[Contribution from the Chemical Laboratory of Iowa State College]

Some Steric Effects of the Isopropyl Group in Organosilicon Compounds

By Henry Gilman and Russell N. Clark

In an earlier paper[1] it was reported that RLi compounds containing a simple alkyl or aryl group reacted promptly with silicon tetrachloride or ethyl orthosilicate or ethyl orthothiosilicate to give R_4Si compounds in high yields.

$$SiCl_4 + 4RLi \longrightarrow R_4Si + 4LiCl$$

Attention was called at that time to the slow introduction of the fourth R group with some sterically hindered radicals in the RLi compounds.

Actually we have since observed that under conventional experimental conditions only three isopropyl groups are introduced in the reaction of isopropyllithium with silicon tetrachloride or ethyl orthosilicate to give tri-isopropylsilyl chloride and tri-isopropylethoxysilane, respectively.

$$SiCl_4 + i\text{-}C_3H_7Li \longrightarrow (i\text{-}C_3H_7)_3SiCl + LiCl$$

Another general procedure[2] for the introduction of a fourth R group is the reaction of a silane with an RLi compound.

$$R_3SiH + RLi \longrightarrow R_4Si + LiH$$

We first prepared tri-isopropylsilane from silicochloroform and three equivalents of isopropyllithium. Then we observed that the tri-isopropylsilane underwent essentially no reaction with isopropyllithium.

The three isopropyl groups about silicon in the chloride and in the silane do not interfere with the introduction of a fourth R group, for phenyllithium with each of these compounds gives tri-isopropylphenylsilane.

$$(i\text{-}C_3H_7)_3SiCl \text{ or } (i\text{-}C_3H_7)_3SiH + C_6H_5Li \longrightarrow (i\text{-}C_3H_7)_3SiC_6H_5$$

However, when a sterically hindered aryllithium compound like *o*-tolyllithium is treated with tri-isopropylsilane there is no apparent reaction.

The difficulty of forming tetraisopropylsilane from a tri-isopropylsilyl compound and isopropyllithium may not be wholly associated with steric factors. The solvent used for the preparation of isopropyllithium was low-boiling petroleum ether in order to circumvent the somewhat rapid cleavage of ethyl ether by this RLi compound.[3a] It is known that the solvent may have a marked effect on the rates of some organometallic reactions.[3] However, other studies[4a] with tri-*o*-tolyl- and dimesityl-silicon types in ethyl ether show that the steric factors are of prime importance.[4b]

The type of organometallic compound that is used is quite significant. For example, a standard procedure for the preparation of R_3SiH compounds is the reaction of silicochloroform with a Grignard reagent.[5] However, from a reaction in ethyl ether between silicochloroform and isopropylmagnesium chloride no tri-isopropylsilane was isolated. Instead only two isopropyl groups were introduced and the somewhat novel products isolated, subsequent to hydrolysis, are apparently di-isopropylsilanol, $(i\text{-}C_3H_7)_2SiH(OH)$, and *sym*-tetra-isopropyldisiloxane, $(i\text{-}C_3H_7)_2Si(H)\text{-}O\text{-}Si(H)\text{-}(C_3H_7\text{-}i)_2$. It is known that the introduction of a fourth R group to prepare an R_4Si compound from silicon tetrachloride or ethyl orthosilicate and the Grignard reagent proceeds slowly and generally gives low to moderate yields. The present studies indicate that even a third group like isopropyl is introduced with difficulty by means of the Grignard reagent.

Apropos the probable influence of steric factors it should be stated that the chlorine in tri-isopropylsilyl chloride undergoes hydrolysis at an appreciably slower rate than that of simple trialkylsilyl and triarylsilyl chlorides. In this connection it should be stated that tri-isopropylsilyl chloride was converted to tri-isopropylethoxysilane by heating with absolute ethanol and pyridine.

Experimental

Reaction of Isopropyllithium with Silicon Tetrachloride and with Ethyl Orthosilicate.—From 6.8 g. (0.04 mole) of silicon tetrachloride and 0.2 mole of isopropyllithium in 250 cc. of petroleum ether (b. p. 28–38°) there was obtained 5.8 g. (68%) of tri-isopropylsilyl chloride distilling at 198° (739 mm.) or 59° (8 mm.); n^{20}_{D} 1.4518; d^{20}_{4} 0.9008; MR_D 57.81 (calcd. MR_D 58.0).

Anal. Calcd. for $C_9H_{21}ClSi$: Cl, 18.42. Found: Cl, 18.13.

