Part II

PHYSICAL PROPERTIES
EVALUATION OF COMPOUNDS AND MATERIALS

Reactions of Chlorodialkoxymethylsilanes with Phenylsodium

C. C. CHAPPELOW, Jr., R. L. ELLIOTT, and J. T. GOODWIN, Jr.[1]
Chemistry Division, Midwest Research Institute, Kansas City, Mo.

Reactions of certain chlorodialkoxymethylsilanes with in situ and preformed phenylsodium were studied under a wide range of reaction conditions. The effect of various factors such as the site of formation of the phenylsodium reagent, the type of alkoxy group in the chlorodialkoxymethylsilane, the reactant ratio, reactant concentration, method of addition, reaction temperature, and rate of stirring were studied. During the course of this investigation, six new compounds were prepared and characterized: chloroethoxymethylphenylsilane, chlorodiisopropoxymethylsilane, chloroisopropoxymethylphenylsilane, diisopropoxymethylphenylsilane, *n*-butoxychloromethylphenylsilane and di-*n*-butoxymethylphenylsilane.

REACTIONS OF chlorodialkoxymethylsilanes with preformed and in situ-formed phenylsodium were studied under a wide range of experimental conditions. The reaction of chlorodiethoxymethylsilane (7) and dichlorodimethoxysilane (6) with in situ-formed phenylsodium have been reported previously. The effect of molecular configuration on the reactivity of various alkoxysilanes with methylmagnesium chloride has also been studied (9). However, up to now little has been published on the relative reactivities of various alkoxy groups and the chlorine atom in chlorodialkoxymethylsilanes toward phenylsodium, or on the stability of silanes of this type in the presence of molten sodium.

EXPERIMENTAL

Examples are given of reactions of chlorodialkomethylsilanes with phenylsodium which demonstrate the experimental techniques used in carrying out the various reaction procedures and the characteristics of the different systems involved. Preparation and characterization of new alkoxy derivatives are discussed.

In Situ-Formed Phenylsodium—Procedure A, Experiment 2. Sodium (16.1 g., 0.350 g. atom) and 350 ml. of toluene were placed in a reaction vessel and heated to 110°. A 500 ml. solution consisting of chlorobenzene (39.4 g., 0.350 mole), chlorodiethoxymethylsilane (147.5 g., 0.875 mole), and 315 ml. of toluene was added dropwise to the molten sodium with stirring at 100 rpm. The reaction mixture was maintained at 110° by controlling the rate of addition. After the ½ hour addition period, the reaction mixture was held at 110° for ½ hour longer by applying heat. The reaction mixture was cooled to 25° and filtered to remove the sodium chloride and unreacted sodium (0.013 mole). Unreacted chlorodiethoxymethylsilane (0.413 mole), methyltriethoxysilane and toluene were removed from the filtrate by an atmospheric distillation in which a maximum pot temperature of 150° was attained. The residue was distilled under vacuum at a rate of ca. 1 ml./min. through a 1-foot section of a ½-inch I.D. column packed with Berl saddles. The following fractions were collected: Fraction A, 43 g., b.p. 90–120°/10 mm., 1.4 wt. % chlorine, a mixture of 3.2 g. (5% yield) of $CH_3SiC_6H_5(OC_2H_5)Cl$, and 39.8 g. (54% yield)

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[1] Present address, Corn Industries Research Foundation, Washington, D. C.

of $CH_3SiC_6H_5(OC_2H_5)_2$; Fraction B, 5.0 g., b.p. 150-180°/10 mm. mainly, $CH_3Si(C_6H_5)_2(OC_2H_5)$; and Fraction C, 4.5 g. of residue.

In Situ-Formed Phenylsodium—Procedure B, Experiment 14. Sodium (17.7 g., 0.77 g. atom), and chlorodiisopropoxymethylsilane (206.5 g., 1.05 moles) were placed in a reaction vessel and heated to 110°. (No solvent was used.) To this mixture, chlorobenzene (39.4 g., 0.35 mole) was added dropwise while it was stirred at ca. 100 r.p.m. The temperature was held at 110° during the ½ hr. addition by controlling the rate of addition and for ½ hr. period thereafter by external heating. Then, the reaction mixture was cooled to room temperature and filtered. The filter cake (43 g.) was washed with a small amount of toluene and found to contain 0.05 g. atom of unreacted sodium. The toluene, unreacted chlorodiisopropoxymethylsilane (0.653 mole), and methyltriisopropoxysilane were removed by an atmospheric distillation in which a final pot temperature of 170° was attained. The residue was subjected to a vacuum distillation at a rate of ca. 1 ml./min. through a 1-foot section of ¾-inch I.D. column packed with ¼-inch Berl saddles. After removal of a small percut (2 g.) distilling below 85°/10 mm., the following fractions were collected: Fraction A, 56.0 g., b.p. 85-115°/10 mm., 1.1 wt % chlorine, a mixture of 4.1 g. (5% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)Cl$ and 51.9 g. (62% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)_2$; Fraction B, 3.5 g., b.p. 115-145°/10 mm.; Fraction C, 2.0 g., b.p., 145-157°/10 mm., mainly, $CH_3Si(C_6H_5)_2O\text{-}i\text{-}C_3H_7$; and Fraction D, 5.5 g., residue.

