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Grignard Reactions of Polyhalocarbons. I. *In Situ* Grignard Reactions of 1,1-Dihalides and 1,1,1-Trihalides with OrganochlorosilanesBY ROBERT L. MERKER AND MARY JANE SCOTT¹

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Grignard reaction procedures have been modified to prepare trimethylsilyl derivatives of bromoform, benzotrichloride, 1,1,1-trichloroethane, diphenyldichloromethane, and tetrabromoethylene. These polyhalides in which the involved carbon atom has more than one halogen traditionally have been considered "inert" or unsuitable to Grignard synthesis. Developments making these preparations practical involve use of tetrahydrofuran and the organochlorosilane which is to be coupled as cosolvents for Grignard reagent formation. Several compounds are here reported for the first time: $C_6H_5C[Si(CH_3)_3]_3$, $C_6H_5CH[Si(CH_3)_3]_2$, $(C_6H_5)_2C[Si(CH_3)_3]_2$, and $CH_3C[Si(CH_3)_3]_3$.

Introduction

Polyhalides, especially those with two or more halogens on the same carbon atom, have been regarded traditionally as poor prospects for Grignard reagent preparations.² Emschwiler,³ in 1926, reported the formation of $[H_2C(MgBr)_2]$ and $[H_2C(MgI)_2]$ which upon hydrolysis yielded methane. In 1932, Chang and Chao-Lun Tseng⁴ described the preparation of $[H_2C(MgI)_2]$ in 10% yield. Their work also established⁵ that chloroform and bromoform do not react with magnesium in ethyl ether. In another article⁶ these same authors report that benzal chloride and benzotrichloride react with magnesium in ethyl ether, but the only products are high molecular weight hydrocarbons.

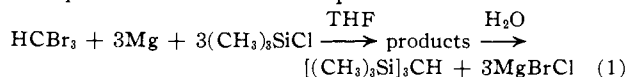
More recently Fidler and co-workers⁷ have prepared $[H_2C(MgI)_2]$ and $[H_2C(MgBr)_2]$ from CH_2X_2 and Mg in ethyl ether. The reactivity of these methylene di-Grignard reagents with coreactants other than hydrolyzing agents was reported to be very low.

Within the past few years many accounts of innovations which have greatly expanded the historical limitations of the Grignard synthesis have appeared.⁸ These innovations involve use of reactive solvents, activated magnesium, entrainment procedures,⁹ and others. Successful Grignard reaction of dihalides such as $Br(CH_2)_{4-10}Br$, *m*- and *p*-dibromobenzene and other dihalogen aromatic derivatives is now possible. Breed¹⁰ and co-workers have prepared *p*-phenylenedisilanes by concurrent addition to magnesium of *p*-dibromobenzene and the reactive silane with which it is to couple. In this Laboratory¹¹ similar synthetic methods have been developed to prepare *p*-(bis-dimethylhydrogensilyl)-benzene, a useful intermediate leading to *p*-silphenylene-siloxane polymers. This paper, the first of a series, describes the *in situ* Grignard and concurrent coupling reactions of some 1,1-dihalides and 1,1,1-trihalides with organochlorosilanes.

Discussion

Trimethylsilyl derivatives of bromoform, benzotrichloride, diphenyldichloromethane, 1,1,1-trichloro-

ethane, and tetrabromoethylene have been prepared by the Grignard reaction. The results of this work are summarized in Table I. A typical reaction may be represented as shown in eq. 1.



Though unsuitable for traditional Grignard reagent preparations, the above polyhalides reacted satisfactorily in a system employing tetrahydrofuran and trimethylchlorosilane as cosolvents. In this manner Grignard formation and simultaneous coupling with the chlorosilane were effected. Trimethylchlorosilane was chosen for this exploratory study since after once coupled no further reaction is possible, hence simplifying the isolation and identification of products.

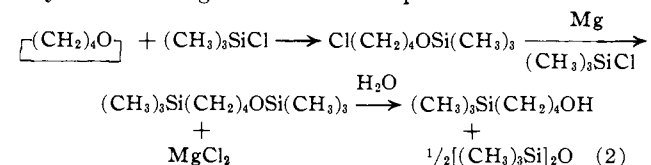
TABLE I
TRIMETHYLSILYL SUBSTITUTED DERIVATIVES PREPARED BY
GRIGNARD REACTION OF POLYHALIDES