In another preparation, the Color Test I[6] was negative directly after adding 0.129 mole of isopropyllithium in 100 cc. of petroleum ether over a period of thirty-five minutes to 7.5 g. (0.043 mole) of cooled silicon tetrachloride. The yield was 8.1 g. (97%); b. p. 59° (8 mm.); n^{20}_{D} 1.4511; d^{20}_{4} 0.9027; MR_D 57.76 (calcd. MR_D 58.0).

Anal. Calcd. for $C_9H_{21}ClSi$: Cl, 18.42. Found: Cl, 18.18.

From 5.2 g. (0.025 mole) of ethyl orthosilicate and an excess of isopropyllithium there was isolated, subsequent to a twenty-four hour period of refluxing in petroleum ether (b. p., 28–38°), 4.8 g. (78%) of tri-isopropylethoxysilane; b. p., 200° (738 mm.); n^{20}_{D} 1.4560; d^{20}_{4} 0.8657; MR_D 63.18 (calcd. MR_D 63.37).

Anal. Calcd. for $C_{11}H_{26}OSi$: Si, 13.88. Found: Si, 14:05.

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(1) Gilman and Clark, This Journal, **68**, 1675 (1946). See, particularly, Fleming, U. S. Patent 2,386,452 [*C. A.*, **40**, 603 (1946)] on the preparation of some unsymmetrical silicon compounds by means of RLi compounds.

(2) (a) Gilman and Massie, This Journal, **68**, 1128 (1946); see, also, (b) Meals, *ibid.*, **68**, 1880 (1946).

(3) (a) Gilman, Moore and Baine, *ibid.*, **63**, 2479 (1941). Gilman, Moore and Jones, *ibid.*, **63**, 2482 (1941); Gilman and Jones, *ibid.*, **62**, 1243 (1940); see, also, ref. 2b.

(4) (a) By Dr. G. N. Russell Smart; (b) see Fuoss, This Journal, **65**, 2406 (1943), for a treatment of consecutive, competitive reactions.

(5) Reynolds, Bigelow and Kraus, This Journal, **51**, 3067 (1929); Kraus and Nelson, *ibid.*, **56**, 195 (1934); Taylor and Walden, *ibid.*, **66**, 842 (1944).

(6) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

Conversion of Tri-isopropylsilyl Chloride to Tri-isopropylethoxysilane.—A solution of 4.1 g. (0.02 mole) of the silyl chloride, 20 cc. of absolute ethanol and 4 g. (0.05 mole) of pyridine[7] was refluxed for eight hours. Most of the ethanol was distilled from the solution; ether was added; the mixture was filtered; and after removing the solvent there was obtained by distillation 2 g. (95%) of tri-isopropylethoxysilane; b. p. 198° (738 mm.); n^{20}_{D} 1.4560; d^{20}_{4} 0.8652; MR_D 63.26.

Anal. Calcd. for $C_{11}H_{26}OSi$: Si, 13.88. Found: Si, 14.01.

Tri-isopropylsilane.—To 13.6 g. (0.1 mole) of silicochloroform[8] in 100 cc. of petroleum ether (b. p., 28–38°) was added, over a three-hour period, 0.3 mole of isopropyllithium in 450 cc. of petroleum ether. The reaction flask was maintained at $-5°$ during the entire addition, and Color Test I was negative when all the RLi solution had been added. The mixture was allowed to stand overnight, filtered, the solvent removed in an atmosphere of purified nitrogen, and the product was fractionally distilled at reduced pressure in an inert atmosphere. The yield of tri-isopropylsilane was 10.2 g. (64%); b. p. 60–61° (3.5 mm.); n^{20}_{D} 1.4358; d^{20}_{4} 0.7726; MR_D 53.42 (calcd. MR_D 53.42).

Anal. Calcd. for $C_9H_{22}Si$: Si, 17.73. Found: Si, 17.56.

After refluxing a solution of 0.05 mole of isopropyllithium and 3 g. (0.019 mole) of tri-isopropylsilane in a total of 175 cc. of petroleum ether for three and one-half days Color Test I was positive. There was recovered 2.6 g. (86%) of the silane; b. p. 71° (5 mm.); n^{20}_{D} 1.4350; d^{20}_{4} 0.7731.

Tri-isopropylphenylsilane.—A. A solution of 3 g. (0.019 mole) of tri-isopropylsilane and 0.05 mole of phenyllithium in 125 cc. of ether was stirred and refluxed for two days, at the end of which time Color Test I was positive. Subsequent to hydrolysis and drying the organic layer over sodium sulfate, the product was fractionated to give 1.2 g. (27%) of tri-isopropylphenylsilane; b. p. 90–91° (4 mm.); d^{20}_{4} 0.9055; n^{20}_{D} 1.5105.

