[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Some Organosilicon Compounds Containing Long-Chained *n*-Alkyl Groups

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A series of tetra-*n*-alkyl-, tri-*n*-alkylaryl-, and *n*-alkyltriarylsilanes, as well as intermediate compounds, have been prepared for potential use as hydraulic fluids or lubricants. Each compound contains at least one long-chained *n*-alkyl group having from ten to eighteen carbon atoms. Some aspects of the various means of preparing these compounds are discussed.

In connection with a study on the preparation of potential hydraulic fluids and lubricating oils, the authors have prepared a series of tetra-*n*-alkyl-, tri-*n*-alkylaryl-, and *n*-alkyltriarylsilanes. For the most part, the *n*-alkyl groups are of the long-chained variety containing from ten to eighteen carbon atoms per group.[1] Other organosilicon compounds having long-chained *n*-alkyl groups have been prepared in this and other laboratories as part of a general synthetic program.[2,3]

The *n*-alkyltriarylsilanes were prepared by the four basic procedures illustrated in equations I, IIa, IIb, and III (R = an alkyl group, Ar = an aryl group and X = Br or Cl).

$$\mathrm{Ar_3SiH + RCH{=}CH_2 \longrightarrow Ar_3SiCH_2CH_2R} \qquad \text{(I)}$$

$$\mathrm{RLi + Ar_3SiCl \longrightarrow Ar_3SiR + LiCl} \qquad \text{(IIa)}$$

$$\mathrm{3\ ArLi + RSiCl_3 \longrightarrow Ar_3SiR + 3LiCl} \qquad \text{(IIb)}$$

$$\mathrm{RX + Ar_3SiK \longrightarrow Ar_3SiR + KX} \qquad \text{(III)}$$

Thus, *n*-decyltriphenylsilane was prepared by method I from *n*-decene-1 and triphenylsilane, by method IIa from *n*-decyllithium and chlorotriphenylsilane and by method III from triphenylsilylpotassium and *n*-decyl bromide. Other related compounds, namely, *n*-dodecyl-, *n*-tetradecyl-, *n*-hexadecyl-, and *n*-octadecyltriphenylsilane, have already been reported;[2b] these compounds were prepared by both methods I and IIa; *n*-heptadecyltriphenylsilane also was made by method IIa. Preparations of *n*-dodecyl- and *n*-octadecyltriphenylsilane, previously reported,[2b] have now been made by method III. The comparative yields obtained by methods I, IIa, and III are given in Table I. *n*-Dodecyltri-*m*-tolylsilane was made using method IIb, *i.e.*, from *m*-tolyllithium and trichloro-*n*-dodecylsilane. The yield was 49%.

TABLE I

PREPARATION OF *n*-ALKYLTRIPHENYLSILANES BY METHODS I, IIa, AND III[a]

	Yield, %		
R (in $RSiPh_3$)	Method I	Method IIa	Method III
n-Decyl	25	75	6
n-Dodecyl	46[b]	67,[b] 67	33
n-Tetradecyl	52[b]	50[b]	. .
n-Hexadecyl	45[b]	30[b]	. .
n-Heptadecyl	. .	43[b]	. .
n-Octadecyl	40[b]	70,[b] 41	6

[a] See text for discussion of the methods. [b] See Ref. 2b for experimental data of these preparations.

The preparation of tri-*n*-alkylarylsilanes in the laboratory also may be carried out in a variety of ways. Methods analogous to I and III are not often, if ever, used because of the difficulty in adding more than one molecule of an olefin to a molecule of the $ArSiH_3$ type[4] and because of the lack of a good preparative method for pure trialkylsilyllithium compounds.[5] However, there are several preparative methods related to methods IIa and IIb; these are given as Equations IV and V (M and M′ = Li or MgBr; X = Cl, Br or H, the latter in Equation V when M′ = Li; R = an alkyl group and Ar = an aryl group). The choice between method IV or V will depend on the availability and reactivity of the various pairs of reagents.

$$\mathrm{3\ RM + ArSiX_3 \longrightarrow R_3SiAr + 3\ MX} \qquad \text{(IV)}$$

$$\mathrm{ArM' + R_3SiX \longrightarrow R_3SiAr + M'X} \qquad \text{(V)}$$

The organometallic compounds (RM and ArM′) are easily prepared in most cases, and the organic halides necessary for the preparations are usually commercially available. However, neither of the two types of silicon containing compounds, R_3SiX or $ArSiX_3$, is available commercially with the obvious exceptions of compounds containing short-

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(1) See, however, R. H. Meen and H. Gilman, *J. Org. Chem.*, **23**, 314 (1958) for some organosilicon compounds containing intermediate-length alkyl groups.

(2) (a) H. Rosenberg, C. Tamborski, J. D. Groves, and E. J. Bartholomew, Wright Air Development Center Technical Report **54-613**, Part I (1955), Part II (1956) and Part III (1957); (b) H. Merten and H. Gilman, *J. Am. Chem. Soc.*, **76**, 5798 (1954); (c) H. Gilman and R. K. Ingham, *J. Am. Chem. Soc.*, **77**, 1680 (1955); (d) H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **21**, 1307 (1956); (e) H. Gilman and D. Miles, *J. Org. Chem.*, **21**, 254 (1956); (f) H. Gilman and J. J. Goodman, *J. Org. Chem.*, **22**, 45 (1957).