In Situ-Formed Phenylsodium—Procedure B, Experiment 21. A methyltrichlorosilane alkoxylation mixture was made by adding isopropyl alcohol to methyltrichlorosilane in a 1 to 1.8 molar ratio and flash distilling the reaction mixture through a Claisen head. Analysis of the distillate with a Perkin-Elmer model 154B Vapor Fractometer using column "C" at 125° C. and 20 p.s.i.g. helium indicated the following mole per cent composition: 0.6% of HCl, 1.2% of $CH_3Si(O\text{-}i\text{-}C_3H_7)Cl_2$, 82.0% of $CH_3Si(O\text{-}i\text{-}C_3H_7)_2Cl$, and 16.2% of $CH_3Si(O\text{-}i\text{-}C_3H_7)_3$. To 19.5 g. of sodium (0.85 g. atom) and 206.5 g. of the above described methyltrichlorosilane-isopropylation mixture at 110° C. was added dropwise 39.4 g. (0.35 mole) of chlorobenzene. It was necessary to initiate the reaction with 0.3 ml. of ethyl acetate, then the reaction mixture was maintained at a temperature of 115° by controlling the rate of addition of the chlorobenzene. After the addition was complete, the reaction mixture was held at 115° for 30 min. The reaction was allowed to cool, and the precipitate was removed by filtration and washed with toluene. The toluene and some of the unreacted chlorodiisopropoxymethylsilane were removed from the filtrate by an atmospheric distillation. The crude reaction mixture was distilled at reduced pressure through a packed Claisen head to give: 56 g. of material, b.p. 85-115° at 10 mm., n_D^{25} 1.4514, d_4^{25} 0.9442, a mixture of 8.5 g. (11% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)Cl$ (calculated from chlorine analysis) and 47.0 g. (59% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)_2$. The total yield of methylphenylsilanes was 70%.

In Situ-Formed Phenylsodium—Procedure B, Experiment 23. Sodium (19.5 g., 0.85 g. atom), methyldi-*n*-butoxy-chlorosilane (158 g., 0.704 mole) and 123 ml. of toluene, which made the initial silane concentration 2.4 molar, were placed in a reaction vessel and heated to 110°. Chlorobenzene (39.5 g., 0.35 mole) was added dropwise to the reaction mixture while stirring at 100 r.p.m. About 30% of the chlorobenzene was added before the reaction was initiated. After the reaction was brought under control, it was completed in the usual manner. The reaction mixture was worked up as previously described, and vacuum distillation of the crude product gave the following fractions: Fraction A, 55 g., b.p. 55-85°/5 mm., mainly unreacted $CH_3Si(O\text{-}n\text{-}C_4H_9)_2Cl$; Fraction B, 66 g., b.p. 85-115°/5 mm., a mixture of 44.7 g. of $CH_3Si(O\text{-}n\text{-}C_4H_9)_3$ and 21.3 g. (27% yield) of $CH_3SiC_6H_5(O\text{-}n\text{-}C_4H_9)Cl$; Fraction C, 37.2 g., b.p. 115-145°/5 mm., a 40% yield of $CH_3SiC_6H_5(O\text{-}n\text{-}C_4H_9)_2$; Fraction D, 10.5 g., b.p. 145-175°/5 mm.; and Fraction E, 3.0 g., residue.

In Situ-Formed Phenylsodium—Procedure C, Experiment 5. Sodium (16.1 g., 0.70 g. atom), 75 ml. of toluene and 1 g. of oleic acid were placed in a 300 ml. Morton flask and stirred at 3000 r.p.m. with a STIR-O-VAC stirrer for ½ hr. while the temperature was maintained at 110°. The resultant sodium dispersion was allowed to cool to 35° and transferred to a 1-liter flask with 25 ml. of toluene. A 500-ml. solution composed of a mixture of chlorobenzene (39.4 g., 0.35 mole), chlorodiethoxymethylsilane (147.5 g., 0.875 mole) and 315 of toluene, was added dropwise to the sodium dispersion, while stirring at ca. 100 r.p.m. During addition, the temperature was maintained at 35° by controlling the rate of addition and cooling. After addition, the reaction continued autogenically to maintain this temperature. After 1 hr., the reaction subsided, and the reaction mixture was worked up as previously described. Distillation of the crude product under reduced pressure gave the following results: Fraction A, 44 g., b.p. 90-120°/10 mm., 0.5 wt. % chlorine, a mixture of 1.2 g. (2% yield) of $CH_3SiC_6H_5(OC_2H_5)Cl$ and 42.8 g. (58% yield) of the compound, $CH_3SiC_6H_5(OC_2H_5)_2$; Fraction B, 10.5 g., b.p. 120-170°/10 mm., mainly $CH_3Si(C_6H_5)_2OC_2H_5$; and Fraction C, 3.0 g., residue.

