were 24,630 calories, −21.4 e.u., and 31,010 calories, respectively; for 99.0% formic acid they were 25,970 calories, −20.0 e.u., and 31,930 calories, respectively. These results are consistent with absolute reaction rate theory.

MANHATTAN, KANSAS RECEIVED MAY 5, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some 1-Naphthylsilicon Compounds

BY HENRY GILMAN AND CECIL G. BRANNEN

Several new 1-naphthylsilicon compounds were synthesized to extend the study of steric hindrance in arylsilanes. Tri-1-naphthylsilane and some of its derivatives exhibited unusual stability toward hydrolytic reagents and were further substituted by organolithium reagents with difficulty. A bimolecular nucleophilic substitution reaction mechanism is employed to account for this stability and to illustrate the steric requirements of these compounds. The value of the halogen–metal interconversion method of preparing organolithium reagents for synthetic purposes is demonstrated.

Several investigators[1] have reported that steric factors are concerned in the reactions of various silanes. It is our belief that the reactions of 1-naphthylsilicon compounds can be explained on a similar basis. We have based this idea on the observations that the tri-1-naphthylsilyl derivatives are relatively inert toward hydrolytic reagents and organolithium compounds, and that tri-1-naphthylsilanol is not converted to the disiloxane by treatment with acid.

Hydrolysis, either acid- or base-catalyzed, of most chlorosilanes is easily effected and usually precautions must be taken to prevent its occurrence. However, hydrolysis does not occur with several triarylchlorosilanes containing an ortho-substituent, such as *o*-tolyl[2], *o*-anisyl[2] and 1-naphthyl, until relatively drastic conditions are imposed. Under some conditions tri-1-naphthylchlorosilane is unaffected by weak base while triphenylchlorosilane is completely hydrolyzed when similarly treated. Likewise, tri-*o*-tolyl- and tri-1-naphthyl-silane do not visibly evolve hydrogen when treated with potassium hydroxide in piperidine,[3] while triphenylsilane in the control experiment gives a vigorous evolution of the gas.

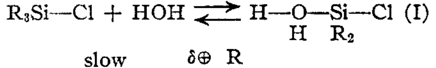
The action of an excess of 1-naphthyllithium on silicon tetrachloride and on ethyl silicate affords only the tri-substituted derivative even though high temperatures and long reaction periods are used. Others have observed similar results with sterically-hindered radicals, such as *o*-tolyl,[1f] *o*-anisyl,[2] isopropyl,[1b] and cyclohexyl,[1e] while *t*-butyllithium[1d] gave only the di-substituted silane.

Formic acid[4] has been used to convert silanols to the corresponding disiloxanes but this reagent is without effect on tri-1-naphthylsilanol. Apparently this disiloxane cannot be made by treating hexachlorodisiloxane with an excess of 1-naphthyllithium.

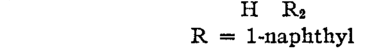
It has been emphasized[5] that steric hindrance should not be associated with a particular reactant or over-all chemical reaction but is a property of a particular reaction mechanism. In order to postulate that steric requirements are the principal factors in the reactions of 1-naphthylsilicon compounds, 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[1c] has shown by kinetic studies that the rate of 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[6] 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 organosilicon compounds may proceed through pentacovalent silicon intermediates. The slow rate of hydrolysis of tri-1-naphthylsilyl chloride 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



$$\overset{\delta\oplus}{\mathrm{R_3Si}}\text{—}\overset{\delta\ominus}{\mathrm{Cl}} + \mathrm{HOH} \overset{\text{fast}}{\rightleftarrows} \mathrm{H}\text{—}\underset{\mathrm{H}}{\overset{\delta\oplus}{\mathrm{O}}}\text{—}\underset{\mathrm{R_2}}{\overset{\mathrm{R}}{\mathrm{Si}}}\text{—}\overset{\delta\ominus}{\mathrm{Cl}}\ (\mathrm{I}) \qquad (1)$$



$$(\mathrm{I}) + \mathrm{HOH} \xrightarrow{\text{slow}} \mathrm{H}\text{—}\underset{\mathrm{H}}{\overset{\delta\oplus}{\mathrm{O}}}\text{—}\underset{\mathrm{R_2}}{\overset{\mathrm{R}}{\mathrm{Si}}}\ \delta\oplus + \mathrm{Cl}\ominus\text{- - -}\mathrm{HOH} \qquad (2)$$

R = 1-naphthyl

The intermediate, I, may be formed with difficulty since the water molecule must encounter the bulky naphthyl groups in step (1).