(3) H. Gilman and D. H. Miles, unpublished studies.

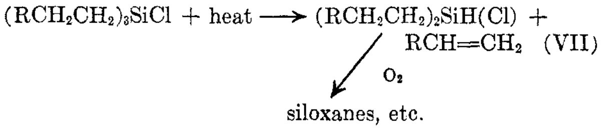
(4) See, however, J. L. Speier, R. Zimmerman, and J. A. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956) for compounds made by adding more than one equivalent of olefin to a silicon hydride compound.

(5) See, for instance, C. A. Eaborn, *J. Chem. Soc.*, 2755 (1949), and H. Gilman, R. K. Ingham, and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953) for preparations and attempted preparations of trialkylsilylmetallic compounds and for references related thereto. See also, H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 607, 608 (1958) for related work.

chained alkyl or phenyl groups.[6] Thus, to prepare a series of tri-*n*-alkylarylsilanes one must either prepare a series of $ArSiX_3$ compounds or a few R_3SiX compounds. The latter choice was preferable to the authors, and they set out to prepare one such tri-*n*-alkylhalosilane, *i.e.*, chlorotri-*n*-hexadecylsilane. Several preparations of this compound were carried out by reaction VI ($R = C_{16}H_{33}$).

$$RSiCl_3 + 2\ RMgBr \longrightarrow R_3SiCl + \text{Mg salts} \quad \text{(VI)}$$

However, during repeated distillations of the product, significant decomposition into two lower boiling materials (in addition to the product) was detected. The lowest boiling material has been tentatively identified as *n*-hexadecene-1 as shown in Table II. The other by-product contained silicon and the infrared spectrum of this impure material indicated it to contain Si—H and Si—O—Si bonds. It is possible that a thermal decomposition such as depicted in Equation VII might have occurred. Such decompositions were observed somewhat earlier at the Wright Air Development Center[7]; Schmidt and Krimmel[8] also found a similar reaction of alkyl-*m*-terphenyl compounds, in which an *alhpa*-olefin was tentatively identified as a decomposition product.



$$(RCH_2CH_2)_3SiCl + \text{heat} \longrightarrow (RCH_2CH_2)_2SiH(Cl) + RCH{=}CH_2 \quad \text{(VII)}$$
$$(RCH_2CH_2)_2SiH(Cl) \xrightarrow{O_2} \text{siloxanes, etc.}$$

The crude chlorotri-*n*-hexadecylsilane made by method VI was used in some preliminary experiments before the impurity was discovered. These experiments were repeated later with material prepared as illustrated in Equations VIII and IX

$$3\ RMgBr + HSiCl_3 \longrightarrow HSiR_3 + MgClBr \quad \text{(VIII)}$$
$$HSiR_3 + Cl_2 \longrightarrow ClSiR_3 + HCl \quad \text{(IX)}$$

($R = C_{16}H_{33}$). This procedure for the preparation of chlorotrialkylsilanes was brought to the attention[7] of the authors during the course of this research and was found to be superior to the method formerly tried. The more recent procedure was used to prepare chlorotri-*n*-hexadecyl-, chlorotri-*n*-decyl-, and tri-*n*-butylchlorosilane with the only difficulty being incomplete chlorination during the first attempt to prepare the tri-*n*-decyl compound. There are several advantages of the two-step method. For instance, the silicon-hydride bond in silicochloroform is relatively unreactive toward a Grignard reagent; hence excess Grignard reagent may be used to assure complete conversion to a trialkylsilane. Since the silicon-hydrogen bond is only slightly effected during acid hydrolysis, the reaction mixture from method VIII may be hydrolyzed and the product extracted with ether (thus eliminating the difficult filtration of the magnesium salts under a nitrogen atmosphere such as is necessary in reaction VI). In many cases the chlorination step is not necessary since reaction V (X is H, M′ is Li) will take place[9] unless steric hindrance or other factors interfere. Thus, the authors prepared tri-*n*-butylphenyl- and tri-*n*-hexadecylphenylsilane from phenyllithium and the corresponding tri-*n*-alkylsilane; however, it was found that the sterically-hindered organolithium compounds, specifically 2-biphenylyllithium, would not react with tri-*n*-butyl-, tri-*n*-decyl-, nor tri-*n*-hexadecylsilane even under some forcing conditions.

TABLE II

COMPARISON OF *n*-HEXADECENE-1 AND THE LOWEST BOILING FRACTION FROM DISTILLATIONS OF CHLOROTRI-*n*-HEXADECYLSILANE

Property	*n*-Hexadecene-1	Literature[a]	Fraction 1[b]	Redistilled Fraction 1[b]
Infrared Spectra	Nearly identical to fraction 1	. . .	Nearly identical to *n*-hexadecene-1	. . .
n_D^{20}	1.4410	1.4419	1.4395	1.4395[c]
B.p., °C.	150–160/15 mm.	157/15 mm.	100–110/0.05 mm.	150–153/13 mm.
Br_2/CCl_4	Decolorizes[d]	. . .	Decolorizes	Decolorizes
MnO_4^-/Me_2CO	Decolorizes when hot	. . .	Decolorizes when cold	Decolorizes when hot

[a] H. T. Waterman, P. Van't Spikjer, and H. A. Van Weston, *Rec. trav. chim.*, *48*, 1103 (1929). [b] Fraction 1 is the lowest boiling fraction from the original distillation, while "Redistilled Fraction 1" is the material collected in a third distillation of the highest boiling fraction from chlorotri-*n*-hexadecylsilane. [c] The refractive index at 25° of fraction 1 from the distillation of 20 g. of chlorotri-*n*-hexadecylsilane was 1.4395; an approximation to 20° would be 1.4410. [d] It requires 42 drops of 5% solution of bromine in carbon tetrachloride to react with 0.5 ml. of each of these compounds.

