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THE REACTION OF ORGANOSILYLMETHYLMAGNESIUM CHLORIDES WITH SILVER HALIDES

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INTRODUCTION

The coupling of organic radicals by the action of heavy metal salts on Grignard reagents has been the subject of considerable study*. Some years ago, Gardner *et al.*$^{2-5}$ investigated the reaction of a number of Grignard reagents with silver halides and disclosed several important features of the reaction. Among them are the following. (*a*) The procedure can be used to couple not only aryl but also certain alkyl radicals. (*b*) The coupling of dissimilar organic radicals is effected when a mixture of two different kinds of Grignard reagents is allowed to react with silver bromide. (*c*) The coupling of radicals from the Grignard reagent(s) arises through the bi- or polymolecular homolytic decomposition of thermally unstable organosilver intermediate(s), in which no free radicals participate; no evidence of attack upon the solvent by radicals was obtained.

During the course of an investigation to prepare $R(CH_3)_2SiCH_2CH_2Si(CH_3)_2R$ compounds through the reaction of $R(CH_3)_2SiCH_2MgCl$ with silver bromide and with silver chloride, we have not only observed that the coupling occurs as expected but also encountered a novel feature of the reaction, *i.e.*, the formation of $R(CH_3)_2SiCH_2CH(CH_3)OC_2H_5$, which is believed to afford convincing evidence for attack upon the solvent by free radicals.

RESULTS AND DISCUSSION

Organosilicon-substituted methylmagnesium chloride $R(CH_3)_2SiCH_2MgCl$, where R is methyl and phenyl, were prepared in ethyl ether and allowed to react with silver bromide or silver chloride according to the procedure of Gardner *et al.* The reaction products (both in the reaction flask and in the trap immersed in Dry Ice/acetone mixture and connected to the flask *via* a reflux condenser) were analyzed by vapor phase chromatography (VPC); in some cases, all the products could be isolated by fractional distillation.

The results for reaction of $(CH_3)_3SiCH_2MgCl$ with silver bromide are listed in Table 1. The most important fact to note is that (2-ethoxypropyl)trimethylsilane was produced, along with tetramethylsilane and expected products, 1,2-bis(trimethylsilyl)ethane and (bromomethyl)trimethylsilane. The structure of (2-ethoxypropyl)trimethylsilane was deduced from the elemental analyses, molar refraction and proton magnetic resonance spectrum (Fig. 1).

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* For a pertinent reference see ref. 1.

TABLE 1

REACTION PRODUCTS FROM (TRIMETHYLSILYL)METHYLMAGNESIUM CHLORIDE AND SILVER BROMIDE

Compound	*Yield (%)*[a]
$(CH_3)_4Si$	*ca.* 10
$(CH_3)_3SiCH_2Br$	3.9
$(CH_3)_3SiCH_2CH_2Si(CH_3)_3$	41.9
$(CH_3)_3CH_2CH(CH_3)OC_2H_5$	17.8

[a] Based on the moles of the Grignard reagent employed, and determined by VPC. Traces of $(CH_3)_3SiOSi(CH_3)_3$ and $(CH_3)_3SiCH_2OH$ were also detected.

The formation of (2-ethoxypropyl)trimethylsilane, as far as we are aware, represents the first instance of coupling of a Grignard-reagent radical with a radical arising from the solvent molecule through hydrogen abstraction. Taking into account the proposed mechanisms for "abnormal" Grignard reactions[1] with silver halides by Bickley and Gardner[5] and for the formation of 1-ethoxyethyl benzoate from the decomposition of benzoyl peroxide in ethyl ether[6], possible mechanisms for the production of four major compounds listed in Table 1 may be described as follows.

