[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

STUDIES IN SILICO-ORGANIC COMPOUNDS. IX. ADDITIONAL DERIVATIVES OF TRICHLOROSILANE AND THEIR ALKALINE HYDROLYSIS[1, 2]

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INTRODUCTION

This work continues the investigation which has already been partially reported by Jenkins, Lavery, Guenther, and Post (1). The emphasis here was placed on the preparation of certain trisubstituted derivatives of trichlorosilane by the conventional Grignard method, then the careful repetition of these processes with different proportions of reactants to prepare partially substituted products. Data covering these products are shown in Table I.

Physical properties of compounds prepared incidental to the identification of the above, or for their own value but which have previously been prepared will be found in Table II.

DISCUSSION

The compounds listed in Table I and some of those in Table II were prepared by the action of trichlorosilane on the proper Grignard reagent as outlined in the Experimental part. Grignard reagents were prepared from chlorides to eliminate possible halogen interchange between unused Grignard reagent and the desired silicon compound. Two Grignard reagents were used in series to prepare compounds with more than one kind of radical per molecule.

The well known reaction of a compound containing silane hydrogen with alkali by which hydrogen is evolved was also studied. It was felt that if a quaternary ammonium hydroxide was used there might be a possibility that the hydrogen anion, instead of forming a hydrogen molecule with a hydrogen cation, might possibly form a hydrocarbon. No tertiary amines or hydrocarbons were isolated in any of the three runs made with these compounds. The only isolable gas was hydrogen. The reaction could be represented as before, by the following equations:

$$\mathrm{HSi(C_2H_5)_3} + \mathrm{(OH)^-} \rightarrow \mathrm{(C_2H_5)_3SiOH} + \mathrm{(H)^+}$$

$$\mathrm{(H)^+} + \mathrm{(H)^-} \rightarrow \mathrm{H_2}$$

$$2\ \mathrm{(C_2H_5)_3SiOH} \rightarrow \mathrm{HOH} + \mathrm{(C_2H_5)_3SiOSi(C_2H_5)_3}$$

These results were obtained by the treatment of triethylsilane with tetramethylammonium hydroxide, triethylsilane with tetraethylammonium hydroxide, and tribenzylsilane with tetraethylammonium hydroxide.

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[1] This paper represents a portion of the thesis presented by the first author in partial fulfillment of the requirements of the degree of Doctor of Philosophy at the University of Buffalo.

[2] The work on which this paper is based comprises a portion of the program of research being carried out under contract with the Office of Naval Research.

EXPERIMENTAL

Triethylsilane was prepared in accordance with methods already in the literature (2), b.p. 107° (755 mm.) [literature (2) 106.8–107.2° (760 mm.)].

n-Butyldichlorosilane. *n*-Butylmagnesium chloride (0.35 mole) was added to 38 cc. (0.38 mole) of trichlorosilane in 200 cc. of anhydrous ether with cooling and stirring. The reaction mixture was refluxed for 17 hours, magnesium salts were removed by filtration, and the filtrate distilled. $n\text{-}C_4H_9SiHCl_2$, b.p. 130–139° (745 mm.), d_{27}^{27} 1.0066, n_D^{20} 1.4275, yield 4%.

TABLE I

New Compounds

COMPOUND	B.P., °C. (MM.)	$d_{t°}^{t°}$	$n_D^{t°}$
$C_4H_9SiHCl_2$	140–139 (745)	1.0066_{27}^{27}	1.4275^{20}
$(C_4H_9)_2SiHCl$	50– 51 (2)	$0.9940_{21.5}^{21.5}$	1.4372^{20}
$HSi(C_4H_9)_3$	86– 87 (2.5)	0.9312_{25}^{25}	1.4400^{20}
iso-$C_4H_9SiHCl_2$	121–124 (760)	1.0009_{26}^{26}	1.4249^{25}
(iso-$C_4H_9)_2SiHCl$	160–167 (749.4)	0.9945_{24}^{24}	1.4340^{20}
iso-$C_5H_{11}SiHCl_2$	143–148 (760)	1.0005_{26}^{26}	1.4304^{28}
(iso-$C_5H_{11})_2SiHCl$	199–202 (741)	0.9944_{28}^{28}	1.4420^{15}
$HSi(C_6H_{11})_3$	170–176 (4)	0.9981_{24}^{24}	1.4968^{20}
$C_6H_5CH_2SiH(CH_3)Cl$	76– 83 (6)	1.0020_{27}^{27}	1.5160^{20}
$C_6H_5CH_2SiH(CH_3)_2$	53– 55 (3)	0.9486_{20}^{20}	1.5040^{20}
$(C_6H_5CH_2)_2SiHCH_3$	131–140 (3)	0.9936_{20}^{20}	1.5650^{20}

TABLE II

Known Compounds

COMPOUND	B.P., °C.	MM.	M.P., °C.	$d_{t°}^{t°}$	n_D^{20}
$HSi(C_2H_5)_3$[a]	107	755			
$(C_2H_5)_3SiOH$[b]	154	760		0.8647_4^{20}	1.4329
$[(C_2H_5)_3Si]_2O$[c]	231	760		$.8590^0$	1.4340
$HSi(CH_2C_6H_5)_3$[d]			91		
$(C_6H_5CH_2)_3SiOH$[e]			106		
$[(C_6H_5CH_2)_3Si]_2O$[f]			205		

[a] B.p. 106.8–107.2° (2). [b] d_4^{20} 0.8647; n_D^{20} 1.4363 (3); d_4^{20} 0.8638, n_D^{20} 1.4329 (5). [c] B.p. 231° (760 mm.), d^0 0.8590 (8); n_D^{20} 1.4340, 1.4332 (4). [d] M.p. 90–91° (1). [e] M.p. 106° (7). [f] M.p. 205° (6).

