

SYNTHESIS OF DIMETHYL VINYLHALOGERMANES AND
RELATED COMPOUNDS

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Relatively few vinylhalo germanes have been reported (1). In connection with other work, we desired a source of dimethylvinylhalo germanes. Attempts to cleave a vinyl group from dimethyldivinylgermane with bromine led to addition products as discovered by Mazerolles and Lesbre (2). In contrast, halogens readily cleaved a vinyl group from dimethyldivinyltin (3).

This report describes several routes to new dimethylvinylhalo germanes, and also includes much improved syntheses of several previously reported compounds.

Experimental

Tetramethylgermane. Previously reported syntheses use relatively expensive n-butyl ether and give yields of ca. 70% (4). In this modification, butyl ether is largely replaced with xylene and yields are in excess of 90%. Technical n-butyl ether (300 ml) was placed in a 3 l., 3-neck flask equipped with a dry ice condenser, stirrer, and a 250 ml equal pressure dropping funnel. After flushing with N₂, 136 g (5.6 mole) of Mg turnings were added followed by 3 ml of methyl iodide. After the vigorous reaction had started, 1.5 l. of xylene, was added and 793 g (5.59 mole) of methyl iodide (or 530 g of methyl bromide) added at a rate to maintain gentle reflux. After addition of iodide was complete, the mixture was stirred for one half hr., then cooled in an ice

bath. Germanium tetrachloride (200 g, 0.93 mole) in 150 ml of xylene was added at a rate to give a gentle reflux. After all the germanium chloride was added, the dry ice condenser was replaced with a Friedrichs condenser and the mixture refluxed overnight. The mixture was then distilled rapidly up to a temperature of 139°. The distillate is redistilled to give product, bp 44-46 (115 g, 93%). The nmr spectrum gives a singlet at $\delta = 0.12$ ppm with no visible contaminants.

Dimethyldichlorogermane. Yields in the method of Sakurai et. al. (5) can be increased to 90% by employing a large excess (50%) of acetyl chloride and aluminum chloride.

Dimethylchlorogermane. This compound was prepared previously in 17% yield by allowing HCl to react with dimethylgermane (6). We have found that Anderson's method (7) gives a 76% yield.

Dimethyldivinylgermane and 1,1,2,2-tetramethyl-1,2-divinyldigermane. Apparently, these compounds have not been previously reported. Dimethyldichlorogermane (86 g, 0.49 mole) was added to a THF solution of 1.50 mole of vinylmagnesium bromide. After hydrolysis, distillation gave 23.4 g (32%) of dimethyldivinylgermane, bp 86-88°. The pot residue was then subjected to vacuum distillation to give 8.8 g (14%) of the digermane, bp 40°/0.2 torr.

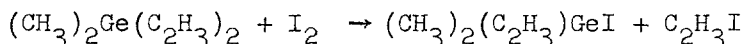
Dimethylvinyliodogermane. Iodine (50 g, 0.20 mole) was placed in the cup of a Soxhlet extractor and allowed to extract over a period of 18 hr into a refluxing chloroform solution of dimethyldivinylgermane (31 g, 0.2 mole). The resulting, pale pink solution was then shaken with zinc dust to remove unreacted iodine, filtered, and then distilled to yield 47.2 g (93%) of product, bp 157-159. The compound darkens slowly on exposure to light. Iodine also cleaves the Ge-Ge bond in tetramethyldivinyl digermane to give dimethylvinyliodogermane.

Dimethylvinylbromogermane. Vinylmagnesium bromide (0.3 mole) was added dropwise to a solution of dimethyldibromogermane (8) (89 g, 0.34 mole) in 50 ml of THF under gentle reflux. After addition was complete, the solution was cooled to 0° to precipitate most of the $MgBr_2 \cdot THF$, and filtered. The mixture was then fractionated to yield dimethyldivinylgermane, dimethylvinylbromogermane (bp 131-133, 15 g, 35% based on unrecovered dibromide), and unreacted dimethyldibromogermane.

(1,2-dimethylvinyl)dimethylchlorogermane. Dimethylchlorogermane (2.5 g, 0.018 mole) and 2-butyne (1.5 g, 0.028 mole) were placed in a Carius tube which was sealed under N_2 . After heating at 115° for several hrs, the tube was opened and the product distilled at 145°.

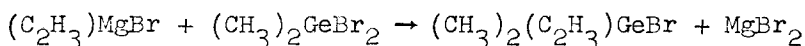
Discussion

It was found that iodine, but not bromine, cleaves the vinylgermanium bond to give high yields of the halogermane:

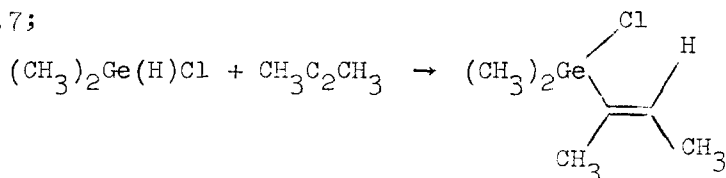


Thus, the behavior of vinyl germanes is intermediate between that of vinylsilanes and vinylstannanes (3).

The corresponding bromo derivative could be prepared in lower yield by adding vinyl magnesium bromide to excess dimethyldibromogermane:



Dimethylchlorogermane added to 2-butyne to give poor yields of (1,2-dimethylvinyl)dimethylchlorogermane (calcd: C, 37.3; H, 6.7;



found: C, 36.0; H, 6.6). The nmr spectrum consisted of broad

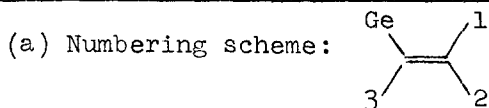
peaks at 1.1, 1.0, 0.85, and 0.55 and sharp peaks at 0.7 and 0.48 ppm. Apparently the methyl (vinyl) resonances are second order and the two sharp peaks may be due to germanium-methyl resonances of cis- and trans-isomers.

Dimethylchlorogermane failed to react with acetylene under a variety of conditions.

The nmr parameters of the unsubstituted vinyl compounds were analyzed by the LAOCN3 computer program (9), and are presented in Table I.

TABLE I.
Nmr Spectra of Vinylgermanes.^{a,b}

<u>Compound</u>	<u>δ (Me)</u>	<u>δ_1</u>	<u>δ_2</u>	<u>δ_3</u>	<u>$J_{1,2}$</u>	<u>$J_{1,3}$</u>	<u>$J_{2,3}$</u>
$\text{Me}_2\text{Ge}(\text{C}_2\text{H}_3)_2$	15.6	333	353	378	5.3	17.9	13.4
$[\text{Me}_2\text{Ge}(\text{C}_2\text{H}_3)]_2$	23.0	341	356	379	5.7	17.1	13.2
$\text{Me}_2(\text{C}_2\text{H}_3)\text{GeBr}$	50.0	344	358	386	4.3	17.9	13.0
$\text{Me}_2(\text{C}_2\text{H}_3)\text{GeI}$	61.2	341	354	386	3.3	18.4	13.0



(b) Chemical shifts and coupling constants in Hz. Std: TMS. Spectra obtained at 60MHz in CCl_4 solution.

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