

1951

Steric hindrance in arylsilicon compounds

Cecil Gray Brannen
Iowa State College

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Organic Chemistry Commons](#)

Recommended Citation

Brannen, Cecil Gray, "Steric hindrance in arylsilicon compounds " (1951). *Retrospective Theses and Dissertations*. 13224.
<https://lib.dr.iastate.edu/rtd/13224>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

STERIC HINDRANCE IN ARYLSILICON COMPOUNDS

by

Cecil Gray Brannen

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements 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

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1951

UMI Number: DP12593

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform DP12593

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

QD412.S6
B7352

11

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Henry Gilman for his advice and encouragement given throughout the course of this investigation.

79859✓

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. HISTORICAL	5
A. Carbon Compounds	6
B. Organosilicon Compounds	14
C. Organogermanium Compounds	20
D. Organo-tin and -lead Compounds	21
E. General References	26
1. Organosilicon Compounds	26
2. Organogermanium Compounds	28
3. Organotin Compounds	28
4. Organolead Compounds	29
III. EXPERIMENTAL	30
A. Organosilicon Compounds	30
1. 1-Naphthyllithium	30
(a) Made by the Direct Method	30
(b) Made by Halogen-Metal Interconversion	31
(c) Solid 1-Naphthyllithium	33
(d) Yield of 1-Naphthyllithium as Determined by Acid Titration versus Carbonation	34
2. 2-Naphthyllithium made by Halogen-Metal Interconversion	35
3. Triphenylsilanol	37
4. Triphenylchlorosilane	37
5. Tri- <i>o</i> -tolylchlorosilane	39
6. Tetra-2-naphthylsilane	39
7. Tri-2-naphthylsilanol (Attempted)	40
(a) From Silicon Tetrachloride and 2-Naphthyllithium made by the Direct Method	40
(b) From Silicon Tetrachloride and 2-Naphthyllithium made by Halogen-Metal Interconversion	40

	Page
8. Tri-2-naphthylethoxysilane (Attempted)	41
9. Tri-2-naphthylsilane (Attempted)	41
✓ 10. Triphenyl-2-naphthylsilane	42
✓ 11. Triphenyl- <i>p</i> -tolylsilane	43
✓ 12. Diphenyldi- <i>p</i> -tolylsilane	44
(a) From Diphenyldichlorosilane and <i>p</i> -Tolylolithium	44
(b) From Silicon Tetrachloride, Phenyl-lithium, and <i>p</i> -Tolylolithium by Systematic Fractional Crystallization	45
✓ 13. Phenyltri- <i>p</i> -tolylsilane	52
14. N-Bromosuccinimide and General Procedures for its Use	53
✓ 15. Triphenyl- <i>p</i> -bromomethylphenylsilane	54
✓ 16. Triphenyl- <i>p</i> -hydroxymethylphenylsilane	55
✓ 17. Triphenyl- <i>p</i> -dibromomethylphenylsilane	57
✓ 18. <i>p</i> -Triphenylsilylbenzaldehyde	58
19. <i>p</i> -Triphenylsilylbenzaldoxime	59
20. Thiosemicarbazone of <i>p</i> -Triphenylsilylbenzaldehyde	60
✓ 21. <i>p</i> -Triphenylsilylbenzoic Acid	60
(a) Oxidation of triphenyl- <i>p</i> -tolylsilane	60
(b) From <i>p</i> -Triphenylsilylbenzyl Alcohol and Potassium Permanganate	62
(c) From <i>p</i> -Triphenylsilylbenzaldehyde and N-Bromosuccinimide Followed by Hydrolysis	62
(d) From <i>p</i> -Triphenylsilylbenzaldehyde and Hydrogen Peroxide (Attempted)	63
✓ 22. 1-Naphthyltriethoxysilane	64
✓ 23. 1-Naphthyltriphenylsilane	65
(a) From 1-Naphthyltriethoxysilane and Phenyllithium	65
(b) From Triphenylchlorosilane and 1-Naphthyllithium	65
✓ 24. Di-1-naphthyldiethoxysilane	66
(a) From Ethyl Silicate and 1-Naphthyl-lithium	66
(b) From 1-Naphthyltriethoxysilane and 1-Naphthyllithium	67

	Page
25. Di-1-naphthyldiphenylsilane	68
26. Tri-1-naphthylchlorosilane	69
27. Tri-1-naphthylethoxysilane	70
(a) From 1-Naphthyllithium and Ethyl Silicate	70
(b) From Di-1-naphthyldiethoxysilane and 1-Naphthyllithium	72
28. Tri-1-naphthylsilane	72
(a) From 1-Naphthyllithium and Trichloro- silane	72
(b) From Tri-1-naphthylethoxysilane or Tri-1-naphthylchlorosilane and Lithium Aluminum Hydride	73
29. Tri-1-naphthylbromosilane	74
30. Tri-1-naphthylsilanol	74
(a) From Tri-1-naphthylchlorosilane	74
(b) From Tri-1-naphthylethoxysilane	76
(c) From Tri-1-naphthylsilane	76
31. Hydrolysis of Tri-1-naphthylchlorosilane and Triphenylchlorosilane	76
32. Tri-1-naphthylsilane and Potassium Hydroxide in Piperidine	77
33. Tri-1-naphthyl- <u>n</u> -butylsilane	78
(a) From Tri-1-naphthylchlorosilane and <u>n</u> -Butyllithium	78
(b) From Tri-1-naphthylethoxysilane and <u>n</u> -Butyllithium	79
(c) From Tri-1-naphthylsilane and <u>n</u> - Butyllithium	79
34. Tri-1-naphthylphenylsilane	80
(a) From Tri-1-naphthylchlorosilane and Phenyllithium	80
(b) From Tri-1-naphthylsilane and Phenyl- lithium	82
(c) From Tri-1-naphthylethoxysilane and Phenyllithium	83
(d) Complex with Chlorobenzene	83

	Page
35. Tri-1-naphthyl-p-tolylsilane	84
(a) From Tri-1-naphthylethoxysilane and p-Tolylolithium	84
(b) From Tri-1-naphthylchlorosilane and p-Tolylolithium	85
(c) From Tri-1-naphthylbromosilane and p-Tolylolithium	86
(d) From Tri-1-naphthylsilane and p-Tolylolithium	86
36. Tri-o-tolyl-p-bromophenylsilane	87
37. Tri-1-naphthyl-p-bromophenylsilane (Attempted)	87
38. Tetra-1-naphthylsilane (Attempted)	88
(a) From 1-Naphthylolithium and Silicon Tetrachloride or Ethyl Silicate	88
(b) From Tri-1-naphthylchlorosilane and 1-Naphthylolithium	89
39. Hexa-1-naphthylidisiloxane (Attempted)	91
(a) From Hexachlorodisiloxane and 1-Naphthylolithium	91
(b) Tri-1-naphthylsilanol and Formic Acid	92
40. Hexa-1-naphthylidisilane (Attempted)	92
(a) From Tri-1-naphthylchlorosilane and Sodium	92
(b) From Hexachlorodisilane and 1-Naphthylolithium	93
41. Tri-1-naphthyl-p-bromomethylphenylsilane (Attempted)	95
42. Tri-1-naphthylsilylbenzoic acid (Attempted)	95
B. By-products Formed During the Preparation and Use of Organolithium Reagents	97
1. Perylene	97
(a) From Naphthalene and Aluminum Chloride	97

	Page
(b) From 1-Bromonaphthalene and Aluminum Chloride	97
(c) From β -dinaphthol	98
2. 1,1'-Binaphthyl	99
(a) From 1-Naphthylmagnesium Bromide and Chromic Chloride	99
(b) From 1-Naphthylmagnesium Bromide and Cupric Chloride	99
3. 1,1'-Binaphthyl and Lithium	100
(a) Followed by Hydrolysis	100
(b) Followed by Carbonation	101
4. 2,2'-Binaphthyl	103
5. 2,2'-Binaphthyl and Lithium	103
6. 9,9'-Biphenanthryl	105
7. 9,9'-Biphenanthryl and Lithium	105
8. 1-n-Butylnaphthalene	106
9. 1-n-Hexylnaphthalene	108
10. 1-Naphthyllithium and Benzyl Chloride	108
11. Attempted Addition of 1-Naphthyllithium to Stilbene	109
12. 1-Naphthylphenylbenzylcarbinol	110
13. 1,2-Diphenyl-1-(1-naphthyl)ethylene (Attempted)	111
14. Attempted Dehydration of 1-Naphthylphenylbenzylcarbinol by Cugaev's Method	111
15. 1-Naphthylphenylbenzylmethyl Chloride (Attempted)	112
IV. DISCUSSION	114
A. Organosilicon Compounds	114
B. By-products from the Preparation and Use of Organolithium Reagents	126
V. SUMMARY	136

I. INTRODUCTION

The term "steric hindrance" was originally used to describe the spatial effects of vicinal groups (1). However, the lack of progress and of a definite viewpoint had the effect that "steric hindrance" tended to deteriorate into a meaningless phrase used to cover a multitude of misunderstood effects. Later, therefore, it became a frequent practice to use a more restricted and cautious nomenclature, such as the description "proximity effect" for the special influence of substituents situated near the site of reaction, and "ortho-effect" for the particular form relating to nuclear substituents. It is in the original sense, that is, the space actually occupied by the group under consideration, that "steric hindrance" is used in this investigation.

Only recently has this theory advanced to a state which is capable of more quantitative treatment. This situation was developed chiefly through a mechanistic view-point when it was realized that the processes by which substances react

(1) For general discussions concerning steric hindrance see (a) J. B. Cohen, "Organic Chemistry for Advanced Students", 5th ed., Edward Arnold and Co., London, 1928, p. 386ff; (b) E. D. Hughes, Quart. Reviews, 2, 107 (1948); (c) G. W. Wheland, "Advanced Organic Chemistry", 2nd ed., John Wiley, New York, 1949, p. 378ff.

are variable for the same reaction, and this mechanism greatly influences the observed rate of reaction. Treatments along these lines have been fruitful in distinguishing between some purely steric effects and polar influences. However, the combination of such effects is, in general, too intricate to enable a quantitative assessment of their influence to be made. The more recent developments obtained by kinetic methods and considerations of transition states have established a basis for a more precise treatment of experimental and theoretical studies of steric hindrance effects generally.

In order to extend the study of steric hindrance in organosilicon compounds, the 1-naphthyl group was particularly suitable because of the presence of a large ortho-substituent. It was the primary objective of this investigation to synthesize a number of 1-naphthylsilicon compounds, to correlate their reactions with non-sterically-hindered types, and to determine the extent of substitution allowed when such groups are bonded to silicon.

In this connection a recent review (2) lists all of the known tetra-alkyl- and -aryl-silanes and the following statement is made concerning this type of compound:

(2) C. E. Burkhard, E. G. Rochow, H. S. Booth, and J. Hartt, Chem. Revs., 41, 105 (1947).

There appears to be no steric hindrance to the attachment of very large groups; the silicon atom has a sufficiently higher atomic volume than carbon so that four tolyl or naphthyl groups may be attached.

However, an examination of the accompanying tables showed that no 1-naphthylsilicon compounds are reported that contain more than one 1-naphthyl group. Furthermore, after considering the reactions of some carbon and silicon compounds, the validity of this statement appears to be in doubt.

During the course of this study a method for introducing functional groups into some methyl-substituted tetra-arylsilanes by means of N-bromosuccinimide was developed. This reaction may prove to be a useful tool for this purpose in a more general way.

A study of the by-products formed during the use and preparation of certain organolithium reagents has extended the knowledge of the limitations and use of this type of reagent, particularly in reference to those reactions which require either a long reaction period or high temperatures. Some of these by-products are the result of a unique cyclo-dehydrogenation reaction involving the addition of lithium to aromatic hydrocarbons (3). Experiments designed to

(3) For a historical account of the addition of alkali metals to aromatic hydrocarbons see F. W. Moore, Doctoral Dissertation, Iowa State College, 1941.

establish the mechanism of this reaction indicate that this method may have synthetic possibilities.

II. HISTORICAL

The purpose of the literature survey to be discussed in the following pages of this section is to bring together the pertinent information that indicates the extent of steric hindrance in compounds of the Group IVB elements. However, as indicated in the "Introduction", the theory of steric hindrance is now treated in such a qualitative manner that many factors must be considered only briefly. Due to this limitation the scope of this treatment has been an attempt to present all of the pertinent compounds that have been reported. From this list certain tentative generalizations are drawn.

The existence of certain highly substituted molecules is at present the only reliable way to indicate the upper limit of substitution. The non-existence of a compound enables one to draw only tentative conclusions, since these same compounds may be synthesized at a later date by different methods. However, an attempted preparation may be used as additional evidence to indicate that steric factors are involved especially in those cases where other effects appear to be equal.

A presentation of all of the factors that enter into the reactions of compounds considered to exhibit steric hindrance

is beyond the scope of this presentation. However, certain factors that have been fairly well established will be mentioned in the appropriate places throughout the text.

It is appropriate to point out here how Wheland summarizes the present status of the theory of steric hindrance (4).

It is therefore evident that steric factors alone are insufficient to explain all the observed variations in rate that are produced by substituents near the reactive centers. Although any complete theory must, to be sure, include these factors, it must nevertheless also include such other factors as the mechanisms of the respective reactions, the electrostatic interactions between atoms and groups, the influence of the solvent (if any), the effects of resonance, and possibly many others which are not at present recognized.

A. Carbon Compounds

There appears to be a definite limit to the number of ortho-substituted phenyl nuclei which may be bonded to a central carbon atom. Although a number of tetraphenylmethane types has been reported, there are only a few compounds (Table I) that contain one or two ortho-substituted nuclei and none containing three or more such substituted groups.

(4) G. W. Wheland, "Advanced Organic Chemistry", John Wiley and Sons, New York, 1949, p. 386.

Table I
Tetraphenylmethanes with Ortho-substituents

A. One o-substituent

Triphenyl-o-anisyl^a

Triphenyl-2,4-dimethoxyphenyl^a

Triphenyl-2,5-dimethoxyphenyl^a

Triphenyl-o-biphenyl^b

B. Two o-substituents

Diphenyl-2,5-dimethoxyphenyl-1-naphthyl^a

C. Three or four o-substituents

None reported

^aM. Gomberg and G. C. Forrester, J. Am. Chem. Soc., 47, 2373 (1925).

^bH. Wieland, K. Heymann, T. Tsatsas, D. Juchum, G. Varvoglis, G. Labriola, O. Dobbelstein, and H. S. Boyd-Barrett, Ann., 514, 145 (1934).

No systematic investigations have been made concerning the possible extent of ortho-substitution in tetraphenylmethane. Conclusions must therefore be drawn only on the basis of the isolated cases reported. Of course, the fact that certain types have been sought after but not isolated strengthens the hypothesis that steric factors prevent the

existence of such molecules. The tremendous volume of work in connection with the dissociation of hexaarylethanes has resulted in the preparation of a large number of triarylmethyl derivatives, and some deductions may be made toward determining the allowable extent of substitution around the central carbon atom. A list of o-substituted triphenylmethyl compounds is presented in Table II.

An answer to the question of how many o-substituents may be introduced into triphenylmethane and its derivatives was attempted by Faber and Nauta (5) in a study of the reactions between aryllithium compounds and diarylketones. The action of mesityllithium on dimesityl ketone and of 2,6-dimethylphenyllithium on its corresponding ketone resulted in unidentified products. They deduced that these products must be the dimers of the original ketones. Evidence to support this contention was the isolation of the same dimerized products when the ketones were treated with phenyllithium. These authors summarize their investigation by stating that it is not known whether the presence of four o-methyl groups is a necessary condition for this dimerization, or whether, with only three o-methyl groups, coupling and triaryl-carbinol formation would occur. It should be noted here that these

(5) A. C. Faber and W. T. Nauta, Rec. trav. chim., 62, 469 (1942).

Table II

References to Compounds of the Group IVB Elements
of the Type R_3MY

A. Y = aryl or alkyl group					
Radical	C	Si	Ge	Sn	Pb
o-tolyl	*	(17) ^{a,b}	*	*	*
mesityl	*	*	*	*	*
1-naphthyl	*	<u>-d</u>	*	*	*
cyclohexyl	*	(14,16) ^e	(23a) ^c (23b) ^f	<u>-g</u>	*
<u>tert</u> -butyl	*	(22) ^e	*	*	*
isopropyl	*	(21) ^c	*	*	*

*Not reported. ^aY = phenyl, p-anisyl. ^bThe numbered references may be found in the text. ^cY = phenyl. ^dY = n-butyl, phenyl, p-tolyl, This Thesis. ^eReference to an attempted preparation. ^fY = methyl, ethyl, n-propyl, n-butyl, n-amyl, and benzyl. ^gY = methyl, ethyl, phenyl, p-tolyl, E. Krause and R. Pohland, Ber., 57, 532 (1924).

Table II (Continued)

B. Y = OH, H, or halogen					
Radical	C	Si	Ge	Sn	Pb
o-tolyl	(5) ^{a,b} (6) ^c	(17) ^d	(24) ^e	(29d) ^f (29c) ^g	(30,31) ^e
mesityl	(5) ^h	(19) ^h	*	*	(28) ⁱ
1-naphthyl	(11,12a) ^j	- ^k	*	- ^l	*
cyclohexyl	(10) ^m	(14) ^k	(23b) ⁿ	- ^r	(28) ^o
<u>tert</u> -butyl	*	(22) ^h	*	(32) ^g	*
isopropyl	(8) ^p	(21) ^d	*	- ^q	(35b,g) ^g

*Not reported. ^aY = Cl, OH. ^bThe numbered references may be found in the text. ^cY = H. ^dY = Cl, H. ^eY = Cl, Br. ^fY = Cl. ^gY = Br, Cl, I. ^hReference to an attempted preparation. ⁱY = I. ^jY = H, OH. ^kY = Br, Cl, H, OH, This Thesis. ^lY = Cl, E. Krause and K. Weinberg, Ber., 62, 2235 (1929). ^mIn all cases reported tricyclohexylmethane was prepared by catalytic hydrogenation of triphenylmethane. ⁿY = Br, Cl, I, OH. Y = Br, H. Bauer and K. Burschkies, Ber., 65, 956 (1932). ^oY = I, F. Hein and E. Nebe, Ber., 75, 1744 (1942); E. Krause, ibid., 62, 135 (1929). Y = Br, Cl, I, OH, E. Krause, ibid., 54, 2060 (1921). ^pY = Cl. Y = H, ^qY = I, A. Cahours, Compt. rend., 88, 725 (1879); Y = OH, A. Cahours and E. Demarcy, ibid., 88, 1112 (1879). ^rY = F, Cl, Br, I, OH, E. Krause and R. Pohland, Ber., 57, 532 (1924).

same authors made tri-o-tolylcarbinol in good yield from di-o-tolyl ketone and o-tolyllithium.

Bartlett and Jones (6) prepared tri-o-tolylmethane from di-o-tolyl phthalide in a six-step synthesis and report that certain reactions strongly indicate that steric hindrance is operative. Metalation of this methane with phenylisopropylpotassium required a reaction period of several hours, in contrast to the immediate metalation of triphenylmethane (7). The metalated product of tri-o-tolylmethane, following carbonation, gave a tribasic acid instead of the expected substituted acetic acid. This product was shown to be 2,2',2''-tricarboxytriphenylmethane.

This behavior is explained on the basis of steric inhibition of resonance, but it is admitted that the hydrogen on the central carbon atom would be just as acidic as those on the methyl groups. The transfer of a central proton to the base, phenyldimethylcarbanion, requires the two molecules to come into direct juxtaposition in the act of effecting the transfer. The hindrance of the groups is probably sufficient to make a collision of this kind very improbable. Another explanation advanced is that a tetrapotassium derivative is

(6) P. D. Bartlett and J. E. Jones, J. Am. Chem. Soc., 64, 1837 (1942).

(7) J. B. Conant and G. W. Wheland, J. Am. Chem. Soc., 54, 1212 (1932).

formed and during carbonation the shielding of the central atom prevents complete carbonation. Subsequent operations involving hydrolysis would form the methane and not the substituted acetic acid. The authors admit that this hypothesis is unlikely, due to the high conversion usually observed of potassium organometallics to carboxyl groups. They conclude that this may be a rare example of steric inhibition of a reaction which is essentially an acid-base exchange.

Although this presentation is largely restricted to a consideration of aryl substituents, some information concerning the extent of substitution around a central carbon atom can be obtained by considering the highly branched alkanes and their derivatives. Tetra-t-butyl- and tetraisopropylmethane have not been reported. The most highly branched alkyl derivative reported is tri-isopropylchloromethane (8). t-Butyldiethylchloromethane (8) and di-t-butylmethane (9) have been synthesized.

The existence of tricyclohexylmethane (10) and the fact

(8) P. D. Bartlett, Abstract of Papers, Tenth National Organic Chemistry Symposium, Boston, Mass., 1947, p. 30.

(9) G. Egloff, "Physical Constants of Hydrocarbons", Vol. I, Reinhold Publishing Corp., New York, 1939, p. 65.

(10) (a) M. Godchet, Bull. soc. chim., 7, 956 (1895); (b) ibid.; Compt. rend., 147, 1057 (1908); (c) V. Ipatiev and B. Dolgof, ibid., 183, 304 (1926); (d) N. D. Zelinski and M. V. Gaverdovskaia, Ber., 60, 713 (1927); (e) H. Adkins, W. H. Zartman, and H. Cramer, J. Am. Chem. Soc., 53, 1425 (1931); (f) O. Neunhoeffer, Ann., 509, 115 (1934); (g) H. Adkins, L. M. Richards, and J. W. Davis, J. Am. Chem. Soc., 63, 1320 (1941).

that tetracyclohexylmethane or tricyclohexylaryl- or -alkylmethane has not been reported indicate that this may be the upper limit of substitution.