The tri-*n*-alkylarylsilanes, prepared from the above reagents utilizing procedures IV and V, included 2-biphenylyltri-*n*-decyl-, 2-biphenylyltri-*n*-hexadecyl-, tri-*n*-hexadecylphenyl-, tri-*n*-dodecylphenyl-, *p*-chlorophenyltri-*n*-hexadecyl-, tri-*n*-hexadecyl-*p*-phenoxyphenyl-, and 4-biphenylyltri-*n*-hexadecylsilane. In addition, 1,1,1-triphenyl-2,2,2-tri-*n*-hexadecyldisilane was made by reaction of triphenylsilyllithium in tetrahydrofuran solution with chlorotri-*n*-hexadecylsilane. Tri-*n*-butylphenyl-

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(6) Anderson Laboratories, Inc., Weston, Mich., have prepared small batches of chlorotri-*n*-dodecylsilane for the authors.

(7) Dr. H. Rosenberg, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, private communication. Also see K. Shiina and M. Kumada, *J. Org. Chem.*, **23**, 139 (1958), for a thermal rearrangement of some organosilicon compounds.

(8) J. J. E. Schmidt and J. A. Krimmel, Denver Research Institute, Wright Air Development Center Technical Report for period of January 15 to April 15, 1957, preprint copy.

(9) R. N. Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946); H. Gilman and S. P. Massie, Jr., *J. Am. Chem. Soc.*, **68**, 1128 (1946); and H. Gilman and H. W. Melvin, Jr., *J. Am. Chem. Soc.*, **71**, 4050 (1949).

silane was prepared, as mentioned earlier, mainly to serve as a model preparation for the long chain compounds made by method V (M′ = Li, X = H).

Five tetraalkylsilanes were prepared, namely, tetra-*n*-dodecyl-, tetra-*n*-tetradecyl-, dibenzyldi-*n*-octadecyl-, di-*n*-octadecylbis(γ-phenylpropyl)-, and *n*-butyltri-*n*-hexadecylsilane. The two tetra long-chained compounds were made from the alkylmagnesium bromide reagents and silicon tetrachloride, while the dialkyldialkyl compounds were made by reactions of benzylmagnesium chloride and γ-phenylpropylmagnesium bromide with dichlorodi-*n*-octadecylsilane. The *n*-butyltri-*n*-hexadecylsilane was made from *n*-butyllithium and chlorotri-*n*-hexadecylsilane.

In addition to making tri-*n*-hexadecylsilane (in 70% yield) by method VIII, it was made also by reaction of crude chlorotri-*n*-hexadecylsilane with lithium aluminum hydride (in 58% yield). Tri-*n*-dodecylphenylsilane was made from phenyllithium and chlorotri-*n*-hexadecylsilane (method V) and from *n*-dodecylmagnesium bromide and trichlorophenylsilane (method IV) in yields of 48 and 51%, respectively.

In preliminary thermal screening tests carried out by heating a small amount of the various compounds in a capillary tube mounted in a copper melting point block, none of the compounds containing long-chained *n*-alkyl groups was found to volatilize above 480°. Some of them showed significant decomposition below this temperature. It is possible that thermal decomposition such as that depicted in Equation VI occurs, and hence is a limiting factor in the thermal stability of organosilicon compounds containing long-chained *n*-alkyl groups.

EXPERIMENTAL[10]

Tri-n-butylsilane. Trichlorosilane (100 g., 0.738 mole), cooled in a Dry Ice–acetone bath, was allowed to react with 0.257 mole of *n*-butylmagnesium bromide in 1800 ml. of ether by addition of the Grignard reagent to the chlorosilane. After stirring for 3 hr., the mixture was hydrolyzed by pouring into a mixture of crushed ice and 100 ml. of hydrochloric acid. Work-up by extraction with 2 portions of ether, drying of the combined extracts and organic layer over sodium sulfate, filtration, and then distillation of the solvent was followed by distillation through a Widmer column; this afforded 110 g. (74%) of a colorless liquid, boiling at 215–220°, n_D^{20} 1.4380, d_4^{20} 0.7788.

Anal. Calcd. for $C_{12}H_{28}Si$: MR_D,[11] 67.88. Found: MR_D, 67.55.

Jenkins and Post[12] report the preparation (5% yield) of tri-*n*-butylsilane, b.p. 86–87°/2.5 mm., n_D^{20} 2.5 mm., n_D^{20} 1.4400, d_{25}^{25} 0.9312. Calculation of the MR_D value using the data of Jenkins and Post for the index of refraction and density gave a value of 56.4, which does not agree with the theoretical value of 67.55.[11]

Tri-n-decylsilane. *n*-Decylmagnesium bromide (0.89 mole, 89% yield) was prepared and added to 42 g. (0.28 mole) of trichlorosilane in the manner just described. Hydrolysis and work-up in the same manner as for tri-*n*-butylsilane, using a Claisen-type flask for the distillation, yielded 66.2 g. (61%) of colorless oil, boiling over the range of 206–210°/0.005 mm., n_D^{20} 1.4582.

