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STUDIES IN SILICO-ORGANIC COMPOUNDS. XXVIII. THE PREPARATION OF *p*-TRIALKYLSILYLPHENYLCARBINOLS

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INTRODUCTION

p-Triethylsilylphenylcarbinols were first prepared by Grüttner and Cauer (1) in 1918. By slowly adding twice the calculated amount of an aldehyde to the chosen Grignard reagent (from *p*-bromophenyltriethylsilane) in ether, and working up the products, a series of viscous colorless liquids was isolated, insoluble in water but soluble in dry ethyl ether, alcohol, benzene and petroleum ether. Acetaldehyde, propionaldehyde, *n*-butyraldehyde and isobutyraldehyde were used but only *p*-triethylsilylphenylmethylcarbinol was isolated in satisfactory amounts.

In this work, *p*-triethylsilylphenylmagnesium bromide was found to react with acetaldehyde, propionaldehyde, *n*-butyraldehyde, isobutyraldehyde, β-methylbutyraldehyde, *n*-heptaldehyde, *n*-caproaldehyde, and benzaldehyde to give satisfactory yields, after hydrolysis, of the corresponding carbinols:

$$\text{I.}\quad p\text{-BrC}_6\text{H}_4\text{MgBr} + \text{SiCl}_4 \rightarrow p\text{-BrC}_6\text{H}_4\text{SiCl}_3 + \text{MgClBr}$$

$$\text{II.}\quad p\text{-BrC}_6\text{H}_4\text{SiCl}_3 + 3\ \text{C}_2\text{H}_5\text{MgBr} \rightarrow p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{Br} + 3\ \text{MgClBr}$$

$$\text{III.}\quad p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{Br} + \text{Mg} \rightarrow p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{MgBr}$$

$$\text{IV.}\quad p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{MgBr} + \text{CH}_3\text{CHO} \rightarrow p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{CH(OMgBr)CH}_3$$

$$\text{V.}\quad p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{CH(OMgBr)CH}_3 + \text{HOH} \rightarrow p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{CH(OH)CH}_3 + \text{Mg(OH)Br.}$$

Similarly to the above, *p*-trimethylsilylphenylmagnesium bromide reacts with benzaldehyde to form, after hydrolysis, *p*-trimethylsilylphenylphenylcarbinol.

p-Triethylsilylphenylmagnesium bromide also has been found to react with ethylene oxide and with propylene oxide:

$$\text{VI.}\quad p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{MgBr} + \overline{\text{CH}_2\text{OCH}_2} \rightarrow p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OMgBr}$$

$$\text{VII.}\quad p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OMgBr} + \text{HOH} \rightarrow p\text{-[(C}_2\text{H}_5)_3\text{Si]C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{Mg(OH)Br}$$

EXPERIMENTAL PART

p-Bromophenyltriethylsilane. In a five-liter, three-necked flask equipped with a mercury-sealed stirrer, dropping-funnel, and reflux condenser, *p*-bromophenyltriethylsilane was prepared by adding dropwise 1.5 moles of *p*-bromophenylmagnesium bromide in 900 cc. of dry ethyl ether to 117.0 cc. (1.5 moles) of tetrachlorosilane in 500 cc. of dry ethyl ether. After refluxing for 24 hours, 5.0 moles of ethylmagnesium iodide in 2000 cc. of dry ethyl ether were

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TABLE I

PHYSICAL PROPERTIES, *p*-TRIALKYLSILYLPHENYLCARBINOLS

Compound	b.p., °C.	mm.	n_D^{25}	d_4^{25}	Yield, %
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)CH_3$	173-174	14			40.6
p-$[(C_2H_5)_3Si]C_6H_4CH_2CH_2OH^a$	131-132	2	1.5161	0.9556	30.0
p-$[(C_2H_5)_3Si]C_6H_4CH_2CH(OH)CH_3{}^a$	141	1	1.5100	.9456	52.0
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)C_2H_5$	185-186	14			37.8
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)C_3H_7$-*n*	197-198	20			33.0
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)C_3H_7$-iso	190-191	18			40.1
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)C_4H_9$-iso^a	165.0-165.5	2	1.5090	.9366	25.1
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)C_6H_{13}$-*n*^{a}	161.0	1	1.5058	.9298	22.0
	194.0	5			
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)C_7H_{15}$-*n*^{a}	161.0	1	1.5020	.9217	42.1
p-$[(C_2H_5)_3Si]C_6H_4CH(OH)C_6H_5{}^a$	180-181	1	1.5656	1.0157	35.4
p-$[(CH_3)_3Si]C_6H_4CH(OH)C_6H_5{}^a$	156-157	2	1.5804	1.0283	51.6