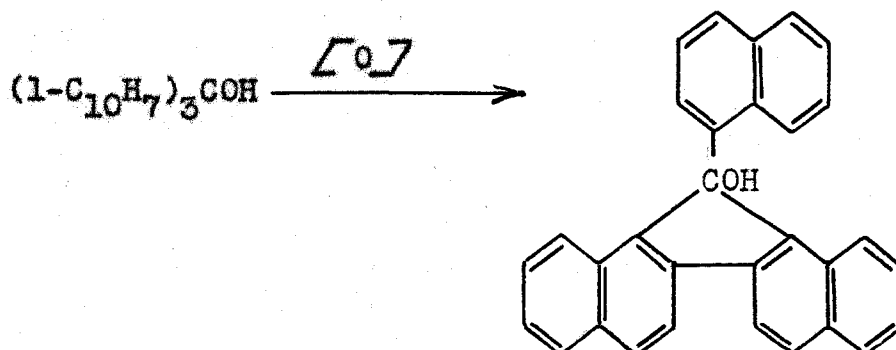
Tri-1-naphthylcarbinol is reported (11) to have been made in low yield (8-21%) by the action of an excess of the Grignard reagent on 1-naphthoyl chloride. The reported compound crystallized from ether with 1.5 molecules of ether and from benzene with 1/3 molecule of benzene. Reduction with hydrogen iodide and phosphorus, a procedure which usually gives the corresponding triarylmethane, gave a dihydrotrinaphthylcarbinol.

Later, Chichibabin (12a) reported that tri-1-naphthylcarbinol was reduced to the corresponding methane by a special technique (12b) with hydrogen iodide in glacial acetic acid.

Chichibabin (13) reinvestigated the reactions of tri-1-naphthylcarbinol and the corresponding reduced product and showed that the latter compound, reported earlier (11) as tri-1-naphthylmethane was actually 1-naphthyl-1,1-naphthofluorene. The carbinol quickly absorbs oxygen from the air and changes to a stable compound that was proved to be

-
- (11) J. Schmidlin and P. Massini, Ber., 42, 2392 (1909).
(12) (a) A. E. Chichibabin, Ber., 44, 1105 (1911);
(b) ibid., Ber., 44, 491 (1911).
(13) (a) A. E. Chichibabin, J. Russ. Phys. Chem. Soc., 43, 1022 (1911), [C. A., 6, 482 (1912)]. (b) ibid., J. Prakt. Chem., 84, 760 (1911), [C. A., 6, 990 (1912)].

1-naphthyl-di-1,1-naphthofluoryl alcohol according to the equation



This same oxidation was accomplished with potassium permanganate. The unstable tri-1-naphthylcarbinol was made by Chichibabin (13) by the action of 1-naphthylmagnesium chloride on di-1-naphthyl ketone in an atmosphere of carbon dioxide. This compound was found to crystallize from ether with 1 mole of ether and from benzene with 1 mole of benzene. The solvent was removed with difficulty from the solvated complexes. Neither the unstable carbinol nor its oxidized product (13) showed an active hydrogen in the Zerewitinoff determination. This latter fact may indicate the effect of a shielding of the hydroxyl group by the large naphthyl groups. However, the reaction mechanism of this type of reaction is not too well understood and electrical effects may be the chief cause (4).

B. Organosilicon Compounds

An inspection of Table III indicates that four o-substituents

References to Symmetrically Tetra-substituted
Compounds of the Group IVA Elements

Table III

Radical	C	SI	Ge	Sn	Pb
<i>o</i> -tolyl	*	(17)(18) ^{a, b}	(24) ^c	(29) ^d	(28, 30)
mesityl	*	(17) ^a	*	*	(28) ^a
<i>o</i> -amyl	*	(17)	*	*	(28)
1-naphthyl	*	- ^d	*	(29c) ^e	(28)
cyclohexyl	*	(14) ^a	(23b) ^a	-f, g	-g, h
tert-butyl	*	(22) ^a	*	*	*
isopropyl	*	(21) ^a	*	*	(25)

* Not reported. ^a Reference to an attempted preparation.

^b The numbered references may be found in the text. ^c J. K.

Simons, J. Am. Chem. Soc., 57, 1299 (1935). ^d Attempted,

This Thesis. ^e C. Guittin, *Ing. chim.*, 14, 205 (1930),

[C. A., 26, 2182 (1932)] P. Pascal, *Compt. rend.*, 218,

57 (1944). ^f E. Krause and R. Poland, *Ber.*, 57, 532 (1924).

^g G. Gruttner, *Ibid.*, 47, 3257 (1914). ^h Ger. pat. 508,667

[*Chem. Zentr.*, 101, II, 3195 (1930)] E. Krause, *Ber.*, 54,

2060 (1921). ⁱ Attempted, P. Pfeiffer, *Z. anorg. Chem.*, 68,

122 (1910).

may be present in tetraphenylsilane types, whereas no such compounds have been reported for the methane series. The existence of tri-*o*-tolyl-alkyl- and -aryl-silanes and similar silanes containing the tri-1-naphthylsilyl group strongly indicates that the silicon atom can accommodate more bulky groups than can carbon. This deduction must be made with reservation since very few thorough investigations have been made regarding the synthesis of tetraarylmethanes. Consequently the synthesis of many methanes of this type may not have been attempted. The fact that such compounds have not yet been reported is, of course, not sufficient evidence to state that they cannot exist, but at this time the information may perhaps be used to make the above tentative generalization.

Tricyclohexylsilane and its derivatives show a certain non-reactivity which may be used to show that more steric hindrance is associated with the cyclohexyl group than with the *o*-tolyl and 1-naphthyl radicals. Tricyclohexylchlorosilane is reported (14) not to react with some organolithium reagents. Methyl-, ethyl-, and phenyllithium, as well as the corresponding Grignard reagents, were employed and even though moderately high temperatures were used no evidence of further substitution

(14) W. H. Nebergall and O. H. Johnson, J. Am. Chem. Soc., 71, 4022 (1949).

was observed. Similar results were obtained using the bromo and iodo derivatives. Tricyclohexylchlorosilane also failed to respond to sodium condensation in boiling xylene, a procedure which gives good yields of hexaphenyldisilane (15) from triphenylchlorosilane.

Cusa and Kipping (16) attempted to prepare tricyclohexylphenylsilane by the action of a large excess of cyclohexylmagnesium bromide on phenyltrichlorosilane and obtained only dicyclohexylphenylsilane. The failure to obtain the expected product was attributed to the steric hindrance associated with the cyclohexyl group.

These experiments illustrate the danger of drawing conclusions as to the absolute limit of substitution permitted around any central atom by examining only those compounds which have been reported. It is conceivable that many of these compounds may be capable of existence and may be synthesized by a proper choice of reagents and conditions. However, these comparisons can still be used to indicate that steric factors are operative. At the present time one of the best hypothesis that can explain all of the facts is that the rate of reaction is

(15) G. E. Dunn, Doctoral Dissertation, Iowa State College, 1951, has obtained 85-90% yields by modifying the directions of W. Schlenk, J. Rennig, and G. Rocky, Ber., 44, 1178 (1911), who do not report their yield.

(16) N. W. Cusa and F. S. Kipping, J. Chem. Soc., 1040 (1933).

retarded due to steric hindrance.

A thorough examination of the action of o-tolyllithium on silicon tetrachloride has been made by Gilman and Smart (17). Tri-o-tolylchlorosilane was made under fairly mild conditions and this compound reacted with organolithium reagents, but only after an extended reaction period. There is some indication that tetra-o-tolylsilane can be made but the product has been characterized by analysis only.

The existence of these o-tolyl derivatives, particularly those containing four o-substituents, is the best evidence, to date, to indicate any appreciable difference in the atomic volume of carbon and silicon in regard to the limit of substitution.

Schumb and Saffer (18) showed that in the reaction of silicon tetrachloride with p-, m-, and o-tolylmagnesium bromides, the yields of the corresponding tetratolylsilanes were 35%, 8%, and 0%, respectively. They were also unsuccessful in their attempts to prepare tetra-o-tolylsilane by a Wurtz reaction involving silicon tetrachloride, o-bromotoluene, and sodium and attribute their failure to steric factors.

(17) H. Gilman and G. N. R. Smart, J. Org. Chem., 15, 720 (1950).

(18) W. C. Schumb and C. M. Saffer, J. Am. Chem. Soc., 61, 363 (1939).

The reaction of mesityllithium with silicon tetrachloride (19) is not yet established but there is evidence (19) that trimesitylsilyl derivatives can be made. Dimesityldiethoxysilane (17) is reported, but on the other hand, dimesitylmethyl derivatives (20) are also reported.

The attempted preparation of tetraisopropylsilane (21) afforded only the trisubstituted derivative. These products, however, did not show the non-reactivity with organolithium reagents as did the tricyclohexylsilyl derivatives. While triisopropylphenylsilane could be prepared, triisopropyl-o-tolylsilane could not.

t-Butyllithium was found (22) much less reactive toward the silicon-chlorine bond than the primary and secondary alkyl-lithium compounds. Attempts to prepare tri- or tetra-t-butylsilicon compounds were unsuccessful. At elevated temperatures (up to 160°) t-butyllithium reacted with t-butyltrichlorosilane to give fair yields of di-t-butyldichlorosilane but none of the tri- or tetra-substituted product.

(19) Unpublished studies by Dr. G. N. R. Smart.

(20) W. T. Nauta and P. J. Weiss, Rec. trav. chim., 56, 535 (1937).

(21) H. Gilman and R. N. Clark, J. Am. Chem. Soc., 69, 1499 (1947).

(22) L. J. Tyler, L. H. Sommer, and F. C. Whitmore, J. Am. Chem. Soc., 70, 2876 (1948).

C. Organogermanium Compounds

Although the total number of organogermanium compounds reported is small in comparison with those of carbon and silicon, some conclusions can be drawn concerning the importance of steric factors in these compounds.

Some information for comparative purposes was obtained in studies with cyclohexylsilanes (14) and cyclohexylgermanes (23). While tricyclohexylsilyl halides did not react with any organolithium or Grignard reagents, the reaction of tricyclohexylbromogermane with alkyl Grignard reagents proceeded smoothly to give the expected product. Additional evidence that steric factors are operative was supplied when it was found that the Wurtz synthesis to prepare hexacyclohexyldigermane from tricyclohexylbromogermane and sodium was successful, while the analogous reaction when used to prepare the corresponding disilane was not.

Simons and coworkers (24) found that the action of the tolyl Grignard reagents alone on germanium tetrachloride gave no tetrasubstituted germanes and only poor yields of the tritolyl derivatives. The prior treatment of the Grignard with

(23) (a) O. H. Johnson and W. H. Nebergall, J. Am. Chem. Soc., 70, 1706 (1948); (b) ibid., 71, 1720 (1949).

(24) J. K. Simons, E. C. Wagner, and J. H. Muller, J. Am. Chem. Soc., 55, 3705 (1933).

zinc chloride and subsequent reaction with germanium tetrachloride afforded 65%, 75%, and 30% yields of the tetra-p-, m-, and o-tolylgermanes, respectively. The conditions used by these workers may be termed mild (not over 100°) in contrast to the procedure that Gilman and Smart (16) were forced to use (baking at 170° for several hours) to effect any reaction between o-tolyllithium and tri-o-tolylchlorosilane.

From these data there appears to be ample evidence that steric hindrance is operative in these reactions and that these factors are more important in the reactions of silicon compounds than in those of germanium.

D. Organo-tin and -lead Compounds

Although reaction mechanisms have not been previously discussed, before considering the Pb compounds, the principle reactions used for the preparation of these compounds should be considered. Lead tetrachloride is an extremely unstable substance and cannot be used in reactions analogous to those of the other four Group IV elements. To be sure, there is considerable variation in the reactivity of the halogen among carbon-, silicon-, germanium- and tin-halides but the reaction $M^{IV}X_4 + RM$ (where M^{IV} = Group IV element, X = halogen, M = Hg, Zn, Mg, Li and R = aryl or alkyl group) can be carried out with all four. In the case of lead, an oxidation-reduction

reaction must be employed to obtain tetra-substituted lead compounds. The reactions $RM + PbCl_2 \longrightarrow R_4Pb + Pb + MCl$, and $Pb-Na + RX \longrightarrow R_4Pb + NaX$, and various combinations of these reagents, are the principle methods of preparing organo-lead compounds (25).

Very little is known concerning the mechanism of the oxidation-reduction reaction (26), and consequently, no definite conclusions may be drawn concerning the results of an attempted reaction. Here, as before, the most important factor is the preparation of the molecule under consideration.

To illustrate this limitation more clearly, consider the fact that tert-butyl alcohol is esterified much less rapidly by a carboxylic acid, but much more rapidly by a hydrogen halide, than is n-butyl alcohol (27). Although the geometrical interpretation of steric hindrance explains the phenomena perfectly in the case of the carboxylic acid, it fails completely with the hydrogen halides. It is now known that these reactions proceed by at least two entirely different mechanisms. The stereochemical theory fails in this respect in that it does not take into account the fact that all reactions do not follow

(25) For a discussion of the reactions of organolead compounds see R. W. Leeper, Doctoral Dissertation, Iowa State College, 1942.

(26) For an excellent discussion of the mechanism of various lead reactions see L. Summers, Doctoral Dissertation, Iowa State College, 1950.

(27) E. D. Hughes, Trans. Faraday Soc., 34, 202 (1938).

the same mechanism.

That a consideration of mechanism is probably necessary is illustrated by an examination of the reported 1-naphthyl-tin and -lead compounds. Considering that the atomic volume of lead is larger than that of tin, it seems odd that tetra-1-naphthyl-tin is reported while experiments designed to prepare the lead analog were unsuccessful. Gilman and Bailie (28) attempted to pyrolyze hexa-1-naphthyl-dilead by employing drastic conditions (heating in a sealed tube at 160° for six hours) but found no isolable product. Although steric hindrance is probably operating in this case, the lack of information concerning the reaction mechanism makes it impossible to draw any valid conclusion.

These same investigators prepared a number of tetraaryl-lead compounds by pyrolysis of the corresponding hexaaryldilead derivatives (*p*-, *m*-, and *o*-tolyl, *o*-anisyl, and *o*- and *p*-ethoxyphenyl). However, hexamesityl-, and hexacyclohexyl-dilead, as well as the hexa-1-naphthyl derivative, did not show any indication of a reaction even after boiling in xylene for three hours.

Very little additional information can be gained from a consideration of the *o*-tolyl- and cyclohexyl-tin and -lead

(28) H. Gilman and J. C. Bailie, J. Am. Chem. Soc., 61 731 (1939).

compounds. Tetra-o-tolyl-tin (29), tri-o-tolyl-tin salts (29 c,d) as well as tetra-o-tolyllead (28,30) and the corresponding triaryllead salts (30,31) have been reported.

Hexamesityldilead merits a consideration from a different point of view. The fact that six o-substituents can be attached to the nuclei bonded to lead strikingly illustrates the greater atomic volume of lead as compared to that of carbon, silicon, or germanium. The effect of the lead-lead bond, however, probably is to permit distortion thus accommodating the o-substituents on the phenyl nuclei. It is unfortunate that mesityltin compounds have not been reported. A comparison of the two series might detect some difference as to the extent of steric hindrance.

Some tert-butyltin- and -lead compounds have been synthesized. Tri-tert-butyltin salts (32) are known while only two tert-butyl groups have been bonded to lead, di-tert-butyldiethyllead (33) and di-tert-butyldiphenyllead (34).

(29) (a) E. Krause, Ber., 51, 913 (1918); (b) E. Krause and M. Schmitz, ibid., 52, 2150 (1919); (c) E. Krause and R. Becker, ibid., 53, 173 (1920); (d) K. A. Kozeschkow, M. M. Nadj, and A. P. Alexandrow, ibid., 67, 1348 (1934).

(30) (a) P. R. Austin, J. Am. Chem. Soc., 53, 1548 (1931); (b) H. Gilman and L. D. Apperson, J. Org. Chem., 4, 162 (1939).

(31) P. R. Austin, J. Am. Chem. Soc., 53, 3514 (1931).

(32) E. Krause and K. Weinberg, Ber., 63, 381 (1930).

(33) J. Robinson, Doctoral Dissertation, Iowa State College, 1929.

(34) H. Gilman and L. Balassa, Iowa State Coll. J. Sci., 3, 105 (1929).

Since the lead atom is known to be larger than the tin atom, factors other than steric hindrance are undoubtedly concerned.

Several investigators (35) report the preparation of tetraisopropyllead while the tin analog has not been obtained. The method used to prepare the lead derivative was the reaction of the Grignard reagent with lead chloride. Triisopropyltin iodide was the principle product when tin amalgam was treated with isopropyl iodide. Once again reaction mechanism as well as steric factors may be involved.

(35) (a) J. Tafel, Ber., 39, 3626 (1906); (b) ibid., 44, 323 (1911); (c) G. Grüttner and E. Krause, Ber., 49, 1415, 1546 (1916); (d) ibid., 50, 576 (1917); (e) ibid., Ann., 415, 338 (1918); (f) F. Fichter and I. Stein, Helv. chim. Acta, 14, 1205 (1931); (g) A. Goldach, ibid., 1436 (1931).

E. General References

1. Organosilicon Compounds

- Andrianov, A. A., A. A. Zhdanov, S. A. Golubtsov, and M. B. Sobolevskii, Uspekhi Khimii, 18, 145 (1949), ∠ C. A., 44, 1404 (1950)✓.
- Apelle, F., Rev. gen. electricite, 55, 99 (1946), ∠ C. A., 41, 621 (1947)✓.
- Barrett, J., H. G. Emblem, D. S. P. Roebuck, and H. P. Scott, Soc. Chem. Ind., Chem. Eng. Group, Advance Copy, May 9, 1950, ∠ C. A., 44, 6191 (1950)✓.
- Burkard, C., E. G. Rochow, H. S. Booth, and J. Hartt, Chem. Revs., 41, 97 (1947).
- Chapman, F., Plastics Inst. Trans., 61 (1948), ∠ C. A., 42, 8485 (1948)✓.
- DeMalde, M., Materie Plastique, 15, 147 (1949).
- Emblem, H. G., and F. L. Sos, Chem. Ind., 450 (1946); ibid., 435 (1947).
- Goddard, A. E., and D. Goddard in J. N. Friend's, "A Text-book of Inorganic Chemistry", Vol. XI, Part 1, Charles Griffin and Co., London, 1928.
- Hardy, D. V. N., Endeavor, 6, 29 (1947).
- Haul, R., Angew. Chem., A60, 225 (1948).
- Hausman, H., J. Chem. Ed., 23, 16 (1946).
- Hunter, M. J., Can. Chem. Process Ind., 30, No. 12, 39 (1946), ∠ C. A., 41, 1206 (1947)✓.
- Jones, F. A., Trans. Inst. Rubber Ind., 23, 46 (1947), ∠ C. A., 42, 517 (1948)✓.
- Kipping, F. S., Proc. Roy. Soc. (London), 159A, 139 (1937).
- Kittel, H., Farben, Lacke, Anstrichstoffe, 2, 50, 65, 113, 137, (1948), ∠ C. A., 43, 561 (1949)✓.

- Kohlschütter, H., Fortschritt chem. Forsch., 1, 1 (1949),
[C. A., 44, 4714 (1950)]/.
- Krause, E., and A. von Grosse, "Die Chemie der Metall-
organischen Verbindungen", Borntraeger, Berlin, 1937,
p. 254ff.
- Marchand, M., Chem. Tech., 2, 139 (1950), [C. A., 44,
7580 (1950)]/.
- Martens, K., Seifen-Öle-Fette-Wachse, 76, 235 (1950),
[C. A., 44, 11161 (1950)]/.
- Miller, D., Can. Chem. Process Ind., 36, 764, 858, 870
(1949), [C. A., 44, 369 (1950)]/.
- Müller, R., Chem. Tech., 2, 7, 41 (1950), [C. A., 44,
369 (1950)]/.
- Noll, W., Fortschr. Mineral., 26, 93 (1947), [C. A., 44,
9720 (1950)]/.
- Nowak, P., Kunststoffe, 40, 177 (1950), [C. A., 44, 8691
(1950)]/.
- Okawara, R., J. Japan. Chem., 4, 20 (1950), [C. A., 44,
3436 (1950)]/.
- Post, H. W., "Silicones and other Organic Silicon Compounds",
Reinhold, New York, N. Y., 1949.
- Remick, A. E., Record Chem. Progress, 11, 52 (1950),
[C. A., 44, 7512 (1950)]/.
- Robinson, S. R., Sci. J. Roy. Coll. Sci. London, 25, 24
(1945).
- Rochow, E. G., "Introduction to the Chemistry of the
Silicones", John Wiley and Sons, New York, N. Y., 1946.
- Rochow, E. G., Trans. Electrochem. Soc., 90 (1946)
(Preprint), [C. A., 40, 7156 (1946)]/.
- Rochow, E. G., and F. J. Norton, Colloid Chemistry, 6, 1092
(1946), [C. A., 40, 2435 (1946)]/.
- Runge, F., "Organometallverbindungen", 2nd ed., Wissenschaftliche
Verlagsgesellschaft, m.b.h., Stuttgart, 1944.

Schmidt, J., "Organometallverbindungen", Wissenschaftliche Verlagsgesellschaft, m.b.h., 1934, Teil II.

Schwarz, R., Naturwiss., 34, 285 (1947); FIAT Rev. Germ. Sci. Chem., Pt. I, 193 (1948); Glastech. Ber., 22, 289 (1949), [C. A., 44, 9719 (1950)]/.

Yakubovich, A. V., and V. A. Ginsberg, Uspekhi Khim., 18, 46 (1949), [C. A., 44, 1404 (1950)]/.

Yamada, T., J. Soc. Org. Syn. Chem. Japan, 7, 142 (1949), [C. A., 44, 4614 (1950)]/.

2. Organogermanium Compounds

Dubien, M., Rev. gen. sci., 37, 366 (1926), [C. A., 20, 3156 (1926)]/.

Goddard, A. E., and D. Goddard, Vol. XI in J. N. Friend's "A Textbook of Inorganic Chemistry", Charles Griffin and Co., London, 1928.

Koeheshkov, K. A., Uspekhi Khim., 3, 83 (1934), [C. A., 28, 5402 (1934)]/.

Krause, E., and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen", Borntraeger, Berlin, 1937.

Runge, F., "Organometallverbindungen", 2nd ed., Wissenschaftliche Verlagsgesellschaft, m.b.h., Stuttgart, 1944.

Schmidt, J., "Organometallverbindungen", Wissenschaftliche Verlagsgesellschaft, m.b.h., 1934, Teil II.

3. Organotin Compounds

Arntzen, C. E., Doctoral Dissertation, Iowa State College, 1942.

Garzuly, R., "Organometalle". In Vol. XIX of Herzl "Sammlung chemisch und chemischtechnischer Vorträge", Enke, Stuttgart (1927).

Goddard, A. E., and D. Goddard, "Organometallic Compounds of Groups I to IV", in J. N. Friend, "A Textbook of Inorganic Chemistry", Charles Griffin Co., London, 1928.

