[Contribution from the Chemical Laboratories of Iowa State College and Muhlenberg College]

STERIC HINDRANCE IN HIGHLY-SUBSTITUTED ORGANOSILICON COMPOUNDS. II. AMINE, ESTER, AND SULFIDE DERIVATIVES IN THE TRI-*o*-TOLYLSILYL SERIES

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The general significance of steric hindrance in reactions leading to the formation of highly-substituted organosilicon compounds was discussed in an earlier paper (1). In the preparation of *o*-tolyl- and mesityl-silanes steric factors were found to be of prime importance, but in the case of phenyl- and *o*-methoxyphenyl-silanes of lesser importance (1). Recently, Nebergall and Johnson (2) have also interpreted studies with cyclohexylsilanes in terms of steric hindrance. The present paper reports the preparation of a disubstituted amine, two esters, and a sulfide in the tri-*o*-tolylsilyl series. The properties of these compounds and the severe conditions required for their preparation are not inconsistent with the view that steric factors operate here.

Organosilicon compounds having silicon-chlorine linkages generally react with ammonia and amines under mild conditions: silicon tetrachloride with aromatic amines giving tetraanilinosilanes (3, 4), triphenylchlorosilane with ammonia giving triphenylaminosilane (5), and trimethylchlorosilane with diethylamine giving trimethyldiethylaminosilane (6). In the present investigation we found that tri-*o*-tolylchlorosilane does not react with di-*n*-butylamine on prolonged refluxing in petroleum ether.[1] However, tri-*o*-tolyldibutylaminosilane was readily prepared by treating the chlorosilane with lithium dibutylamide at elevated temperatures:

$$(o\text{-}CH_3C_6H_4)_3SiCl + (n\text{-}C_4H_9)_2NLi \xrightarrow{ca.\ 180^\circ} (o\text{-}CH_3C_6H_4)_3SiN(C_4H_9\text{-}n)_2 + LiCl \quad 1.$$

This method may be used for the preparation of other triaryl(dialkylamino)-silanes (7). When tri-*o*-tolylsilanol[2] was refluxed with acetic anhydride the acetate formed readily:

$$(o\text{-}CH_3C_6H_4)_3SiOH + (CH_3CO)_2O \xrightarrow{\text{Reflux}} (o\text{-}CH_3C_6H_4)_3SiOCOCH_3 + CH_3COOH \quad 2.$$

This is the same procedure that was used by Nebergall and Johnson (2) for the preparation of tricyclohexylacetoxysilane and by Ladenburg (8) for the preparation of triphenylacetoxysilane. Tri-*o*-tolylacetoxysilane appears to be more stable than triphenylacetoxysilane, in that the latter compound deteriorates rapidly in moist air (9). We were unable to prepare an ester from triphenylsilanol and

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[1] The petroleum ether referred to in this paper had b.p. 60–70°.

[2] The preparation of tri-*o*-tolylsilanol from the chlorosilane and other related compounds will be described later.

phthalic anhydride. However, tri-*o*-tolylsilyl stearate was made by heating a mixture of tri-*o*-tolylchlorosilane, sodium stearate, and powdered copper to about 230°:

$$(o\text{-}CH_3C_6H_4)_3SiCl + NaOOC(CH_2)_{16}CH_3 \xrightarrow{ca.\ 230°,\ Cu} (o\text{-}CH_3C_6H_4)_3SiOOC(CH_2)_{16}CH_3 + NaCl \quad 3.$$

These reaction conditions are considerably more drastic than those described by Barry (10) for the preparation of tridodecylacetoxysilane and dodecyldiphenylacetoxysilane from the silyl chlorides and sodium acetate, and much more drastic than those described by Schuyten and co-workers (11) for the preparation of trimethylacetoxysilane.

Tri-*o*-tolyl-*p*-tolylmercaptosilane was prepared by heating tri-*o*-tolylchlorosilane with sodium *p*-thiocresoxide to 250° in the presence of copper powder:

$$(o\text{-}CH_3C_6H_4)_3SiCl + p\text{-}NaSC_6H_4CH_3 \xrightarrow{ca.\ 250°,\ Cu} (o\text{-}CH_3C_6H_4)_3SiSC_6H_4CH_3\text{-}p + NaCl \quad 4.$$

An earlier attempt to prepare this product from the chlorosilane and sodium *p*-thiocresoxide in refluxing alcohol was unsuccessful. Furthermore, we were unable to make triphenylphenylmercaptosilane[3] by heating triphenylsilane with sodium thiophenoxide and diphenyl sulfide at 260° or by heating triphenylphenoxysilane (12) with sulfur at 320°. And, again, triphenyl-*p*-tolylmercaptosilane was not formed when triphenylsilane was heated to 200° with sodium *p*-thiocresoxide. The conditions which obtained in the successful preparation of tri-*o*-tolyl-*p*-tolylmercaptosilane were much more drastic than those used by Backer and co-workers (13–16) for the preparation of thio and seleno esters of silicic acid and certain siliconic acids. It is also of interest to note that triphenylsilane reacts readily with sodium phenoxide giving triphenylphenoxysilane (12) while it does not react at all with sodium thiophenoxide or sodium *p*-thiocresoxide under corresponding conditions.

