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

STERIC HINDRANCE IN HIGHLY-SUBSTITUTED ORGANOSILICON COMPOUNDS. III. THE PREPARATION AND PROPERTIES OF SOME TRIARYLSILYL ETHERS

HENRY GILMAN and G. N. RUSSELL SMART

Received August 27, 1953

In the preceding papers of this series (1, 2) evidence was presented which supports the views of other investigators (3–7) concerning the importance of steric factors in highly-substituted organosilicon compounds. A study of the reactions leading to the formation of triarylsilyl ethers has led to results which also may be interpreted in terms of steric hindrance.

The preparation of triarylsilyl ethers by the action of aryllithium compounds on ethyl orthosilicate and the isolation of tri-*o*-tolyl-*o*-toloxysilane and tri-*o*-tolylethoxysilane in experiments where silicon tetrachloride was treated with *o*-tolyllithium have already been described (1). Ethers of this general type can also be prepared from related triarylsilyl derivatives by a variety of methods.

The most direct preparation involves the reaction of the triarylchlorosilane with an alcohol:

$$Ar_3SiCl + ROH \rightarrow Ar_3SiOR + HCl$$

This method has been widely used in the preparation of other types of alkoxy- and phenoxy-silanes (8, 9) and it is eminently suited to the preparation of the methyl, ethyl, propyl, and *beta*-dimethylaminoethyl ethers of tri-*o*-tolylsilanol. However, when tri-*o*-tolylchlorosilane was treated with higher alcohols or with phenol, the corresponding ethers could be isolated only in small yield, if at all.

A more satisfactory method for the preparation of triarylsilylethers involves the use of sodium alkoxides or phenoxides along with the triarylchlorosilane in a modified Williamson reaction (10):

$$Ar_3SiCl + RONa \xrightarrow{ROH} Ar_3SiOR + NaCl$$

The propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, benzyl, and *o*-cresyl ethers were readily made in this manner. However, when tri-*o*-tolylchlorosilane was treated with sodium *tert*-butoxide most of the chlorosilane was recovered unchanged and, in addition, there was isolated a small amount of a high-melting material, apparently hexa-*o*-tolyldisiloxane. This experiment with sodium *tert*-butoxide is of interest not only because it provides an example of steric hindrance [triphenylchlorosilane appears to react even with *tert*-butyl alcohol (11)], but also because it has apparently produced a compound which we have been unable to prepare by any of the classical methods. Post and his co-workers have obtained anomalous results with *tert*-butyl alcohol and chlorosilanes under somewhat different circumstances (12, 13). Modified experiments using sodium *tert*-butoxide, tri-*o*-tolylchlorosilane, and tri-*o*-tolylsilanol indicate that what is believed to be hexa-*o*-tolyldisiloxane is also formed in a reaction between the sodium salt of the silanol and the chlorosilane:

$$(o\text{-}CH_3C_6H_4)_3SiOH + (CH_3)_3CONa \xrightarrow{(CH_3)_3COH} (o\text{-}CH_3C_6H_4)_3SiONa + (CH_3)_3COH$$

$$(o\text{-}CH_3C_6H_4)_3SiONa + (o\text{-}CH_3C_6H_4)_3SiCl \rightarrow [(o\text{-}CH_3C_6H_4)_3Si]_2O + NaCl$$

This series of reactions is presently being investigated as a possible method for the preparation of unsymmetrically-substituted disiloxanes; for example, $(o\text{-}CH_3C_6H_4)_3Si\text{-}O\text{-}Si(C_6H_5)_3$.

An interesting exchange of alkoxyl groups occurs when the propyl ether or isopropyl ether of tri-*o*-tolylsilanol is refluxed with methanol in the presence of sulfuric acid; in each case tri-*o*-tolylmethoxysilane is formed in excellent yield:

$$(o\text{-}CH_3C_6H_4)_3SiOR + CH_3OH \xrightarrow{H_2SO_4} (o\text{-}CH_3C_6H_4)_3SiOCH_3 + ROH$$

While the generality of this reaction has not been fully determined, it is apparent from the present studies that methanol is more effective than other aliphatic alcohols in promoting this exchange. Furthermore, it was shown that tri-*o*-tolylbenzyloxysilane does not react with methanol under the conditions of the above experiments. Alkoxyl group exchanges have been observed frequently with other types of organosilicon compounds (14, 15).

Triarylsilanes can be converted into triarylsilyl ethers by treatment with sodium alkoxides or phenoxides:

$$Ar_3SiH + RONa \rightarrow Ar_3SiOR + NaH$$

This method is especially suited to the preparation of triarylsilyl ethers in cases where the triarylsilane is more readily available, more stable, or easier to work with than the related chlorosilane; triphenylsilane, for example, may be used in place of triphenylchlorosilane in certain preparations. Nebergall (17) has described the conversion of phenylsilane to phenyltriethoxysilane through the use of ethanol and lithium ethoxide.