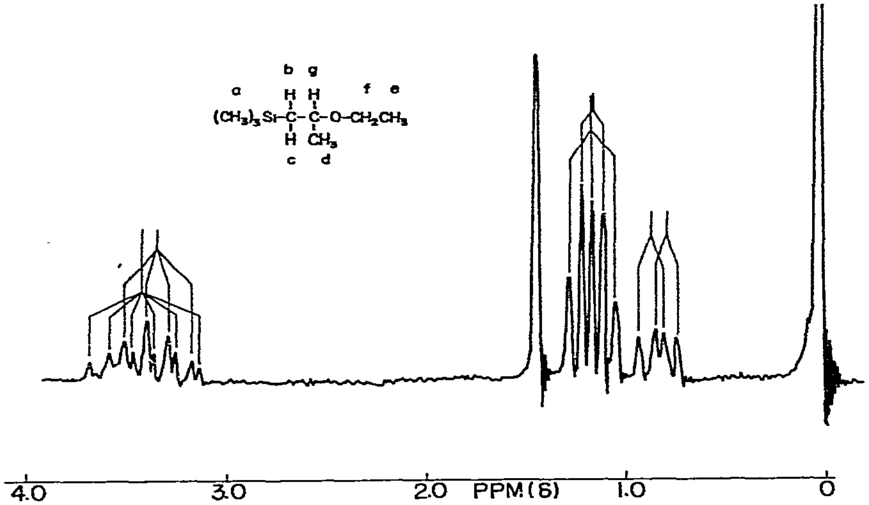

Fig. 1. Proton NMR spectrum of (2-ethoxypropyl)trimethylsilane. Chemical shifts in δ value and coupling constants in cps (given in parentheses) are: a, 0.01; b, 0.78 (6.5); c, 0.86 (7.0); d, 1.14 (5.8); e, 1.15 (6.8); f, 3.32 (6.8); and g, 3.40 (6.5).

$$(CH_3)_3SiCH_2MgCl + AgBr \rightarrow (CH_3)_3SiCH_2Ag + \tfrac{1}{2}\,MgCl_2 + \tfrac{1}{2}\,MgBr_2 \qquad (1)$$

$$2x\,(CH_3)_3SiCH_2Ag \rightarrow x\,(CH_3)_3SiCH_2CH_2Si(CH_3)_3 + 2x\,Ag \qquad (2)$$

$$(CH_3)_3SiCH_2^{\cdot} + Ag \qquad (3)$$

$$(CH_3)_3SiCH_2Ag \rightarrow (CH_3)_3SiCH_2^{\cdot} + Ag \qquad (3)$$

$$(CH_3)_3SiCH_2^{\cdot} + C_2H_5OC_2H_5 \rightarrow (CH_3)_4Si + CH_3\dot{C}HOC_2H_5 \qquad (4)$$

$$CH_3\dot{C}HOC_2H_5 + (CH_3)_3SiCH_2Ag \rightarrow (CH_3)_3SiCH_2CH(CH_3)OC_2H_5 + Ag \qquad (5)$$

$$(CH_3)_3SiCH_2Ag + MgBr_2 \rightarrow (CH_3)_3SiCH_2Br + Ag + \dot{M}gBr \qquad (6)$$

TABLE 2

REACTION PRODUCTS FROM (TRIMETHYLSILYL)METHYLMAGNESIUM CHLORIDE WITH SILVER CHLORIDE AND BROMIDE IN THE PRESENCE OF CUMENE

Compound	*Yield (%)*[a]	
	AgCl	*AgBr*
$(CH_3)_4Si$	11.3	[b]
$(CH_3)_3SiCH_2X$	6.1 (X = Cl)	7.5 (X = Br)
$(CH_3)_3SiCH_2CH_2Si(CH_3)_3$	17.2	24.7
Bi-α-cumyl	27.1	10.6

[a] See Table 1. [b] Not determined.