B. A solution of 9.7 g. (0.05 mole) of tri-isopropylchlorosilane and 0.05 mole of phenyllithium in 115 cc. of ether was stirred and refluxed for two days. There was isolated, in the usual manner, 4.2 g. (36%) of tri-isopropylphenylsilane; b. p. 90–91° (4 mm.); d^{20}_{4} 0.9049; n^{20}_{D} 1.5102; MR_D 77.40 (calcd. MR_D 77.62).

Anal. Calcd. for $C_{15}H_{26}Si$: Si, 11.96. Found: Si, 11.78 and 11.81.

Subsequent to refluxing a solution of 3 g. (0.019 mole) of tri-isopropylsilane and 0.05 mole of *o*-tolyllithium in 150 cc. of ether for thirty-six hours Color Test I was positive. There was recovered, by customary procedures, 2.5 g. (82%) of tri-isopropylsilane; b. p., 64–65° (4 mm.); d^{20}_{4} 0.7735.

Reaction of Silicochloroform with Isopropylmagnesium Chloride.—To a solution of 1.5 moles of isopropylmagnesium chloride in 1800 cc. of ether was added 46 g. (0.34 mole) of silicochloroform in 100 cc. of ether. The flask was cooled in an ice–salt-bath to $-10°$ and the temperature of the reaction mixture was maintained at -10 to $-5°$ during the addition. When all of the silicochloroform solution had been added, the mixture was stirred at room temperature for fifteen hours and then at reflux temperature for twenty-one hours. Hydrolysis was effected by slowly pouring the cooled mixture into a dilute sulfuric acid–ice mixture, maintaining the temperature during the hydrolysis between -10 and $-5°$. The organic layer was separated and dried, and after removing the solvent in a nitrogen atmosphere, the residue was fractionated at reduced pressure in a nitrogen atmosphere. Two fairly sharp fractions were obtained. One of these may be di-isopropylsilanol; b. p. 74–75° (6 mm.); d^{20}_{4} 0.8435; n^{20}_{D} 1.4350; MR_D 40.50 (calcd. MR_D 40.46). The yield was 5.6 g. (11%).

Anal. Calcd. for $C_6H_{16}OSi$: Si, 21.12. Found: Si, 20.98. A second fraction may be *sym*-tetra-isopropyldisiloxane; 129–130° (6 mm.); d^{20}_{4} 0.8899; n^{20}_{D} 1.4692; MR_D 76.61 (calcd. MR_D 76.90). The yield was 15.8 g. (42%).

Anal. Calcd. for $C_{12}H_{30}OSi_2$: Si, 22.70. Found: Si, 22.47. An intermediate fraction (10.2 g.) distilled over the range 76–128° (6 mm.).

In another preparation a significant difference was noted, and this may be due in part to the hydrolysis mixture used. The reaction mixture from 68 g. (0.5 mole) of silicochloroform and 2.2 moles of isopropylmagnesium chloride was hydrolyzed by pouring into a mixture of hydrochloric acid and ice. Again the reaction temperature during hydrolysis was maintained between $-10°$ and $-5°$. This time fractionation under reduced pressure and in an inert atmosphere gave but one fraction which appears to be di-isopropylsilanol; b. p. 64–65° (4 mm.); d^{20}_{4} 0.8431; n^{20}_{D} 1.4356. The yield was 67 g. (85%).

Both the supposed di-isopropylsilanol and *sym*-tetra-isopropyldisiloxane evolved a gas when treated with potassium hydroxide in piperidine. This is a modified test[9] for the Si–H linkage, as well as for the Si–Si bond. A control test with an authentic specimen of triphenylsilane was also positive, but the evolution of gas (hydrogen) in this case was more prompt than with the other two compounds. It might be mentioned that these sterically hindered types are being examined for the possibility of preparing silicon compounds with unsaturation stemming from silicon, as well as for regulated or controlled polymerization and copolymerization.

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Summary

Probably because of steric factors, isopropyllithium reacts with silicon tetrachloride and with ethyl orthosilicate to give tri-isopropylsilyl chloride and tri-isopropylethoxysilane, respectively, instead of tetra-isopropylsilane. Furthermore, with tri-isopropylsilane and isopropyllithium there is no evidence for the formation of appreciable quantities of the R_4Si compound.

From a reaction between isopropylmagnesium chloride and silicochloroform only two isopropyl groups are introduced to give apparently di-isopropylsilanol and *sym*-tetra-isopropyldisiloxane.

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[7] Pyridine has been used in related reactions by Sauer, THIS JOURNAL, **66**, 1707 (1944).

[8] The authors are grateful to Dr. Edgar Britton of the Dow Chemical Company for the silicochloroform.

[9] Kipping and Sands, *J. Chem. Soc.*, **119**, 848 (1921).