That triarylsilanes are less reactive than are the triarylchlorosilanes in substitution reactions of this type is shown by the fact that, with sodium *o*-cresoxide, tri-*o*-tolylchlorosilane but not tri-*o*-tolylsilane is converted into the *o*-cresyl ether. This result is consistent with the data presented earlier (1, 2). Since triphenylsilane reacts with sodium phenoxide and tri-*o*-tolylsilane reacts with sodium ethoxide to give the corresponding ethers, it would appear that the failure of tri-*o*-tolylsilane to react with sodium *o*-cresoxide is dictated by steric factors.[1]

Triarylsilyl esters may be converted into the related ethers by reaction with alcohols:

$$Ar_3SiOCOCH_3 + 2ROH \rightarrow Ar_3SiOR + CH_3COOR + H_2O$$

While the above equation employs an acetate ester, there is no reason to believe that the reaction is not general. However, while triphenylsilyl acetate is quantita-

---

[1] It has not been possible as yet to convert triphenylsilane into the thiophenoxy or *p*-thiocresoxy derivatives under analogous conditions (2, 16).

tively converted into triphenylethoxysilane on standing for 24 hours at room temperature in benzene-ethanol solution, tri-*o*-tolylsilyl acetate is unaffected under these mild conditions.[2] The latter compound may be converted into an ether by refluxing a benzene-alcohol solution for a few hours in the presence of a trace of sulfuric acid. The reaction described by the above equation is, from the practical viewpoint, a reversal of that described by Post and Hoffrichter (18) in which orthoesters of silicic acid and substituted siliconic acids are converted into carboxylic acid derivatives through treatment with acid anhydrides.

It is possible to convert tri-*o*-tolyldi-*n*-butylaminosilane into tri-*o*-tolylethoxysilane by heating the silylamine with ethanol in the presence of anhydrous hydrogen chloride:

$$(o\text{-}CH_3C_6H_4)_3SiN(C_4H_9\text{-}n)_2 + C_2H_5OH \xrightarrow{HCl} (o\text{-}CH_3C_6H_4)_3SiOC_2H_5 + (n\text{-}C_4H_9)_2NH_2Cl$$

Although of questionable value as a method for the preparation of silyl ethers, this reaction and related reactions have proved useful in characterization work. The ethoxy compound, of all the compounds prepared in the tri-*o*-tolylsilyl series, is the most easily purified (by recrystallization) and identified (by melting and mixture melting points); it is stable and is sparingly soluble in ethanol and petroleum ether. Since many triarylsilyl derivatives can be converted into the ethoxysilane by treatment with ethanol and in some cases also with sulfuric acid, its importance as an identifying derivative cannot be overemphasized.

In view of the structural analogy between silanols and carbinols (22), it might be expected that the triarylsilanols would serve as suitable starting materials for the preparation of triarylsilyl ethers. However, in this connection success has been limited. Triphenylsilanol did not react with phenol under any of a variety of conditions. When this silanol was refluxed for an extended period of time with ethanol in the presence of anhydrous zinc chloride, triphenylethoxysilane formed slowly:[3]

$$(C_6H_5)_3SiOH + C_2H_5OH \xrightarrow{ZnCl_2} (C_6H_5)_3SiOC_2H_5 + H_2O$$

When tri-*o*-tolylsilanol was treated in a similar fashion, no reaction occurred. However, tri-*o*-tolylsilanol has been converted into the methyl ether by first changing it into the acetate (2).

EXPERIMENTAL

Properties of the triarylsilyl ethers. All of the triarylsilyl ethers were found to be white crystalline solids. Table I lists the melting ranges[4] and analyses for the compounds. With the exception of the hydrochloride of tri-*o*-tolyl-*beta*-dimethylaminoethoxysilane, all of

---

[2] This experiment was performed by Mr. George R. Mack, senior student at Muhlenberg College.

[3] Dolgov and Volnov (19) have suggested that triphenylsilane is formed in this reaction. No mention of this is made in a recent publication by Nametkin, Topchiev, and Machus (20). The present work appears to exclude the possibility that triphenylsilane is a reaction product.

[4] Unless otherwise noted, melting points are corrected. A flame-heated copper block was used in determining the melting points.

