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VINYLMETALLOIDS *

I **. COUPLING REACTIONS OF GROUP IV METALLOIDAL HALIDES WITH MAGNESIUM IN TETRAHYDROFURAN

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Summary

The reaction of vinyl bromide with a mixture of magnesium and either dichlorodimethylsilane or dichlorodiethylgermane in tetrahydrofuran was found to give the corresponding coupled products: 1,1,2,2-tetramethyl-1,2-divinyldisilane (II) and 1,1,2,2-tetraethyl-1,2-divinyldigermane (XI), respectively, in ca. 30% yield. Other vinyl bromides also were investigated. The reaction of dichlorodimethylsilane with vinyl bromide/magnesium appears to proceed via chloro(dimethyl)vinylsilane (III) which was found to react directly with magnesium in THF to give II in 53% yield. It is shown that the reaction of a vinylsilyl halide with magnesium, if carried out in the presence of chlorotrimethylsilane or chlorotriethylgermane, leads to pentamethylvinyldisilane (VI) or triethyl(vinyldimethylsilyl)germane (V) in yields of 67 and 43%, respectively. However, the reaction of III and chlorotrimethylgermane with magnesium in THF gives a 40/60 mixture of trimethyl(vinyldimethylsilyl)germane (VII) and hexamethyldigermane (VIII). Under similar conditions, chlorotrimethylgermane was found to give VIII directly with magnesium in THF in 48% yield while chlorotriethylgermane is inert to Mg. These results are discussed in terms of the formation of metalloidal—magnesium bonds.

Introduction

In connection with our studies [2] on the hydroboration/oxidation of unsaturated derivatives of silicon, germanium and tin, it was necessary to prepare

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* Dedicated to Prof. H.C. Brown on the occasion of his 66th birthday.

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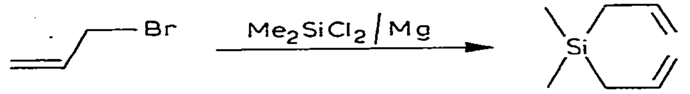
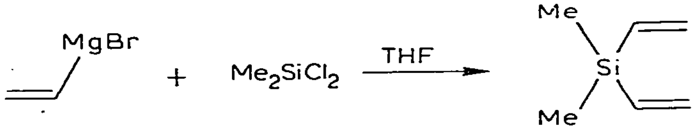
several divinyl compounds. The Grignard method using pre-formation of the vinylmagnesium halide in THF, followed by addition of the appropriate diorganometalloidal dihalide, provides a convenient route to such systems [3]. An alternative procedure might involve the trapping of the nascent organomagnesium compound by the metalloidal dihalide. Such a procedure, known as the Barbier method, has enjoyed considerable success for many organometallic reactions [4], especially for allylsilanes [5]. For example, diallyldimethylsilane has been prepared in 94% yield from the insitu trapping of allylmagnesium bromide by dichlorodimethylsilane in THF [6] *. This method depends on the fact that silyl halides, except for arylsilyl halides, are unreactive toward magnesium.



Since no information was available for the Barbier procedure in the vinylsilyl bromide case, we undertook a study of the reaction of vinyl bromides with dichlorodimethylsilane in the presence of magnesium using tetrahydrofuran solvent **.

Results and discussion

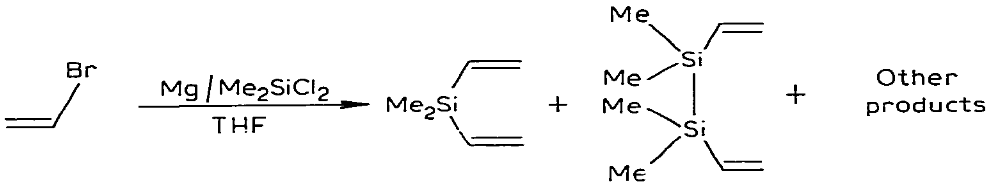
For comparison purposes, dimethyldivinylsilane (I) was prepared in 60% yield from vinylmagnesium bromide in THF and dichlorodimethylsilane.



