  $(CH_3)_3Si-Si(CH_3)_3$ , is prepared by the action of excess dimethylzinc upon an ether solution of hexachlorodisilane; the reaction is effected in a sealed tube at 85° for several hours (135). It boils at 112.5°, melts at 14.0-14.4° and has a vapor pressure of 141 mm. at 61.2°. The value of the silicon to silicon bond is given as 2.34±0.10 Å, and of the silicon to silicon to carbon angle as 109±4°.

Hexaethyldisilane,  $(C_2H_5)_3Si-Si(C_2H_5)_3$ , is obtained from the action of ethylmagnesium bromide upon an ether solution of hexachlorodisilane (49). A small amount of tetraethylsilane is also isolated in this reaction. Diethylzinc gives no reaction with hexachlorodisilane even when the reactants are heated in a sealed tube at 130° (142). The product boils at 250°.

Hexa-n-propyldisilane,  $(n-C_3H_7)_3Si-Si(C_3H_7-n)_3$ , cannot  
142. Brockway and Davidson, ibid., 63, 3287 (1941).

be prepared from the Grignard reagent and hexachlorodisilane in an ether solution (49); however, the action of *n*-propylmagnesium bromide upon this reagent in the absence of ether furnishes an excellent yield of the desired product. It distills at 114° at 3 mm.;  $n_D^{20}$  1.4740; and  $d_4^{26}$  0.8693. It is insoluble in water and soluble in the common organic solvents.

Aryl Derivatives of the Type  $R_3Si-SiR_3$

Hexaphenyldisilane,  $(C_6H_5)_3Si-Si(C_6H_5)_3$ , is produced by the action of phenylmagnesium bromide upon hexachlorodisilane in the absence of ether after these reactants are heated together for four hours at 165-185°; only very little tetraphenylsilane is found in this reaction mass (49). No product whatsoever is isolated from the normal Grignard reaction between phenylmagnesium bromide and hexachlorodisilane. Both of these results are in contrast to the work of Schwarz and Sexaur (143) who claim that the silicon to silicon bond in disilanes is split during the "ordinary" Grignard reaction. This product is isolated in small yield from octachlorotrisilane in the "forced" Grignard reaction; no octaphenylcompound was isolated, however.

Hexabromodisilane gives this compound under exactly the same conditions as the hexachlorocompound. When hexachlorodisilane, sodium, and chlorobenzene are heated together, a

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143. Schwarz and Sexaur, Ber., 59B, 333 (1926).

vigorous reaction ensues, but only tetraphenylsilane is isolated (37, 76). If, however, phenylsodium is first prepared and then added to this hexachloro-compound, the major reaction product is hexaphenyldisilane (76). This would indicate that the energy generated in the formation of phenylsodium cleaves the silicon to silicon bond. The product melts at 352°.

Hexabenzylidisilane,  $(C_6H_5CH_2)_3Si-Si(CH_2C_6H_5)_3$ , is made by the reaction of benzylmagnesium chloride or benzylsodium with hexachlorodisilane (76). In the first case ether is absent, while in the second it is present. The compound melts at 194°.

Hexa-p-tolyldisilane,  $(p-CH_3C_6H_4)_3Si-Si(C_6H_4CH_3-p)_3$ , is produced from the Grignard reagent and hexachlorodisilane in the absence of ether (49). It melts at 345° and is only soluble in hot benzene or xylene. It is very stable melting without decomposition and it is not hydrolyzed by water or a dilute sodium hydroxide solution.

### Silicon Polymers

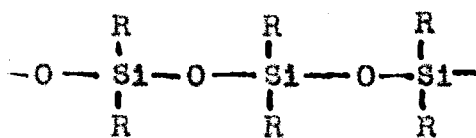
Silicones as a novel class of high polymers had their beginning as a result of basic research conducted in the Corning Glass Works (144). The investigations were centered in

144. Kolderman, Can. Chem. Process Inds., 29, 147 (1945)  
[C. A., 39, 2429 (1945)].

the field of polymers situated between the glasses and silicates, on the one side, and the truly organic polymers on the other. Initially the impelling force of these investigations arose from research in pure glass chemistry; finally, it was derived from the possibility of securing a glass-like plastic or other materials useful with glass (144, 145).

In general, the term "silicones" has been applied to silicon polymers. The name has its derivation in the organic term "ketone". Originally the silicones were believed to be monomers of the formula  $R_2Si=O$ , a molecule analogous to the organic ketone. Although silicon polymers have the same empirical formula  $R_2SiO$ , their bonding is polymeric and of the nature  $R - \underset{O}{Si} - R$ , thus making a name such as silicone chemically quite inappropriate. However, in this case euphony as well as long usage seems to have outweighed chemical considerations and the term so persists.

The first and fundamental silicon polymer was known to have the general formula  $-R_2SiO-$  (79, 146, 147) and was shown to have this structure (148):



These polymers are prepared with greatest care. A

145. Black, Mech. Eng., 67, 267 (1945) [C. A., 39, 2588 (1945)].  
 146. Rochow, Chem. Eng. News, 23, 612 (1945).  
 147. Yarsley, Chem. Trade J. 110, 371 (1942). [C. A., 36, 3872 (1942)].  
 148. Hunter, Hyde, Warrick, and Fletcher, J. Am. Chem. Soc., 68, 667 (1946).

dialkyl- or diaryldichlorosilane, prepared in the usual manner, is merely hydrolyzed and polymerization occurs without inducement (79, 111, 148, 150, 151). The real difficulty arises from attempting to direct this polymerization to a desired product. The organic groups may be aryl or alkyl or one of each. The properties of the polymer as well as their rate of polymerization vary with the types of organic groups present. These groups may also be substituted with such radical as OR (152). Various modifications of this basic type are known. For example, a linear polymer of the type  $R_3Si(OSiHR')_n$  is prepared by hydrolyzing an alkyldichlorosilane in the presence of a hexaalkyldisiloxane (153).

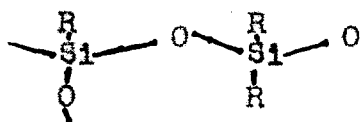
These polymers may be readily depolymerized by slowly heating them from  $350^\circ$  to  $400^\circ$  in the absence of air (148, 154). This forms low molecular weight cyclic siloxanes which may be separated by distillation. This type of cyclic polymer is also furnished by the careful hydrolysis of the appropriate methylchlorosilane (148, 154).

One of these cyclic products, that obtained from the cyclic condensation of diphenylsilanediol, has been in dispute in the literature. Kipping, who originally conducted this reaction

149. Bass, Hyde, Britton, and McGregor, Modern Plastics, 28, 70 (1944).
150. Kroton, J. Applied Chem. U.S.S.R., 12, 1435 (1939).  
C. A., 34, 6242 (1940).
151. The British Thomson-Houston Co. Ltd., Brit. Pat. 542,655, January 21, 1942. C. A., 36, 3877 (1942).
152. Rochow, U. S. Pat. 2,258,221, October 7, 1941. C. A., 36, 858 (1942).
153. Sauer, Schreiber, and Brewer, J. Am. Chem. Soc., 68, 962 (1946).
154. Patnode and Wilcock, ibid., 68, 358 (1946).

(155), indicated that it was a cyclotetrasiloxane. Hyde and Delong, on the other hand, in reviewing Kipping's work claimed that the true product of this reaction was a trimer and that Kipping's material must have been impure trimer (79). Burkhard recently has repeated these experiments and has rather conclusively established the product as the tetramer (156).

A second type of silicone is the so-called cross-linked polymer represented by this structural formula:

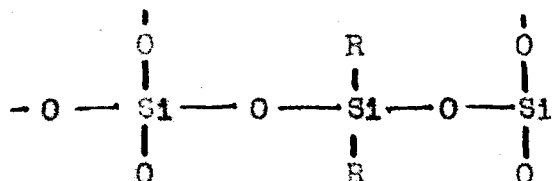


This is prepared simply from the hydrolysis of a mixture of dialkyl- or diaryldichlorosilane and similar trichlorosilanes (149, 157, 158). The same type of product is isolated from the interaction of a partially condensed siloxane with a triaryl- or trialkylethoxysilane in the presence of water (159). Such products are more viscous than those prepared by concurrently hydrolyzing mixtures of various siloxanes (159). This type of polymer also gives cyclic degradation products on slowly heating in the absence of air from 350° to 600° (160).

A third type of linear polymer is the one represented by

- 
155. Kipping, J. Chem. Soc., 101, 2138 (1912).  
 156. Burkhard, Decker, and Harker, J. Am. Chem. Soc., 67, 2174 (1945).  
 157. Rochow and Gilliam, ibid., 63, 798 (1941).  
 158. Rochow, U. S. Pat. 2,258,220, October 7, 1942. C. A., 36, 858 (1942).  
 159. Warrick, U. S. Pat. 2,397,895, April 2, 1946. C. A., 40, 3767 (1946).  
 160. Scott, J. Am. Chem. Soc., 68, 365 (1946).

the structural formula:



This is synthesized by hydrolyzing dialkyl- or diaryldichlorosilanes in a solution of silicon tetrachloride (145, 157).

A fourth type of polymer, a tridimensional one, results from hydrolyzing an aryl- or alkyltrichlorosilane (79, 147, 151, 157) or similar triethoxysilanes (42, 161).

All of these polymeric preparations which are essentially dehydration reactions are accelerated and productive of more pliable and less tacky products, if they are conducted in the presence of such catalysts as ethyl borate (162), hydrated ferric chloride (163, 164), boric oxide (165), hydrated stannic chloride, copper sulfate, or ferrous chloride (164).

A fifth type of silicone is the silicon co-polymer. This kind of product is produced when the appropriate alkyl- or arylchlorosilanes are hydrolyzed in the presence of some other substance capable of polymer formation as polyhydroxyalcohols (86), ketones (165), novalac resins (166), phenolic compounds

161. Andrianov, *Khim. Referat. Zhur.*, No. 12, 73 (1940).  
C. A., 37, 1527 (1943)].
162. Rochow, U. S. Pat. 2,371,068, March 6, 1945. C. A.,  
 39, 4899 (1945)].
163. Sprung, U. S. Pat. 2,383,827, August 28, 1945. C. A.,  
 39, 5553 (1945)].
164. Wright and Marsden, U. S. Pat. 2,389,477, November 20,  
 1945. C. A., 40, 2033 (1946)].
165. McGregor and Warrick, U. S. Pat. 2,375,998, May 15,  
 1945. C. A., 40, 245 (1945)].
166. Marsden, U. S. Pat. 2,390,378, December 4, 1945.  
C. A., 40, 4250 (1946)].



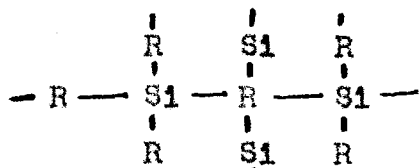
(167, 168), methyl methacrylates (169, 170), or vinyl compounds (171, 172, 173).

Cross-linking may be induced or increased in all of the above polymers by one of two methods. The first employs the oxidative treatment of the various polymers at elevated temperatures (79, 174, 175, 176). In this process the alkyl radicals are oxidized so splitting the silicon to carbon bond and substituting a new silicon to oxygen bond which is capable of further cross-linking. The second method employs cleavage of the aryl to silicon bond by aqueous hydrogen chloride under the influence of heat (79, 175) which again creates a new silicon to oxygen bond with its cross-linking potentialities. This process also allows the polymerization of the cyclic siloxanes already described thus forming a modified cross-linked polymer.

A sixth type of polymer reported is the one of this

- 
167. Ushakov, Russ. Pat. 53,752, August 31, 1938. C. A., 35, 1547 (1941)7.
168. Holzappel, Kolloid-Z., 100, 380 (1942). C. A., 38, 4251 (1944)7.
169. Nason, U. S. Pat. 2,182,208, December 5, 1939. C. A., 34, 2100 (1940)7.
170. Rothrock, U. S. Pat. 2,276,094, March 10, 1942. C. A., 36, 4630 (1943)7.
171. Garner, U. S. Pat. 2,396,692, March 19, 1946. C. A., 40, 3766 (1946)7.
172. McGregor and Warrick, U. S. Pat. 2,299,552, October 20, 1942. C. A., 37, 1842 (1942)7.
173. Staudinger, Ger. Pat. 707,393, May 21, 1941. C. A., 39, 5553 (1945)7.
174. Hyde, U. S. Pat. 2,386,467, Oct. 9, 1945. C. A., 40, 246 (1946)7.
175. Hyde, U. S. Pat. 2,386,466, October 9, 1945. C. A., 40 1062 (1946)7.
176. Daudt, U. S. Pat. 2,397,727, April 2, 1946. C. A., 40, 3938 (1946)7.

formula (177):



The radical, R, is a bivalent organic radical such as phenylene, methylene, etc. (178, 179, 180). The polymer is formed by allowing various alkyl- or arylmagnesium halides to react with silicon tetrachloride. Variations in the procedure allow the introduction of siloxane linkages into the molecule (178, 179, 180).

Various substances such as phenols (181, 182), and assorted amines (183, 184, 185, 186) have been used to stabilize these organosiloxanes.

The number of uses to which silicon polymers is being put is so great that it defies listing. However, certainly one of the most important and most advantageous uses to which

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177. Hyde, U. S. Pat. 2,371,050, March 6, 1945. C. A., 39 4888 (1945)7.
178. Rochow, U. S. Pat. 2,383,817, August 28, 1945. C. A. 39, 5556 (1945)7.
179. Rochow, U. S. Pat. 2,352,974, July 4, 1944. C. A., 39 225 (1944)7.
180. The British Thomson-Houston Co. Ltd., Brit. Pat. 552,640, April 19, 1943. C. A., 38, 5058 (1944)7.
181. McGregor and Warrick, U. S. Pat. 2,389,806, November 27, 1945. C. A., 40, 1536 (1946)7.
182. McGregor and Warrick, U. S. Pat. 2,389,804, November 27, 1945. C. A., 40, 1536 (1946)7.
183. McGregor and Warrick, U. S. Pat. 2,389,805, November 27, 1945. C. A., 40, 1536 (1946)7.
184. McGregor and Warrick, U. S. Pat. 2,389,807, November 27, 1945. C. A., 40, 1537 (1946)7.
185. McGregor and Warrick, U. S. Pat. 2,389,803, November 27, 1945. C. A., 40, 1536 (1946)7.
186. McGregor and Warrick, U. S. Pat. 2,389,802, November 27, 1945. C. A., 40, 1536 (1946)7.

these polymers is adapted is that of an electrical insulator (178, 187, 188, 189, 190). The particular property of these polymers that makes them especially adaptable to this use is that a very thin film of the polymer insulates as well as, or better than great thicknesses of other insulators. This greatly diminishes the weight of motors and allows their much more efficient cooling. Another important use is for special lubricants (149, 177, 191, 192, 193, 194). Silicones may be made which give a very small change of viscosity with temperature, which are quite thermally stable, and which do not freeze even at  $-100^{\circ}$ . All of these properties are desirable in various special lubricants.

For a more intensive study of the silicones some recent reviews might be consulted (20, 24, 145, 146, 149, 195, 196, 197).

187. Moses, Westinghouse Engr., 4, 138 (1944). C. A., 38, 6006 (1944)/.
188. Bass and Kauppi, Proc. Inst. Radio Engrs., 33, 441 (1945). C. A., 39, 5125 (1945)/.
189. Kauppi, Grant, Moses, and Horrell, Westinghouse Engr., 5, 135 (1945). C. A., 40, 493 (1946)/.
190. McGregor and Warrick, Brit. Pat. 463,995, September 8, 1944. C. A., 40, 3127 (1946)/.
191. Kauppi and Pederson, Natl. Petroleum News, 37, R944 (1945). C. A., 39, 5125 (1945)/.
192. Andrianov, Khimicheskaya Prom., No. 2, 1 (1945). C. A., 40, 2352 (1946)/.
193. Kauppi, Inst. Spokesman, 10, No. 3, 1 (1946). C. A., 40, 5554 (1946)/.
194. McGregor and Warrick, U. S. Pat. 2,382,082, August 14, 1945. C. A., 40, 148 (1946)/.
195. Foster, Oil Gas J., 44, No. 22, 86, 112 (1945) C. A., 39, 5551 (1945)/.
196. Davis, Pacific Plastics Mag., 3, No. 6, 28, No. 7, 40 (1945) C. A., 39, 4519 (1945)/.
197. Penn, Plastics (London), 9, 273 (1945) C. A., 40, 2683 (1946)/.

## EXPERIMENTAL

## A. Silicon Compounds

Tetraethylsilane.

To 3.4 g. (0.02 mole) of silicon tetrachloride in 25 ml. of anhydrous ether was slowly added 0.082 mole of ethyllithium (198) in 62 ml. of anhydrous ether. The whole system was maintained in a nitrogen atmosphere and the reaction flask was encased in an ice-bath. The addition was controlled so as to maintain a very gentle reflux of ether. Color Test I (199) was found to be negative immediately after the addition of the first, second, third, and fourth equivalent of the ethyllithium solution. When the excess (0.002 mole) was added the Color Test became positive and remained so even after 30 minutes' heating at reflux. This stirred and cooled solution was hydrolyzed and the ether layer was separated. The ether was removed and the residue was washed with concentrated sulfuric acid to remove any silanol present (200). The organic layer was separated, taken up in ether, and this ether solution was washed with water and then dried over sodium sulfate. The ether was removed and the residue was fractionated. There was

198. Gilman, Moore, and Baine, J. Am. Chem. Soc., 63, 2479 (1941).

199. Gilman and Schulze, ibid., 47, 2002 (1925).

200. Friedel and Crafts, Ann. chim. phys., 4, 19 (1895).

obtained 2.64 g., a yield of 92%, of tetraethylsilane boiling at 150-151° at 739 mm.;  $d_4^{20}$  0.7664; and  $n_D^{20}$  1.4250. The literature reports the boiling point as 152-154° (2);  $d_4^{20}$  0.7659; and  $n_D^{20}$  1.4246 (201).

#### Tetra-n-butylsilane

To 17 g. (0.1 mole) of silicon tetrachloride dissolved in 100 ml. of absolute ether was slowly added 0.41 mole of n-butyllithium (202, 203, 204) in 350 ml. of anhydrous ether. The system was arranged as in the previous preparation. Again the organometallic compound was added at such a rate as to maintain very gentle reflux. At the end of the addition of the first, second, and third equivalents of the n-butyllithium Color Test I was negative (199). However, at the end of the addition of the fourth equivalent this Color Test was positive. It remained so even after 30 minutes' heating at reflux; however, Color Test II-A (205) which is specific, in this case, for n-butyllithium was negative. The solution was then hydrolyzed and worked up in the same manner as the tetraethylsilane preparation. The compound, 24.9 g. or a yield of 97%, boiled at 156-157° at 22 mm.;  $d_4^{20}$  0.8008, and  $d_4^{22}$  0.8002;  $n_D^{20}$  1.4465; and  $n_D^{22}$  1.4460;  $MR_D$  calcd., 85.49; and  $MR_D$  found 85.19. This

201. Bygdén, Dissertation, Uppsala, 1916.

202. Gilman, Zoellner, and Selby, J. Am. Chem. Soc., 55, 1252 (1933).

203. Gilman and Stuckwisch, ibid., 65, 1461 (1943).

204. Gilman and Haubein, ibid., 66, 1515 (1944).

205. Gilman and Swiss, ibid., 62, 1847 (1940).

would seem to substantiate Sauer's doubt (30) of Post's "tetra-*n*-butylsilane" (42).