TABLE I

MELTING RANGES AND ANALYSES OF SOME TRI-*o*-TOLYLSILYL ETHERS (o-Tol_3SiOR)

R	MOLECULAR FORMULA	SILICON ANALYSIS, %		MELTING RANGE, °C.[a]
		Calcd.	Found	
CH_3	$C_{22}H_{24}OSi$	8.44	8.44, 8.2	101.5–102.0
C_2H_5	$C_{23}H_{26}OSi$	8.10	7.99, 8.00 7.88, 8.21	143.5–144.0
C_3H_7-*n*	$C_{24}H_{28}OSi$	7.79	7.79, 7.78	101.0–101.5
C_3H_7-*iso*	$C_{24}H_{28}OSi$	7.79	7.85, 7.77 7.73	106.5–107.5
C_4H_9-*n*	$C_{25}H_{30}OSi$	7.49	7.43	81.5–82.5
C_4H_9-*iso*	$C_{25}H_{30}OSi$	7.49	7.49, 7.47	109.5–110.0
C_4H_9-*sec*	$C_{25}H_{30}OSi$	7.49	7.38	57.5–59.0
$C_6H_5CH_2$	$C_{28}H_{28}OSi$	6.87	6.85, 6.93	158.5–159.5
$CH_3C_6H_4$-*o*	$C_{28}H_{28}OSi$	6.87	6.97	153.0–154.0 (uncorr.)
$(CH_3)_2NCH_2CH_2$	$C_{25}H_{31}NOSi$	7.22	7.33	68.5–69.5 (uncorr.)
$(CH_3)_2{}^{+}NHCH_2CH_2\ Cl^{-}$	$C_{25}H_{32}ClNOSi$	6.61	6.60[b]	188.5–189.5 (uncorr.)

[a] Melting points are corrected except where otherwise specified.

[b] Calc'd for $C_{25}H_{32}ClNOSi$: Cl, 8.35. Found: Cl, 8.45.

the compounds are heat stable and can be distilled at reduced pressure without decomposition. There appears to be no tendency to sublime. The triarylsilyl ethers can be separated from the other components of the reaction mixtures and be partially purified by distillation. Final purification is best effected by recrystallization.

With the exception of the *beta*-dimethylaminoethoxy derivative and its hydrochloride, the solubilities of the compounds reported in Table I can be predicted with reasonable accuracy by referring to the melting points. All are insoluble in water and are unaffected by prolonged standing with hot or cold water. (Techniques by which these ethers may be hydrolyzed will be described in a later report.) All are very soluble in benzene. The higher-melting compounds are sparingly soluble in methanol, ethanol, and petroleum ether[5] in the cold and moderately soluble in the hot solvents. The lower-melting compounds are considerably more soluble in these solvents. In general, the triarylsilyl ethers are somewhat less soluble in the alcohols than in the petroleum ether. Recrystallization is best effected by the solvent pairs benzene-methanol, benzene-ethanol, and benzene-petroleum ether. When an alcohol is present in the recrystallization system, the possibility of reaction between the triarylsilyl ether and the alcohol should not be overlooked. A reaction is most likely to occur if a mineral acid is also present in the solution.

The triarylsilyl ethers were assigned structures on the basis of their methods of preparation, and of their conversions to more common triarylsilyl compounds. These structures are supported by silicon analyses. Tri-*o*-tolylethoxysilane and tri-*o*-tolyl-*o*-toloxysilane were compared by mixture melting points with specimens prepared by other methods (1). Triphenylethoxysilane was identified by mixture melting point with a sample isolated by Dr. L. F. Cason after treating triphenylchlorosilane with sodium ethoxide and ethanol.

---

[5] The petroleum ether referred to in this report boils from 60–68°. This low-boiling petroleum ether and ligroin appear to be superior to commercial heptane and cyclohexane for recrystallization of these compounds.

TABLE II

THE REACTION OF TRI-*o*-TOLYLCHLOROSILANE (*o*-Tol_3SiCl) WITH VARIOUS ALCOHOLS (ROH) AND PHENOL

ROH OR C_6H_5OH	Moles ROH or C_6H_5OH[a] / Moles *o*-Tol_3SiCl	REACTION CONDITIONS		PRODUCT(S) ISOLATED	YIELD, %
		Time, min.	Temp., °C.		
CH_3OH	40	10	Reflux	*o*-Tol_3SiOCH_3	97
C_2H_5OH	40	10	Reflux	*o*-$Tol_3SiOC_2H_5$	97
C_3H_7OH-*n*	25	15	Reflux	*o*-$Tol_3SiOC_3H_7$-*n*	30
C_3H_7OH-*iso*	25	20	Reflux	*o*-Tol_3SiOCH_3[b]	96
C_4H_9OH-*iso*	25	15	Reflux	*o*-Tol_3SiOCH_3[b]	35
$C_6H_5CH_2OH$	2	20	180	*o*-Tol_3SiCl	62
$C_6H_5CH_2OH$	2	240	130	*o*-Tol_3SiCl *o*-$Tol_3SiOCH_2C_6H_5$	50 11
$C_6H_5CH_2OH$	35	240	120	*o*-$Tol_3SiOCH_2C_6H_5$[c]	3
C_6H_5OH	2	30	100	*o*-Tol_3SiCl	80
C_6H_5OH	2[d]	60	100	*o*-Tol_3SiCl	80
C_6H_5OH	2[e]	240	Reflux	No crystalline products	