Preformed Phenylsodium—Procedure D, Experiment 16. A sodium (16.1 g., 0.350 g. atom) dispersion in toluene (50 ml.) was prepared as previously described. Then, the phenylsodium reagent was prepared by adding chlorobenzene (39.4 g., 0.350 mole) dropwise to the sodium dispersion with gentle stirring. The reaction was initiated at 50°, and then maintained between 25° and 30° by controlling the rate of addition and by applying external cooling. Then, the phenylsodium reagent as a slurry in toluene was added dropwise with stirring at ca. 100 r.p.m. to undiluted chlorodiisopropoxymethylsilane (210.5 g., 1.07 moles). The reaction was maintained at 50° C. by controlling the rate of addition and for an additional ½ hr. thereafter by applying heat. The reaction mixture was cooled to room temperature and filtered. The filter cake was washed with toluene, dried (44 g. dry) and found to contain 0.02 g. atom of unreacted sodium. The combined filtrate and washings were subject to an atmospheric distillation and all material distilling below 145° was removed. The residue was vacuum-distilled in the distillation apparatus previously described, and the following fractions were collected: Fraction A, 83.0 g., b.p. 25-55°/10 mm., a mixture 68 g. of the unreacted $CH_3Si(O\text{-}i\text{-}C_3H_7)_2Cl$ and 15.0 g. of $CH_3(O\text{-}i\text{-}C_3H_7)_3$; Fraction B, 1.0 g., b.p. 55-85°/10 mm.; Fraction C, 60.5 g., b.p. 85-115°/10 mm. (90% between 102-104°/10 mm.), a mixture of 4.2 g. (6% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)Cl$ and 56.3 g. (68% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)_2$, Fraction D, 2.5 g., b.p. 115-175°/10 mm., and Fraction E, 6.0 g., residue.

Preformed Phenylmagnesium Bromide—Procedure D, Experiment 19. The Grignard reagent was prepared by adding bromobenzene (55.0 g., 0.350 mole) dropwise to magnesium turnings (9.4 g., 0.385 g. atom) suspended in 335 ml. of diethyl ether. The reaction was maintained at ca. 35° during the preparation. The resultant ethereal solution of phenylmagnesium bromide (0.350 mole) was added dropwise with stirring at ca. 100 r.p.m. to chlorodiisopropoxymethylsilane (207.5 g., 1.055 moles) diluted with 225 ml. of diethyl ether to make its initial concentration 2.40 molar. The temperature was held at ca. 25° during the ½ hr. addition of the Grignard reagent and for ½ hr. thereafter. The initial precipitate was gelatinous, but continued stirring converted it to a white granular form. After the reaction was complete, toluene was added to the reaction mixture and the ether distilled off at atmospheric pressure. The resultant slurry was filtered and the filter cake washed with toluene. The filtrate was subjected to an atmospheric distillation in which all of the solvent and some of the unreacted chlorodiisopropoxymethylsilane were removed. The residue was vacuum-distilled according to the procedure previously described, and the following fractions were collected: Fraction A, 91.5 g., b.p. 25–55°/10 mm., a mixture of 56.2 g. of the unreacted $CH_3Si(O\text{-}i\text{-}C_3H_7)_2Cl$ and 35.3 g. of $CH_3Si(O\text{-}i\text{-}C_3H_7)_3$; Fraction B, 0.5 g., b.p. 55–95°/10 mm.; Fraction C, 36.5 g., b.p. 95–105°/10 mm., a mixture of 22.4 g. (30% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)Cl$, and 14.1 g. (17% yield) of $CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)_2$; Fraction D, 1.5 g., b.p. 105–145°/10 mm., Fraction E, 10.0 g., b.p. 145–200°/10 mm.; and Fraction F, 8.5 g., residue.

Chlorodiisopropoxymethylsilane. Methyltrichlorosilane (448 g., 3.0 moles) was placed in reaction vessel and isopropyl alcohol (333 g., 5.55 moles) was added dropwise with stirring over a 1-hour period. The reaction was endothermic and heat had to be applied to maintain the mixture at 25°. After addition, the reaction mixture was purged with dry nitrogen for approximately 15 min. to remove the dissolved hydrogen chloride. Then, it was distilled through a packed column to obtain the product. A 50-gram sample of the diisopropoxylated product distilling at 145° at 760 mm. was taken for characterization: b.p. 38°/10 mm., 50°/20 mm., 64°/40 mm., 80°/80 mm., n_D^{25} 1.3899, d_4^{25} 0.3899, d_4^{25} 0.9398, MR_D calcd. 49.95, found 49.55.

Anal. Calcd. for $SiC_7H_{17}O_2Cl$: Cl, 18.1. Found: Cl, 17.8.