Anal.[13] Calcd. for $C_{30}H_{64}Si$: Si, 6.20. Found: Si, 6.18.

Tri-n-hexadecylsilane. In a manner similar to the two previous experiments, 0.87 mole of *n*-hexadecylmagnesium bromide and 0.237 mole of trichlorosilane in 500 ml. of ether were allowed to react. Work-up yielded 117.8 g. (70.5%) of an oil, boiling at 300–305°/0.008 mm., which solidified to a white waxy solid, m.p. 34–36°.

Anal. Calcd. for $C_{48}H_{100}Si$: Si, 3.98. Found: Si, 4.08, 4.08.

An impure sample of the same compound was made by the reaction of 18.5 g. (0.025 mole) of chlorotri-*n*-hexadecylsilane with 0.7 g. (0.0185 mole) of lithium aluminum hydride in 40 ml. of ether. The yield was 10.4 g. (58%) of a white waxy material, m.p. 33–35°.

Chlorotri-n-butylsilane. A solution of 41.5 g. (0.206 mole) of tri-*n*-butylsilane in 100 ml. of carbon tetrachloride was allowed to react, using ice cooling, with 25 g. (0.35 mole) of chlorine gas. After the theoretical amount of chlorine had passed through the solution, the reaction mixture became yellow. Distillation of the solvent and then of the crude oil, avoiding contact with moisture, gave 33.5 g. (75%) of a colorless oil, boiling at 134–139°/16 mm.

Anal.[14] Calcd. for $C_{12}H_{27}ClSi$: Cl, 15.0. Found: Cl, 14.75, 14.75.

Chlorotri-*n*-butylsilane has been made by at least two other methods. Gilman and Marshall[15] made it in 51% yield by reaction of ethyl orthosilicate with *n*-butylmagnesium bromide to form ethoxytriethylsilane, acidification to give the disiloxane and finally treatment with ammonium chloride in sulfuric acid to give tri-*n*-butylchlorosilane. In 1952, Noller and Post[16] and Petrov and Chernyshev[17] prepared it by direct reaction of silicon tetrachloride with *n*-butylmagnesium bromide.

Chlorotri-n-decylsilane. As in the previous example, chlorine gas (a total of 0.7 mole) was allowed to react with 0.14 mole of tri-*n*-decylsilane. Distillation of the solvent and then of the residual oil yielded 35 g. (51.3%) of product, boiling over the range 240–250°/1.0 mm.

Anal. Calcd. for $C_{30}H_{63}ClSi$: Cl, 7.27. Found: Cl, 7.30, 7.35.

Chlorotri-n-hexadecylsilane. A. From tri-n-hexadecylsilane. As in the previous two examples, chlorine gas (0.2 mole) and 0.167 mole of tri-*n*-hexadecylsilane in 75 ml. of carbon tetrachloride were allowed to react. The yield of product was *ca.* 80% with a boiling range of 275–280°/0.005 mm.

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[10] All melting points are uncorrected. Preparations utilizing reactive organometallic compounds or chlorosilanes were carried out under a dry, oxygen-free nitrogen atmosphere.

[11] Molecular refractions were calculated using the values reported by A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *Chem. & Ind.* (*London*), 358 (1950); 376 (1951); *J. Chem. Soc.*, 514 (1952); W. T. Cresswell, J. Leicester, and A. I. Vogel, *Chem. & Ind.* (*London*), 19 (1953); *J. Phys. Chem.*, **58**, 174 (1954).

[12] J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 552 (1950).

[13] The silicon content was determined by the method of H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

[14] The hydrolyzable chlorine was determined by titrating *ca.* 0.1-g. samples dissolved in a mixture of 50 ml. of absolute ethanol and 50 ml. of ether, using 0.1*N* sodium hydroxide as the titrant.

[15] H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

[16] D. C. Noller and H. W. Post, *J. Am. Chem. Soc.*, **74**, 1361 (1952).

[17] A. D. Petrov and E. A. Chernyshev, *Doklady Akad. Nauk S.S.S.R.*, **86**, 737 (1952) [*Chem. Abstr.*, **47**, 8010 (1953)].

An infrared spectrum indicated that all the silane had reacted. No decomposition was noted as in the compound prepared by method B, possibly due to the slightly lower distillation temperature.

B. From trichloro-n-hexadecylsilane. Several different preparations from trichloro-*n*-hexadecylsilane and *n*-hexadecylmagnesium bromide gave yields of *ca.* 45%. A typical preparation is given.

n-Hexadecylmagnesium bromide (0.804 mole) in 400 ml. of ether was added to 130 g. (0.336 mole) of trichloro-*n*-hexadecylsilane in ether. The mixture was stirred at ether reflux for 3 days. The ether then was replaced by 400 ml. of xylene and the mixture refluxed overnight. The solution was filtered in a nitrogen pressure apparatus which had been thoroughly dried. The solvents were distilled from the filtrate leaving an oil. This was distilled at reduced pressure giving three fractions, 25 g., boiling at 100–110°/0.05 mm.; 25 g., boiling at 230–235°/0.1 mm.; and 150–200 g., boiling at 320°/0.1 mm. Redistillation of the last fraction again gave three fractions: 1, boiling over the range 92–107°/0.05 mm.; 2, boiling over the range 230–265°/0.05 mm.; and 3, 118 g., boiling at 295–300°/0.05 mm. Since it appeared that decomposition was taking place during the distillation, 20 g. of the product was redistilled and again three fractions of similar boiling ranges to those of the preceding distillations were obtained. The low boiling fraction tentatively was identified as an *alpha*-olefin, presumably 1-hexadecene (see Table II). The second fraction appears on the basis of infrared spectra to be an Si—H type compound, while the high boiling material is slightly impure product contaminated with Si—H and Si—O—Si components.