[a] The *o*-Tol_3SiCl was prepared as described in Reference 1. In most runs, 6.8 g. (0.02 mole) of the chlorosilane was used. The alcohols were dried and purified by distillation with benzene. [b] The methoxy group is derived from the methanol used in working up the crude product. [c] Tri-*o*-tolylbenzyloxysilane was first isolated and analysed by Mr. William F. Witmer. [d] The C_6H_5OH and *o*-Tol_3SiCl were dissolved in benzene and the solution was saturated with HCl gas. The benzene was then distilled off and the residue was heated strongly. The procedure was repeated before working up the reaction mixture. [e] The C_6H_5OH and *o*-Tol_3SiCl were dissolved in pyridine. At the end of the heating period, the volatile materials were removed by distillation.

The methyl and the *n*-propyl and isopropyl ethers of tri-*o*-tolylsilanol cannot be distinguished by melting point; furthermore, the isopropyl and isobutyl ethers, the silanol, and the chlorosilane all melt somewhere between 105 and 115°. In recognition of these facts, careful checks of the identity of crystalline products by mixture melting points with known, analysed samples were made in every reasonable case. As an additional precaution, melting point determinations on mixtures of analysed samples of the ethers, the silanol, and the chlorosilane were made; in every instance the melting point of the mixture was much lower than the melting points of the pure specimens.

Tri-o-tolylsilyl ethers. (a) From the chlorosilane and alcohols or phenol. The conditions of the experiments and the results are summarized in Table II. The general procedure was to heat the reaction mixture of chlorosilane and excess alcohol for the stated time and then to remove most of the unconsumed alcohol by distillation (at reduced pressure in the case of benzyl alcohol). If crystallization did not occur after cooling and standing, the alcohol was completely removed and petroleum ether was added. If crystallization still did not occur, the petroleum ether was replaced with methanol. In the experiments with *n*-propyl, isopropyl, and isobutyl alcohols it was found necessary to use methanol. Since tri-*o*-tolylmethoxysilane was recovered rather than the isopropyl and isobutyl ethers in their respective runs, it must be inferred that the methanol reacted with ether the expected product or the unchanged chlorosilane, or with both. In the experiment with *n*-propyl alcohol, tri-*o*-tolyl-*n*-propoxysilane was isolated although the yield was low; no methoxysilane could be isolated in this case. Hydrogen chloride was evolved during the regular heating periods indicating that reaction does occur between tri-*o*-tolylchlorosilane and *n*-propyl, isopropyl, and isobutyl alcohols. Kinetic studies, too, show that tri-*o*-tolylchlorosilane reacts with these alcohols, although the rate of reaction is slower than with methanol and ethanol.[6] These facts suggest that the poor results obtained with this method in the above cases should be attributed, in part, to the difficulty of isolating products rather than to failure of the reaction itself.

In those runs where tri-*o*-tolylchlorosilane was treated with phenol, the excess phenol was removed by washing the diluted reaction mixture with aqueous sodium carbonate before any attempt was made to isolate a product.

In the early experiments with the tri-*o*-tolylchlorosilane-ethanol reaction, hydrogen chloride was bubbled through the boiling solution. In later work, it was found that the hydrogen chloride had no beneficial effect,[7] and the reaction was found to be very rapid at the boiling point of the solution even when precautions were taken to remove all possible traces of hydrogen chloride.

Tri-o-tolyl-beta-dimethylaminoethoxysilane. *beta*-Dimethylaminoethanol boiling at 131.0–131.5° (uncorr.)/750 mm. (n_D^{20} 1.4268) was used in these experiments.

A solution of 15.1 g. (0.045 mole) of tri-*o*-tolylchlorosilane (1) in 50 ml. of petroleum ether (b.p. 60–68°) was treated with 8.0 g. (0.090 mole) of *beta*-dimethylaminoethanol. No attempt was made to separate the crystalline salts that formed on mixing. After refluxing for one hour, the mixture was poured onto an excess of 1 *N* alkali and ice. The organic layer was separated and dried. It was then diluted to 200 ml. with petroleum ether (b.p. 60–68°) and treated with hydrogen chloride. There was separated 20 g. of hygroscopic salt, m.p. 155–165°. This was washed with hot carbon tetrachloride and was twice recrystallized from a 1:1 benzene-acetone solution. In this way 5.0 g. (28%) of pure tri-*o*-tolyl-*beta*-dimethylaminoethoxysilane hydrochloride was isolated, m.p. 188.5–189.5°, (uncorr.). This compound appears to deteriorate slowly in moist air. It is sparingly soluble in petroleum ether and carbon tetrachloride, but appreciably soluble in benzene and very soluble in methanol and ethanol.