Anal. Calcd. for  $C_{16}H_{36}Si$ : Si, 10.93. Found: Si, 11.12.

The previous preparation was repeated using 20.8 g. (0.1 mole) of tetraethoxysilane (206) and 0.41 mole of *n*-butyllithium. Color Test I (199) was again negative after the addition of the first three equivalents of *n*-butyllithium, and again it was positive after the addition of the fourth equivalent. After 30 minutes' heating at reflux Color Test II-A (205) was negative. Upon fractionation of the residue there was obtained 24.4 g. (95%) of tetra-*n*-butylsilane boiling at 156-157° at 22 mm.;  $n_D^{20}$  1.4463; and  $d_4^{20}$  0.8010.

Tetraisopropylsilane (Attempted).

To 5.2 g. (0.025 mole) of tetraethoxysilane in 50 ml. of anhydrous ether was added an excess of isopropyllithium (198). The same precautions for this addition were taken as for those previously described. The resulting mixture was refluxed for 24 hours. The isolated product was washed with concentrated sulfuric acid and then treated in the usual manner. Distillation gave 4.8 g. (78%) of a product boiling at 200° at 738 mm.;  $n_D^{20}$  1.4560;  $d_4^{20}$  0.8657; and  $MR_D$  63.18. The calculated molecular refraction for tetraisopropylsilane is 67.21, and for

206. The tetraethoxysilane and silicon tetrachloride used in these preparations were redistilled commercial reagents.

triisopropylethoxysilane, 63.37. Therefore this compound was probably triisopropylethoxysilane.

Anal. Calcd. for  $C_{11}H_{26}OSi$ : Si, 13.88. Found: Si, 14.05.

Another preparation was conducted in exactly the same manner except that silicon tetrachloride was used in place of the tetraethoxysilane. From 6.8 g. (0.04 mole) of silicon tetrachloride and 0.2 mole of isopropyllithium in 251 ml. of anhydrous Skelly A, there was obtained 5.8 g., a 68% yield, of product distilling at  $198^{\circ}$  at 739 mm., and  $59^{\circ}$  at eight mm.;  $n_D^{20}$  1.4518;  $d_4^{20}$  0.9008; and  $MR_D$  57.81. According to the molecular refraction this compound cannot be tetraisopropylsilane. However, the calculated molecular refraction of triisopropylchlorosilane is 58.00; this indication was confirmed by this analysis.

Anal. Calcd. for  $C_9H_{21}ClSi$ : Cl, 18.42. Found: Cl, 18.13.

This same compound was prepared from 7.5 g. (0.043 mole) of silicon tetrachloride and 0.129 mole of isopropyllithium in 99 ml. of anhydrous Skelly A. The isopropyllithium was added to the cooled silicon tetrachloride over the course of 35 minutes. At this time Color Test I (199) was immediately negative. There was isolated 8.1 g., a yield of 97%, of triisopropylchlorosilane boiling at  $59^{\circ}$  at eight mm.;  $n_D^{20}$  1.4511;  $d_4^{20}$  0.9027;  $MR_D$  calcd., 58.00; and  $MR_D$  found, 57.76.

Anal. Calcd. for  $C_9H_{21}ClSi$ : Cl, 18.42. Found: Cl, 18.18.

A solution of 4.1 g. (0.02 mole) of triisopropylchlorosilane, 20 ml. of absolute ethanol, and four g. (0.05 mole) of

pyridine was heated at reflux for eight hours. Most of the ethanol was distilled from the solution and ether was added. The mixture was filtered and the filtrate was distilled free of solvent. The residue was fractionated to give two g., a 95% yield, of triisopropylethoxysilane distilling at  $198^{\circ}$  at 738 mm.;  $n_D^{20}$  1.4560;  $d_4^{20}$  0.8652;  $MR_D$  calcd., 63.26; and  $MR_D$  found, 63.37.

Anal. Calcd. for  $C_{11}H_{26}OSi$ : Si, 13.88. Found: Si, 14.01.

#### Tetra-t-butylsilane (Attempted)

This preparation was made by a modification of the directions of Bartlett (207) in which he formed tri-t-butylcarbinol and various other highly branched carbinols through the agency of a supposed intermediate t-butylsodium compound.

In a 500 ml. round-bottomed, three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel were placed 40 g. (1.73 g.-atoms) of sodium, 94 g. (1.01 mole) of t-butyl chloride, and 100 ml. of anhydrous ether. The whole system was swept with nitrogen before the reaction was begun and it was maintained in a nitrogen atmosphere during the entire course of the reaction. To this well stirred mixture was added dropwise 20.3 g. (0.1 mole) of tetraethoxysilane dissolved in 30 ml. of anhydrous ether. After ten ml. of this solution had been added, the flask was warmed. As

207. Bartlett and Schneider, J. Am. Chem. Soc., 67, 141 (1945).



soon as reflux commenced, a vigorous reaction set in. The sodium soon became black in color and spontaneous reflux was maintained as more of the tetraethoxysilane was added. Color Test I (199) was positive at this time. After all of the tetraethoxysilane was added, the solution was refluxed for 72 hours. This mixture was filtered and the solvent was removed from the filtrate. There was isolated a thick red oil which would not crystallize and which did not yield any distillate when heated to  $280^{\circ}$  at 0.5 mm. pressure. The residue in the flask solidified to a glassy solid on cooling; this was insoluble in the common organic solvents indicating that polymerization may have occurred. Conceivably, this thick red oil might have been a mixture of t-butyltriethoxysilane and di-t-butyldiethoxysilane which could polymerize on heating.

#### Tetraphenylsilane

To 8.5 g. (0.05 mole) of freshly distilled silicon tetrachloride dissolved in 50 ml. of anhydrous ether was slowly added a solution of 0.21 mole of phenyllithium (202) in 146 ml. of anhydrous ether. The whole system was maintained under nitrogen and the reaction flask was encased in an ice-bath. Color Test I (199) was made after the addition of each equivalent of phenyllithium. In each case it was negative just as soon as the equivalent was added. The reaction mixture was

hydrolyzed and filtered. The ether layer was then separated and distilled free of solvent. The residue was combined with the precipitate obtained by filtration; this combined solid was recrystallized from benzene. There was isolated 16.6 g. (99%) of tetraphenylsilane melting at 232-233°. The product was identified by the mixed melting point method.

This preparation was repeated using 8.3 g. (0.04 mole) of tetraethoxysilane in place of the silicon tetrachloride. Again Color Test I was negative as soon as each one of the four equivalents was added. There was obtained 13.1 g. (98%) of tetraphenylsilane melting at 232-233° after one recrystallization from benzene.

This synthesis was again conducted using in place of the silicon tetrachloride tetrathioethoxysilane prepared by the method of Baaker (101). From 8.1 g (0.03 mole) of tetrathioethoxysilane there was isolated 9.9 g. (98%) of tetraphenylsilane melting at 233°.

#### Triphenyl-*p*-tolylsilane

To 5.1 g. (0.03 mole) of silicon tetrachloride in 40 ml. of anhydrous ether was added 90 ml. of one molar (0.09 mole) phenyllithium (202) solution. The addition was, as before, just fast enough to cause very gentle reflux. Color Test I (199) was taken and found to be immediately negative. Then to this stirred solution was added 0.031 mole of *p*-tolyl-lithium (207) in 28 ml. of anhydrous ether. Color Test I

(199) was immediately negative after this addition. The solution was hydrolyzed and the clear ether layer was separated. This solution was dried and distilled free of solvent. The residue, which crystallized, was recrystallized once from Skelly B and twice from a methanol-ethyl acetate solution. This gave 9.5 g. (91%) of triphenyl-p-tolylsilane melting at 134-135°.

Anal. Calcd. for  $C_{25}H_{22}Si$ : Si, 8.00. Found: Si, 7.92.

#### Tri-p-tolylphenylsilane

To 5.1 g. (0.03 mole) of freshly distilled silicon tetrachloride in 40 ml. of anhydrous ether was slowly added 0.09 mole of p-tolyllithium (202) in 82 ml. of anhydrous ether. Color Test I (199) was negative as soon as this addition was complete. To this stirred and cooled solution was slowly added 0.031 mole of phenyllithium (202) in 31 ml. of anhydrous ether. The reaction mass was hydrolyzed and worked up in the same manner as before. The crystalline residue was recrystallized once from Skelly B and twice from a methanol-ethyl acetate solution. There was so isolated 10.1 g. (89%) of tri-p-tolylphenylsilane melting at 127-128°.

Anal. Calcd. for  $C_{27}H_{26}Si$ : Si, 7.42. Found: Si, 7.35.

#### $\Delta$ -Picolyltriphenylsilane (Attempted)

To a cooled solution of 16.64 g. (0.08 mole) of tetra-

ethoxysilane in 80 ml. of anhydrous ether was slowly added 0.24 mole of phenyllithium (202) in 227 ml. of anhydrous ether. Color Test I (199) was negative as soon as this addition was complete. The addition was regulated so as to maintain a very gentle ether reflux. To this stirred mixture was added 0.16 mole of  $\alpha$ -picolyllithium (208) in 178 ml. of anhydrous ether. During this addition there was no evidence of reaction; the deep brown-red color of the  $\alpha$ -picolyllithium solution was not discharged as it normally is when it is consumed, nor did the ether reflux even when the solution was added in a rapid stream. The resulting mixture was heated at reflux for 38 hours and then hydrolyzed. The ether layer was separated and the aqueous layer was extracted with three 100 ml. portions of ether. The ether solutions were combined and dried over sodium sulfate. After the ether was removed, there was isolated by distillation 9.8 g. of  $\alpha$ -picoline. This was identified by its picrate which melted at 167-169<sup>o</sup> and which gave no depression when a mixed melting point was taken with an authentic sample. The residue from this distillation was taken up in 95 per cent ethanol and treated with an ethanol solution of picric acid. There was isolated 11.6 g. of the picrate of  $\alpha$ -picoline melting at 168-169<sup>o</sup>; this was equivalent to 3.3 g. of  $\alpha$ -picoline indicating an over all return of 88 per cent of the  $\alpha$ -picoline used. By concentrating the ethanol filtrate

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208. Walter, Org. Syn., 23, 83 (1943).

from the picrate formation there was obtained 18.1 g. of triphenylsilanol melting at 149-150<sup>o</sup> and 1.6 g. of hexaphenyldisiloxane melting at 220-221<sup>o</sup>. These products were identified by the mixed melting point method, and they account for 90 per cent of the triphenylethoxysilane used.

#### Diphenyldi-p-tolylsilane

To a solution of 6.8 g. (0.04 mole) of silicon tetrachloride in 60 ml. of anhydrous ether was added dropwise 0.08 mole of phenyllithium (202) in 72 ml. of absolute ether. At the end of this addition a negative Color Test I (199) was obtained. Then 0.081 mole of p-tolyllithium (202) in 66 ml. of anhydrous ether was added dropwise. The solution was hydrolyzed and worked up in the same way as the previous preparation. The residue, which crystallized on cooling, was recrystallized once from a dilute ethanol solution and twice from a methanol-ethyl acetate solution. There was isolated 11.3 g. (78%) of diphenyldi-p-tolylsilane melting at 176-177<sup>o</sup>.

Anal. Calcd. for C<sub>26</sub>H<sub>29</sub>Si: Si, 7.70. Found: Si, 7.60.

This preparation was repeated using 6.8 g. (0.04 mole) of silicon tetrachloride in 60 ml. of ether and adding first 0.08 mole of p-tolyllithium (202) in 63 ml. of ether and then 0.081 mole of phenyllithium (202) in 75 ml. of ether. Upon hydrolyzing the reaction mixture and working it up in the same

manner as before, there was isolated 11.5 g. (79%) of diphenyldi-p-tolylsilane melting at 176-177°. The product had been recrystallized three times from an ethyl acetate-methanol solution. The two products were shown to be identical by the mixed melting point method.

### Triphenylmethylsilane

To a solution of 5.1 g. (0.03 mole) of silicon tetrachloride in 60 ml. of anhydrous ether was added dropwise 0.09 mole of phenyllithium (202) in 77 ml. of anhydrous ether. To this stirred solution was added 0.031 mole of methyllithium (209) in 21 ml. of anhydrous ether. Five minutes was required for Color Test I (199) to become negative. The resulting mixture was worked up in the usual manner. The residue obtained when the ether was distilled away was recrystallized from Skelly B to give 7.6 g. (92%) of triphenylmethylsilane melting at 66-67°. This was positively identified by the mixed melting point method with a sample prepared by H. Melvin from methyllithium and triphenylsilane (210).

This preparation was repeated using 6.8 g. (0.04 mole) of silicon tetrachloride in 70 ml. of ether. However, this time one equivalent of methyllithium (0.04 mole in 13.5 ml. of ether) was added first and this was followed by three equivalents of phenyllithium (0.12 mole in 100 ml. of ether). The solution

209. Zoellner, Doctoral Dissertation, Iowa State College (1933) p. 70.

210. Melvin, Unpublished studies, Iowa State College (1946).

was hydrolyzed and worked up as before. There was isolated a thick oil from which there was finally obtained 2.5 g., a 23% yield, of triphenylmethylsilane melting at 66-67° after three recrystallizations from Skelly B. The residual oil could not be crystallized.

#### Trimethylphenylsilane

To 12.48 g. (0.06 mole) of freshly distilled tetraethoxysilane dissolved in 75 ml. of anhydrous ether was added 0.18 mole of methyllithium (209) in 200 ml. of absolute ether. This mixture gave a negative Color Test I (199) after 5 minutes' stirring. Then 0.06 mole of phenyllithium (202) in 108 ml. of anhydrous ether was added. The solution was hydrolyzed and the ether layer was separated and dried over sodium sulfate. On removal of ether and fractionation of the residue there was isolated 8.0 g. (89% yield) of trimethylphenylsilane boiling at 163-164° at 737 mm.;  $n_D^{20}$  1.4938; and  $n_D^{25}$  1.4890. The literature gives these values: boiling point 170° at 758 mm.; and  $n_D^{25}$  1.4883 (201).

#### Triphenylsilanol

To a solution of 6.8 g. (0.04 mole) of silicon tetrachloride in 50 ml. of anhydrous ether was slowly added 0.12 mole of phenyllithium (202) in 88 ml. of anhydrous ether. The whole system was maintained under nitrogen and the reaction flask was encased in ice. As soon as the third equivalent was

added Color Test I (199) was negative. The solution was hydrolyzed and the ether layer was separated and dried over sodium sulfate. The ether was removed from this dry solution and the residue was recrystallized twice from Skelly D. This gave 10.8 g., a yield of 97%, of triphenylsilanol melting at 150-151°. This was identified positively by the mixed melting point method.

A larger run was then made. From 82.48 g. (0.485 mole) of silicon tetrachloride and 1.455 moles of phenyllithium in 1472 ml. of ether there was obtained 127.2 g. of triphenylsilanol melting at 150-151°. This was a yield of 95%.

#### Triphenylethoxysilane

To a solution of 8.32 g. (0.04 mole) of tetraethoxysilane in 50 ml. of anhydrous ether was slowly added 0.12 mole of phenyllithium (202) in 99 ml. of anhydrous ether. The resulting mixture was filtered by suction and the resulting solution was freed of most of its ether by distillation under reduced pressure. This mixture was filtered, and 100 ml. of anhydrous benzene was added to the filtrate. This mixture was also filtered and then distilled free of solvent. The residue was recrystallized from ethanol. There was first obtained 3.2 g. of a product that was only slightly soluble in hot ethanol and melted at 220-221°. This was shown to be hexaphenyldisiloxane by the mixed melting point method. This 3.2



g. thus accounted for 28 percent of the tetraethoxysilane used. Beside this, there was obtained 8.3 g., a 68% yield, of triphenylethoxysilane melting at 64-65<sup>o</sup>. This was identified by a mixed melting point with an authentic sample (211).

#### Trimethyl-p-bromophenylsilane

p-Bromophenylmagnesium bromide was prepared according to the method of Pink (212). Since this investigator gave no experimental directions, the following ones are given.

To a vigorously stirred mixture of 1.9 g. (0.08 g.-atom) of magnesium in 20 ml. of anhydrous ether was slowly added a solution of 9.44 g. (0.04 mole) of p-dibromobenzene in 100 ml. of anhydrous ether. After complete addition of this solution the resulting mixture was heated at reflux for six hours. During this time the Grignard reagent precipitated as a thick oil which immediately separated into a layer when stirring was stopped. The ether was then removed from this mixture and replaced by 100 ml. of anhydrous benzene. The Grignard reagent was soluble on the addition of this solvent and was immediately filtered from the excess magnesium. Titration indicated a 99% yield of the reagent.

This prepared Grignard reagent was slowly added to 6.8 g. (0.04 mole) of silicon tetrachloride in 70 ml. of anhydrous

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211. Cason, Unpublished studies, Iowa State College (1946).

212. Pink, J. Chem. Soc., 123, 3418 (1923).

ether. After 20 minutes' stirring, Color Test I (199) was negative. Thereupon, 0.121 mole of methyllithium (209) in 81 ml. of anhydrous ether was added in a slow stream. Color Test I was negative five minutes after this addition. This mixture was hydrolyzed and the ether layer was separated and dried over anhydrous sodium sulfate. The ether was distilled away and the residue was fractionated at reduced pressure.

There was isolated 4.1 g. (45% yield) of trimethyl-*p*-bromophenylsilane boiling at 95-96° at 3 mm.;  $n_D^{20}$  1.5271 and  $n_D^{28}$  1.5239;  $d_4^{20}$  1.2022;  $MR_D$  calcd., 57.52; and  $MR_D$  found 57.48.

This same product was obtained from *p*-bromophenyltrichlorosilane and methylmagnesium iodide (213) and gave this refractive index:  $n_D^{28}$  1.5241.

Anal. Calcd. for  $C_9H_{13}BrSi$ : Br, 34.84. Found: Br, 34.59.

This preparation was repeated using seven g. (0.035 mole) of triethoxychlorosilane in place of the silicon tetrachloride. Upon fractionation there was isolated 5.8 g. (73% yield) of trimethyl-*p*-bromophenylsilane boiling at 94-96° at 2.5 mm. and having these properties:  $n_D^{20}$  1.5272; and  $d_4^{20}$  1.2023.

This compound has recently been prepared in 53% yield from *p*-bromophenylmagnesium bromide and trimethylchlorosilane (214). It distills at 146-148° at 50 mm.;  $d_4^{20}$  1.2197;  $n_D^{20}$  1.5302; and  $MR_D$  found, 58.03.

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213. Wiley, Unpublished studies, Iowa State College (1946).  
 214. Burkhard, J. Am. Chem. Soc., 68, 2103 (1946).

