[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION AND CLEAVAGE OF SOME HEXASUBSTITUTED DISILOXANES

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In this communication are reported the results obtained in studies on the cleavage of some hexasubstituted disiloxanes by organolithium compounds and by alkali metal hydroxides. As most of the disiloxanes used in these studies are not readily available, a general method for their synthesis is described.

A survey of the literature (1) reveals the preparation of a number of disiloxanes by a variety of methods, the most generally applicable methods being intermolecular condensation of silanols, intermolecular equilibration of a mixture of disiloxanes, and reaction of organometallic compounds with halo- or alkoxydisiloxanes. One of the better methods for preparing symmetrical disiloxanes is the intermolecular condensation of the silanol effected by 98% formic acid (2); this method would be expected to prove less satisfactory for the preparation of the unsymmetrical compounds.

It has been previously shown (3) that under somewhat different conditions siloxanes may be prepared from alkali metal silanolates and halosilanes. The present investigation has shown this to be a method of general applicability, with certain notable exceptions.

$$R_3SiOM + R'_3SiCl \rightarrow R_3SiOSiR'_3 + MCl$$

Sodium tri-α-naphthylsilanolate did not form a disiloxane when allowed to react with trimethylchlorosilane, triphenylchlorosilane, or tri-*p*-tolylchlorosilane. The fact that these chlorosilanes did react with other silanolates indicates that the failure of disiloxane formation is due to some property of the tri-α-naphthyl salt, presumably of a steric nature (4).

Also unsuccessful was the preparation of 1,1,1-triphenyl-3,3,3-tris-(*p*-dimethylaminophenyl)-disiloxane from sodium triphenylsilanolate and tris-(*p*-dimethylaminophenyl)-chlorosilane. The failure of triphenylchlorosilane to react with sodium tris-(*p*-dimethylaminophenyl)-silanolate was also observed. It should be mentioned that earlier workers (6) were unable to prepare hexakis-(*p*-dimethylaminophenyl)disiloxane under similar conditions.

References to the cleavage of siloxanes by organometallic compounds and alkali metal hydroxides may be found in the literature (1, 7). In the present work the cleavages were restricted to the reactions of organolithium compounds, or of sodium or potassium hydroxide, with hexasubstituted disiloxanes.

When a symmetrical hexasubstituted disiloxane is cleaved by an organolithium compound, the products are a tetrasubstituted silane and the lithium salt of a silanol. The yields of the two cleavage products in a given reaction are

$$R_3SiOSiR_3 + R'Li \rightarrow R_3SiR' + R_3SiOLi$$

thus the same, but because isolation and purification procedures may not lend themselves as well for the one compound as for the other, the actual yields of the two products may differ considerably. In any event, one may assume the cleavage to have taken place to an extent at least as great as is indicated by the product obtained in the higher yield.

It may be seen from the experimental results that methyllithium failed to cleave hexaphenyldisiloxane or hexa-*p*-tolyldisiloxane. This failure of methyllithium to bring about cleavage is not greatly surprising in view of its lower reactivity, as compared with other alkyllithium compounds, in such reactions as metalation (8), metal-metal interconversion (9), and cleavage of diethyl ether (5, 10).

When an unsymmetrical hexasubstituted disiloxane is cleaved by an organolithium reagent, four cleavage products are possible, depending upon which

$$R_3SiOSiR'_3 + R''Li \rightarrow R_3SiR'' + R'_3SiOLi + R'_3SiR'' + R_3SiOLi$$

silicon-oxygen bond is cleaved. The distribution of products is consistent with the relative electronegativities of the silicon atoms in the substituted disiloxanes as determined by the electron-releasing powers of the substituents on each silicon atom, if nucleophilic attack of the RLi compound on the siloxane is taken as the rate-determining step.

In nearly all of the cleavages of the unsymmetrical disiloxanes by organolithium compounds, the organolithium compound chosen was such that the cleavage products possible were a symmetrical tetrasubstituted silane, an unsymmetrical tetrasubstituted silane, and, upon hydrolysis, two silanols. It was desirable that the cleavage products include each of these three types, for crystallization techniques of separation applied quite well under such conditions. For example, a symmetrical tetraarylsilane could be separated from the other three possible cleavage products by virtue of its low solubility in ether, and tetraarylsilanes in general could be separated from the silanols as a result of the greater solubility of silanols in 90% methanol. Unfortunately, no suitable solvent was found for separating the individual triarylsilanols.