Polyhalide	Products	
	Structure	Yield, ^b %
HCBBr ₃	$[(CH_3)_3Si]_2CH_2$ $[(CH_3)_3Si]_3CH$	18.5 24.2
C ₆ H ₅ CCl ₃	$[(CH_3)_3Si]_2HCC_6H_5^a$ $[(CH_3)_3Si]_3CC_6H_5^a$	21.9 15.8
(C ₆ H ₅) ₂ CCl ₂	$[(CH_3)_3Si]_2C(C_6H_5)_2^a$ $(CH_3)_3SiHC(C_6H_5)_2$	7.6 11.8
CH ₃ CCl ₃	$[(CH_3)_3Si]_3CCH_3^a$	4.3
Br ₂ C=CBBr ₂	$(CH_3)_3SiC\equiv CSi(CH_3)_3$	60.2

^a Compound here reported for first time. ^b Based on polyhalide.

The polyhalide, dissolved in tetrahydrofuran, was added to magnesium shavings suspended in tetrahydrofuran and trimethylchlorosilane. Reaction began immediately and continued vigorously controlled by the rate of addition. After the addition and short reflux period, the reaction mixture was hydrolyzed, washed with water, then fractionally distilled.

A side product, 4-trimethylsilylbutanol, was isolated in small amounts in the reactions studied. This probably arises through the reaction sequence



which is similar to the reaction shown by Kratochvil¹² in which refluxing tetrahydrofuran with silicon tetrachloride yields mixtures of chlorobutoxysilanes.

Since the primary interest of this initial research was the exploration of the possibilities of this modified Grignard synthesis, no attempt for optimum yields was made. It is expected that yields in the reactions

(12) M. Kratochvil and J. Frejka, *Chem. Listy*, **52**, 151 (1958).

(1) Multiple Fellowship on Silicones Sustained by Dow Corning Corporation and Corning Glass Works.

(2) M. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice Hall, Inc., New York, N. Y., 1954, p. 32.

(3) G. Emschwiler, *Compt. rend.*, **183**, 665 (1926).

(4) Chang and Chao-Lun Tseng, *Trans. Sci. Soc. China*, **7**, 243 (1932); *Chem. Abstr.*, **26**, 5544 (1932).

(5) Chao-Lun Tseng, *Natl. Central Univ. Sci. Rept. Ser. A*, **1**, No. 2, 1 (1931); *Chem. Abstr.*, **26**, 2166 (1932).

(6) Chang and Chao-Lun Tseng, *Trans. Sci. Soc. China*, **7**, 239 (1932); *Chem. Abstr.*, **26**, 5544 (1932).

(7) D. Fidler, J. Jones, S. Clark and H. Stange, *J. Am. Chem. Soc.*, **77**, 6634 (1955).

(8) I. Millar and H. Heaney, *Quart. Rev. (London)*, **11**, 109 (1957).

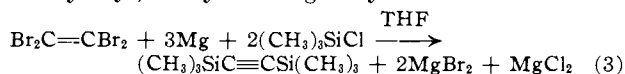
(9) D. E. Pearson, D. Cowan and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

(10) L. Breed, W. Haggerty and F. Baiocchi, *ibid.*, **25**, 1633 (1960).

(11) R. L. Merker and M. J. Scott, *J. Polymer Sci.*, in press.

described could be somewhat improved by finding the most favorable reactant concentrations, addition rates, rate of agitation, and so on.

The conversion of tetrabromoethylene to bis-(trimethylsilyl)-acetylene in good yield *via* the reaction



furnishes an interesting and useful example of a combined elimination and coupling reaction employing the *in situ* method.

In Table I it can be seen that bis-(trimethylsilyl)-methane is one product of the Grignard reaction of bromoform and trimethylchlorosilane. In this and other similar reactions in which reduced products were observed the origin of the hydrogen atom has not as yet been established. It could result conceivably from the hydrolysis of uncoupled Grignard reagent or through the abstraction of hydrogen by a free radical intermediate. Little is known at present concerning the nature of the intermediates or mechanism of this extremely complex reaction. The fact that conventional Grignardization of benzal chloride,⁶ benzotrichloride,⁶ and carbon tetrabromide¹³ leads only to insoluble carbon-containing residues suggests that under *in situ* conditions the intermediate formed through reaction of the polyhalide and magnesium reacts to a large extent with organochlorosilane rather than additional polyhalide. If the primary intermediate involves only one halogen atom on the carbon—that is, a typical Grignard reagent and not some unknown free radical intermediate—the reaction path can be envisioned as stepwise with each step yielding an additional silicon on the carbon atom. These very interesting questions are presently under investigation in this Laboratory.

