

PRELIMINARY COMMUNICATION

SYNTHESIS OF CATENATED ETHYLGERMANIUM COMPOUNDS BY GRIGNARD REACTION

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The reaction of a Grignard reagent with germanium tetrachloride has long been used for the preparation of tetrasubstituted germanes¹. In reactions of this type derivatives of digermane are also obtained, and in the presence of excess magnesium, such derivatives are major products of the reaction². Digermanes also result from the similar reaction of germanium tetrachloride with alkyllithium reagents^{3,4}. Derivatives of higher germanes have been found on separation of the products of the Grignard reaction using gas chromatography⁴. When the phenyl Grignard reagent is used, the maximum yield of tetraphenylgermane is obtained if the reaction is carried out in refluxing toluene, while hexaphenyldigermane is the major product in a mixture of toluene and diethyl ether, refluxing at a lower temperature⁵. This suggests that the mechanism of formation of the Ge-Ge bond may be influenced by the reaction temperature, the choice of solvent, or both.

A series of reactions has been carried out to determine the effect of these variables on the formation of catenated germanes in the reaction between ethyl magnesium bromide and germanium tetrachloride. Unless otherwise noted, reactions were carried out by addition of a solution of germanium tetrachloride in the desired solvent to a solution of ethylmagnesium bromide in the same solvent, in the presence of a suspension of magnesium powder, the mole ratio $\text{EtMgBr}/\text{GeCl}_4$ being 5:1. Addition was carried out slowly so as to allow a constant reaction temperature to be maintained, using either an ice bath or constant temperature bath. The reaction was allowed to continue for one hour after addition was complete, then quenched with acetic acid. The reaction mixture was washed with sodium carbonate solution, and most of the solvent removed by a preliminary distillation before samples were analyzed on the chromatograph. An F&M 720 Dual Column Programmed Temperature Gas Chromatograph was used with a 3 ft column consisting of 3% Analabs Silicone SE 52 on Anakrom ABS. The temperature was programmed from 75 to 300° at 20°/min. The results are summarized in Table 1.

Those reactions marked "mixed addition" in the table were carried out by addition of a mixture of ethyl bromide and germanium tetrachloride to a suspension of magnesium in the desired solvent. One reaction was carried out in the absence of excess

TABLE I

RELATIVE YIELDS OF PRODUCTS FROM GRIGNARD REACTIONS

Relative yields (mole percent) estimated from areas of peaks on gas chromatographic analysis. Total yield of products obtained on chromatograph taken as 100%. Retention temperatures are on programmed temperature from 75 to 300° at 20°/min with 40 cc/min carrier gas flow (helium).

Solvent, reaction temperature and conditions	Et ₃ GeH	Et ₄ Ge	Grignard by-product	Et ₃ GeCl	Grignard by-product	Et ₆ Ge ₂	Grignard by-product	Et ₈ Ge ₃	Et ₁₀ Ge ₄ (?)
	99°	120°	134°	141°	187°	194°	201°	249°	280°
Ether 0-3°	—	94.8	0.13	3.46	1.18	0.76	—	—	—
Ether 20-24°	3.72	91.5	1.01	2.37	0.75	0.81	0.08	0.02	—
Ether 35°	0.80	92.6	1.68	0.49	0.98	2.19	0.57	0.82	—
Ether 35° (no Mg)	0.05	91.2	2.07	3.62	1.84	0.99	—	—	—
Ether 35° (blank)	—	—	63.2	—	29.1	—	2.8	—	—
Ether 35° (mixed addition)	4.06	71.0	—	10.6	—	9.66	0.97	2.90	1.11
Toluene 35°	<i>a</i>	91.8	0.78	3.90	0.78	1.95	0.78	trace	—
Toluene 90-94°	<i>a</i>	79.8	1.71	5.58	2.57	4.72	2.14	0.17	2.57
THF 35°	—	15.6	2.72	1.57	4.5	43.2	0.22	21.6	9.69
THF 35° (mixed addition)	0.52	46.55	—	7.01	0.52	29.3	—	12.0	4.62
THF 67° (mixed addition)	0.60	57.4	—	—	1.4	24.5	—	10.4	4.3

a Peak blocked by solvent peak.

magnesium, and one blank reaction was run without the addition of germanium tetrachloride, but with all other steps in the procedure and work-up of products unchanged.

Tetraethylgermane, hexaethyldigermane, and octaethyltrigermane were separated and purified by fractional distillation from the combined products of several reactions. The physical constants and infrared spectra of tetraethylgermane^{1,6} and hexaethyldigermane⁷ thus obtained agreed with literature values. Octaethyltrigermane had recently been prepared by reaction of triethylgermyl potassium with chloropentahyldigermane⁸ and by the Grignard reaction⁹. We were able to obtain this product in only 92% purity as determined by gas-chromatographic analysis; however, the refractive index (n_D^{28} 1.5312; literature n_D^{20} 1.5350, 1.5321)^{8,9} and boiling points (172°/2mm; literature 133–137°/0.05, 152–156°/0.08)^{9,8} were in agreement with those reported. Analysis for C, H, and Ge agree with the values calculated for a mixture of 92% Et₈Ge₃ and 8% Et₆Ge₂. (Found: C, 42.52, 43.39; H, 9.10, 9.15; Ge, 47.38, 47.50%; calcd.: C, 42.89; H, 9.01; Ge, 47.16%).