Klarmann, E., "Darstellung metallorganischer Verbindungen", in Abderhalden's "Handbuch der biologischen Arbeitsmethoden", Urban and Schwarzenberg, Berlin, 1929, Abt. I, Chemische Methoden, Teil 2, 2 Hälfte, Heft 4 [Lieferung 294], pp. 2203-2214.

Krause, E., and A. von Grosse, "Die Chemie der metallorganischen Verbindungen", Borntraeger, Berlin, 1937.

Runge, F., "Organometallverbindungen", 2nd ed., Wissenschaftliche Verlagsgesellschaft, m.b.h., Stuttgart, 1944.

Schmidt, J., "Organometallverbindungen", Wissenschaftliche Verlagsgesellschaft, m.b.h., 1934, Teil II.

4. Organolead Compounds

Calingaert, G., Chem. Revs., 2, 43 (1925).

Garzuly, R., "Organometalle", in Vol. XIX of Herz', "Sammlung chemisch und chemischtechnischer Vorträge", Enke, Stuttgart, 1927.

Goddard, A. E., and D. Goddard in J. N. Friend's "A Textbook of Inorganic Chemistry", Vol. XI, Part 1, Charles Griffin and Co., London, 1928.

Klarman, E., "Darstellung metallorganischen Arbeitsmethoden", in Abderhalden's "Handbuch der biologischen Arbeitsmethoden", Urban and Schwarzenberg, Berlin, 1929, Abt. I, Chemische Methoden, Teil 2, 2 Hälfte, Heft 4.

Krause, E., and A. von Grosse, "Die Chemie der metallorganischen Verbindungen", Borntraeger, Berlin, 1937.

Leeper, R. W., Doctoral Dissertation, Iowa State College, 1942. (Past reviews).

Runge, F., "Organometallverbindungen", 2nd ed., Wissenschaftliche Verlagsgesellschaft, m.b.h., Stuttgart, 1944.

Schmidt, J., "Organometallverbindungen", Part 2, Wissenschaftliche Verlagsgesellschaft, m.b.g., 1934.

Summers, L., Doctoral Dissertation, Iowa State College, 1950.

III. EXPERIMENTAL

A. Organosilicon Compounds

Most of the silicon analyses reported in this investigation were carried out in essential accordance with a published procedure (36a). In those cases where a micro-method (36b) was employed, a notation is made in the report of analytical results.

1. 1-Naphthyllithium

(a) Made by the Direct Method.- During the course of this investigation about twenty-five 1-naphthyllithium preparations were made from 1-bromonaphthalene and lithium metal in diethyl ether. Consistent 90-95% yields (as determined (37) by acid titration) were obtained by following the procedure outlined by Gilman Zoellner, and Selby (38). Lower yields (60-75%) were obtained when the reaction was carried out at 0° by cooling with an ice bath.

(36) (a) H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1950); (b) H. Gilman and L. S. Miller, ibid., 73 (Feb. or Mar.) (1951).

(37) H. Gilman, P. D. Wilkinson, W. P. Fischel, and C. H. Meyers, J. Am. Chem. Soc., 45, 150 (1923).

(38) H. Gilman, E. A. Zoellner, and W. M. Selby, J. Am. Chem. Soc., 54, 1957 (1932).

Several experiments were made in attempts to obviate the formation of the red and purple colored substances that invariably accompany the preparation of 1-naphthyllithium when made by the direct procedure. These colored materials are probably lithium addition products of naphthalene (39) and binaphthyl. Scott and coworkers (40) have shown that sodium addition to naphthalene proceeds faster and to a greater extent in highly oxygenated solvents (such as methyl ether and the dimethyl ether of ethylene glycol). It was believed that the use of hydrocarbon solvents might prevent the formation of the colored material. However, when benzene and petroleum ether (b. p. 30-60°) were used alone and in various combinations with ether, lithium was not attacked by 1-bromonaphthalene except when the hydrocarbon concentration was below 30%. In those preparations that showed a positive Color Test I, a rose to purple color was invariably present in the reaction mixture.

(b) Made by Halogen-Metal Interconversion.- The effect of different solvents, etc., on the yield of this particular organometallic reagent is described elsewhere (41), and this procedure is merely a standardization of technique. A typical preparation is described.

(39) W. Schlenk and E. Bergmann, Ann., 463, 1 (1928).

(40) N. D. Scott, J. F. Walker, and V. L. Hansley, J. Am. Chem. Soc., 58, 2442 (1936).

(41) H. Gilman and F. W. Moore, J. Am. Chem. Soc., 62, 1843 (1940).

To an ethereal solution of ca. 100 ml. of dry ether and 257 g. (1.24 moles) of 1-bromonaphthalene was added 1030 ml. (1.24 moles) of a 1.2 N solution of n-butyllithium (prepared in an 83% yield by a recently described procedure (42) from 205.5 g. (1.5 moles) of n-butyl bromide and 22.4 g. (3.2 g. atoms) of lithium). (The order of addition is immaterial. Comparable yields were obtained when the 1-bromonaphthalene was added to the n-butyllithium.) The internal temperature was kept at $0 \pm 5^{\circ}$ with a Dry-Ice-acetone bath. After about one quarter of the n-butyllithium solution had been added, a white solid started separating from the mixture. The time for complete addition was fifteen minutes and the mixture was allowed to stir an additional five minutes before using.

Several small runs gave consistent 90-92% yields of pure 1-naphthoic acid when the entire batch was carbonated by pouring on a slurry of ether and Dry Ice after stirring for twenty minutes. When an ethereal solution of this preparation was poured on Dry Ice alone, varied color changes, yellow to orange to green, were observed and the acid obtained after separating the layers and acidifying the ether-washed basic aqueous layer was tan to brown in color, melting about four degrees low ($155-156^{\circ}$). If an ether slurry of Dry Ice was

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

used, the acid, after the same treatment, was pure white and of excellent purity, m. p. 159-160°.

(c) Solid 1-Naphthyllithium.- Equivalent amounts (1.47 moles) of 1-bromonaphthalene and n-butyllithium were mixed in the same manner as described in the previous section. The solvent, from the white precipitate that had formed, was drawn off through a filter stick by the procedure outlined by Gilman, Langham, and Moore (43). The resulting residue was washed separately with three 100 ml. portions of cold dry ether (-40°). The addition of 800 ml. of anhydrous benzene dissolved most of the white residue but a fine suspension of white solid remained. After the benzene solution was decanted, the normality was found by acid titration to be 0.766 (a 40% overall yield). Two 25 ml. aliquots were carbonated and these gave a weight of 1-naphthoic acid equivalent to a normality of 0.745. These normality values indicate that the carbonation reaction in this case was 97% efficient.

Another preparation of the solid was made and a weighed sample was hydrolyzed and titrated. The weighing apparatus consisted of a 30 mm. coarse sintered glass crucible with 3 mm. stopcocks fused onto 30 mm. glass tube extensions on each end of the crucible. A 1 mm. stopcock was sealed onto the

(43) H. Gilman, W. Langham, and F. W. Moore, J. Am. Chem. Soc., 62, 2327 (1940).

upper portion of the glass cylinder about one inch below the 3 mm. stopcock. This latter opening was found to be necessary to allow more efficient filling of the cylinder during filtration. If the 1 mm. stopcock is omitted, the solid of the slurry of 1-naphthyllithium will not be carried over into the cylinder.

The same arrangement of equipment was used as that reported for filtration in an inert atmosphere (43). The weighing apparatus described above was used in place of a regular filter. The procedure that was found most satisfactory was: leave all stopcocks open in order to charge the apparatus, close the small stopcock, apply enough nitrogen pressure to force the liquid through the sintered glass filter, close all stopcocks, detach the apparatus, and then attach to an efficient vacuum pump for 1/2 to one hour with the appropriate stopcock open. After this treatment the apparatus was weighed with all openings closed.

A sample of 23.750 g. required 96 me. of acid to neutralize the base liberated after hydrolysis of the solid with water. This represents a purity of 55%. By the same treatment two other samples indicate that the solid was 53% and 51% 1-naphthyllithium.

(d) Yield of 1-Naphthyllithium as Determined by Acid Titration versus Carbonation.- The yield by acid titration of a

1-naphthyllithium preparation was 85% whereas an aliquot of the same preparation that was carbonated gave a 40% yield of yellow 1-naphthoic acid melting at 152-156°. The yields from a different preparation were 89% by acid titration and 63% by carbonation. Several reasons can be advanced for this difference. First, the carbonation reaction may not be quantitative; second, the amount of water condensed on the Dry Ice is variable; and third, the purple color is probably due to dilithio addition compounds that will yield alkali on hydrolysis and consequently indicate a higher yield of naphthyllithium than is actually present.

2. 2-Naphthyllithium made by Halogen-Metal Interconversion.

Other investigations (41) concerning the yield of 2-naphthyllithium made by halogen-metal interconversion with 2-bromonaphthalene and *n*-butyllithium were done at room temperature only and no yields are recorded for reaction periods longer than ten minutes. An inspection of the published data reveals that the yields of 2-naphthyllithium may not have reached a maximum. It is possible that higher yields may be formed by extending the reaction time or by varying the conditions. The following quantitative studies were carried out to obtain this data.

To a vigorously stirred solution of 5.00 g. (0.0242 mole) of 2-bromonaphthalene in ether (total volume 78 ml.) was added

22 ml. (0.0242 mole) of a 1.1 N ethereal solution of *n*-butyllithium. Aliquots of 10 ml. were withdrawn periodically. Each aliquot was poured directly onto a Dry Ice-ether slurry and after all the solid Dry Ice had disappeared the mixture was extracted thrice with dilute hydrochloric acid, then five times with distilled water (44) and the layers were carefully separated. The ethereal layer was then titrated with standard sodium hydroxide. The results are presented in Table IV.

Table IV
Effect of Temperature on % Yields of 2-Naphthoic Acid

Time, min.	Temperature		
	-15°	5°	32°
0	4	66	60
5	18	--	61
10	65	77	64
20	69	75	67
60	76	74	76
120	61	68	72

(44) Thorough washing with water was necessary to remove valeric acid. Separate experiments with small amounts of pure valeric acid showed that this acid was completely removed from the ether layer by four extractions with water.

The ethereal solutions containing the acid were combined from the 5° run, and the weight of 2-naphthoic acid that was recovered was 94% of the titration value. The acid was recovered from all aliquots and the purity was checked by melting point. All solid samples had a melting point of 181-183°.

In preliminary experiments a 0.1 molar run was made at 5° and the 2-naphthoic acid was isolated, dried, and weighed, checking the melting point after the weighing. The yields were much lower than those reported above, probably due to the loss during manipulation of the small quantities of material.

3. Triphenylsilanol.-- Although the procedure of Clark (45) was followed as closely as the directions permitted, lower yields (60% and 63%) of the same quality material (m. p. 150-151°) was isolated than that reported (97%). Clark added the silicon tetrachloride solution "slowly" to the phenyllithium, while the solution was added in this investigation at the rate of 100 ml. per hour.

4. Triphenylchlorosilane.-- This compound was made by treating triphenylsilanol with dry hydrogen chloride in strict accordance with the directions of Kraus and Rosen (46). The

(45) R. N. Clark, Doctoral Dissertation, Iowa State College, 1946, p. 104.

(46) C. A. Kraus and R. Rosen, J. Am. Chem. Soc., 47, 2739 (1925).

published directions report a 90% yield but no melting point is given. A yield of 83% of product melting at 97-98^o was found in this investigation.

Another preparation of triphenylchlorosilane was made from silicon tetrachloride and phenyllithium by following the directions of Smart (19). The purpose of this preparation was to obtain a sample of highest purity for use in some phase diagram studies (19).

Ethereal solutions of phenyllithium (340 ml., 1.77 N, 0.6 mole) and silicon tetrachloride (33.9 g., 0.2 mole, in 200 ml. of ether) were reacted under the same conditions as those described in the section on triphenylsilanol. After the mixture had stirred for thirty minutes, the ether was distilled from the flask. The white residue was digested separately with four 300 ml. portions of dry petroleum ether (b. p. 60-80^o) and the solutions were filtered through a filter stick into a clean dry flask. Fairly warm solutions were filtered since triphenylchlorosilane is insoluble in the cold solvent. This extraction treatment was necessary in order to remove the lithium salts. If these salts are allowed to remain in the mixture during vacuum distillation, an insulating layer is formed which prevents distillation of the volatile components from the center of the mass.

After the solvent had been removed, the residue was

distilled through an 8 inch Vigreux column at 0.3 mm. The fraction boiling at 160-170° was collected. There was obtained 16.5 g. (28%) of triphenylchlorosilane after the distilled material had been recrystallized twice from petroleum ether (b. p. 60-80°) and dried at 70° at reduced pressure. The melting point in a capillary tube was 101-102° while the entire mass melted from 100° to 113°. A crude cooling curve showed the freezing point to be 108-109°.

5. Tri-p-tolylchlorosilane.- This compound, melting at 115-116°, was made in 72% yield in essential accordance with the procedure of Gilman and Smart (17) who report a 70% yield of material melting at 113-116°. While the reaction mixture is reported to have been stirred at room temperature for twenty hours followed by refluxing for one hour, only a three hour reaction period at reflux temperature was used in this preparation to obtain a comparable yield.

6. Tetra-2-naphthylsilane.- This silane was easily made (47) by the action of 2-naphthyllithium, prepared either by the direct procedure or by halogen-metal interconversion, on silicon tetrachloride, trichlorosilane, or ethyl silicate. The pure product, melting at 216-217° (cor.), was obtained in yields ranging from 40-80%.

(47) H. Gilman and C. G. Brannen, J. Am. Chem. Soc., 72, 4280 (1950).

7. Tri-2-naphthylsilanol (Attempted)

(a) From Silicon Tetrachloride and 2-Naphthyllithium made by the Direct Method.- A 0.322 N ethereal solution containing 0.071 mole of 2-naphthyllithium was made from 20.7 g. (0.1 mole) of 2-bromonaphthalene and 2.3 g. (0.33 g. atom) of lithium. This solution was added at a rate of 2 drops per second to a vigorously stirred mixture of 4.08 g. (0.024 mole) of freshly distilled silicon tetrachloride in 200 ml. of ether while cooling the reaction flask with an ice-salt bath. After hydrolyzing the mixture with dilute ammonium chloride and removing the solvent from the organic layer, an oil was obtained. No solid products could be obtained from this oil by attempted crystallization from the common organic solvents. A chromatogram using the combination alumina and petroleum ether (b. p. 60-80°) was successful only in that a few mg. of 2,2'-binaphthyl was isolated.

(b) From Silicon Tetrachloride and 2-Naphthyllithium made by Halogen-Metal Interconversion.- 2-Naphthyllithium was made as described previously by mixing equimolar quantities (0.0625 mole) of 2-bromonaphthalene and n-butyllithium at 5°. On the basis of the carbonation studies, the yield was assumed to be 75%. This solution was added at a rate of 4 ml. per minute to a mixture of 2.72 g. (0.016 mole) of freshly distilled silicon tetrachloride in 50 ml. of ether while cooling the reaction flask in an ice bath. After hydrolysis and solvent

removal, a yellow oil was obtained. Crystallization of this oil from ethyl acetate gave 1.2 g. (14%) of tetra-2-naphthylsilane melting at 212-213°. The remainder of the material was chromatographed on alumina from petroleum ether (b. p. 60-80°) to yield an additional 0.21 g. of tetra-2-naphthylsilane and 0.31 g. (2%) of 2,2'-binaphthyl. Identification was made by the mixed melting point method. All of the other fractions were oils that resisted further purification.

8. Tri-2-naphthylethoxysilane. (Attempted).- An ethereal solution of 2-naphthyllithium (0.095 mole) was made in 66% yield by the direct method (38) and added slowly to a mixture of 6.25 g. (0.03 mole) of ethyl silicate in 300 ml. of ether at 10°. After the mixture had stirred for two hours, the solvent was replaced by benzene and the inorganic salts were removed by filtration. Distillation of the filtrate at 0.1 mm. gave two fractions: 3.4 g. of b. p. 250-300°, and 2.6 g. of b. p. 300-325°. 2,2'-Binaphthyl (28%) was obtained from both of these fractions by crystallization from petroleum ether (b. p. 90-110°). After several unsuccessful attempts to purify the ether soluble oils by crystallization from other common organic solvents, the material was discarded.

9. Tri-2-naphthylsilane. (Attempted).- An ethereal solution of 2-naphthyllithium was prepared by mixing 10.3 g.

(0.05 mole) of 2-bromonaphthalene in 100 ml. of ether and 62.5 ml. of a 0.8 N (0.05 mole) of n-butyllithium at 32°. After stirring the mixture for ten minutes, this solution was transferred to a dropping funnel and added over a period of one hour to 1.76 g. (0.013 mole) of trichlorosilane in 100 ml. of ether. After hydrolysis and removal of the solvent from the organic layer, the residue was fractionally crystallized by a scheme similar to that outlined in Table V to give 12% of 2,2'-binaphthyl, 26% of tetra-2-naphthylsilane and several impure fractions melting over 6-20° intervals in the vicinity of 100-150°.

A similar run was made (47) in which the trichlorosilane was added to the 2-naphthyllithium. The yield of pure tetra-2-naphthylsilane was 40%.

10. Triphenyl-2-naphthylsilane.- This compound was made to obtain its physical properties to compare with the 1-naphthyl silicon compound. An ethereal solution of 20.7 g. (0.1 mole) of 2-bromonaphthalene in 25 ml. of solvent was added to 132 ml. of a 0.76 N (0.1 mole) solution of n-butyllithium at room temperature. After stirring this mixture for ten minutes, an ethereal solution of 15.1 g. (0.051 mole) of triphenylchlorosilane was added over a period of twenty minutes. Even after refluxing the resulting solution for seventeen hours, Color Test I was positive. The reaction mixture was poured

onto dilute hydrochloric acid to yield considerable white solid floating between the layers. The aqueous layer was drained off, keeping the solid with the ethereal layer. Removal of the solvent from the organic material gave a yellow oil. Digestion of this oil with 50 ml. of petroleum ether (b. p. 60-80°) gave 12.4 g. of white solid, m. p. 130-133°, and a second crop of 3.1 g., m. p. 120-125°. The solids were combined and recrystallized from 100 ml. of petroleum ether (b. p. 90-110°) to give 12.2 g. (32%) of white crystals melting at 150-151°.

Anal. Calcd. for $C_{28}H_{22}Si$: Si, 7.26. Found: Si, 7.23, 7.22.

Since the melting point of triphenyl-2-naphthylsilane is the same as that of triphenylsilanol, a mixed melting point was run to furnish additional proof that this material was not triphenylsilanol formed by hydrolysis of the starting material, triphenylchlorosilane. A large depression of the melting point proved that the two compounds are not the same.

11. Triphenyl-p-tolylsilane.- About 0.4 mole of p-tolyl-lithium in 300 ml. of ether was added to a solution of 80.0 g. (0.27 mole) of triphenylchlorosilane, m. p. 96-97°, in about 300 ml. of ether over a period of twenty minutes while cooling the mixture with an ice bath. After stirring overnight, Color Test I (64) was positive. The mixture was poured onto

crushed ice, about 50 ml. of dilute hydrochloric acid was added to dissolve the inorganic salts, and the insoluble white solid was removed by filtration. The solvent was removed from the ether layer of the filtrate and the residue, a white solid, was added to the previously obtained solid. After drying under a heat lamp for two hours, the crude product melted at 137-139° and weighed 97.0 g. (100%). Recrystallization from ethyl acetate gave 89.0 g. (92%) of pure triphenyl-p-tolylsilane, m. p. 140-141°.

Although this melting point is higher than that reported (45) earlier (135-136°), a mixed melting point with a reference sample showed no depression. The reference specimen was obtained from the compounds of F. J. Marshall, was labeled "triphenyl-p-tolylsilane", and melted at 135-136°.

12. Diphenyldi-p-tolylsilane

(a) From Diphenyldichlorosilane and p-Tollyllithium.-

To a vigorously stirred solution of 12.6 g. (0.05 mole) of diphenyldichlorosilane in 300 ml. of dry ether was added 0.13 mole of p-tollyllithium in 325 ml. of ether over a period of twenty minutes. The mixture was stirred three hours at room temperature and then poured into about 400 ml. of 1% hydrochloric acid. The layers were separated, the solvent was removed from the ethereal layer, and the residual oil was dissolved in 40 ml. of boiling ethyl acetate. About 80 ml. of methanol was added to the refluxing

solution, the mixture was filtered hot, and set aside to crystallize. After six hours 14.8 g. (87%) of white crystals melting at 118-119° were removed by filtration. Recrystallization from ethyl acetate-petroleum ether (b. p. 90-115°) (1:1) gave 13.1 g. (77%) of product melting at 121-122°. This melting point could not be raised by two more recrystallizations from ethyl acetate.

Diphenyldi-*p*-tolylsilane is reported (48) to have a melting point of 176-177°, consequently this material was analyzed.

Anal. Calcd. for C₂₆H₂₄Si: Si, 7.70. Found: Si, 7.70, 7.73.

(b) From Silicon Tetrachloride, Phenyllithium, and *p*-Tolylithium by Systematic Fractional Crystallization.- This experiment was made to check the results of Gilman and Clark (48). These workers reported a 78% yield of diphenyldi-*p*-tolylsilane melting at 176-177°.

To a mixture of 17.8 g. (0.105 mole) of freshly-distilled silicon tetrachloride and 1.5 l. of dry ether was added 600 ml. of 0.35 N phenyllithium (0.21 mole) while the reaction flask was cooled with an ice-salt bath. The phenyllithium was added at a rate of 100 ml. per hour. Immediately

(48) H. Gilman and R. N. Clark, J. Am. Chem. Soc., 68, 1675 (1946).

after this addition was complete, 0.29 mole of *p*-tolyllithium (49) in 300 ml. of ether was added over a period of thirty minutes. Color Test I was positive after stirring the mixture for one hour under gentle reflux conditions. The mixture was then poured onto about 1 l. of water and the organic layer was separated. After the solvent was removed from the ethereal layer, 3.0 g. of solid (R) melting at 133-140° was filtered from the oil after the residue was cooled.

The results of the systematic fractional crystallization of the residual oil are listed in the following table. The scheme that was followed has been amply discussed elsewhere (50), but certain features used here are unique.