(1)

(I)

However, in the Barbier procedure with Me_2SiCl_2 present in the magnesium/THF mixture, a very low yield (4%) of I was obtained; the major product (18%) was found to be 1,1,2,2-tetramethyl-1,2-divinyldisilane (II). A GC trace of the residue revealed the presence of at least 20 high-boiling products.



(2)

(I)

(II)

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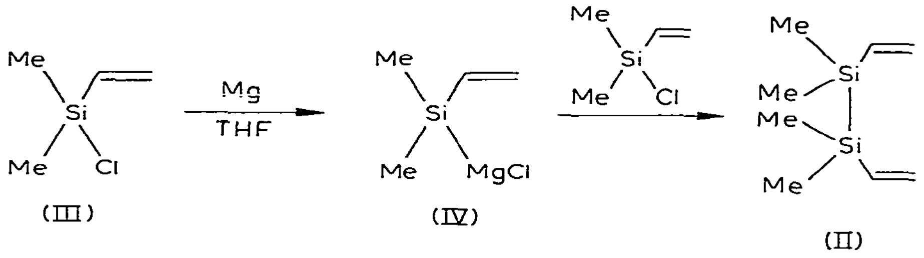
* Under conditions (rapid addition at reflux temperature) where allyl bromide is quantitatively converted to biallyl in the absence of a silicon halide, allyltrimethylsilane is formed in 98% (GC) yield with one equivalent of chlorotrimethylsilane present in the magnesium/THF mixture.

** After this work was completed, we became aware of a similar study by Mironov et al. [7] using vinyl chloride with Mg and III with Mg. However, these authors employed 1,2-dibromoethane as an initiator.

The formation of II as the major product was somewhat surprising in light of the fact that only arylsilyl chlorides had been found to undergo coupling reactions with magnesium [8,9].

Mironov and coworkers [7] showed that the reaction of vinyl chloride with magnesium, initiated by 1,2-dibromoethane, in the presence of Me_2SiCl_2 leads to II. The reaction probably is sped up by the presence of $MgBr_2$. In fact, in the presence of magnesium bromide, Me_2SiCl_2 was found to give an oxasilacyclohexane (from ring-opening of solvent) with magnesium in THF, without polysilane formation [11]. While germanium halides normally give considerable amounts of digermane products on reaction with vinylmagnesium bromide in THF [3b,3c,10], addition of excess vinylmagnesium bromide to dichlorodimethylsilane (eq. 1) did not lead to the formation of II. Addition of one equivalent of vinylmagnesium bromide to the Me_2SiCl_2/Mg/THF mixture followed by heating at reflux temperature for 24 h resulted in an 8% yield of II. Finally, when one equivalent (only) of vinyl bromide was added to the Me_2SiCl_2/Mg/THF mixture followed by heating at reflux temperature for 24 h, the yield of II was increased to 30%. These results suggested that an initially formed chloro(dimethyl)vinylsilane (III) might undergo direct reaction with magnesium in THF leading to II via a "silyl Grignard" [7,12] species such as IV.



(3)

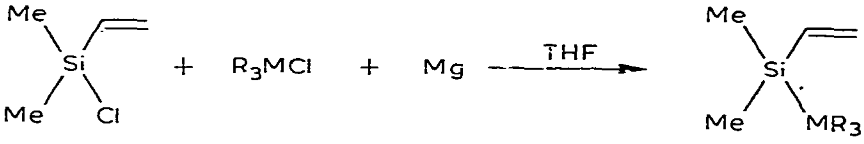
To test this hypothesis we synthesized III [13] and heated it at reflux temperature for 48 h in THF with excess magnesium. Like Mironov [7] who in the presence of dibromoethane obtained II, we isolated disilane II in good yield. In our case no initiator was added to the mixture and when high-purity magnesium was used a similar yield of II was realized even though the reaction time was cut to 24 h. Hence, it seems unlikely that trace amounts of metallic impurities in the magnesium are responsible for the formation of II.