However, the reactions studied by the previously mentioned workers[6,1d] were relatively rapid and it is possible that the S_N1 reaction was not evident only

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[1] (a) F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946); (b) H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947); (c) F. P. Price, *ibid.*, **69**, 2600 (1947); (d) L. J. Tyler, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2876 (1948); (e) W. H. Nebergall and O. H. Johnson, *ibid.*, **71**, 4022 (1949); (f) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

[2] Unpublished studies from this Laboratory by Dr. G. N. R. Smart.

[3] A test devised by F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 848 (1921), and modified by Gilman and Clark.[1b]

[4] Unpublished studies from this Laboratory by H. W. Melvin.

[5] I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 174 (1946).

[6] C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

because of the speed of the competing process. With tri-1-naphthylsilyl compounds the very slow rate indicates that the ionization process is strongly inhibited by changing carbon to silicon. It is possible that these compounds do react by ionization but if this is the case, the rate of ionization is of a completely different order of magnitude from that to be expected of the carbon analogs.

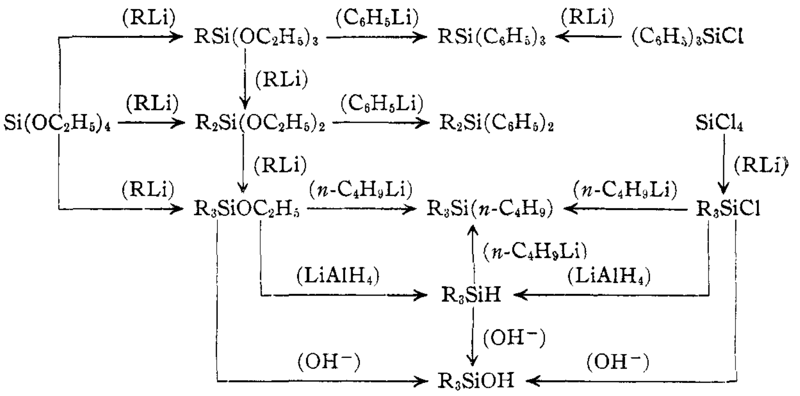
It was mentioned earlier that formic acid has been used for condensing silanols to the corresponding disiloxanes. This acid-catalyzed disiloxane formation may proceed as

$$R_3SiOH \xrightarrow{H^+} R_3SiOH_2^{\oplus} \xrightarrow{R_3SiOH} \left[R_3SiO\cdots\overset{H}{\underset{R_3}{Si}}\cdots.OH_2^{\oplus} \right] \longrightarrow R_3SiOSiR_3 + H_3O^{\oplus}$$

Brown and Sujishi[7] have demonstrated the steric requirements of tri-1-naphthylboron toward methyl amines and attribute this effect to the exceedingly high F-strain[7] factor. This type of strain, and B-strain,[8] 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.

SERIES OF REACTIONS FOR STRUCTURE PROOF OF 1-NAPHTHYLSILICON COMPOUNDS

$R = 1\text{-}C_{10}H_7\text{-}$



The compounds used in this study were prepared in the conventional manner by the action of organolithium reagents on silicon tetrachloride, ethyl silicate or trichlorosilane. However, the 1-naphthyllithium reagent was not made by the conventional method from 1-bromonaphthalene and lithium metal,[9] but was made by halogen–metal interconversion.[10] These syntheses afford a striking illustration of the value of the halogen–metal interconversion method of making organometallic reagent for preparative purposes. 1-Naphthyllithium made by the direct method, has been shown to give by-products[11] which are extremely difficult to eliminate whereas the reagent made from *n*-butyllithium and 1-bromonaphthalene gives a clean product. The acid obtained by carbonation of the former mixture contains a colored impurity while the acid obtained from the latter type of preparation gives an analytically pure product.

Structure proof for these compounds was obtained by the series of reactions shown schematically in the accompanying chart.

Acknowledgment.—The authors are grateful to Dr. G. S. Hammond for assistance.

Experimental

All reactions involving organometallic reagents were performed in an atmosphere of nitrogen in a three-neck flask fitted with a reflux condenser, motor stirrer with a glycerol seal, and a nitrogen inlet tube. Melting points are uncorrected unless otherwise noted and yields are calculated on the basis of the silicon compound used as a starting material.

1-Naphthyllithium (Halogen–Metal Interconversion).—Unless otherwise noted the 1-naphthyllithium preparations mentioned in this paper were made by this procedure. The effect of different solvents, etc., on the yield of this particular organometallic reagent is described elsewhere,[10] and this procedure is merely a standardization of technique. A typical preparation is described.

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[12] 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 ± 5° with a Dry Ice–acetone-bath. After about one quarter of the *n*-butyllithium solution had been added, a white solid[13] started separating from the mixture. The time for complete addition was 15 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 20 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°). If an ether slurry of Dry Ice was used, the acid, after the same treatment, was pure white and of excellent purity, m.p. 159–160°.