The filtrates and wash liquors yielded 8.0 g. (50%) of crude tri-*o*-tolylsilanol, m.p. 100–108°. This was recrystallized from petroleum ether to give pure tri-*o*-tolylsilanol, m.p. 107–108° (uncorr.), identified by mixture melting point.[8]

The free amine was obtained either from the purified hydrochloride or from a reaction such as that described above without the intermediate isolation of the hydrochloride. One gram (0.0024 mole) of the pure hydrochloride was dissolved in 5 ml. of absolute ethanol and the solution was treated with 3 ml. of 5% alcoholic potassium hydroxide (0.0027 mole). Potassium chloride formed immediately and, on cooling to −40°, 0.50 g. (55%) of the crude amine, m.p. 58–63°, crystallized out. This was recrystallized from petroleum ether at −40° to give pure tri-*o*-tolyl-*beta*-dimethylaminoethoxysilane, m.p. 68.5–69.5° (uncorrected). In an experiment where the original reaction mixture was used instead of the purified hydrochloride, the product was isolated by distillation after treatment with alkali and evaporation of the solvent. The fraction distilling from 185–195°/2 mm. crystallized on cooling (55% yield) and melted at 65–66° (uncorr.). This material was further purified by recrystallization from petroleum ether at −40°. The compound is extremely soluble in organic solvents.

The *picrate* was obtained by treating 0.05 g. of tri-*o*-tolyl-*beta*-dimethylaminoethoxysilane in 2 ml. of absolute ethanol with excess saturated ethanolic picric acid. This picrate melted at 198–199° (uncorr.) as recovered from the reaction mixture and the melting point was not raised by recrystallization. The compound was not analysed.

Tri-o-tolylsilyl ethers. (b) From the chlorosilane and sodium alkoxides or phenoxides. In

---

[6] The results of studies on the rates of reaction of triphenylchlorosilane and tri-*o*-tolychorosilane with various alcohols will be presented in a later report.

[7] This work was done by Mr. William F. Witmer, senior student at Muhlenberg College.

[8] The preparation of the silanol from the chlorosilane and other derivatives will be described in a later report.

the preparation of the *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *sec*-butyl ethers of tri-*o*-tolylsilanol, 0.50 g. of sodium (0.022 g.-atom) was dissolved in 5–10 ml. of the dry, freshly-distilled alcohol[9] and to the resulting solution was added 6.8 g. (0.020 mole) of tri-*o*-tolylchlorosilane (1). Reaction was rapid as evidenced by the precipitation of sodium chloride. The mixture was heated for 20–60 minutes and was then poured onto a mixture of ice and dilute hydrochloric acid. The oil which settled out was allowed to harden and was then filtered off. The crude material, after drying, was recrystallized several times from heptane, petroleum ether,[5] benzene-methanol solution, or methanol. In these reactions, methanol did not create any difficulties by reacting with the products.

The crude and recrystallized yields of the tri-*o*-tolylsilyl ethers were as follows: *n*-propyl, 96% and 71%; isopropyl, 98% and 41%; *n*-butyl, 99% and 86%; isobutyl, 98% and 85%; and *sec*-butyl, 84% and 68%. Re-working of the mother liquors would have given higher yields of recrystallized material in every case.

In the attempted preparation of the *tert*-butyl ether, the same procedure was followed except that the chlorosilane was refluxed with the sodium *tert*-butoxide–*tert*-butyl alcohol mixture for 24 hours. This reaction, like the others in this group, was protected from atmospheric moisture. When the crude product was worked up in the usual manner, there was isolated 62% of unchanged tri-*o*-tolylchlorosilane and 9% of a compound melting at 270–273° (uncorrected). This latter compound has not been completely characterized but it appears to be hexa-*o*-tolyldisiloxane, not hitherto reported. The essential features of this run were confirmed by two additional experiments and, in addition, it was shown that some tri-*o*-tolylsilanol is formed during the reaction. There is also some evidence of the formation of small amounts of the silanol and the high-melting compound in the experiment with *sec*-butyl alcohol.

For the preparation of the tri-*o*-tolylbenzyloxysilane, sodium benzyloxide was made by adding excess benzyl alcohol to a solution of sodium methoxide in methanol; the methanol was subsequently removed by strong heating. When the sodium benzyloxide was treated with the chlorosilane in the presence of excess benzyl alcohol, a rapid reaction occurred. After heating for 10 minutes, the reaction mixture was hydrolyzed and the product was worked up in the usual way. The crude yield approximated 100%, and the recrystallized yield was 80%.