The actual yields of the cleavage products are based on the amount of disiloxane which underwent reaction, as determined by subtracting the amount of disiloxane recovered from the amount originally taken. On this basis, one may assume that the yield of R_3SiR'' plus that of $R_3'SiR''$ should equal 100%, a lower total yield indicating incomplete separation of one of the silanes or incomplete recovery of the unreacted disiloxane. Similarly, the sum of the yields of the silanols should equal 100%. The yield of each of the products formed by cleavage of a given silicon-oxygen bond must, of course, be equal. Thus, one can realize the course of the cleavage reaction even though one or two of the products is isolated in poor yield or not at all.

Although the results of the reaction of 1,1,1-triphenyl-3,3,3-tri-*p*-tolyldisiloxane with phenyllithium did not demonstrate conclusively any preferential cleavage, the reaction of the same disiloxane with *p*-tolyllithium did give results to show that there was preferential cleavage at the triphenylsilicon-oxygen bond. This preferential cleavage is in accord with that predicted on the basis that the nucleophilic attack will take place more readily at that silicon atom which is made the less electronegative by the electronic effects of the organic substituents.

Similarly, the cleavage of 1,1,1-trimethyl-3,3,3-triphenyldisiloxane with *p*-tolyllithium was found to take place preferentially at the triphenylsilicon-oxygen bond. The cleavage of this disiloxane with phenyllithium, however, did not give conclusive results owing to the relatively poor total yield of cleavage products isolated.

It is interesting to note that even under conditions more drastic than those usually employed, no cleavage of 1,1,1-triphenyl-3,3,3-tri-*o*-tolyldisiloxane by phenyllithium was observed. Possibly steric factors may have been involved, although this appears improbable in view of the fact that any cleavage which might occur would be expected to take place preferentially at the triphenylsilicon-oxygen bond.

The hydrolysis of hexaphenyldisiloxane, of 1,1,1-triphenyl-3,3,3-tri-*p*-tolyldisiloxane, and of 1,1,1-triphenyl-3,3,3-tri-*o*-tolyldisiloxane by an aqueous acetone mixture of an alkali metal hydroxide resulted in the formation of the expected silanols, presumably by the same type of nucleophilic attack as given for the cleavage of disiloxanes by organolithium compounds.

EXPERIMENTAL

All reactions involving an organometallic compound, a chlorosilane, or a lithium or sodium salt of a silanol were carried out in an atmosphere of dry nitrogen. The ether used as solvent was previously dried over sodium. Compounds were analyzed for silicon by sulfuric acid oxidation (11) or by the Parr bomb method (12). The latter procedure was used for compounds containing the trimethylsilyl group, as such compounds are relatively volatile. All melting points are uncorrected, and those solid compounds which were not analyzed were identified by the method of mixture melting points with authentic specimens.

The method of preparation of the disiloxanes is illustrated below as given for hexaphenyldisiloxane. The preparation and attempted preparation of other disiloxanes are tabulated in Table I.

Hexaphenyldisiloxane. Sodium triphenylsilanolate was prepared by dissolving 6 g. (0.0218 mole) of the silanol in 100 ml. of ether and refluxing the solution with a 10% excess of metallic sodium cut into small cubes. When hydrogen evolution ceased, the ethereal solution was decanted from the remaining sodium.[1] To this solution was added at one time 5.95 g. (0.0201 mole) of triphenylchlorosilane dissolved in 20 ml. of ether. After refluxing for 12 hours and hydrolyzing with water, the ethereal layer was separated, and the solvent was removed to give 8.9 g. (96%) of crude product melting over the range 215–225°.[2] Two recrystallizations from benzene gave 8 g. (74.5%) of hexaphenyldisiloxane melting at 224–224.5°, identified by a mixture melting point with an authentic specimen.

Cleavage of hexaphenyldisiloxane with phenyllithium. A solution of 0.06 mole of phenyllithium (13) in 102 ml. of ether was added rapidly with stirring to a xylene solution of 10 g.

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[1] Some of the sodium triarylsilanolates were insoluble in ether, and hence this decantation was omitted for these salts.