Identification of triethylgermane and chlorotriethylgermane in the products was made by comparison of retention temperatures with those of authentic samples of these compounds. Triethylgermane was prepared by reduction of bromotriethylgermane using LiAlH₄¹⁰, chlorotriethylgermane by the redistribution reaction of tetraethylgermane with germanium tetrachloride in the presence of aluminum trichloride at 154°¹¹.

The products with retention temperatures of 134, 187, and 201° have not been identified, but since they were also obtained in the reaction without germanium tetrachloride, they cannot be organogermanium compounds.

The product with retention temperature of 280° has not been isolated in pure form, but considering the trend in retention temperatures from tetraethylgermane to octaethyltrigermane, is almost certainly a tetragermane.

Comparison of the relative yields from reactions in ether at different temperatures indicates that increasing temperature favors formation of the digermane. Parallel to this is a decrease in the yield of chlorotriethylgermane. The yield of triethylgermane shows an increase from 0 to 20°, but a decrease from 20 to 35°. This is in agreement with the mechanism proposed by Glockling and Hooton².



Triethylgermane will arise from the hydrolysis of triethylgermylmagnesium halide during the work-up of the products. A similar intermediate has been proposed for the formation of hexaphenyldisilane when chlorotriphenylsilane reacts with Grignard reagents in tetrahydrofuran¹².

Our results indicate that reaction (1) takes place at 20° (the decrease in the yield of Et₃GeCl parallels the increase in Et₃GeH) but that a higher temperature (in this case 35°) is necessary for an appreciable proportion of the second reaction to occur (the decrease in yield of Et₃GeH and the corresponding increasing in Et₆Ge₂).

Further confirmation of Glockling and Hooton's results has been obtained by using Grignard reagent filtered to remove magnesium. Here the yield of Et₃GeCl in-

creases, corresponding to a decrease in the yields of Et_3GeH and Et_6Ge_2 . However the decrease in the yield of Et_6Ge_2 is not as great as that of Et_3GeH , suggesting that an alternative mechanism for the formation of the digermane without formation of Et_3GeMgX may also occur.

The reaction in toluene at 35° gives results comparable to those in refluxing ether. Reaction in refluxing toluene ($90\text{--}104^\circ$) shows further increase in the yield of digermane as well as the appearance of the tetragermane. This suggests that the mechanism of coupling in the two solvents is the same, and is increasingly favored, in competition with formation of tetraethylgermane, with increasing temperature.

A considerable increase in the yield of catenated germanes is obtained if the reaction is carried out by addition of a mixture of ethyl bromide and germanium tetrachloride to a magnesium suspension in ether ("mixed addition"). This might be taken as support for a mechanism involving reduction of GeCl_4 by reaction with the Grignard reagent¹³ or magnesium¹⁴, were it not for the parallel increase in the yields of Et_3GeCl and Et_3GeH . While such mechanisms cannot be ruled out, it seems more likely that the explanation for the lower yield of Et_4Ge as compared with other products of the reaction, is that formation of Et_4Ge requires a large excess of Grignard reagent over GeCl_4 , a condition not obtained during the course of a mixed addition. On the other hand the excess of magnesium required for formation of Et_3GeMgX is present.

The results in tetrahydrofuran (THF) are different from those obtained in ether or toluene. At 35° hexaethyldigermane is now the principle product of the reaction, exceeding the yield of tetraethylgermane by a factor of three, and the proportion of higher germanes is correspondingly increased. In THF solution, both mixed addition and increased temperature result in a decreased yield of catenated germanes rather than an increase.

It would seem that this difference in results indicates that the mechanism of formation of the Ge—Ge bond in THF solution differs from that in ether and toluene. However Glockling and Hooton² have reported that the reaction in THF solution does not give digermane in the absence of magnesium, but instead always gives tetra-substituted germanes in good yield. This is true even in the case of tetrabenzylgermane. Since steric hinderance by the bulky benzyl group makes this particular case more than ordinarily unfavorable for formation of R_4Ge in competition with R_6Ge_2 , it is most likely, then, that even in THF solution a mechanism involving reductive coupling of R_3GeCl with excess magnesium is responsible for the greater part of the formation of catenated compounds. It is possible that reaction intermediates leading to catenation are more stabilized by the solvent in THF than in ether or toluene.

Further study is planned on the effect of other solvents and on whether the above observations hold true for other organic groups than ethyl.

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