[a] New compound.

added with stirring over a period of 6 hours. Reflux was continued for 48 hours. Acidified ice water was added until the white solid had dissolved, then the ether layer was separated, washed three times with 300-cc. portions of distilled water, and dried over calcium chloride. On distillation *p*-bromophenyltriethylsilane was obtained, 224 g., b.p. (found) 149° (14 mm.); (literature) (2) 149° (14 mm.), yield 40%. The action of magnesium on *p*-bromophenyltriethylsilane in dry ethyl ether readily gave the corresponding Grignard reagent.

p-Bromophenyltrimethylsilane. In a similar three-liter apparatus, *p*-bromophenyltrimethylsilane was prepared by adding dropwise trimethylchlorosilane (325 g., 3.0 moles) in 300 cc. of dry ethyl ether to *p*-bromophenylmagnesium bromide (3.0 moles) in 1200 cc. of dry ethyl ether, over a three-hour period with stirring. The mixture then was refluxed for 72 hours. Acidulated ice water was added dropwise until the whole solid had dissolved. The ether and water layers were separated after which the former was washed with three 500-cc. portions of water and dried over calcium chloride for several days. Distillation of the dried ether layer gave a mixture b.p. 136-138° (50 mm.), which froze in Dry Ice and acetone. This mixture was allowed to thaw on a Büchner filter under suction. The filtrate was frozen and thawed until no residue remained. Fractionation of the filtrate gave *p*-bromophenyltrimethylsilane, b.p. (found) 136-138° (50 mm.), (literature) (6) 146-148° (50 mm.), n_D^{25} (found) 1.5250, (literature) (6) 1.5302, d_4^{25} (found) 1.2010, (literature) (6) 1.2197, yield 52%.

Anal. Calc'd for $C_9H_{13}BrSi$: Si, 12.24; M.R., 57.63.
Found: Si, 12.31, 12.21; M.R., 58.55.

p-Triethylsilylphenylmethylcarbinol. Acetaldehyde (22.4 cc., 0.4 mole), in 50 cc. of dry ethyl ether was added dropwise to 100 cc. of a dry ethyl ether solution of *p*-triethylsilylphenylmagnesium bromide (0.14 mole) with cooling at 0° and stirring. The reaction mixture was refluxed for 4 hours. Ice cold dilute hydrochloric acid (200 cc.) was added with stirring. The ether layer was washed several times with 100-cc. portions of water, then dried over magnesium sulfate. Distillation gave 13.5 g. of *p*-triethylsilylphenylmethylcarbinol, b.p. (found) 173-174° (14 mm.); (literature) (1) 173-174° (14.5 mm.), 40.6% yield.

p-Triethylsilylphenylethylcarbinol. Propionaldehyde (28.8 cc. 0.4 mole) in 50 cc. of dry ethyl ether was allowed to react with *p*-triethylsilylphenylmagnesium bromide (0.18 mole in 100 cc. of dry ethyl ether) with cooling at 0° and stirring. Distillation yielded *p*-triethylsilylphenylethylcarbinol, 94.5 g., b.p. (found) 185-186° (11.5 mm.); (literature) (1) 188° (14.8 mm.), 37.8% yield.

p-Triethylsilylphenyl-n-propylcarbinol. *n*-Butyraldehyde (36.3 cc., 0.3 mole) was allowed to react with *p*-triethylsilylphenylmagnesium bromide (0.2 mole in 100 cc. of dry ethyl ether). Distillation gave *p*-triethylsilylphenyl-*n*-propylcarbinol, 35 g.; b.p. (found) 197–198° (20 mm.); (literature) (1) 199–201° (21 mm.), yield 33%.