Trimethyl-*p*-lithiophenylsilane

To 0.25 g. (0.036 g.-atom) of lithium in five ml. of anhydrous ether was slowly added a solution of 4.1 g. (0.018 mole) of trimethyl-*p*-bromophenylsilane in 25 ml. of anhydrous ether. A spontaneous reaction commenced and continued while the reagent was being added to the lithium. The resulting reaction mixture was refluxed for 30 minutes after addition was complete and spontaneous reflux had ceased. It was then poured into a slurry of ether and dry ice. When the dry ice had spontaneously evaporated, the resulting mixture was hydrolyzed and made acid with dilute hydrochloric acid. The ether layer was separated and dried over anhydrous sodium sulfate. The ether was removed from this solution and the residue was recrystallized twice from ether to give 2.3 g. (60% yield) of *p*-carboxyphenyltrimethylsilane melting at 110-111°. This acid gave a neutral equivalent, calcd. 194; found, 195.

Anal. Calcd. for  $C_{10}H_{14}O_2Si$ : Si, 14.43. Found: Si, 14.29.

Benzyltriethoxysilane

The directions used in the first preparation were adapted from the general procedure given by Andrianov and Gribanova (75, 118).

To a stirred mixture of 2.43 g. (0.1 g.-atom) of magnesium and 100 ml. of tetraethoxysilane was added 12.7 g. (0.1

mole) of benzyl chloride in 20 ml. of tetraethoxysilane. After the addition of the first 10 per cent of this halide, a spontaneous reaction set in and continued until all of the halide had been added. The resulting mixture was digested for three hours at 80-100°, and then filtered. The filtrate was distilled free of solvent and the residue was fractionated. There was obtained 12.1 g., a 47% yield, of benzyltriethoxysilane boiling at 245-248° at 739 mm. The literature value is 250-258° at 763 mm. (16).

To 40 g. (0.2 mole) of triethoxychlorosilane in 100 ml. of anhydrous ether was added 0.2 mole of benzylmagnesium chloride (215) in 235 ml. of anhydrous ether. The resulting mixture was heated at reflux for 30 minutes at which time Color Test I (199) was negative. This mixture was then filtered and the solvent was distilled from the filtrate. The residue was fractionated and there was obtained 18.5 g., a 65% yield, of benzyltriethoxysilane boiling at 245-247° at 740 mm.

The following method of attempted preparation was adapted from the general procedure proposed by Fleming (62).

To a vigorously stirred mixture of 20.8 g. (0.1 mole) of tetraethoxysilane, 1.4 g. (0.2 g.-atom) of lithium, and 100 ml. of ether was added 12.7 g. (0.1 mole) of benzyl chloride in 50 ml. of anhydrous ether. A vigorous reaction commenced

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215. Gilman, Zoellner, and Dickey, *ibid.*, 51, 1576 (1929).

and continued during the addition of the halide and for 30 minutes thereafter. Color Test I (199) was negative as soon as this spontaneous reaction had ceased. This reaction mixture was filtered and the filtrate was fractionated after the solvent had been distilled away. There was obtained a low boiling fraction distilling at 163-165° at 745 mm. and amounting to 18.8 g.; and a high boiling fraction distilling at 280-282° at 745 mm. and amounting to 7.4 g. The low boiling material was tetraethoxysilane, a return of 90 per cent of the starting material; the high boiling fraction was dibenzyl which was formed in 81% yield. This was shown by the fact that it crystallized to a solid from dilute ethanol melting at 50-52° which gave no depression upon a mixed melting point with an authentic sample of dibenzyl.

#### Trimethylbenzylsilane

To 25.4 g. (0.1 mole) of benzyltriethoxysilane in 50 ml. of anhydrous ether was added 0.3 mole of methyllithium (209) in 189 ml. of anhydrous ether. Color Test I (199) was negative five minutes after this addition was complete. The reaction mixture was hydrolyzed and the ether layer was separated and dried over sodium sulfate. The ether was removed from this solution and the residue was fractionated. There was isolated 15.3 g., a yield of 93%, of trimethylbenzylsilane boiling at 185-187° at 736 mm.; and  $n_D^{25}$  1.4912. The literature gives these values: boiling point 191° at 759 mm.; and

$n_D^{25}$  1.4909 (201).

To 12.7 g. (0.05 mole) of benzyltriethoxysilane in 100 ml. of anhydrous ether was added 0.15 mole of methylmagnesium iodide in 456 ml. of anhydrous ether. The solution was heated at reflux for two days; Color Test I (199) was still positive. Nevertheless, the mixture was hydrolyzed and the ether layer was separated and dried over sodium sulfate. The ether was removed from this dried solution and the residue was fractionated at 741 mm. There was obtained 6.2 g., a yield of 79%, of product distilling at 318-320° at 735 mm.;  $n_D^{20}$  1.5209;  $d_4^{20}$  0.9991;  $MR_D$  calcd. 97.20; and  $MR_D$  found, 97.01.

This calculated value\* for the molecular refraction is for sym.-dibenzyltetramethyldisiloxane which also satisfies the following analysis.

Calcd. for  $C_{18}H_{26}OSi_2$ :  $\bar{M}$ , 17.83. Found:  $\bar{M}$ , 17.97.

#### Attempted bromination of trimethylbenzylsilane

To a cooled solution of 8.2 g. (0.05 mole) of trimethylbenzylsilane in 100 ml. of carbon tetrachloride was added eight g. (0.05 mole) of bromine in 50 ml. of carbon tetrachloride.

\* These calculations of the molecular refraction were made using the values given by Sauer (30). For the convenience of the reader the various references discussing molecular refractions for the several silicon types are repeated here: Bygden, Ber., 44, 2640 (1911); ibid., 45, 707 (1912); ibid., 48, 1236 (1915); and Z. physik. Chem., 90, 243 (1915) [C. A., 9, 3014 (1915)]. Whitmore and co-workers, J. Am. Chem. Soc., 68, 475 (1946). Sauer, ibid., 68, 954 (1946).

The dropwise addition was complete in 30 minutes. Only a very small amount of hydrogen bromide was evolved. The resulting solution was distilled free of solvent and the residue was fractionated. There was isolated 6.9 g. (81%) of benzyl bromide boiling at 193-194° at 740 mm.;  $d_0^{22}$  1.4280. The literature gives the boiling point as 198-199° and the density  $d_0^{22}$  1.4380 (216). From this product there was formed benzyl 3,5-dinitrobenzoate according to the directions of Mulliken (217). It melted at 112-113° and gave no depression with a mixed melting point of an authentic sample prepared from a known sample of benzyl bromide.

#### Attempted nitration of trimethylbenzylsilane

To a cooled solution of 8.2 g. (0.05 mole) of trimethylbenzylsilane in 100 ml. of acetic anhydride was slowly added a cooled solution of 2.98 g. (0.05 mole) of concentrated nitric acid in ten ml. of acetic anhydride. The addition was regulated so as to maintain the reaction temperature below 0°. The resulting mixture was stirred at -5 -0° for six hours, and then poured into a liter of a 20 per cent ammonium hydroxide solution. This mixture was extracted with three 100 ml. portions of ether. These extracts were combined and dried over sodium sulfate. The ether was removed from this dried extract and

216. Kekulé, Ann., 137, 190 (1866).

217. Mulliken, "Identification of Pure Organic Compounds," Vol. IV, John Wiley and Sons, Inc., New York (1922). p. 89.

the residue was fractionated. There was obtained 5.2 g. of product boiling at 135-145° at 30 mm. This was refractionated to give 3.2 g. (48%) of phenylnitromethane boiling at 135-137° at 30 mm.;  $n_D^{20}$  1.5309; and  $d_4^{20}$  1.1577. The literature gives the boiling point as 141-142° at 35 mm.;  $n_D^{20}$  1.532; and  $d_4^{20}$  1.1598 (218).

This phenylnitromethane was reduced in accordance with the general directions of Gabriel (219).

The product was dissolved in 20 ml. of a 50-50 mixture of 20 per cent hydrochloric acid and absolute ethanol. To this solution was added four g., (0.037 g.-atom), of tin granules and this mixture was heated at reflux until the tin had dissolved. This solution was diluted with 20 ml. of ethanol and to it was added a hot solution of five g. of picric acid in ten ml. of ethanol. The precipitated picrate of benzylamine was filtered and recrystallized from benzene. It melted at 194° and gave no depression with an authentic sample of benzylamine picrate (220) clearly identifying the original product as phenylnitromethane.

#### Phenyltriethoxysilane

To 40 g. (0.2 mole) of triethoxychlorosilane in 100 ml. of anhydrous ether was added 0.2 mole of phenylmagnesium

218. Konowalow, Ber., 28, 1861 (1895).

219. Gabriel, ibid., 18, 1254 (1885).

220. Jerusalem, J. Chem. Soc., 95, 1283 (1909).



bromide (215) in 346 ml. of anhydrous ether. The resulting mixture was refluxed for 30 minutes after this addition at which time Color Test I (199) was negative. It was then filtered and the filtrate was distilled free of solvent. The residue was fractionated giving 26.2 g., a 66% yield, of phenyltriethoxysilane boiling at 228-30° at 741 mm.; and  $d_0^{10}$  1.0051. The literature gives these values: boiling point 232-234°; and  $d_0^{10}$  1.0055 (221).

#### Attempted nitration of phenyltriethoxysilane

To eight g. (0.033 mole) of phenyltriethoxysilane in 100 ml. of acetic anhydride was added 2.1 ml. (0.033 mole) of concentrated nitric acid in 25 ml. of acetic anhydride. The addition was conducted at -5° and the reaction mixture was stirred for six hours at -5°. The reaction mixture was poured over 100 g. of ice. To this mixture was added 100 ml. of concentrated ammonium hydroxide. This acid solution was extracted with three 100 ml. portions of ether. The extracts were combined, washed, and dried over sodium sulfate. The ether was distilled away and distillation of the residue was attempted at 0.1 mm. No distillate was collected and the contents of the flask solidified to a resin on cooling.

#### p-Aminophenyltriethoxysilane

This compound is described in the patent literature (62)  
221. Khotensky and Seregenkoff, Ber., 41, 2948 (1908).

but no details were indicated for its preparation. Therefore these experiments were undertaken.

In 100 ml. of anhydrous ether were placed 20.8 g. (0.1 mole) of tetraethoxysilane and 1.4 g. (0.2 g.-atom) of lithium. To this vigorously stirred solution was added dropwise a solution of 17.2 g. (0.1 mole) of *p*-bromoaniline in 50 ml. of anhydrous ether. After the vigorous reaction had ceased, the resulting mixture was heated at reflux for 30 minutes. Then the reaction mass was filtered and the filtrate was distilled free of solvent. The residue was fractionated and there was obtained 8.1 g., an 88% yield, of aniline boiling at 180-181<sup>o</sup> at 738 mm. This compound was identified by its conversion to *p*-toluenesulfonanilide (222) melting at 102-3<sup>o</sup> and giving no depression upon a mixed melting point with an authentic sample.

Since this procedure was unproductive of the desired compound, the following one was tried.

To a solution of 17.2 g. (0.1 mole) of *p*-bromoaniline in 100 ml. of anhydrous ether was added slowly 0.2 mole of *n*-butyllithium (202, 203, 204) in 402 ml. of anhydrous ether. The reaction mixture was cooled during the addition and then heated for 30 minutes at reflux. This solution was then added to 20.8 g. (0.1 mole) of tetraethoxysilane in 100 ml. of ether. The resulting mixture was stirred at reflux for two hours at which time Color Test I (199) was negative. Ethanol

222. Shriner and Fuson, "The Systematic Identification of Organic Compounds", John Wiley and Sons, Inc., New York (1940). p. 48.

was now added to the cooled mixture and the resulting mixture was filtered. The filtrate was distilled free of solvent and the residue was fractionated. There was obtained 6.8 g., a yield of 27%, of *p*-aminophenyltriethoxysilane boiling at 148-153° at 16 mm. The literature gives a boiling point of 145-150° at 14 mm. (62). These constants were also measured for this compound:  $n_D^{20}$  1.4950;  $d_4^{20}$  1.0702;  $MR_D$  calcd., 69.63; and  $MR_D$  found 68.99.

### Triethylchlorosilane

In accord with the directions of Whitmore and co-workers, (223) there was prepared 48.3 g., a 68% yield, of triethylchlorosilane from 98.0 g. (0.47 mole) of tetraethoxysilane and 1.4 mole of ethylmagnesium bromide. The product distilled at 143-144° at 735 mm. The literature value is 144° at 735 mm.

### Reformatsky reaction with triphenylchlorosilane

To a vigorously stirred refluxing mixture of 100 ml. toluene, 5.4 g. (0.05 mole) of benzaldehyde, and 3.3 g. (0.05 g.-atom) of sandpapered zinc foil, was slowly added a solution of 0.05 mole of triphenylchlorosilane in 50 ml. of anhydrous toluene. The resulting mixture was heated at reflux for 24 hours and then cooled and hydrolyzed. The toluene layer was separated and dried over sodium sulfate. The solvent was

223. DiGiorgio, Strong, Sommer, and Whitmore, J. Am. Chem. Soc., 68, 1380 (1946).

distilled from this solution and the residue solidified on cooling. It was recrystallized from Skelly D to give 11.2 g., an 81 per cent return, of triphenylsilanol melting at 150-151°. This was positively identified by the mixed melting point method.

#### Reformatsky reaction with triethylchlorosilane

The previous experiment was repeated using 5.4 g. (0.05 mole) of benzaldehyde, 3.3 g. (0.05 g.-atom) of sandpapered zinc foil, and 7.5 g. (0.05 mole) of triethylchlorosilane. When the solvent was removed, the residue was fractionated to give 5.2 g. (84%) of hexaethyldisiloxane boiling at 225-228° at 735 mm.;  $n_D^{20}$  1.4450;  $d_4^{20}$  0.8599;  $MR_D$  calcd. 76.12; and  $MR_D$  found, 75.95. The literature gives  $d_4^{20}$  0.8590 and a boiling point of 231° (221).

#### Ethyl triethylsilylacetate (Attempted)

To a vigorously stirred, refluxing mixture of 7.5 g. (0.05 mole) of triethylchlorosilane, 3.3 g. (0.05 g.-atom) of sandpapered zinc foil, and 100 ml. of toluene was slowly added 8.4 g. (0.05 mole) of ethyl bromoacetate. The addition required three hours. The reaction mixture became tan soon after this addition was begun and finally after three hours' reflux a brown tar began to separate. This mixture was stirred at reflux for six hours in all and was then filtered.

The solvent was distilled away from this filtrate and the residue was fractionated. There was obtained 6.2 g., a return of 83%, of triethylchlorosilane boiling at 142-144° at 735 mm. and giving the following analysis:

Anal. Calcd. for  $C_6H_{15}ClSi$ : Cl, 23.58. Found: Cl, 23.33.

The literature boiling point is 144° at 735 mm. (224).

Ethyl triphenylsilylacetate (Attempted).

The previous experiment was repeated using 13.8 g. (0.05 mole) of triphenylchlorosilane, 3.3 g. (0.05 g.-atom) of sand-papered zinc foil, and 8.4 g. (0.05 mole) of ethyl bromoacetate. The addition of this ethyl bromoacetate required three hours and the reaction mixture was heated for six hours after this addition. The solvent was distilled away and the thick brown tar that resulted was extracted for two days with Skelly D. This extract was distilled free of solvent. This residue melted at 96-98°, the melting point of triphenylchlorosilane, and was converted by treatment with water to triphenylsilanol melting at 150-151°. The return of chloride was 8.7 g., or 63%.

Reaction between triethylchlorosilane and ethyl sodioacetoacetate

The ethyl sodioacetoacetate used in this preparation was made by a modification of the directions of Breslow and co-

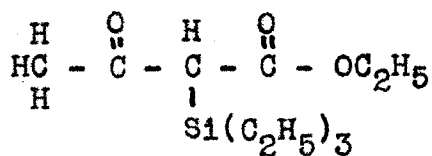
224. Friedel and Ladenburg, Ann., 147, 355 (1868).

workers (225).

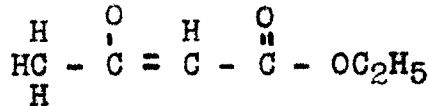
To a vigorously stirred mixture of 1.12 g. (0.05 g.-atom) of sodium sand and 100 ml. of anhydrous toluene was added 6.5 g. (0.05 mole) of ethyl acetoacetate in 30 ml. of anhydrous toluene. The resulting mixture was stirred until a clear solution was obtained; then, to this solution was added a solution of 7.5 g. (0.05 mole) of triethylchlorosilane in 30 ml. of anhydrous toluene. The resulting mixture was heated at 80-100° for 12 hours, filtered, and the filtrate was distilled free of solvent. The residue was fractionated to give 7.4 g., a yield of 61%, of product distilling at 108-110° at 6 mm.;  $n_D^{20}$  1.4560;  $d_4^{20}$  0.9590; and  $MR_D$  69.42.

This product could have the triethylsilyl-radical attached to the  $\alpha$ -carbon atom and so be ethyl  $\alpha$ -triethylsilylacetoacetate, or to the  $\beta$ -oxygen atom and so be ethyl  $\beta$ -triethylsiloxyacrylate (II). The calculated molecular refraction for the first compound is  $MR_D$  69.16, and for the second,  $MR_D$  69.12.

Anal. Calcd. for  $C_{12}H_{14}O_3Si$ : Si, 11.48. Found: Si, 11.54.



I



II

225. Breslow, Yost, Walker, and Hauser, J. Am. Chem. Soc., 66, 1921 (1944).

When the 2,4-dinitrophenylhydrazone (226) was attempted to be made, only ethyl acetoacetate 2,4-dinitrophenylhydrazone, melting at 94-95°, was isolated. The identity of this compound was confirmed by the mixed melting point method.

In 50 ml. of 10 per cent hydrochloric acid was placed 2.44 g. (0.01 mole) of this reaction product and the resulting mixture was heated at reflux for 30 minutes and then cooled. The organic layer was separated and dissolved in ether and the ether solution was dried over sodium sulfate. After the ether was distilled away, the residue displayed these properties: boiling point 226-228° at 739 mm.;  $d_4^{20}$  0.8599;  $n_D^{20}$  1.4440;  $MR_D$  calcd., 76.12; and  $MR_D$  found, 75.88. The product was hexaethyldisiloxane. The aqueous portion was made basic and treated with benzaldehyde (227) and heated at reflux. On cooling there was obtained dibenzalacetone melting at 110-111°. The compound was further identified by the mixed melting point method.

A solution of 4.9 g. (0.02 mole) of ethyl  $\beta$ -triethylsiloxycrotonate and 1.58 g. (0.02 mole) of freshly distilled acetyl chloride was heated for six hours at 135-150°. The resulting solution was fractionated. There was first isolated a fraction distilling at 139-143° at 736 mm.; triethylchlorosilane boils at 144° at 735 mm. (223). This product was shown to be triethylchlorosilane by analysis.

226. Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley & Sons, Inc., New York (1941). p. 255.

227. Huntress and Mulliken, ibid., p. 374.

Anal. Calcd. for  $C_6H_{15}ClSi$ : Si, 18.62. Found: Si, 18.85.