Chloroethoxymethylphenylsilane. To 57.3 g. (0.30 mole) of dichloromethylphenylsilane was added dropwise 13.8 g. (0.30 mole) of ethyl alcohol. After the addition was complete, the reaction mixture was purged with dry nitrogen for 20 min. After refluxing for 3 hr., the reaction mixture was distilled through a packed Claisen head under reduced pressure and a 20 g. sample of the monosubstituted product was taken for characterization: b.p. 86°/10 mm., 101°/20 mm., 117°/40 mm., 135°/80 mm., n_D^{25} 1.4880, d_4^{25} 1.0453, MR_D (molecular refraction) calcd. 55.12, found 55.26.

Anal. Calcd. for $SiC_9H_{13}OCl$: Cl, 17.7. Found: Cl, 17.5.

Chloroisopropoxymethylphenylsilane. In a similar manner, dichloromethylphenylsilane (56 g., 0.28 mole) was reacted with 15 g. (0.25 mole) of isopropyl alcohol. A 15 g. sample of the monoisopropoxylated product was collected for characterization: b.p. 93°/10 mm., 108°/20 mm., 125°/40 mm., 144°/80 mm., n_D^{25} 1.4820, d_4^{25} 1.0420, MR_D calcd. 58.69, found 59.75.

Anal. Calcd. for $SiC_{10}H_{15}OCl$: Cl, 16.6. Found: Cl, 16.3.

***n*-Butoxychloromethylphenylsilane.** A reaction similar to the above run was carried out using 47.8 g. (0.25 mole) of dichloromethylphenylsilane and 18.5 g. (0.25 mole) of *n*-butyl alcohol. A 20-gram sample of *n*-butoxychloromethylphenylsilane was taken for characterization: b.p. 101°/5 mm., 117°/10 mm., 130°/20 mm., 147°/40 mm., n_D^{25} 1.4836, d_4^{25} 1.0154, MR_D calcd. 64.38, found 64.37.

Anal. Calcd. for $SiC_{11}H_{17}OCl$: Cl, 15.5. Found: Cl, 15.1.

Diisopropoxymethylphenylsilane. To 47.8 g. (0.25 mole) of dichloromethylphenylsilane was added 47.1 g. (0.79 mole) of isopropyl alcohol. After addition, the reaction mixture was purged with nitrogen for 15 minutes and refluxed for 2 hours. The excess isopropyl alcohol was removed by atmospheric distillation and the residue vacuum distilled through a packed column. A 10-gram sample of the diisopropoxy derivative distilling at 103° at 10 mm. was taken for characterization: b.p. 117°/20 mm., 134°/40 mm., 152°/80 mm., n_D^{25} 1.4611, d_4^{25} 0.9377, MR_D calcd. 70.34, found 69.84. Analysis indicated the product contained 0.63% chlorine.

Di-*n*-butoxymethylphenylsilane. In a similar manner, dichloromethylphenylsilane (47.8 g., 0.25 mole) was treated with *n*-butyl alcohol (48.5 g., 0.65 mole). A small amount of sodium was used to drive the reaction to completion. A 20-gram sample of the dibutoxy derivative distilling at 142° at 10 mm. was collected for characterization: b.p. 127°/5 mm., 156°/20 mm., 173°/40 mm., n_D^{25} 1.4643, d_4^{25} 0.9288, MR_D calcd. 79.40, found 79.06.

Expt. No.	$CH_3Si(OR)_2Cl$ R	Mole	Organometallic Reagent[a]
1	C_2H_5	0.35	C_6H_5Na[g]
2	C_2H_5	0.88	C_6H_5Na[g]
3	C_2H_5	0.70	C_6H_5Na[g]
4	C_2H_5	1.37	C_6H_5Na[g]
5	C_2H_5	0.88	C_6H_5Na[g]
6	C_2H_5	0.35	C_6H_5Na[h]
7	C_2H_5	0.88	C_6H_5Na[h]
8	C_2H_5	0.88	C_6H_5Na[h]
9	C_2H_5	0.88	C_6H_5Na[h]
10	$i\text{-}C_3H_7$	0.35	C_6H_5Na[g]
11	$i\text{-}C_3H_7$	0.70	C_6H_5Na[g]
12	$i\text{-}C_3H_7$	1.05	C_6H_5Na[g]
13	$i\text{-}C_3H_7$	1.40	C_6H_5Na[g]
14	$i\text{-}C_3H_7$	1.05	C_6H_5Na[g]
15	$i\text{-}C_3H_7$	1.05	C_6H_5Na[h]
16	$i\text{-}C_3H_7$	1.05	C_6H_5Na[h]
17	$i\text{-}C_3H_7$	1.05	C_6H_5Na[h]
18	$i\text{-}C_3H_7$	1.05	C_6H_5Na[h]
19	$i\text{-}C_3H_7$	1.05	C_6H_5MgBr[h]
20	$i\text{-}C_3H_7$	1.05	C_6H_5MgBr[h]
21	$i\text{-}C_3H_7$[e]	1.05	C_6H_5Na[g]
22	$i\text{-}C_3H_7$[f]	1.05	C_6H_5Na[g]
23	$n\text{-}C_4H_9$	0.70	C_6H_5Na[g]
24	$n\text{-}C_4H_9$	1.40	C_6H_5Na[g]