In order to gain support for the intermediacy of a species such as IV, several trapping reagents were chosen and their behavior toward magnesium was examined. Both chlorotrimethylsilane and chlorotriethylgermane have been reported not to undergo dimetallane formation on treatment with magnesium in THF at reflux temperature [8,9,10].

$$R_3MCl \xrightarrow[THF]{Mg} R_3M{-}MR_3 \qquad (4)$$

(M = Si, R = Me; M = Ge, R = Et)

Indeed, we confirmed that under our conditions, neither compound forms the coupled product even after three days at reflux temperature. However, in the presence of III, chlorotrimethylsilane gives pentamethyl(vinyl)disilane (VI) in 67% yield [7], and chlorotriethylgermane gives triethyl(vinyldimethylsilyl)germane (V) in 43% yield.



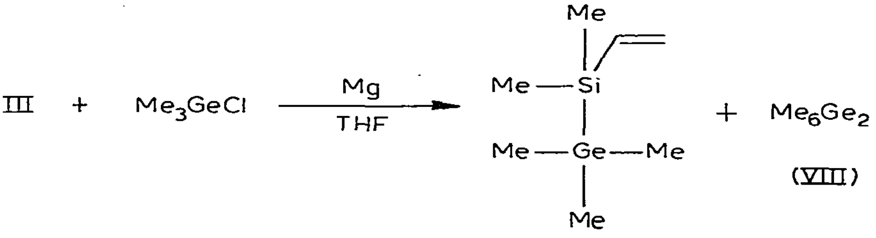
(5)

(III)

(VI, MR = $SiMe_3$;
V, MR = $GeEt_3$)

These findings are taken as strong evidence for the reaction of III with magnesium leading to a vinylsilylmagnesium species such as IV with subsequent reaction with a metalloidal halide leading to dimetallanes such as II, V, and VI.

A particularly unexpected result was obtained when chlorotrimethylgermane was used to trap IV. Using a 1/2 mole ratio of III to this germyl chloride, a 40/60 mixture of trimethyl(vinyldimethylsilyl)germane (VII) and hexamethyldigermane (VIII) was obtained (eq. 6). Chlorotrimethylgermane reportedly does



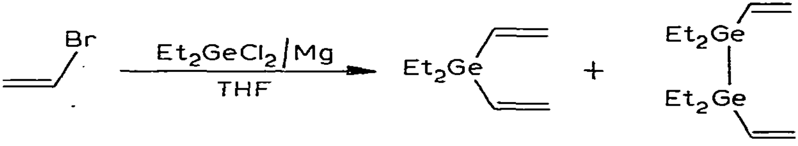
(6)

(VIII)

(VII)

not undergo coupling reactions with magnesium in THF [10] or in other ether solvents [3b]. However, our conditions were evidently more severe and THF is reported to be the solvent of choice for such coupling reactions [8,9]. Indeed, when chlorotrimethylgermane (unlike the triethyl homolog) was heated at reflux temperature with magnesium in THF for 24 h, VIII was obtained in 48% yield.

The Barbier conditions were examined for several other systems as well. Whereas 2-bromopropene gave a low yield (5%) of 1,1,2,2-tetramethyl-1,2-di-2-propenyldisilane (IX), no comparable disilane products were obtained from α-bromostyrene or trimethyl(α-bromovinyl)silane under the conditions illustrated in eq. 2 (using one equivalent of the vinyl bromide). However, treatment of vinyl bromide with a dichlorodiethylgermane/magnesium/THF mixture does give the digermane XI in 30% yield, together with the divinylated product X (8%).



(7)

(X)

(XI)

Surprisingly, the tetramethyl analog of XI could not be prepared by a similar procedure using dichlorodimethylgermane and this chloride is stable to magnesium in refluxing THF. While the origin of disilane II appears to be the reaction of the vinylsilyl chloride III with magnesium, a similar pathway need not necessarily be involved in the formation of XI since the occurrence of digermanes has been shown to be due to several different pathways [14].

