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α-Hydroxygermanes and Substituted Vinylgermanes

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The preparation of several α-hydroxygermanes from triphenylgermyllithium and ketones is described. Dehydration of the α-hydroxygermanes gives olefins with germyl and organic groups on the same carbon atom. Ozonolysis of 1-triphenylgermyl-1-phenylethylene led to a low yield of benzoyltriphenylgermane.

Introduction

The addition of triphenylgermyllithium to the carbonyl group of formaldehyde and benzophenone gives triphenylhydroxymethylgermane and triphenylgermyldiphenylcarbinol, respectively.[2] Triphenylsilylpotassium adds to formaldehyde to give the expected α-hydroxysilane[3] but the abnormal addition products, diarylmethoxytriphenylsilanes, are obtained when triphenylsilylpotassium is allowed to react with benzophenone and 4,4′-dimethylbenzophenone.[4] Triphenylsilyllithium adds normally to acetone, cyclohexanone, and 2-nonadecanone,[5] but abnormally to benzaldehyde.[6] Triphenyltinsodium acts as a reducing agent toward benzophenone.[7]

The first examples of vinyl compounds of germanium were prepared by the reaction of germanium tetrachloride and vinylmagnesium bromide in tetrahydrofuran.[8] Vinyltrichlorogermane has been prepared by the reaction[9]

$$GeCl_4 + (CH_2{=}CH)_2Hg \xrightarrow{80^\circ} CH_2{=}CHGeCl_3 + CH_2{=}CHHgCl$$

and by dehydrochlorination of 2-chloroethyltrichlorogermane with quinoline.[10]

Most of the known examples of substituted vinylgermanium compounds have the substituent on the β carbon atom and were prepared by the addition of alkylgermanes to the triple bond of derivatives of acetylene[11,12]

$$R_3GeH + HC{\equiv}CR' \longrightarrow R_3GeCH{=}CHR'$$

From the reaction of triethylgermane and 2,5-dimethyl-3-hexyne-2,5-diol, 2,5-dimethyl-3-triethylgermyl-3-hexene-2,5-diol was obtained in 40% yield.[12]

The vinylgermanes $((CH_3)_3Ge)_2CH{=}CH_2$ and $(CH_3)_3GeCH{=}CHGe(CH_3)_3$ were prepared by a procedure involving dehydrochlorination of $ClCH_2CHClGeCl_3$ and subsequent reactions with methylmagnesium chloride and then with sodium and trimethylchlorogermane.[13]

This research was undertaken to prepare a series of new α-hydroxygermanes and then to prepare by dehydration vinylgermanes with other substituents on the α-carbon.

Experimental

Tetrahydrofuran, ethyl ether, and benzene were purified by refluxing over lithium aluminum hydride and distilling immediately before use.

Yields of alcohols are based on the amount of unrecrystallized product isolated. Analysis and spectra were obtained from recrystallized samples.

Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Infrared spectra (Nujol mulls) were taken with a Beckman IR-9 recording spectrophotometer.

Proton magnetic resonance spectra of the samples in carbon tetrachloride with tetramethylsilane as the internal reference were taken with a Varian Associates, Inc., A-60 spectrometer.

Triphenylgermyllithium was prepared from triphenylgermane and *n*-butyllithium according to the method of Gilman and Gerow.[14,16]

1-Triphenylgermyl-1-phenyl-1-ethanol.—The following preparation of a triphenylgermyl substituted alcohol is typical of the procedures employed in this investigation. Minor variations are noted in the footnotes for Table I.

A solution of 0.01 mole triphenylgermyllithium in 100 ml. of ethyl ether was placed in a stirred three-necked flask and cooled to 0°. To this solution was added a solution of 0.01 mole of acetophenone in 100 ml. of ethyl ether. The resulting colorless solution was stirred at 0° for 0.5 hr., allowed to return to room temperature, and then stirred for another 0.5 hr. This yellow solution was hydrolyzed with an equal volume of dilute hydrochloric acid. The ether layer was separated and dried and the ether was replaced with hexane. Upon cooling, a white solid (2.9 g.) formed. A portion of this solid was recrystallized from hexane. Data for characterization of the product are presented in Table I.

1,1-Bis(triphenylgermyl)ethylene.—The following procedure was also followed in the preparation of the other compounds listed in Table II.

