

procedure was used in cases where R' = aralkyl and 2-pyridyl; 2-chloropyridine is sufficiently reactive to participate in the Williamson synthesis. In certain cases, as noted in Table I, the hydrochloride of the product precipitated on extraction of the toluene solution with acid; the salt was collected by filtration and purified by recrystallization.

Method B. β -Chlorophenethylpiperidine hydrochloride¹⁰ (72.0 g., 0.28 mole) was stirred at room temperature with an equivalent amount of 56% potassium hydroxide and the liberated base extracted with two portions of toluene. The combined extracts (150 ml.) were dried by shaking for 2 hr. with anhydrous potassium carbonate. The filtered toluene solution was then added dropwise to a hot, stirred, suspension of sodium phenoxide. This suspension had been prepared by adding 26.0 g. (0.28 mole) of phenol to 6.7 g. (0.28 mole) of sodium hydride in 150 ml. of toluene. After the reaction mixture had been refluxed for 16 hr., it was cooled and shaken with 10% hydrochloric acid. The aqueous layer was made strongly basic and extracted several times with benzene. The benzene extracts were dried and distilled to give 57.3 g. of I (R' = phenyl, NR₂ = piperidino).

α -Phenoxy- α -phenylacetopiperidide (VI). A solution of 44.0 g. (0.19 mole) of α -phenoxyphenylacetic acid¹¹ and 34.5 g. (0.29 mole) of thionyl chloride in 150 ml. of ether to which 3 drops of pyridine had been added was stirred at reflux for 4 hr. The residue which remained on evaporation of the solvent was taken up in 150 ml. of Skellysolve B. A solid separated, and was collected by filtration. This solid was identified as recovered acid; 18.8 g., 43% recovery. The solvent was evaporated from the filtrate, leaving a residue of 28.7 g. which failed to crystallize. This crude acid chloride was taken up in 100 ml. of benzene and added dropwise to a stirred solution of 25.5 g. of piperidine in 100 ml. of benzene.

(11) C. O. Guss, *J. Am. Chem. Soc.*, **71**, 3460 (1949).

Heat was evolved, and a white solid formed. After the addition had been completed, the reaction mixture was stirred at reflux for 1 hr., then allowed to stand overnight at room temperature. The mixture was then poured in water (solid dissolved); the benzene layer was separated and extracted twice with saturated sodium bicarbonate solution. Evaporation of the solvent from the dried benzene solution left a residue which spontaneously solidified. Two recrystallizations from dilute methanol gave 25.7 g. of VI, m.p. 115.0–117.0°. An analytical sample melted at 116.0–117.0°.

Anal. Calcd. for C₁₉H₂₁NO₂: C, 77.3; H, 7.2. Found: C, 77.2; H, 7.2.

1-(β -Phenoxyphenethyl)piperidine (VII). A suspension of 5.9 g. (0.02 mole) of VI and 3.7 g. (0.1 mole) of lithium aluminum hydride in 300 ml. of ether was stirred at reflux for 2 hr., then allowed to stand overnight at room temperature. The mixture was hydrolyzed by cautious addition of ice; the white solid which formed was collected by filtration and washed several times on the filter with fresh ether. The filtrate and washings were combined and the solvent evaporated. Distillation at 0.8 mm. gave 4.8 g. of colorless liquid, b.p. 158–159° (86% yield).

Anal. Calcd. for C₁₉H₂₃NO: C, 81.1; H, 8.2. Found: C, 81.3; H, 8.3.

Hydrochloride: melting point alone and when mixed with a sample prepared by the alternate route (Method B), 196.5–198.0°.

Anal. Calcd. for C₁₉H₂₃NO·HCl: C, 71.8; H, 7.6. Found: C, 71.8; H, 7.6.

Further evidence for the identity of the basic ethers prepared by the two routes was afforded by the infrared spectra, which were indistinguishable.

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Some Organosilicon Compounds Derived from Phenyl Ether

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Received April 24, 1958

This article reports the preparation of several organosilicon compounds derived from either *o*- or *p*-phenoxyphenyllithium, or from (oxydi-*o*- or oxydi-*p*-phenylene)dilithium. These compounds are of interest as synthetic lubricants or hydraulic fluids because of their low melting points and relatively high volatilization points.