Anal. Calcd. for $C_{48}H_{99}ClSi$: Si, 3.80. Found: Si, 3.79, 3.59.

Tetra-n-dodecylsilane. *n*-Dodecylmagnesium bromide (1.7 moles, made in 85% yield) was prepared as usual in 1100 ml. of ether and then added slowly to 44 g. (0.26 mole) of silicon tetrachloride in 250 ml. of xylene. After stirring overnight at reflux, the ether was distilled as completely as possible and replaced by additional xylene. The resulting suspension was refluxed with stirring for 80 hr., cooled, and then hydrolyzed by the addition of saturated ammonium chloride solution. The layers were separated; the water layer was extracted with two large portions of ether; the combined organic layers were dried over sodium sulfate; and the solvent, after filtration of the sodium sulfate, was distilled. The resulting oil was distilled at reduced pressure to yield 150 g. (82%) of product boiling over the range of 240–250°/0.06 mm. This was redistilled in a Hickman molecular still using a sand-bath temperature of 370° at a pressure of 0.03 mm. This gave 145 g. (79%) of product, n_{D}^{27} 1.4633, d_{27}^{27} 0.8304.

Anal. Calcd. for $C_{48}H_{100}Si$: Si, 3.98; MR$_{\text{D}}$, 234.7. Found: Si, 4.39, 4.40; MR$_{\text{D}}$, 234.7.

Tetra-n-tetradecylsilane. In a method similar to the previous example, 0.149 mole of *n*-tetradecylmagnesium bromide in 250 ml. of ether was added to 0.037 mole of silicon tetrachloride. After stirring at reflux for 4 hr., most of the ether was distilled (not replaced by xylene as in the previous example) and the material was heated in the absence of any added solvent at 150–160° for 4 hr., cooled, the original ether added and the mixture refluxed overnight. Work-up as in the previous example (no molecular distillation) gave 12 g. (40%) of an oil, b.p. 253–255°/0.6 mm., n_{D}^{27} 1.4590, d_{27}^{27} 0.831.

Anal. Calcd. for $C_{56}H_{116}Si$: C, 82.26; H, 14.30; Si, 3.44; MR$_{\text{D}}$, 271.89. Found: C, 81.88, 82.01; H, 14.37, 14.47; Si, 3.56, 3.66; MR$_{\text{D}}$, 269.2.

Dibenzyldi-n-octadecylsilane. Benzylmagnesium chloride (0.068 mole) was prepared in the usual manner (96% yield) and then added to 12.1 g. (0.02 mole) of dichlorodi-*n*-octadecylsilane dissolved in 100 ml. of sodium-dried xylene. The ether (from the Grignard preparation) was distilled as completely as possible, and the reaction mixture was then refluxed for 7 hr. The cooled mixture was hydrolyzed by the addition of 100 ml. of 3*N* hydrochloric acid solution and then worked up by extractive procedures similar to those described previously and the product distilled under reduced pressure to yield 7.8 g. (54.5%) of an oil, boiling at 317–322° (0.9 mm.), n_{D}^{20} 1.5005.

Anal. Calcd. for $C_{50}H_{88}Si$: Si, 3.92. Found: Si, 3.92, 4.05.

Di-n-octadecylbis(γ-phenylpropyl)silane. Twelve and one-tenth grams (0.02 mole) of dichlorodi-*n*-octadecylsilane in 50 ml. of sodium-dried xylene was reacted with 0.05 mole of γ-phenylpropylmagnesium bromide in 70 ml. of ether (the Grignard reagent was prepared in the normal way in 71% yield). The reaction was carried out as in the previous experiment and worked up in the usual manner. Distillation under reduced pressure yielded 4.8 g. (31%) of an oil, boiling at 275–282° (0.001 mm.), n_{D}^{20} 1.4921, d_4^{20} 0.8872.

Anal. Calcd. for $C_{54}H_{96}Si$: Si, 3.63; MR$_{\text{D}}$,[11] 255.0. Found: Si, 3.83, 3.73; MR$_{\text{D}}$, 254.86.

n-Butyltri-n-hexadecylsilane. *n*-Butyllithium[18] (0.019 mole) was added with stirring to 14.0 g. (0.019 mole) of chlorotri-*n*-hexadecylsilane. After stirring the ethereal solution overnight, Color Test I[19] was still positive. After stirring for one more hour, the mixture was hydrolyzed by the addition of a saturated ammonium chloride solution. Work-up in the usual fashion left *ca.* 15.0 g. of white solid which could not be crystallized satisfactorily. After distilling the ethyl acetate–ethanol mixture used for the attempted crystallization, the residual material was distilled twice at reduced pressure to yield 4.4 g. (29.0%) of an oil, boiling at 270–280°/0.001 mm.