Anal. Calc'd for $C_4H_{10}Cl_2Si$: Cl, 45.25. Found: Cl, 45.20.

Di-n-butylchlorosilane. The above procedure was repeated but with 0.4 mole of Grignard and 0.2 mole of trichlorosilane. $(n\text{-}C_4H_9)_2SiHCl$, b.p. 50–51° (2 mm.), $d_{21.5}^{21.5}$ 0.9940, n_D^{20} 1.4372.

Anal. Calc'd for $C_8H_{19}ClSi$: Cl, 19.89. Found: Cl, 19.65.

Tri-n-butylsilane. The above procedure was again repeated using 0.5 mole of Grignard and 0.1 mole of trichlorosilane. $HSi(C_4H_9\text{-}n)_3$, b.p. 86–87° (2.5 mm.), d_{25}^{25} 0.9312, n_D^{20} 1.4400, yield 5%.

Anal. Calc'd for $C_{12}H_{28}Si$: Mol. wt., 200. Found: Mol. wt. (cryoscopic in benzene) 206.

Isobutyldichlorosilane. The Grignard to trichlorosilane molar ratio in this preparation was 0.25 to 0.30. iso-$C_4H_9SiHCl_2$, b.p. 121–124° (760 mm.), d^{26}_{26} 1.0009, n^{25}_D 1.4249, yield 3.5%.

Anal. Calc'd for $C_4H_{10}Cl_2Si$: Cl, 45.25. Found: Cl, 45.20.

Diisobutylchlorosilane. This preparation was carried out using 0.3 mole of Grignard reagent and 0.15 mole of trichlorosilane. (iso-$C_4H_9)_2SiHCl$, b.p. 160–167° (749.4 mm.), d^{24}_{24} 0.9945, n^{20}_D 1.4340, yield 2%.

Anal. Calc'd for $C_8H_{19}ClSi$: Cl, 19.89. Found: Cl, 19.80.

Isoamyldichlorosilane. Isoamylmagnesium chloride (350 cc., 0.35 mole) was added to 40 cc. (0.4 mole) of trichlorosilane in 500 cc. of anhydrous ether with cooling to 0° and stirring. The reaction mixture was allowed to stand for 16 hours, then refluxed for 2 hours. After removal of solid inorganic products the filtrate was distilled. iso-$C_5H_{11}SiHCl_2$, b.p. 143–148° (760 mm.), d^{26}_{26} 1.0005, n^{28}_D 1.4304.

Anal. Calc'd for $C_5H_{12}Cl_2Si$: Cl, 41.55. Found: Cl, 41.55, 41.50.

Diisoamylchlorosilane. The procedure outlined above was again followed save that the molar amounts of Grignard and trichlorosilane were 0.30 and 0.15 respectively. (iso-$C_5H_{11})_2SiHCl$, b.p. 199–202° (741 mm.), d^{28}_{28} 0.9944, n^{15}_D 1.4420, yield 1.5%.

Anal. Calc'd for $C_{10}H_{23}ClSi$: Cl, 17.20. Found: Cl, 17.00.

Tricyclohexylsilane. Trichlorosilane (20 cc., 0.2 mole) in 100 cc. of anhydrous ether was added to 0.8 mole of cyclohexylmagnesium chloride in 1200 cc. of the same solvent. Addition was spread through one hour with cooling to 0° and stirring, then refluxing for 4 hours. As before, solid products were filtered off and the filtrate fractionated. Tricyclohexylsilane, b.p. 170–176°, d^{24}_{24} 0.9981, n^{20}_D 1.4968, yield 4.4%.

Anal. Calc'd for $C_{18}H_{34}Si$: Mol. wt., 278. Found: Mol. wt. (cryoscopic in benzene), 274.

Benzylmethylchlorosilane. Benzylmagnesium chloride (175 cc., 0.5 mole) was added to 50 cc. (0.5 mole) of trichlorosilane in 400 cc. of anhydrous ether at 0° with stirring. The mixture was refluxed for 4 hours after which an additional 300 cc. of anhydrous ether was added. Methylmagnesium chloride (167 cc., 0.5 mole) was then added dropwise to the reaction mixture and refluxed for 16 hours. Solid material was filtered off and the filtrate fractionated. Benzylmethylchlorosilane, b.p. 76–83° (6 mm.), d^{27}_{27} 1.002, n^{20}_D 1.5160, yield 2.4%.