The preparation in this laboratory of several organosilicon compounds derived from aryl ethers has already been reported.^{1–3} These compounds were prepared, as a part of a current research problem, for the purpose of finding thermally stable organosilicon compounds for possible use as synthetic lubricants or hydraulic fluids. A second aim of this research is to develop such thermally stable compounds which are also low-melting, preferably being liquids at room temperature.

Among the phenyl ether derivatives previously reported are two complete series of compounds of

the general formula (C₆H₅)_xSiR_(4-x); where x is 0, 1, 2 or 3, and R is either *o*-phenoxyphenyl¹ or *p*-phenoxyphenyl² except for the compound where x is 3 and R is *p*-phenoxyphenyl. In addition, *n*-dodecyltris(*p*-phenoxyphenyl)silane was prepared.² The compounds were prepared by reaction of organolithium compounds with chlorosilanes. The preparations of the organolithium compounds were carried out by either halogen-metal interconversion or metalation reactions using *n*-butyllithium^{4,5} as the metalating agent.

In another study, dimetalation of phenyl ether using slightly more than two equivalents of *n*-butyllithium to one equivalent of phenyl ether was

(1) K. Oita and H. Gilman, *J. Org. Chem.*, **21**, 1009 (1956).

(2) H. Gilman and J. J. Goodman, *J. Org. Chem.*, **22**, 45 (1957).

(3) K. Oita and H. Gilman, *J. Am. Chem. Soc.*, **79**, 339 (1957).

(4) W. Langham, R. Q. Brewster, and H. Gilman, *J. Am. Chem. Soc.*, **63**, 545 (1941).

(5) H. Gilman and R. L. Bebb, *J. Am. Chem. Soc.*, **61**, 109 (1939).

found to yield (oxydi-*o*-phenylene)dilithium.³ This reagent further reacted with dichlorodimethyl- and dichlorodiphenyl silane to give the cyclic compounds 10,10-dimethyl- and 10,10-diphenyl-phenoxasilin and with silicon tetrachloride to form 10,10'-spirobiphenoxasilin.

All of the compounds previously reported,¹⁻³ with the exceptions of *n*-dodecyltris(*p*-phenoxyphenyl)silane (a liquid) and 10,10-dimethylphenoxasilin (m.p. 78.5–79.0°), were solids melting above 140°. Since it was desired to prepare low-melting compounds having high thermal stability, attempts have now been made to incorporate either long-chained *n*-alkyl groups or benzyl groups into organosilicon compounds derived from phenyl ether.

Reactions of (oxydi-*o*-phenylene)dilithium with dibenzylchloro- and dichlorodi-*n*-dodecylsilane have given 10,10-dibenzyl- and 10,10-di-*n*-dodecylphenoxasilin. Attempts to prepare 10-benzyl-10-chloro- and 10-chloro-10-*n*-dodecylphenoxasilin by reactions of (oxydi-*o*-phenylene)dilithium with benzyltrichloro- and trichloro-*n*-dodecylsilane have yielded materials containing little or no hydrolyzable chloride ion, although careful precautions were taken to avoid contact with moisture.

Chlorotri-*n*-hexadecylsilane⁶ was treated with *p*-phenoxyphenyllithium to give tri-*n*-hexadecyl-*p*-phenoxyphenylsilane. Reaction of *p*-phenoxyphenyllithium with tri-*n*-hexadecylsilane, (C₁₆H₃₃)₃SiH, apparently yielded a small amount of tri-*n*-hexadecyl-*p*-phenoxyphenylsilane since the infrared spectra of several fractions were similar to that of the pure compound. The spectra, however, showed the presence of the Si-H bond (4.75 μ) indicating that unreacted tri-*n*-hexadecylsilane was still present. Dichlorodi-*n*-dodecylsilane yielded upon reaction, in separate experiments, with 2 equivalents each of *o*- and *p*-phenoxyphenyllithium, the compounds di-*n*-dodecylbis(*o*- and *p*-phenoxyphenyl)silane.