Anal. Calcd. for $C_{52}H_{108}Si$: Si, 3.69; MR$_{\text{D}}$, 253.75. Found: Si, 3.63, 3.64; MR$_{\text{D}}$, 251.58.

Tri-n-butylphenylsilane. Phenyllithium (0.038 mole) and 0.035 mole of tri-*n*-butylsilane were refluxed together for 6 hr. A white precipitate slowly formed during this period. When Color Test I[19] was negative, the mixture was hydrolyzed and worked up as usual. Reduced pressure distillation gave 3.2 g. (33.2%) of tri-*n*-butylphenylsilane, b.p. 163–166°, n_{D}^{20} 1.4940, d_4^{20} 0.8757. Reported values[15] are n_{D}^{20} 1.4891 and d_4^{20} 0.8719.

2-Biphenylyltri-n-alkylsilanes. A. From chlorotri-n-alkylsilanes. Two 2-biphenylyltri-*n*-alkylsilanes, 2-biphenylyltri-*n*-hexadecyl-, and 2-biphenylyltri-*n*-decylsilane were prepared by method A. The former preparation is here described; the other compound was prepared in a similar manner and the product (b.p. 235–238°/0.001 mm., n_{D}^{20} 1.5096, d_4^{20} 0.909) obtained in a 25% yield. The analyses for both compounds are given.

Chlorotri-*n*-hexadecylsilane (4.8 g., 0.02 mole) was allowed to react with 2-biphenylyllithium (0.015 mole, prepared by direct reaction of 2-bromobiphenyl with lithium metal) in ethereal solution. The mixture was refluxed overnight and then the ether was distilled and replaced by 100 ml. of toluene. After refluxing for 8 hr. Color Test I[19] was negative. Another 0.015 mole of 2-biphenylyllithium was added and reflux continued (with distillation of the ether) for 48 hr. Color Test I was again negative, so the mixture was hydrolyzed and worked up in the usual manner. The biphenyl present in the product was removed by vacuum sublimation at 5 mm., and the resulting oil distilled to yield 41% of product, b.p. 283–290°/0.001 mm., n_{D}^{20} 1.4840, d_4^{20} 0.870.

Anal. Calcd. for $C_{42}H_{72}Si$: (2-biphenylyltri-*n*-decylsilane): Si, 4.64; MR$_{\text{D}}$, 198.43. Found: Si, 4.66, 4.56; MR$_{\text{D}}$, 198.02.

Anal. Calcd. for $C_{60}H_{108}Si$ (2-biphenyltri-*n*-hexadecylsilane): Si, 3.27; MR$_{\text{D}}$, 283.40. Found: Si, 3.44, 3.48; MR$_{\text{D}}$, 282.8.

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(18) Prepared by method of 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) using a temperature of −40 to −30°.

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

2-Biphenylyltri-n-alkylsilanes. B. From tri-n-alkylsilanes (attempted). Using conditions similar to those described for the preparation of 2-biphenyltri-*n*-hexadecylsilane from the chlorosilane in the preceding experiment but refluxing in toluene for 9 days failed to yield any of the desired product when tri-*n*-butylsilane, tri-*n*-decylsilane, and tri-*n*-hexadecylsilane were reacted with 2-biphenylyllithium.

Tri-n-dodecylphenylsilane. A. From phenyllithium and chlorotri-n-dodecylsilane. Phenyllithium (0.01 mole) and 5.0 g. (0.0088 mole) of chlorotri-*n*-dodecylsilane[6] were allowed to react. After stirring overnight, Color Test I was negative, and the mixture was hydrolyzed with water and worked up in the usual way to yield 2.6 g. (48.2%) of product, b.p. 224–225°/0.001 mm., n_D^{20} 1.4673.

B. From n-dodecylmagnesium bromide and trichlorophenylsilane. n-Dodecylmagnesium bromide (0.16 mole) in 160 ml. of ether was reacted with 8.5 g. (0.04 mole) of trichlorophenylsilane in 20 ml. of toluene. The ether was distilled and an additional 130 ml. of toluene added. After refluxing overnight, the mixture was cooled, hydrolyzed, and worked up as usual. Reduced pressure distillation of the product afforded 12.5 g. (51%) of product, b.p. 250–253°/0.001 mm., n_D^{20} 1.4800, d_4^{20} 0.8595.

Anal. Calcd. for $C_{42}H_{58}Si$: Si, 4.58; MR_D, 202.89. Found: Si, 4.65, 4.77; MR_D, 201.3.

Tri-n-hexadecylphenylsilane. A. From trichlorophenylsilane. In essential accordance with the procedure just described, 0.1 mole of *n*-hexadecylmagnesium bromide and 0.0187 mole of trichlorophenylsilane were refluxed together in toluene-ether mixtures. Work-up yielded 6.0 g. (42%) of product, b.p. 279°/0.2 mm., n_D^{20} 1.4897, d_{27}^{27} 0.857.

Anal. Calcd. for $C_{54}H_{104}Si$: C, 82.99; H, 13.41; Si, 3.60. Found: C, 83.11, 83.27; H, 13.39, 13.39; Si, 3.66, 3.38.