From a practical viewpoint it is distinctly easier to record the results and carry out the procedure if the flasks are marked in the manner indicated in the following diagram rather than by the system given in the reference. For example, flask "1" may be permanently marked (51) and as each crop of crystals is removed, merely change the last number. When

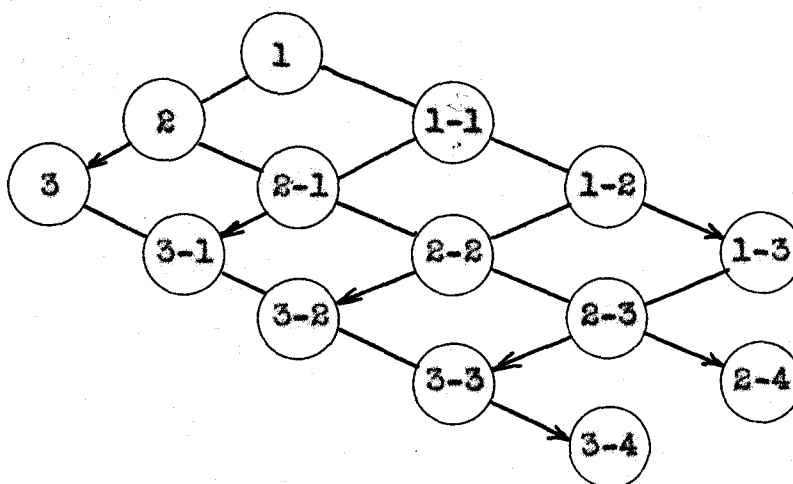
(49) An excess of tolyllithium was used in order to avoid the formation of silanols which may unnecessarily complicate subsequent crystallization.

(50) R. S. Tipson, in A. Weissberger's "Technique in Organic Chemistry", Vol. III, Interscience Publishers, Inc., New York, 1950, p. 420ff.; A. A. Morton, "Laboratory Technique in Organic Chemistry", McGraw-Hill Book Co., New York, 1938, p. 162.

(51) In the present case the flasks were marked with a Burgess vibrator tool.

impure solids, such as that obtained from "1-1" (52), are added to filtrates, such as "2-1", then this information is marked on the flask. The flask "2-1" then would have the identifying mark "2-1/1-1". Immediately after the solid is removed from this flask, the notation is changed to read "2-2". Then after addition of the solid from "1-2", the notation is "2-2/1-2", etc. Since this procedure may require days or even weeks to complete, the method adopted must be used consistently to avoid confusion.

Table V
Fractional Crystallization of the Residual Oil

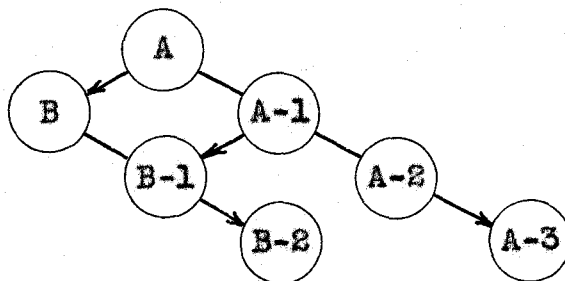


(52) The underscored number indicates a permanent mark on the flask.

Table V (Continued)

Flask No.	Solvent	Volume of Solvent (ml.)	Material Obtained From the Flask Weight (g.)	Melting Point
1	ethyl acetate	180	3.80	174-178
1-1	"	60	1.10	145-150
1-2	"	40	0.35	140-150
1-3	"	10	1.60	185-130
2	"	80	2.65	190-196
2-1	ethyl acetate	40	1.40	170-176
2-2	"	20	1.50	163-167
2-3	"	15	0.70	155-162
2-4	"	5	2.2	113-116
3	"	60	2.00	198-200
3-1	ethyl acetate	40	0.40	187-192
3-2	"	20	1.80	102-104
3-3	"	15	0.35	172-180
3-4	"	5	1.7	143-150

The solvent from the solution in flasks 1-4, 2-4, 3-5, and 3-1 was removed and the residue was distilled at 0.1 mm. Two fractions were collected: 0.5 g., b. p. 60-230°, and 3.6 g., b. p. 230-260°. The first fraction gave 0.10 g. of white solid, m. p. 146-60°, when recrystallized from 20 ml. of ethanol. The second fraction was fractionally crystallized from petroleum ether (m. p. 60-80°) according to the following scheme:



Flask Number	Volume of Solvent ml.	Material Obtained From the Flask	
		g.	m. p.
A	800	1.30	118-122
A-1	100	0.06	102-105
A-2	50	0.20	117-121
A-3	10	0.60	125-130
B	100	0.8	129-135
B-1	50	0.25	108-114
B-2	10	0.55	80-83

Since none of these fractions was sufficiently pure for positive identification by the mixed melting point method, the fractions with reasonably close melting points were combined and recrystallized. It was found expedient for recording purposes to use different colored inks or indelible pencils to mark in the notebook those fractions that were combined. For the sake of illustration this notation will be used here (Table VI).

Table VI
Combination of the Solid Fractions

Designation	M. p. range of the solids combined	Total weight (g.)	Solids combined
Green	80-120	5.55	2-2, 2-3, 3-3, 3-4
Blue	125-140	5.10	R, 1-4, B
Red	160-180	4.25	2-2, 2-3, 3-3, 3-4

These combined solids were separately dissolved in the least amount of ethyl acetate, about 10 ml. in all three cases, and allowed to crystallize. The various crops that were removed, after the solvent was slowly evaporated, are recorded in Table VII.

Table VII
Crystallization of the Combined Fractions

Crop Number	Weight (g.)	Melting Point
Green 1	1.1	135-137
" 2	1.5	111-113
" 3	1.3	105-106
Blue 1	2.4	148-153
" 2	1.7	110-112
Red 1	1.3	168-178
" 2	1.0	183-187
" 3	0.6	138-158

The fractions Green-2, Green-3, and Blue-2, 4.5 g., were combined and recrystallized from 10 ml. of ethyl acetate to give 3.7 g. of crude diphenyldi-*p*-tolylsilane, m. p. 111-112°. A mixed melting point with an authentic specimen of m. p. 118-119° was 112-117°.

No further crystallizations were attempted since this procedure appears to be ample proof that high yields of the desired compound cannot be obtained by the existing directions for the stepwise addition of two organolithium reagents to silicon tetrachloride.

Diphenyldi-*p*-tolylsilane is reported (45,48) to melt at 176-177° and the accompanying analysis given is acceptable for this compound. It is possible that a mixture of tetraphenyl- and tetra-*p*-tolyl-silane could be formed in high yield when the reaction is carried out according to the published directions. If two equivalents of the first-added organolithium reagent are mixed too rapidly with silicon tetrachloride, then a substantial quantity of the corresponding tetrasubstituted silane may be formed. This would leave a proportionate amount of unreacted silicon tetrachloride to react with the second organolithium reagent to form the tetrasubstituted silane. The resulting mixture of tetraphenyl- and tetra-*p*-tolyl-silane might form a eutectic mixture and give a perfect silicon analysis for diphenyldi-*p*-tolylsilane.

In order to check this possibility, equivalent amounts of the two pure silanes were recrystallized together from ethyl acetate. Even after three recrystallizations the melting point had not changed from that of the original mixture which melted at 199-201°.

This experiment was repeated except that the p-tolyl-lithium was added first, followed by phenyllithium. Substantially negative results were obtained from the systematic fractional crystallization. The only identifiable solids isolated were a trace of p,p'-bitolyl, and 6% of triphenyl-p-tolylsilane of m. p. 134-136°.

13. Phenyltri-p-tolylsilane.- This compound was made for an authentic specimen for use in the immediately preceding preparation. To a stirred mixture of 6.5 g. (0.0312 mole) of phenyltrichlorosilane was added 88.5 ml. of a 1.13 N ethereal solution of p-tolyllithium (0.10 mole). No attempt was made to cool the reaction flask and addition was made at such a rate as to permit gentle refluxing. After the mixture was poured into water, the organic layer was washed well with dilute hydrochloric acid and the layers were separated. The solvent was removed to yield 10.2 g. of a dirty-white solid melting at 176-180°. Crystallization of this solid from petroleum ether (b. p. 90-110°) followed by recrystallization of the resulting material gave 3.85 g. of white crystals

melting at 182-183°. This melting point was not improved after two recrystallizations from ethyl acetate. After removing the solvent from the combined mother liquors and recrystallizing the residue from petroleum ether (b. p. 60-80°), an additional 4.5 g. of product melting at 180-181° was isolated in two crops. The yield of good quality phenyltri-p-tolylsilane was 71%.

Since phenyltri-p-tolylsilane is reported (45) to melt at 127-128°, the material melting at 182-183° was analyzed.

Anal. Calcd. for $C_{27}H_{26}Si$: Si, 7.42. Found: Si, 7.40, 7.39.

14. N-Bromosuccinimide and General Procedures for Its Use.-

The reactions using N-bromosuccinimide (hereafter abbreviated as NBS) were performed in the conventional apparatus (43) used in reactions involving organolithium preparations and a nitrogen atmosphere was employed. These precautions are not essential since adequate protection from moisture can be achieved with appropriately placed calcium chloride tubes.

NBS was prepared and the active bromine of the product was determined in essential accordance with a published procedure (53). Practically the same yield (78%) and purity

(53) K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, Ann., 551, 109 (1942).

(97% active bromine) of product was isolated as that reported.

During the preparation of NBS, when the crude product was filtered through a 9 cm. Buchner funnel the filtration time was excessive (about thirty minutes) and consequently a low yield of 40% was isolated. The use of an 18.5 cm. funnel in subsequent preparations reduced the filtration time to five minutes and the yields were comparable to those reported. It should be emphasized that exceptionally vigorous stirring should be used during the addition of bromine to the sodium succinimide.

15. Triphenyl-p-bromomethylphenylsilane.- Five grams (0.0143 mole) of triphenyl-p-tolylsilane was dissolved in about 300 ml. of commercial carbon tetrachloride, 2.54 g. (0.0143 mole) of finely powdered NBS was added, and the mixture was refluxed for twenty-four hours. The NBS had not disappeared from the bottom of the flask. A starch-iodide paper test for active bromine was positive. The use of ultraviolet irradiation for fifteen minutes on the refluxing mixture induced complete reaction as evidenced by the disappearance of the NBS and a negative active bromine test. After cooling and filtering, there was collected 1.35 g. (0.011 mole, a 95% recovery) of succinimide (mixed m. p.) melting at 122-123°. The white solid obtained after removing the solvent was dissolved in about 100 ml. of acetone, decolorized with charcoal,

filtered, and set aside to crystallize slowly. In three crops, 4.5 g. (73%) of pure triphenyl-*p*-bromomethylphenylsilane, m. p. 175-176°, was obtained.

Anal. Calcd. for $C_{25}H_{21}BrSi$: Br, 18.62; Si, 6.53.

Found: Br, 18.6; Si, 6.62, 6.60.

Several attempts were made to react highly purified samples of this compound with magnesium. However, the reaction failed to start and the silane was recovered unchanged even though the following precautions and devices were used: the apparatus was thoroughly dried; the ether used was especially dried with calcium hydride and filtered directly into a nitrogen swept flask; magnesium-copper alloy and powdered magnesium as well as the metal turnings activated by heating with iodine were used; and the usual crystal of iodine and drop of methyl iodide were added. This failure is surprising since benzyl halide types form the Grignard reagent with especial ease.

16. Triphenyl-*p*-hydroxymethylphenylsilane.- Three grams (0.007 mole) of triphenyl-*p*-bromomethylphenylsilane was dissolved in about 300 ml. of methyl cellosolve, 3.0 g. (0.017 mole) of silver nitrate dissolved in 40 ml. of water was added, and the mixture was refluxed for thirty minutes. The greenish precipitate was removed by filtration of the hot mixture, most of the solvent was distilled away at reduced

pressure, and the remainder by steam distillation. The residue was extracted with ether and the ethereal solution was dried with sodium sulfate. After removal of the ether, crystallization of the yellow viscous oil was induced by the addition of a few ml. of methanol, and external cooling. A crop of 1.95 g. (76%) of white crystals, m. p. 53-54^o, was isolated by cooling with Dry Ice. The analytical sample had a melting point of 54-55^o and was obtained by slow crystallization from methanol.

Anal. Calcd. for C₂₅H₂₂OSi; Si, 7.65; active hydrogen, 1. Found: Si, 7.53; active hydrogen (Zerewitinoff), 0.95.

Poor yields were obtained by hydrolyzing triphenyl-*p*-bromomethylphenylsilane with potassium hydroxide in acetone or ethanol. A solution of 2.0 g. (0.0046 mole) of the silane in 100 ml. of acetone was mixed with a solution of 0.5 g. of potassium hydroxide in 2 ml. of water, and the resulting solution was refluxed for thirty minutes. After cooling this solution, about 300 ml. of ether was added and the acetone and inorganic salts were extracted out by several extractions with water. A gummy solid was obtained after removing the solvent from the organic layer. After several recrystallizations of the resulting oils from methanol, 0.2 g. (12%) of triphenyl-*p*-hydroxymethylphenylsilane, m. p. 52-3^o, was isolated.

A 10% yield of the alcohol was obtained by the same procedure when ethanol was used as solvent instead of acetone.

17. Triphenyl-p-dibromomethylphenylsilane.- Five grams (0.0143 mole) of triphenyl-p-tolylsilane was dissolved in 250 ml. of commercial carbon tetrachloride (the silicon compound was easily soluble at room temperature) and 5.2 g. (0.029 mole) of finely divided NBS was added. After refluxing the mixture for forty minutes while irradiating with a mercury-vapor lamp, a homogeneous solution was formed and a test for free bromine (starch-iodide paper) was negative. The solution after cooling deposited 2.8 g. (96%) of succinimide which was removed by filtration. The solvent was removed from the filtrate to give a slightly yellow solid. This solid was dissolved in 75 ml. of ethyl acetate which, on cooling, gave 3.30 g. of white crystals, m. p. 180-182°. The filtrate was diluted with an equal volume of petroleum ether (b. p. 90-110°) to give a second crop of 2.4 g., m. p. 177-180°. Recrystallization from 100 ml. of 1:1 ethanol-ethyl acetate gave 5.3 g. (63%) of pure triphenyl-p-dibromomethylphenylsilane melting at 184-184.5°.

Anal. Calcd. for $C_{25}H_{20}Br_2Si$: Br, 31.5; Si, 5.52.
Found: Br, 30.0; Si, 5.65, 5.64.

For the purpose of characterization triphenyl-p-dibromomethylphenylsilane was made by the action of NBS on

the mono-bromo derivative. A mixture of 4.00 g. (0.0093 mole) of triphenyl-*p*-bromomethylphenylsilane, 150 ml. of carbon tetrachloride, and 1.66 g. (0.0093 mole) of NBS was refluxed with stirring and ultra-violet irradiation for thirty minutes. The reaction was apparently complete since the NBS had disappeared from its place on the bottom of the flask. After cooling and removing the succinimide by filtration, the solvent was removed from the filtrate. The residue was crystallized from a 1:1 acetone-petroleum ether (b. p. 90-110°) mixture to yield 1.6 g. (34%) of a white solid melting at 184-184.5°. This material showed no depression of melting point when mixed with an analyzed sample of triphenyl-*p*-dibromomethylphenylsilane.

18. *p*-Triphenylsilylbenzaldehyde.- Five grams (0.0099 mole) of triphenyl-*p*-dibromomethylphenylsilane was dissolved in hot commercial methyl cellosolve and a mixture of 5.0 g. (0.03 mole) of silver nitrate in about 40 ml. of water was added dropwise with stirring to the refluxing solution over a period of ten minutes. The silver bromide precipitated immediately. After the mixture was stirred for an additional twenty minutes to insure the removal and subsequent reaction of any of the bromosilicon compound that might be entrapped in the precipitate, the green solid was removed by filtration of the hot mixture. The solvent was removed from the filtrate

by distillation at reduced pressure, and the residual yellow oil was dissolved in 75 ml. of ethanol. After standing for two days, 1.40 g. of white solid, m. p. 110-111^o, was removed, and a second crop of 1.00 g., m. p. 108-110^o, was obtained after reducing the volume to 30 ml. The final yield was 67%. The analytical sample melted at 110-111^o.

Anal. Calcd. for C₂₅H₂₀OSi: Si, 7.70. Found: Si, 7.78, 7.72.

This aldehyde was also prepared in good overall yields (79%) by starting with triphenyl-*p*-tolylsilane and not isolating the intermediate dibromosilicon compound formed after treatment with NBS. This procedure was carried out in the same manner as is given in the preceding sections describing the preparation of triphenyl-*p*-dibromomethylphenylsilane and the corresponding aldehyde. It was found necessary to change the solvent after the first step in the reaction sequence. When carbon tetrachloride was used throughout the reaction, a 60% yield of the dibromosilicon compound was isolated instead of the expected aldehyde. Apparently this is due to the extreme immiscibility of water and carbon tetrachloride. Although some silver bromide was formed, the two phase system apparently allowed very little reaction of the silver ions with the halogen compound.

19. *p*-Triphenylsilylbenzaloxime.-- The general procedure given

in Shriner and Fuson (54) was used in this preparation. A 98% yield of p-triphenylsilylbenzaloxime melting at 194-195° was obtained from p-triphenylsilylbenzaldehyde and hydroxylamine hydrochloride.

Anal. Calcd. for $C_{25}H_{21}NOSi$: N, 3.70; Si, 7.38. Found: N, 3.56, 3.62; Si (micro), 7.24, 7.28.

20. Thiosemicarbazone of p-Triphenylsilylbenzaldehyde.- A published procedure (55) was followed to effect reaction between p-triphenylsilylbenzaldehyde and thiosemicarbazide. A 62% yield of white crystals melting at 234-235° was obtained after the crude product was recrystallized from a 6:1 ethanol-ethyl acetate mixture.

Anal. Calcd. for $C_{26}H_{26}NSSi$: S, 7.32; Si, 6.40. Found: S, 7.21, 7.28; Si, 6.28, 6.31.

21. p-Triphenylsilylbenzoic Acid.- This compound was made in an attempt to find some method for introducing the carboxyl group into tetraarylsilanes.

(a) Oxidation of triphenyl-p-tolylsilane.- Triphenyl-p-tolylsilane, 1.80 g. (0.0052 mole), was suspended in a mixture

(54) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds", 2nd ed., John Wiley, New York, 1940, p. 167.

(55) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis", Thomas Y. Crowell Co., New York, 1947, p. 249.

of 100 ml. of glacial acetic acid and 30 ml. of acetic anhydride, and 3 ml. of concd. sulfuric acid was added, followed by 10 g. (0.1 mole) of anhydrous chromic oxide (Baker and Adams, "98% pure") in three portions. The reaction flask was immersed in a large water bath maintained at $17^{\circ} \pm 2^{\circ}$. After stirring for fifteen minutes, the dark green mixture was poured rapidly onto about 500 g. of crushed ice and stirred for several minutes. About 300 ml. of water was added and the white solid was removed by filtration. This solid, melting at $195-197^{\circ}$, after recrystallization from 300 ml. of petroleum ether (b. p. $90-110^{\circ}$), weighed 1.6 g. and had a melting point of $213-214^{\circ}$. The yield was 90%.

Anal. Calcd. for $C_{25}H_{20}O_2Si$: Si, 7.37; neut. eq., 380; active hydrogen, 1.00. Found: Si, 7.38, 7.30; neut. eq., 377; active hydrogen (Zerewitinoff), 1.02, 1.1.

The above procedure is a modification of the directions outlined elsewhere (56) for the oxidation of *p*-nitrotoluene to the corresponding aldehyde. The only essential difference was changing the reaction temperature from 0° to 17° . When this reaction was carried out at 0° in the same manner as outlined above, no products could be obtained from the oils and tars.

(56) S. V. Lieberman and R. Connor in A. H. Blatt's "Organic Syntheses", Collective Vol. 2, John Wiley, New York, 1943, p. 441.

Several unsuccessful attempts were made to oxidize triphenyl-p-tolylsilane with potassium permanganate in acetone.

(b) From p-Triphenylsilylbenzyl Alcohol and Potassium Permanganate.- One gram (0.0027 mole) of p-triphenylsilylbenzyl alcohol was dissolved in 200 ml. of acetone (previously treated with permanganate), 1.5 g. (0.009 mole) of potassium permanganate was added, and the mixture was refluxed for eighteen hours. During this treatment the permanganate was completely reduced. The manganese dioxide was removed by filtration, and the residue was washed twice with fresh boiling acetone. The solvent was removed from the combined filtrates, and the white residue was dissolved in about 100 ml. of petroleum ether (b. p. 90-110°). No solid separated from this solution after standing for five days. The solvent was replaced with ether and the ethereal solution was extracted with concd. ammonium hydroxide. About 0.2 g. of white solid melting at 184-187° was obtained after acidifying the aqueous layer. Recrystallization from petroleum ether (b. p. 90-110°) gave 0.12 g. (12%) of crystals melting at 203-205°. A mixed melting point with an analyzed specimen of p-triphenylsilylbenzoic acid showed no depression.

(c) From p-Triphenylsilylbenzaldehyde and N-Bromosuccinimide Followed by Hydrolysis.- Six grams (0.0165 mole) of p-triphenylsilylbenzaldehyde were dissolved in 300 ml. of commercial carbon tetrachloride, 3.0 g. (0.019 mole) of finely

powdered NBS was added, and the mixture was refluxed with stirring for twenty minutes while irradiating the flask with a mercury-arc lamp. After cooling and filtering off the succinimide, the solvent was removed from the red colored filtrate by the use of a steam bath and oil pump. The solid was white when first formed but turned black after fifteen minutes while the last traces of solvent were being removed. This solid was taken up in ether and the ethereal solution was extracted with concd. ammonium hydroxide. The addition of about 50 ml. of saturated sodium chloride solution broke up the emulsion and precipitated a white solid between the layers. This solid was filtered off and combined with the solid obtained from the acidified basic aqueous layer. Recrystallization from petroleum ether (b.p. 90-110°) gave 1.2 g. (19%) of white solid, m. p. 212-214°. This material was shown to be p-triphenylsilylbenzoic acid by a mixed melting point.