1-Naphthyltriethoxysilane.[14]—A slurry of 1-naphthyllithium (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 30 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 31.0 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°.

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[7] H. C. Brown and S. Sujishi, THIS JOURNAL, **70**, 2793 (1948).

[8] H. C. Brown, H. Bartholomay and M. D. Taylor, *ibid.*, **66**, 435 (1944).

[9] H. Gilman, E. A. Zoellner and W. M. Selby, *ibid.*, **54**, 1957 (1932).

[10] H. Gilman and F. W. Moore, *ibid.*, **62**, 1842 (1940).

[11] H. Gilman and C. G. Brannen, *ibid.*, **71**, 657 (1949).

[12] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *ibid.*, **71**, 1499 (1949).

[13] Qualitative experiments indicate that this solid is 1-naphthyllithium but to date the highest yield of 1-naphthoic acid obtained from carbonation of the apparently dry solid is 52%. More quantitative results will be published later.

[14] 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,[9] 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.

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° (cor.).

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°, 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° (cor.). A mixed melting point with the analyzed sample in A above showed no depression.

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°), and set aside to crystallize. White crystals, 32.4 g., m.p. 85–89°, formed overnight and were filtered from the mixture. Two crystallizations from petroleum ether (b.p. 90–115°) gave 28.2 g. (42%) of white solid, m.p. 100.5–101°. 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-naphthyldiethoxysilane, 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[9] was added to the ethyl silicate, the yield of colorless solid was low (12%). Since colored impurities are known to be present,[11] 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[9] from 1-bromonaphthalene and lithium metal). The orange-colored mixture was immediately poured into *ca.* 100 ml. of water, the layers were separated, and the solvent was replaced with benzene. After cooling the orange-colored 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 superheated steam.[15] 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.

Di-1-naphthyldiphenylsilane.—An ethereal solution of 0.72 g. (0.0019 mole) of di-1-naphthyldiethoxysilane was added 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 $C_{32}H_{24}Si$: Si, 6.43. Found: Si, 6.50, 6.48.

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 20 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 $C_{30}H_{21}ClSi$: Cl, 8.00; Si, 6.31. Found: Cl, 8.3, 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 of these runs low yields (10–30%) of tri-1-naphthylchlorosilane resulted. Since appreciable amounts (10–70%) of 1-*n*-butylnaphthalene[16] were isolated from the resulting oils, the reaction of 1-naphthyllithium with *n*-butyl bromide took place at a surprisingly fast rate. This coupling reaction is being investigated further.

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 20.8 g. (0.1 mole) of ethyl silicate in 50 ml. of ether was added with stirring over a period of 20 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. 290–310°, 15.0 g., was tri-1-naphthylethoxysilane, m.p. 185–186°. The crude yield was

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

(16) B.p. 287–288° at 745 mm., $n^{20}D$ 1.5811, d^{20}_4 0.977. These data are consistent with the constants reported by A. S. Bailey, G. B. Pickering and J. C. Smith, *J. Inst. Petroleum*, **35**, 105 (1949). Positive identification was made by melting point, 70–71°, and mixed m.p. 70–71°, of the trinitrobenzene complex. The authors are grateful to Dr. Bailey for supplying the reference sample of the trinitrobenzene complex of 1-*n*-butylnaphthalene.

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[17] 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.[9] 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.

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 30 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 Fischer 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 methyl cellosolve apparently plays an important role in this reaction. Other alcohols, ethanol and methanol, apparently do not effect this hydrolysis since they have been used for the recrystallization of tri-1-naphthylchlorosilane. This also appears to be more than a temperature effect since di-*n*-butyl ether (b.p. 142°) is an excellent solvent for the purification of tri-1-naphthylchlorosilane.

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 24 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 20 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°, with petroleum ether (b.p. 60–80°), there was obtained 2.4 g. (78%) of pure tri-1-naphthylsilanol, m.p. 208–209°. A mixed melting point with samples from A and B above showed no depression.

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 20 minutes. After stirring for one hour, the mixture, a red solution with a white precipitate, was poured 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.[16,18]—A mixture of the silicon compound in ether was added to an excess of lithium aluminum hydride in ether and refluxed for 30 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 and a 95% yield when tri-1-naphthylchlorosilane was used.

Tri-1-naphthyl-*n*-butylsilane. A. From Tri-1-naphthylchlorosilane and *n*-Buthyllithium.—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 1.2 *N* ethereal solution of *n*-butyllithium was added, and the mixture was refluxed for 20 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 $C_{34}H_{30}Si$: 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 24 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°, was recrystallized from 100 ml. of petroleum ether (b.p. 90–115°). This material was purified by exhaustive digestion[17] with small portions of cyclohexane. The final yield was 3.3 g. (71%) of pure tri-1-naphthyl-*n*-butylsilane, m.p. 187–188°.