Since (oxydi-*p*-phenylene)bis[triphenylsilane]⁷ had shown good thermal stability, but was a high-melting solid, the corresponding benzyl compound, (oxydi-*p*-phenylene)bis[tribenzylsilane], and methyl compound, (oxydi-*p*-phenylene)bis[trimethylsilane], were prepared. The methyl compound was found to melt near room temperature (45.0–45.5°); therefore its somewhat less symmetrical isomer, (oxydi-*o*-phenylene)bis[trimethylsilane], was prepared by reaction of two equivalents of chlorotrimethylsilane with (oxydi-*o*-phenylene)dilithium. The *p,p'*-disubstituted phenyl ether compounds were made by reaction of two equivalents of tri-

benzylsilane and chlorotrimethylsilane, in separate experiments, with (oxydi-*p*-phenylene)dilithium.

All of the new compounds, with the exceptions of (oxydi-*p*-phenylene)bis[trimethylsilane] and (oxydi-*p*-phenylene)bis[tribenzylsilane] (a glass), and 10,10-dibenzylphenoxasilin (melting near room temperature), were liquids. The two (oxydiphenylene)bis[trimethylsilane] compounds have good thermal stability, but boil around 320° at atmospheric pressure. The (oxydi-*p*-phenylene)bis[tribenzylsilane] volatilizes at 540–550° with only slight decomposition; this compares favorably with the corresponding bis[triphenylsilane] compound (m.p. 306–307°) which volatilizes at 557–560°. The other compounds all volatilize in the range from 440–480°, which is comparable to the mono- and di-(*o*-phenoxyphenyl)phenylsilanes¹ and to 10,10-diphenylphenoxasilin,³ but is somewhat lower than the other compounds prepared previously.¹⁻³ Thus far no compound containing a long-chained *n*-alkyl group has been found to be stable above 480°.

EXPERIMENTAL⁸

10,10-Dibenzylphenoxasilin. A four-necked flask was equipped with a reflux condenser, Trubore mechanical stirrer, and two dropping funnels. Into one funnel was placed a solution of 28 g. (0.1 mole) of dibenzylchlorosilane⁹ in 300 ml. of ether; into the other was placed a solution of ca. 0.1 mole of (oxydi-*o*-phenylene)dilithium³ in 500 ml. of ether. The two reagents then were added slowly to a stirred mixture of 50 ml. of benzene and 100 ml. of ether at a rate to avoid excess of either reagent. The addition required 2 hr. The mixture was then stirred 72 hr. after which time Color Test I¹⁰ was negative. Hydrolysis of the mixture was accomplished by the addition of 100 ml. of water. The layers were separated and the water layer was extracted with 100 ml. of ether. The ethereal layers were combined, dried over sodium sulfate, and filtered, and the ether was distilled. The benzene solution was then placed on a column of alumina and eluted with 500 ml. of benzene. The benzene was distilled to leave 33 g. of a crude oil. Distillation of this oil at reduced pressure gave two liquid fractions: 8.5 g. (27%), boiling at 188–194° (0.003 mm.), n_D^{20} 1.6305; and 7.8 g. (25%), b.p. 194–195° (0.003 mm.), n_D^{20} 1.6322. Both fractions gave identical infrared spectra and the spectra indicated them to be the desired compound. The fraction boiling at 194–195° (0.003 mm.) was analyzed. *Volatilization point:* Microbubbles begin at 400°, and the compound volatilizes at 470–480°. Some decomposition is noted.

*Anal.*¹¹ Calcd. for C₂₆H₂₂OSi: Si, 7.44. Found: Si, 7.21, 7.30.

*10,10-Di-*n*-dodecylphenoxasilin.* By essentially the same procedure described for 10,10-dibenzylphenoxasilin, except using 0.05 mole quantities, 10,10-di-*n*-dodecylphenoxasilin was prepared from (oxydi-*o*-phenylene)dilithium and dichlorodi-*n*-dodecylsilane. The main product, 4.3 g. (16.5%)

(8) All melting points are uncorrected. Reactions were carried out under dry, oxygen-free nitrogen when involving organolithium reagents or chlorosilanes. Volatilization points were determined by heating the compounds in a capillary tube mounted in a flame-heated copper block.

(9) Prepared by Mr. E. A. Zuech of this Laboratory.

(10) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **27**, 2002 (1925).

