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The Thermal Reactions of Allyl-substituted Germyl Radicals

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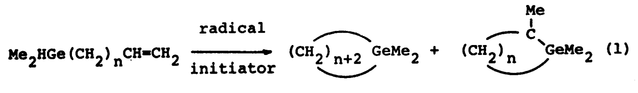
Synopsis. The allyldibutylgermyl and dibutyl(2-methylallyl)germyl radicals in benzene at 80 °C afforded diallyldibutylgermane and dibutylgermane, and dibutylbis(2-methylallyl)germane and dibutylgermane, respectively. The mechanism of these reactions is discussed.

Although numerous publications on addition of organogermyl radicals to olefinic double bonds have appeared,[1] there are few reports on the reactions of olefinic germyl radicals.[1a,2] The reactions of olefinic germyl radicals lead to cyclic products and are of interest both in synthesis and in mechanistic problems. In a previous paper,[2] we have reported on the reactions of ω-alkenyldimethylgermyl radicals, $Me_2\dot{G}e(CH_2)_n$-$CH{=}CH_2$, (n=2—5) (Eq. 1). ω-Alkenyldimethylgermyl



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radicals afford cyclization products, with the exo isomer (**1**) predominating. These results are in striking contrast to those of the corresponding ω-alkenyl radicals.[3] This paper deals with the thermal reactions of allyl-substituted germyl radicals which are one group of the ω-alkenylgermyl radicals. It is interesting to compare the present findings with those for carbon analogs.

Results and Discussion

The reactions of allyldibutylgermane (**3**, R=H) and dibutyl(2-methylallyl)germane (**3**, R=Me) were carried out in sealed, degassed tubes in benzene as solvent and dibenzoyl peroxide (BPO) as initiator at 80 °C. Products were isolated by preparative GLC and their structures were verified by comparing the retention times on GLC and IR and NMR spectra with those of authentic samples. The main products obtained in the thermal reactions of allyldibutylgermane (**3**, R=H) and dibutyl(2-methylallyl)germane (**3**, R=Me) under various conditions are summarized in Table 1.

As shown in Table 1, the allyldibutylgermyl radical (**4**, R=H) in benzene afforded diallyldibutylgermane (**6**, R=H) and dibutylgermane. The dibutylbis(2-methylallyl)germyl radicals (**4**, R=Me) in benzene gave dibutylbis(2-methylallyl)germane (**6**, R=Me) and dibutylgermane. Several organic products with much higher boiling points were also detected in both reactions. No cyclization products were detected. The allyldibutylgermyl radical (**4**, R=H) was more reactive than the dibutyl(2-methylallyl)germyl radical (**4**, R=Me). The thermal reactions of allyl-substituted germanes were promoted by BPO, radical generator.

The reversibility of the addition to an olefinic double bond is not a favorable process for carbon radicals at least at low temperature, but is progressively favored for elements lower in group 4B in the periodic table.[4] Therefore, the formation of diallyldibutylgermanes (**6**) and dibutylgermane suggests that the following addition-elimination process may occur in the thermal reactions of allyl-substituted germanes (Scheme **1**):

$$\underset{\mathbf{3}}{CH_2{=}CRCH_2GeHBu_2} \xrightarrow[\text{initiator}]{\text{radical}} \underset{\mathbf{4}}{CH_2{=}CRCH_2\dot{G}eBu_2} \quad \text{R=H, Me} \tag{2}$$

$$\mathbf{4}+\mathbf{3} \longrightarrow \underset{\mathbf{5}}{CH_2{=}CRCH_2GeBu_2CH_2\dot{C}RCH_2GeHBu_2} \tag{3}$$

$$\mathbf{5} \longrightarrow \underset{\mathbf{6}}{(CH_2{=}CRCH_2)_2GeBu_2} + Bu_2\dot{G}eH \tag{4}$$

$$Bu_2\dot{G}eH + \mathbf{3} \longrightarrow Bu_2GeH_2 + \mathbf{4}. \tag{5}$$

Thus, the addition of the germyl radicals (**4**) generated from the hydrogermanes (**3**) to the carbon-carbon double bond of the hydrogermanes (**3**) intermolecularly gives the intermediate radicals (**5**). The intermediate

Table 1. Thermal reactions of allyl-substituted germanes

Reactants(mmol)			Conditions		Products, Yield/%[a)]		
$(CH_2{=}CRCH_2)Bu_2GeH$, **3**	BPO,	C_6H_6	Temp/°C	Time/h	$(CH_2{=}CRCH_2)_2GeBu_2$, **6**	Bu_2GeH_2,	**3**
R=H							
1.01	0.02	31.00	80	15	5.9	7.3	42.2
0.72	0.07	21.52	80	15	3.1	4.8	42.2
0.98	0	30.90	80	15	trace	trace	95.1
0.51	0.02	50.64	80	15	5.5	8.1	48.8
0.59	0.05	53.64	80	15	5.2	7.1	44.4
R=Me							
0.72	0.07	21.20	80	15	4.0	4.0	84.4
0.72	0.05	22.92	80	15	3.3	3.5	88.1
0.51	0	21.20	80	15	trace	trace	98.0
0.77	0.07	77.71	80	15	4.9	6.2	87.6
0.51	0.05	53.28	80	15	3.9	5.2	83.1

a) Based on the consumed hydrogermanes **3**.