[a] 0.350 mole of reagent used in all experimenta. [b] See experimental for examples. [c] Toluene except as noted. [d] Yield calculations based 0n 0.350 mole of product representing 100%. [e] Composition via VPC analysis (in mole %): 0.6%-HCL; 1.2%-$CH_3Si(OR)Cl_2$, 82.0%-$CH_3Si(OR)_2Cl$ and 16.2%-$CH_3Si(OR)_3$. [f] Composition via VPC analysis (in mole %): 1.4%-HCl, 16.6%-$CH_3Si(OR)Cl_2$, 81.5%-$CH_3Si(OR)_2Cl$, and 1.5%-$CH_3Si(OR)_3$. [g] Reagent was formed in situ. [h] Reagent was preformed. [i] Employed stirring rate of 5000 r.p.m., whereas a stirring rate of about 100 r.p.m. was used in all other experiments. [j] Ether used as solvent. [k] Duplicate experiment gave values of 3, 45, . . . , 11, 46, respectively. [l] Duplicate experiment gave values of 13, 45, . . . , 2, 42, respectively. [m] Duplicate experiment gave values of 1, 50, 6, 5, 73, respectively. [n] Duplicate experiment gave values of 4, 59, . . . , 11, 61, respectively. [o] Duplicate experiment gave values of 7, . . . , . . . , 45, 16, respectively. [p] Duplicate experiment gave values of 5, . . . , . . . , 38, 12, respectively.

RESULTS

The results of this study are summarized in Table I. During this work, several sets of duplicate experiments were performed at random so that an estimation of the precision of the over-all experimental work could be made. Statistical analyses of the results in terms of total yield of monophenylated products (yield of alkoxychloromethylphenylsilane plus yield of dialkoxymethylphenylsilane) which were obtained from the duplicate experiments, indicated a standard deviation of ±5.9%. Thus, at the 95% confidence limits for a difference between the yields of monophenylated products of two different experiments to be considered significant the difference must be greater than

Table I. Reactions of Chlorodialkoxymethylsilanes with Phenylsodium

				$CH_3Si(OR)_2Cl$, %		Products, % Yield[d]	
Procedure[b]	Rxn. Temp., °C.	Solvent[c] Ml.	Na, % Recovd. as NaOH	Recovd. Unchanged	Recovd. as $CH_3Si(OR)_3$	$CH_3SiC_6H_5(OR)Cl$	$CH_3SiC_6H_5(OR)_2$
A	110	450	3	0	...	0	35
A	110	665	2[k]	47[k]	...[k]	5[k]	54[k]
B	110	665	1	27	20	23	32
B	110	340	6	71	8	9	39
C	35	415	3[l]	50[l]	...[l]	2[l]	58[l]
D	0	270	3	0	...	0	63
D	0	480	1[m]	51[m]	5[m]	8[m]	67[m]
D	−60	480	0	54	...	11	63
D	0	130	3	50	...	10	69
B	110	73	8	3	...	1	50
B	110	143	12	45	18	11	51
B	110	220	9[n]	60[n]	...[n]	4[n]	69[n]
B	110	286	11	70	4	5	67
B	110	None	7	62	...	5	62
D[i]	110	None	6	58	0	2	80
D	50	130	3	62	8	6	68
D	25	130	10	38	21	51	20
D	0	130	1	72	2	3	67
D	25	560[j]	...	19	20	30	17
D	25	335[j]	...	68	7	19	21
B	110	None	4[o]	...[o]	...[o]	11[o]	59[o]
B	110	None	1[p]	...[p]	...[p]	22[p]	30[p]
B	110	123	7	38	36	27	40
B	110	246	15	65	18	28	40

11.8%. The ratio of alkoxychloromethylphenylsilane to dialkoxymethylphenylsilane in the reaction products of duplicate experiments varied so greatly that no interpretation of the results was made on this basis. Apparently, this ratio is affected by a complex of interactions not directly related to any one variable.

Chlorodiethoxymethylsilane. Under similar reaction conditions, preformed phenylsodium gave significantly higher yields of monophenylated products than in situ-formed phenylsodium.

In reactions with in situ-formed phenylsodium, increasing the reactant ratio (phenylsodium:silane reactant) from 1:1 to 1:2.5 significantly increased the yield of monophenylated products. However, increasing the reactant ratio from 1:2.5 to 1:4 did not produce a significant increase in the yields.

In reactions with preformed phenylsodium increasing the reactant ratio from 1:1 to 1:2.5 produced a significant increase in the yield of monophenylated products. Neither lowering the reaction temperature from 0° to −60° nor diluting the silane reactant from 5.81 molar to 1.75 molar, affected the yield of monophenylated products.