(11) Silicon analyses of most compounds were by the method of H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

(6) This compound has been prepared by two different methods and has been shown to decompose, if the distillation temperature exceeds 300°, into hexadecene-1 and an organosilicon residue. Results of this investigation will be published later.

(7) Unpublished studies, J. J. Goodman, doctoral dissertation, Iowa State College, 1955.

of an oil, boiled at 247–255° (0.009 mm.), n_D^{20} 1.5135, d_4^{20} 0.9359. *Volatilization point*: Microbubbles form at 355°, the compound volatilizes at 460–470° with some decomposition.

Anal. Calcd. for $C_{26}H_{38}OSi$: Si, 5.25; MR_D ,¹² 171.98. Found: Si, 4.98, 4.90, 4.89; MR_D , 171.93.

(*Oxydi-o-phenylene*)bis[trimethylsilane]. (*Oxydi-o-phenylene*)dilithium (0.073 mole) in 140 ml. of ether was prepared by a published procedure.³ To the stirred organodilithium compound in solution was added 19 ml. (16.2 g., 0.15 mole) of chlorotrimethylsilane. After refluxing overnight Color Test I¹⁰ was negative. The mixture was hydrolyzed and worked up as in the previous experiments to leave 19.2 g. (87%) of a crude oil. This oil was distilled at reduced pressure to give 13.7 g. (59.7%) of product, boiling at 117–120° (0.001 mm.), n_D^{20} 1.5415, d_4^{20} 1.432. *Volatilization point*: Microbubbles form at 300°, the compound volatilizes at 315–320° leaving no residue.

*Anal.*¹³ Calcd. for $C_{18}H_{26}OSi_2$: Si, 17.86; MR_D ,¹² 99.92. Found: Si, 17.56, 17.60; MR_D , 100.35.

(*Oxydi-p-phenylene*)bis[trimethylsilane]. (*Oxydi-p-phenylene*)dilithium was prepared by the reaction¹⁴ of 23 g. (0.1 mole) of bis(*p*-bromophenyl) ether in 200 ml. of benzene and 244 ml. of a 1.23*N* ethereal solution of *n*-butyllithium. To the resulting mixture was added slowly 30 g. (0.277 mole) of chlorotrimethylsilane. After two days at reflux temperature, the reaction mixture was hydrolyzed and then worked up in the usual manner. There was obtained 24.2 g. (77.3%) of an oil, boiling at 124–130° (0.02 mm.), n_D^{20} 1.5372, d_4^{20} 0.993.

*Anal.*¹³ Calcd. for $C_{18}H_{26}OSi_2$: Si, 17.86; MR_D ,¹² 99.92. Found: Si, 17.7, 17.5; MR_D , 98.84.

Following distillation of part of the product under a nitrogen atmosphere at slightly greater than atmospheric pressure, the product obtained was found to crystallize into large rhombohedral crystals. These melted at 44.5–46.5° and were used to seed the material which was not distilled and which gave finer crystals melting at 44.5–46.5°. Recrystallization of the crystals gave 6.3 g. (20%) of product, m.p. 45.0–45.6°.

J. J. Goodman¹⁵ also prepared this compound by the same method, but found the index of refraction to be n_D^{20} 1.5430, and the density to be d_4^{20} 1.0251 giving an MR_D value of 96.2 which does not agree with the calculated value¹² of 99.92. The authors checked the density and index of refraction and found them to be n_D^{20} 1.5420 and d_4^{20} 1.013 giving an MR_D value of 97.7, which is still quite low.

During the nitrogen atmosphere distillation mentioned previously, no decomposition of the material prepared by the authors was noted. *Volatilization point*: Microbubbles begin at 300°, the compound distills at 315–320° and no decomposition is noted.

(*Oxydi-p-phenylene*)bis[tribenzylsilane]. (*Oxydi-p-phenylene*)dilithium was prepared as in the previous experiment (0.025 mole) and allowed to react with 15 g. (0.05 mole) of tribenzylsilane.⁹ After the reaction mixture had stirred for 1 hr., Color Test I¹⁰ was weak and the reaction mixture was hydrolyzed and worked up in the usual manner to leave 8.0 g. (41.3%) of an oil, b.p. 320–322° (0.001 mm.). This oil is very viscous and glassy. *Volatilization point*: Microbubbles

are formed at 420°, the compound volatilizes at 540–550° with very little decomposition.