There was also isolated a second fraction boiling at 206-209° at 736 mm.;  $n_D^{15}$  1.4466; and  $d_4^{15}$  1.0664. This second product would be ethyl diacetoacetate if the acetyl radical were attached to the  $\alpha$ -carbon atom or ethyl  $\beta$ -acetoxyacrylate if it were attached to the oxygen atom. The literature constants for these compounds are: ethyl diacetoacetate: boiling point 209-211° (228),  $n_D^{17.6}$  1.4460; and  $d_{15}^{15}$  1.0967 (229); and ethyl  $\beta$ -acetoxyacrylate: boiling point 212° (230),  $n_D^{15}$  1.4470; and  $d_4^{15}$  1.0644 (231). Therefore the compound could be either one of these. Consequently this reaction product was refluxed for one hour with 10 per cent hydrochloric acid and the cooled product was split into two parts. The first part was tested with a ferric chloride solution and gave no test as acetylacetone should have (232). This solution was made basic with a sodium hydroxide solution and treated with hydrazine hydrate. No precipitate was obtained as there should have been if acetylacetone were present (232).

The other half was made basic with a sodium hydroxide solution and treated with benzaldehyde. A precipitate was obtained which was dibenzalacetone melting at 109-110° and was identified by the mixed melting point method (227).

The compound that would give acetone on this ketonic

228. Claisen and Zedel, Ann., 277, 164 (1893).  
 229. Perkin, J. Chem. Soc., 61, 858 (1895).  
 230. Nef, Ann., 266, 104 (1891).  
 231. Auwers, ibid., 415, 228 (1918).  
 232. Huntress and Mulliken, loc. cit., p. 253.



cleavage would be ethyl  $\beta$ -acetoxycrotonate. This compound in turn would be formed from the corresponding  $\beta$ -triethylsiloxyc compound. Consequently, the product from the action of ethyl sodioacetoacetate with triethylchlorosilane was probably ethyl  $\beta$ -triethylsiloxycrotonate.

#### Reaction of triphenylchlorosilane and ethyl sodioacetoacetate

A solution of 0.05 mole of ethyl sodioacetoacetate in 130 ml. of anhydrous toluene was made according to the directions given in the previous experiment. To this stirred solution was added a solution of 0.05 mole of triphenylchlorosilane in 150 ml. of anhydrous ether. The resulting mixture was heated at reflux for 12 hours and then cooled and filtered. The solvent was removed from this filtrate and there was obtained a thick brown oil. The only crystalline product able to be obtained from this material was 3.2 g. of hexaphenyldisiloxane melting at 220-221<sup>o</sup> and identified by the mixed melting point method. This accounted for 24% of the triphenylchlorosilane used.

#### Reaction between triphenylchlorosilane and diethyl sodiomalonate

To a vigorously stirred mixture of 1.12 g. (0.05 g.-atom) of sodium sand and 100 ml. of anhydrous toluene was added a solution of 8.5 g. (0.05 mole) of diethyl malonate in 30 ml. of anhydrous toluene. The resulting mixture was stirred until a clear solution was obtained, then to this was added a

solution of 14.8 g. (0.05 mole) of triphenylchlorosilane in 130 ml. of anhydrous ether. The resulting mixture was heated at 80-100° for 12 hours, cooled, filtered, and the filtrate was distilled free of solvent. The residue was a thick oil which neither would crystallize upon standing nor could be crystallized from any solvent.

Reaction of triethylchlorosilane with diethyl sodiomalonate

To a vigorously stirred mixture of 1.12 g. (0.05 g.-atom) of sodium sand and 100 ml. of anhydrous toluene was added a solution of 8.5 g. (0.05 mole) of diethyl malonate in 30 ml. of anhydrous toluene. The resulting mixture was stirred and warmed until a clear solution was obtained; then to this was added a solution of 7.5 g. (0.05 mole) of triethylchlorosilane in 25 ml. of anhydrous ether. The resulting mixture was heated at 80-100° for 12 hours, cooled, filtered, and the filtrate was distilled free of solvent. The residue was fractionated at reduced pressure; no silicon-containing distillate was isolated and the residue in the flask solidified to a resinous mass on cooling.

B.  $\beta$ -Lactams of  $\beta$ -Anilino- $\beta$ -phenylpropionic Acids

$\beta$ -Lactam of  $\beta$ -anilino- $\beta$ -phenylpropionic acid

$$\begin{array}{c} \text{H} \\ | \\ \text{C}_6\text{H}_5\text{C}-\text{NC}_6\text{H}_5 \\ | \\ \text{H}_2\text{C}-\text{CO} \end{array}$$

This  $\beta$ -lactam was prepared in 50% yield from 36.2 g. (0.2 mole) of benzalaniline according to the directions of

Gilman and Speeter (233). The melting point was 153-154<sup>o</sup>, that of the literature.

Basic hydrolysis of the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenylpropionic acid

Two g. (0.01 mole) of the  $\beta$ -lactam was placed in 50 ml. of a 20 per cent aqueous solution of potassium hydroxide. This mixture was refluxed until a clear solution was obtained. The murky yellow solution was decolorized with Norite A. This cleared solution was cooled and exactly neutralized with dilute acetic acid. The taffy-like solid that separated was filtered and allowed to dry and harden. This material was twice recrystallized from water. There was obtained 0.6 g. of  $\beta$ -anilino- $\beta$ -phenylpropionic acid melting at 134-135<sup>o</sup>. The literature melting point is 134<sup>o</sup> (234). The yield is 25%.

Acid hydrolysis of the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenylpropionic acid.

Two g. (0.01 mole) of the  $\beta$ -lactam was placed in 50 ml. of a 20 per cent hydrochloric acid solution. This mixture was refluxed until a clear solution was obtained. This yellow solution was decolorized with Norite A. The clear solution was cooled, made basic with dilute ammonium hydroxide, and then just neutral with dilute acetic acid. The white

233. Gilman and Speeter, J. Am. Chem. Soc., 65, 2256 (1943).  
 234. Fourneau and Billeter, Bull. soc. chim., 7, 593 (1942).  
[C. A., 36, 2849 (1942)].

precipitate that was obtained was filtered and recrystallized from water. There was obtained 0.9 g. of  $\beta$ -anilino- $\beta$ -phenylpropionic acid melting 134-135<sup>o</sup>. This represented a yield of 45%. A mixed melting point between this and the product obtained on basic hydrolysis showed no depression.

#### Ethyl $\beta$ -anilino- $\beta$ -phenylpropionate

Two g. (0.008 mole) of  $\beta$ -anilino- $\beta$ -phenylpropionic acid was dissolved in 20 ml. of absolute ethanol. This cooled, stirred solution was saturated with dry hydrogen chloride gas. This saturated solution was refluxed for one hour, after which time the ethanol was removed by distillation. The residue was taken up in ether and the ether solution was washed with a sodium bicarbonate solution and then with water. This washed solution was dried over sodium sulfate and the ether was removed. The residue, which solidified on cooling, was recrystallized from 95 per cent ethanol. There was so obtained 1.2 g. of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate, a yield of 69%. The melting point was 74-75<sup>o</sup>.

Anal. Calcd. for C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>N: N, 5.21. Found: N, 5.38.

#### Ethyl $\beta$ -anilino- $\beta$ -phenylpropionate

Ten g. (0.055 mole) of the  $\beta$ -lactam was dissolved in 100 ml. of absolute ethanol. This solution was saturated with dry hydrogen chloride gas. The resulting solution was heated at reflux for one hour and then the ethanol was removed. The

residue was dissolved in ether and this ether solution was washed first with a dilute solution of sodium carbonate and then with water. The washed solution was dried over sodium sulfate and the ether was removed. The residue was recrystallized from 95 per cent ethanol to give 10.1 g. of product melting 74-75°. This was ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate in 85% yield as was shown by the mixed melting point method with the authentic sample already prepared.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with methylmagnesium iodide

To 5.3 g. (0.02 mole) of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate in 100 ml. of absolute ether was slowly added 0.02 mole of methylmagnesium iodide (235) in 76 ml. of anhydrous ether. The entire system was maintained in a nitrogen atmosphere. The reaction mixture was stirred for one hour at which time Color Test I (199) was negative. Then the reaction mixture was hydrolyzed in the usual manner. The ether layer was removed, dried over sodium sulfate, and distilled free of ether. The residue was recrystallized from methanol to give 4.4 g. of the  $\beta$ -lactam melting at 153-154°. A mixed melting point with an authentic sample gave no depression. This was a yield of 98%.

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235. Zoellner, Doctoral Dissertation, Iowa State College (1933). p. 59.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with n-butyllithium

In the manner described above 0.02 mole of n-butyllithium (202, 203, 204) was allowed to react with 5.3 g, (0.02 mole) of the ethyl ester. On removal of the solvent there was obtained a sticky brown oil which after two recrystallizations from benzene gave 1.9 g. of the lactam melting at 152-153<sup>o</sup>. This was a yield of 43%. A mixed melting point with an authentic sample gave no depression.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with lithium diethylamide

According to the directions given above, 0.02 mole of lithium diethylamide, prepared from 0.02 mole diethylamine and 0.02 mole of n-butyllithium (202, 203, 204), was permitted to react with 5.3 g. (0.02 mole) of the ethyl ester. The reaction mixture was allowed to stir for 12 hours before it was hydrolyzed. There was obtained from the residue of the ether distillation a semi-solid mass which, after three recrystallizations from benzene, gave two g., a yield of 41%, of the lactam. Its melting point was 153-154<sup>o</sup>; a mixed melting point with an authentic sample of the lactam gave no depression.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with diethylzinc

In the previously described manner three ml. (approximately 0.02 mole) of diethylzinc was allowed to react with

5.3 g. (0.02 mole) of the ethyl ester. Again the reaction mixture was allowed to stir 12 hours before hydrolysis. There was isolated a sticky gum which would not crystallize from any solvent. Consequently, the sticky mass was placed in a Soxhlet extractor through which ether was condensed for 24 hours. From this ether solution there was obtained a product which, after air drying and four recrystallizations from benzene, gave a melting point of 152-153°. This was shown to be the  $\beta$ -lactam by the mixed melting point method. The yield was 0.5 g. or 10%.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with phenyllithium

In the same manner as before 0.02 mole of phenyllithium (202) was permitted to react with 5.3 g. (0.02 mole) of the ethyl ester. There was obtained a thick brown paste from which no crystalline material could be isolated.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with methyl-lithium

In the manner previously described 0.02 mole of methyl-lithium (209) was allowed to react with 5.3 g. (0.02 mole) of the ethyl ester. The ether solution furnished a semi-solid mass which in turn gave 0.9 g. of product melting at 153-154° after one recrystallization from methanol and two from benzene. This was the  $\beta$ -lactam in 19% yield as was shown by

the mixed melting point method.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with phenylethynylmagnesium iodide

According to the method described above 0.02 mole of phenylethynylmagnesium iodide, prepared from phenylacetylene and methylmagnesium iodide (235) was allowed to react with 5.3 g. (0.02 mole) of the ethyl ester. In working up the reaction mixture, the ether solution was washed with an ammoniacal solution of cuprous chloride to remove any phenylacetylene present. From this ether solution there was obtained a brown oil which gave 0.3 g., a yield of 6%, of the lactam after two recrystallizations from methanol followed by two from benzene. The lactam was verified by a mixed melting point with an authentic sample.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with phenylethynyllithium

In the above manner 0.02 mole of phenylethynyllithium, prepared from phenylacetylene and methyllithium (209) was allowed to react with 5.3 g. (0.02 mole) of the ethyl ester. Again the ether solution was washed with an ammoniacal solution of cuprous chloride. A brown oil was obtained which resisted all attempts at crystallization.



Acetomesitylene

According to the method of Meyer and Molz (236) acetomesitylene was prepared from 0.42 mole of mesitylene and 1.9 mole of acetyl chloride. There was obtained a yield of 58 g. (80%) of product boiling at 234-256°. The literature records a boiling point of 234-236°.

Reaction of ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate with acetomesitylmagnesium bromide

In the same manner as in the reaction with methylmagnesium iodide, 0.02 mole of acetomesitylmagnesium bromide, prepared from acetomesitylene and phenylmagnesium bromide (237), was mixed with 5.3 g. (0.02 mole) of the ester. From the ether solution there was obtained an oil which was crystallized from Skelly B. Recrystallization from 95 per cent ethanol gave one gram of starting material melting at 75°, a return of 19%. The product was identified by the mixed melting point method.

Variation of solvent in the preparation of the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenylpropionic acid

In the manner described before (p. 123) a 0.05 mole run was made using freshly distilled anisole as the solvent; the yield was 2.4 g. (22%) of the lactam which melted at 152-154°.

236. Meyer and Molz, Ber., 30, 1271 (1889).

237. Gilman and Jones, J. Am. Chem. Soc., 63, 1162 (1941).

When a 0.05 mole run was made employing a 50 per cent solution of anisole in anhydrous ether as a solvent, the yield was 2.6 g. (23%) of the lactam which melted at 153-154°.

When a 0.05 mole run was made using a 50 per cent solution of anisole in anhydrous benzene as the solvent, the yield was 3.8 g. (35%) of the lactam melting at 152-153°.

When a 0.05 mole run was made using anhydrous dioxane as the solvent, 5.5 g., 50%, of the lactam was obtained. This melted at 153-154°.

When a 0.05 mole run was made using anhydrous xylene as the solvent, four g., 36%, of the lactam was isolated. This melted at 153-154°.

Variation of the zinc employed in the preparation of the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenylpropionic acid

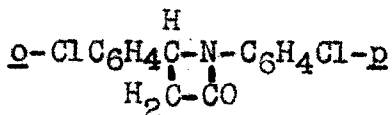
A 0.1 mole run of the lactam was made in the same manner as before (p. 123) except that an alloy containing 92% Zn and 8% Cu was used instead of the sandpapered zinc foil. There was obtained 11.2 g. (51%) of the lactam melting at 153-154°.

$o$ -Chlorobenzal- $p$ -chloroaniline

This compound was prepared according to the procedure of Hantzsch and Schwab (238). From 19.2 g. (0.15 mole) of  $p$ -chloroaniline and 21.1 g. (0.15 mole) of  $o$ -chlorobenzaldehyde 238. Hantzsch and Schwab, Ber., 34, 829 (1901).

there was obtained 37 g. (98%) of o-chlorobenzal-p-chloroaniline after one recrystallization from 95 per cent ethanol. The melting point was 68° which was identical with the literature melting point.

$\beta$ -Lactam of  $\beta$ -p-chloroanilino- $\beta$ -o-chlorophenylpropionic acid



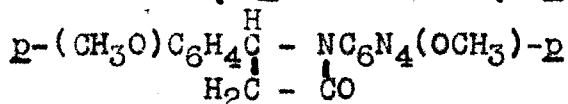
In the usual manner (p. 123) this lactam was prepared from 25 g. (0.1 mole) of o-chlorobenzal-p-chloroaniline. After two recrystallizations from benzene there was obtained 11 g. (38%) of the  $\beta$ -lactam of  $\beta$ -p-chloroanilino- $\beta$ -o-chlorophenylpropionic acid melting at 129-130°.

Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{ONCl}_2$ : Cl, 24.91. Found: Cl, 25.02.

p-Anisal-p-anisidine

This preparation was effected according to the directions of Senier and Forster (239). From 20.1 g. (0.15 mole) of anisaldehyde and 18 g. (0.15 mole) of p-anisidine there was formed 33.1 g. (91%) of p-anisal-p-anisidine. The melting point was 146° after one recrystallization from absolute ethanol; the literature gives a melting point of 146-147°.

$\beta$ -Lactam of  $\beta$ -p-anisidino- $\beta$ -p-anisylpropionic acid



239. Senier and Forster, J. Chem. Soc., 107, 1171 (1915).

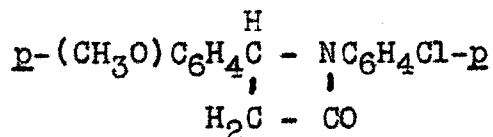
In the manner described above this lactam was prepared from 24.1 g. (0.1 mole) of p-anisal-p-anisidine. After one recrystallization from benzene and one from methanol, there was obtained 7.2 g. (25%) of the  $\beta$ -lactam of  $\beta$ -p-anisidino- $\beta$ -p-anisylpropionic acid which melted at 154-155.5°.

Anal. Calcd. for C<sub>17</sub>H<sub>17</sub>O<sub>3</sub>N: N, 4.95. Found: N, 5.16.

p-Anisal-p-chloroaniline

This compound was formed in accordance with the directions of Senier and Forster (240). This anil was obtained in 93% yield from 19.2 g. (0.15 mole) of p-chloroaniline and 20.1 g. (0.15 mole) of p-anisaldehyde. The melting point, 93-94°, was in agreement with that of the literature and was obtained after one recrystallization from 95 per cent ethanol.

$\beta$ -Lactam of  $\beta$ -p-chloroanilino- $\beta$ -p-anisylpropionic acid



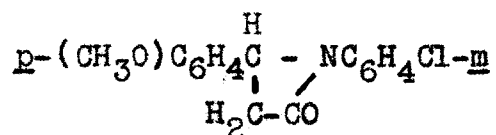
In the usual manner this lactam was obtained from 24.5 g. (0.1 mole) of p-anisal-p-chloroaniline in a yield of 10.3 g. (36%). The melting point, after one recrystallization from methanol, was 108-109°.

Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>ONCl: Cl, 12.33. Found: Cl, 12.41.

240. Senier and Forster, ibid., 105, 2467 (1913).

p-Anisal-m-chloroaniline

This compound was prepared according to the method of Senier and Forster (238) in 88% yield from 20.1 g. (0.15 mole) of p-anisaldehyde and 19.2 (0.15 mole) of m-chloroaniline. The melting point, after one recrystallization from absolute ethanol, was 53-54°, identical with that of the literature.

β-Lactam of β-m-chloroanilino-β-p-anisylpropionic acid

In the manner described above this lactam was formed from 24.5 g. (0.1 mole) of p-anisal-m-chloroaniline in a yield of five g. (17.5%). The melting point, after three recrystallizations from methanol, was 110.5-112°.

Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>ONCl: Cl, 12.33. Found: Cl, 12.35.

p-Anisal-o-chloroaniline

This preparation was effected through the procedure of Fischer and Neber (241) in a yield of 18 g. (72%) from 20.1 g. (0.15 mole) of p-anisaldehyde and 19.2 g. (0.15 mole) of o-chloroaniline. The melting point, after two recrystallizations from anhydrous petroleum ether, was 58-60°; the literature melting point is 58-61°.

241. Fischer and Neber, Ber., 45, 1095 (1912).

Attempted preparation of the  $\beta$ -lactam of  $\beta$ -*o*-chloroanilino-  
 $\beta$ -*p*-anisylpropionic acid.

In the usual manner this preparation was attempted from 24.5 g. (0.1 mole) of *p*-anisal-*o*-chloroaniline. There was obtained a thick oil which had a very sharp odor and which would not crystallize upon standing for six months or from a variety of solvents.

*o*-Chlorobenzal-*o*-chloroaniline

This compound was made in the manner of Mayer and Levis (242) in a yield of 37.4 g. (96%) from 19.2 g. (0.15 mole) of *o*-chloroaniline and 21.1 g. (0.15 mole) of *o*-chlorobenzaldehyde. The melting point, after one recrystallization from Skelly B, was 111-112° which was in accord with the literature melting point.