Tri-o-tolyl-o-toloxysilane from tri-o-tolylchlorosilane.[10] Sodium *o*-cresoxide was made by treating sodium methoxide (0.020 mole) in methanol with an equivalent amount of freshly-distilled *o*-cresol; the methanol was removed by strong heating under reduced pressure. The dry salt was then mixed with 3.4 g. (0.010 mole) of tri-*o*-tolylchlorosilane and 0.3 g. of "precipitated" copper powder.[11] The mixture was heated for 5 hours at 230° and for 30 minutes at 270°. After cooling, the mixture was extracted with benzene, and the extract was washed quickly with dilute hydrochloric acid, dried, and distilled. The fraction distilling from 180–235°/5 mm. (chiefly, 225–230°) crystallized on treatment with petroleum ether, and there was isolated 1.8 g. (50%) of tri-*o*-tolyl-*o*-tolyloxysilane, m.p. 149–152° (uncorr.), and considerable material of poorer quality. Recrystallization from petroleum

---

[9] The *n*-propyl and *n*-butyl alcohols dissolved the sodium readily. Isobutyl alcohol (10 ml.) required 1 hour to dissolve 0.5 g. of sodium at the boiling point. Isopropyl, *sec*-butyl, and *tert*-butyl alcohols dissolved the sodium very slowly: *sec*-butyl alcohol required 10 hours and *tert*-butyl alcohol required 14 hours at the boiling point. These sodium alkoxides, once formed, are sparingly soluble.

[10] In the first paper of this series (Reference 1), p. 729, Table IV, the by-product in Run 4 is listed "$R_3SiOC_2H_5$," that is, tri-*o*-tolylethoxysilane; this should read "$R_3SiOC_6H_4CH_3$-*o*," that is, tri-*o*-tolyl-*o*-toloxysilane. The product is correctly described in the text of the paper (p. 733).

[11] It is not certain that copper is an essential component of the reaction mixture; see further, the preparations of tri-*o*-tolylsilyl stearate and tri-*o*-tolyl-*p*-tolylmercaptosilane (Reference 2).

ether (b.p. 60–68°) containing a little benzene gave the desired compound, m.p. 153–154° (uncorr.), in nearly quantitative recovery.

Triphenylethoxysilane from triphenylsilanol. Triphenylsilanol (0.1 g., 0.0004 mole) was treated with 0.1 g. of anhydrous zinc chloride and 5 ml. of absolute ethanol under reflux for 7 days. The syrupy residue which remained after removal of the ethanol was vacuum-distilled onto a cold finger. In this way there was recovered 0.07 g. (64%) of a crystalline solid melting at 57–60°. Redistillation gave a sample melting at 61–62° (uncorr.) which did not depress the melting point of authentic triphenylethoxysilane, m.p. 63–64° (uncorr.) [reported: 65° (20)].

The formation of the ethoxysilane was very slow. After 24 hours of reflux no triphenylethoxysilane could be isolated, although the melting point of the recovered silanol had dropped from 154° to about 140°. No triphenylsilane could be detected and it appears certain that reduction does not occur since samples of the crude product gave no hydrogen when treated with potassium hydroxide in pyridine (21, 5). The formation of the ethoxysilane and the non-formation of the reduction product were confirmed in a larger run (10 g. of silanol) by Dr. G. E. Dunn. Dr. Dunn was also able to show that, when a five-fold excess of anhydrous zinc chloride is used in a reaction lasting 15 minutes, hexaphenyldisiloxane is formed in small amounts; no ethoxysilane could be isolated in this case. When a five-fold excess of zinc chloride was used in a reaction lasting 4 hours, however, neither hexaphenyldisiloxane nor the ethoxysilane could be isolated. Under no circumstances could triphenylsilane be isolated or detected.

When tri-*o*-tolylsilanol was treated with ethanol and zinc chloride at the boiling point for 7 days, the silanol was recovered unchanged. Triphenylsilanol could not be converted into its phenoxy ether by refluxing it with an equivalent amount of phenol in xylene solution where conditions were arranged to permit the continuous removal of water. When the reaction mixture was treated with anhydrous HCl (19) and, eventually, with anhydrous zinc chloride, no crystalline products could be isolated when the reaction mixtures were worked up in the usual way.