Chloroisopropoxymethylsilane. Under comparative reaction conditions both in situ and preformed phenylsodium gave significantly higher yields than preformed phenylmagnesium bromide.

With in situ-formed phenylsodium, significantly higher yields were obtained at reactant ratios of 1:4 and 1:3 than ratios of 1:2 and 1:1. Increasing the rate of stirring from 100 to 5000 r.p.m. significantly increased the yield. Dilution of the silane reactant with toluene from 4.78 to 2.40 molar did not appreciably affect the yield.

In reactions with preformed phenylsodium no difference in the yields of monophenylated products was obtained by increasing the temperature from 0° to 50°.

Chlorodi-*n*-butoxymethylsilane. Approximately the same yield of monophenylated products was obtained at a reactant ratio of 1:2 as at a reactant ratio of 1:4.

Methyltrichlorosilane Isopropoxylation Mixtures. In reactions with in situ-formed phenylsodium significantly higher yields of monophenylated products were obtained with 80% diisopropoxy-20% triisopropoxy mixture than with 80% diisopropoxy-20% monoisopropoxy mixtures.

Chlorodialkomethylsilanes with In Situ-Formed Phenylsodium: The effect of the type of alkoxy group in the chlorodialkoxymethylsilane reactant employed in the reactions which were carried out at a 1:2 reactant ratio was not significant. However, in the reactions which were carried out at a 1:4 reactant ratio significantly higher yields were obtained with the *n*-butoxy compound and the isopropoxy compound than with the ethoxy compound.

DISCUSSION

The reactions of chlorodiisopropoxymethylsilane with phenylmagnesium bromide did not show a difference between the reactivities of the silicon-chlorine bond and the silicon-alkoxy bond toward the Grignard reagent. Two types of reactions (Equations 1 and 2) appeared to proceed simultaneously at approximately the same rate.

$$CH_3Si(OR)_2Cl + C_6H_5MgBr \rightarrow CH_3SiC_6H_5(OR)_2 + MgBrCl \quad (1)$$

$$CH_3Si(OR)_2Cl + C_6H_5MgBr \rightarrow CH_3SiC_6H_5(OR)Cl + MgBr(OR) \quad (2)$$

However, in nearly all the reactions of the three types of chlorodialkomethylsilanes with the phenylsodium reagents, the silicon-chlorine bonds were more reactive towards phenylsodium than the silicon-alkoxy bonds, so that chlorine substitution (Equation 3) was favored over alkoxy substitution (Equation 4):

$$CH_3Si(OR)_2Cl + C_6H_5Na \rightarrow CH_3SiC_6H_5(OR)_2 + NaCl \quad (3)$$

$$CH_3Si(OR)_2Cl + C_6H_5Na \rightarrow CH_3SiC_6H_5(OR)Cl + NaOR \quad (4)$$

Although the reactions of chlorodiispropoxymethylsilane and chlorodi-*n*-butoxymethylsilane gave higher yields of monophenylated products than chlorodiethoxymethylsilane, the distribution of products indicated that the silicon-chlorine bonds of diethoxy and diisopropoxy compounds were more reactive towards the organosodium reagent than the silicon-chlorine bonds of the di-*n*-butoxy compound. Of the chlorodialkoxymethylsilanes studied, chlorodiisopropoxymethylsilane gave the highest yield of monophenylated products and the highest yield of dialkoxymethylphenylsilane.

However, the production of fairly large amounts of the methyltrialkoxysilane byproduct indicates that one or more dominant side reactions occurred in many of the experiments with the chlorodialkomethylsilanes and the phenylsodium reagent. There are several possible routes by which methyltrialkoxysilane could be produced. Most of these routes also provide a means whereby the chloroalkoxymethylphenylsilane could be produced.

One route might involve the replacement of an alkoxy group in the chlorodialkoxymethylsilane (Equation 4) to produce the alkoxychloromethylphenylsilane and the corresponding sodium alkoxide. This alkoxide can react with the chlorodialkoxymethylsilane to yield the methyltrialkoxysilane (Equation 5).

$$CH_3Si(OR)_2Cl + NaOR \rightarrow CH_3Si(OR)_3 + NaCl \qquad (5)$$

Another possible route involves the sodium alkoxide catalyzed disproportionation of the chlorodialkoxymethylsilane (Equation 6) to yield the methyltrialkoxysilane and the alkoxydichloromethylsilane. The latter compound may react with the phenylsodium (Equation 7) to yield the alkoxychloromethylphenylsilane.

$$2CH_3Si(OR)_2Cl \rightarrow CH_3Si(OR)Cl_2 + CH_3Si(OR)_3 \qquad (6)$$

$$CH_3Si(OR)Cl_2 + C_6H_5Na \rightarrow CH_3SiC_6H_5(OR)Cl + NaCl \qquad (7)$$

The redistribution reaction of the chlorodialkoxymethylsilane and the dialkoxymethylphenylsilane (Equation 8) might be another means whereby the methyltrialkoxysilane and the alkoxychloromethylphenylsilane could be produced.

$$CH_3Si(OR)_2Cl + CH_3SiC_6H_5(OR)_2 \rightarrow CH_3Si(OR)_3 + CH_3SiC_6H_5(OR)Cl \qquad (8)$$

Since both of the materials involved in this reaction and catalytical amounts of the sodium alkoxide were present in the final reaction mixtures of most experiments, this type of side reaction is feasible.