Attempted preparation of the  $\beta$ -lactam of  $\beta$ -*o*-chloroanilino-  
 $\beta$ -*o*-chlorophenylpropionic acid

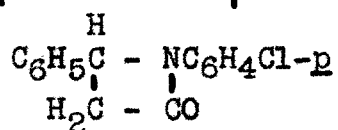
In the manner described above this preparation was attempted from 26 g. (0.1 mole) of *o*-chlorobenzal-*o*-chloroaniline. There was isolated a thick brown oil which resisted all attempts at crystallization and which did not crystallize of itself on standing for six months.

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242. Mayer and Levis, ibid., 52, 1641 (1919).

Benzal-p-chloroaniline

According to the method of Hantzsch and Schwab (238) this compound was made in a yield of 30 g. (94%) from 19.2 g. (0.15 mole) of p-chloroaniline and 15.9 g. (0.15 mole) of benzaldehyde. The melting point, after one recrystallization from absolute ethanol, was 61.5-62°; the literature melting point is 62°.

β-Lactam of β-p-chloroanilino-β-phenylpropionic acid

In the same manner as for the preparation of the other lactams, this lactam was made from 21.6 g. (0.1 mole) of benzal-p-chloroaniline. The yield was 12.8 g. (49.6%); the melting point, after one recrystallization from methanol, was 110-111°.

Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{ONCl}$ : Cl, 13.76. Found, 13.89.

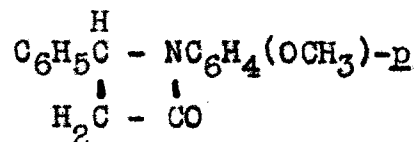
Benzal-p-anisidine

This compound was synthesized according to the method of Muller, Plöchl, and Shetz (243) from 15.9 g. (0.15 mole) of benzaldehyde and 18.5 g. (0.15 mole) of p-anisidine in a yield of 30.5 g. (95%). The melting point of this compound, after

243. Muller, Plöchl, and Shetz, ibid., 31, 2706 (1898).

one recrystallization from 95 per cent ethanol, was  $72^{\circ}$ , identical with that of the literature.

$\beta$ -Lactam of  $\beta$ -p-anisidino- $\beta$ -phenylpropionic acid



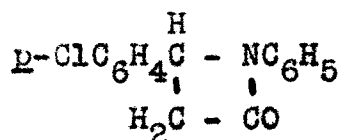
In the usual manner this lactam was prepared from 31.4 g. (0.1 mole) of benzal-p-anisidine in a yield of 10.9 g. (43%) after two recrystallizations from benzene. The melting point was  $96^{\circ}$ .

Anal. Calcd. for  $\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}$ : N, 5.49. Found: N, 5.72.

o-Chlorobenzalaniline

According to the directions of Bamberger and Müller (244) o-chlorobenzalaniline was prepared from 14 g. (0.15 mole) of freshly distilled aniline and 21.1 g. (0.15 mole) of o-chlorobenzaldehyde in a yield of 29 g. (90%). Its constants were these:  $d_4^{20}$  1.1809; and  $n_D^{20}$  1.6455. The constants given by the literature are  $d_4^{20}$  1.180; and  $n_D^{20}$  1.64544. (245).

$\beta$ -Lactam of  $\beta$ -anilino- $\beta$ -o-chlorophenylpropionic acid



In the usual manner this compound was prepared from 21.6 g.

244. Bamberger and Müller, Ann., 313, 118 (1900).

245. Auwers, Ber., 61, 1041 (1928).



(0.1 mole) of o-chlorobenzalaniline in a yield of 8.8 g. (34%). This compound was first obtained as a thick oil which required two months to crystallize. The melting point, after three recrystallizations from methanol, was 93-94°.

Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>ONCl: Cl, 13.76. Found: Cl, 14.01.

N,N'-Benzal-bis- $\alpha$ -pyridylamine  $C_6H_5C(NC_5H_4N-\alpha)_2$

This compound was prepared from 37.8 g. (0.4 mole) of  $\alpha$ -pyridylamine and 21.2 g. (0.2 mole) of benzaldehyde according to the method of Steinhauser and Diepolder (246). The yield was 51 g. (91%) after one recrystallization from Skelly B. The melting point was 108-109°, that of the literature.

Benzal- $\alpha$ -pyridylamine  $(C_6H_5C^H=NC_5H_4N-\alpha)$

According to the method of Kirpal and Reiter (247) there was obtained 30 g. (91%) of benzal- $\alpha$ -pyridylamine from 50 g. (0.18 mole) of N,N'-benzal-bis- $\alpha$ -pyridylamine. The boiling point at 25 mm. was 212-214°; the literature gives a boiling point at 18 mm. of 200°.

Attempted preparation of the  $\beta$ -lactam of  $\beta$ - $\alpha$ -pyridylamino- $\beta$ -phenylpropionic acid

In the usual manner the preparation of this lactam was attempted from 18.2 g. (0.1 mole) of benzal- $\alpha$ -pyridylamine.

246. Steinhauser and Diepolder, J. prakt. Chem. 93, 392 (1916).

247. Kirpal and Reiter, Ber., 60, 664 (1927).

There was obtained a thick, brown oil which could not be crystallized from any solvent and which did not crystallize on standing for five months.

Attempted preparation of benzal-*o*-chloroaniline

This preparation was attempted according to the directions of Fischer and Neber (241) from 16.4 g. (0.15 m.) of benzaldehyde and 19.2 g. (0.15 m.) of *o*-chloroaniline. There was isolated 17.6 g. of a solid melting at 45° after one recrystallization from Skelly B. The literature melting point for benzal-*o*-chloroaniline is 34-35°. This compound was found to be N,N'-benzal-bis-*o*-chloroaniline.

Anal. Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>2</sub>: Cl, 20.69. Found: Cl, 20.61.

Benzal-*o*-chloroaniline

This compound was prepared in the manner Kirpal and Reiter (247) used to prepare benzal-*d*-pyridylamine.

Twenty-five g. (0.073 mole) of N,N'-benzal-bis-*o*-chloroaniline was placed in a distilling flask and the compound was subjected to distillation at reduced pressure. One fraction came across at 70-75° at four mm.; another fraction was obtained at 165-170° at four mm. This second fraction, which amounted to 15 g. (97%), solidified on cooling, giving benzal-*o*-chloroaniline melting 34-35°. The first fraction was treated with benzenesulfonyl chloride to give a derivative which melted

at 129<sup>o</sup>. This is the melting point given in the literature (248) for benzenesulfon-o-chloroanilide. This compound was identified by the mixed melting point method.

Attempted preparation of the  $\beta$ -lactam of  $\beta$ -o-chloroanilino- $\beta$ -phenylpropionic acid

In the usual manner this preparation was attempted from 21.6 g. (0.1 mole) of benzal-o-chloroaniline. There was obtained a thick oil which would not crystallize from any solvent or upon standing.

C. Phenylpyridine Derivatives

2-Phenylpyridine

This compound was prepared according to the method of Edward (249). From 15.8 g. (0.2 mole) of pyridine and 0.2 mole of phenyllithium (202) there was obtained 18 g. (57%) of 2-phenylpyridine boiling at 142-144<sup>o</sup> at five mm. and at 85-87<sup>o</sup> at 0.1 mm. These were the literature boiling points.

2-Nitrophenylpyridines

When 62 g. (0.4 mole) of 2-phenylpyridine was nitrated with a mixture of potassium nitrate and sulfuric acid according to the method of Edward (249), there was obtained a mixture

248. Rapiet, Thompson, and Cohen, J. Chem. Soc., 85, 372 (1904).  
249. Edward, Unpublished studies, Iowa State College (1943).

of the three 2-(nitrophenyl)pyridines. These were separated as the literature described. There was obtained 30 g. (37%) of 2-(4'-nitrophenyl)pyridine melting at 130-131<sup>o</sup>; 25 g. (31%) of 2-(3'-nitrophenyl)pyridine melting at 72-73<sup>o</sup>; and 3.2 g. (4%) 2-(2'-nitrophenyl)pyridine melting at 60-61<sup>o</sup>. The literature (250) melting points are 130-131<sup>o</sup>; 73-74<sup>o</sup>; and 60-61<sup>o</sup>, respectively.

#### 2-(4'-Aminophenyl)pyridine

2-(4'-Aminophenyl)pyridine has been prepared in 86% yield (250) by the use of tin and hydrochloric acid and by the use of sodium sulfide (249) in 32% yield. It was found that this compound could be made most easily and in the highest yield by the following procedure.

Twenty-four g. (0.12 mole) of 2-(4'-nitrophenyl)pyridine was placed in 200 ml. of absolute ethanol along with five g. of activated Raney nickel. This was placed in a low-pressure Parr hydrogenation apparatus which was then charged with a pressure of 45 lbs. of hydrogen. At room temperature, the hydrogen was taken up very slowly; however, upon heating the reaction mixture to 65-70<sup>o</sup>, hydrogen was consumed rather rapidly. In the course of an hour, the theoretical amount of hydrogen was used. The reaction mass was removed from the bomb, filtered free of the Raney nickel, and the clear filtrate

250. Forsyth and Pyman, J. Chem. Soc., 2912 (1926).

was distilled free of solvent. The residue was recrystallized from dilute ethanol giving 19 g. (95%) of 2-(4'-aminophenyl)pyridine melting at 97-98°.

2-(4'-Benzalaminophenyl)pyridine

To ten g. (0.1 mole) of benzaldehyde was added a solution of 17 g. (0.1 mole) of 2-(4'-aminophenyl)pyridine in 50 ml. of ethanol. The solution warmed of itself upon this addition, and was heated at reflux for two hours. Upon cooling, a precipitate formed which was filtered. This was 24 g. (95%) of 2-(4'-benzalaminophenyl)pyridine melting at 102-103°, after one crystallization from absolute ethanol.

Anal. Calcd. for  $C_{18}H_{14}N_2$ : N, 10.86. Found: N, 11.01.

2-(4'-Salicylalaminophenyl)pyridine

In the same manner as above 2-(4'-salicylalaminophenyl)pyridine was prepared from one g. (0.006 mole) of 2-(4'-aminophenyl)pyridine and 0.7 g. (0.006 mole) of salicylaldehyde. There was obtained 1.5 g. (93%) of product melting at 137-138° after one recrystallization from absolute ethanol.

Anal. Calcd. for  $C_{18}H_{14}ON_2$ : N, 10.22. Found: N, 10.35.

2-[4'-(2",5"-Dimethylpyrryl-1")phenyl]pyridine

There was dissolved in ten ml. absolute ethanol 3.4 g. (0.02 mole) of 2-(4'-aminophenyl)pyridine, 2.28 g. (0.02 mole)

of acetylacetone, and one ml. of glacial acetic acid. This stirred solution was heated for four hours at reflux. On cooling there was obtained 5.1 g. (90%) of 2-(4'-(2",5"-dimethylpyrryl-1")phenyl)pyridine melting at 98.5-99<sup>o</sup>, after recrystallization from dilute ethanol. Since this compound was reported in the literature (251) as having a melting point of 93-94<sup>o</sup> it was analyzed.

Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>: N, 11.29. Found: N, 11.50.

#### 2-(4'-Formylaminophenyl)pyridine

In 20 ml. of 98 per cent formic acid there was dissolved one g. (0.006 mole) of 2-(4'-aminophenyl)pyridine; this solution was refluxed for three hours. The resulting solution was transferred to a distilling flask containing 20 ml. of anhydrous toluene. This was distilled free of solvent, the very last traces being removed under diminished pressure. The residue was recrystallized from benzene and so gave 0.9 g. (88%) of 2-(4'-formylaminophenyl)pyridine melting at 127-128<sup>o</sup>.

Anal. Calcd. for C<sub>12</sub>H<sub>10</sub>ON<sub>2</sub>: N, 14.14. Found: N, 14.02.

#### 2-(4'-Acetaminophenyl)pyridine

Twenty ml. of acetic anhydride, 20 ml. of anhydrous benzene, and five g. (0.03 mole) of 2-(4'-aminophenyl)pyridine were placed in a 25 ml. flask and heated at reflux for one-half an hour. The resulting solution was treated with 20 ml.

251. Gilman, Stuckwisch, and Nobis, J. Am. Chem. Soc., 68, 326 (1946).

of a nine molar alcoholic hydrogen chloride solution. The precipitated hydrochloride was filtered, dried, dissolved in water, and treated with a sodium bicarbonate solution. The precipitated acetamino-compound was recrystallized from 95 per cent ethanol. There was obtained 5.9 g. (94%) of 2-(4'-acetaminophenyl)pyridine melting at 134-135°. The literature (252) melting point is 134-135°. The yield of the literature preparation is not given.

2-(3'-Nitro-4'-acetaminophenyl)pyridine

This compound was reportedly (252) prepared in 84% yield by the action of fuming nitric acid on 2-(4'-acetaminophenyl)pyridine. The following procedure was found to be more consistent and to furnish higher yields.

There was dissolved five g. (0.024 mole) of 2-(4'-acetaminophenyl)pyridine in 20 ml. of cold, concentrated sulfuric acid. The sulfuric acid was cooled and stirred during this addition. To this ice-cooled solution was added a cooled solution of 2.4 g. (0.024 mole) of potassium nitrate in 20 ml. of concentrated sulfuric acid. Addition was regulated so as to maintain the temperature of the reaction below 10°. After addition the reaction mixture was stirred at 15-20° for three hours; then it was poured into 300 ml. of ice and water. This mixture was made basic with dilute ammonium hydroxide. The precipitate was filtered and yielded 6.4 g. (94%) of 2-(3'-nitro-4'-acetamino-

252. Coates, Cook, Heilbron, Hey, Lambert, and Lewis, J. Chem. Soc., 401 (1943).

phenyl)pyridine after one recrystallization from absolute ethanol. The melting point was 142-143<sup>o</sup>, the same as that of the literature.

2-(3'-Nitro-4'-aminophenyl)pyridine

This compound was obtained in a yield of 5.1 g. (91%) upon the basic hydrolysis of six g. (0.023 mole) of 2-(3'-nitro-4'-acetaminophenyl)pyridine according to the directions of Heilbron and co-workers (252). The melting point, after recrystallization from absolute ethanol, was 148-149<sup>o</sup>, identical with that of the literature.

2-(3'-Nitro-4'-formylaminophenyl)pyridine

Employing the procedure used to prepare 2-(4'-formylaminophenyl)pyridine, 2-(3'-nitro-4'-formylaminophenyl)pyridine was prepared from one g. (0.0046 mole) of 2-(3'-nitro-4'-aminophenyl)pyridine and 20 ml. of 98 per cent formic acid. There was obtained 0.9 g. (82%) of product melting at 102-104<sup>o</sup> after one recrystallization from benzene. This melting point had to be taken rapidly, otherwise the compound slowly decomposed and ultimately gave the melting point of the free amine. The compound was very slowly decomposed in hot water.

Anal. Calcd. for C<sub>12</sub>H<sub>9</sub>O<sub>3</sub>N<sub>3</sub>: N, 17.28. Found: N, 17.16.

p-Anisyllithium

These directions are a variation of those of Edward (249).



A solution of 49.5 g. (0.4 mole) of p-bromoanisole in 75 ml. of anhydrous ether was added in 12 minutes with vigorous stirring to 5.6 g. (0.8 g.-atom) of lithium in eight ml. of anhydrous ether. In order to realize this short time of reaction, the lithium had been hammered to a thickness of about 0.5 mm., and cut into very small pieces, and the reaction flask was cooled with an ice-bath as soon as refluxing had set in. The reaction mass was stirred for five minutes longer and then used. The total time of reaction was 15 minutes.

#### 2-(4'-Methoxyphenyl)pyridine

This compound was synthesized by a variation of the method of Edward (249).

The p-anisyllithium, prepared from 49.5 g. (0.4 mole) of p-bromoanisole, was added slowly with stirring to 31.6 g. (0.04 mole) of anhydrous pyridine (253) in 30 ml. of anhydrous ether. During this preparation the whole system was maintained under a nitrogen atmosphere. Ten minutes after the addition of the pyridine, its reaction with p-anisyllithium was complete as indicated by a red color with Color Test I (199). Subsequently, dry and carbon dioxide-free air was passed over the stirred mixture, heated to maintain a gentle reflux of the ether, for 18 hours; at the end of this time, the reaction mixture gave no Color Test I. Consequently, it was hydrolyzed with 20 g. of ammonium chloride and approximately 300 g. of ice. The ether 253. Karl Fischer Reagent pyridine (Eastman Kodak 214-H) was found satisfactory for use in this reaction.

layer was separated from the aqueous layer and from a heavy brown gum; this gum was triturated twice with ether. The combined ether fractions were dried over sodium sulfate for three hours. After removal of the ether, the residue was distilled at one mm. pressure. A yellow oil boiling at 120-135° was collected; this solidified upon cooling to an oily solid. It weighed 31.5 g. (42.5% yield). It was recrystallized from petroleum ether to give 26 g. (35% yield) of 2-(4'-methoxyphenyl)pyridine melting at 48-50°. Haworth, Heilbron, and Hey (254) give a melting point of 49-50° for this compound.

#### 2-(4'-Hydroxyphenyl)pyridine

A solution of 50 ml. of 48 per cent hydrobromic acid and 20.4 g. (0.11 mole) of 2-(4'-methoxyphenyl)pyridine was refluxed for 14 hours and then poured into a liter of an ice-water mixture. The precipitated hydrobromide was redissolved and the solution was decolorized with charcoal. The reprecipitated hydrobromide was filtered. There was isolated 25 g. (90% yield) of 2-(4'-hydroxyphenyl)pyridine hydrobromide giving a melting point of 195-198° with decomposition.

Anal. Calcd. for  $C_{11}H_{10}ONBr$ : Br, 31.67. Found: Br, 31.51.

The free base, obtained by treating a solution of the hydrobromide with dilute ammonium hydroxide, gave a melting point of 164-165° after one recrystallization from dilute 254. Haworth, Heilbron, and Hey, J. Chem. Soc., 359 (1940).

ethanol. Chichibabin (255) synthesized a compound that was "probably" 2-(4'-hydroxyphenyl)pyridine, melting at 159-160°, by treating phenol with a solution of sodium 2-pyridineisodiazoxide. Besides this product he also isolated 2-phenoxy-pyridine and another compound that was "probably" 2-(2'-hydroxyphenyl)pyridine. Because of the uncertainty of the identify of this product, and because of the difference in melting point between it and ours, our compound was analyzed.

Anal. Calcd. for  $C_{11}H_9ON$ : N, 8.19. Found: N, 8.34.

2-(3'-Nitro-4'-hydroxyphenyl)pyridine

This compound has been prepared (256) by the prolonged action of an aqueous solution of potassium hydroxide on 2-(3'-nitro-4'-aminophenyl)pyridine. We obtained this compound directly from 2-(4'-hydroxyphenyl)pyridine by this procedure.