[2] Some of the disiloxanes were only partially soluble in the ether layer; therefore, the solid present in the hydrolyzed mixture was filtered and combined with the residue from the solvent removal for subsequent purification.

TABLE I—SYNTHESES OF DISILOXANES

R_3SiOM	R'_3SiCl	REFLUX TIME, hrs.	$R_3SiOSiR'_3$	YIELD, %	M.P., °C.	ANALYSES Si	
						Calc'd	Found
$(C_6H_5)_3SiONa$	$(C_6H_5)_3SiCl$	12	$(C_6H_5)_3SiOSi(C_6H_5)_3{}^{a}$	74.5	224–224.5		
$(o\text{-}CH_3C_6H_4)_3SiONa^{b}$	$(C_6H_5)_3SiCl$	48	$(C_6H_5)_3SiOSi(C_6H_4CH_3\text{-}o)_3{}^{c,\ d}$	76.7	212–213	9.73	9.80
$(m\text{-}CH_3C_6H_4)_3SiONa^{b}$	$(C_6H_5)_3SiCl$	36	$(C_6H_5)_3SiOSi(C_6H_4CH_3\text{-}m)_3{}^{e}$	77	191–191.5	9.73	9.85
$(p\text{-}CH_3C_6H_4)_3SiONa^{f}$	$(C_6H_5)_3SiCl$	12	$(C_6H_5)_3SiOSi(C_6H_4CH_3\text{-}p)_3{}^{c}$	88	164–164.5	9.73	9.77
$(C_6H_5)_3SiONa$	$(p\text{-}CH_3C_6H_4)_3SiCl^{g}$	14	$(C_6H_5)_3SiOSi(C_6H_4CH_3\text{-}p)_3{}^{h}$	83	164–164.5		
$(p\text{-}CH_3C_6H_4)_3SiOH^{f,\ i}$	$(C_6H_5)_3SiCl$	52	$(C_6H_5)_3SiOSi(C_6H_4CH_3\text{-}p)_3$	0^{j}			
$(o\text{-}CH_3C_6H_4)_3SiONa^{b}$	$(p\text{-}CH_3C_6H_4)_3SiCl^{g}$	24	$(o\text{-}CH_3C_6H_4)_3SiOSi(C_6H_4CH_3\text{-}p)_3{}^{k}$	70	197–197.5	9.05	9.05
$(m\text{-}CH_3C_6H_4)_3SiONa^{b}$	$(p\text{-}CH_3C_6H_4)_3SiCl^{g}$	18	$(m\text{-}CH_3C_6H_4)_3SiOSi(C_6H_4CH_3\text{-}p)_3{}^{l}$	62	136–137	9.05	9.10
$(\alpha\text{-}C_{10}H_7)_3SiONa^{m}$	$(C_6H_5)_3SiCl$	15	$(C_6H_5)_3SiOSi(C_{10}H_7\text{-}\alpha)_3$	0^{n}			
$(\alpha\text{-}C_{10}H_7)_3SiONa^{m}$	$(p\text{-}CH_3C_6H_4)_3SiCl^{g}$	30	$(p\text{-}CH_3C_6H_4)_3SiOSi(C_{10}H_7\text{-}\alpha)_3$	0^{o}			
$(C_6H_5)_3SiONa$	$[p\text{-}(CH_3)_2NC_6H_4]_3SiCl^{p}$	48	$(C_6H_5)_3SiOSi[C_6H_4N(CH_3)_2\text{-}p]_3$	0^{q}			
$[p\text{-}(CH_3)_2NC_6H_4]_3SiONa^{r}$	$(C_6H_5)_3SiCl$	21	$(C_6H_5)_3SiOSi[C_6H_4N(CH_3)_2\text{-}p]_3$	0^{s}			
$(C_6H_5)_3SiONa$	$(CH_3)_3SiCl$	14	$(CH_3)_3SiOSi(C_6H_5)_3{}^{t}$	67	49–50	16.05	16.11
$(o\text{-}CH_3C_6H_4)_3SiOLi^{b,\ u}$	$(CH_3)_3SiCl$	24	$(CH_3)_3SiOSi(C_6H_4CH_3\text{-}o)_3{}^{v}$	74.3	91–91.5	14.35	14.25
$(m\text{-}CH_3C_6H_4)_3SiONa^{b}$	$(CH_3)_3SiCl$	16	$(CH_3)_3SiOSi(C_6H_4CH_3\text{-}m)_3{}^{w}$	56.5		14.35	14.26
$(p\text{-}CH_3C_6H_4)_3SiONa^{f}$	$(CH_3)_3SiCl$	8	$(CH_3)_3SiOSi(C_6H_4CH_3\text{-}p)_3{}^{x}$	73	81–81.5	14.35	14.41
$(\alpha\text{-}C_{10}H_7)_3SiONa^{m}$	$(CH_3)_3SiCl$	45	$(CH_3)_3SiOSi(C_{10}H_7\text{-}\alpha)_3{}^{y}$	0			

