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STUDIES IN SILICO-ORGANIC COMPOUNDS. VII. THE PREPARATION AND PROPERTIES OF CERTAIN SUBSTITUTED SILANES[1]

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INTRODUCTION

It was the purpose of this work to prepare certain simple derivatives of silane of the general formulas $RSiHCl_2$, R_2SiHCl, and R_3SiH to be used later in more extensive work covering their properties. Interaction of trichlorosilane with organometallic compounds was selected as the method of preparation.

Pape (1, 2) prepared two types of silanes by the use of zinc dipropyl:

$$\text{I.}\quad 2HSiCl_3 + 4Zn(C_3H_7)_2 \rightarrow (C_3H_7)_3SiH + Si(C_3H_7)_4 + 3ZnCl_2 + Zn + C_3H_8.$$

Taurke (3) and Ladenburg (4) continued the work. Triphenylsilane has been prepared through the action of the Grignard reagent (5) and through the medium of a lithium derivative (6):

$$\text{II.}\qquad (C_6H_5)_3SiLi + NH_4Br \rightarrow (C_6H_5)_3SiH + LiBr + NH_3.$$

Other references complete the bibliography (7 through 17).

In 1885, Polis (20) prepared tetraphenylsilane, tetra-*p*-tolylsilane and tetrabenzylsilane by the interaction of the proper chloride, tetrachlorosilane, and sodium. Triphenylchlorosilane reacts with sodium (21) to form hexaphenyldisilane, and 1,3-diethyl-1,3-diphenyl-1,3-dipropyldisilane has been prepared by the action of sodium on ethylphenylpropylchlorosilane (22). On the other hand, Kipping and Steele (23) reported that the action of sodium on dibenzyldichlorosilane at the boiling point of toluene produced tetrabenzylsilane. Kraus and Nelson (7) prepared hexaethyldisilane by the interaction of sodium and triethylbromosilane. Other work followed (24, 25, 26). The use of lithium metal in syntheses of silicon compounds of these types has also been investigated (6, 9, 27, 28, 29, 30).

DISCUSSION

In view of the high degree of reactivity of the chlorine atoms in trichlorosilane it was felt that the Grignard reagents, in cases where these were used, should be added in high dilution. The work of Kraus and Nelson (7) was here repeated with satisfactory yields of triethylsilane. Interaction of 0.6 mole of benzylmagnesium chloride and 0.1 mole of trichlorosilane produced tribenzylsilane in good yields. The silicon compound was added to the Grignard. Adding in reverse order and decreasing the molar ratio of Grignard to trichlorosilane resulted in the preparation of benzyldichlorosilane and dibenzylchlorosilane.

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Dibenzyl was frequently observed as a by-product. The use of Grignard reagents which contained bromide was avoided whenever only partial replacement of chlorines was desired because of the possibility of halogen interchange.

The preparation of allylmagnesium bromide proceeded smoothly. Good yields of triallylsilane were obtained from the interaction of this reagent with trichlorosilane.

Using the method of Polis (20), *p*-ethylchlorobenzene, sodium, and tetrachlorosilane were allowed to react with the production of tetra-*p*-ethylphenylsilane:

$$\text{III} \quad 4\,p\text{-}C_2H_5C_6H_4Cl + SiCl_4 + 8Na \rightarrow 8NaCl + Si(C_6H_4C_2H_5\text{-}p)_4.$$

When Taurke's (3) method for the preparation of similar derivatives of trichlorosilane was used, only tetra-*p*-ethylphenylsilane was isolated. Here, sodium, trichlorosilane and *p*-ethylchlorobenzene were allowed to interact with ethyl acetate as the catalyst. Tetra-*p*-ethylphenylsilane was the only product when the experiments were repeated using hexachlorodisilane. No results were obtained with *m*-ethylchlorobenzene or with *o*-ethylchlorobenzene. Similar attempts to prepare tetra-*p*-propylphenylsilane and tetra-*p*-butylphenylsilane were unsuccessful. Lithium, trichlorosilane, and *p*-ethylchlorosilane reacting, produced only a small amount of tetra-*p*-ethylphenylsilane.

TABLE I

PHYSICAL PROPERTIES

SUBSTANCE	B.P., °C	M.P., °C	*d*	*n*
$HSi(C_2H_5)_3$	105–115			
$HSi(CH_2C_6H_5)_3$	200–210	90–91		
$(C_6H_5CH_2)_2SiHCl$[a]	155–151 (6 mm.)		1.0863(20°/20°)	1.5734(20°/D)
$C_6H_5CH_2SiHCl_2$[a]	53–55 (2 mm.)		1.1770(27°/27°)	1.5316(20°/D)
$HSi(CH_2CH{=}CH_2)_3$[a]	160–165		0.8705(25°/25°)	1.4678(25°/D)
$Si(C_6H_4C_2H_5-p)_4$[a]		199–201		

[a] New compound.