However, in all the reactions which contain appreciable amounts of the byproducts, the methyltrialkoxysilane was always present in greater amounts than the alkoxychloromethylphenylsilane. This fact suggests that the methyltriethoxysilane is the sole product of a side reaction, or that some of the coproduced alkoxychloromethylphenylsilane is consumed in a subsequent side reaction.

Most of the other results which were obtained during this study—such as the effect of high-speed stirring, the concentration of the reactant, and the reaction temperature—are consistent with the heterogeneity of the reactions of methyldialkoxychlorosilanes with phenylsodium reagents in nonpolar solvent systems.

For the alkoxyderivatives of methyltrichlorosilane and dichloromethylphenylsilane, three chlorodialkoxymethylsilanes, and the three alkoxychloromethylphenylsilanes were prepared by the partial alcoholysis of parent chlorosilanes. Five of the completely alkoxylated derivatives were prepared by alcoholysis of the chlorosilanes with an excess of the alcohol followed by the addition of a small amount of sodium to drive the reaction to completion. By these two general procedures six new silanes were prepared: chloroethoxymethylphenylsilane, chlorodiisopropoxymethyl silade, chloroisopropoxymethylphenylsilane, diisopropoxymethylphenylsilane, *n*-butoxychloromethylphenylsilane and di-*n*-butoxymethylphenylsilane. The physical properties of these new silanes along with the known (1–15) silicon compounds which were prepared and characterized during this study, are listed in Table II.

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Table II. Compounds Prepared and Characterized In this Study

Compound	B.P., (° C./Mm.)	n_D^{25}	d_4^{25}	MR_D Calcd.	MR_D Found
$CH_3Si(OC_2H_5)_2Cl$	36/20[b]	1.3881[c]	0.9755[d]	49.36	49.36
$CH_3Si(OC_2H_5)_3$	24.6/10[e]	1.3887[f]	0.9166[g]	46.45	45.97
$CH_3SiC_6H_5(OC_2H_5)Cl$[a]	86/10[h]	1.4880	1.0453	55.12	55.26
$CH_3SiC_6H_5(OC_2H_5)_2$	98/10[i]	1.4672[j]	0.9650[k]	60.88	60.50
$CH_3Si(O\text{-}i\text{-}C_3H_7)_2Cl$[a]	38/10[l]	1.3899	0.9398	49.95	49.55
$CH_3Si(O\text{-}i\text{-}C_3H_7)_3$	50/10[m]	1.3849[n]	0.8531[o]	60.34	60.43
$CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)Cl$[a]	93/10[p]	1.4820	1.0420	58.69	59.75
$CH_3SiC_6H_5(O\text{-}i\text{-}C_3H_7)_2$[a]	103/10[q]	1.4611	0.9377	70.34	69.84
$CH_3Si(O\text{-}n\text{-}C_4H_9)_2Cl$	69/5[r]	1.4091	0.9422	59.21	58.94
$CH_3Si(O\text{-}n\text{-}C_4H_9)_3$	101/5[s]	1.4078[t]	0.8726[u]	74.23	74.04
$CH_3SiC_6H_5(O\text{-}n\text{-}C_4H_9)Cl$[a]	101/5[v]	1.4836	1.0154	64.38	64.37
$CH_3SiC_6H_5(O\text{-}n\text{-}C_4H_9)_2$[a]	127/5[w]	1.4643	0.9288	79.40	79.06