Anal. Calcd. for $C_{24}H_{30}OSi_2$: Si, 7.29. Found: Si, 7.40, 7.35.

Tri-n-hexadecyl-p-phenoxyphenylsilane. *p*-Phenoxyphenyllithium (0.045 mole) was prepared from *n*-butyllithium and *p*-bromophenyl phenyl ether⁴ and then was added to 10 g. (0.035 mole) of chlorotri-*n*-hexadecylsilane. Color Test I was negative within 15 min. and the mixture was hydrolyzed and worked up in the usual fashion. There was obtained 6.9 g. (58.5%) of an oil, boiling over the range 305–315° (0.005 mm.), n_D^{20} 1.4960, d_4^{20} 0.8971. *Volatilization point*: Microbubbles form at 340°, the compound volatilizes at 450–460°.

Anal. Calcd. for $C_{26}H_{40}OSi$: Si, 3.22; MR_D ,¹² 285.18. Found: Si, 3.39, 3.28; MR_D , 284.61.

A slightly impure sample was made by the same method using somewhat impure chlorotri-*n*-hexadecylsilane. When tri-*n*-hexadecylsilane was allowed to react with *p*-phenoxyphenyllithium at reflux for 12 hr., no pure product was obtained, but a crude fraction was obtained whose infrared spectrum was similar to that of the authentic material prepared as previously described. However, complete reaction did not occur as evidenced by the presence of the Si-H band at 4.75 μ in the infrared spectrum.

Di-n-dodecylbis(o-phenoxyphenyl)silane. To 13.6 g. (0.08 mole) of phenyl ether in 100 ml. of ethyl ether was added 63 ml. (0.084 mole) of 1.34 *N* *n*-butyllithium. After stirring at room temperature for 24 hr., Color Test II¹⁶ was negative. To the resulting solution was added 17.5 g. (0.04 mole) of dichlorodi-*n*-dodecylsilane. After refluxing overnight, Color Test I¹⁰ was negative. Hydrolysis and work-up in the usual manner yielded 8 g. (28.8%) of product, boiling over the range 260–270° (0.001 mm.), n_D^{20} 1.5290, d_4^{20} 0.9680. Another 7 g. (25.2%) of crude product also was obtained. *Volatilization point*: Microbubbles form at 370°, the compound volatilizes at 460–470° leaving no residue.

Anal. Calcd. for $C_{28}H_{48}O_2Si_2$: Si, 3.98; MR_D ,¹² 224.19. Found: Si, 4.14, 4.12; MR_D , 224.67.

Di-n-dodecylbis(p-phenoxyphenyl)silane. To *p*-bromophenyl phenyl ether (14.98 g., 0.06 mole) in 100 ml. of ether was added 50 ml. (0.061 mole) of a 1.22*N* ethereal solution of *n*-butyllithium. When Color Test II¹⁶ was negative, the mixture was treated with 13.1 g. (0.03 mole) of dichlorodi-*n*-dodecylsilane. As soon as Color Test I was negative, the mixture was hydrolyzed and worked up as usual to give 21 g. of an oil. Reduced pressure distillation of the oil gave 5.0 g. (25%) of product, boiling at 275–280° (0.001 mm.), n_D^{20} 1.5380, d_4^{20} 0.9776, as well as a slightly impure sample amounting to 6.5 g. *Volatilization point*: Microbubbles form at 400°, the compound volatilizes at 450–470°.

Anal. Calcd. for $C_{28}H_{48}O_2Si_2$: Si, 3.98; MR_D ,¹² 224.10. Found: Si, 4.00, 3.83; MR_D , 225.6.

Infrared spectra of the compounds. Infrared spectra of each of the above compounds were run and compared to those of related compounds. Except where otherwise noted, the spectra indicated the compound obtained to be the desired product.

Acknowledgments. This research was supported by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The Authors are grateful to the Institute for Atomic Research, Iowa State College and to Dr. V. A. Fassel and Mr. E. M. Layton, Jr. for preparing the infrared spectra.

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