A solution of 6.8 g. (0.0104 mole) of 1,1-bis(triphenylgermyl)-1-ethanol[15] and 12.0 g. (0.044 mole) of phosphorus tribromide in 250 ml. of benzene was refluxed 16 hr. A yellow oil began to collect on the side of the flask after 0.5 hr. of refluxing, and evolution of hydrogen bromide was observed during the first 2 hr. At the end of the reflux period the solution was hydrolyzed with dilute hydrochloric acid and the organic layer was separated. After being dried over anhydrous sodium sulfate, the benzene

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TABLE I

PRODUCTS OBTAINED FROM THE ADDITION OF TRIPHENYLGERMYLLITHIUM TO KETONES[a]

		Alcohols			Stretching		C, %		H, %		
Ketone	Triphenylgermane % recovered[b]	Formula	Yield, %	M.p., °C.	freq., OH[c]	cm.$^{-1}$ C_6H_5–Ge[c]	Calcd.	Found	Calcd.	Found	Comments
$C_6H_5C(O)CH_3$	...	$(C_6H_5)_3GeC(OH)(C_6H_5)CH_3$	68	116–118	3520	1081 1426	73.5	73.2	5.7	5.9	d, f
$CH_3C(O)CH_3$	42	$(C_6H_5)_3GeC(OH)(CH_3)_2$	46	156–158	3445	1090 1430	69.5	69.3	6.1	6.1	e, g
$C_6H_5C(O)C_6H_5$	...	$(C_6H_5)_3GeC(OH)(C_6H_5)_2$	81	150–152	3520	1086 1430	76.4	76.3	5.4	5.5	h
$C_6H_5C(O)CH(CH_3)_2$	...	$(C_6H_5)_3GeC(OH)(C_6H_5)CH(CH_3)_2$	84	144–146.5	3580	1087 1430	74.2	74.3	6.2	6.3	
$CH_3C(O)C(CH_3)_3$	93	...	...		...	...					
$CH_3CH_2C(O)CH_3$	45	$(C_6H_5)_3GeC(OH)(CH_3)CH_2CH_3$	37	96–98	3580	1086 1428	70.1	69.8	6.4	6.4	
$CH_3CH_2C(O)CH_2CH_3$	...	$(CH_3CH_2)_2C(OH)Ge(C_6H_5)_3$	70	88.5–89.5	3560	1090 1431	70.6	70.8	6.7	6.6	
$CH_3(CH_2)_2C(O)(CH_2)_2CH_3$	...	$(CH_3CH_2CH_2)_2C(OH)Ge(C_6H_5)_3$	48	77–79	3540	1090 1430	71.6	70.9	7.2	7.2	i
$\underline{CH_2(CH_2)_2C(O)CH(CH_3)CH_2}$	83	...	...								

[a] The solvent was diethyl ether unless otherwise noted. [b] Triphenylgermane was obtained from the filtrate from which the alcohol had been separated by stripping the hexane solvent and recrystallizing the triphenylgermane from methanol–water. [c] Data for alcohols. [d] With tetrahydrofuran as the solvent, 89% of the triphenylgermane was recovered. [e] With tetrahydrofuran as the solvent, 87% of the triphenylgermane was recovered. [f] δ_{CH_3} −1.86 p.p.m., δ_{OH} −1.68 p.p.m. [g] δ_{CH_3} −1.48 p.p.m., δ_{OH} −1.14 p.p.m. [h] The reaction mixture turned from green to yellow while being stirred for 2 hr. at 25°. [i] Recrystallized from methanol–water since an oil forms with hydrocarbon solvents. [j] A white solid product (0.5 g.) was shown to be triphenylgermanium hydroxide by comparison of its infrared spectrum with that of an authentic sample, by a mixture melting point (133.7–134.2°), and by analysis. *Anal.* Calcd. for $C_{18}H_{16}GeO$: C, 67.4; H, 5.0. Found: C, 67.7; H, 5.2.