Experimental

Starting Materials.—The magnesium used for this work was J. T. Baker purified shavings. Commercial tetrahydrofuran was dried by distillation from lithium aluminum hydride. Commercial polyhalides were used without further purification. The trimethylchlorosilane was supplied by Dow Corning Corporation.

Analyses.—The carbon and hydrogen analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. Further verification of structures was provided by H^1 n.m.r. and infrared spectral analyses. Reported melting points are uncorrected. All yields cited are based on the amount of polyhalide used.

Grignard Reaction of Bromoform.—Into a 3-necked flask equipped with a condenser, stirring rod, and dropping funnel was placed 57.6 g. (2.37 g.-atom) of magnesium. After drying the apparatus and magnesium by heating under a stream of dry nitrogen, 258 g. (2.37 moles) of trimethylchlorosilane and 1000 ml. of tetrahydrofuran were added to the flask and heated to reflux. The external heat was removed and through the dropping funnel at a rate to maintain reflux was added 200 g. (0.79 mole) of bromoform in 200 ml. of tetrahydrofuran. Following a 2.5-hour addition period and 1.5-hour reflux the reaction mixture was poured over crushed ice. The unreacted magnesium was filtered off—7 g. remaining. The liquid layers were separated, the organic phase washed three times with water, then dried over sodium sulfate. Solvents and hexamethyldisiloxane were removed at atmospheric pressure and fractional distillation at reduced pressures yielded the products: 23.3 g. (18.5%) of bis-(trimethylsilyl)-methane, b.p. 71° at 100 mm., n_D^{25} 1.4150, reported¹⁴ n_D^{20} 1.4170, d_4^{25} 0.753, reported¹⁴ d_4^{20} 0.752; R_D calcd. for $\text{C}_7\text{H}_{20}\text{Si}_2$ 0.3347, found 0.3326; 44.6 g. (24.2%) of tris-(trimethylsilyl)-methane, b.p. 101° at 20 mm., n_D^{25} 1.4605, reported¹⁵ n_D^{20} 1.4630, d_4^{25} 0.8275, reported¹⁵ d_4^{20} 0.826; R_D calcd. for $\text{C}_{10}\text{H}_{28}\text{Si}_3$ 0.3320, found 0.3313; calcd. mol. wt. 232.6, found (ebullioscopic) 240.

Also separated in the distillation was 13.3 g. of 4-trimethylsilylbutanol, b.p. 182° at atm. pressure, n_D^{25} 1.4332, reported¹⁶ n_D^{25} 1.4215, d_4^{25} 0.833, reported¹⁶ d_4^{25} 0.820; R_D calcd. for $\text{C}_7\text{H}_{18}\text{SiO}$ 0.3121, found R_D 0.3122.

Grignard Reaction of Benzotrichloride.—Following the general procedure described above, 41.1 g. (1.69 g.-atom) of magnesium,

183.2 g. (1.69 moles) of trimethylchlorosilane, and 420 ml. of tetrahydrofuran were placed in a 3-necked flask. Through a dropping funnel was added a solution of 100 g. (0.512 mole) of benzotrichloride in 140 ml. of tetrahydrofuran. At the completion of the addition period, 50 g. of trimethylchlorosilane was added to the reaction mixture which was then refluxed for 1 hr. and poured over crushed ice. The remaining magnesium, 0.9 g., was filtered off and the filtrate neutralized with sodium bicarbonate. The organic layer was washed with water and dried over sodium sulfate; the solvents and hexamethyldisiloxane were removed at atmospheric pressure. This mixture after the addition of 200 ml. of methanol was chilled to the temperature of Dry Ice-acetone. The precipitate which had formed was removed by filtration and recrystallized from 200 ml. of 75% methanol-25% ethanol giving a yield of 25.0 g. (15.8%) of tris-(trimethylsilyl)-phenylmethane, m.p. 158-160°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{32}\text{Si}_3$: C, 62.24; H, 10.46; Si, 27.30; mol. wt., 308.7. Found: C, 62.10; H, 10.49; Si, 27.35; mol. wt. (cryoscopic), 302.

The above filtrate was then distilled at reduced pressure yielding 26.5 g. (21.9%) of bis-(trimethylsilyl)-phenylmethane, b.p. 166° at 99 mm., d_4^{25} 0.884, n_D^{25} 1.4992.

Anal. Calcd. for $\text{C}_{13}\text{H}_{24}\text{Si}_2$: C, 66.01; H, 10.23; Si, 23.76; mol. wt., 236.5; R_D 0.3304. Found: C, 66.11; H, 10.22; Si, 23.73; mol. wt. (cryoscopic), 230; R_D 0.3321.