Triarylsilyl ethers from triarylsilanes. (*a*). *Triphenylphenoxysilane.* To a solution of 0.46 g. (0.020 g.-atom) of sodium in 20 g. (0.213 mole) of dry phenol was added 5.2 g. (0.020 mole) of triphenylsilane[12] of melting range 43–44°. The mixture was stirred at 120° for four hours (precipitate present) and at 190° for one hour (homogeneous solution). The cooled mass was extracted with dry benzene, the benzene was evaporated from the extract, and the residue was distilled at reduced pressure. The fraction distilling at about 200°/4 mm. solidified in the receiver. This 5.4 g. of material melted at 100–103° and represented a 75% yield of crude triphenylphenoxysilane. Recrystallization from petroleum ether (b.p. 60–68°) gave 4.8 g. of pure triphenylphenoxysilane, m.p. 103–104° (uncorr.). Triphenylphenoxysilane (not listed in Table I) is very stable to heat and is unaffected by water or by dilute aqueous acids or bases. It has similar solubility properties to the tri-*o*-tolylsilylethers. Attempts to prepare this compound from triphenylsilanol and phenol were unsuccessful.

The structure of triphenylphenoxysilane was confirmed in the following manner. Triphenylphenoxysilane (0.30 g., 0.00085 mole), m.p. 102–104°, (uncorr.), was refluxed for 45 minutes with 4 ml. of 90% ethanol containing 0.15 g. (0.0027 mole) of potassium hydroxide. After dilution and neutralization of the excess alkali, there was isolated 0.16 g. (70%) of triphenylsilanol, m.p. 145–152° (uncorr.), identified by mixture melting point. The filtrate from which the silanol had been separated was treated with excess bromine and, after working up in the usual manner, there was isolated 0.20 g. (70%) of tribromophenol, m.p. 88–90° (uncorr.), identified by mixture melting point.

(*b*). *Tri-o-tolylethoxysilane.* One gram (0.0033 mole) of tri-*o*-tolylsilane (1) was refluxed for 28 hours with 20 ml. of an ethanol solution containing 1.0 g. (0.044 g.-atom) of dissolved sodium. After partial evaporation of the solvent and cooling, a 60% yield of crude tri-*o*-tolylethoxysilane was isolated which melted at about 125°. This material was recrystal-

---

[12] This compound was prepared by Dr. R. A. Siebert from trichlorosilane and phenylmagnesium bromide.

lized from ethanol to give 0.4 g. (35%) of tri-*o*-tolylethoxysilane, m.p. 144.5–145.0° (uncorr.), identified by mixture melting point.

(*c*). *Attempted preparation of tri-o-tolyl-o-tolyloxysilane from tri-o-tolylsilane.* Tri-*o*-tolyl-*o*-toloxysilane could not be made from tri-*o*-tolylsilane and sodium *o*-cresoxide. A mixture of 0.46 g. (0.020 g.-atom) of sodium, 6.8 g. (0.020 mole) of tri-*o*-tolylsilane (1), and 20.0 g. (0.19 mole) of redistilled *o*-cresol was heated under nitrogen for 12 hours at 120° and for 5 hours at 200°. The cooled mixture was then treated with 50 ml. of benzene and an additional 0.5 g. (0.02 g.-atom) of sodium and was refluxed for 48 hours. The benzene was distilled off and the residue was heated for one more hour at 200°. A benzene extract of the resulting mixture gave 5.4 g. (80%) of unchanged tri-*o*-tolylsilane on distillation at reduced pressure. This material melted at 83–85° and was identified by mixture melting point.

Tri-o-tolylethoxysilane from tri-o-tolyldi-n-butylaminosilane. A solution of 0.08 g. (0.0002 mole) of tri-*o*-tolyldi-*n*-butylaminosilane (2) in 5 ml. of refluxing ethanol was treated with a slow stream of dry hydrogen chloride for 30 minutes. The solvent was evaporated and the syrupy residue was partitioned between ether and water. The ether layer gave 0.035 g. (55%) of tri-*o*-tolylethoxysilane, m.p. 143–144° (uncorr.), identified by mixture melting point. The water layer gave 0.005 g. (17%) of di-*n*-butylammonium chloride, m.p. 283° (uncorr.), identified by mixture melting point.

Tri-o-tolylmethoxysilane from tri-o-tolylsilyl acetate. Tri-*o*-tolylsilyl acetate (2) (0.50 g., 0.0014 mole) and a microdrop of concentrated sulfuric acid were dissolved in 9 ml. of methanol. The solution was refluxed for 3.5 hours. After distilling off one-half of the methanol and cooling, there was isolated 0.37 g. (80%) of tri-*o*-tolylmethoxysilane in two crops, m.p. 100–102° and 99–101°. These samples did not depress the melting point of pure tri-*o*-tolylmethoxysilane.