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[a] Recrystallized twice from benzene; identified by a mixture melting point with an authentic specimen. [b] The silanol was prepared from silicon tetrachloride and the tolyllithium compound by the general method of Gilman and Clark (16). [c] Recrystallized three times from petroleum ether (b.p. 77–115°). [d] Unpublished studies by Gilman and Smart show that no reaction occurs when a mixture of sodium triphenylsilanolate and tri-*o*-tolylchlorosilane are refluxed in ether for 36 hours. [e] Recrystallized twice from petroleum ether (b.p. 77–115°). [f] The silanol was prepared by the method of Steele and Kipping, *J. Chem. Soc.*, 357 (1929). [g] Prepared by the method of Steele and Kipping, *J. Chem. Soc.*, 357 (1929). [h] Recrystallized once from petroleum ether (b.p. 77–115°); identified by a mixture melting point with an authentic specimen. [i] The silanol was added to triphenylchlorosilane dissolved in dry pyridine. [j] There was recovered 74.6% of the triphenylchlorosilane and 58.6% of the tri-*p*-tolylsilanol, which were separated, following distillation of the pyridine, by fractional crystallization from petroleum ether (b.p. 60–70°). [k] Recrystallized once from petroleum ether (b.p. 77–115°). [l] Recrystallized twice from petroleum ether (b.p. 60–70°). [m] The silanol was prepared by the method of Gilman and Brannen (4). [n] There was isolated a 91.5% yield of tri-α-naphthylsilanol and an 89.5% yield of triphenylsilanol. [o] Distillation of the solvent followed by extraction of the residue with petroleum ether (b.p. 60–70°) gave an 89.4% recovery of tri-*p*-tolylchlorosilane. Hydrolysis of the petroleum ether-insoluble material resulted in a 98% recovery of tri-α-naphthylsilanol. [p] Prepared by the method of Gilman, Plunkett, and Dunn (6). [q] Without subjecting the reaction mixture to hydrolysis, there were recovered 80% of the chlorosilane and 86% of the sodium triphenylsilanolate. [r] The silanol was prepared by the method of Gilman, Plunkett, and Dunn (6). [s] There was obtained a 70% recovery of the tris-(*p*-dimethylaminophenyl)silanol, and 95.5% of the triphenylchlorosilane was recovered as the silanol. [t] Purified by distillation, b.p. 156–157°/0.7 mm. [u] Prepared from the silanol and phenyllithium (13). [v] Purified by distillation, b.p. 176–177°/0.3 mm. [w] Purified by distillation, b.p. 165–166°/1.25 mm., n_D^{20} 1.5545, d_4^{20} 1.0150. [x] Purified by distillation, b.p. 187–188°/0.3 mm. From the distillation residue there was obtained an 8.6% yield of hexa-*p*-tolyldisiloxane. [y] Without sub- distilled to give a quantitative recovery of sodium tri-

(0.0187 mole) of hexaphenyldisiloxane. Most of the ether was removed, and 4 g. of copper bronze catalyst[3] was added. The reaction mixture was refluxed for 20 hours at an internal temperature of 125°, during which time Color Test I (14) remained positive. Upon cooling, a white solid crystallized from solution. Subsequent to hydrolysis, the solid material was filtered off and taken up in 75 ml. of warm benzene. After complete solution of the organic material, the copper bronze was removed by filtration. The filtrate was concentrated and cooled, whereupon 5.4 g. (86%) of tetraphenylsilane melting at 233–234° precipitated. The previously filtered xylene and water were separated, and the organic layer was dried over sodium sulfate. The xylene was distilled at 15 mm., and the residue was recrystallized twice from petroleum ether (b.p. 77–115°) to give 4.5 g. (87.5%) of triphenylsilanol melting at 150–150.5°. Each cleavage product was identified by a mixture melting point determination. No hexaphenyldisiloxane was recovered.