In 30 ml. of glacial acetic acid was dissolved 6.5 g. (0.038 mole) of 2-(4'-hydroxyphenyl)pyridine. The flask was encased in a water bath and with vigorous stirring 12 ml. of fuming (d., 1.5) nitric acid was slowly added. The resulting solution was then heated at reflux for one-half hour and then poured into a concentrated solution of sodium bicarbonate. The

255. Chichibabin, J. Russ. Phys.-Chem. Soc., 50, 502 (1920); C. A., 18, 1495 (1924). See also Chichibabin and Shemyakina, J. Russ. Phys.-Chem., 53, 217 (1921); C. A., 18, 2342 (1924).
256. Coates, Cook, Heilbron, Hey, Lambert, and Lewis, J. Chem. Soc., 406 (1943).

precipitate was filtered and dried. There was obtained 7.2 g. (88%) of 2-(3'-nitro-4'-hydroxyphenyl)pyridine melting at 126-127° after one recrystallization from 95 per cent ethanol. The melting point indicated in the literature (256) is 125°.

#### p-Bromothiophenol

This compound was prepared very much in the manner that Schwarzenbach and Egli used to prepare the o-isomer (257).

In a one-liter three-necked flask a solution of 69 g. (0.4 mole) of p-bromoaniline in 67 ml. (0.8 mole) of concentrated hydrochloric acid diluted by 180 ml. of water was prepared by heating the mixture. Prior to diazotization the hot solution was cooled to -5° while being stirred very rapidly. The stirring was continued and a solution of 28.3 g. (0.41 mole) of 95 per cent sodium nitrite in 50 ml. of water was added dropwise to the mixture. The temperature was maintained at -5° during the whole addition. When an excess of nitrous acid was observed in the diazonium mixture, the solution of the diazonium chloride was transferred portionwise in a thin stream to a stirred solution of 172 g. (1 mole) of potassium ethylxanthate (258) in 600 ml. of water maintained at 80°. The mixture was allowed to stand overnight. The red oil that formed was extracted with a minimum amount of benzene and the extract was

257. Schwarzenbach and Egli, Helv. Chim. Acta., 17, 1176 (1934); See also Martin, Doctoral Dissertation, Iowa State College (1945), p. 34.  
 258. Sacc, Ann., 51, 346 (1884); see also Martin, Doctoral Dissertation, Iowa State College (1945), p. 33.

slowly added to a refluxing stirred solution of 112 g. (2 moles) of potassium hydroxide in 200 ml. of ethanol and 100 ml. of water. The mixture was refluxed and stirred for three hours. At this time the solution was concentrated until the benzene had been eliminated from the solution. The remaining solution was then poured into a liter of water. A small amount of red oil that separated was then removed by extraction with ether. The basic solution was then cooled and acidified with concentrated sulfuric acid. The oil that separated on acidification was extracted with ether and the extract was dried for a short time over sodium sulfate. Upon distillation of the ether and subsequent fractionation of the residue under reduced pressure there was obtained 30 g. (37.5%) of *p*-bromothiophenol melting at 74-75° and boiling at 99-100° under six mm. pressure. This compound has been prepared by Hübner and Alsberg (259) by the action of zinc and hydrochloric acid on *p*-bromobenzenesulfonyl chloride; they record a melting point of 75°, but give no yield.

#### *p*-Mercaptophenyllithium

A solution of 0.05 mole of *n*-butyllithium (202, 203, 204) in 90 ml. of anhydrous ether was added slowly to a stirred solution of 4.7 g. (0.025 mole) of *p*-bromothiophenol in 50 ml. of anhydrous ether. The first half was added with cooling, the 259. Hübner and Alsberg, Ann., 156, 327 (1870).

second, in a rapid stream. The solution was then heated at reflux. After 15 minutes a white precipitate formed; and in 30 minutes Color Test II-A (205) was negative showing the absence of *n*-butyllithium. This mixture was poured into a slurry of ether and dry-ice. After the dry-ice disappeared, the mixture was hydrolyzed with dilute hydrochloric acid. The ether layer was extracted with a sodium carbonate solution. The carbonate solution was neutralized and the precipitated acid was filtered and dried. There was obtained 2.9 g. (74%) of *p*-mercaptobenzoic acid melting 213-215° after one recrystallization from Skelly B.

Mr. Gainer, working independently in these laboratories, has obtained this acid by this general procedure in 65-70% yields.

This acid was previously prepared by Smiles and Harrison (260) by the reduction of *p*-carboxybenzenesulfonyl chloride. These investigators indicated a melting point of 250°. Bromley and Chamberlain (261) upon refining this process reported a compound melting at 216-217°. We discovered that, whereas this acid initially melted at 213-215°, it resolidified on further heating to 220°, remelting sharply at 254-255°. This higher melting compound on recrystallization from ether gave once more the lower melting compound.

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260. Smiles and Harrison, *J. Chem. Soc.*, 121, 2024 (1922).  
261. Bromley and Chamberlain, *ibid.*, 376 (1942).

2-(4'-Mercaptophenyl)pyridine

A 0.125 mole run of p-mercaptophenyllithium was prepared in the manner described above. To this stirred solution was added 10 g. (0.125 mole) of pyridine. After one-half hour of stirring at reflux a pasty precipitate separated and Color Test I (199) was negative demonstrating the absence of any RLi compound. This stirred mixture was treated with dry-carbon dioxide-free air for 48 hours, and the resulting mass was hydrolyzed with dilute hydrochloric acid. The aqueous layer was separated and made basic with a sodium carbonate solution. After extraction of the resulting mixture with ether, the aqueous layer was made acid with dilute acetic acid. The mercaptan that separated was extracted with ether and this extract was dried over sodium sulfate. The dried ether solution was treated with ethanolic hydrogen chloride; the precipitated hydrochloride was filtered and recrystallized from ethanol. There was obtained 5.8 g. (21%) of 2-(4'-mercaptophenyl)pyridine melting at 172-174°.

Anal. Calcd. for  $C_{11}H_{10}NClS$ : Cl, 15.89. Found: Cl, 16.33.

The boiling point of the free base was 190-193° at one mm. pressure. Distillation, even at this low pressure, was accompanied by a moderate amount of decomposition.

 $\gamma$ -(p-Nitrophenyl)propyl chloride (262)

262. Brown and Deutsch, Ber., 45, 2504 (1912).

To 45 g. of ice-cooled fuming nitric acid (d., 1.5) 15 g. (0.1 mole) of  $\gamma$ -phenylpropyl chloride was slowly added at such a rate as to maintain the reaction temperature between  $-10$  and  $-20^{\circ}$ . At the end of the addition the reaction mass was poured into a liter of water. This mixture was extracted with three 100 ml. portions of ether. These extracts were combined and dried over sodium sulfate. The ether was distilled away and the residue was distilled at reduced pressure. There was obtained 17 g. (87%) of  $\gamma$ -(*p*-nitrophenyl)propyl chloride boiling at  $177-180^{\circ}$  at six mm.

Diethyl- $\gamma$ -(*p*-nitrophenyl)propyl-amine

A solution of 50 ml. of diethylamine and 50 ml. ethanol was refluxed with 25 g. (0.125 mole) of  $\gamma$ -(*p*-nitrophenyl)propyl chloride for 30 hours. This mixture was cooled and to it was added 100 ml. of anhydrous ether. The diethylamino-hydrochloride that precipitated was filtered; there was isolated 10.8 g. of the hydrochloride, the theoretical amount. The solvent was removed from the filtrate and the residue was fractionated. There was obtained 21 g. (70%) of diethyl- $\gamma$ -(*p*-nitrophenyl)propyl-amine boiling at  $145-146^{\circ}$  at one mm. pressure.

Anal. Calcd. for  $C_{13}H_{20}O_2N_2$ : N, 11.89. Found: N, 12.16.

Diethyl- $\gamma$ -(*p*-aminophenyl)propyl-amine

There was placed in 100 ml. of absolute ethanol 9.44 g.



(0.04 mole) of diethyl- $\gamma$ -(*p*-nitrophenyl)propylamine and five g. of activated Raney nickel. This mixture was placed in a Parr low-pressure hydrogenation apparatus and subjected to 60 lbs. pressure of hydrogen. In the course of one hour the theoretical amount of hydrogen was consumed. The reaction mixture was removed from the apparatus and filtered free of Raney nickel. The clear filtrate was distilled free of solvent and the residue was fractionated. There was obtained 7.6 g. (92%) of diethyl- $\gamma$ -(*p*-aminophenyl)propylamine boiling at 152-153° at two mm. pressure.

Anal. Calcd. for  $C_{13}H_{22}N_2$ : N, 13.60. Found: N, 13.72.

### 2-Nitrophenylpyridines

These nitrophenylpyridines were prepared by a modification of the procedure of Haworth, Heilbron, and Hey (263). The essential variation employed was in the preparation of the diazonium chloride solution; no exact details were recorded for this preparation by these investigators. We discovered that the amount of acid used, as well as the fineness of division of the *o*-nitroaniline hydrochloride before diazotization, had a marked effect on the yield. The subsequent preparation of the 2-nitrophenylpyridines was accomplished in the manner described by these workers.

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263. Haworth, Heilbron, and Hey, J. Chem. Soc., 349 (1940).

a. Preparation of the 2-nitrobenzenediazonium chloride solution. Seventy grams (0.5 mole) of 2-nitroaniline was mixed with 160 ml. of 32 per cent hydrochloric acid. This mixture was heated until all the amine was in solution as the hydrochloride; then the solution was placed in an ice-bath and stirred vigorously while the mixture was cooling to 0°. Such a procedure furnished very small needles of the hydrochloride which were very suitable for diazotization. To this cooled, stirred mixture was slowly added a saturated solution of 37 g. (0.55 mole) of 95 per cent sodium nitrite in cold water. The addition was controlled so as to keep the reaction temperature between 5° and 10°.

b. Preparation and separation of the 2-nitrophenylpyridine isomers. This preparation and separation was effected through the method of Haworth, Heilbron and Hey (263). There was isolated 88 g. of the mixed picrates from which there was obtained 45 g. of the picrate of 2-(2'-nitrophenyl)pyridine melting at 151-152°; 33 g. of the picrate of 3-(2'-nitrophenyl)pyridine melting at 182-183°; and 0.5 g. of the picrate of 4-(2'-nitrophenyl)pyridine melting at 205-207°. From these picrates there were isolated 21.5 g. of 2-(2'-nitrophenyl)pyridine melting at 60-61°, and 15.8 g. of 3-(2'-nitrophenyl)pyridine, an oil boiling at 190-192° under one mm. pressure. These represented yields of 21.5 and 15.8 per cent, respectively.

2-(2'-Aminophenyl)pyridine

In 50 ml. of absolute ethanol there was placed four g. (0.02 mole) of 2-(2'-nitrophenyl)pyridine and three g. of Raney nickel. This mixture was placed in a low-pressure Parr hydrogenation apparatus and subjected to 45 lbs. hydrogen pressure. In an hour the theoretical amount of hydrogen was consumed. The reaction mixture was removed and filtered free of Raney nickel. The clear filtrate was distilled free of solvent and the residue was fractionated. There was obtained three grams (89%) of 2-(2'-aminophenyl)pyridine boiling at 192-194° under one mm. pressure. This was identified by the formation of its picrate which melted at 185-186° which was the melting point recorded in the literature (264).

This compound was prepared in lower yield by these investigators (252) through wet reduction.

2-(2'-(2",5"-Dimethylpyrrol-1")phenyl)pyridine

There was dissolved in five ml. of absolute ethanol one g. (0.006 mole) of 2-(2'-aminophenyl)pyridine, 0.75 g. (0.006 mole) of acetylacetone, and one ml. of glacial acetic acid. This solution was heated at reflux for four hours. On cooling there was obtained 1.5 g. (93%) of product melting at 101-102°, after one recrystallization from ethanol.

Anal. Calcd. for  $C_{17}H_{16}N_2$ : N, 11.29. Found: N, 11.36.  
264. Petrow, Stock, and Wragg, ibid., 316 (1943).

3-(2'-Aminophenyl)pyridine

Using the same method as was employed for the preparation of 2-(2'-aminophenyl)pyridine, there was isolated nine g. (90%) of 3-(2'-aminophenyl)pyridine from 12 g. (0.06 mole) of 3-(2'-nitrophenyl)pyridine. This compound boiled at 210-212° at three mm. pressure. The incidental preparation of this compound was recorded (259) by Heilbron and his co-workers. No constants or analysis were reported, though.

Anal. Calcd. for  $C_{11}H_9N_2$ : N, 16.47. Found: N, 16.62.

2-(2'-Salicylalaminophenyl)pyridine

Five-tenths g. (0.003 mole) of 2-(2'-aminophenyl)pyridine was heated with 0.35 g. (0.003 mole) of salicylaldehyde for three hours in the absence of solvent. This mass was cooled and recrystallized from methanol. There was obtained 0.4 g. (48%) of 2-(2'-salicylalaminophenyl)pyridine.

Anal. Calcd. for  $C_{18}H_{14}ON_2$ : N, 10.22. Found: N, 10.46.

3- $\overline{2}$ '-(2'',5''-Dimethylpyrryl-1'')phenyl $\overline{7}$ pyridine

According to the method used to prepare the 2-isomer, 3- $\overline{2}$ '-(2'',5''-dimethylpyrryl-1'')phenyl $\overline{7}$ pyridine was synthesized from one g. (0.006 mole) of 3-(2'-aminophenyl)pyridine and 0.75 g. (0.006 mole) of acetonylacetone in a yield of 1.4 g. (89%). This compound melted at 66-7°, after one recrystallization from

ethanol.

Anal. Calcd. for  $C_{17}H_{16}N_2$ : N, 11.29. Found: N, 11.53.

### 3-Nitrophenylpyridines

These compounds were synthesized and separated by a modification of the method of Haworth, Heilbron, and Hey (263). The essential variations made were in the preparation of the diazonium chloride solution and in the separation of the prepared 3-nitrophenylpyridines. As in the synthesis of the 2-nitrophenylpyridines it was discovered that the amount of acid used as well as the state of division of the m-nitroaniline hydrochloride had a pronounced effect on the yield. The separation of these isomers was accomplished very easily through the formation and fractional crystallization of their picrates. These investigators employed the fractional crystallization of their various acid salts for this separation, a process that was more tedious and longer than ours.

a. Preparation of the 3-nitrobenzenediazonium chloride solution. This solution was prepared from 70 g. (0.5 mole) of 3-nitroaniline in exactly the same manner as the 2-nitrobenzenediazonium solution was formed (p. 155).

b. Preparation of the 3-nitrophenylpyridines. This prepared diazonium solution was added slowly to 500 ml. of pyridine contained in a liter three-necked, round-bottomed flask equipped with a condenser, dropping funnel, thermometer, and mechanical

stirrer. Only small portions of the diazonium solution were placed in the dropping funnel; the major portion was kept cold in an ice-bath during the addition. This addition was regulated so as to maintain the reaction temperature between 38° and 43°. After complete addition, the stirred mixture was heated at 100° for one hour, then cooled, and then made strongly basic with ammonium hydroxide. The pyridine was steam distilled from the solution and the resulting mixture was extracted with four 100 ml. portions of benzene. The benzene extracts were dried and then distilled free of benzene. Fractionation of the residue under diminished pressure furnished 39 g. of a yellow oil that distilled at 160-190° under one mm. pressure.

c. Separation of the three 3-nitrophenylpyridines. This 39 g. of oil was dissolved in 100 ml. of 95 per cent ethanol. This warmed solution was added to a refluxing solution of 50 g. of picric acid in 450 ml. of 95 per cent ethanol. The resulting mixture was immediately filtered. The precipitate was a mixture of the picrates of the 3- and 4-(3'-nitrophenyl)-pyridines. When the ethanol filtrate cooled there separated the picrate of the 2-isomer. This precipitate, together with that obtained by concentrating the ethanolic solution to 130 ml., gave 61 g. of the picrate of 2-(3'-nitrophenyl)pyridine melting at 152-155°. One recrystallization from acetone gave 59 g. of the pure picrate melting at the literature melting point of 156-157°. On treatment with a hot, dilute ammonium hydroxide

solution this picrate furnished 26 g. (26%) of 2-(3'-nitrophenyl)pyridine melting at 73-74°. This yield and purity was obtained after two recrystallizations of the crude product from dilute ethanol. The picrates that were insoluble in hot ethanol were repeatedly treated with 100 ml. of acetone. The refluxing acetone mixtures were filtered while hot. The portion soluble in the hot acetone solution was the picrate of the 3-isomer; the portion insoluble in hot acetone was the picrate of the 4-isomer. From six g. of the picrate of the 3-isomer, melting at 250-251° there was isolated 2.1 g (2.1%) of 3-(3'-nitrophenyl)pyridine melting at 109-110° by the ammonium hydroxide method. By this same method there was isolated from seven g. of the picrate of the 4-isomer, melting at 200-201°, 3.2 g. (3.2%) of 4-(3'-nitrophenyl)pyridine melting at 101-102°.

#### 4-(3'-Aminophenyl)pyridine

In 50 ml. of absolute ethanol there was placed 3 g. of activated Raney nickel and 1.2 g. (0.006 mole) of 4-(3'-nitrophenyl)pyridine. This mixture was placed in a low-pressure Parr hydrogenation apparatus and subjected to 45 lbs. pressure of hydrogen. In the course of a half-hour the theoretical amount of hydrogen was consumed. From the filtered reaction mixture there was isolated 0.9 g. (89%) of 4-(3'-aminophenyl)pyridine melting at 164-166°. This yield and purity was obtained after two recrystallizations from Skelly B. This compound

was prepared by wet reduction of the corresponding nitro-compound by Heilbron, Hey, and Lambert (265) with a melting point of 165-166°.

### 3-(3'-Aminophenyl)pyridine

Employing the above procedure there was obtained 0.9 g. (89%) of 3-(3'-aminophenyl)pyridine from 1.2 g. (0.006 mole) of the corresponding nitro-compound. The compound was initially an oil but it crystallized from Skelly B to give a melting point of 77-78°. This was the melting point obtained when the compound was made by wet reduction (265).

This amine can be converted quantitatively to the monohydrochloride by treating its ether solution with an ethanolic solution of hydrogen chloride. This hydrochloride melts at 286-288° with decomposition.

Anal. Calcd. for  $C_{11}H_{11}N_2Cl$ : Cl, 17.19. Found: 17.38.

### 2-(3'-Aminophenyl)pyridine

Using the above procedure there was obtained 5.6 g. (93%) of 2-(3'-aminophenyl)pyridine from seven g. (0.035 mole) of 2-(3'-nitrophenyl)pyridine. The melting point was 72-73° in accord with that Edward (249) obtained when he isolated the amine in 50 per cent yield from sodium sulfide reduction of the corresponding nitrocompound. Heilbron and co-workers (265) also 265. Heilbron, Hey, and Lambert, ibid., 1279 (1940).



prepared the compound by the action of stannous chloride and hydrochloric acid on the corresponding nitro-compound. They merely obtained a "thick, viscous oil" that distilled at  $213^{\circ}$  at 20 mm. The yield of the oil was 82%.