radicals (**5**) undergo degradation to form diallyldibutylgermanes (**6**) and dibutylgermyl radical. The dibutylgermyl radical abstracts a hydrogen atom from the hydrogermanes (**3**) to give dibutylgermane and the germyl radicals (**4**). The reactions of allyl-substituted germyl radicals proceed by a free-radical chain mechanism. However, the mass balance in these reactions is bad. Moreover, the theoretical ratio of diallyldibutylgermanes (**6**) and dibutylgermane is not always obtained. These facts suggest that the intermolecular addition of organogermyl radicals to olefinic bonds and/or dimerization of organogermyl radicals, along with the addition-elimination process shown in Scheme 1, may proceed in these reactions resulting in the formation of unidentified materials.

The present results of the thermal reactions of allyl-substituted germyl radicals are clearly different from those of the corresponding 3-butenyl and allylsilyl radicals. 1,2-Vinyl shifts proceeding *via* cyclopropylmethyl radicals are well known in the reactions of 3-butenyl radicals.[3a,4b] It has been reported that vinylsilanes are formed by loss of methylene from the allyl groups[5] or by loss of a methyl group originallyl bound to silicon[6] in the reactions of allylsilyl radicals.

Experimental

Materials. Bu_2GeCl_2: bp 120 °C/10 mmHg,[7] Bu_2GeH_2: bp 86 °C/46 mmHg,[8] Bu_2GeHCl: bp 105 °C/17 mmHg,[8] and $(CH_2{=}CHCH_2)GeBu_2H$: bp 36 °C/0.2 mmHg[9] were prepared as described in the cited references.

Preparation of Dibutyl(2-methylallyl)germane. A (2-methylallyl)magnesium chloride was prepared from 2-methylallyl chloride (3.3 g, 36.0 mmol) and magnesium (0.9 g, 36.0 mmol) in 50 ml of dry THF. To this, (2-methylallyl)magnesium chloride, dibutylchlorogermane (2.0 g, 9.0 mmol) dissolved in 10 ml of dry ether was added. The reaction mixture was stirred with reflux for 3 h. After hydrolysis with water, organic substances were extracted with ether and the extract was dried over sodium sulfate. Fractional distillation gave dibutyl(2-methylallyl)germane (1.6 g, 6.6 mmol, 73.5%), bp 38.5—39.5 °C/0.04 mmHg; n^{20} 1.4689; NMR (δ in $CDCl_3$) 0.88—1.73 (m, 23H), 3.80 (m, 1H), 4.52 (s, 2H); IR (neat, cm^{-1}) 2050 (Ge–H). Found: C, 59.20: H, 10.64%, Calcd. for $C_{12}H_{26}Ge$: C, 59.33; H, 10.79%.

Preparation of Diallyldibutylgermane. An allylmagnesium chloride was prepared from allyl chloride (1.0 g, 14.0 mmol) and magnesium (0.32 g, 14.0 mmol) in 50 ml of dry THF. To this, allylmagnesium chloride, dibutyldichlorogermane (1.5 g, 58 mmol) dissolved in 10 ml of dry ether was added. The reaction mixture was stirred with reflux for 4 h. After hydrolysis with water, organic substances were extracted with ether and the extract was dried over sodium sulfate. Fractional distillation gave diallyldibutylgermane (1.2 g, 4.5 mmol, 76.9%). bp 125 °C/18 mmHg; n^{20} 1.4766; NMR (δ in $CDCl_3$) 0.88—1.32 (m, 18H), 1.69 (d, J=8.0 Hz, 4H), 4.70—4.92 (m, 4H), 5.53—6.02 (m, 2H). Found: C, 62.76: H, 10.24%. Calcd for $C_{14}H_{28}Ge$: C, 62.52: H, 10.49%.

Preparation of Dibutylbis(2-methylallyl)germane. Dibutylbis(2-methylally)germane was prepared from 2-methylallylmagnesium chloride and dibutyldichlorogermane in 76.3% yield, bp 83 °C/0.8 mmHg; n^{20} 1.4818; NMR (δ in CCl_4) 0.80—1.83 (m, 28H), 4.51 (m, 2H). Found: C, 64.64: H, 10.92%. Calcd for $C_{16}H_{32}Ge$: C, 64.70: H, 10.86%.

Thermal Reactions of Hydrogermanes in Benzene. A hydrogermane, BPO, and benzene were placed in a Pyrex glass tubes. The tube was sealed after degassing and immersed in a constant temperature bath kept at 80 °C. The reaction mixture was analyzed by GLC (Shimadzu GC 6A with SE30 20% or Apiezen L 30% 2m). The amounts of products were determined by an internal-standard method. Each product was isolated by preparative GLC and the structure was verified by comparing the retention time on GLC and IR and NMR spectra with those of authentic samples.

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