Grignard Reactions of Polyhalocarbons. II. *In Situ* Grignard Reactions of Carbon Tetrahalides with Organochlorosilanes

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Tseng has reported[2] that carbon tetrabromide in ether reacts vigorously with magnesium; no statement is made concerning the products of this reaction. He also observed that under the same conditions there is no reaction between magnesium and carbon tetrachloride. Reychler[3] had earlier established that carbon tetrachloride is not only unreactive but inhibits, perhaps mechanically by the formation of a coating on the magnesium, the Grignard reaction in ether of such active halides as methyl iodide, ethyl iodide, ethyl bromide, and bromobenzene. In addition to these few papers the literature also contains accounts of reactions of carbon tetrahalides with preformed Grignard reagents, but no other reports of attempted reaction between a carbon tetrahalide and magnesium were found.

Discussion

Carbon tetrabromide in tetrahydrofuran solution was found to react vigorously with magnesium shavings. No products could be isolated from the resulting carbonaceous residue. When an organochlorosilane was added to the tetrahydrofuran in which the magnesium was suspended and the carbon tetrahalide was added dropwise at a rate just sufficient to maintain reflux, the reaction was just as vigorous, and, after hydrolysis and distillation, fair to good yields of tetrakis-, tris-, and bissilylmethanes were obtained. This suggests that the conditions imposed by the *in situ* procedure, *i.e.*, a high concentration of organochlorosilane in the immediate vicinity of the magnesium surface where the carbon tetrahalide at relatively low concentrations reacts, tend to favor ensuing reaction of the Grignard intermediate with organochlorosilane rather than with additional carbon tetrahalide.

The general reaction is summarized in eq. 1 following.

$$\mathrm{CX_4 + Mg + R_3SiCl \xrightarrow{\text{tetrahydrofuran}}}$$

$$\text{products} \xrightarrow{\mathrm{H_2O}} \left\{\begin{array}{l}\mathrm{(R_3Si)_4C}\\ \mathrm{(R_3Si)_3CH}\\ \mathrm{(R_3Si)_2CH_2}\end{array}\right. + \mathrm{MgXCl} \qquad (1)$$

Although carbon tetrachloride did react under the conditions employed, the reaction was too slow to be of synthetic value. Carbon tetrabromide, bromotrichloromethane, and dibromodichloromethane reacted readily to give fair to good yields of the products shown in Table I.

In addition to the tetrasubstituted methanes, it can be seen in both eq. 1 and Table I that considerable quantities of tri- and disubstituted methanes were obtained. This was also true for *in situ* Grignard reactions of 1,1-dihalides which yielded monosilyl as well as disilyl products and the reactions of 1,1,1-trihalides which yielded monosilyl and disilyl as well as trisilyl substituted products.[4] It is of interest that no tetra- or trisubstituted methanes were isolated in the reaction employing dimethylphenylchlorosilane, the most sterically hindered organochlorosilane. The least sterically hindered organochlorosilane, dimethylchlorosilane, gave the highest yield of tetrasubstituted methane. The significance of this remains obscure until the origin of the hydrogen atoms in the reduced products and the nature of the reaction intermediates are established.

TABLE I

In Situ GRIGNARD REACTIONS OF CARBON TETRAHALIDES AND ORGANOCHLOROSILANES

Tetrahalide	Silane	Products Structure	 Yield, %[a]
CBr_4	$(CH_3)_3SiCl$	$[(CH_3)_3Si]_4C$[b]	27.6
		$[(CH_3)_3Si]_3CH$	39.8
		$[(CH_3)_3Si]_2CH_2$	4.9
$BrCCl_3$	$(CH_3)_3SiCl$	$[(CH_3)_3Si]_4C$	20.2
		$[(CH_3)_3Si]_3CH$	21.3
Br_2CCl_2	$(CH_3)_3SiCl$	$[(CH_3)_3Si]_4C$	29.6
		$[(CH_3)_3Si]_3CH$	26.0
		$[(CH_3)_3Si]_2CH_2$	4.5
CBr_4	$(CH_3)_2HSiCl$	$[(CH_3)_2HSi]_4C$[b]	59.5
CBr_4	$(CH_3)_2C_6H_5SiCl$	$[C_6H_5(CH_3)_2Si]_2CH_2$	67.5

[a] Based on carbon tetrahalide. [b] Compounds here reported for the first time.

The tetrasilylmethanes are structurally interesting compounds because of their molecular geometry. The large and spherically symmetrical tetrakis(trimethylsilyl)methane molecule (the carbon analog of which has never been reported) has a surface comprised of twelve geometrically equivalent methyl groups. Somewhat surprisingly, it is a high melting crystalline material which appears from visual observations to undergo a phase transition to another solid form at about 195–210°. Such behavior is similar to that of tetramethylmethane and some other spherically symmetrical molecules in which free rotation of the molecule within the crystal lattice occurs.