The cleavage reaction was repeated in diethyl ether. To a suspension of 6.9 g. (0.013 mole) of hexaphenyldisiloxane in 45 ml. of ether was added 0.039 mole of phenyllithium in 5.2 ml. of ether. No catalyst was added. The reaction mixture was refluxed for 24 hours and then hydrolyzed. Filtration gave 3.9 g. of white solid melting at 226–232°. Two recrystallizations from benzene gave 3.5 g. (80%) of tetraphenylsilane melting at 234–234.5°, identified by a mixture melting point. The filtered ether-water mixture was separated, and the aqueous layer was extracted three times with 25-ml. portions of ether. The combined ethereal extracts were dried over sodium sulfate, and the solvent was distilled to give 3.4 g. of crude material melting over the range 136–147°. Two recrystallizations from petroleum ether (b.p. 77–115°) gave 2.82 g. (78.7%) of triphenylsilanol (mixture m.p.) melting at 150–151°. Again no disiloxane was recovered.

Cleavage of hexaphenyldisiloxane with p-tolyllithium. To 93 ml. of ether containing 0.045 mole of *p*-tolyllithium (15) was added 8 g. (0.015 mole) of hexaphenyldisiloxane. The mixture was refluxed for 15 hours, much of the disiloxane apparently remaining undissolved. Filtration of the mixture gave 3.8 g. of white solid melting at 220–224°. After two recrystallizations from benzene, 3.28 g. (41%) of hexaphenyldisiloxane melting at 223–224° was recovered. The ethereal layer was evaporated to dryness, and a white residue weighing 8.25 g. was obtained. As this substance did not melt when held in a free flame, it was presumed that salts were present. To remove these salts, the solid was digested with 135 ml. of refluxing benzene and filtered hot. Upon cooling, 0.8 g. of hexaphenyldisiloxane melting at 223–224° separated from the benzene solution. This increased the total recovery of the disiloxane to 4.08 g. (51%). The mother liquor was evaporated to dryness by distillation at about 15 mm. to give 4 g. of residue melting over the range 126–145°. This solid was stirred with 15 ml. of 90% methanol and filtered to separate the silanol from the tetraarylsilane. The filtered solid was recrystallized from petroleum ether (b.p. 77–115°) to yield 1.85 g. (71.5% based on the amount of disiloxane actually cleaved) of triphenyl-*p*-tolylsilane (16) melting at 134–135° and identified by a mixture melting point. The solvent was distilled from the methanol solution, and the residue was recrystallized twice from petroleum ether (b.p. 60–70°) to give 1.53 g. (75% based on the amount of disiloxane cleaved) of triphenylsilanol (mixture m.p.) melting at 149–150°.

Attempted cleavage of hexaphenyldisiloxane with methyllithium. A solution of 0.06 mole of methyllithium (15) in 90 ml. of ether was added to 10.7 g (0.02 mole) of hexaphenyldisiloxane suspended in 30 ml. of ether. Copper bronze (4 g.) was added, and the mixture was refluxed for 26 hours. Color Test I remained positive. Following hydrolysis, the reaction mixture was worked up in the usual manner to give 9.2 g. (85% recovery) of hexaphenyldisiloxane melting at 223–224°. Neither of the expected cleavage products, triphenylsilanol and methyltriphenylsilane (17), was found.

The reaction was repeated in the same manner, except that the copper bronze catalyst was not used. Only hexaphenyldisiloxane (93% recovery) was isolated from the reaction mixture.

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[3] Purchased from the General Chemical Company, New York.

Cleavage of hexa-p-tolyldisiloxane with phenyllithium. A mixture of 4 g. (0.0065 mole) of hexa-*p*-tolyldisiloxane and 0.033 mole of phenyllithium in 142 ml. of ether was refluxed for 24 hours. Color Test I remained positive. An insoluble fraction weighing 3.1 g. and melting at 218–223° was filtered from the reaction mixture and recrystallized from benzene to give 2.5 g. (62.5% recovery) of hexaphenyldisiloxane melting at 223–224°. The ether solution was hydrolyzed with water, and the two layers were separated. The organic layer was dried over sodium sulfate, and the ether was distilled to give 1.2 g. of residue melting over the range 106–190°. This solid was digested with 15 ml. of petroleum ether (b.p. 60–70°) and filtered hot to give an additional 0.5 g. of hexa-*p*-tolyldisiloxane melting at 222–223°, thus bringing the total recovery of the disiloxane to 3 g. (75%). Upon cooling, a small amount of solid melting at 149–150° separated from the mother liquor, and was identified as triphenylsilanol by a mixture melting point. The extent of cleavage (25%) was not sufficiently significant, so further investigation of this reaction was not carried out.