Anal. Calc'd for $C_8H_{11}ClSi$: Cl, 20.78; Silane hydrogen, 0.587.
Found: Cl, 20.80; Silane hydrogen 0.572.

Benzyldimethylsilane. Benzylmagnesium chloride (0.8 mole) was added to 80 cc. (0.8 mole) of trichlorosilane in 800 cc. of anhydrous ether at 0° with stirring. The mixture was refluxed for 1 hour, and 400 cc. of dry ether and 1.6 moles of methylmagnesium chloride were added. It was refluxed for 6 hours, acidulated ice-water (200 cc.) was slowly added, and the ether layer separated. The latter was dried over calcium chloride and fractionated. Benzyldimethylsilane, b.p. 53–55° (3 mm.), d^{20}_{20} 0.9486, n^{20}_D 1.5040, yield 16.5%.

Anal. Calc'd for $C_9H_{14}Si$: Mol wt., 150.0; Silane hydrogen, 0.666.
Found: Mol. wt. (cryoscopic in benzene), 145.5; Silane hydrogen, 0.645.

Dibenzylmethylsilane. Benzylmagnesium chloride (0.9 mole) was added to 45 cc. (0.45 mole) of trichlorosilane in 600 cc. of anhydrous ether with cooling to 0° and stirring. The mixture was refluxed for 3 hours, methylmagnesium chloride (167 cc., 0.5 mole) was added with stirring, refluxed for 4 hours, and 600 cc. of acidulated ice-water slowly added. The ether was dried over calcium chloride for 16 hours, and fractionation gave dibenzylmethylsilane, b.p. 131–140° (3 mm.), d_{20} 0.9936, n^{20}_D 1.5650, yield 22.1%.

Anal. Calc'd for $C_{15}H_{18}Si$: Mol. wt., 226; Silane hydrogen, 0.4425.
Found: Mol. wt. (cryoscopic in benzene), 220; Silane hydrogen, 0.425.

Tribenzylsilane was prepared according to the method already in the literature (1); m.p. 91° [literature, (1) 90–91°].

Interaction of triethylsilane and tetramethylammonium hydroxide. Aqueous tetramethylammonium hydroxide (80 cc., 0.15 mole) dissolved in 50 cc. of 96% ethanol was added to 23.3 cc. (0.15 mole) of triethylsilane. The reaction mixture was stirred. A glass tube led from the top of the reflux condenser to a trap immersed in Dry Ice and acetone, with an outlet arranged for gas collection. As the base was added, the flask was gently heated until the ethanol refluxed. A gas was evolved. After the addition of 60 cc. of the hydroxide, no more gas was observed coming off. No trimethylamine was collected in the trap. The material in the reaction flask consisted of two layers; the top layer was fractionated, yielding *triethylhydroxysilane,* b.p. 154° (760 mm.), d_4^{20} 0.8647 [literature, 0.8647 (3), 0.8638 (5)]; n_D^{20} 1.4329 [literature, 1.4363 (3), 1.4329 (5)]. *Hexaethyldisiloxane* was also isolated from this layer, b.p. 231° (760 mm.) *cf.* (8), d^0 0.8590 (8), n_D^{20} 1.4342 [literature, 1.4340, 1.4332 (4)]. The gas evolved was *hydrogen,* unmixed with *methane* because (a) on contact with hot copper oxide, the latter was reduced to copper, (b) no portion of the gas underwent liquefaction in liquid nitrogen (about −196°), and (c) on combustion, the water formed gave no precipitate with calcium hydroxide.

Interaction of triethylsilane and tetraethylammonium hydroxide. The procedure in this experiment was approximately the same as in the preceding, save that 0.1-molar quantities were used. Refluxing was carried out at 100° for 3 hours, after which the system was allowed to stand at room temperature for 16 hours. A second reflux period at 70° for 2 hours followed. The upper layer yielded triethylhydroxysilane and hexaethyldisiloxane. As before, the gas was shown to contain only hydrogen.

Interaction of tribenzylsilane and tetraethylammonium hydroxide. Reactants were mixed using 0.05 mole of each and the experiment carried out as above, with 4 hours of refluxing. A gas came off during the first 30 minutes only. The only silicon compound isolable was *hexabenzyldisiloxane,* m.p. 205°, *cf.* (6).

SUMMARY

1. By interaction of the proper Grignard reagent and trichlorosilane in regulated ratios, there have been prepared butyldichlorosilane, dibutylchlorosilane, tributylsilane, isobutyldichlorosilane, diisobutylchlorosilane, isoamyldichlorosilane, diisoamylchlorosilane, and tricyclohexylsilane.

2. By successive action of benzylmagnesium chloride and methylmagnesium chloride in regulated ratios, benzylmethylchlorosilane, benzyldimethylsilane, and dibenzylmethylsilane have also been prepared.

3. Contact between (a) triethylsilane and tetramethylammonium hydroxide, (b) triethylsilane and tetraethylammonium hydroxide, and (c) tribenzylsilane and tetraethylammonium hydroxide produced no evidence of hydrocarbon formation. The products of these reactions were hydrogen, triethylhydroxysilane, hexaethyldisiloxane, tribenzylhydroxysilane, and hexabenzyldisiloxane.

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