Experimental

Materials.—J. T. Baker purified magnesium turnings were used in this work. Commercial tetrahydrofuran was dried by distillation from lithium aluminum hydride. Commercial carbon tetrahalides were used without further purification. The organochlorosilanes were supplied by Dow Corning Corp.

Analytical.—The carbon and hydrogen analyses and the silicon analyses of tetrakis(trimethylsilyl)methane and tetrakis(dimethylsilyl)methane were done by Galbraith Laboratories, Knoxville, Tenn. The melting points are uncorrected. The structures of the two new compounds were confirmed by H^1 n.m.r. analysis. A Varian A-60 spectrometer was used. Yields are based on weight of tetrahalide used.

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(1) Multiple Fellowship on Silicones sustained by Dow Corning Corp. and Corning Glass Works.

(2) C.-L. Tseng, *Trans. Sci. Soc. China*, **7**, 233 (1932).

(3) A. Reychler, *Bull. soc. chim. France*, [3]**35**, 803 (1906).

(4) R. L. Merker and M. J. Scott, *J. Am. Chem. Soc.*, **85**, 2243 (1963).

Grignard Reactions with *in Situ* Trimethylchlorosilane.—In a three-necked flask equipped with dropping funnel, stirring rod, and condenser, was placed 58.8 g. (2.42 g.-atoms) of magnesium. The apparatus was dried by heating under a stream of dry nitrogen. To the flask was added 262 g. (2.42 moles) of trimethylchlorosilane and 600 ml. of tetrahydrofuran. This was heated to reflux, external heat was removed, and, at a rate to maintain reflux, 200 g. (0.603 mole) of carbon tetrabromide in 200 ml. tetrahydrofuran were added. After the addition which required 2.5 hr. and 2 hr. reflux, the mixture was poured over cracked ice and filtered. The unchanged magnesium weighed 3.2 g. Solvent and hexamethyldisiloxane were removed from the organic layer at atmospheric pressure. From the crude products 36 g. of precipitate was filtered. The filtrate was fractionated at reduced pressures yielding the products that follow: (1) 20.2 g. of 4-trimethylsilybutanol (see ref. 4 for origin of this product), b.p. 125° at 100 mm.; n^{25}_{D} 1.4332, lit.[5] n^{25}_{D} 1.4315; d^{25}_{4} 0.833, lit.[5] d^{25}_{4} 0.830. r_D Calcd.: 0.3121. Found: 0.3122. (2) 4.7 g. (4.9%) of bis(trimethylsilyl)methane, b.p. 71° at 100 mm.; n^{25}_{D} 1.4134, lit.[6] n^{20}_{D} 1.4170; d^{25}_{4} 0.750, lit.[6] d^{20}_{4} 0.752. r_D Calcd.: 0.3347. Found: 0.3328. (3) 55.7 g. (39.8%) of tris(trimethylsilyl)methane, b.p. 101° at 20 mm.; n^{25}_{D} 1.4605, lit.[7] n^{20}_{D} 1.4630; d^{25}_{4} 0.8275, lit.[7] d^{20}_{4} 0.836. r_D Calcd.: 0.3320. Found: 0.3313.

From the residue, 16.5 g. of solid was extracted with benzene. After removal of the benzene, this was combined with the precipitate filtered from the crude products above and recrystallized from absolute ethanol, yielding 50.5 g. (27.6%) of tetrakis(trimethylsilyl)methane, melting point, sublimes.

Anal. Calcd. for $C_{13}H_{36}Si_4$: C, 51.20; H, 11.90; Si, 36.86; mol. wt., 304.8. Found: C, 51.40; H, 11.81; Si, 36.60; mol. wt. (ebullioscopic), 323.

The H^1 n.m.r. spectrum consists of a single peak at $\tau = 9.8$ p.p.m. using cyclohexane as the internal reference. Grignard reactions of bromotrichloromethane and dibromodichloromethane were run in the way described above for carbon tetrabromide. A trace of iodine was used to initiate reaction with the bromotrichloromethane. Products were characterized as above; yields are given in Table I.

Reaction with *in Situ* Dimethylchlorosilane.—To 56.8 g. (2.34 g.-atoms) of magnesium, 276 g. (2.92 moles) of dimethylchlorosilane, and 600 ml. of tetrahydrofuran was added at a rate to maintain reflux 200 g. (0.603 mole) of carbon tetrabromide in 200 ml. of tetrahydrofuran. The addition period of 2.75 hr. was followed by 5-hr. reflux. The mixture was poured over crushed ice, neutralized with sodium bicarbonate, and the organic layer was washed with water. The crude products, after the addition of 500 ml. of methanol, were cooled to the temperature of Dry Ice–acetone and 63.1 g. of precipitate was filtered off. The filtrate was distilled and in fractions boiling at about 160° at 50 mm. an additional 28.6 g. of solid crystallized. The two crystalline products were mixed and recrystallized from 95% methanol–5% ethanol, yielding 88.7 g. (59.5%) of tetrakis(dimethylsilyl)methane, m.p. 115°.