p-Triethylsilylphenylisopropylcarbinol. The reaction between isobutyraldehyde (26.3 cc., 0.4 mole) in 50 cc. of dry ethyl ether and *p*-triethylsilylphenylmagnesium bromide (0.18 mole in 100 cc. of dry ethyl ether) yielded *p*-triethylsilylphenylisopropylcarbinol, 42 g., b.p. (found) 190–191° (18 mm.); (literature) (1) 190–192° (18 mm.), yield 40.1%.

p-Triethylsilylphenylisobutylcarbinol. The interaction of 63.6 cc. (0.6 mole) of β-methylbutyraldehyde in 50 cc. of dry ethyl ether and 0.30 mole of *p*-triethylsilylphenylmagnesium bromide in 160 cc. of dry ethyl ether gave, after distillation, 21.0 g. of *p*-triethylsilylphenylisobutylcarbinol, b.p. 165.0–165.5° (2 mm.), n_D^{25} 1.5090, d_4^{25} 0.9366, yield 25.1%.

Anal. Calc'd for $C_{17}H_{30}OSi$: Si, 10.07; M.R., 88.54; Mol. Wt., 278.5.

Found: Si, 10.30, 10.29; M.R., 88.83; Mol Wt., 279.8 (cryoscopic in benzene).

p-Triethylsilylphenyl-n-hexylcarbinol. In the same manner, 0.1 mole of *p*-triethylsilylphenylmagnesium bromide and 23 cc. (0.2 mole) of *n*-heptaldehyde reacted to form *p*-triethylsilylphenyl-*n*-hexylcarbinol, 3.5 g., b.p. 161° (1 mm.), 194° (5 mm.), n_D^{25} 1.5058, d_4^{25} 0.9298, 11% yield.

Anal. Calc'd for $C_{19}H_{34}OSi$: Si, 9.18; M.R., 97.50; Mol. Wt., 306.5.

Found: Si, 9.00, 8.88; M.R., 97.88; Mol. Wt., 310.3 (cryoscopic in benzene).

p-Triethylsilylphenyl-n-heptylcarbinol. Caproaldehyde (93.6 cc., 0.6 mole) reacted with 0.3 mole of *p*-triethylsilylphenylmagnesium bromide to form *p*-triethylsilylphenyl-*n*-heptylcarbinol, 24 g., b.p. 161° (1 mm.), n_D^{25} 1.5020, d_4^{25} 0.9217, 25% yield.

Anal. Calc'd for $C_{20}H_{36}OSi$: Si, 8.75, M.R., 102.43; Mol. Wt., 320.5.

Found: Si, 8.26, 8.34; M.R., 102.88; Mol. Wt., 329.8 (cryoscopic in benzene).

p-Triethylsilylphenylphenylcarbinol. Similarly, 0.16 mole of *p*-triethylsilylphenylmagnesium bromide reacted with 40.4 cc. (0.4 mole) of benzaldehyde, giving *p*-triethylsilylphenylphenylcarbinol, 16.9 g., b.p. 180–181° (1 mm.), n_D^{25} 1.5656, d_4^{25} 1.0157, yield 35.4%.

Anal. Calc'd for $C_{19}H_{26}OSi$: Si, 9.40; M.R., 94.26; Mol. Wt., 298.5.

Found: Si, 9.84, 9.56; M.R., 95.51; Mol. Wt., 295.2 (cryoscopic in benzene).

p-Triethylsilylbenzylcarbinol. Ethylene oxide (20 cc., 0.44 mole) in 100 cc. of dry ethyl ether, at 0°, was added dropwise to 0.065 mole of *p*-triethylsilylphenylmagnesium bromide in 50 cc. of the same solvent. The product was *p*-triethylsilylbenzylcarbinol, 4.5 g., b.p. 131–132° (2 mm.), n_D^{25} 1.5161, d_4^{25} 0.9558, yield 30.0%.

Anal. Calc'd for $C_{14}H_{24}OSi$: Si, 11.89; M.R., 74.65.