2-(3'-(2",5"-Dimethylpyrryl-1")phenyl)pyridine

There was dissolved in five ml. of absolute ethanol one g. (0.006 mole) of 2-(3'-aminophenyl)pyridine, 0.75 g. (0.006 mole) of acetylacetone, and one ml. of glacial acetic acid. This solution was heated at reflux for two hours. On cooling this reaction mixture there was obtained 1.4 g. (89%) of product melting at  $83.5-84^{\circ}$ , after one recrystallization from ethanol.

Anal. Calcd. for  $C_{17}H_{16}N_2$ : N, 11.29. Found: N, 11.33.

2-(3'-Salicylalaminophenyl)pyridine

In ten ml. of 95 per cent ethanol there were dissolved one g. (0.006 mole) of 2-(3'-aminophenyl)pyridine and 0.7 g. (0.006 mole) of salicylaldehyde. After this solution was refluxed for one hour, there separated upon cooling 1.2 g. (72%) of product melting at  $77-78^{\circ}$  after one recrystallization from dilute ethanol.

Anal. Calcd. for  $C_{18}H_{14}ON_2$ : N, 10.22. Found: N, 10.24.

### 4-Nitrophenylpyridines

These compounds were synthesized and separated by a modification of the method of Haworth, Heilbron, and Hey (259). Essentially, the variation applied here was in the preparation of the diazonium chloride solution. Heilbron and his co-workers (259) gave no specific directions for the formation of this solution; we found that the concentration of the acid used as well as the fineness of the precipitated p-nitroaniline hydrochloride critically affected the yield.

a. Preparation of the 4-nitrobenzenediazonium chloride solution. This solution was prepared from 70 g. (0.5 mole) of 4-nitroaniline in exactly the same manner as the 2-nitrobenzenediazonium chloride solution was formed (p. 155).

b. Preparation of the 4-nitrophenylpyridines. This preparation was carried out in the same manner as that for the 3-nitrophenylpyridines (p. 155). There was isolated 75 g. of a yellow oil boiling at 165-190° under one mm. pressure.

c. Separation of the 4-nitrophenylpyridines. When these pyridine derivatives were separated according to the method of Forsyth and Pyman (250), there were isolated 37 g. (37%) of 2-(4'-nitrophenyl)pyridine melting at 131-132°; 8.1 g. (8.1%) of 3-(4'-nitrophenyl)pyridine melting at 146-147°; 0.2 g. (0.2%) of 4-(4'-nitrophenyl)pyridine melting at 122-123°; and 0.6 g. (0.5%) of 2,6-(4',4''-dinitrodiphenyl)pyridine melting at 296-298°.

2,6-(4',4"-Diaminodiphenyl)pyridine

In 25 ml. of absolute ethanol there were placed one g. of activated Raney nickel and 0.4 g. (0.0012 mole) of 2,6-(4',4"-dinitrodiphenyl)pyridine. The reaction mixture was placed in a low-pressure Parr hydrogenation apparatus and subjected to 60 lbs. pressure of hydrogen. In one hour the theoretical amount of hydrogen was consumed. After filtration of the reaction mixture and removal of the ethanol by distillation, there was obtained 0.28 g. (86%) of 2,6-(4',4"-diaminodiphenyl)pyridine melting at 216-218°.

Anal. Calcd. for  $C_{17}H_{15}N_3$ : N, 16.09. Found: N, 16.21.

3-(4'-Aminophenyl)pyridine

Using the general procedure described above three g. (0.015 mole) of 3-(4'-nitrophenyl)pyridine was reduced to 2.3 g. (90%) of the amine melting at 116-118° after one recrystallization from dilute ethanol. This melting point was in agreement with that for the product obtained by wet reduction (265).

3-(4'-(2",5"-Dimethylpyrryl-1")phenyl)pyridine

In five ml. of absolute ethanol there was dissolved one g. (0.006 mole) of 3-(4'-aminophenyl)pyridine, one ml. of acetic acid, and 0.7 g. (0.006 mole) of acetylacetone. This solution was heated at reflux for four hours. The reaction

mixture was then cooled and there separated 1.4 g. (89%) of product melting at 116-117°. A mixed melting point between this compound and starting material gave a marked depression, melting from 45° to 70°.

Anal. Calcd. for  $C_{17}H_{16}N_2$ : N, 11.29. Found: N, 11.40.

### 3-Nitro-4-aminoanisole

According to the method of Reverdin, (266) 3-nitro-4-aminoanisole was synthesized in 82% yield. The compound melted at 123-124°, the melting point of the literature.

### 3-Nitro-4-bromoanisole

The procedure used for this preparation was a variation of that of Hodgson and Dyson (267). The final product was steam distilled by these investigators; we found that 3-nitro-4-bromoanisole could be isolated more rapidly and in high yield and purity by its distillation under diminished pressure. These workers recorded neither directions for the formation of the diazonium solution nor yield.

Seventy g. (0.42 mole) of 3-nitro-4-aminoanisole was dissolved in a solution of 80 ml. of conc. sulfuric acid and 300 ml. of water, and the solution was cooled to 0°. To this stirred mixture there was slowly added a solution of 30 g. (0.4 mole) of 95 per cent sodium nitrite in 100 ml. of water. This

266. Reverdin, Ber., 29, 2595 (1896).

267. Hodgson and Dyson, J. Chem. Soc., 946 (1935).

diazotized solution was added dropwise to a hot solution (90-95°) of 50 g. of sodium bromide and 140 g. of copper sulfate in 800 ml. of water. The resulting mixture was cooled, and extracted with three 100 ml. portions of ether. The ether extracts were washed with dilute base and water, and dried. After removal of the ether, the residue was fractionated to give 74.8 g. (70%) of 3-nitro-4-bromoanisole distilling at 158-160° under 5 mm. pressure. The compound solidified on cooling and melted at 31-32° after one recrystallization from ethanol. The melting point recorded in the literature is 32° (267).

#### 3-Amino-4-bromoanisole

In 100 ml. of absolute ethanol there was placed 13.5 g. (0.058 mole) of 3-nitro-4-bromoanisole and five g. of activated Raney nickel. This mixture was placed in a low-pressure Parr hydrogenation apparatus and subjected to 45 lbs. pressure of hydrogen. As soon as shaking was begun, an exothermic reaction set in and the theoretical amount of hydrogen was consumed in 12 minutes. The reaction mixture was filtered and then distilled free of solvent. The residue was fractionated to give 11 g. (94%) of product distilling at 101-103° under 0.5 mm. pressure. The hydrochloride of this compound was prepared. It melted at 186°, the melting point recorded in the literature for this compound (267). The highest yield reported by the wet reduction method for preparing this compound is 71% (267). This compound

solidified on cooling and melted at 23-24°.

2-Amino-4-methoxybenzoic acid

One hundred ml. of an ether solution of 0.06 mole of n-butyllithium (202, 203, 204) was added to a solution of four g. (0.02 mole) of 3-amino-4-bromoanisole in 50 ml. of anhydrous ether. The whole system was under a nitrogen atmosphere. After addition, the reaction mixture was stirred for 30 minutes at room temperature and for one hour at 0°. Then it was poured into a slurry of anhydrous ether and dry ice. After spontaneous disappearance of the dry ice, the reaction mixture was hydrolyzed with water and hydrochloric acid. The aqueous layer was separated and made just basic with dilute ammonium hydroxide and then just neutral with dilute acetic acid. This mixture was extracted with ether and the ether extract was dried and distilled free of solvent. The residue was recrystallized from water to give 1.7 g. (51%) 2-amino-4-methoxybenzoic acid melting at 170-171°. The literature (268) melting point is 172°.

Attempted preparation of 2-(2'-amino-4'-methoxyphenyl)pyridine

A solution of 0.1 mole of 2-amino-4-methoxyphenyllithium in 400 ml. of anhydrous ether was made as described above. To this mixture was slowly added 15.8 g. (0.2 mole) of pyridine. The resulting mixture was heated at reflux for two hours at which

268. Ullmann and Dootson, Ber., 51, 20 (1918).

time the mixture was deep brown in color. The reaction mass was cooled and hydrolyzed. The ether layer was separated and treated with 50 ml. of nitrobenzene and allowed to stand over night. The ether from this solution was distilled away and the residue was steam distilled until 47 ml. of nitrobenzene was recovered. The residue was taken up in ether and this ether solution was dried. The ether was removed from this dried solution and the residue was fractionated. There was obtained five g. of a yellow oil boiling at 175-181<sup>o</sup> under 0.5 mm. pressure. This oil would not crystallize, nor would it give a picrate or hydrochloride although it did contain nitrogen.

This experiment was repeated three times but each time there was just obtained this yellow oil in yields of 3.5, 6, and 2.2 grams, respectively.

#### 2-Nitro-4-methoxyphenylpyridines

a. 2-Nitro-4-methoxybenzenediazonium chloride. Sixty-seven g. (0.4 mole) of 3-nitro-4-aminoanisole was dissolved in 125 ml. of 32 per cent hydrochloric acid. This hot solution was cooled rapidly with stirring to 0<sup>o</sup>. The resulting mixture was diazotized with a saturated solution of 28 g. (0.41 mole) of 95 per cent sodium nitrite in cold water.

b. Preparation of the 2-nitro-4-methoxyphenylpyridines. This diazonium solution was added portionwise to 500 ml. of pyridine at such a rate as to maintain the reaction temperature

at 38-40°. This addition required two hours. After this, the reaction mixture was heated at 95° for an hour and then cooled and made strongly basic with an ammonium hydroxide solution. The pyridine was then removed by steam distillation. The residue in the flask was cooled and extracted with three 100 ml. portions of benzene. These combined benzene extracts were dried and distilled free of solvent. The residue was fractionated to give 12 g. of an oil boiling at 190-220° at 0.1 mm.

c. Separation of the 2-nitro-4-methoxyphenylpyridines.

This 12 g. of oil was dissolved in 100 ml. of 95 per cent ethanol. This hot solution was added to a refluxing solution of 15 g. of picric acid in 150 ml. of 95 per cent ethanol. The fraction that was insoluble in the hot ethanol solution was collected and recrystallized from acetone three times. This gave five grams of the picrate of 3(?)-(2'-nitro-4'-methoxyphenyl)pyridine melting at 200-202°.

Anal. Calcd. for  $C_{18}H_{13}O_4N_5$ : N, 15.23. Found: N, 15.51.

This picrate was decomposed by warming it with dilute ammonium hydroxide. An oil separated which solidified on cooling and gave 2.1 g. (2.3%) of 3(?)-(2'-nitro-4'-methoxyphenyl)pyridine melting at 66-67°.

Anal. Calcd. for  $C_{12}H_{10}O_3N_2$ : N, 12.17. Found: N, 12.15.

This product was supposed to be the 3-isomer since the other product isolated was the 2-isomer and since in these



coupling reactions with pyridine the 2- and 3-isomers are formed to a very much greater extent than the 4-isomer. The compound could not be proven in the same fashion as the 2-isomer was because this nitro-compound would not reduce to the amine.

The ethanolic solution containing the picrate soluble in ethanol was distilled free of solvent and the residue was recrystallized three times from methanol. There was so isolated three g. of the picrate of 2-(2'-nitro-4'-methoxyphenyl)pyridine melting at 153-155°.

Anal. Calcd. for  $C_{18}H_{13}O_3N_5$ : N, 15.23. Found: N, 15.52.

This product was decomposed with dilute ammonium hydroxide to the free amine which first appeared as an oil but which solidified readily on cooling. Recrystallization of this solid from methanol gave 1.2 g. (1.3%) of 2-(2'-nitro-4'-methoxyphenyl)pyridine melting at 89-90°.

Anal. Calcd. for  $C_{12}H_{10}O_3N_2$ : N, 12.17. Found: N, 12.23.

#### 2-(2'-Amino-4'-methoxyphenyl)pyridine

One g. (0.005 mole) of 2-(2'-nitro-4'-methoxyphenyl)pyridine was placed in ten ml. of hot ethanol along with one-half g. of activated Raney nickel. This hot mixture was subjected to 60 lbs. pressure of hydrogen in a low-pressure Parr hydrogenation apparatus. The theoretical amount of hydrogen was consumed in five minutes. The reaction mixture was removed,

filtered free of Raney nickel, and diluted with ten ml. of anhydrous ether. To this solution was added three ml. of a nine molar solution of hydrogen chloride in ethanol. The precipitated hydrochloride was recrystallized from an ether-ethanol solution to give 1.2 g. (80%) of the dihydrochloride of 2-(2'-amino-4'-methoxyphenyl)pyridine melting at 199-200° with decomposition.

Anal. Calcd. for  $C_{12}H_{14}ON_2Cl_2$ : Cl, 26.00. Found: Cl, 25.99.

#### Deamination of 2-(2'-amino-4'-methoxyphenyl)pyridine

This procedure was fashioned after the general directions proposed by Mai (269).

One g. (0.004 mole) of the dihydrochloride of 2-(2'-amino-4'-methoxyphenyl)pyridine was placed in 0.5 ml. of water and one ml. of concentrated hydrochloric acid. To this cooled mixture there was added six ml. of 50 per cent hypophosphorus acid. The cold solution was stirred for two hours and then placed for 24 hours in a refrigerator at 12°. The acid solution was neutralized and the oily precipitate was filtered and recrystallized from ether giving 0.3 g. (40%) of 2-(4'-methoxyphenyl)pyridine melting at 49-50°. This was identified by the mixed melting point method. This procedure definitely established the 2-(2'-nitro-4'-methoxyphenyl)pyridine and 2-(2'-amino-4'-methoxyphenyl)pyridine.

269. Mai, Ber., 35, 163 (1902).

Attempted Reduction of 3(?)-(2'-Nitro-4'-methoxyphenyl)pyridine

In the same manner as for the 2-isomer 1.15 g. (0.005 mole) of 3(?)-(2'-nitro-4'-methoxyphenyl)pyridine was subjected to catalytic reduction. Pressures varying from 30 to 60 lbs. of hydrogen were used as well as temperatures varying from room temperature to 100°. In every case, the starting material was recovered in a 96 per cent yield or better.

The wet reduction procedure using tin and hydrochloric acid was also employed in the following manner.

In ten ml. of absolute ethanol was dissolved 1.15 g. (0.005 mole) of 3(?)-(2'-nitro-4'-methoxyphenyl)pyridine. To this solution was added 20 ml. of 20 per cent hydrochloric acid and 11.8 g. (0.1 g.-atom) of tin. This stirred mixture was heated at reflux until all of the tin was consumed. When the reaction mixture was worked up there was obtained one g. of pure starting material, a return of 90%.

2-(4'-Nitrophenyl)thiophene

A nitrophenylthiophene was first synthesized by Gomberg and Bachman (270) by the addition of a sodium hydroxide solution to a mixture of a p-nitrobenzenediazonium chloride solution and thiophene. We found that this general procedure developed by Elks, Haworth, and Hey (271) which involves the substitution of

270. Gomberg and Bachman, J. Am. Chem. Soc., 46, 2339 (1924).

271. Elks, Haworth, and Hey, J. Chem. Soc., 1285 (1940).

the sodium hydroxide solution by a sodium acetate solution, gave a superior yield.

A hot solution of 13.8 g. (0.1 mole) of *p*-nitroaniline was prepared and cooled, with vigorous stirring, to 0° and diazotized with a solution of seven g. (0.11 mole) of 95 per cent of sodium nitrite in 14 ml. of water. The diazo-solution was intimately mixed with 200 ml. of thiophene. Then, to this stirred mixture was slowly added a solution of 16 g. of sodium acetate trihydrate in 32 ml. of water. The resulting emulsion was stirred for three hours. The reaction mixture was then acidified and filtered. The dark thiophene layer of the filtrate was separated and the thiophene was removed by steam distillation. The black tarry mass that remained in the water of the distilling flask was filtered and dried. It was then ground and placed in a distilling flask. Distillation of this mass under diminished pressure gave ten g. of a distillate boiling at 130-150° under 0.1 mm. pressure and melting 120-125°. Recrystallization from acetone gave 7.3 g. (36%) of 2-(4'-nitrophenyl)thiophene melting at 136-137°. Gomberg and Bachman (266) report a 23% yield of product melting at 137-138°, but they do not state the position in the ring.

#### 2-(4'-Aminophenyl)thiophene

To a hot mixture of 3.1 g. (0.015 mole) of 2-(4'-nitrophenyl)thiophene and 25 ml. of absolute ethanol was added three

g. of a suspension of commercial Raney nickel in absolute ethanol. This mixture was placed in a Parr low-pressure hydrogenation apparatus and subjected to 60 lbs. pressure of hydrogen. When the theoretical amount of hydrogen was consumed, the mixture was filtered free of Raney nickel and the solution was distilled free of solvent. The residue was crystallized from ethanol. This gave two g. of product melting at 69-71°, a yield of 67%.

Anal. Calcd. for  $C_{10}H_8N_2S$ : S, 18.29. Found: S, 18.52

#### Deamination of 2-(4'-aminophenyl)thiophene

Along with their report of a p-nitrophenylthiophene, Gomberg and Bachman (270) noted the production of a phenylthiophene whose melting point was 42-43°. Kues and Pool (272) prepared 2-phenylthiophene from benzoylpropionic acid and phosphorus pentasulfide with a melting point of 40-41°. Mohlau and Berger (273), by the action of benzenediazonium chloride on thiophene isolated a phenylthiophene melting at 57°. Bamberger (274) later considered this to be a mixture of 2- and 3-phenylthiophenes much as the product of benzenediazonium chloride and naphthalene gave a mixture of 1- and 2-phenylnaphthalene (273). Thus the phenylthiophene of Gomberg and Bachman melting at 42-43° might be a mixture of 2- and 3-phenylthiophenes as their "phenylpyridine"

272. Kues and Pool, Ber., 19, 3142 (1886).

273. Mohlau and Berger, ibid., 26, 1994 (1893).

274. Bamberger, ibid., 30, 367 (1897).

(270) melting at  $57^{\circ}$ , was evidently a mixture of at least two of the possible phenylpyridines. The 2- (275) and 3-phenylpyridines (276) are liquids whereas 4-phenylpyridine is a solid melting at  $97^{\circ}$  (277). Moreover, Bamberger (274) prepared 3-phenylthiophene melting at  $90-90.5^{\circ}$ , by the action of nitrosoacetanilide on thiophene indicating that arylation may also occur mainly in the 3-position of thiophene as well. Since the sodium diazotate, sodium acetate and nitrosoacetylamine method of diazo-arylation are thought to proceed through the same free radical mechanism (278, 279, 280), the position of any one arylation is obviously uncertain. The determination of the *p*-nitrophenyl-position in thiophene was thus undertaken. The proof was the hypophosphorus acid deamination (269) of the corresponding amine to the known phenylthiophene.