Table 2 lists the results of the reaction of $(CH_3)_3SiCH_2MgCl$ with silver chloride and with silver bromide in ether in the presence of cumene. It should be noted that in these cases the hydrogen abstraction by the $(CH_3)_3SiCH_2^{\cdot}$ radical took place from cumene instead of ethyl ether [no (2-ethoxypropyl)trimethylsilane could be detected] and that the formation of self-coupling product $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ occurred to approximately the same extent as in the absence of cumene. These results seem to be consistent with eqn. (2), which represents the coupling of Grignard reagent radicals as involving bi- or polymolecular decomposition of the organosilver intermediate, with no free radicals taking part.

TABLE 3

REACTION PRODUCTS FROM (PHENYLDIMETHYLSILYL)METHYLMAGNESIUM CHLORIDE WITH SILVER CHLORIDE AND BROMIDE

Compound	*Yield (%)*[a]	
	AgCl	*AgBr*
$(CH_3)_3SiC_6H_5$	20.0	24.7
$(C_6H_5)(CH_3)_2SiCH_2X$	4.0 (X = Cl)	10.0 (X = Br)
$(C_6H_5)(CH_3)_2SiCH_2CH(CH_3)OC_2H_5$	16.8	26.2
$[(C_6H_5)(CH_3)_2SiCH_2-]_2$	49.3	27.5

[a] See Table 1. A trace of $(C_6H_5)(CH_3)_2SiCH_2OH$ was also detected.

Table 3 lists the results obtained for the reaction of (phenyldimethylsilyl)methylmagnesium chloride with silver chloride and with silver bromide in ethyl ether. Here again, we observe the formation of considerable amounts of the product which resulted from a combination of the Grignard reagent radical and the radical arising from the solvent by hydrogen abstraction, namely, (2-ethoxypropyl)phenyldimethylsilane, in addition to the expected coupling product, 1,2-bis(phenyldimethylsilyl)ethane, and others. Structure proof for (2-ethoxypropyl)phenyldimethylsilane was afforded by its proton magnetic resonance spectrum which is reproduced in Fig. 2.

The mechanism for the formation of (bromomethyl)trimethylsilane from the reaction of (trimethylsilyl)methylmagnesium chloride with silver bromide (eqn. 6) is analogous to that described by Bickley and Gardner[5] for the formation of n-butyl iodide from the reaction of n-butylmagnesium bromide with magnesium iodide in the presence of silver bromide.

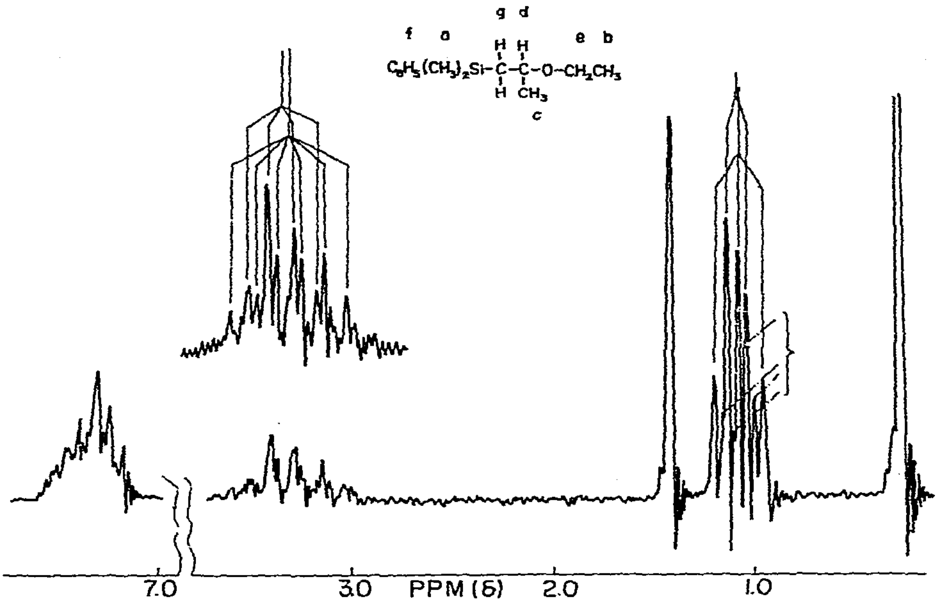

Fig. 2. Proton NMR spectrum of (2-ethoxypropyl)phenyldimethylsilane. Chemical shifts in δ value and coupling constants in cps (given in parentheses) are: a, 0.30; b, 1.10 (7.0); c, 1.11 (5.8); d, 3.35 (7.0); e, 3.38 (7.0); f, 7.30; and g, 1.10.