Attempted cleavage of hexa-p-tolyldisiloxane with methyllithium. A mixture of 5 g. (0.0081 mole) of hexa-*p*-tolyldisiloxane and 0.03 mole of methyllithium in 75 ml. of ether was refluxed for 30 hours. Color Test I remained positive. After hydrolysis and working up of the reaction mixture in the usual manner, 4.5 g. (90% recovery) of hexa-*p*-tolyldisiloxane melting at 223–224° was obtained.

Cleavage of 1,1,1-triphenyl-3,3,3-tri-p-tolyldisiloxane with phenyllithium. A solution of 0.0456 mole of phenyllithium in 60 ml. of ether and 7 g. (0.0122 mole) of 1,1,1-triphenyl-3,3,3-tri-*p*-tolyldisiloxane was refluxed for 16 hours. Color Test I remained positive. The reaction mixture, containing a suspended white solid, was hydrolyzed with water. The aqueous layer was separated and extracted with three 25-ml. portions of ether. Removal of the solvent from the combined ethereal extracts gave a residue (A-1) weighing 8.75 g. This crude material was digested with 40 ml. of refluxing 90% methanol; the mixture was cooled and filtered to give 4.43 g. of solid (A-2) melting over the range 124–220°. The filtrate, which was believed to contain triphenylsilanol and tri-*p*-tolylsilanol, was evaporated to dryness; and the residue, weighing 4.3 g., was digested with 40 ml. of petroleum ether (b.p. 77–115°). The mixture was cooled and filtered to give 0.28 g. (8.3%) of triphenylsilanol (mixture m.p.) melting at 150–151°. A small amount of tri-*p*-tolylsilanol melting at 97–99°, identified by a mixture melting point, was obtained from the petroleum ether filtrate by fractional crystallization. However, no suitable method was found to resolve the remainder of this fraction, and the total yield of each silanol remained unknown.

The methanol-insoluble fraction (A-2) was dissolved in 50 ml. of hot benzene. Upon cooling, there separated 1.95 g. (47.6%) of tetraphenylsilane (mixture m.p.) melting at 231–232°. The solvent was distilled from the mother liquor, and the residue was recrystallized from petroleum ether (b.p. 77–115°) to give 1.4 g. of solid melting over the range 125–220°. Further recrystallizations from the same solvent yielded 0.9 g. (12.8% recovery) of 1,1,1-triphenyl-3,3,3-tri-*p*-tolyldisiloxane melting at 163–164°. The mother liquors from which the disiloxane was purified were combined and concentrated to give a solid weighing about 0.01 g. and melting at 127–128°, identified as phenyltri-*p*-tolylsilane (18) by a mixture melting point.

The theoretical yield of each cleavage product was taken in this work to be the yield which would result from a quantitative cleavage of the disiloxane at the appropriate silicon-oxygen bond, first subtracting the number of grams of recovered material from the original amount taken. The results of other runs, given on the same basis, are included in Table II.

Attempted cleavage of 1,1,1-triphenyl-3,3,3-tri-o-tolyldisiloxane with phenyllithium. A mixture of 8 g. (0.0138 mole) of the disiloxane and 0.0468 mole of phenyllithium in 70 ml. of ether was refluxed for 20 hours, Color Test I remaining positive. After hydrolysis, the ether layer was separated along with some undissolved white crystals. Removal of the solvent left 7.9 g. of material melting over the range 195–205°. Recrystallization from a benzene-methanol solution gave 7.6 g. (95% recovery) of the disiloxane melting at 212–213°.