Experimental

All glassware was dried for at least 4 h at 110° C, assembled hot, and allowed to cool under a nitrogen (or argon) purge prior to use in these reactions. An inert atmosphere was maintained throughout the reactions. Magnesium (Fischer or Alfa-High Purity) was used without pretreatment as was vinyl bromide (Aldrich). The 2-bromopropene was distilled from calcium hydride prior to use as was dichlorodimethylsilane and chloromethylsilane (Aldrich). The halogermanes (Laramie Chemical Company) were found to be of consistently high purity and were used without purification. THF was freshly distilled from lithium aluminum hydride prior to use. All spectra were recorded under standard conditions using commercial instrumentation (i.e., Perkin—Elmer 457, Varian EM360, Varian MAT CH5). The mass spectral data given for the germanium compounds reflect only uncorrected values for the ^{74}Ge isotope. Spectra and analytical data are given in Table 1.

TABLE 1

SYNTHESIS AND SPECTRA OF ORGANOSILANES AND GERMANES

Compound	Yield (%)	NMR in CCl_4 (δ, ppm)	*m/e* (% abundance) [a]	Analysis (Found (calcd.) (%))	
				C	H
II [b]	53	0.11 (s, 12); 5.12 (m, 6)	170 (3); 59 (100)	56.62 (56.39)	10.73 (10.73)
III	[c]	0.57 (s, 6); 6.10 (m, 3)		39.98 (39.82)	7.57 (7.52)
V	43	0.18 (s, 6); 0.5—1.2 (m, 15); 5.4—6.6 (m, 3)	246 (15); 161 (100)	49.27 (49.03)	9.88 (9.86)
VI	67	0.0 (s, 9); 0.05 (s, 6); 5.97 (m, 3)	158 (29); 73 (100)	53.03 (53.08)	11.45 (11.45)
VII	[d]	0.27 (s, 6); 0.32 (s, 9); 6.05 (m, 3)	204 (39) [e]; 85 (100)		
VIII [f]	[d]	0.26 (s)	206 (23); 119 (100) [e]	see ref. 17	
IX [g]	5	0.13 (s, 12); 1.8 (t, *J* 4.5 and 1.3 Hz); 5.4 (m, 2)	198 (5); 73 (100)	60.69 (60.52)	11.19 (11.17)
XI	32	1.02 (m, 10); 5.3—6.6 (m, 6)	316 (2); 103 (100) [e]	45.70 (45.68)	8.30 (8.31)

[a] Only parent and base peaks are given. [b] B.p. 152°C/744 Torr, prepared from III and Mg in THF, reflux 2 days, or from (30%). [c] Prepared according to ref. 13, b.p. 81—83°C/740 Torr. [d] Relative ratio by NMR. [e] Isotopic distribution indicates Ge species. [f] Also obtained in 48% yield from Me_3GeCl and Mg. [g] From 2-bromopropene, Mg and Me_2SiCl_2.

Dimethyldivinylsilane (I)

To vinylmagnesium bromide in an ice bath (prepared from 2.0 g-atom of Mg and 2.0 mol of vinyl bromide in 800 ml of refluxing THF) was added dichlorodimethylsilane (121 g, 1.00 mol). The solution was heated at reflux for 1 h and the mixture allowed to stand at room temperature for 12 h. The solid mass was heated to give a fluid mixture which was poured onto ice (ca. 1 kg). Pentane (500 ml) was added and, after separation of the aqueous layer, the resulting organic material was washed with water (2 × 200 ml), dried over $MgSO_4$ and distilled using a Nester—Faust lab-size spinning band column to give 67 g (60%) of I, b.p. 78—79°C/740 Torr (lit [15] 80.8—81.6°C/760 Torr).