(d) From p-Triphenylsilylbenzaldehyde and Hydrogen Peroxide (Attempted).- Three grams (0.00825 mole) of p-triphenylsilylbenzaldehyde in 50 ml. of acetone was added dropwise with stirring at 70° to a solution containing 0.4 g. (0.01 mole) of sodium hydroxide and 10 ml. of 30% hydrogen peroxide. After stirring for ten minutes, 10 ml. of 30% hydrogen peroxide in 50 ml. of acetone was added and the mixture

was refluxed ten minutes. The solution was acidified and steam-distilled. After extracting the residue with ether, the ethereal layer was extracted with concd. ammonium hydroxide. No solid was obtained from the acidified aqueous layer. The solvent was removed from the neutral ethereal layer to obtain a red-brown oil. Attempts to induce crystallization from ethanol, petroleum ether, benzene, and acetone were unsuccessful. No products were isolated from the various fractions.

22. 1-Naphthyltriethoxysilane (57).- A slurry of 1-naphthyl-lithium (made from equimolar quantities (0.2 mole) of 1-bromonaphthalene and n-butyllithium) was added to an excess of 52 g. (0.25 mole) of freshly distilled ethyl silicate in ether and stirred at room temperature for thirty minutes. The solvent was replaced by petroleum ether (b. p. 60-80°) (or benzene) and the lithium salts were removed by filtration. Vacuum distillation of the filtrate gave a considerable amount of naphthalene and 21.0 g. of a yellow oil, b. p. 125-130° at 1.5 mm. After another distillation at 753 mm., there was obtained 29.0 g. (56%) of 1-naphthyltriethoxysilane of b. p. 291-293°.

(57) E. Khotinsky and B. Seregenkoff, Ber., 41, 2951 (1908), made this compound from the Grignard reagent and ethyl silicate but no yield is reported.

This compound can be made in comparable yields by using 1-naphthyllithium made by the direct procedure, but the product is more highly colored (red to dark yellow) even after several fractionations.

When the ethyl silicate was added to the 1-naphthyllithium (made by halogen-metal interconversion) under the same conditions, there was isolated a 20% yield of di-1-naphthyldiethoxysilane, 22% of tri-1-naphthylethoxysilane, and only 8% of 1-naphthyltriethoxysilane.

23. 1-Naphthyltriphenylsilane

(a) From 1-Naphthyltriethoxysilane and Phenyllithium.-

To a solution of 4.20 g. (0.014 mole) of 1-naphthyltriethoxysilane in 20 ml. of dry ether in the usual apparatus was added with stirring 24.3 ml. (0.043 mole) of a 1.77 N ethereal solution of phenyllithium. After pouring into ca. 50 ml. of water, separating the layers, and removing the solvent from the ether layer, 3.3 g. of white solid, m.p. 165-169°, was obtained. Two crystallizations from benzene-petroleum ether (b. p. 90-115°) (1:1) gave 2.83 g. (51%) of white crystals, m. p. 172-172.5°.

Anal. Calcd. for $C_{16}H_{22}O_3Si$: Si, 7.25. Found: Si, 7.29, 7.34.

(b) From Triphenylchlorosilane and 1-Naphthyllithium.-

A solution of 23.5 g. (0.08 mole) of triphenylchlorosilane,

m. p. 95-96^o, in 200 ml. of ether was added to a preparation of 1-naphthyllithium made in the usual manner by mixing 31 g. (0.15 mole) of 1-bromonaphthalene and 0.15 mole of n-butyllithium. The mixture was allowed to reflux and stirring was continued for one hour. After working up as described in (a) above, there was obtained 21.0 g. (69%) of 1-naphthyltriphenylsilane of m. p. 172-172.5^o (cor.). A mixed melting point with the analyzed sample in (a) above showed no depression.

24. Di-1-naphthyldiethoxysilane

(a) From Ethyl Silicate and 1-Naphthyllithium.- A solution of 37.5 g. (0.18 mole) of freshly distilled ethyl silicate and 30 ml. of ether was added dropwise with stirring to a mixture of 94.0 g. (0.45 mole) of 1-bromonaphthalene and 0.45 mole of n-butyllithium in 600 ml. of ether. After pouring into ca. 300 ml. of water, separating the layers, steam-distilling the ether layer, and extracting the residue with benzene, the benzene layer was dried by distillation, reduced to a small volume, diluted with an equal volume of petroleum ether (b. p. 90-115^o), and set aside to crystallize. White crystals, 32.4 g., m. p. 85-89^o, formed overnight and were filtered from the mixture. Two crystallizations from petroleum ether (b. p. 90-115^o) gave 28.2 g. (42%) of white solid, m. p. 100.5-101^o. All of the filtrates were combined, the solvent

was removed, and the residue was vacuum distilled. A fraction, 10.1 g., b. p. 215-225° at 0.2 mm., when washed with petroleum ether (b. p. 30-60°), proved to be pure di-1-naphthyl-diethoxysilane, m. p. 100-101° (cor.), by a mixed melting point determination. Yields ranging from 45% to 60% have been obtained by this method.

Anal. Calcd. for $C_{24}H_{24}OSi$: Si, 7.49. Found: Si, 7.52, 7.54.

When 1-naphthyllithium made by the direct procedure from 1-bromonaphthalene and lithium metal was added to the ethyl silicate, the yield of colorless solid was low (12%). Since colored impurities are known to be present (58), this is believed to be the explanation for the low yield. Although the material can be vacuum-distilled, the product is yellow, and even after treatment with charcoal, diatomaceous earth, and alumina the color remained. Only through the wasteful procedure of repeated crystallizations could a colorless product be obtained.

(b) From 1-Naphthyltriethoxysilane and 1-Naphthyllithium.

To a solution of 13.1 g. (0.045 mole) of 1-naphthyltriethoxysilane was added dropwise with stirring 70.5 ml. (0.045 mole) of 0.65 N 1-naphthyllithium (prepared by the direct procedure

(58) H. Gilman and C. G. Brannen, J. Am. Chem. Soc., 71, 657 (1949).

from 1-bromonaphthalene and lithium metal). The orange-colored mixture was poured into ca. 100 ml. of water, the layers were separated, and the solvent was replaced with benzene. After cooling the solution, 4.2 g. (25%) of yellow solid, m. p. 98-99°, were filtered off and washed with a few ml. of cold acetone. This solid did not depress the melting point of an analyzed sample of di-1-naphthyldiethoxysilane made by the procedure described in (a) above. Three crystallizations from acetone finally removed the yellow color but the yield of white solid was only 1.8 g. (7%).

The residue from the above preparation was steam-distilled with super-heated steam (59). After the more volatile components were removed at 100°, a yellow viscous oil appeared in the distillate at 240°. About 0.8 g. of yellow colored di-1-naphthyldiethoxysilane, m. p. 98-99°, (identified by a mixed melting point determination) was recovered from the oil after extraction and crystallization. This organosilicon compound may have been merely carried over mechanically by the stream of vapor rather than actually existing in a vapor state, but these experiments indicate a remarkable stability of this compound toward water.

25. Di-1-naphthyldiphenylsilane.- An ethereal solution of 0.72 g. (0.0019 mole) of di-1-naphthyldiethoxysilane was added

(59) The apparatus used is that described in A. A. Morton, "Laboratory Technique in Organic Chemistry", McGraw-Hill Book Co., New York, 1938, p. 144.

to an excess of 0.005 mole of phenyllithium and refluxed for one hour. After working up as described in section (a) on 1-naphthyltriphenylsilane and crystallization from petroleum ether (b. p. 90-110°), there was obtained 0.81 g. (97%) of white solid, m. p. 194-195° (cor.).

Anal. Calcd. for C₃₂H₂₄Si: Si, 6.43. Found: Si, 6.50, 6.48.

26. Tri-1-naphthylchlorosilane.- An ethereal solution of 1.07 moles of 1.8 N n-butyllithium was added with vigorous stirring at 0 to -5° (internal temperature) to 222 g. (1.07 moles) of 1-bromonaphthalene in about 100 ml. of dry ether. After stirring for twenty minutes, 51.0 g. (0.3 mole) of freshly distilled silicon tetrachloride in about 200 ml. of dry ether was added at such a rate as to keep the internal temperature at 0 to -5°. Stirring was continued for two hours at this temperature before the mixture was poured onto 500 ml. of dil. hydrochloric acid. The organic layer was washed well with water and the solvent removed using a steam bath and water pump. The viscous oil deposited 96 g. (72%) of crude tri-1-naphthylchlorosilane, m. p. 194-198°, in three crops. Recrystallization from ethanol using a Soxhlet extractor (or n-butyl ether used in the ordinary manner) gave 85 g. (64%) of the pure product, m. p. 210-211° (cor.).

Anal. Calcd. for C₃₀H₂₁ClSi: Cl, 8.00; Si, 6.31. Found:

Cl, 8.1, 8.2; Si, 6.31, 6.32.

When only three equivalents of 1-naphthyllithium to one equivalent of silicon tetrachloride were used, a low boiling fraction, b. p. 150-250° at 0.3 mm., was isolated (possibly the silanediol or mixed *n*-butyl-1-naphthylsilicon compounds) which makes purification of the desired tri-1-naphthylchlorosilane difficult. Attempts to isolate the product by vacuum distillation using conventional procedures were unsuccessful. The product does not distil even at 350° (vapor temperature) at 0.3 mm. and at that temperature decomposition is indicated by the rise in pressure (from 0.3 mm. to ca. 6 mm.) and a darkening of the residue. A pure sample was distilled in a Hickman molecular still at 340-350° at 20 microns, but the method was not practical for large runs due to the extremely slow rate of distillation.

Several preparations were made by allowing the mixture to gently reflux during the addition of the silicon tetrachloride and in all these runs low yields (10-30%) of tri-1-naphthylchlorosilane resulted. Since appreciable amounts (10-70%) of 1-*n*-butylnaphthalene were isolated from the resulting oils, the reaction of 1-naphthyllithium with *n*-butyl bromide took place at a surprisingly fast rate.

27. Tri-1-naphthylethoxysilane

(a) From 1-Naphthyllithium and Ethyl Silicate.- A mixture

of 82.8 g. (0.40 mole) of 1-bromonaphthalene and 0.40 mole of n-butyllithium in 400 ml. of ether was made under the usual conditions and 20.83 g. (0.1 mole) of ethyl silicate in 50 ml. of ether was added with stirring over a period of twenty minutes. After refluxing for four hours, the mixture was poured into about 500 ml. of dil. hydrochloric acid, the layers separated, and the solvent removed from the ether layer. A white solid, 16.1 g., m. p. 180-183°, was vacuum-distilled from the residue at 0.7 mm. The fraction with a b. p. of 290-310°, 15.0 g., was tri-1-naphthylethoxysilane, m. p. 185-186°. The crude yield was 32.6 g. (72%) of material melting at 185-186.5°. Recrystallization with ethanol by the use of a Soxhlet extractor gave 30.2 g. (68%) of white solid, m. p. 186-186.5° (cor.), unchanged by repeated crystallizations.

Anal. Calcd. for $C_{32}H_{26}OSi$: Si, 6.18. Found: Si, 6.13, 6.15.

The highest yields were obtained by using a molar ratio of 1-naphthyllithium to ethyl silicate greater than three. Runs made using a ratio of three (on the basis of a 90% interconversion yield of 1-naphthyllithium) gave from 10-25% of di-1-naphthyldiethoxysilane and the yield of tri-1-naphthylethoxysilane was only 35-45%. The procedure outlined above gave a 66% yield in another run except that purification was

accomplished by exhaustive digestion (60) with ethanol instead of by crystallization.

(b) From Di-1-naphthyldiethoxysilane and 1-Naphthyllithium.-

A 36% yield of tri-1-naphthylethoxysilane was obtained by treating di-1-naphthyldiethoxysilane with 1-naphthyllithium made by the direct procedure. The product could not be obtained from the highly colored tars by the ordinary crystallization techniques and only after partial purification by vacuum distillation followed by several recrystallizations could the tri-1-naphthylethoxysilane be isolated. The probable reason for the low yield is given in the section (a) on di-1-naphthyldiethoxysilane. Since this reaction was run to establish the structure of these compounds, the conditions for a higher yield were not worked out.

28. Tri-1-naphthylsilane

(a) From 1-Naphthyllithium and Trichlorosilane.- One hundred and forty grams (0.68 mole) of 1-bromonaphthalene and 0.68 mole of n-butyllithium were brought into reaction as usual, and 27.7 g. (0.205 mole) of trichlorosilane in 200 ml. of ether was added dropwise with stirring and cooling over a period of twenty minutes. After stirring for one hour, the mixture, a red solution with a white precipitate, was poured

(60) A. A. Morton, "Laboratory Technique", op. cit., p. 228.

into about 500 ml. of dil. hydrochloric acid and the layers were separated. The solvent was removed from the ether layer and 81.5 g. (97%) of crude tri-1-naphthylsilane, m. p. 226-228°, was obtained in three crops. The red color of the product at this stage was removed with slight loss of product by washing with a small volume of cold acetone. Recrystallization from ethanol by the use of a Soxhlet extractor gave 68 g. (81%) of pure tri-1-naphthylsilane, m. p. 235-236° (cor.).

Anal. Calcd. for $C_{30}H_{22}Si$: Si, 6.84. Found: Si, 6.87, 6.93.

(b) From Tri-1-naphthylethoxysilane or Tri-1-naphthylchlorosilane and Lithium Aluminum Hydride (61).- A mixture of the silicon compound in ether was added to an excess of lithium aluminum hydride in ether and refluxed for thirty minutes. The excess lithium aluminum hydride was destroyed by adding ethanol dropwise to the mixture. After extracting out the inorganic salts with dilute hydrochloric acid and removing the solvent from the organic layer, the crude tri-1-naphthylsilane melted only two degrees low, m. p. 233-234° (cor.). Recrystallization from acetone gave a 90% yield of pure tri-1-naphthylsilane starting with tri-1-naphthylethoxysilane

(61) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947); W. H. Nebergall and O. H. Johnson, ibid., 71, 4022 (1949).

and a 95% yield when tri-1-naphthylchlorosilane was used.

29. Tri-1-naphthylbromosilane.- This compound was made in an effort to obtain a more reactive intermediate to prepare tri-1-naphthylphenyl derivatives. A solution of 53.0 g. (0.13 mole) of tri-1-naphthylsilane in 1.2 l. of carbon tetrachloride was effected by heating and 20.7 g. (0.13 mole) of bromine was added in one portion. The mixture was refluxed with stirring for two hours and allowed to stir at room temperature for an additional fifteen hours. The residual bromine was removed by shaking the solution with a saturated solution of sodium bisulfite, the layers were separated, the organic layer was dried with calcium chloride, and the solvent was removed until the volume was about 200 ml. After several hours, 43.0 g. of white solid melting at 200-202° was filtered from the solution. Recrystallization from butyl ether gave 34 g. (54%) of white crystals melting at 212-213° (cor.). This melting point could not be raised by repeated recrystallization.

Anal. Calcd. for $C_{30}H_{21}BrSi$: Br, 16.4; Si, 5.72. Found: Br, 16.0, 15.8; Si, 5.70, 5.75.

30. Tri-1-naphthylsilanol

(a) From Tri-1-naphthylchlorosilane.- Twenty grams (0.045 mole) of tri-1-naphthylchlorosilane was dissolved in 250 ml. of 95% ethanol, 50 ml. of 10% potassium hydroxide was

added, and the mixture was refluxed for two hours. After pouring into about 500 ml. of water, filtering and drying, 15.5 g. (91%) of crude tri-1-naphthylsilanol, m. p. 201-203°, was obtained. Purification by crystallization with ethanol by the use of a Soxhlet extractor gave 14.5 g. (76%) of product melting at 208-209° (cor.).

Anal. Calcd. for $C_{30}H_{22}OSi$: Si, 6.58. Found: Si, 6.54, 6.51.

When dioxane or acetone was used as solvent, the product was tan in color and several recrystallizations, with attendant decrease in yield, were required to obtain a colorless material.

Another procedure that gives nearly quantitative yields is also described. Ten grams (0.023 mole) of tri-1-naphthylchlorosilane was refluxed for thirty minutes in 100 ml. of monomethyl ether of ethylene glycol (methyl cellosolve) (containing 0.02 mole of water per liter as determined by titration with Karl Fisher reagent). It was shown that hydrogen chloride was expelled during this treatment. After cooling the reaction mixture, 5.9 g. (60%) of tri-1-naphthylsilanol, m. p. 205-206°, was removed by filtration. Another 3.8 g. (39%) crop was obtained by removing the solvent at reduced pressure and recrystallizing the residue from petroleum ether (b. p. 90-115°). The overall yield of good quality product

was 99%.

(b) From Tri-1-naphthylethoxysilane.- A 75% yield of tri-1-naphthylsilanol was obtained from tri-1-naphthylethoxysilane and potassium hydroxide in 95% ethanol. The mixture was allowed to reflux for twenty-four hours, but this may be a longer time than is necessary. Another run made under similar conditions but refluxed for only one hour was incomplete as evidenced by the recovery of about 35% of the starting tri-1-naphthylethoxysilane.

(c) From Tri-1-naphthylsilane.- After 3.0 g. (0.13 g. atom) of sodium metal was dissolved in 75 ml. of 95% ethanol, 3.0 g. (0.0073 mole) of tri-1-naphthylsilane was added and the mixture was refluxed for twenty hours. The solution was poured into ca. 300 ml. of water, cooled, and the tan-colored solid was collected on a filter. After digesting the 2.8 g. of solid, m. p. 200-203^o, with petroleum ether (b. p. 60-80^o), there was obtained 2.4 g. (78%) of pure tri-1-naphthylsilanol, m. p. 208-209^o. A mixed melting point with samples from (a) and (b) above showed no depression.

31. Hydrolysis of Tri-1-naphthylchlorosilane and Triphenylchlorosilane.- Stock solutions of 7.00 g. (0.0158 mole) of tri-1-naphthylchlorosilane in 1 l. of Merck reagent grade acetone and 12.00 g. (0.0406 mole) of triphenylchlorosilane in 1 l. of the same solvent were prepared and placed in a 25^o

thermostat. Five ml. of water per 100 ml. of stock solution was added and 25 ml. aliquots were removed at timed intervals and titrated with 0.0536 N sodium hydroxide using phenolphthalein as the indicator. Even after five days the tri-1-naphthylchlorosilane run did not show any increase in the consumption of base over the value obtained at zero time. The reading at zero time was 0.25 ml. and the blank, using the same concentration of acetone and water, was 0.20 ml. The triphenylchlorosilane aliquot at zero time required a volume of base equivalent to 100% hydrolysis. This hydrolysis of the triphenylchlorosilane may not have proceeded at an appreciable rate in the aqueous acetone, but, if not, reaction must have occurred during the titration with the weak base. Since tri-1-naphthylchlorosilane was unaffected by the low concentration of base, these experiments indicate the relative stability of these two silicon compounds toward dilute alkali.

The solvent from the acetone solutions of tri-1-naphthylchlorosilane was allowed to evaporate at room temperature. Well-formed crystals were isolated directly and these melted at 206-207^o, and showed no depression of melting point when mixed with an authentic specimen.

32. Tri-1-naphthylsilane and Potassium Hydroxide in Piperidine
(62).- The reagent was made by dissolving one pellet of

(62) A test devised by F. S. Kipping and J. E. Sands, J. Am. Chem. Soc., 119, 348 (1921) and modified by Gilman and Clark (21).

potassium hydroxide in 3 ml. of piperidine containing 5 drops of water. When about 0.05 g. of tri-1-naphthylsilane was added and the mixture warmed to effect solution, no gas evolution was noted even after standing for several days. Under corresponding conditions, tri-o-tolylsilane showed no gas evolution, while triphenylsilane gave an immediate, rapid stream of gas.

33. Tri-1-naphthyl-n-butylsilane

(a) From Tri-1-naphthylchlorosilane and n-Butyllithium.-

Ten grams (0.0225 mole) of tri-1-naphthylchlorosilane was dissolved in ca. 75 ml. of dry thiophene-free benzene, 30 ml. (0.034 mole) of a 1.8 N ethereal solution of n-butyllithium was added, and the mixture was refluxed for twenty hours. After washing the benzene-ether layer with water and removing the solvent, 8.2 g. of a light yellow solid, m. p. 110-138°, remained. Crystallization from several solvents failed to yield a sharp-melting product. The solid was dissolved in 500 ml. of petroleum ether (b. p. 90-115°) and poured onto 90 g. of alumina in a 4 cm. absorption tube and developed with 2.5 l. of the same solvent. After removal of the solvent from the middle liter of the eluant, 2.2 g. (22%) of white crystals of tri-1-naphthyl-n-butylsilane, m. p. 189-190° (cor.), remained.

Anal. Calcd. for C₃₄H₃₀Si; Si, 6.00. Found: Si, 5.98, 5.99.

(b) From Tri-1-naphthylethoxysilane and n-Butyllithium. -

Five grams (0.011 mole) of tri-1-naphthylethoxysilane and 20 ml. (0.022 mole) of a 1.1 N ethereal solution of n-butyllithium were mixed, 75 ml. of dry xylene was added, and the mixture was refluxed for twenty-four hours. After pouring into ca. 300 ml. of water and working up as in (a) above, 5.25 g. of a yellow solid, m. p. 135- 155^o, was recrystallized from 100 ml. of petroleum ether (b. p. 90-115^o). This material was purified by exhaustive digestion (60) with small portions of cyclohexane. The final yield was 3.3 g. (71%) of pure tri-1-naphthyl-n-butylsilane, melting at 187-188^o.

(c) From Tri-1-naphthylsilane and n-Butyllithium. - Ten

grams (0.0244 mole) of tri-1-naphthylsilane and 30 ml. (0.036 mole) of a 1.2 N ethereal solution of n-butyllithium were mixed, 100 ml. of dry thiophene-free benzene was added, and the mixture was refluxed for twelve hours. After pouring into water and removing the inorganic salts as above, 11.3 g. of yellow solid, m. p. 90- 135^o, was obtained. Attempts to purify by crystallization from a number of different solvents gave solids melting over the range 130-160^o. The exhaustive digestion treatment mentioned in (b) above did not change the melting point. Two grams of the solid was dissolved in 200 ml. of petroleum ether (b. p. 90-115^o) and poured through 20 g. of alumina in a 1 cm. adsorption column and developed with 1 l. of

the same solvent. After removal of the solvent from the first 300 ml. of filtrate, 0.11 g. of white solid, m. p. 95-115°, was obtained. With similar treatment, the next 700 ml. of filtrate contained 1.63 g. of solid, m. p. 173-179°, which gave 1.35 g. (12%) of tri-1-naphthyl-n-butylsilane, m. p. 186-187°, after two crystallizations from benzene-petroleum ether (b. p. 60-80°). This material showed no depression of melting point when mixed with the products from (a) and (b) above. The contents of the column were eluted with benzene and the filtrate contained 0.20 g. of yellow solid, m. p. 195-200°, from which a few crystals of pure tri-1-naphthylsilane (identified by a mixed melting point) were obtained after recrystallization from ethanol.