We attempted to oxidize tri-*o*-tolyl-*p*-tolylmercaptosilane to the sulfone. Oxidation did take place when the mercaptosilane was treated with potassium permanganate in glacial acetic acid; on working up the reaction mixture, however, only tri-*o*-tolylsilanol[2] could be isolated. There is evidence that the sulfoxide or sulfone may have been produced but that, because of a general weakening of the sulfur-silicon linkage, the product hydrolyzed under the conditions of the experiment.

EXPERIMENTAL

Tri-o-tolyl-di-n-butylaminosilane. Tri-*o*-tolylchlorosilane (8.4 g., 0.025 mole) dissolved in 20 ml. of boiling anhydrous petroleum ether[1] was treated with 12.9 g. (0.100 mole) of

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[3] Triphenylchlorosilane and sodium thiophenoxide probably gave this product when heated to 250° in the presence of copper powder. Since the product was not adequately characterized, the experiment is not described here. Crude triphenylphenylmercaptosilane distills in the range 170–200°/1 mm.

dry, freshly-distilled di-*n*-butylamine. No reaction took place, and when the solvent was removed after 15 hours reflux, 7.4 g. (88%) of pure tri-*o*-tolylchlorosilane was recovered unchanged (m.p. 114–115.5°, identified by mixed melting point). In another experiment, in which the dibutylamine was not dried before use, the chlorosilane hydrolyzed and there was isolated dibutylammonium chloride (m.p. 283°) and tri-*o*-tolylsilanol[2] (m.p. 104–105°). Each product was identified by mixed melting point. Although the yields were not determined, it is probable that the reaction is quantitative in the presence of sufficient water.

Tri-*o*-tolyldi-*n*-butylaminosilane was successfully prepared by the action of lithium dibutylamide on tri-*o*-tolylchlorosilane. To an ether solution containing 0.080 mole of *p*-anisyllithium[4] was added 20 ml. (0.119 mole) of dry di-*n*-butylamine. An exothermic reaction took place and the resulting red solution gave a negative Color Test I (17), indicating the absence of unchanged RLi. About 70% of the solvent was removed by distillation, and to the residue was added a solution of 9 g. (0.027 mole) of tri-*o*-tolylchlorosilane in 150 ml. of hot anhydrous petroleum ether.[1] The reaction mixture was heated to 180° under nitrogen for one hour (with removal of the solvent) and the cooled mass was extracted with boiling petroleum ether. After evaporation of the solvent, 2.3 g. of crude tri-*o*-tolyldi-*n*-butylaminosilane, m.p. 118–124°, was isolated. Distillation of the non-crystalline residues gave 1.3 g. (15%) of crude tri-*o*-tolylsilanol, m.p. 99–103° (subsequently recrystallized from petroleum ether and identified by mixed melting point[2]), and 4.2 g. of crude tri-*o*-tolyldi-*n*-butylaminosilane, boiling about 190°/2 mm., m.p. 116–120°. The aminosilane (55% over-all yield) was readily purified by recrystallization from 95% ethanol to give the pure product, m.p. 123.5–125.0°, in 35% over-all yield. This was characterized by analysis and by conversion to the ethoxysilane on treatment with hot ethanol and hydrogen chloride (12).

Anal. Calc'd for $C_{29}H_{39}NSi$: Si, 6.53. Found: Si, 6.46.

Tri-*o*-tolyldibutylaminosilane is very soluble in benzene, moderately soluble in petroleum ether, and slightly soluble in ethanol.

Tri-o-tolylacetoxysilane. Tri-*o*-tolylsilanol[2] (1.5 g., 0.0047 mole) was dissolved in 3.5 ml. (0.037 mole) of acetic anhydride. After refluxing for 15 hours the acetic anhydride was distilled. The syrupy residue crystallized on cooling and treatment with petroleum ether,[1] and tri-*o*-tolylacetoxysilane was separated in 77% yield (1.3 g., m.p. 120–120.5°). This product after recrystallization from petroleum ether had m.p. 121–121.5° (1.1 g.).

Anal. Calc'd for $C_{23}H_{24}O_2Si$: Si, 7.79. Found: Si, 7.82.

Tri-*o*-tolylacetoxysilane is very soluble in benzene; it is sparingly soluble in cold ethanol and petroleum ether, but appreciably soluble in the hot solvents. The product can be recrystallized from hot ethanol without decomposition.