1,1,2,2-Tetramethyl-1,2-divinyldisilane (II)

A one liter round-bottomed flask, equipped with addition funnel and dry-ice condensor was charged with magnesium (24.3 g, 1.00 g-atom), dichlorodimethylsilane (58.5 g, 0.50 mol) and THF (300 ml) and the resulting mixture was heated to reflux. Vinyl bromide (54.4 g, 0.50 mol) in THF (100 ml) was added dropwise (reaction begins immediately) and the mixture was heated at reflux temperature for 2 h. The dry-ice condenser was replaced with a water condenser and the stirred mixture was heated at reflux temperature for 24 h (approximately 6 g of magnesium remains unreacted). The mixture was poured onto ice, separated, dried, filtered and distilled to give 10 g (30%) of II b.p. 140°C/630 Torr (lit. [9] 69.5°C/24 Torr).

Triethyl(vinyldimethylsilyl)germane (V)

Into a 50 ml round-bottomed flask was placed magnesium (0.60 g, 0.025 g-atom), III (3.0 g, 0.025 mol), chlorotriethylgermane (5.0 g, 0.026 mol) and THF (25 ml). The stirred mixture was refluxed for one week. After quenching with saturated ammonium chloride, the organic layer was dried and distilled to give 2.6 g (43%) of V (b.p. 102—105°C/16 Torr)).

Pentamethylvinyldisilane (VI)

Into a 250 ml round-bottomed flask was placed magnesium (2.4 g, 0.10 g-atom), III (12.1 g, 0.10 mol), chlorotrimethylsilane (54.3 g, 0.50 mol), and THF (75 ml). The stirred mixture was refluxed for one week. After the usual work-up (see V), 10.5 g (67%) of VI was obtained (b.p. 132°C/740 Torr) (lit. [16] 132°C). The use of 2 equivalents of chlorotrimethylsilane gave ~14% of II in addition to VI.

Trimethyl(vinyldimethylsilyl)germane (VII) and hexamethyldigermane (VIII)

Into a 100 ml round-bottomed flask was placed magnesium (1.2 g, 0.050 g-atom), III (6.1 g, 0.050 mol), chlorotrimethylgermane (15.4 g, 0.10 mol) and THF (35 ml). The stirred mixture was refluxed for two days. After the usual work-up (see V), 4.5 g (b.p. 130—136°C/740 Torr) was obtained which was found to be a mixture of VII and VIII, separated by preparative GC (column 60°C) (9′ × 3/8″, 10% QF-1).

Hexamethyldigermane (VIII)

Into a 100 ml round-bottomed flask was placed magnesium (0.40 g, 0.016

g-atom), chlorotrimethylgermane (5.0 g, 0.033 mol) and THF (20 ml). The stirred mixture was refluxed for 20 h. After the usual work-up (see V), 1.85 g (48%) of VIII (b.p. 135°C/740 Torr) (lit. [17] 137°C/772 Torr) was obtained.

1,1,2,2-Tetramethyl-1,2-di-2-propenylsilane (IX)

1,1,2,2-Tetramethyl-1,2-di-2-propenylsilane was prepared by the procedure used for II (except that the dry-ice condenser was replaced by a normal reflux condenser). From magnesium (3.7 g, 0.15 g-atom), dichlorodimethylsilane (12.9 g, 0.10 mol), 2-bromopropene (12.1 g, 0.10 mol), and THF (40 ml) was obtained 1.5 g (b.p. 90—120°C/16 Torr) of impure IX. This fraction was collected (140°C) by preparative GC to obtain 0.50 g (5%) of IX (lit. [18] 97—98°C/32 Torr).

1,1,2,2-Tetraethyl-1,2-divinyldigermane (XI)

From magnesium (0.90 g, 0.037 mol), dichlorodiethyldigermane (5.0 g, 0.025 mol) in THF (50 ml), and vinyl bromide (2.7 g, 0.025 mol) in THF (5 ml) (as for II) there was obtained 0.38 g (8%) diethyldivinylgermane (X) (b.p. 48—50°C/15 Torr) [3b] and 1.25 g (32%) of XI (b.p. 122°C/15 Torr).

Acknowledgement

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