34. Tri-1-naphthylphenylsilane

(a) From tri-1-naphthylchlorosilane and Phenyllithium.-

To a solution of 15.0 g. (0.034 mole) of tri-1-naphthylchlorosilane in 200 ml. of dry benzene was added 0.24 mole of an ethereal solution of phenyllithium (made in 96% yield in the usual manner but filtered through a pressure filter (63) immediately before use). Most of the ether was removed by distillation and the mixture was refluxed at 54° for thirty hours. Color Test I was still positive after this treatment.

(63) A Hormann laboratory filter was used with a No. 1 asbestos pad.

Following hydrolysis with dilute hydrochloric acid and extraction of the inorganic salts, the organic layer was set aside to crystallize, the solvent being allowed to slowly evaporate. After seven days 11.25 g. of white solid melting at 135-150° was collected in two crops. Recrystallization from benzene, ethyl acetate, petroleum ether (b. p. 90-110°), and ethanol failed to change the melting point. Chromatography using the combination of alumina and petroleum ether (b. p. 60-80°) gave several fractions of the same melting point. This material was finally purified by exhaustive digestion (60) of the finely pulverized material with four 20 ml. portions of ethanol. This procedure gave a yield of 8.7 g. (53%) of white solid melting at 192-193°.

Anal. Calcd. for $C_{36}H_{26}Si$: Si, 5.76. Found: Si, 5.75, 5.84.

This experiment was repeated several times in an effort to obtain higher yields and to further investigate the possibility of the existence of a diastereoisomer of tri-1-naphthylphenylsilane. In all cases the crude product melted at 135-150° and this material resisted attempts at purification by all of the common laboratory methods except by digestion and the method outlined in (d) of this section (crystallization from chlorobenzene). The yields varied from 40% to 60%. Silicon analysis of the low-melting material

showed it to contain 5.89%. A sodium fusion test showed the absence of halogen. The silicon analysis indicates that the impurity does not contain silicon since the expected impurities contain a higher percentage of silicon than trinaphthylphenylsilane.

(b) From Tri-1-naphthylsilane and Phenyllithium.- Ten grams (0.024 mole) of tri-1-naphthylsilane was dissolved in 250 ml. of dry ether and 0.02 mole of phenyllithium (made in 92% yield) was added to the refluxing mixture. Even after stirring and refluxing for four days, Color Test I was positive. An additional 0.02 mole of phenyllithium was added, the ether was replaced with benzene, and the resulting mixture was refluxed at 60° for three days. Although Color Test I was still positive the material was worked up in the usual manner to obtain 12.8 g. of a white solid melting at 140-150°. Purification by digestion with six 20 ml. portions of ethanol gave 7.3 g. (63%) of crude product melting at 187-189°. After three recrystallizations from benzene a pure sample of tri-1-naphthylphenylsilane melting at 192-193° was obtained. A mixed melting point with an analyzed specimen showed no depression.

Attempts to fractionate the remaining solids by crystallization were unsuccessful and only impure low-melting solids could be obtained.

(c) From Tri-1-naphthylethoxysilane and Phenyllithium.-

To a solution of 5.0 g. (0.011 mole) of tri-1-naphthylethoxysilane in about 100 ml. of dry xylene was added 0.022 mole of an ethereal solution of phenyllithium. After refluxing for thirty-six hours, the opaque purple mixture gave a positive Color Test I. Following hydrolysis and removal of the inorganic salts, the solvent was distilled away to yield a yellow semi-solid. Digestion of this oil with several small portions of ethanol followed by three recrystallizations from benzene gave 0.8 g. (14%) of tri-1-naphthylphenylsilane melting at 189-190°. Identification was made by a mixed melting point. Since this preparation was made for the purpose of synthesizing tri-1-naphthylphenylsilane by another method, no further attempts were made to purify the crude solids and oils.

(d) Complex with Chlorobenzene.- Five grams (0.011 mole) of tri-1-naphthylphenylsilane, m. p. 190-191°, was dissolved in about 40 ml. of hot chlorobenzene and the solution was allowed to cool slowly. After four hours, 2.6 g. of large colorless crystals melting at 108-109° were removed by filtration. Recrystallization from the same solvent did not change the melting point.

Anal. Calcd. for $C_{42}H_{31}ClSi$: Cl, 5.92; Si, 4.68. Found: Cl, 5.80; Si, 4.61.

Three recrystallizations of 1.3 g. of this material from petroleum ether (b. p. 90-110°) were necessary before the melting point was constant at 192-193°. A 60% recovery of material was realized.

Attempts to purify the crude product, melting at 135-150°, (obtained by the treatment of tri-1-naphthylchlorosilane with phenyllithium) by crystallization from chlorobenzene gave inferior yields to those obtained by the exhaustive digestion treatment but some of the complex was isolated.

35. Tri-1-naphthyl-p-tolylsilane.- This compound was prepared by the action of p-tolylolithium on tri-1-naphthylsilane, -chlorosilane, -bromosilane, and -ethoxysilane, but only the latter compound gave high yields. It is believed that this is the case only because of the ease of purification and not because the other compounds do not react completely.

(a) From Tri-1-naphthylethoxysilane and p-Tolylolithium.- A solution of 110 g. (0.24 mole) of tri-1-naphthylethoxysilane and 1 l. of dry benzene was effected by heating and 0.34 mole of an ethereal solution of p-tolylolithium (made in 90% yield in the usual manner) was added. Color Test I was positive after refluxing the mixture for four days. The brown mixture was poured into dilute hydrochloric acid, the inorganic salts were removed by extraction, and the solvent was removed

from the organic layer. The hard, brittle brown solid was melted, poured into a large mortar, and pulverized. There was obtained 112 g. (92%) of crude product melting at 220-223°. Exhaustive digestion with small portions of boiling acetone gave 98 g. (80%) of pure tri-1-naphthyl-p-tolylsilane melting at 232-233°. The analytical sample was recrystallized twice from ethyl acetate but the melting point did not change.

Anal. Calcd. for $C_{37}H_{28}Si$; Si, 5.60. Found: Si, 5.68, 5.72.

In another run xylene was used for a solvent instead of benzene in an attempt to reduce the reaction time. Although Color Test I was negative after twenty hours when equivalent quantities of silicon compound and organolithium reagent were used, the mixture turned dark brown and the final product was difficult to purify with attendant decrease of yield. A check run of p-tollyllithium, when refluxed in xylene for twenty hours, gave the same color change and a brown to yellow ether solution after hydrolysis.

(b) From Tri-1-naphthylchlorosilane and p-Tollyllithium. Preparations starting with tri-1-naphthylchlorosilane gave variable results. The procedure used was essentially the same as that outlined in (a) above. From some of these runs only the corresponding silanol was isolated, while in others fair yields (40-60%) of the expected product were isolated.

In all of the instances where the silanol was isolated the yield of *p*-tolyllithium was between 50% and 60%. It is believed that the organolithium reagent was consumed by coupling with the unused *p*-bromotoluene and that the starting chlorosilane was hydrolyzed incidental to the process of isolation. Here again the use of xylene as a solvent gave colored impurities that were difficult to remove. A reaction period of three days in benzene appeared to be the optimal conditions.

(c) From Tri-1-naphthylbromosilane and *p*-Tollyllithium.- Equivalent quantities of tri-1-naphthylbromosilane and *p*-tolyllithium reacted in only two hours in refluxing ether to give a 60% yield of the expected product. Again the crude product, melting ca. 190-195^o, was difficult to purify by crystallization and this yield was isolated by digestion with small portions of acetone.

(d) From Tri-1-naphthylsilane and *p*-Tollyllithium.- Tri-1-naphthylsilane did not react with one equivalent of *p*-tolyllithium until the mixture in benzene had refluxed for six days. After this treatment the product was contaminated with colored impurities. The digestion procedure was not effective in this case probably due to the extreme insolubility of tri-1-naphthylsilane in acetone. Only after a long systematic crystallization procedure using ethyl acetate was a 12% yield of tri-1-naphthyl-*p*-tolylsilane isolated from the

colored oils and low-melting solids.

36. Tri-*o*-tolyl-*p*-bromophenylsilane.- Equimolar quantities of ethereal solutions of 0.425 mole of *p*-dibromobenzene and *n*-butyllithium were mixed at 5° in accord with published directions (43). The solution was stirred at that temperature until Color Test II became negative, a period of two hours, then 30.0 g. (0.09 mole) of tri-*o*-tolylchlorosilane was added to the stirred solution. After the mixture had refluxed for eighteen hours, Color Test I was negative. The inorganic salts were eliminated in the usual manner by extraction and the solvent was removed from the organic layer to obtain an oil. Attempts to crystallize this oil from the common organic solvents were unsuccessful.

All of the organic material was combined and distilled at 1.0 mm. The fraction boiling at 215-260°, after digestion with 20 ml. of petroleum ether (b. p. 90-110°), gave 12.6 g. of white solid melting at 172-173°. After two recrystallizations from the same solvent, there was obtained 9.3 g. (23%) of white solid melting at 185-187°.

Anal. Calcd. for $C_{27}H_{25}BrSi$: Br, 17.4; Si, 6.13. Found: Br, 16.3, 16.2; Si, 6.24, 6.20.

37. Tri-1-naphthyl-*p*-bromophenylsilane (Attempted).- An ethereal solution of *p*-bromophenyllithium was made as described in the previous section from 153 g. (0.65 mole) of

p-dibromobenzene and an equimolar quantity of n-butyllithium. To the stirred solution was added 34 g. (0.077 mole) of tri-1-naphthylchlorosilane and after this mixture had refluxed for fifteen hours, Color Test I (64) was positive. The solvent was then replaced with dry benzene and after refluxing for four hours Color Test I was negative. This run was worked up as described in the previous section and the solvent was finally removed at 0.1 mm. at 100°. After considerable manipulation of the red oil, there was obtained from acetone 22 g. (68%) of crude tri-1-naphthylsilanol melting at 202-203°.

38. Tetra-1-naphthylsilane (Attempted)

(a) From 1-Naphthyllithium and Silicon Tetrachloride or Ethyl Silicate.- To an ethereal solution of 15.3 g. (0.09 mole) of silicon tetrachloride was added 0.45 mole of 1-naphthyllithium (made from 67 g. (0.5 mole) of 1-bromonaphthalene and 8 g. (1.1 g. atom) of lithium) in 400 ml. of ether. Color Test I was negative until 3.1 equivalents of the organolithium reagent were added and positive even after refluxing for three days after four equivalents had been added. The purple mixture was hydrolyzed in the usual manner to yield a yellow organic layer. The solvent was removed and after

(64) H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

considerable manipulation of the black tar, 1.8 g. of crude perylene melting at 262-264° was crystallized from benzene. Practically all of the common organic solvents were used in various combinations and some of the yellow solids were distilled at 20 microns but no sharp-melting products could be isolated. A few mg. of a white solid melting at 325-340° were obtained but this high melting material could not be isolated from two other runs made under similar conditions.

When an excess of 1-naphthyllithium was added to ethyl silicate, only traces of perylene were isolated from the black tars.

(b) From Tri-1-naphthylchlorosilane and 1-Naphthyllithium.- Ten grams (0.022 mole) of tri-1-naphthylchlorosilane was added to the suspension resulting from mixing 0.1 mole of 1-bromonaphthalene to 0.1 mole of n-butyllithium in ether and refluxed for three days. Color test I was then negative. Following hydrolysis and removal of the inorganic salts, the organic layer was steam-distilled and the residue was extracted with ether. After removal of the solvent from the ether extract and crystallization from petroleum ether (b. p. 90-115°), 7.5 g. (75%) of crude tri-1-naphthylchlorosilane melting at 201-203° was recovered in three crops. This material showed no depression of melting point when mixed with an authentic specimen.

1-n-Butylnaphthalene was isolated from these runs. Apparently the failure of this experiment was due to the faster rate of the coupling reaction of 1-naphthyllithium with n-butyl bromide as compared to the desired reaction of 1-naphthyllithium with tri-1-naphthylchlorosilane.

When 1-naphthyllithium made by the direct procedure was mixed with tri-1-naphthylchlorosilane in xylene and baked at 150-180° for three days, no isolable products could be obtained from the black tars.

In an attempt to eliminate the highly colored by-products, solid 1-naphthyllithium (65) was prepared by halogen-metal interconversion, dissolved in benzene, an excess was added to a benzene solution of tri-1-naphthylchlorosilane, and the mixture was refluxed for twenty hours. After this treatment Color Test I was positive and the mixture had turned dark brown in color. Hydrolysis in the usual manner and removal of the inorganic salts by extraction gave a yellow organic layer. Attempted crystallizations from a number of common organic solvents gave a 10% recovery of tri-1-naphthylchlorosilane (mixed m. p.) and a number of unidentified solid mixtures and tars.

(65) This Thesis.

39. Hexa-1-naphthylidisiloxane (Attempted)

(a) From Hexachlorodisiloxane and 1-Naphthyllithium.- A 0.766 N benzene solution of 1-naphthyllithium was made by following the directions previously outlined (65). Five ml. (7.75 g., 0.027 mole) of hexachlorodisiloxane was added to about 100 ml. of dry benzene in the usual apparatus, 190 ml. (0.116 mole, RLi/silicon compound = 4.3) of the organolithium reagent was added, and the mixture was refluxed until Color Test I became negative (thirty-six hours). A benzene solution of 0.05 mole of the 1-naphthyllithium solution that was run under the same conditions showed a strong positive Color Test I after refluxing for six days. An excess of 0.06 mole of the organolithium reagent was then added and the mixture was refluxed an additional two days. Although Color Test I was still positive, the mixture was hydrolyzed and the inorganic salts removed by extraction in the usual manner. A tan solid, suspended between the ether and aqueous layers, was filtered from the solution. This material weighed 15.5 g., melted at 300-400^o, left a white ash not alkaline to litmus when ignited, contained no halogen or lithium, and was very insoluble in all the common organic solvents. A sharp-melting product could not be obtained by crystallization, digestion, or extraction. This material may be the crude hexa-1-naphthylidisiloxane or possibly a naphthylpolysiloxane.

(b) Tri-1-naphthylsilanol and Formic Acid (66).- Ten grams (0.023 mole) of tri-1-naphthylsilanol and 100 ml. of 99-100% formic acid were mixed and refluxed for fifteen hours. The solution was diluted with water, neutralized with sodium carbonate, and extracted with benzene. The benzene layer was concentrated and allowed to stand. After two days, 8.5 g. (85%) of tri-1-naphthylsilanol (determined by a mixed melting point) was recovered in two crops.

40. Hexa-1-naphthyldisilane (Attempted)

(a) From Tri-1-naphthylchlorosilane and Sodium.- This procedure was patterned after a published method (15) for making hexaphenyldisilane from triphenylchlorosilane and sodium. Ten grams (0.0225 mole) of tri-1-naphthylchlorosilane was dissolved in 300 ml. of hot dry p-xylene, 7.5 g. (0.32 g. atom) of bright clean sodium metal was added in small slices, and the resulting mixture was refluxed with vigorous stirring for five hours. The excess sodium was removed by hot filtration and the light yellow filtrate was set aside to crystallize. After one week 0.4 g. (4%) of impure tri-1-naphthylchlorosilane melting at 198-200° was removed from the solution. The solvent was removed from the mother liquor to yield a yellow viscous oil. After considerable manipulation from

(66) Unpublished studies by H. W. Melvin.

several different solvents, 1.8 g. (18%) of impure tri-1-naphthylchlorosilane (mixed m. p.) was separated. No other products were isolated from the yellow oils.

This experiment was repeated using the same quantities of starting materials but the mixture was refluxed for thirty-six hours. A recovery of 12% of the tri-1-naphthylchlorosilane was the only product that was isolated.

(b) From Hexachlorodisilane and 1-Naphthyllithium.- To a solution of 10 g. (0.037 mole) of hexachlorodisilane in ether was added dropwise with stirring 0.3 mole of 1-naphthyllithium (made by the direct procedure) (RLi/silicon compound = 8) in 300 ml. of ether. Even after refluxing the mixture for three days, Color Test I was positive. The mixture was hydrolyzed and the inorganic salts were removed in the usual manner and the organic layer was steam-distilled. A considerable quantity of naphthalene was collected from the distillate and the orange residue was extracted with ether. After replacing the ether with benzene and cooling, 1.1 g. of a yellow solid melting at 220-225° was collected. This material after two recrystallizations melted at 261-263° and was shown to be perylene by a mixed melting point. The filtrates were combined and by using petroleum ether (b. p. 60-80°) as a diluant and collecting several solids after slow evaporation of the solutions, 1.6 g. of a yellow solid melting

at 230-233° was obtained. By treating this material with a few ml. of cold concd. sulfuric acid, 0.3 g. of a white solid melting at 230-231° was obtained after washing the residue with ethanol.

This experiment was repeated in an effort to obtain more of the last mentioned solid but none could be found. Perylene and naphthalene were the only products isolated.

In an attempt to eliminate the colored by-products, the 1-naphthyllithium was made by halogen-metal interconversion and reacted with the silicon compound. Equivalent amounts (0.36 mole) of 1-bromonaphthalene and n-butyllithium were mixed as usual at -5°, stirred for twenty minutes, and 11.9 g. (0.041 mole) of hexachlorodisilane in 50 ml. of ether was added with vigorous stirring. Color Test I was not negative until the mixture had refluxed for two days. Following the usual hydrolysis and extraction, the organic layer was dried and the solvent was replaced with petroleum ether (b. p. 90-110°). About 0.8 g. of white solid melting at 176-180° was collected after the solution had stood at 0° for two days. Attempted purification by recrystallization from ethanol, benzene, or petroleum ether (b. p. 90-110°) gave only sticky solids and oils. The main filtrate gave only gums and oils when crystallization was attempted from the common organic solvents.

41. Tri-1-naphthyl-p-bromomethylphenylsilane. (Attempted).-

The procedure for obtaining triphenyl-p-bromomethylphenylsilane from triphenyl-p-tolylsilane and N-bromosuccinimide was used in this preparation. Fifteen grams (0.03 mole) of tri-1-naphthyl-p-tolylsilane were dissolved in 600 ml. of carbon tetrachloride, 5.35 g. (0.03 mole) of finely powdered NBS was added, and the mixture was refluxed with stirring for thirty minutes while irradiating the reaction flask with a mercury vapor lamp. The NBS had disappeared from its place on the bottom of the flask and a test for active bromine was negative. After cooling and filtering off the succinimide, the solvent was removed from the filtrate to give a yellow oil. Digestion of this oil with about 200 ml. of petroleum ether (b. p. 90-110°), followed by filtration, gave 14.0 g. of yellow solid melting over the range 150-155°. Even after several recrystallizations from ethanol, ethyl acetate, and petroleum ether (b. p. 90-110°), the melting point range could not be raised above 160-165°.

This experiment was repeated twice with essentially the same negative results.

42. Tri-1-naphthylsilylbenzoic acid. (Attempted).- Several attempts were made to oxidize tri-1-naphthyl-p-tolylsilane with chromium trioxide by the same procedure that was used to prepare p-triphenylsilylbenzoic acid from triphenyl-p-

tolylsilane (63). A typical experiment is described. Ten grams (0.02 mole) of tri-1-naphthyl-p-tolylsilane was suspended in 400 ml. of glacial acetic acid and 6.0 g. (0.06 mole) of chromium trioxide was added in small portions to the stirred mixture. After stirring for an additional hour, the green solution was poured onto crushed ice and filtered. There resulted an 80% recovery of tri-1-naphthyl-p-tolylsilane as evidenced by the mixed melting point method.

In a similar experiment the mixture was refluxed for fifteen minutes and a 15% recovery of the starting organosilicon compound was obtained. Extraction of the organic material with potassium and ammonium hydroxide followed by neutralization of the aqueous layer did not reveal any acid. (It was expected that some benzoic or phthalic acid might be formed from oxidation of cleavage products.)

Three runs were made in which 1, 3, and 10 ml. of concd. sulfuric acid were added to the respective mixtures which were all stirred at room temperature throughout the reaction. Tri-1-naphthyl-p-tolylsilane was not isolated from these attempts but the resulting oils and tars resisted purification. These latter substances apparently were not acidic. Essentially the same negative results were obtained by using sulfuric acid at 50° and 100° except that some charring occurred at 100°. These modifications of the basic procedure may have been too severe.

B. By-products Formed During the Preparation and
Use of Organolithium Reagents

1. Perylene.- The hydrocarbon, perylene, was isolated from several mixtures while attempting to prepare 1-naphthylsilicon compounds by the reaction of 1-naphthyllithium with various chloro- and ethoxysilanes. In every case where perylene was found the 1-naphthyllithium had been made by the direct procedure from 1-bromonaphthalene and lithium metal. This hydrocarbon was also found (58) in 3% yield when a preparation of 1-naphthyllithium was hydrolyzed. The following experiments were carried out in an attempt to determine the mechanism of the formation of perylene.

Authentic specimens of perylene were made by the three methods given below.

(a) From Naphthalene and Aluminum Chloride.- This preparation was made in essential accordance with published directions (67). These workers reported a yield of 10% of product melting at 264-265°. The material in our investigation was obtained in only 3% yield melting at 268-269° (cor.).

(b) From 1-Bromonaphthalene and Aluminum Chloride.- The directions of Weitzenbock and Seer (68) were followed. A

(67) R. Scholl, C. Seer, and R. Weitzenbock, Ber., 43, 2203 (1910).

(68) R. Weitzenbock and C. Seer, Ber., 46, 1996 (1913).

yield of 4% is reported and the product melted at 264-265°. A 6% yield of product melting at 268-269° (cor.) was found in our investigation.

(c) From β -dinaphthol.- The β -dinaphthol used was made in essential accordance with published directions (69). These investigators report a 90% yield of crude product melting at 212-213° while a yield of 82% melting at 215-216° was obtained in our study.

Perylene of m. p. 268-269° (cor.) was made in 65% yield by treating β -dinaphthol with phosphorus pentachloride and phosphorous acid by following the directions of Brass and Tengler (70). These workers reported a 72% yield of product melting at 264-265°. The phosphorus acid that was used in our investigation was made by an established procedure (71) from phosphorus trichloride and hydrochloric acid.