Found: Si, 11.50, 12.00; M.R., 74.88.

p-Triethylsilylbenzylmethylcarbinol. Propylene oxide (30 cc., 0.43 mole) in 100 cc. of dry ethyl ether reacted with 0.08 mole of *p*-triethylsilylphenylmagnesium bromide in 100 cc. of the same solvent at 0°. The mixture gelled after four hours of reflux but distillation gave *p*-triethylsilylbenzylmethylcarbinol, 8.0 g., b.p. 141° (1 mm.), n_D^{25} 1.5100, d_4^{25} 0.9456, yield 40.0%.

Anal. Calc'd for $C_{15}H_{26}OSi$: Si, 11.20: M.R., 79.28.

Found: Si, 11.40, 11.40; M.R., 79.23.

Phenyltriethylsilane was isolated as a by-product, 4.5 g., b.p. 78–80° (1 mm.), n_D^{25} 1.4950 (found), n_D^{20} 1.4900 (literature) (4), d_4^{25} 0.8968 (found), d_4^{25} 0.8964 (literature) (4).

p-Trimethylsilylphenylphenylcarbinol. Benzaldehyde (84 cc., 0.8 mole) in 100 cc. of dry ethyl ether was added slowly to 0.4 mole of *p*-trimethylsilylphenylmagnesium bromide in 160 cc. of dry ethyl ether. The reaction mixture was refluxed for four hours, yielding *p*-trimethylsilylphenylphenylcarbinol, 20 g., b.p. 156–157° (2 mm.), n_D^{25} 1.5804, d_4^{25} 1.0283, yield 20%.

Anal. Calc'd for $C_{16}H_{20}OSi$: Si, 10.94; M.R., 80.37; Mol. Wt., 258.4.

Found: Si, 10.52, 10.70; M.R., 80.64; Mol. Wt., 258.5 (cryoscopic in benzene).

Materials. Aldehydes and *p*-dibromobenzene were purchased from reputable sources and were purified before using. Their physical properties were satisfactory. Grignard reagents were prepared from *p*-dibromobenzene by standard methods (3). In the usual apparatus (500 cc.) *p*-trimethylsilylphenylmagnesium bromide was prepared by adding dropwise *p*-bromophenyltrimethylsilane (18 cc., 0.1 mole) in 40 cc. of dry ethyl ether. A crystal of iodine was added and heat was applied before the reaction started. The reaction proceeded very smoothly and upon analysis a 91% yield of Grignard reagent was found. Similarly, *p*-triethylsilylphenylmagnesium bromide was also prepared. Grignard reagents were standardized by titration with hydrochloric acid and back titration with sodium hydroxide. Tetrachlorosilane, trimethylchlorosilane, and other reagents were purchased from reputable sources and were found to have satisfactory physical constants. Molar refractions were calculated from the data of Warrick (5).

Determination of silicon. A sample weighing between 0.3 g. and 0.5 g., contained in a weighed, platinum crucible, was treated with 30 to 40 drops of fuming sulfuric acid and was heated first over a hot plate for three to four hours, then over a Fischer burner to drive off all volatile matter including sulfur trioxide. Fuming nitric acid then was added, repeatedly when necessary, until the residue was white. Silica was determined by difference in weight after ignition to constant weight and cooling in a phosphorus pentoxide desiccator.

SUMMARY

1. Eight substituted carbinols have been prepared by the interaction of *p*-triethylsilylphenylmagnesium bromide and acetaldehyde, propionaldehyde, *n*-butyraldehyde, isobutyraldehyde, β-methylbutyraldehyde, *n*-heptaldehyde, *n*-caproaldehyde, and benzaldehyde.

2. *p*-Triethylsilylphenylmagnesium bromide has been found to react with ethylene oxide and with propylene oxide to form *p*-triethylsilylbenzylcarbinol and *p*-triethylsilylbenzylmethylcarbinol, respectively.

3. *p*-Trimethylsilylphenylmagnesium bromide reacts with benzaldehyde to form *p*-trimethylsilylphenylphenylcarbinol.

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