Post and Hofrichter (18) were able to prepare mixed ester-anhydride types by treating ethyl silicate and related compounds with acetic anhydride. However, we found that tri-*o*-tolylethoxysilane does not react with boiling acetic anhydride, with boiling acetic anhydride in the presence of hydrogen chloride, nor with benzoyl or 3,5-dinitrobenzoyl chlorides at 200°.

Tri-o-tolylsilyl stearate. To a solution of 0.46 g. (0.02 g.-atom) of sodium in 30 ml. of absolute ethanol was added 6.5 g. (0.023 mole) of pure, powdered stearic acid. The alcohol was then evaporated and the residue dried for 15 hours at 120°. The sodium stearate was thoroughly mixed with 0.5 g. of precipitated copper powder[5] and 6.9 g. (0.020 mole) of tri-*o*-tolylchlorosilane.

The mixture was heated at 170° for 15 hours in an inert atmosphere and subsequently at 230° for one hour. The black, syrupy crude product was extracted with benzene; crystallization could not be induced at this stage so the solvent was evaporated and the residue was molecularly-distilled. A small amount of unreacted stearic acid was first removed, and when the bath temperature was 290° (pressure 0.001 mm.) the main product dis-

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[4] Any active organolithium compound could be used.

[5] The role of the copper powder is not clear and, indeed, it is not certain that it is an essential component of the mixture.

tilled smoothly and crystallized in the receiver. Eight grams of a wax-like solid was obtained, m.p. 39–41°; this represents a 70% yield of tri-*o*-tolylsilyl stearate. The product was very soluble in benzene and slightly soluble in petroleum ether[1] and ethanol; however, the material could not be further purified by recrystallization. It was characterized by analysis and by saponification to stearic acid and the silanol.[6]

Anal. Calc'd for $C_{39}H_{56}O_2Si$: Si, 4.80. Found: Si, 4.90.

Tri-o-tolyl-p-tolylmercaptosilane. To a solution of 0.46 g. (0.02 g.-atom) of sodium in 7 ml. of absolute ethanol was added 2.5 g. (0.02 mole) of *p*-thiocresol. The excess alcohol was evaporated and the sodium *p*-thiocresoxide was dried at 110° for 15 hours. The brownish residue was thoroughly mixed with 0.1 g. of precipitated copper powder[5] and 6.7 g. (0.02 mole) of tri-*o*-tolylchlorosilane. The mixture was heated in an atmosphere of dry nitrogen at 230–250° for five hours. It was cooled and extracted with hot benzene; the benzene was evaporated from the extract and the residue distilled. The material distilling at 190–230°/5 mm. (4.0 g.) gave, after treatment with petroleum ether,[1] 0.5 g. of impure tri-*o*-tolylsilanol (m.p. 86–102°). The fraction distilling at 230–250°/5 mm. (3.2 g.) gave, after treatment with petroleum ether, 1.3 g. of impure tri-*o*-tolyl-*p*-tolylmercaptosilane (m.p. 110–113°). The distillation residue together with the non-crystalline portions of the distillates was redistilled and there was eventually obtained over-all yields of 20% impure silanol and 50% impure mercaptosilane. Each product was purified with small loss by recrystallizing it from petroleum ether. The purified silanol (m.p. 102–104°) was characterized by a mixed melting point with an authentic sample.[2] The purified tri-*o*-tolyl-*p*-tolylmercaptosilane (m.p. 112–113°) was characterized by analysis and by hydrolysis to the silanol and *p*-thiocresol.[6]

Anal. Calc'd for $C_{28}H_{28}SSi$: Si, 6.61. Found: Si, 6.66.

The mercaptosilane is very soluble in benzene, appreciably soluble in hot ethanol and petroleum ether, but sparingly soluble in cold ethanol and petroleum ether.

As has already been indicated, tri-*o*-tolyl-*p*-tolylmercaptosilane could not be prepared by treating tri-*o*-tolylchlorosilane with sodium *p*-thiocresoxide in the presence of ethanol; the ethoxysilane was formed under these conditions. Further, triphenyl-*p*-tolylmercaptosilane could not be prepared by heating equivalent quantities of sodium *p*-thiocresoxide and triphenylsilane to 200° in the presence of excess *p*-thiocresol; the unchanged triphenylsilane was recovered in 85% yield after a one-hour reaction. In an attempt to prepare triphenylphenylmercaptosilane, equivalent quantities of sodium thiophenoxide and triphenylsilane were heated to 260° for 48 hours in the presence of a slight excess of thiophenol and ten parts of diphenyl sulfide. The anticipated product could not be isolated and, although we did not actually recover the triphenylsilane in the crystalline state, we characterized the crude distilled triphenylsilane by chemical test.