EXPERIMENTAL

Proton magnetic resonance spectra were obtained by Dr. K. Tori, Shionogi Research Laboratory, in carbon tetrachloride solutions containing cyclohexane as an internal reference. (Trimethylsilyl)methyl- and (phenyldimethylsilyl)methylmagnesium chlorides were prepared in ethyl ether in the usual way from the corresponding (organosilyl)methyl chlorides in 96–98 and 93–96% yield, respectively (determined by titrating the acid hydrolyzate).

Reaction of $(CH_3)_3SiCH_2MgCl$ with silver bromide

In a 500-ml three-necked flask equipped with a stirrer, a dropping funnel and a reflux condenser leading to a Dry Ice/acetone trap there was placed a mixture of 75.2 g (0.40 mole) of freshly prepared and dried silver bromide suspended in 200 ml of absolute ether. To this mixture was added dropwise 200 ml of 2 *M* ethereal solution of $(CH_3)_3SiCH_2MgCl$ with stirring and cooling in an ice bath over a 1-h period. After being stirred for an additional 1 h at 0°, the reaction mixture was gradually brought to room temperature and then heated to reflux for 12 h. VPC analysis of the liquid collected in the Dry Ice/acetone trap revealed that *ca.* 2.5 g of tetramethylsilane was contained. The contents in the flask were hydrolyzed with 200 ml of 1 *N* hydrochloric acid. An insoluble solid mass was separated by filtration. The organic layer and ether extracts from the aqueous phase were combined, washed with sodium bicarbonate solution and dried over calcium chloride. After removal of the solvent ether, the residual liquid (33.5 g) was analyzed by VPC (Silicone-DC 550, 2.5 m, 125°). The results are given in Table 1. Fractional distillation of it through a spinningband coulumn rated at about 30 theoretical plates gave three fractions: (*1*) 2.6 g of (bromomethyl)trimethylsilane, b.p. 115.5–117.5°, the retention time in the vapor phase chromatograph and IR spectrum being superimposable with those of an authentic sample, b.p. 115.5° (reported[7] b.p. 116°), prepared from the action of methylmagnesium bromide on (bromomethyl)dimethylchlorosilane[8]; (*2*) 11.4 g of (2-ethoxypropyl)trimethylsilane; b.p. 143°, n_D^{20} 1.4110, d_4^{20} 0.7832, MR_D 50.83 (calcd. 50.57), its NMR spectrum being illustrated in Fig. 1 (Found: C, 59.81; H, 12.65. $C_8H_{20}OSi$ calcd.: C, 59.93; H, 12.57%.); and (*3*) 14.6 g of 1,2-bis(trimethylsilyl)ethane, b.p. 150°, n_D^{20} 1.4204, completely identical with an authentic sample (reported[7] b.p. 150–151°, n_D^{20} 1.4204) in every respect.

Treatment of (2-ethoxypropyl)trimethylsilane with cold concentrated sulfuric acid followed by hydrolysis converted it quantitatively into hexamethyldisiloxane, b.p. 100°. Therefore, separation of 1,2-bis(trimethylsilyl)ethane by fractionation was facilitated considerably after this treatment.

The insoluble mass that resulted upon hydrolysis of the reaction mixture was treated with concentrated nitric acid to give 11.5 g (15.2%) of unchanged silver bromide and a solution, from which 62.5 g (82.8%) of silver bromide was produced.