[a] New compound. [b] 50°/40, 66°/80, 129°/760 (*8*), 126.5–127.5°/760 (*1*). [c] n_D^{25} 1.393 (*1*). [d] d_4^{20} 0.983 (*8*), d_4^{20} 1.010 (*1*). [e] 140–145°/760 (*9*), 135–138°/731.3 (*11*), 144.5°/760 (*14*), 141.5°/775 (*12*), 142–4°/745 (*3*), 143.5°/760 (*15*). [f] n_D^{20} 1.3821 (*9*), n_D^{25} 1.3838–1.3867 (*11*), n_D^{25} 1.3811 (*14*), n_D^{20} 1.38327 (*12*), n_D^{25} 1.3820 (*15*) [g] d_4^{25} 0.877 (*11*), d_4^{20} 0.8948 (*12*), d_4^{25} 0.885 (*15*). [h] 101°/20, 117°/40, 135°/80. [i] 112°/12, 118°/31, 218°/760, 117–18°/31 (7), 105–10°/13 (*5*), 112°/18 (*4*), 218°/760 (*4*), 216°/760 (2). [j] n_D^{20} 1.4678 (*4*), n_D^{20} 1.4704 (2). [k] d_4^{20} 0.962 (*4*), d_4^{20} 0.9627 (2). [l] 50°/20, 60°/40, 80°/80, 145°/763. [m] 64°/20, 79°/40, 96°/80, 161–2°/760 (*9*), 69°/20 (*14*), 163°/749 (*3*), 102°/100 (*13*). [n] n_D^{22} 1.3846 (*9*). n_D^{25} 1.3841 (*14*), n_D^{25} 1.3830 (*3*), n_D^{20} 1.3869 (*13*). [o] d_4^{25} 0.8481 (*14*), d_4^{25} 0.8557 (*3*). [p] 108°/20, 125°/40, 144°/80. [q] 117°/20. 134°/40, 152°/80. [r] 82°/10, 97°/20, 113°/40, 206°/752, 98–9°/22 (*9*). [s] 115°/10, 128°/20, 145°/40, 120°/15 (*9*), 134.0–134.5°/20 (*14*), 122°/17 (*12*), 145°/43 (*13*), 115°/10 (*10*). [t] n_D^{21} 1.4083 (*9*), n_D^{25} 1.4081 (*14*), n_D^{20} 1.41085 (*12*), n_D^{20} 1.4110 (*13*), n_D^{20} 1.4106 (*10*). [u] d_4^{25} 0.8715 (*14*), d_4^{20} 0.8772 (*12*), d_4^{20} 0.8775 (*10*). [v] 117°/10, 130°/20, 147°/40. [w] 142°/10, 156°/20, 173°/40.

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Reaction of Benzoin with Aminobenzoic Acids and with *p*-Ethylaniline

CHARLES D. HURD and JAMES MOFFAT[1]
Department of Chemistry, Northwestern University, Evanston, Ill.

Brief studies of the reaction of benzoin with the three aminobenzoic acids and with *p*-aminophenylacetic acid are reported.

DURING STUDIES on the reactions of amino acids with sugars, several simplified model systems (*3, 4*) were examined.

Weckowicz had already studied the ortho isomer, anthranilic acid, in this reaction (*5*), and Cameron and co-workers had reported the use of ethyl *p*-aminobenzoate and of *p*-aminophenylacetic acid (*1*). These workers had thoroughly proved the structures of their products. In general, the equation was

$$C_6H_5\text{-}CO\text{-}CHOH\text{-}C_6H_5 + ArNH_2 \rightarrow C_6H_5CH(NHAr)\text{-}CO\text{-}C_6H_5 + H_2O$$

As exaplained (*3*), the amine group initially attacks the carbonyl position to yield an unstable α-hydroxy imine [$PhC(=NAr)CHOHPh$] which tautomerizes to the α-amino ketone.

Several points about the previous work need clarification. Cameron's group ran most of their reactions at 100° C., and under these conditions found that *o*-substituted anilines would not react with benzoin. Weckowicz, however, had previously shown that anthranilic acid reacted smoothly with aniline in the melt at higher temperatures. We confirm this. This study was extended to the *m*- and *p*-aminobenzoic acids. The expected *m*- and *p*-(desylamino)benzoic acids

$$C_6H_5CH(COC_6H_5){-}NHC_6H_4COOH$$

were formed in about the same yields as that found for the ortho isomer.

Weckowicz treated his *N*-desylanthranilic acid with an excess of phenylhydrazine in acetic acid and obtained a compound, m.p. 229–230°, for which the empirical formula $C_{33}H_{27}N_5$ was suggested based on analytical data. Since this is the melting point of benzoin phenylosazone and since his analytical data correspond better with the osazone formulation ($C_{26}H_{22}N_4$) than with the C_{33} formula, we have repeated this reaction. We find that the substance of m.p. 229–230° is indeed the phenylosazone and we find that the other two (desylamino)benzoic acids as well as *p*-(desylamino)phenylacetic acid also give rise to this osazone:

$$PhCOCHPh\text{-}NHAr + 3PhNHNH_2 \rightarrow PhNHN{=}CPh\text{-}CPh{=}NNHPh + ArNH_2 + PhNH_2 + NH_3 + H_2O.$$

The Schiff base reported (*2*) by Emerson and co-workers from the reaction of benzoin and *p*-ethylaniline is surely

Table I. (Desylamino)benzoic Acids

Isomer	M.P., ° C.	Anal., % N, Found, (Calc'd., 4.23)
Ortho	226.5–228.5 (dec., gas)[a]	4.25
Meta	182–184	4.38
Para	246–256 (dec., gas)[b]	4.28

[a] Weckowicz reported m.p. 231–232° (*5*).
[b] This compound turns bright yellow at 235°.

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[1] Present adress, Department of Chemistry, University of Kansas City, Kansas City 10, Mo.