TABLE II

PRODUCTS FROM THE DEHYDRATION OF α-HYDROXYGERMANES

					C, %		H, %	
Alcohol	Product	Yield, %	M.p., °C.	C_6H_5–Ge str., cm.$^{-1}$ [a]	Calcd.	Found	Calcd.	Found
$((C_6H_5)_3Ge)_2C(OH)CH_3$	$((C_6H_5)_3Ge)_2C{=}CH_2$[b]	62	145–146	1090 1432	72.0	71.7	5.1	5.7
$(C_6H_5)_3GeC(OH)(CH_3)CH_2CH_3$	$((C_6H_5)_3Ge)(CH_3)C{=}C(H)CH_3$ + $((C_6H_5)_3Ge)(CH_3CH_2)C{=}CH_2$	39	116–120	1090 1430	73.6	73.5	6.2	6.1
$(C_6H_5)_3GeC(OH)(CH_3)_2$	$((C_6H_5)_3Ge)(CH_3)C{=}CH_2$	58	96–97	1089 1429	73.1	73.2	5.8	6.0
$(C_6H_5)_3GeC(OH)(C_6H_5)CH_3$	$((C_6H_5)_3Ge)(C_6H_5)C{=}CH_2$	63	119–120	1090 1432	76.7	76.9	5.4	5.5
$(C_6H_5)_3GeC(OH)(C_6H_5)CH(CH_3)_2$	$(C_6H_5)_3GeC(Br)(C_6H_5)CH(CH_3)_2$[c]	47	135.5–137	...	65.2	65.4	5.3	5.5
$(CH_3CH_2)_2C(OH)Ge(C_6H_5)_3$	$((C_6H_5)_3Ge)_2O$	84	183–184	...	69.3	69.2	4.8	5.0

[a] Olefin. [b] δ_{CH_2} −6.73 p.p.m. [c] The molecular weight was determined osmometrically in benzene: calcd., 516.02; found, 502.

solution was stripped and hexane was added. The resulting hexane solution was eluted with 500 ml. of hexane–pentane solution from an alumina column. This eluent was stripped and ethanol was added. Addition of water until cloudiness appeared at the boiling point of the ethanol solution, followed by cooling of the solution to 0°, led to the crystallization of a white solid. Recrystallization of this solid from ethanol–water yielded 4.1 g. of 1,1-bis(triphenylgermyl)ethylene, characterized as indicated in Table II.

Ozonolysis of 1-Triphenylgermyl-1-phenylethylene.—Oxygen gas containing approximately 5% ozone was allowed to pass through a solution of 2.0 g. (0.0049 mole) of 1-triphenylgermyl-1-phenylethylene in 40 ml. of anhydrous ethyl acetate at −78° for 25 min. Excess ozone was removed by passing a stream of nitrogen through the solution for another 0.5 hr. The ethyl acetate solution was then reduced with hydrogen over a 5% Pd-C catalyst. The ethyl acetate was removed with a solvent stripper and replaced by 50 ml. of pentane. Cooling this solution produced a small amount of impure yellow solid, m.p. 90–110°. This solid was redissolved and the solution was chromatographed on alumina. The column was eluted with 400-ml. portions of hexane, heptane, and carbon tetrachloride. The hexane and heptane eluents yielded no products. The yellow band on the column was eluted with carbon tetrachloride. On workup, 0.1 g. (5%) of a yellow solid was isolated; m.p. 98–100°. A mixture melting point with authentic benzoyltriphenylgermane showed no depression.

Ozonolysis of other olefins was attempted, but no ketones were isolated after hydrogenation.

Results

The reaction of triphenylgermyllithium with an organic ketone yields either an α-hydroxygermane or triphenylgermane. In some instances both products were obtained. The following α-hydroxygermanes were isolated: 1-triphenylgermyl-1-phenyl-1-ethanol, 2-triphenylgermyl-2-propanol, triphenylgermyldiphenylcarbinol, 1-triphenylgermyl-1-phenyl-2-methyl-1-propanol, 2-triphenylgermyl-2-butanol, 3-triphenylgermyl-3-pentanol, and 4-triphenylgermyl-4-heptanol. Some properties are listed in Table I.

Some of the α-hydroxygermanes react with phosphorus tribromide in refluxing benzene to yield substituted vinylgermanes. As indicated in Table II, the following vinylgermanes were prepared: 1,1-bis(triphenylgermyl)ethylene, 2-triphenylgermyl-2-butene, 2-triphenylgermyl-1-butene, 2-triphenylgermylpropene, and 1-triphenylgermyl-1-phenylethylene. Reaction of 1-triphenylgermyl-1-phenyl-2-methylpropanol with phosphorus tribromide yields the corresponding bromide. The only product isolated from the attempted dehydration of 3-triphenylgermyl-3-pentanol was hexaphenyldigermoxane.

Ozonolysis of vinylgermanes and subsequent reduction of the ozonide was explored in an effort to find a general preparative method for α-germyl ketones. Germyl substituted phenyl ketones, but not germyl alkyl ketones, can be prepared from acid chlorides and triphenylgermyllithium.[15] A low yield of benzoyltriphenylgermane was obtained from the ozonolysis of 1-triphenylgermyl-1-phenylethylene, but, as summarized in Table III, either hexaphenyldigermoxane or the unreacted olefin was recovered from the ozonolysis of other vinylgermanes.