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 12 hours. After pouring into water and removing the inorganic salts as above, 11.3 g. of yellow solid, m.p. 90–135°, was obtained. Attempts to purify by crystallization from a number of different solvents gave solids melting over the range 130–160°. 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°) and poured through 20 g. of alumina in a 1 cm. absorption 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 crystalli-

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[17] A. A. Morton, ref. 15, p. 228.

[18] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

zations 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.

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[19] was then negative. The mixture was poured into crushed ice and dilute hydrochloric acid and the layers were separated. The ether layer was steam distilled and the residue 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%), in three crops, of crude tri-1-naphthylchlorosilane, m.p. 201–203°, was recovered, which showed no depression of melting point when mixed with an authentic specimen.

1-*n*-Butylnaphthalene[16] was isolated from these runs. Apparently the failure of this experiment is 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[9] was mixed with tri-1-naphthylchlorosilane and baked at 150–180° for three days, no isolable products have yet been obtained from the black tars. However, tetra-*o*-tolylsilane was obtained under similar conditions and it is possible that tetra-1-naphthylsilane may yet be made by modifying the conditions.

Tri-1-naphthylsilanol and Formic Acid.—Ten grams (0.023 mole) of tri-1-naphthylsilanol and 100 ml. of 99–100% formic acid were mixed and refluxed for 15 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.

Tri-1-naphthylsilane and Potassium Hydroxide in Piperidine.[3]—The reagent was made by dissolving one pellet of 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.

In connection with some rate studies by G. E. Dunn, this evolution of hydrogen has been observed in a series of non-sterically-hindered silanes.

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° 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°, and showed no depression of melting point when mixed with an authentic specimen.

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[19] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2202 (1925).

[CONTRIBUTION OF THE CARVER FOUNDATION, TUSKEGEE INSTITUTE]

A Study of the Friedel–Crafts Synthesis with Alkoxychloroalkanes[1]

BY CLARENCE T. MASON AND LEWIS A. GIST, JR.

The behavior of alkoxychloroalkanes in a Friedel–Crafts reaction with benzene under varying conditions is used to explain the apparent discrepancies found in the earlier literature. The reaction does not take place through disproportionation of the alkoxychloromethane since: (1) dichloromethane could not be isolated, and (2) dibutoxymethane does not react in the Friedel–Crafts reaction under conditions comparable to those used for the alkoxychloromethane. Under similar conditions, alkoxychloromethanes and alkoxy-1-chloroethanes give analogous reactions, indicating that the mechanism of the reaction does not involve the elimination of hydrogen chloride to give an intermediate vinyl ether. The chlorine in alkoxy-1-chloroalkanes can react with benzene at low temperatures to give benzyl alkyl ethers, while under the same conditions the chlorine in 1-alkoxy-2-chloroethane does not react. Under more drastic conditions the latter suffers rupture of the carbon–oxygen bond.

Introduction

The stability of alkoxychloromethanes in the presence of easily hydrolysable metal halides has already been established,[2a,b,3,4] but at different temperatures, reaction times, and catalyst concentrations, many products are possible resulting from chloromethylation, condensation, polymerization, and decomposition of the alkoxychloromethane.

Verley[2a] reported isolating diphenylmethane as the chief product of the reaction of ethoxychloromethane with an excess of benzene in the presence of aluminum chloride and showed the presence of benzyl chloride and small amounts of benzyl ethyl ether. The latter he postulated as being split to give benzyl chloride, which condensed with the benzene to give diphenylmethane.

$$\mathrm{ClCH_2OEt} \xrightarrow[\mathrm{AlCl_3}]{\mathrm{C_6H_6}} \mathrm{C_6H_5CH_2OEt} \xrightarrow[\mathrm{AlCl_3}]{\mathrm{HCl}}$$

$$\mathrm{C_6H_5CH_2Cl} \xrightarrow[\mathrm{AlCl_3}]{\mathrm{C_6H_6}} \mathrm{(C_6H_5)_2CH_2}$$

Huston and Friedemann,[5] using the same reactants, found anthracene and diphenylmethane as the chief products, but did not isolate benzyl

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[1] A portion of this paper was presented before the Organic Section of the American Chemical Society, September, 1950.

[2] (a) M. A. Verley, *Bull. soc. chim.*, [3] **17**, 914 (1897); (b) M. Sommelet, *Compt. rend.*, **157**, 1443 (1913).

[3] E. I. du Pont de Nemours and Co., British Patent 423,520, Feb. 4, 1935; *C. A.*, **29**, 4374^9 (1935).

[4] F. Straus and T. Thiel, *Ann.*, **525**, 151 (1936).

[5] R. C. Huston and T. E. Friedemann, THIS JOURNAL, **38**, 2527 (1916).