In addition to the mechanisms reported (58), perylene may be formed during the preparation of 1-naphthyllithium by the direct method by the action of lithium metal on the intermediate, 1,1'-binaphthyl. Many hydrocarbons have been shown to add alkali metals (39) but no instances could be found

(69) R. Pummerer, E. Prell, and A. Rieche, Ber., 59, 2160 (1926).

(70) K. Brass and E. Tengler, Ber., 64B, 1646 (1931).

(71) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry", Prentice-Hall, New York, 1944, p. 198.

where dehydrogenation and cyclization were effected by this treatment. The following experiments with 1,1'-binaphthyl, 2,2'-binaphthyl, and 9,9'-biphenanthryl were carried out to determine the extent of this cyclization.

2. 1,1'-Binaphthyl

(a) From 1-Naphthylmagnesium Bromide and Chromic Chloride.-

Although this preparation was carried out in strict accordance with a published procedure (72), there was obtained a crude yield of only 40% as compared to the reported practically quantitative yield. Bennett and Turner do not report a pure yield, but when the crude material obtained in the present investigation was recrystallized from ethanol, there resulted a 90% recovery of pure material: a 36% yield.

(b) From 1-Naphthylmagnesium Bromide and Cupric Chloride.-

The treatment of phenylmagnesium bromide with anhydrous cupric chloride is reported to give an 80% yield of diphenyl (73). However, this method afforded only a 30% yield of pure 1,1'-binaphthyl in this study. The crude product, melting at 146-153°, was dissolved in petroleum ether (b. p. 90-110°) and this solution was poured through a column of alumina. After the solvent was removed from the filtrate, 95% of the weight

(72) G. M. Bennett and E. E. Turner, J. Chem. Soc., 105, 1057 (1914).

(73) J. Krizewsky and E. E. Turner, J. Chem. Soc., 115, 559 (1919).

of the crude product was recovered as pure 1,1'-binaphthyl melting at 155-155.5°.

3. 1,1'-Binaphthyl and Lithium

(a) Followed by Hydrolysis.- The binaphthyl used in this experiment was purified by treatment with alumina as described in Section (b) of the preparation of 1,1'-binaphthyl. To a solution of 0.50 g. (0.00325 mole) of 1,1'-binaphthyl in 150 ml. of dry ether was added 0.8 g. (0.11 g. atom) of lithium wire. This mixture was stirred for two hours at room temperature (23°) in a nitrogen atmosphere. After stirring for five minutes the mixture turned dark purple in color. The lithium metal was held back with a plug of glass wool and the liquid was poured onto about 300 ml. of water. After the inorganic salts were removed by extraction, the solvent of the ethereal layer was replaced with about 20 ml. of benzene. In three crops 0.26 g. of yellow solid melting at 240-250° was filtered from the solution. Recrystallization from benzene gave 0.21 g. (42% based on the binaphthyl) of perylene melting at 264-266°. A mixed melting point with an authentic specimen showed no depression. No other solids could be obtained from the orange and red oils obtained from the filtrates.

This experiment was repeated and worked up by chromatographic methods in an attempt to isolate either a higher

yield of perylene or other products that may have been formed. The same quantities of starting materials and solvent were used and the mixture was refluxed with stirring for ten hours in a nitrogen atmosphere. The mixture was worked up as before, replacing the ether with 600 ml. of dry benzene. One liter of petroleum ether (b. p. 90-110^o) was added, the solution was poured through a 2 by 8 inch column of alumina, and the progress of the bands was followed with the aid of mercury-arc lamp. After development with petroleum ether (b. p. 60-80^o) and benzene, several bands developed on the column but oils only were isolated by extrusion, cutting, and elution of the zones.

(b) Followed by Carbonation.- A mixture of 1.0 g. (0.0064 mole) of 1,1'-binaphthyl (purified by chromatography), 0.65 g. (0.092 g. atom) of lithium, and about 150 ml. of dry ether was refluxed under the usual anhydrous conditions for nine hours. After straining the solution through a small glass wool plug to separate the unreacted lithium, the volume was 155 ml. A 5 ml. aliquot was titrated with standard acid and showed that the solution was 0.153 N in base (phenolphthalein indicator). This value corresponds to 0.0237 mole of base. If all of the base was present in a carbon-lithium linkage, this indicates that about four equivalents of lithium reacted with one equivalent of binaphthyl. The ether solution

was carbonated by pouring onto a slurry of Dry Ice and ether.

By conventional extraction procedures there was obtained 0.98 g. of an orange solid melting at 230-236° which had a neutral equivalent of 316. The melting point could not be raised by recrystallization from benzene and ethyl acetate. By extraction of this material with methanol in a Soxhlet apparatus, a crop of 0.31 g. of red solid melting at 190-220° and having a neutral equivalent of 296 was collected. It is believed that this acid may be 8-carboxy-1,1'-binaphthyl (74) (molecular weight 298, m. p. 240°).

This experiment was repeated using 10.00 g. (0.064 mole) of 1,1'-binaphthyl and 1.4 g. (0.2 g. atom) of lithium in ether refluxing for two hours before carbonation. The ethereal layer after treatment with Dry Ice was extracted six times with 200 ml. portions of dilute hydrochloric acid, followed by water, then with 10% potassium hydroxide. The basic layer was extracted in a liquid-liquid extractor with ether for sixteen hours. This step was done in an attempt to free the basic layer of all neutral substances. During this treatment 1.55 g. of a yellow solid separated which was insoluble in acid, base, and most of the common organic solvents.

The basic layer was acidified to give, after drying,

(74) J. Meisenheimer and O. Beisswenger, Ber., 65, 32 (1932).

2.9 g. of an orange-red solid. This solid melted at about 120° with considerable frothing and the neutral equivalent was 195.

The neutral ether solutions were combined, the solvent was replaced by 50 ml. of benzene, and allowed to crystallize. After two weeks 2.3 g. of black solid, m. p. 220-232°, was filtered from the solution. Two recrystallizations from benzene, gave 0.3 g. of perylene (mixed m. p.), melting at 262-264°.

4. 2,2'-Binaphthyl.- A 43% yield of 2,2'-binaphthyl melting at 182-183° was obtained from 2-naphthylmagnesium bromide and cupric chloride by the same procedure given in section (b) of the preparation of 1,1'-binaphthyl.

5. 2,2'-Binaphthyl and Lithium.- A mixture of 0.5 g. (0.0019 mole) of 2,2'-binaphthyl, 1.6 g. (0.23 g. atom) of lithium wire, and 125 ml. of ether was refluxed with stirring in a nitrogen atmosphere for twenty hours. The mixture turned dark purple and opaque in about two minutes and Color Test I was positive immediately after the purple color appeared. After the solution was strained through coarse glass wool, aliquots were titrated with standard acid in the usual manner as with an aryllithium reagent (37). The normality was 0.065 which corresponds to 0.0078 moles of alkali. This indicates that four equivalents of lithium had reacted with one equivalent

of binaphthyl ($0.0078/0.0019 = 4.1$). After the mixture was hydrolyzed and the layers were separated, the solvent was removed from the organic layer to yield a yellow solid melting from 120° to 250° . Several unsuccessful attempts were made to purify this solid by crystallization from ethanol, benzene, and petroleum ether (b. p. $60-80^{\circ}$) but only small amounts of gummy solids were isolated.

Chromatographic purification using the combination of alumina and petroleum ether (b. p. $60-80^{\circ}$) indicated that several components were present. After extruding, cutting, and eluting there resulted 0.50 g. (10%) of 2,2'-binaphthyl (mixed m. p.) and a number of yellow oils.

Another run was made using the same quantities of starting material in the same manner. This mixture was carbonated in an attempt to establish the location of the carbon-lithium linkage by characterization of the resulting acid. Carbonation was effected in the usual manner by pouring the reaction mixture onto a Dry Ice-ether slurry. The resulting ethereal solution was carefully extracted with 10% potassium hydroxide. The basic layer after acidification gave 0.10 g. of a yellow solid melting over the range $117-135^{\circ}$ with gas evolution. This melting point range was not changed by several recrystallizations from benzene-petroleum ether (b. p. $60-80^{\circ}$) mixtures. After the neutral ether layer had stood for several days, there

was removed 70 mg. of crude 2,2'-binaphthyl melting at 177-179°.

6. 9,9'-Biphenanthryl.- This preparation was made in essential accordance with a published procedure (75) from 9-phenanthryl-magnesium bromide and anhydrous ceric chloride. A 62% yield of product melting at 183-184° was obtained while Bachmann reports an 82% yield of material melting at 181-182°.

7. 9,9'-Biphenanthryl and Lithium.- A mixture of 0.10 g. (0.00028 mole) of 9,9'-biphenanthryl, 1.00 g. (0.14 g. atom) of lithium, and 50 ml. of dry ether was refluxed with stirring in an atmosphere of nitrogen for three days. The mixture was purple within three minutes. The contents of the flask were poured onto about 400 ml. of water, the layers were separated, and the ethereal layer (yellow in color) was dried overnight with sodium sulfate. The solvent was removed and the residue was dissolved in 300 ml. of dry petroleum ether (b. p. 90-110°). This solution was poured through 20 g. of alumina in a one inch column and developed with petroleum ether (b. p. 60-80°), benzene, and finally ether. After the solvent was removed from the benzene and ether eluants, there was obtained 20 mg. of a brown solid melting at 315-317°. This material may be a dibenzperylene.

(75) W. E. Bachmann, J. Am. Chem. Soc., 56, 1363 (1934).

The alumina was extracted with methanol and after reducing the volume there resulted 26 mg. of brown solid melting over the range 130-142°.

8. 1-n-Butylnaphthalene.- Incidental to the preparation of some organosilicon compounds, this hydrocarbon was isolated in 40-60% yields when 1-naphthyllithium was made by a halogen-metal interconversion. A survey of the literature (76) revealed considerable discrepancy in regard to the physical constants of the n-butylnaphthalenes. Consequently, the following studies were carried out to determine the extent of this reaction in regard to a preparative method for synthesizing reference specimens of hydrocarbons.

Equivalent quantities (0.49 mole) of 1-bromonaphthalene and n-butyllithium were mixed and allowed to reflux gently. After the exothermic reaction had subsided, the solution was heated to maintain reflux conditions until Color Test I became negative (a period of thirty-six hours). The mixture was hydrolyzed, inorganic salts were removed by extraction, and the organic layer was distilled at 3.5 mm. The fraction boiling at 136-143° was collected: 78.0 g., n_D^{20} 1.5865. Careful fractionation of this material through a column of

(76) The literature is reviewed by A. S. Bailey, G. B. Pickering, and H. C. Smith, J. Inst. Petroleum, 35, 103 (1949).

eleven theoretical plates gave 71.0 g. (83%) of a colorless oil: b. p. 287-288° at 745 mm., n_D^{20} 1.5812, D_{20}^{20} 0.978. These physical constants are in good agreement with the published values (76).

The sym-trinitrobenzene complex was prepared (76) by mixing and fusing weighed equivalent quantities of the components to obtain a yellow solid melting at 72-74°. A mixed melting point with a reference specimen (77) melting at 70-71° showed no depression. A mixed melting point with the corresponding complex of 2-n-butyl-naphthalene (m. p. 75°) (77) showed a large depression.

This experiment was repeated in essentially the same manner except that 20% excess n-butyl bromide was added to the refluxing solution immediately after the n-butyllithium and 1-bromonaphthalene were mixed. In this case it was necessary to reflux the reaction for only twenty-four hours before Color Test I was negative. After the material had been fractionated, an 87% yield of pure product was obtained.

In another run the ether was replaced with benzene immediately after mixing the starting materials. Color Test I was negative after refluxing the reaction for fifteen hours, but the yield of pure product was only 38%.

(77) Kindly supplied by A. S. Bailey, The Dyson Perrins Laboratory, Oxford University.

9. 1-n-Hexylnaphthalene.-- This experiment was carried out to check the method outlined in the previous section. An ethereal solution of 0.41 mole of n-hexyllithium was made in the usual manner (42) in 70% yield and was added to an equivalent amount of 1-bromonaphthalene. A 20% excess of 1-bromohexane was added and even after this mixture had been refluxed for five days Color Test I was positive. The solution was poured onto a Dry Ice-ether slurry and the acid was isolated in the conventional manner by extraction. A 4.2% yield of 1-naphthoic acid (mixed m. p.) melting at 155-156° was isolated.

The neutral ether solution was worked up by fractional distillation in essentially the same manner as that described in the 1-n-butylnaphthalene section to obtain a 61% yield of product: n_D^{20} 1.5652, D_{20}^{20} 0.957. These physical constants are in good agreement with the reported values: n_D^{20} 1.5652, D_4^{20} 0.958 (76).

10. 1-Naphthyllithium and Benzyl Chloride.-- Equivalent amounts (1.0 mole) of 1-bromonaphthalene and n-butyllithium were mixed at -5°, stirred for thirty minutes, and an excess of 190 g. (1.5 moles) of freshly distilled benzyl chloride was slowly added to the stirred mixture. Color Test I was negative immediately after all of the benzyl chloride had been added. After pouring into water and separating the layers, the organic

material was distilled at reduced pressure. The fraction boiling at 250-270° at 3.5 mm. was digested with petroleum ether (b. p. 30-60°) and the solution was allowed to crystallize undisturbed. After two days 33 g. of white solid melting at 81-83° was removed. Recrystallization from ethanol raised the melting point to 82-83°. (The expected product, 1-benzyl-naphthalene (78), melts at 58°.) A sodium fusion test showed halogen to be absent, the material was insoluble in concentrated sulfuric acid, and a picrate could not be made. An ultra-violet absorption spectra was made on the Carey recording spectrophotometer which showed maxima at 273, 283.5, 292.5, and 376 m μ .

On the basis of this data and that reported by other investigators concerning a similar reaction (79), it is believed that this compound is 1-naphthylphenylbenzylmethane. The following experiments were carried out in an attempt to synthesize this hydrocarbon.

11. Attempted Addition of 1-Naphthyllithium to Stilbene.

This procedure was patterned after that of Ziegler and co-workers (80) who obtained α, β -diphenyl- n -heptylic acid by

(78) G. Egloff, "Physical Constants of Hydrocarbons", Vol. IV, Reinhold, New York, 1947, p. 227.

(79) G. Wittig and H. Witt, Ber., 74, 1474 (1941).

(80) K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, Ann., 473, 1 (1929).

carbonating the mixture resulting from adding n-butyllithium to stilbene.

An ethereal solution of 5.0 g. (0.028 mole) of stilbene and 0.056 mole of 1-naphthyllithium (made in 86% yield by the direct procedure) was refluxed for sixteen hours. Following hydrolysis and separation of the layers, the organic material was distilled at 3.0 mm. The fraction boiling at 240-305°, a red oil, was digested with about 4 ml. of petroleum ether (b. p. 30-60°) and cooled. There was obtained 2.3 g. of stilbene (mixed m. p.) melting at 118-120°. All of the filtrates were combined, dissolved in petroleum ether (b. p. 30-60°) and chromatographed on alumina. About six distinct bands developed on the column indicating that the mixture contained an excessive amount of impurities. After extruding and separating the six bands on the alumina, the organic material was eluted with methanol. All fractions gave only colored oils which could not be crystallized.

12. 1-Naphthylphenylbenzylcarbinol.- Ethereal solutions of 0.13 mole of benzylmagnesium chloride and 15.0 g. (0.065 mole) of 1-naphthylphenyl ketone were mixed in the usual apparatus and refluxed for thirty minutes. After hydrolysis with water and separation of the layers, the solvent was removed from the organic layer to give a yellow solid. Two digestions with 20 ml. portions of petroleum ether (b. p.

90-110°) removed the yellow color to leave a white solid. Crystallization from ethanol gave 14 g. (67%) of white crystals melting at 148-149°. This compound is reported to melt at 150° (81).

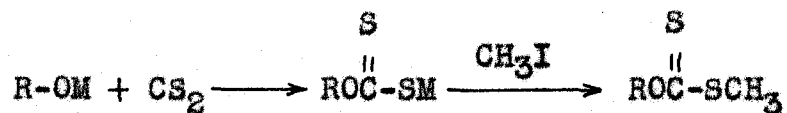
13. 1,2-Diphenyl-1-(1-naphthyl)ethylene (Attempted).- A number of substituted stilbenes has been prepared (82) by distilling the corresponding carbinol at reduced pressure in the presence of a trace of sulfuric acid. Seven grams (0.021 mole) of 1-naphthylphenylbenzylcarbinol were distilled at 0.1 mm. after adding 3 drops of 50% sulfuric acid to the dry solid. The fraction boiling at 215-220°, 6.0 g. of a yellow viscous oil, was collected and dissolved in petroleum ether (b. p. 60-80°). Only oils were obtained from methanol, ethanol, petroleum ether, and various combinations of these solvents.

14. Attempted Dehydration of 1-Naphthylphenylbenzylcarbinol by Cugaev's Method.- The Cugaev (83) reaction consists essentially in the formation of the methyl xanthate of the alcohol by reaction of the alkali metal derivative of the alcohol successively with carbon disulfide and methyl iodide:

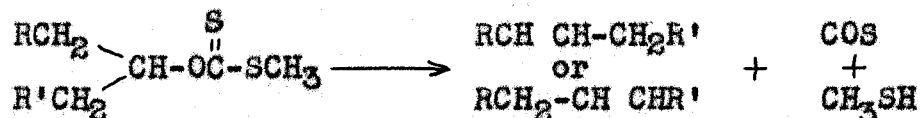
(81) H. Bauer, Ber., 42, 2589 (1909).

(82) W. Tadros, K. Farahat, and J. M. Robson, J. Chem. Soc., 439 (1949).

(83) "Tschugaeff" is an alternate spelling that often is used.



Distillation of the methyl xanthate results in its breakdown to methyl mercaptan, carbon oxysulfide, and the dehydrated alcohol:



Although this reaction was carried out in essential accordance with the procedure outlined by Alexander and Mudrak (84) for use with a similar carbinol, a 92% recovery of our starting carbinol was isolated.

Since it was believed that the sodium salt of the carbinol was not formed initially in the three step reaction, the lithium salt was made by adding an equivalent amount of *n*-butyllithium to the alcohol. The above reported procedure was then followed but an 84% recovery of the carbinol was isolated.

15. 1-Naphthylphenylbenzylmethyl Chloride (Attempted).-- This preparation was attempted in order to obtain 1-naphthylphenylbenzylmethyl chloride for subsequent reduction to the hydrocarbon by the use of lithium aluminum hydride. Two grams

(84) E. R. Alexander and A. Mudrak, J. Am. Chem. Soc., 72, 1810 (1950).

(0.006 mole) of 1-naphthylphenylbenzylcarbinol was refluxed in benzene with 5 g. (0.042 mole) of thionyl chloride (freshly-distilled from quinoline) for two hours. The solvent and excess thionyl chloride were removed by distillation at reduced pressure to give a yellow oil. This material could not be crystallized from petroleum ether (b. p. 60-80°), ethanol, or benzene.

IV. DISCUSSION

A. Organosilicon Compounds

Syntheses of the 1-naphthylsilicon compounds in this investigation illustrate the value of the halogen-metal interconversion method for preparing organolithium reagents. The use of 1-naphthyllithium made by the direct procedure introduces colored impurities (58) which are extremely difficult to eliminate from the final product. When the organolithium reagent was made by halogen-metal interconversion, a white product was easily obtained. However, this method can not be used when an extended reaction period and/or high temperatures are required. This is due to the two reactants of the interconversion coupling with each other rather than with the desired compound. These reactions are discussed more completely in Section B.

Since there was no obvious reason for believing that tetra-2-naphthylsilane would not be formed as easily as tetraphenylsilane, the former compound was synthesized to compare its physical properties with other tetraarylsilanes.

Tetra-2-naphthylsilane (47) was made easily from silicon halides and 2-naphthyllithium but the tri-2-naphthylsilyl derivatives could not be isolated. It is believed that the

chief difficulty here was the absence of an accurate method for determining the amount of 2-naphthyllithium. Negative results were obtained when the organolithium reagent was prepared by either the direct procedure or by halogen-metal interconversion.

When 2-naphthyllithium is made by the former method, the reaction mixture is highly colored. This color is probably due to the addition of lithium metal to the intermediary binaphthyl. This intermediate has been isolated from reactions using 2-naphthyllithium made by the interconversion procedure in yields as high as 20% and it is likely that a comparable amount is formed when the direct procedure is employed. 2,2'-Binaphthyl has been shown to add four equivalents of lithium which on hydrolysis yields four equivalents of alkali. The acid titer of the organolithium preparation, then, would show a higher yield of 2-naphthyllithium than is actually present. Another complicating factor may be the variable amount of binaphthyl formed during the reaction due to slight variations in temperature, rate of addition, state of division of the metal, etc.

The only satisfactory method for determining the extent of halogen-metal interconversion is by carbonating aliquots at timed intervals and isolating the resulting acid. Several indeterminate factors are present here: appreciable amounts of

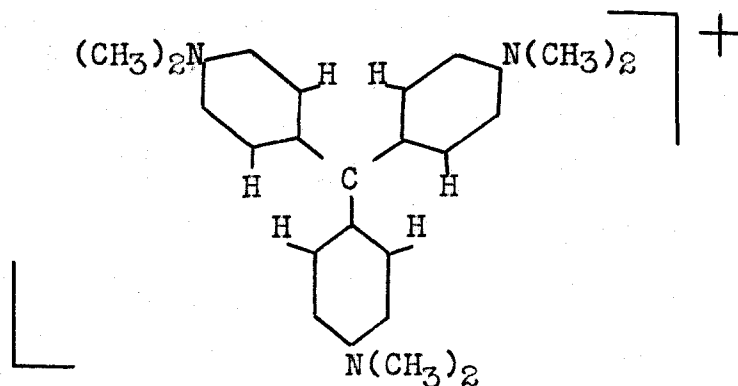
water may be present in Dry Ice, the carbonation reaction may not be quantitative, and some material may be lost while isolating the acid.

The work reported in the experimental section for synthesizing diphenyldi-p-tolylsilane shows that the organolithium reagent must be added extremely slowly to replace only two chlorine atoms in silicon tetrachloride. Moreover, since the reaction of most organolithium reagents with silicon tetrachloride is vigorous, the exact amount of organolithium reagent must be added in order to prevent more substitution than is desired. If the yield of the organolithium compound varies appreciably over a comparatively short period of time, i.e., that period during which it is added to the silicon halide, then the amount of organolithium reagent again becomes merely an approximation.