EXPERIMENTAL PART

Triethylsilane. Trichlorosilane (5 cc. 0.05 mole) in 100 cc. of anhydrous ether was added dropwise to 50 cc. (0.15 mole) of ethylmagnesium chloride in 100 cc. of anhydrous ether with cooling to 0° and stirring. The system was allowed to warm up to room temperature and was refluxed for eight hours with constant stirring. Ice-water, 100 cc., containing 5 cc. of sulfuric acid was added. The ether layer was removed and dried over calcium chloride. Distillation yielded 3 cc., b.p. 105–115°, soluble in acetone and 95% ethanol. The product evolved hydrogen when treated with warm alcoholic sodium hydroxide. A repetition of this run using double quantities yielded 10 cc. of triethylsilane.

Tribenzylsilane. Trichlorosilane (10 cc., 0.1 mole) in 100 cc. of anhydrous ether was added dropwise to 300 cc. (0.6 mole) of benzylmagnesium chloride in ether with constant stirring. The system was kept at 0°. After standing sixty-six hours the mixture was refluxed for twenty-three hours. Acidified water was added and the ether layer separated.

After distillation of the ether and cooling, white crystals appeared, m.p. 91°, yield 67%, mol. wt. (cryoscopic from benzene) 309; calc'd, 302. Hydrogen was evolved with sodium hydroxide in ethanol. On repetition using 0.3 mole of benzylmagnesium chloride and 0.1 mole of trichlorosilane the entire reaction mixture was filtered by suction and the ethereal solution distilled. There were obtained crystals, b.p. 150–160° (22 mm.), m.p. 52–53° and a non-distillable residue. The crystals were dibenzyl. After three days, crystals of tribenzylsilane deposited from the residue, m.p. 90°. Benzylmagnesium chloride (0.2 mole) in anhydrous ether was added dropwise to 10 cc. (0.1 mole) of trichlorosilane in 400 cc. of anhydrous ether with stirring at 0°. The system was allowed to stand at room temperatures for sixty-four hours, then refluxed for four hours. Vacuum distillation of the ether layer produced 7 cc. of a colorless liquid, b.p. 200–210° which crystallized on cooling, m.p. 90°, tribenzylsilane. A small amount (2 cc.) of a low-boiling product was obtained, Cl (found) 4.93; calc'd dibenzylchlorosilane, 14.4.

Dibenzylchlorosilane. From the interaction of 0.6 mole of benzylmagnesium chloride in anhydrous ether and 0.3 mole of trichlorosilane, also in anhydrous ether, there was formed after seventeen hours standing and eight hours refluxing, 26 cc. of a colorless liquid b.p. 155–161° (6 mm.), Cl (found) 13.77; calc'd dibenzylchlorosilane, 14.4: $d(20°/20°) = 1.0863$, $n(20°/\text{D}) = 1.5734$. Tribenzylsilane was isolated from the residue.

Benzyldichlorosilane. When benzylmagnesium chloride and trichlorosilane reacted as above but in the molar ratio of 1:1, there was obtained 10 cc. of a distillate, b.p. 53–55° (2 mm.), Cl (found) 37.58, 37.70; calc'd benzyldichlorosilane, 37.20; $n(20°/\text{D}) = 1.5316$, $d(27°/27°) = 1.1770$. Subsequent runs confirmed these results, with the formation of dibenzylchlorosilane as well. At times isolable amounts of tribenzylsilane were also formed here.

Triallylsilane. A three-neck, 3-liter flask filled with anhydrous ether was used to prepare 1.0 mole of the Grignard reagent made from allyl bromide and magnesium. After forty-eight hours, 0.1 mole of trichlorosilane was added dropwise, diluted with about five volumes of anhydrous ether. The reaction commenced immediately without preheating, in fact ice cooling was necessary throughout. After one hour, the system was refluxed for twelve hours, with formation of a grey pasty mass on the sides of the flask. Excess Grignard reagent was destroyed by the addition of 100 cc. of ice and water slightly acidified with 15 cc. of sulfuric acid. The ether extract of this mixture, dried over calcium chloride, yielded fractions b.p. 75–80° and 155–165°. Subsequent runs showed increased yields. It was later found that instead of a 10:1 molar ratio of Grignard reagent to trichlorosilane, 8:1 proved sufficient. The first fraction was allyl bromide, the second b.p. 160–165° was triallylsilane. Triallylsilane has a mint-like odor, is flammable with a smoky flame, $d(25°/25°) = 0.8705$, $n(25°/\text{D}) = 1.4678$, insoluble in water, neutral, soluble in acetone, ether, and alcohol. Triallylsilane reacted violently with concentrated sulfuric acid with evolution of smoke and formation of a black mass. Silver in silver nitrate was reduced to a black powcer. Hydrogen gas was evolved on treatment with alcoholic potassium hydroxide. Mol Wt. (cryoscopic from benzene) 144; calc'd, 152.