TABLE II

CLEAVAGE[a] OF 1,1,1-TRIPHENYL-3,3,3-TRI-p-TOLYLDISILOXANE WITH PHENYLLITHIUM

RUN	YIELD OF RECOVERED DISILOXANE, %	YIELD OF TETRAPHENYLSILANE, %	YIELD OF TRIPHENYLSILANOL	YIELD OF TRIPHENYL-p-TOLYLSILANE, %	YIELD OF TRI-p-TOLYLSILANOL, %
I	0	38.6	trace	0	0
II	0	41	0	4	0
III[b, c]	70	33	0	0	0
IV[d]	35	trace	0	0	0
V[b]	85	0	0	0	0
VI	9.2	39	8	2	trace
VII[e]	12.8	47.6	8.3	trace	trace

[a] Three equivalents of phenyllithium were used, the reflux period was 15 hours, and Color Test I was positive in all runs, unless otherwise stated; all yields were calculated as described in the detailed procedure. [b] One equivalent of phenyllithium was used. [c] Color Test I was negative. [d] Two equivalents of phenyllithium were used. [e] This run is reported in the detailed procedure.

The reaction was repeated with a more concentrated phenyllithium solution (1.2 *M*), but again a practically quantitative recovery (93%) of the disiloxane was obtained.

Cleavage of 1,1,1-triphenyl-3,3,3-tri-p-tolyldisiloxane with p-tolyllithium. A mixture of 10 g. (0.0174 mole) of the disiloxane and 0.0523 mole of p-tolyllithium in 65.5 ml. of ether was refluxed for 19 hours and then hydrolyzed. The ether layer, along with some suspended solid, was separated and filtered. The insoluble material, weighing 1.6 g. and melting at 227–230°, was identified as tetra-p-tolylsilane (19) by a mixture melting point. The solvent was distilled from the ethereal solution, and the residue was filtered. The filtrate, containing toluene from the hydrolysis of the excess p-tolyllithium, was diluted with about 4 ml. of petroleum ether (b.p. 60–70°) and allowed to stand. The first fraction of crystals which separated melted at 163–164° and was identified as recovered disiloxane by a mixture melting point. Upon further standing, a solid melting at 120–130° separated. This solid was stirred with 90% methanol to dissolve any silanol which might be present as an impurity. After filtering this methanol solution, the insoluble material was combined with the residue resulting from evaporation of the petroleum ether; the entire mass, weighing 7.15 g., was suspended in 20 ml. of 90% methanol, stirred, and filtered. The filtered methanol solutions containing the silanols were not investigated. The filtered solid was fractionally crystallized from methanol-ethyl acetate mixtures to give as the first product 0.7 g. of tetra-p-tolylsilane melting at 226–228°, increasing the total yield of this silane to 2.3 g. (39%). On slow evaporation of the mother liquor, a material melting over the range 120–138° precipitated. After several recrystallizations of this solid, there were obtained 1.4 g. (14.5% recovery) of 1,1,1-triphenyl-3,3,3-tri-p-tolyldisiloxane melting at 163–164° and 2.94 g. (56%) of triphenyl-p-tolylsilane (16) melting at 137–138°, identified by a mixture melting point. In order to obtain the silane in the state of purity given above, it was necessary to resort to recrystallization of the crude material from ethyl acetate-methanol mixtures. A residual fraction weighing 0.25 g. could not be resolved. The yields given are on the basis of disiloxane actually cleaved.

Cleavage of 1,1,1-trimethyl-3,3,3-triphenyldisiloxane with phenyllithium. To 10 g. (0.0287 mole) of the disiloxane was added 0.087 mole of phenyllithium in 110 ml. of ether. The mixture was refluxed for only 3 hours, for there was evidence that the cleavage was complete by this time as indicated by the precipitation of a white solid after 1 hour of refluxing. Subsequent to hydrolysis, this solid was filtered off to give 3.85 g. (40%) of tetraphenylsilane (mixture m.p.) melting at 234–234.5°. The ethereal layer was separated and dried over calcium sulfate. Removal of the solvent at atmospheric pressure followed by distillation of other volatile material at 3 mm. left 2 g. (25%) of triphenylsilanol (mixture m.p.) melting at 146–148°. The distillate was not investigated further, due to the azeotropic mixture of ether, benzene, and either trimethylsilanol or hexamethyldisiloxane which would result upon further distillation (20).