TABLE III

PRODUCTS OBTAINED FROM THE OZONOLYSIS OF VINYLGERMANES

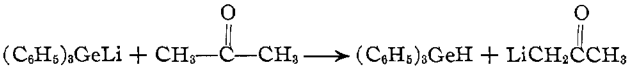
Olefin	Solvent	Temp., °C.	Product(s)	Yield, %
$(C_6H_5)_3Ge(C_6H_5)C{=}CH_2$	C_2H_5OAc	−78	$C_6H_5C(O)Ge(C_6H_5)_3$	5
$((C_6H_5)_3Ge)_2C{=}CH_2$	C_2H_5OAc	−78	$((C_6H_5)_3Ge)_2O$	45
$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	Heptane	−78	$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	27
			$((C_6H_5)_3Ge)_2O$	22
$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	CCl_4	−20	$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	53
$(C_6H_5)_3Ge(C_6H_5)C{=}CH_2$	CCl_4	−20	$(C_6H_5)_3Ge(C_6H_5)C{=}CH_2$	42

Discussion

The strong solvent dependence of the reaction of triphenylgermyllithium with ketones is demonstrated by the reactions of acetophenone and acetone in ether and in tetrahydrofuran. The sole product isolated from the reaction of acetophenone or acetone with triphenylgermyllithium in tetrahydrofuran was triphenylgermane. With ethyl ether as the solvent, the corresponding alcohol is obtained in good yield.

Triphenylgermane can result from one of two pathways. First, the triphenylgermane could arise from hydrolysis of unreacted triphenylgermyllithium; and second, it could result from abstraction of an acidic hydrogen from the ketone. The second path seems to be more likely. Triphenylgermyllithium has been shown earlier to react with carbonyl groups in carboxylic acid chlorides even at temperatures as low as −78°.[15] Benzophenone, which has no α-hydrogens available for reaction, gives the corresponding alcohol in 52% yield when allowed to react with triphenylgermyllithium in tetrahydrofuran.[16]

$$(C_6H_5)_3GeLi + H_2O \rightarrow (C_6H_5)_3GeH + LiOH$$



$$(C_6H_5)_3GeLi + CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3 \longrightarrow (C_6H_5)_3GeH + LiCH_2\overset{\overset{\large O}{\|}}{C}CH_3$$

Steric effects are probably important in explaining the failure to observe any alcohol resulting from reactions of *t*-butyl methyl ketone and 2-methylcyclohexanone with triphenylgermyllithium. Approach to the carbonyl group is severely hindered in each case.

No rearrangement of the α-hydroxygermanes to α-germyl ethers was observed. Formation of silyl ethers generally is observed in similar silicon systems.[17] The rearrangement in the silicon systems probably is due to the abnormally high Si–O bond energy.

The preparation of vinylgermanes from the dehydration of α-hydroxygermanes is especially useful in the synthesis of monosubstituted vinylgermanes in which the substituent is bonded to the same carbon atom as the germanium. Alternate Grignard syntheses or addition reactions leading to the preparation of such compounds have not been reported. Addition of triphenylgermane to monosubstituted acetylenes leads to the anti-Markownikoff product, *i.e.*, the germanium bonded to the least hindered carbon atom.

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Scrambling of Oxygen with Halogens on Dimethylgermanium: Labile α,ω-Dihalopolydimethylgermoxanes

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Several new families of germanium compounds are described. These are the α,ω-dihalopolydimethylgermoxanes—with the halogen being either chlorine, bromine, or iodine. Proton nuclear magnetic resonance of the methyl groups shows that the chain compounds making up these families rapidly equilibrate (<1 sec.) with respect to exchange of parts. They also equilibrate somewhat more slowly with the trimeric and tetrameric cyclic dimethylgermoxanes—so that the ring molecules coexist with the chain molecules at equilibrium. Exchange of halogen with the methoxyl group on the dimethylgermanium moiety was also studied. In all cases, the minimum number of equilibrium constants needed to define the molecular distributions quantitatively were determined.

In a related study[1] of the exchange of bridging sulfur with halogen atoms on the dimethylgermanium moiety, we demonstrated the existence of α,ω-dihalopolydimethylgermanium sulfides and described the equilibria involving these compounds and the dimethylgermanium sulfide ring trimer. The ring compound was found to

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