Additional two runs carried out under the same conditions as above gave, respectively, $(CH_3)_3SiCH_2Br$ 4.3 and 5.9 g, $(CH_3)_3SiCH_2CH(CH_3)OC_2H_5$ 8.5 and 13.5 g, and $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$, 15.5 and 13.3 g.

Reaction of $(CH_3)_3SiCH_2MgCl$ with silver chloride and with silver bromide in the presence of cumene

To 100 ml of 2 *M* ethereal solution of $(CH_3)_3SiCH_2MgCl$ was added 120 g of freshly distilled cumene. About 50 ml of the solvent ether was removed from the mixture by distillation. To the residue was added 29 g (0.2 mole) of freshly prepared silver chloride at 0°, and afterwards the mixture was heated at 100° for 6 h. After a work-up in a similar way to that described above, the reaction products were analyzed by VPC. By distillation 3.5 g of bi-α-cumyl, m.p. 117–118° (reported[9] 118–119°), was isolated. Unchanged cumene weighed 107 g. The reaction with silver bromide (38 g, 0.2 mole) used in place of silver chloride was carried out in essentially the same way as above, and the product was analyzed by VPC. The results are given in Table 2.

Reaction of $(C_6H_5)(CH_3)_2SiCH_2MgCl$ with silver chloride and with silver bromide

In substantially the same manner as described above, 22 g (0.15 mole) of silver chloride suspended in 150 ml of ether was allowed to react with 100 ml of 1.5 *M* ethereal solution of $(C_6H_5)(CH_3)_2SiCH_2MgCl$. VPC analysis of the reaction product gave the results listed in Table 3. By fractional distillation there were isolated 4.5 g of phenyltrimethylsilane, b.p. 72.5°/31 mm, 1.1 g of (chloromethyl)phenyldimethylsilane, b.p. 120°/31 mm, 5.6 g of (2-ethoxypropyl)phenyldimethylsilane, b.p. 135°/31 mm, n_D^{20} 1.4954, d_4^{20} 0.9233, MR_D 70.29 (calcd. 70.46), its NMR spectrum being given in Fig. 2 (Found: C, 70.21; H, 9.78. $C_{13}H_{22}OSi$ calcd.: C, 70.21; H, 9.97%.), and 11.0 g of 1,2-bis(phenyldimethylsilyl)ethane, m.p. 60° (Found: C, 71.65; H, 8.74. $C_{18}H_{26}Si_2$ calcd.: C, 72.41; H, 8.78%).

In the product from the analogous reaction with silver bromide used in place of silver chloride, (bromomethyl)phenyldimethylsilane was detected by VPC in addition to phenyltrimethylsilane, (2-ethoxypropyl)phenyldimethylsilane and 1,2-

bis(phenyldimethylsilyl)ethane (see Table 3). The authentic sample of (bromomethyl)phenyldimethylsilane for VPC, b.p. 113.0–113.5°/16 mm, n_D^{20} 1.5426, d_4^{20} 1.2490 (Found: C, 47.41; H, 5.43. $C_9H_{13}BrSi$ calcd.: C, 47.16; H, 5.72%), was prepared by the action of phenylmagnesium bromide on (bromomethyl)dimethylchlorosilane[8].

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SUMMARY

The reaction of two (organosilyl)methylmagnesium chlorides, $R(CH_3)_2SiCH_2MgCl$ ($R = CH_3$ and C_6H_5), with silver chloride and with silver bromide in diethyl ether has been studied. It has been found that the reaction proceeds with the formation of significant amounts of compounds of the formula $R(CH_3)_2SiCH_2CH(CH_3)OC_2H_5$ in addition to the expected coupling products $[R(CH_3)_2SiCH_2-]_2$ and others. This result shows that the attack of free radicals arising from the Grignard reagents upon the solvent takes place concurrently with the self-coupling reaction.

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