Grignard Reaction of Diphenyldichloromethane.—As outlined above, to 20.5 g. (0.844 g.-atom) of magnesium, 91.6 g. (0.844 mole) of trimethylchlorosilane, and 210 ml. of tetrahydrofuran was added dropwise a solution of 100 g. (0.422 mole) of diphenyldichloromethane in 70 ml. of tetrahydrofuran. The mixture was then refluxed 2 hr. with an additional 25 g. of trimethylchlorosilane. After hydrolysis, filtration (1.5 g. of magnesium left), neutralization with sodium bicarbonate, and washing, the solvents and hexamethyldisiloxane were distilled at atmospheric pressure. After the addition of 200 ml. of ethanol, 11 g. (15.7%) of tetraphenylethylene was filtered from the crude products. The tetraphenylethylene was recrystallized from toluene; m.p. 226°, reported¹⁷ m.p. 227°. The filtrate was fractionated at reduced pressure. In cuts distilling at 180° at 10 mm., 10 g. (7.6%) of bis-(trimethylsilyl)-diphenylmethane was isolated as a crystalline product. This material was recrystallized from absolute ethanol; m.p. 103°.

Anal. Calcd. for $\text{C}_{19}\text{H}_{28}\text{Si}_2$: C, 73.00; H, 9.03; Si, 17.97; mol. wt., 312.6. Found: C, 73.20; H, 9.05; Si, 18.11; mol. wt. (cryoscopic), 297.

Methanol was added to the fraction which distilled at 214-216° at 100 mm. and the solution cooled to the temperature of Dry Ice-acetone. From this was filtered 12 g. (11.8%) of trimethylsilyldiphenylmethane, which was recrystallized from absolute methanol; m.p. 73-74°, reported¹⁸ m.p. 74.5-75.5°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{Si}$: C, 79.93; H, 8.38; Si, 11.68; mol. wt., 240.4. Found: C, 79.82; H, 8.32; Si, 11.69; mol. wt. (cryoscopic), 225.

Grignard Reaction of 1,1,1-Trichloroethane.—To 54.7 g. (2.25 g.-atom) of magnesium, 244 g. (2.25 moles) of trimethylchlorosilane, and 560 ml. of tetrahydrofuran was added through a dropping funnel a solution of 100 g. (0.75 mole) of 1,1,1-trichloroethane in 93 ml. of tetrahydrofuran. The reaction mixture was treated as is outlined above. No products were isolated by fractional distillation at atmospheric pressure to a temperature of 242°. The residue was cooled in a bath of ice-water and 8 g. (4.3%) of tris-(trimethylsilyl)-methylmethane filtered off. This compound was recrystallized from absolute ethanol; m.p. 115°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{30}\text{Si}_3$: Si, 34.18; mol. wt., 246.6. Found: Si, 34.02; mol. wt. (cryoscopic), 243.

Grignard Reaction of Tetrabromoethylene.—A solution of 50 g. (0.145 mole) of tetrabromoethylene in 50 ml. of tetrahydrofuran was allowed to react with 14.1 g. (0.582 g.-atom) of magnesium suspended in 94.4 g. (0.87 mole) of trimethylchlorosilane and 150 ml. of tetrahydrofuran. The reaction mixture was treated as described above—4.5 g. of magnesium not consumed. Fractional distillation yielded 14.8 g. (60.2%) of bis-(trimethylsilyl)-acetylene, b.p. 135°, n_D^{25} 1.4240, reported¹⁹ n_D^{25} 1.4259, d_4^{25} 0.762, reported¹⁹ d_4^{25} 0.763.

Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{Si}_2$: Si, 32.98; R_D 0.3330. Found: Si, 32.27; R_D 0.3347.

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(13) R. L. Merker and M. J. Scott, to be published.

(14) L. Sommer, G. Goldberg, J. Gold and F. Whitmore, *J. Am. Chem. Soc.*, **69**, 980 (1947).

(15) R. Müller and G. Seitz, *Chem. Ber.*, **91**, 22 (1958).

(16) J. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

(17) "Handbook of Chemistry and Physics," C. D. Hodgeman, Ed., Chemical Rubber Publishing Co., Cleveland, O., 1956.

(18) C. H. Hauser and C. Hance, *J. Am. Chem. Soc.*, **73**, 5846 (1951).

(19) K. Frisch and R. Young, *ibid.*, **74**, 4853 (1952).