Krafft and Steiner (19) were able to prepare diphenyl sulfide in small yield by heating diphenyl ether with the theoretical amount of sulfur for 15 hours at 350°. They reported that the less-stable, unsymmetrical ethers gave better yields and that diphenyl selenide and diphenyl telluride were converted into diphenyl sulfide under comparatively mild conditions. In the conversion of diphenyl ether to the sulfide it was suggested that the sulfoxide was formed at an intermediate stage. We have sought to extend the work of Krafft and Steiner into the field of organosilicon chemistry in an attempt to convert triphenylphenoxysilane to triphenylphenylmercaptosilane by heating it with sulfur.

One gram (0.0028 mole) of triphenylphenoxysilane (12) and 0.09 g. (0.0028 g.-atom) of sulfur were heated to 320° in an atmosphere of nitrogen for one hour. The black mass was cooled and the sublimed sulfur was washed back into the reaction mixture with a little benzene (the odor of hydrogen sulfide was very strong). The benzene was evaporated and the mixture was heated for one additional hour at 320° and then for 15 hours at 220°. The black, oily reaction product was extracted with hot petroleum ether[1] and a clear yellow

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[6] The hydrolysis of tri-*o*-tolylsilyl stearate and tri-*o*-tolyl-*p*-tolylmercaptosilane will be described later.

solution was obtained which deposited white crystals on cooling. The black residue proved to be partially soluble in benzene. From the combined extracts could be recovered about 40% of unchanged triphenylphenoxysilane and, in addition, 6 mg. (0.5%) of a sparingly soluble crystalline material, m.p. 226–227°. This material appeared to be reasonably pure; it contained sulfur and depressed the melting points of tetraphenylsilane and hexaphenyldisiloxane. No extensive attempt was made to characterize it in view of the small amounts of material available, but we wish to indicate the possibility that it may be triphenylsilyl phenyl sulfoxide, $(C_6H_5)_3Si\text{-}SO\text{-}C_6H_5$.

Oxidation of tri-o-tolyl-p-tolylmercaptosilane. Tri-*o*-tolyl-*p*-tolylmercaptosilane (0.183 g., 0.00043 mole) and 0.136 g. (0.00086 mole) of potassium permanganate were ground together in a mortar. The mixture was suspended in a solution containing 10 ml. of acetic acid and 0.5 ml. of acetic anhydride. The solution assumed a brownish color almost at once, and after shaking at room temperature for two hours most of the mercaptosilane and permanganate had dissolved. The reaction mixture was hydrolyzed during a 20-minute period by adding it to 50 g. of ice-water along with 15% aqueous alkali and strong sodium bisulfite solution containing a known amount of the reducing agent. The alkali was added at such a rate that the hydrolysis mixture was but slightly acidic at all times, and the bisulfite solution was added at such a rate that the unreacted potassium permanganate and the by-product manganese dioxide were smoothly reduced but at the same time the introduction of any large excess of the reducing agent was avoided. It was estimated that 0.134 g. of sodium bisulfite was required to reduce the unused oxidizing agent. Using this value, it may readily be shown that the equivalent of 0.000344 mole of potassium permanganate was reduced in the anhydrous reaction mixture from the permanganate to the manganous level. This corresponds to the liberation of 0.00086 g.-atom of oxygen (*i.e.*, 0.000344 × 2.5); since 0.00043 mole of tri-*o*-tolyl-*p*-tolylmercaptosilane was introduced, the oxygen consumption was 2.00 g.-atom *per* mole. The simplicity of this ratio is probably coincidental in view of the rough techniques used, but there is certainly a strong suggestion that the oxidation went right through to the sulfone stage. Unfortunately, no product could be isolated here. The precipitate which formed on dilution turned into an oil when filtered and it could not be crystallized from any of a variety of solvents. In another run where the acetic acid was not neutralized on dilution, a 10% yield of tri-*o*-tolylsilanol was isolated. This may have resulted from hydrolysis of the sulfone.

When tri-*o*-tolyl-*p*-tolylmercaptosilane in acetone solution was treated either with potassium permanganate and aqueous acetic acid for 15 minutes or with hydrogen peroxide for 34 hours, the starting material was recovered in near-quantitative yield.

SUMMARY

1. The preparation of four new aromatic organosilicon compounds of the tri-*o*-tolylsilyl series is reported.
2. The drastic reaction conditions required for the preparation of these compounds and their unusual stability are not inconsistent with the view that steric factors may operate here.
3. There is new evidence that a triarylchlorosilane is more reactive than a related triarylsilane: the former will react with a sodium thiophenoxide, but not the latter.
4. Tri-*o*-tolyl-*p*-tolylmercaptosilane is easily oxidized. However, the silanol and not the sulfone is isolated after the reaction.

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