B. From tri-n-hexadecylsilane. Phenyllithium (0.02 mole) and 0.014 mole of tri-*n*-hexadecylsilane were reacted together in the same manner as were phenyllithium and tri-*n*-butylsilane (described earlier) to yield 29% of an oil, boiling over the range 223–230°/0.003 mm., n_D^{20} 1.4804.

p-Chlorophenyltri-n-hexadecylsilane. *p*-Chlorophenyllithium[20] was prepared by the halogen-metal interconversion of 3.8 g. (0.02 mole) of *p*-bromochlorobenzene and 20 ml. (0.02 mole) of *n*-butyllithium at −10 to −20°. To this stirred mixture was added 11.1 g. (0.015 mole) of chlorotri-*n*-hexadecylsilane and stirring was continued until the mixture reached room temperature. Work-up in the usual manner afforded 10.1 g. (82%) of product, b.p. 295–300°/0.005 mm.; redistillation gave 7.5 g. (61%) of an oil, b.p. 250°/0.001 mm., n_D^{20} 1.4855, d_4^{20} 0.882.

Anal. Calcd. for $C_{54}H_{103}ClSi$: Si, 3.44; MR_D, 266.15. Found: Si, 3.48, 3.49; MR_D, 265.38.

Tri-n-hexadecyl-p-phenoxyphenylsilane. Using a method similar to that described for *p*-chlorophenyltri-*n*-hexadecylsilane, *p*-phenoxyphenyllithium[20] (0.045 mole prepared from *p*-bromophenyl phenyl ether and *n*-butyllithium) and 0.035 mole of chlorotri-*n*-hexadecylsilane were found to yield 58.5% of product, boiling at 305–315°/0.005 mm., n_D^{20} 1.4960, d_4^{20} 0.897.

4-Biphenylyltri-n-hexadecylsilane. 4-Biphenylyllithium (0.025 mole) and 13.3 g. (0.018 mole) of chlorotri-*n*-hexadecylsilane were stirred together for 15 min., hydrolyzed, and worked up in the usual manner to yield 6.2 g. (40.2%) of product, boiling at 310–323°/0.002 mm.; redistillation gave 4.15 g. (27%) of product, boiling at 300–310°/0.001 mm., n_D^{20} 1.5000, d_4^{20} 0.884.

Anal. Calcd. for $C_{60}H_{108}Si$: Si, 3.27; MR_D, 283.40. Found: Si, 3.36, 3.56; MR_D, 285.50.

1,1,1-Triphenyl-2,2,2-tri-n-hexadecyldisilane. Triphenylsilyllithium (*ca.* 0.05 mole) was prepared by the lithium metal cleavage[21] of 13.3 g. (0.025 mole) of hexaphenyldisilane using tetrahydrofuran as the solvent. The resulting solution was added in two portions to 17.2 g. (0.02 mole) of chlorotri-*n*-hexadecylsilane. Color Test I was negative after the first addition, but positive after the second addition. After refluxing for 24 hr., Color Test I was still weakly positive. The mixture was hydrolyzed and worked up as usual to yield, after chromatography on alumina to remove any silanol, 15 g. (78%) of a colorless oil, boiling at 320–325°/0.001 mm., n_D^{20} 1.5142, d_4^{20} 0.9081.

Anal. Calcd. for $C_{66}H_{114}Si$: Si, 5.83; MR_D, 320.04. Found: Si, 5.70, 5.66; MR_D, 320.99.

n-Decyltriphenylsilane. A. From decene-1 and triphenylsilane. By a method previously described[2b] for related compounds, 0.3 mole of triphenylsilane, and 0.05 mole of *n*-decene-1 in the presence of 0.5 g. of benzoyl peroxide were found to give 25% of product, m.p. 66–67°, which did not depress the melting point of samples made by methods B and C.

B. From n-decyllithium and chlorotriphenylsilane. Using the method described previously[2b] for related compounds, *n*-decyllithium (*ca.* 0.025 mole) and 0.025 mole of *n*-decyl bromide were allowed to react and work-up yielded 75% of the desired product, m.p. 68.5–69° (after recrystallization from 95% ethanol).

C. From triphenylsilylpotassium and n-decyl bromide. The triphenylsilylpotassium from the cleavage of 10 g. (0.0193 mole) of hexaphenyldisilane with sodium-potassium alloy was placed in a flask and 8.53 g. (0.0386 mole) of *n*-decyl bromide in 30 ml. of ether was added. After stirring for 1 hr., Color Test I[19] was negative, so 100 ml. of water was added to hydrolyze the mixture. After stirring for 10 min., the ether layer was separated and filtered to give 6.3 g. (62%) of hexaphenyldisilane, melting at 357–362°. The filtrate was dried over sodium sulfate and the solvent distilled to leave a residue which was recrystallized several times from ethanol and then methanol to finally give 0.1 g. of eicosane (m.p. 37.5–38.5°, mixed melting point undepressed) and 0.6 g. (6.32%) of triphenyl-*n*-decylsilane, m.p. 68–69°.