In another experiment tri-*o*-tolylsilyl acetate was recovered unchanged after standing at room temperature for 24 hours in benzene-ethanol solution (no sulfuric acid). Under these conditions triphenylsilyl acetate[13] was changed into triphenylethoxysilane (apparently quantitatively).

Tri-o-tolylmethoxysilane from the n-propyl and isopropyl ethers. Tri-*o*-tolylisopropoxysilane (0.50 g., 0.0014 mole) and two microdrops of sulfuric acid were dissolved in a solution containing 10 ml. of methanol and 5 ml. of benzene. After refluxing for 16 hours, the solvent was distilled off. The residue was treated with methanol and there was obtained 0.38 g. (82%) of tri-*o*-tolylmethoxysilane in three crops, m.p. 100–101°, 99–102°, and 97–99°. These samples depressed the melting point of tri-*o*-tolylisopropoxysilane but not the melting point of tri-*o*-tolylmethoxysilane.

When tri-*o*-tolyl-*n*-propoxysilane was treated in similar fashion, tri-*o*-tolylmethoxysilane was isolated in 82% yield. Tri-*o*-tolylbenzyloxysilane, under the same conditions was recovered unchanged in 85% yield.

SUMMARY

1. Ten new triarylsilyl ethers have been prepared. These are the methyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, and benzyl ethers of tri-*o*-tolylsilanol, tri-*o*-tolyl-*beta*-dimethylaminoethoxysilane and its hydrochloride, and triphenylphenoxysilane.

2. Triphenylethoxysilane, tri-*o*-tolylethoxysilane, and tri-*o*-tolyl-*o*-toloxysilane have been prepared by new methods.

3. New evidence is presented to support the view that triarylsilanes are less reactive than triarylchlorosilanes.

4. Triarylsilyl ethers have been prepared from the related triarylchlorosilanes,

---

[13] The preparation of triphenylsilyl acetate from the chlorosilane, sodium acetate, and acetic acid will be described in a later report.

triarylsilanes, triarylsilanols, triarylsilyl esters, triarylsilyl amines, and from other triarylsilyl ethers. The results obtained are consistent with the view that steric factors are of prime importance in tri-*o*-tolylsilyl compounds.

AMES, IOWA
ALLENTOWN, PA.

REFERENCES

(1) GILMAN AND SMART, *J. Org. Chem.*, **15**, 720 (1950).
(2) GILMAN AND SMART, *J. Org. Chem.*, **16**, 424 (1951).
(3) CUSA AND KIPPING, *J. Chem. Soc.*, 2205 (1932).
(4) SCHUMB AND SAFFER, *J. Am. Chem. Soc.*, **61**, 363 (1939).
(5) GILMAN AND CLARK, *J. Am. Chem. Soc.*, **69**, 1499 (1947); GILMAN AND BRANNEN, *J. Am. Chem. Soc.*, **73**, 4640 (1951).
(6) TYLER, SOMMER, AND WHITMORE, *J. Am. Chem. Soc.*, **69**, 981 (1947); *J. Am. Chem. Soc.*, **70**, 2876 (1948).
(7) NEBERGALL AND JOHNSON, *J. Am. Chem. Soc.*, **71**, 4022 (1949).
(8) NAGEL AND POST, *J. Org. Chem.*, **17**, 1382 (1952).
(9) SPEIER, *J. Am. Chem. Soc.*, **74**, 1003 (1952).
(10) WILLIAMSON, *Ann.*, **81**, 77 (1851).
(11) SMART AND KEEFER, Unpublished results.
(12) JOFFE AND POST, *J. Org. Chem.*, **14**, 421 (1951).
(13) BOYE AND POST, *J. Org. Chem.*, **16**, 391 (1951).
(14) FRIEDEL AND CRAFTS, *Ann.*, **136**, 203 (1865).
(15) REILLY AND POST, *J. Org. Chem.*, **16**, 383 (1951).
(16) GILMAN AND MELVIN, *J. Am. Chem. Soc.*, **71**, 4050 (1949).
(17) NEBERGALL, *J. Am. Chem. Soc.*, **72**, 4702 (1950).
(18) POST AND HOFRICHTER, *J. Org. Chem.*, **5**, 443 (1940).
(19) DOLGOV AND VOLNOV, *Zhur. Obshchei Khim., Khim. Ser.*, *I*, 91 (1931); [*Chem. Abstr.*, **25**, 4536 (1931)].
(20) NAMETKIN, TOPCHIEV, AND MACHUS, *Doklady Akad. Nauk S.S.S.R.*, **83**, 705 (1952); [*Chem. Abstr.*, **47**, 2723 (1953)].
(21) KIPPING AND SANDS, *J. Chem. Soc.*, **119**, 848 (1921).
(22) GILMAN AND DUNN, *Chem. Revs.*, **52**, 77 (1953).