Anal. Calcd. for $C_9H_{28}Si_4$: C, 43.46; H, 11.34; Si, 45.19. Found: C, 43.60; H, 11.43; Si, 45.27.

The H^1 n.m.r. spectrum consists of two peaks, a doublet at $\tau = 9.8$ p.p.m. and a septet at $\tau = 5.9$ p.p.m. with a coupling constant of 4 c.p.s. The intensity ratio of the doublet to the septet is approximately 6:1 and tetramethylsilane is the internal reference.

Reaction with *in Situ* Phenyldimethylchlorosilane.—To 14.6 g. (0.60 g.-atoms) of magnesium, 102.2 g. (0.60 mole) of phenyldimethylchlorosilane, and 150 ml. of tetrahydrofuran was added dropwise 50 g. (0.15 mole) of carbon tetrabromide in 50 ml. of tetrahydrofuran. The reaction mixture was treated as described above. Distillation yielded 28.8 g. (67.5%) of bis(phenyldimethylsilyl)methane, b.p. 131° at 1 mm.; n^{25}_{D} 1.5404, lit.[8] n^{25}_{D} 1.5426; d^{25}_{4} 0.960, lit.[8] d^{25}_{4} 0.961. r_D Calcd.: 0.3285. Found: 0.3270.

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[5] J. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

[6] L. Sommer, G. Goldberg, J. Gold, and F. Whitmore, *ibid.*, **69**, 980 (1947).

[7] R. Müller and G. Seitz, *Chem. Ber.*, **91**, 22 (1958).

[8] J. T. Goodwin, U. S. Patent 2,544,079 (1951).

Hydrogenolysis of the Grignard Reagent

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In the course of some studies on the Grignard reagent, we had occasion to investigate the hydrogenolysis reaction. While hydrogenolysis of organometallic compounds is not new, there has been no report of hydrogenolysis of the Grignard reagent.

We found that ether solutions of the Grignard reagent react readily and cleanly with hydrogen without a catalyst according to the following equation.

$$2RMgX + 2H_2 \longrightarrow 2RH + MgX_2 + MgH_2$$

This reaction is general for a large number of Grignard reagents. The reaction conditions and results obtained with a variety of Grignard reagents are summarized in Table I. Runs of shorter duration with ethylmagnesium chloride at 100° showed that the reaction was 28% complete in 1 hr. and 43% complete in 3 hr.

It is obvious from Table I that some Grignard reagents react with hydrogen more readily than others. There appears to be no simple correlation of relative reactivity with the structure of the alkyl group. Such factors as the molecular aggregation of the Grignard reagent and the equilibria among the various species, monomer, dimer, dialkylmagnesium, and magnesium halide could affect the rate of the hydrogenolysis reaction. Furthermore, the system is heterogeneous and even the relative solubilities of the Grignard reagents at elevated temperatures are unknown.

We have found further that Grignard reagents are stable with respect to olefin elimination. Deuterium reacted with isopropylmagnesium chloride at 75° and at 125°. In both cases mass spectrometer analysis of the gaseous products showed that the propane produced contained only one deuterium atom. Hydrolysis of the ether-insoluble product with H_2O produced HD. The deuterium reaction can thus be written as shown.

$$2\ i\text{-PrMgCl} + 2D_2 \longrightarrow 2\ i\text{-PrD} + MgD_2 + MgCl_2$$

These experiments also show that hydrogenolysis does not proceed by an olefin elimination mechanism.

Experimental

Fisher certified reagent grade ethyl bromide, ethyl iodide, allyl bromide, *n*-butyl chloride, phenyl chloride, phenyl bromide, and benzyl chloride were used as received. Isopropyl chloride and *sec*-butyl chloride (Eastman) and neopentyl chloride (Matheson, Coleman and Bell) also were used as received. Eastman *t*-butyl chloride was distilled prior to use, and both methyl chloride and ethyl chloride (Ethyl Corporation) were vaporized through a calcium chloride drying tube. Mallinckrodt anhydrous ether and Domal high purity sublimed magnesium granules (Dominion Magnesium Co., Ltd., Haley, Ont.) were used without purification.

Grignard Preparation.—In general the Grignard reagents were prepared in 1-mole quantities from 27 g. of magnesium, 300 ml. of ether, and 1 mole of halide. A three-necked, 1-l. creased flask equipped with an air-driven stirrer, Dry Ice condenser, and addition funnel served as the reaction vessel. A blanket of argon was maintained on the reaction mixture at all times. The