Anal. Calcd. for $C_{28}H_{36}Si$: Si, 7.00. Found: Si, 7.21, 6.87.

n-Dodecyltriphenylsilane. Triphenylsilylpotassium was prepared from 10 g. of hexaphenyldisilane as in the preceding experiment and reacted with 7.9 g. (0.0386 mole) of *n*-dodecyl chloride in 30 ml. of ether. Work-up of the mixture obtained after hydrolysis yielded 9% of hexaphenyldisilane melting at 359° and 33% of *n*-dodecyltriphenylsilane melting at 67.5–68°. A mixed melting point with authentic material prepared earlier[2b] was not depressed. Another sample of material (in 66.7% yield) was made by the *n*-dodecyllithium method described previously.[2b]

n-Octadecyltriphenylsilane. As in the preceding two experiments, triphenylsilylpotassium (from 10 g. of hexaphenyldisilane) was stirred with *n*-octadecyl bromide. Work-up gave 59% of hexaphenyldisilane melting at 356–360°, 35% of hexatricontane melting at 77.5–78°, and 6% of *n*-octadecyltriphenylsilane melting at 75.5–76.5°. Reported[2b] melting point is 72–73°. Another sample was made by the *n*-octadecyllithium method already described[2b] and found to melt at 78–79°. The yield in the latter case was 41%.

n-Dodecyltri-m-tolylsilane. To 15 g. (0.0495 mole) of trichloro-*n*-dodecylsilane was added 200 ml. (0.15 mole) of 0.8*N* *m*-tolyllithium in ether (the *m*-tolyllithium was prepared by direct reaction of lithium metal with *m*-bromotoluene). After stirring for 15 min., Color Test I[19] was negative, and the mixture was hydrolyzed with water and worked up as usual. Reduced pressure distillation of the crude product yielded 11.4 g. (49.0%) of product, boiling over the range of 196–206° (0.001 mm.), n_D^{20} 1.5488, d_4^{20} 0.9624.

Anal. Calcd. for $C_{33}H_{46}Si$: Si, 5.97; MR_D, 154.56. Found: Si, 6.08, 6.07; MR_D, 155.56.

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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Oxidative Ring Cleavage of Some Substituted Nitronaphthalenes[1]

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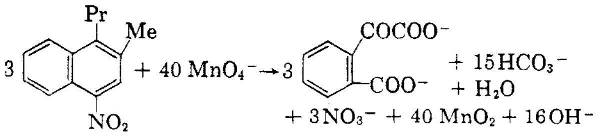
The oxidative ring cleavage of 2-methyl-1-propyl-4-nitronaphthalene, 1-bromo-5-nitronaphthalene, and 1,5-dinitronaphthalene by alkaline permanganate has been studied. The nitrated ring is cleaved preferentially by this reagent with the formation of substituted phthalonic acids. The hitherto unknown 3- and 6-bromophthalonic acids have been obtained in pure form and structures assigned. The data prove that 1-nitronaphthalenes are not cleaved by alkaline permanganate exclusively between carbons 1 and 2 or 3 and 4, but do not permit unequivocal designation of the point of ring cleavage.

As part of an investigation aimed at elucidation of satisfactory methods for selective ring cleavage of substituted naphthalenes, we became interested in the alkaline permanganate oxidation of naphthalene and certain of its derivatives. It is well known[2] that naphthalene is oxidized in good yield by that reagent to phthalonic acid. Under similar conditions alkylated naphthalenes are preferentially cleaved in the less-alkylated ring, but the degree of selectivity is not high.[3] An early report[4] states that 1-nitronaphthalene is slowly oxidized by permanganate but fails to specify conditions or products for the reaction. In view of the fact that 1-nitronaphthalene is cleaved by chromic anhydride to give 3-nitrophthalic acid,[4] it is interesting that Gardner[5] has reported the oxidation by alkaline permanganate of that compound to phthalonic acid in good yield. No further examples of this interesting oxidative cleavage have appeared. The high yield (74% as the aniline derivative), indicating a considerable degree of selectivity in this reaction, prompted a further investigation to determine its generality and hence utility for directed ring cleavage.

We have prepared and submitted to oxidation 1-bromo-5-nitronaphthalene and 2-methyl-1-propyl-4-nitronaphthalene. The results show that the nitro group does indeed direct the ring scission into the nitrated ring. In the case of 2-methyl-1-propyl-4-nitronaphthalene a mediocre yield of phthalic acid (36–40%) was obtained after isolation and purification. In this case no attempt was made to isolate the phthalonic acid undoubtedly formed in the alkaline medium, but the reaction mixture was acidified and permanganate added to a permanent color. The ether extraction employed for the isolation of phthalic acid permitted the recovery of substantially all of that substance from test solutions, but when phthalic acid was introduced in place of the naphthalene derivative only about 70% could be recovered under the normal oxidation conditions employed. However, no benzoic acid was found in such tests indicating probable destruction of the ring. For comparison purposes a sample of 2-methyl-1-propylnaphthalene was oxidized under identical conditions and only 13% of phthalic acid could be obtained. Thus the directive effect of the nitro group is indeed apparent but the presence of the alkyl groups reduced its effectiveness. The influence is also dependent on the alkalinity of the medium, for a run started in neutral solution produced only 20% phthalic acid despite the increasing pH of the medium as the reaction proceeds.



Oxidation of 1-bromo-5-nitronaphthalene under alkaline conditions gave a mixture of acidic products in good yield (76%). The crude product showed a wide melting range (*ca.* 125–165°), and contained no nitrogen as indicated by fusion tests and by Dumas analysis. That this mixture consisted substantially of the isomeric 3- and 6-bromophthalonic acids was denoted by its neutral equivalent

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