Cleavage of 1,1,1-trimethyl-3,3,3-triphenyldisiloxane with p-tolyllithium. A solution of 10 g. (0.0287 mole) of the disiloxane and 0.087 mole of *p*-tolyllithium in 110 ml. of ether was refluxed for 18 hours, Color Test I remaining positive. After the reaction mixture was hydrolyzed with water, the organic layer was separated and dried over sodium sulfate. The ether was distilled at 38–39°, indicating that perhaps trimethylsilanol or hexamethyldisiloxane, possible cleavage products, were co-distilling with the solvent, for the distillation temperature of pure ether under identical conditions was 34°. The residual oil partially crystallized on standing; filtration gave 4.4 g. of triphenyl-*p*-tolylsilane (mixture m.p.) melting at 133–135°. Dilution of the filtrate with petroleum ether (b.p. 60–70°) caused the precipitation of 2.6 g. (33%) of triphenylsilanol (mixture m.p.) melting at 147–150°. After distillation of the solvent from the mother liquor, the residue was distilled to give 1.1 g. (21%) of trimethyl-*p*-tolylsilane (21) boiling at 73–75°/2 mm., n_{D}^{20} 1.4918. The residue from this distillation crystallized on cooling; recrystallization from a 1:1 methanol-ethyl acetate solution gave 1.45 g. of triphenyl-*p*-tolylsilane melting at 137–137.5°, increasing the total yield to 5.85 g. (58.5%).

Hydrolysis of hexaphenyldisiloxane with sodium hydroxide. Using a modification of the method of Kipping and Lloyd (22), 5 g. (0.0093 mole) of the disiloxane, 40 ml. of acetone, and 10 g. of water in which had been dissolved 5 g. of sodium hydroxide was refluxed until the suspended solid dissolved (2 to 3 hours). (If the mixture is refluxed for longer periods, extensive decomposition apparently occurs, and the solution becomes dark red. This may be due to the polymerization of acetone by the strong alkali.) The reaction mixture was poured with stirring into a large volume of water, and the resulting solid was filtered to give 5.0 g. of material melting at 145–152°. Two recrystallizations from petroleum ether (b.p. 77–115° gave 4.1 g. (79.5%) of triphenylsilanol (mixture m.p.) melting at 151–151.5°.

Hydrolysis of 1,1,1-triphenyl-3,3,3-tri-p-tolyldisiloxane with potassium hydroxide. The hydrolysis was carried out in essential accordance with the method given above except that potassium hydroxide was substitued for the sodium hydroxide. Fractional crystallization of the crude product from petroleum ether (b.p. 60–70°) gave 1.4 g. (58%) of triphenylsilanol melting at 147–149° and 1.1 g. (39.9%) of tri-*p*-tolylsilanol melting at 97–99°. Both cleavage products were identified by mixture melting points.

Hydrolysis of 1,1,1-triphenyl-3,3,3-tri-o-tolyldisiloxane with potassium hydroxide. The reaction was carried out as above except that the reflux period was extended to 9 hours. After the reaction product had been poured into water, the mixture was acidified with hydrochloric acid and filtered. This filtered solid was stirred with 90% methanol, and the mixture was filtered to give a 48.6% recovery of the disiloxane melting at 211–213°. The solvent was distilled from the methanol solution, and the residue was recrystallized from benzene to givea a 45.6% yield of tri-*o*-tolylsilanol melting at 105–106°. Distillation of the benzene gave a residue which, upon recrystallization from petroleum ether (b.p. 77–115°), constituted a a 37% yield of triphenylsilanol melting at 148–150°. Each silanol was identified by a mixture melting point.

SUMMARY

1. It has been shown that the preparation of a symmetrical or unsymmetrical hexasubstituted disiloxane from a trisubstituted chlorosilane and the sodium salt of a triarylsilanol is a generally useful method, and a number of new disiloxanes have been prepared.

2. The cleavage of hexasubstituted disiloxanes with organolithium compounds

has been found to be a relatively general reaction. However, neither methyllithium nor 1,1,1-triphenyl-3,3,3-tri-*o*-tolyldisiloxane entered this reaction.

3. Although cleavage by organolithium compounds occurs at both silicon-oxygen bonds of unsymmetrical disiloxanes, preferential cleavage appears to occur at the bond to the silicon atom having the lower electron density and hence providing the better site for nucleophilic attack.

4. The cleavage of some hexaaryldisiloxanes with alkali metal hydroxides has been reported.

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