An inspection of the Stewart model of tri-1-naphthylphenylsilane indicates that steric hindrance may cause restricted rotation and hence, in this case, the existence of stereoisomers. If a model of this compound be seized by the phenyl groups, it becomes apparent that the right- and left-handed "propellers" which are formed are not superimposable and, if these two forms actually exist, are enantiomorphous. Holding the phenyl group pointing downward, the three naphthyl groups can be placed in three other positions: (1) all three

benz-substituents pointing down; (2) one up, two down; and (3) two up, one down. Theoretically, then, four sets of enantiomorphs or eight diastereoisomers are possible. However, some of these configurations may be forbidden in that the energy relationships of the more highly strained positions would be excessively high in comparison to the less-strained arrangements. The energy barrier, i.e. steric hindrance, may be so small between some of these configurations that the more highly strained isomers would be non-existent.

The possibility of this type of isomerism in such substances as triphenylmethyl and its ions was pointed out recently (85) and somewhat later evidence (86) was submitted to substantiate this prediction. These workers present spectral studies concerning the crystal violet ion, tris-*p*-dimethylaminophenylmethyl carbonium ion,



(85) G. N. Lewis and M. Calvin, Chem. Rev., 25, 273 (1939).

(86) G. N. Lewis, T. T. Magel, and D. Lipkin, J. Am. Chem. Soc., 64, 1774 (1942).

and interpret the data as indicating the existence of two isomers. This phenomenon is referred to as the "windmill" or "propellor" type of isomerism. These investigators refer to a form "A" in which the phenyl nuclei are all twisted about the central carbon atom in the same direction, termed helical symmetry. Isomer "B", asymmetric helical symmetry, has one of the nuclei twisted in the opposite direction from the other two groups.

The forces which hold the groups in this fixed position are ascribed to repulsion of the ortho hydrogen atoms and an opposing force, the tendency of the ions to revert to a planar configuration. An equilibrium position is reached in which these two forces are balanced. To present a more clear illustration the central carbon-phenyl bonds may be thought of as having one-third double bond character. This opposition of forces, then, becomes a matter of the repulsive forces set up between the ortho hydrogens tending to twist the "rigid" carbon-carbon double bond.

It is interesting to note that Lewis found no difference in the energy content of the two isomers of the crystal violet ion. The energy of activation for isomerization was estimated to be 2-3 kcal.

The same type of evidence indicates that the phenyl group in a compound such as malachite green (phenyl-bis-p-dimethyl-

aminophenyl carbonium chloride) is free to rotate about its axis. This is probably true because the phenyl group does not participate in the main resonance of the molecule. There is, then, little double bond character in the central carbon-phenyl bond. Hence, since no force is in opposition to the repulsive action of the ortho hydrogen atoms, the phenyl groups are not held in a fixed position.

To extend this idea to the silicon compounds it is necessary that steric factors alone must be relied on to hold the particular group in a fixed position before isomers can exist. Ortho-substituents may force the nuclei in one direction or another but some force must hold that group in a more or less fixed position so that it does not rotate far enough to revert to the position occupied by its diastereoisomer. For example, consider a right- and left-handed propellor, it is known that these are not superimposable. However, if the blades are free to rotate through an arc of only 90° then, although some force may twist the blades from a planar arrangement, the new positions attained will give two propellors identical in all respects. In the case of the crystal violet ion, this opposing force is the tendency of the ion to assume a planar configuration (or stated in the older terminology, the energy required to twist a double bond). But since there is no evidence that silicon-carbon double bonds

exist, steric hindrance alone must prevent this free rotation in order to satisfy the conditions for the existence of isomers.

In order to prove this hypothesis by synthetic methods, it is necessary to isolate one set of diastereoisomers and resolve the pair of enantiomorphs. In this investigation a procedure was developed for brominating the methyl group in triphenyl-*p*-tolylsilane. By this method the number of functional groups that can be introduced into tetraphenylsilane is limited only by the number of reactions of a reactive bromine atom. In this study the following functional groups were attached to tetraphenylsilane: bromomethyl, dibromomethyl, hydroxymethyl, formyl, cyanomethyl and carboxyl.

However, when this method was used to prepare the corresponding tri-1-naphthylphenyl derivative by starting with the *p*-tolyl compound, no sharp-melting products could be isolated. It is believed that the bromination reaction proceeds smoothly and that the failure of this method is merely a failure to develop the proper conditions for purifying the crude product. On the other hand, one or more of the naphthalene nuclei may have been brominated as well as the side chain to give a complex mixture. Or the free bromine that is invariably formed in *N*-bromosuccinimide reactions may have partially cleaved one of the groups from the silane.

The preparation of tri-1-naphthylphenylsilane and tri-1-naphthyl-p-tolylsilane was an arduous task in that the crude product was invariably extraordinarily difficult to purify. After a procedure had been developed for obtaining a good yield of the pure silane, the mother liquors were carefully examined in an effort to find another compound that might be an isomer of the isolated product. However, no other compounds could be isolated from the resulting oils and tars. The diastereoisomers would have different physical properties and hence would retard crystallization and are likely to be isomorphous and depress the melting point of the predominant product. On the other hand, the problem may have been merely the elimination of a combination of impurities that had similar physical properties only and hence were difficult to remove by ordinary techniques.

p-Bromophenyllithium (43) prepared by halogen-metal interconversion failed to react with tri-1-naphthylchlorosilane. This experiment was designed to provide a functional group in tri-1-naphthylphenylsilane for the purpose of attempting resolution.

These failures again illustrate a limitation of the halogen-metal interconversion procedure used when extended reaction periods are needed. In both cases the organolithium reagent disappeared within about eighteen hours and no

substitution had occurred in the silane. The main reaction is probably the coupling of one molecule of the active species, p-bromophenyllithium, with another of the same kind. Other reactions are undoubtedly involved but no new data has been presented in this investigation and this subject is discussed elsewhere (43).

The reactions of the tri-l-naphthylsilicon derivative indicate that steric factors are operating. Hydrolysis of most chlorosilanes is easily effected and usually precautions must be taken to prevent its occurrence. However, hydrolysis of tri-l-naphthylchlorosilane as well as tri-o-tolylchlorosilane (19) does not occur until relatively drastic conditions are imposed. Likewise, tri-l-naphthylsilane and tri-o-tolylsilane do not visibly evolve hydrogen when treated with potassium hydroxide in piperidine (62), while triphenylsilane in the control experiment gives a vigorous evolution of the gas.

The action of an excess of l-naphthyllithium on silicon tetrachloride and on ethyl silicate affords only the tri-substituted derivative, even though high temperatures and long reaction periods are used.

Hexa-l-naphthyldisiloxane could not be made by treating the tri-substituted silanol with formic acid (66) or by treating hexachlorodisiloxane with an excess of l-naphthyl-

lithium. The former method was used to prepare hexaphenyl-disiloxane (64) and hexakis-(p-chlorophenyl)-disiloxane (87) and this procedure may prove to be a general reaction. However, this method failed in the case of tri-(p-dimethylamino-phenyl)-silanol. Additional evidence must, therefore, be obtained before this reaction may be used as a criterion that steric factors are concerned.

It has been emphasized (88) that steric hindrance should not be associated with a particular reactant or over-all chemical reaction but is a property of a particular reaction mechanism. In order to postulate that steric requirements are the principal factors in the reactions of 1-naphthylsilicon compounds, an S_N2 mechanism must be assumed to operate ordinarily in the hydrolysis of silanes. There appears to be ample data from recent reports to justify this assumption and these reactions furnish additional evidence for this postulation. Furthermore, it follows that the ionization (S_N1) mechanism is much slower than is the case with carbon compounds.

Price (89) has shown by kinetic studies that the rate of

(87) L. S. Miller, Doctoral Dissertation, Iowa State College, 1950, p. 49.

(88) I. Dostrovsky, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 174 (1946).

(89) F. P. Price, J. Am. Chem. Soc., 69, 2600 (1947).

alkaline cleavage of the Si-H bond in trialkylsilanes decreases with increasing bulk of the alkyl groups. This order is the same as that observed in carbon compounds undergoing nucleophilic attack and this cleavage is postulated as proceeding by an S_N2 mechanism. Actual steric requirements are not mentioned, but an explanation is given in terms of the field effects of the entering and constitutive groups. In the present case the groups are larger, leading to the expectation that in this type of mechanism the rate should be retarded.

Swain (90) has shown that the data of reaction rate studies of the hydrolysis of triarylsilyl fluorides is inconsistent with the idea of a siliconium ion intermediate (an S_N1 type) and suggests that many reactions of organo-silicon compounds may proceed through pentacovalent silicon intermediates. The slow rate of hydrolysis of tri-1-naphthylchlorosilane is predicted on the basis of these experiments if large steric requirements are postulated for the naphthyl groups. As presented by Swain the reaction may proceed as follows:

(90) C. G. Swain, R. M. Esteve, Jr. and R. H. Jones, J. Am. Chem. Soc., 71, 965 (1949).

Brown and Sujishi (91) have demonstrated the steric requirements of tri-1-naphthylboron toward methyl amines and attribute this effect to the exceedingly high F-strain (91) factor. This type of strain, and B-strain (92), may not be directly involved in the hydrolysis reaction, but these observations emphasize the importance of the space actually occupied by the 1-naphthyl group.

B. By-products from the Preparation and Use of Organolithium Reagents

As reported elsewhere (58), perylene formation from the treatment of 1-bromonaphthalene with lithium metal may proceed by the disproportionation of free radicals or by a cyclodehydrogenation of 1,1'-binaphthyl by means of organolithium compounds. However, the formation of free radicals of this type (1,8-dinaphthylene) requires a considerable amount of energy and therefore an ionic mechanism as set forth below is believed to be a more probable mechanism.

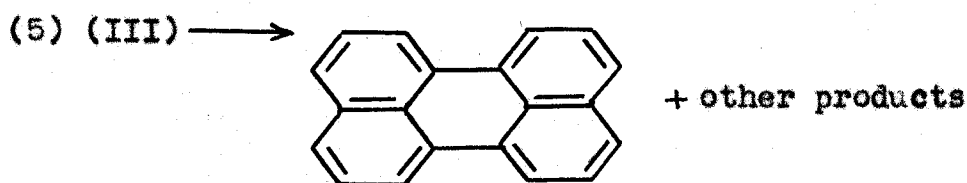
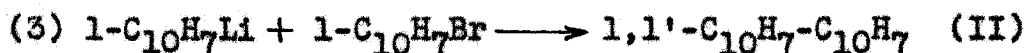
Although there is little doubt that perylene was detected in the mixtures resulting from treating pure 1,1'-binaphthyl and phenyl- and p-dimethylaminophenyllithium, the

(91) H. C. Brown and S. Sujishi, J. Am. Chem. Soc., 70, 2793 (1948).

(92) H. C. Brown, H. Bartholomay, and M. D. Taylor, J. Am. Chem. Soc., 66, 435 (1944).

formation of perylene is now believed to have resulted from the action of lithium metal on 1,1'-binaphthyl. The solutions of organolithium compounds used on the reported experiments (58) may well have contained appreciable amounts of finely divided lithium metal.

Considering the high yield (50%) of perylene isolated from the reaction between pure 1,1'-binaphthyl and lithium metal, the reaction is now believed to proceed by an ionic mechanism as follows:

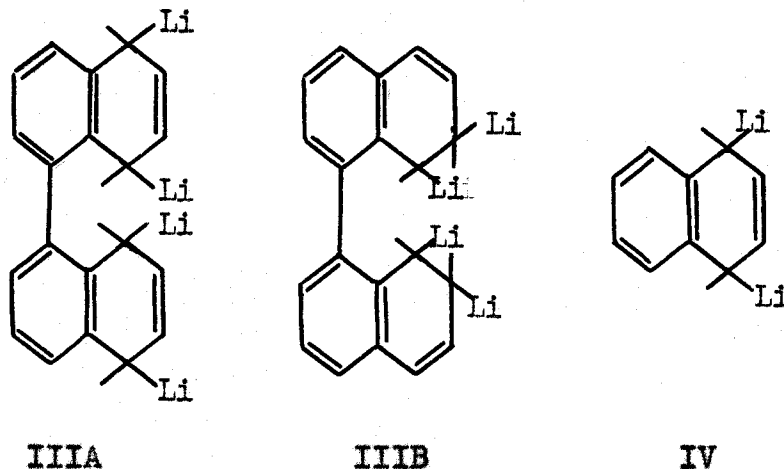


Equation (3) has been observed in a large number of reactions and requires no further explanation.

The fact that four equivalents of alkali are found for each equivalent of binaphthyl, after the mixture is hydrolyzed, is strong evidence for the correctness of equation (4). On the basis of analogous reactions (39,40), the addition complex (III) may have a structure (93) such as IIIA or IIIB

(93) For an analogous addition product of phenanthrene and sodium see A. Jeanes and R. Adams, J. Am. Chem. Soc., 59, 2608 (1937).

of the following

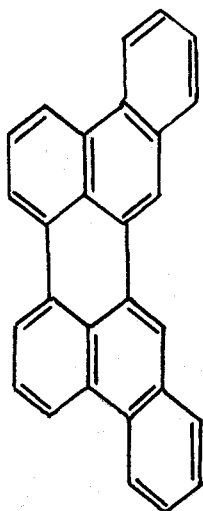


The addition complex of naphthalene (IV) is included for comparison. Even this addition product is not well established (40).

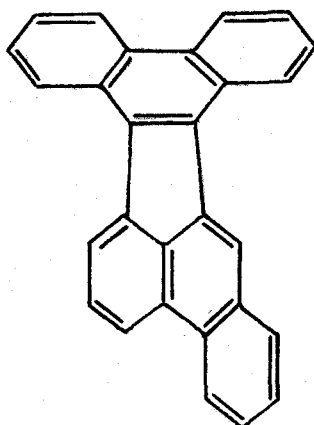
The "other products" of equation (5) may well be di- or tetra-hydro-1,1'-binaphthyl compounds. Although there is no direct evidence at present to substantiate this idea, analogous reactions have been reported (39) to yield dihydro derivatives following the addition of lithium and subsequent hydrolysis. The fact that a high yield of perylene and acidic organic material is isolated after carbonation of the addition product, indicates the existence of carbon-lithium bonds even after the perylene has been formed.

If the above mechanism is correct, then 2,2'-binaphthyl and metallic lithium might possibly yield one or more of the following compounds:

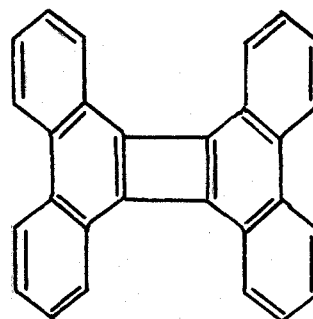
To extend these studies, 9,9'-biphenanthryl was reacted with lithium metal. The products that would be formed if equations (3-5) are correct would be one or more of the following:



VIII



IX



X

Compounds IX and X are not reported and unfortunately there is some doubt concerning the physical constants of VIII. An article by Schauenstein and Burgermeister (97) summarizes the previous work concerning these dibenzperylenes. Some evidence is also presented to aid in establishing the location of the benz-substituents. These workers concluded that 2,3,10,11-dibenzperylene (VIII) melts at 329-332°.

(97) E. Schauenstein and E. Burgermeister, Ber., 76B, 205 (1943).

A substance melting at 315-317° was isolated in our investigation from the reaction of 9,9'-biphenanthryl and lithium. However, attempts to obtain specimens of the dibenzperylene for identification by the mixed melting point method were unsuccessful. A letter sent to Kurt Brass requesting a sample of 2,3,10,11-dibenzperylene (98) was returned with a notation that Prof. Brass died in 1945. Another note was posted January 19, 1949 to Prov. Zinke (99) and has not yet been returned or answered.

At least one reaction between each of the above mentioned biaryls (1,1'- and 2,2'-binaphthyl, and 9,9'-biphenanthryl) and lithium was carbonated in an attempt to locate the position of the carbon-lithium bonds. In all cases organic acids were found but none of these could be purified sufficiently for identification. These acids may be dihydrocarboxylic acids which are in general, extremely difficult to purify (93).

When 1-naphthyllithium made from 1-bromonaphthalene and n-butyllithium was used in reactions requiring a long reaction period and/or high temperatures, appreciable amounts of 1-n-butylnaphthalene were isolated. This result is not surprising since this type of coupling reaction has been observed

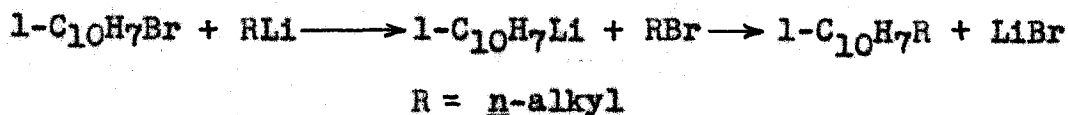
(98) K. Brass and E. Fanta, Ber., 65, 1 (1936).

(99) A. Zinke, E. Ziegler, H. Gottschall, and K. Lercher, Ber., 75B, 148 (1942).

frequently. However, a search of the literature revealed that there are very few synthetic methods for obtaining alkylnaphthalenes and related hydrocarbons in good yield. Some of the methods described, particularly the Friedel-Craft syntheses, leave much to be desired concerning the structure of the isolated product. The Wurtz-Fittig reaction apparently leaves the alkyl residue intact during the reaction but the yields are low (76).

Preliminary experiments indicated that the reaction of an RLi type with an RX type is to be preferred for the synthesis of authentic specimens of hydrocarbons. This method was tested by preparing 1-n-butylnaphthalene in 83% yield and 1-n-hexylnaphthalene in 61% yield by treating 1-bromonaphthalene with the corresponding n-alkyllithium.

The following two facts leave little doubt as to how this reaction proceeds. 1-Naphthoic acid is obtained in 90% yield by carbonating the 1-bromonaphthalene-n-butyllithium mixture after the reagents have stirred for twenty minutes. Color Test II becomes negative after stirring the reaction mixture for two hours while Color Test I remains positive for three days. This reaction, then, takes place as follows:

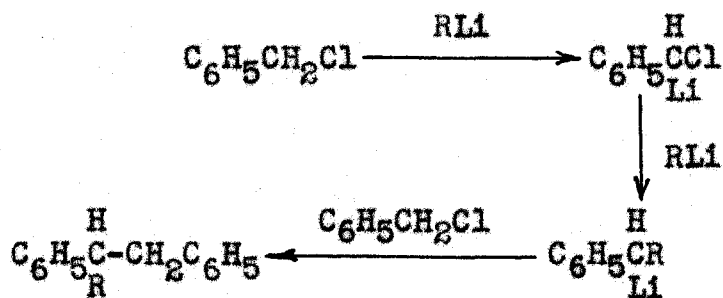


Although the comparative reactivity of alkyl halides may not require further proof, these reactions illustrate this activity in a striking manner. Methyl iodide is reported to react immediately with 1-naphthyllithium (41) to give an 80% yield of 1-methylnaphthalene, n-butyl bromide required three days to react completely, while with n-hexyl bromide a color test showed the presence of 1-naphthyllithium even after six days.

An experiment designed to obtain additional proof of the superiority of the above method for obtaining authentic hydrocarbon samples gave an unidentified product. This reaction was the treatment of benzyl chloride with 1-naphthyllithium. The colorless product that was isolated in good yield melted at 82-83°. A search of the literature in connection with even the least likely end-product of this reaction failed to develop a clue as to its identity. However, the ultra-violet spectral curve of this compound shows four maxima, all of which are within 1 $m\mu$ of the nine maxima shown by 1-benzyl-naphthalene. This evidence strongly indicates that the product is a benzyl-naphthalene type and not a phenyl-naphthalene derivative. The latter type of compound shows a definite bathochromic shift due to the interaction of the two aromatic nuclei. The presence of a methylene group between the nuclei inhibits this interaction.

The spectrum of the benzylnaphthalenes can be fairly accurately described by superimposing the spectrum of benzene on that of naphthalene.

The reaction between phenyllithium and benzyl chloride is reported (79) to give a 53% yield of 1,1,2-triphenylethane and the mechanism that is given to account for this product is summarized in the following reaction sequence:



The end-product, if R = 1-naphthyl, would be 1-naphthyl-phenylbenzylmethane.

It should be mentioned that Wittig and Witt do not claim to have proved the above reaction sequence but merely consider it as a possibility. In their case R=C₆H₅⁻ and, considering the intermediate in the first step, it seemed much more likely to them that diphenylmethane should be formed. However, they found in a separate experiment that diphenylmethane was not metalated to any appreciable extent by phenyllithium. This experiment does not satisfy the experimental facts since the reaction between benzyl chloride

and phenyllithium is vigorous and immediate.

Efforts to prepare 1-naphthylphenylbenzylmethane were unsuccessful. Well known procedures were adopted in attempts to (1) dehydrate the corresponding carbinol to the ethylene for subsequent catalytic hydrogenation by distillation with sulfuric acid and by Cugaev's method, and (2) to prepare the chloride for subsequent reduction with lithium aluminum hydride.

V. SUMMARY

A survey of the literature was made concerning steric hindrance in organic compounds of the Group IVB elements.

Several new 1-naphthylsilicon compounds were synthesized and their reactions were studied. It is believed that some reactions of tri-1-naphthylsilyl derivatives may be adequately explained only by postulating that steric hindrance is present.

A theoretical discussion is presented to point out the possibility of providing additional evidence for the existence of a new type of isomerism recently proposed by G. N. Lewis. This "windmill" or "propellor" type of isomerism is possible only if steric factors are operative within the molecule. It is believed that tri-1-naphthylphenylsilane derivatives may be capable of being resolved into optical isomers due to this special type of isomerism.

1,1'-Binaphthyl was observed to undergo a unique cyclodehydrogenation reaction when treated with lithium. Some unsuccessful experiments were made to elucidate the mechanism of this type of reaction.

The value of the halogen-metal interconversion method for preparing organolithium reagents is illustrated. The use of this method eliminates certain highly colored by-products

that are invariably present when the naphthyllithium reagents are made by the direct method from the aryl bromide and lithium metal.

A number of functional groups, carboxyl, bromomethyl, dibromomethyl, cyanomethyl, and formyl, were introduced into a para position in tetraphenylsilane. However, this method failed when attempted with the tri-1-naphthylsilicon compounds.

The reaction of an aryllithium reagent with an alkyl halide was shown to give good yields of aryl-alkyl hydrocarbons which are not readily available through other syntheses. However, benzyl chloride was shown to react in an unexpected manner with 1-naphthyllithium. Several unsuccessful syntheses were attempted in an effort to prove the structure of the product.