Tetra-p-ethylphenylsilane. Thinly sliced sodium (11.5 g., 0.5 mole) under 150 cc. of anhydrous ether was treated with 35 g. (0.25 mole) of *p*-ethylphenylchlorobenzene in 100 cc. of anhydrous ether. Under continuous stirring and cooling in an ice-bath, 10.6 g. (0.063 mole) of tetrachlorosilane was added. The reaction proceeded by itself for about two hours and was brought to completion by the heat of a water-bath. A blue color developed and a blue precipitate separated. After standing overnight, the reaction mixture was filtered and the remaining liquid cooled to 10° for twelve hours. Long needles appeared and were purified from ether, weight 8 g., m.p. 199–201°, Si (found) 6.66, 5.98; calc'd, tetra-*p*-ethylphenylsilane, 6.26, mol. wt., (cryoscopic from benzene) 432.0, 451.0; calc'd, 448.5. In a similar manner, using 0.25 mole of trichlorosilane, 4.0 g. of tetra-*p*-ethylphenylsilane were obtained, m.p. 199–201°, m.p. (mixed with first sample) 198–201°, mol. wt., (cryoscopic from benzene) 460.5. Repetition of the experiment using 0.041 mole of hexachlorodisilane and 3 cc. of ethyl acetate as catalyst produced 5 g. of tetra-*p*-ethylphenylsilane, m.p. 199–201°, mol. wt. (cryoscopic from benzene) 465.

Butylbenzene was prepared by the interaction of 141 g. of bromobenzene, 123 g. of butyl bromide, and 57.6 g. of sodium in 200 cc. of anhydrous ether. A vigorous reaction set in which proceeded for three hours without application of heat. A blue precipitate formed and the sodium was covered with a blue deposit. The reaction mixture was then refluxed for five hours and filtered. Butylbenzene b.p. 175–179° (750 mm.), 53 g.

p-Butylchlorobenzene was formed when butylbenzene was subjected to the action of a stream of chlorine gas with iron nails as catalyst. The reaction flask was surrounded by an ice-bath while the chlorine was bubbled through the hydrocarbon. *p*-Butylchlorobenzene, b.p. 220–223° (751 mm.), 217–224° (748 mm.), average yield 72%, b.p. [literature (31) 225–228° (761 mm.)].

p-Propylchlorobenzene was prepared as was the butyl compound above, b.p. 195–198° (758 mm.), [literature (32) 190–192° (760 mm)].

Trichlorosilane was obtained from a reliable source. Its physical properties were satisfactory.

Ethylmagnesium chloride was purchased from Arapahoe Chemicals Inc., Boulder, Colorado.

Benzylmagnesium chloride was prepared in this laboratory by the usual procedure.

Diethyl ether was made anhydrous by further drying the purchased anhydrous grade over sodium and distilling.

Chlorine was determined by the method of Rochow (19).

Silicon was determined by the perchloric acid method.

SUMMARY

1. The preparation of trethylsilane has been repeated with good yields.

2. The interaction of benzylmagnesium chloride and trichlorosilane in molar proportions varying from 6:1 to 1:1 produces tribenzylsilane, dibenzylchlorosilane, and benzyldichlorosilane. Dibenzyl is formed in small amounts as a by-product.

3. The preparation of triallylsilane through the interaction of allylmagnesium bromide and trichlorosilane is reported and the physical properties of the product are described.

4. Tetra-*p*-ethylphenylsilane can be prepared by the action of *p*-ethylchlorobenzene and sodium on tetrachlorosilane. The ortho and meta isomers have not been prepared by this method nor have the corresponding *p*-propyl and *p*-butyl derivatives.

5. When trichlorosilane or hexachlorodisilane is used instead of tetrachlorosilane in the above synthesis, tetra-*p*-ethylphenylsilane is the only product formed under the conditions set forth herein.

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