A mixture of 0.5 g. (0.002 mole) of 2-(4'-aminophenyl)thiophene hydrochloride and one ml. of concentrated hydrochloric acid was heated to boiling and rapidly cooled to  $-5^{\circ}$ . This mixture was diazotized with a solution of 0.2 g. of sodium nitrite in one ml. of water. To this diazotized solution was added 4.7 ml. of 50 per cent hypophosphorus acid that had previously been cooled to  $0^{\circ}$ . The resulting mixture was stirred

275. Skraup and Cobenzl, Monatsh., 4, 472 (1871).  
 276. Pictet, Ber., 38, 1948 (1905).  
 277. Hantzsh, ibid., 17, 1518 (1886).  
 278. Hey and Waters, Chem. Revs., 21, 109 (1937).  
 279. Adams, "Organic Reactions", Vol. II, John Wiley and Sons, Inc., New York (1944). p. 228-9.  
 280. Hey, Ann. Repts., 37, 278 (1940).

at 0° for an hour and kept at 12° for 24 hours. This mixture was diluted with water and filtered. The precipitate was sublimed and the sublimate was recrystallized from dilute ethanol. There was obtained 0.2 g. of product melting at 40-41°, a yield of 63%. Kues and Pool (268) give a melting point of 40-41° for 2-phenylthiophene. Therefore these compounds must be derivatives of the 2-isomer.

## DISCUSSION

## A. Silicon Compounds

Before endeavoring to prepare any substituted organosilanes, it was thought desirable to ascertain the best possible way of synthesizing the typical organosilanes that would be employed throughout the course of these studies.

The existing methods of preparation of tetraalkyl- or tetraaryl-substituted silanes are encumbered with one or more distinct disadvantages. Either the yields are very low, or the method is quite involved and employs troublesome reagents, or the reaction time is long, or the conditions are severe leading to many by-products and subsequent difficulty in isolating a pure product. Often a particular preparation is saddled with all of these disadvantages. For example, tetraethylsilane is prepared either from silicon tetrachloride and diethylzinc by heating these reactants in a sealed tube for three hours at  $160^{\circ}$  (2), or by heating the Grignard reagent with silicon tetrachloride in ether for 18 hours (34). In the former instance no yield is given, in the latter, the yield is only 45 per cent. Moreover, as the alkyl chain grows in length the conditions of these reactions must grow in severity and the reaction time must become longer.



The formation of tetraalkyl- or tetraaryl-substituted silanes of the general types  $R_3R'Si$  or  $R_2R'_2Si$  heretofore has always involved two distinct stages. First the  $R'SiX_3$  or  $R'_2SiX_2$  compound is prepared by the conventional methods and then isolated. In general, this type of compound is difficult to handle, decomposing in the presence of moist air. Then this  $R'SiX_3$  or  $R'_2SiX_2$  compound is reacted with the appropriate R-reagent to furnish the fully substituted silane. Evidently, this procedure involves two low yield reactions and so is most troublesome.

Fleming has demonstrated the possibility of using organolithium reagents in place of the Grignard reagents to introduce alkyl or aryl radicals into the silane molecule (62). He was primarily concerned with the production of monoalkyl- or monoaryl-silanes and has recorded the synthesis of several of these.

By the use of organolithium compounds we have found that these reagents beautifully gave most of the organosilanes in which we were interested.

In preparing the simple tetraalkyl- or tetraaryl-silanes, the use of these reagents has no parallel. In all cases, the reaction conditions were extremely mild, involving temperatures no higher than the reflux temperature of ether; and the reaction time was extremely short, requiring only the length of time for slow and careful addition of the reagents. A case in point was the synthesis of the already mentioned tetraethylsilane. A 92

per cent yield was obtained merely by adding an ether solution of silicon tetrachloride. The reaction was complete almost as soon as the reagents were together. Even when the length of the alkyl chain was increased, the fully substituted silane was still formed with ease and in high yield. Tetra-n-butylsilane, for example, was isolated in yields of 97 per cent. Tetraaryl-silanes, such as tetraphenylsilane, were produced in equally high yields under equally mild conditions.

Unfortunately, not even these more reactive organolithium reagents seem to facilitate the tetrasubstitution of sterically hindered radicals such as the isopropyl radical. The prolonged action of more than four equivalents of isopropyllithium on either silicon tetrachloride or tetraethoxysilane merely furnished triisopropylchlorosilane or triisopropylethoxysilane. The effect that the three isopropyl groups attached to the silicon atom had upon the fourth substituent was really remarkable. If this fourth group was chlorine, it was so stable to hydrolysis that water, when shaken with it for a prolonged time, still produced no hydrolysis. Normally, such a trialkylchlorosilane hydrolyzes rapidly in moist air and immediately in the presence of water. Similarly, if this fourth substituent was ethoxy, it was so shielded that concentrated sulfuric acid had no effect upon it or the molecule. Ordinarily, such trialkylethoxysilanes react with cold concentrated sulfuric to yield a disiloxane which dissolves immediately in the acid.

Recent investigations in these laboratories (281) have attained similar conclusions in the case of tri-o-tolylchlorosilane. This compound was also very stable to hydrolysis. Moreover, a fourth o-tolyl group could not be introduced by normal means and as yet has not been introduced even under forced conditions. It will be recalled that Schumb and his co-workers were unable to synthesize tetra-o-tolylsilane either by the "forced" Grignard or by the Wurtz procedure (49).

During the synthesis of tetra-n-butylsilane a negative Color Test I (199) was not obtained immediately after the fourth equivalent of n-butyllithium had been added to the silicon tetrachloride or the tetraethoxysilane. However, hydrolysis and subsequent working up of the reaction in the usual manner still furnished this product in very high yield. It was also noted that at the end of the addition Color Test II-A (206), which is less sensitive than Color Test I, was negative. Evidently then, the concentration of n-butyllithium present at the end of the reaction was high enough to react with the Michler's ketone of Color Test I, but not high enough to react with the slight concentration of tri-n-butylchloro- or tri-n-butylethoxysilane still present. In other words, in this reaction there seems to be a concentration level below which the reagents will not interact.

As has already been noted (p. 9), the tetra-n-butylsilane  
281. Smart, Unpublished studies, Iowa State College (1946).

of the literature is in doubt. Sauer (30) has pointed out that the molecular refraction for the reported tetra-n-butylsilane does not agree with the calculated molecular refraction ( $MR_D$  found 81.12 as against  $MR_D$  calculated, 85.49). He also indicated that this compound might well be tri-n-butylethoxysilane in which case the calculated and found molecular refractions would agree within 0.2 of a unit. Tsen and Chu have also recorded the preparation of this compound (34) but they give no refractive index and so the molecular refraction of this compound cannot be calculated. Our preparation of a compound whose molecular refraction and whose analysis agrees with that for tetra-n-butylsilane substantiates Sauer's doubt of the tetra-n-butylsilane in the literature (92).

It was noted that either silicon tetrachloride, or tetraethoxysilane, or tetrathioethoxysilane could be used to prepare these tetraalkyl- or tetraaryl-silanes. As far as yield, or time of reaction, or mildness of conditions is concerned, there is little to choose among these reagents. It can be said that silicon tetrachloride evolves the most heat in these reactions and tetraethoxysilane the least. Consequently, silicon tetrachloride is probably the most reactive reagent of the three. Nevertheless, all of these reagents reacted with such ease that this factor scarcely makes silicon tetrachloride more advantageous for these general simple reactions. However, it can be argued that tetraethoxysilane is the best reagent to use

in these reactions. In the first place, of these reagents only silicon tetrachloride and tetraethoxysilane are available commercially; consequently, all factors being equal, as they are, these latter two have a distinct advantage over the other. Of these two, tetraethoxysilane is by far the simpler to handle. It does not hydrolyze readily, as silicon tetrachloride does, and so can be weighed in the air without any fear of inaccuracy. Moreover, silicon tetrachloride has a particularly high vapor pressure and so must be weighed in a closed vessel and introduced into the reaction mixture with special precautions. Tetraethoxysilane has a low vapor pressure at room temperature and so does not evidence this difficulty. Finally, it was observed that silicon tetrachloride was slowly lost from a refluxing ether solution; even a very efficient condenser did not return all of the silicon tetrachloride.

It was also ascertained that organosilanes of the general type  $R_3R'Si$  can be efficaciously synthesized by the use of organolithium reagents. The general procedure that gave excellent yields of these compounds involved the careful and slow addition of three equivalents of the  $RLi$  compound to the silicon tetrachloride or the tetraethoxysilane in an ether solution followed by the addition of one equivalent of the  $R'Li$  compound. Manifestly this procedure does not involve the troublesome isolation of the intermediate  $R_3SiX$  or  $R'SiX_3$  compound. The whole addition may be made in one reaction mixture. These

experiments indicated that three alkyl or three aryl groups enter the silicon molecule before a fourth one enters. In other words there is a definite step between the introduction of the third and fourth radical into the silane molecule.

This property allowed the synthesis of triphenylsilanol in high yield and with great ease; the three equivalents of phenyllithium were slowly added to an ether solution of silicon tetrachloride and then the triphenylchlorosilane formed was hydrolyzed by water. Previously, the preparation of this compound involved the heating of an excess of phenylmagnesium bromide with an ether solution of silicon tetrachloride for three days (282).

The production of trimethylphenylsilane by this same general manner showed that alkyl radicals enter the silane molecule in this same stepwise fashion.

$\alpha$ -Picolyllithium was particularly noteworthy in these reactions since it alone of the many organolithium reagents tested did not react with triphenylethoxysilane. No fully satisfying reason can be proposed for this non-reactivity; perhaps this non-reactivity is related to the failure of  $\alpha$ -picolyllithium to give Color Test I as the majority of the other organolithium reagents do. It might also be noted that, as yet, no silane containing a heteronitrogen atom has been recorded.

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282. Dilthey and Eduardoff, Ber., 37, 1140 (1904).

Great care must be taken during the addition of the first three equivalents of the organolithium compound if this stepwise addition is to be obtained. The best results are achieved if the ether solution of the organometallic compound is approximately one molar and if this solution is added to the ether solution of silicon tetrachloride or tetraethoxysilane at such a rate as to produce little or no reflux. When silicon tetrachloride is used the reaction flask should be encased in an ice-bath to prevent any loss of this reagent.

The formation of silanes of the type  $R_2R'_2Si$  by the addition of two equivalents of an  $RLi$  compound followed by two of  $R''Li$  and  $R'Li$  compound to silicon tetrachloride or tetraethoxysilane was accomplished in only 78-80 per cent yields demonstrating that the step between the substitution of two alkyl or two aryl groups and three is not as definite as that between the substitution of three and four. However, this type of silane was still synthesized in relatively high yield without the necessity of isolating the intermediate  $R_2SiX_2$  compound.

The introduction of one alkyl or one aryl group into silicon tetrachloride or tetraethoxysilane by this general method was only accomplished in small yield. The  $RLi$  compound seemed just as ready to react with the monoalkyl- or the monoaryl-trichlorosilane, or the similar triethoxysilanes, as with the unsubstituted silicon tetrachloride or tetraethoxysilane. Thus, methyltriphenylsilane was prepared only in 23 per cent yield

from the addition of one equivalent of methyllithium to silicon tetrachloride followed by the addition of three equivalents of phenyllithium. This type of molecule,  $R_3R'Si$ , in which the  $R'$  must be introduced first was best synthesized by adding the Grignard reagent of this radical to triethoxychlorosilane, then following this addition with three equivalents of the lithium derivative of the second radical. The Grignard reagent reacts preferentially with the chlorine atom and so allows the synthesis of this type of compound in yields averaging 70 per cent. Here again the isolation of the troublesome trichloro-derivative could be avoided.

The production of triphenylethoxysilane from the careful addition of three equivalents of phenyllithium to tetraethoxysilane offered special technical difficulties. The lithium ethoxide formed in the reaction was most difficult to free from the reaction mixture. Bases of this type catalyze the conversion of such ethoxysilanes to the corresponding hexasubstituted disiloxanes. Consequently, in this case, quite a quantity of hexaphenyldisiloxane was always isolated as a by-product.

The introduction of halogen atoms into alkylphenylsilanes was most easily accomplished by the addition of a halophenylmagnesium halide solution to triethoxychlorosilane followed by the addition of three equivalents of the alkylithium compound. Thus, *p*-bromophenyltrimethylsilane was prepared in 73 per cent yield. This bromo-derivative was readily converted to the



corresponding lithio-compound in 63 per cent yield by the direct action of an ether solution of this compound upon lithium.

Since it was evident that the alkyl to silicon linkage was relatively stable to the common cleavage reagents, it was hoped that trimethylbenzylsilane could be brominated or nitrated without concurrently cleaving the molecule at the benzyl to silicon bond. However, it was discovered that the phenyl ring apparently so weakened this bond that it was split very easily with either reagent. Thus, the use of this method of direct substitution of a halogen into this type of aryl substituted silane was precluded. The possibility still exists, though, that such substitution may occur if the phenyl ring is further removed from the silicon atom, as on the  $\beta$ - or  $\gamma$ -carbon atom; for example,  $\gamma$ -phenylpropyltrimethylsilane.

The reaction of triethylchlorosilane with ethyl sodioacetate furnished a compound in which the triethylsilyl radical was attached to the  $\beta$ -oxygen atom rather than to the  $\alpha$ -carbon atom as was desired. This denied the possibility of the formation of such a compound as ethyl  $\alpha$ -triethylsilylacetoacetate which by ketonic cleavage would have given triethylsilylacetone, a molecule capable of furnishing others containing a variety of functional groups.

The isolation of a triphenyl-derivative corresponding to the triethylsilyl-compound just described could not be accomplished. Here again was encountered the same difficulty as

was met in the isolation of the corresponding ethoxy-derivative. In all likelihood the ether linkage was formed, but the molecule that was so obtained decomposed most readily into hexaphenyldisiloxane, the only solid that could be obtained from these reaction mixtures.

Primarily, the synthesis and attempted synthesis of the variously substituted silanes was undertaken to ascertain if they could be accomplished, and if so, the best way to accomplish them. Secondly, though, these preparations were made to investigate the general relationships between the chemistry of similar silicon and carbon molecules. In view of this purpose an effort was made to synthesize some nitrogen-containing silanes to compare their properties, and incidentally their biological activity, with various nitrogen-containing carbon compounds. The nitrogen containing molecules that were chosen for these studies were those of biological interest that are discussed in the following sections:

#### B. $\beta$ -Lactams of $\beta$ -Anilino- $\beta$ -phenylpropionic Acids

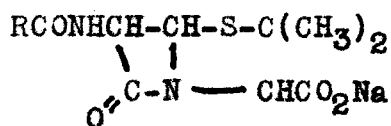
Recently the apparent structure of penicillin (I) has been demonstrated (283, 284) and shown to have the  $\beta$ -lactam grouping (II). At the time these studies were undertaken the presence of

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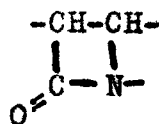
283. Medical Research Committee, Washington, and Medical Research Council, London, Science, 102, 627 (1945).

284. duVigneaud, Carpenter, Holley, Levermore, and Rachele, ibid., 104, 431 (1946).

the  $\beta$ -lactam structure in penicillin was known. It was thought



(I)



(II)

desirable to synthesize variously substituted  $\beta$ -lactams of  $\beta$ -anilino- $\beta$ -phenylpropionic acids which, it will be noted, contained this  $\beta$ -lactam structure. The substituents were chosen as those that were particularly effective in the benzophenones prepared by Freedlander as anti-tuberculous compounds (285, 286).

Incidental to these preparations several facts of theoretical interest were noted. First of all it was found possible either to open these lactams in an aqueous medium and so obtain the corresponding acid, or to open them in an alcoholic medium and so form the corresponding esters. This general procedure offers a way to the formation of the otherwise difficultly obtainable  $\beta$ -anilino- $\beta$ -phenylpropionic acids and esters.

It was also determined that dioxane and toluene are the most favorable solvents to use in the Reformatsky reaction in which these lactams are prepared.

Finally it was demonstrated that methylmagnesium iodide

285. Freedlander, Proc. Soc. Exptl. Biol. Med., 51, 153 (1942) C. A., 37, 405 (1943).
286. Freedlander, Am. Rev. Tuberc., 49, 543 (1944) C. A., 38, 5246 (1944).

was the mildest organometallic reagent that would close ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate to the corresponding lactam in high yield. Reagents of greater reactivity gave lower yields probably because of the secondary reactions into which they were able to enter.

### C. The Phenylpyridines

It was known that 2-(4'-aminophenyl)pyridine was a powerful anti-tuberculous reagent; however, indications were that this compound concurrently displayed undesirable toxic effects. Consequently, this molecule was modified in several ways in an endeavor to obtain another compound that was still as effective but either less toxic or not toxic at all.

In the first place, most of the other isomeric aminophenylpyridines were prepared to determine what effect such a change had upon effectivity and toxicity.

Secondly, the molecule was fundamentally altered in two ways. The grouping in the 4'-position was changed to hydroxy, and mercapto; and the nucleus was changed from pyridine to thiophene.

Thirdly, the 4'-amino radical was blocked with various hydrolyzable groups such as formyl, acetyl, and benzal with the hope that this would reduce the toxicity. This was the method found effective in the case of *p,p'*-diaminodiphenyl-

which was an active, but toxic, reagent (287). It was ascertained that the blocking of these amino groups by such radicals as formyl gave a derivative that was no longer toxic but still quite as active. It was thought that these derivatives were hydrolyzed to the free base at the point in the animal body where they could exert their effect.

Finally, the basicity of this molecule was diminished with the thought that there might be some relationship between that and the toxicity. The introduction of a nitro-group into the 3'-position of the phenyl ring gave a compound that was far less basic than the parent molecule as was clearly indicated by the fact that its hydrochloride decomposed upon contact with water.

Incidental to these studies it was noted that these nitrophenylpyridines, in general, could be readily reduced with hydrogen using active Raney nickel as a catalyst. This method had the distinct advantage over the tin-hydrochloric acid or sodium sulfide methods in that it furnished the amines in much higher yield, much more rapidly, and much more easily. This was quite important in the preparation of the various isomeric aminophenylpyridines since the nitrophenylpyridines were so difficult to obtain and often were obtained in very small amounts.

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287. Heymann and Fieser, J. Am. Chem. Soc., 67, 1979 (1945).

## SUMMARY

A brief survey was made of organosilicon chemistry from its inception to 1927; whereas a thorough review of this chemistry from 1936 to date was presented.

Methods of preparing alkyl or aryl substituted silanes of the general types  $R_4Si$ ,  $R_3R'Si$ ,  $R_2R'_2Si$ ,  $R_3SiOH$ , and  $RSi(OC_2H_5)_3$  from silicon tetrachloride, or tetraethoxysilane, or tetra-thioethoxysilane and organolithium reagents were described.

Studies were conducted into the possibility of introducing functional groups into various organosilanes. A general method for preparing halo-substituted phenylsilanes was given. It was shown that the direct substitution of the nitro or bromo group into benzylorganosilanes could not be accomplished.

The reaction of triethylchlorosilane and ethyl sodio-acetoacetate gave ethyl  $\beta$ -triethylsiloxyacrylate rather than the hoped for ethyl  $\beta$ -triethylsilylacetoacetate.

In connection with a study of some nitrogen-containing silicon compounds, several  $\beta$ -lactams of  $\beta$ -anilino- $\beta$ -phenylpropionic acids have been synthesized. The biologically active 2-(4'-aminophenyl)pyridine has been modified in various ways in an attempt to diminish its toxicity and so make it a more effective anti-tuberculous agent.

Most of the isomeric aminophenylpyridines were produced

from the corresponding nitro-compounds through the use of hydrogen and Raney nickel as a catalyst.