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RING CLOSURE REACTIONS OF ω-ALKENYLDIMETHYLGERMYL RADICALS

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Summary

Ring closure reactions of ω-alkenyldimethylgermyl radicals, $CH_2{=}CH(CH_2)_n$-$GeMe_2^{\cdot}$ (n = 2—5), were investigated. The 3-butenyldimethylgermyl radical (n = 2) afforded 1,1-dimethyl-1-germacyclopentane as the only cyclization product in low yields. The 4-pentenyldimethylgermyl radical (n = 3) afforded 1,1-dimethyl-1-germacyclohexane almost exclusively and the 5-hexenyldimethylgermyl radical (n = 4) afforded 1,1-dimethyl-1-germacycloheptane predominantly. The 6-heptenyldimethylgermyl radical (n = 5) cyclized to give only 1,1-dimethyl-1-germacyclooctane in low yields. The mechanism of these ring closure reactions is discussed.

Introduction

It is well known that organogermyl radicals add to olefinic double bonds. The organogermyl radicals so formed undergo further reactions such as abstraction of hydrogen or halogen. This type of reaction has been reviewed [1].

The addition of organogermyl radicals to carbon—carbon double bonds can also occur intramolecularly. Such reactions lead to cyclic products and are of interest both in synthesis and for mechanistic problems. However, no examples of ring closure reactions of organogermyl radicals have been reported.

In this paper, we present the first examples of ring closure reactions of ω-alkenyldimethylgermyl radicals, $CH_2{=}CH(CH_2)_nGeMe_2^{\cdot}$ (n = 2—5).

Numerous ring closure reactions of ω-alkenyl radicals have been known and studied [2]. It is of interest to compare the present findings with those for carbon analogs.

Results

ω-Alkenyldimethylgermanes, $HMe_2Ge(CH_2)_nCH{=}CH_2$ (I, n = 2—5), were prepared by partial alkenylation of dimethyldichlorogermane followed by reduc-

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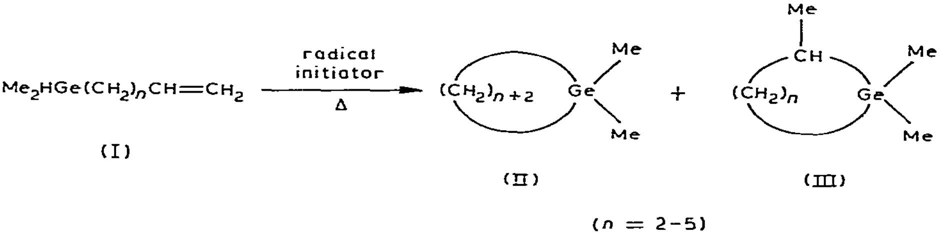
tion with lithium aluminum hydride. Authentic samples of 1,1-dimethyl-1-germacycloalkanes (II) and 1,1-dimethyl-2-methyl-1-germacycloalkanes (III), possible products of cyclization, were prepared by reactions of di-Grignard reagents from α,ω-dibromoalkanes with dimethyldichlorogermane. Physical properties and analytical data of these organogermanium compounds are summarized in Table 3.

The reactions of compounds I were carried out in sealed, degassed tubes with benzene as solvent and azobisisobutyronitrile (AIBN) as initiator at 42° C for 15 h or with dibenzoyl peroxide (BPO) as initiator at 80°C for 20 h. Compounds I are expected to afford mixtures of cyclization products II and III (eq. 1).



(1)

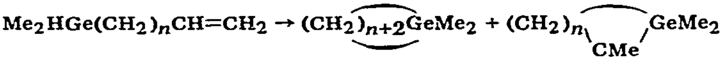
All products were isolated by preparative GLC (SE30 20% 5 m) and identified by comparing the IR, NMR, and mass spectra and retention times on GLC with those of authentic samples except for 1,1-dimethyl-1-germacyclooctane (II, $n = 5$). The latter compound was identified by careful examination of the IR, NMR, and mass spectra. The results obtained in the reactions of compounds I are summarized in Table 1.

The 3-butenyldimethylgermyl radical ($n = 2$) afforded 1,1-dimethyl-1-germacyclopentane (II, $n = 2$) as the only cyclization product in low yields. No 1,1-dimethyl-2-methyl-1-germacyclobutane (III, $n = 2$) was detected. The 4-pentenyldimethylgermyl radical ($n = 3$) afforded 1,1-dimethyl-1-germacyclohexane (II, $n = 3$) almost exclusively in good yields. 1,1-Dimethyl-2-methyl-1-germacyclopentane (III, $n = 3$) was also detected as the minor cyclization product. The 5-hexenyldimethylgermyl radical ($n = 4$) afforded 1,1-dimethyl-1-germacycloheptane (II, $n = 4$) predominantly, while 1,1-dimethyl-2-methyl-1-germacyclohexane (III, $n = 4$) was also detected as the minor cyclization product. The ratios of the cyclization products II to III increase with decreasing reaction temperatures or decreasing the concentrations of the hydrogermanes I in the reactions of 4-pentenyldimethylgermyl and 5-hexenyldimethylgermyl radicals. The 6-hexenyldimethylgermyl radical ($n = 5$) cyclized to give only 1,1-dimethyl-1-germacyclooctane (II, $n = 5$) in low yields.

The present results of ring closure reactions of ω-alkenyldimethylgermyl radicals are clearly different from those of the corresponding ω-alkenyl radicals [2]. The results also differ from those of 4-pentenylsilyl radicals [3]. As a typical example, the ratios of the cyclization products II to III in ring closure reactions of 5-hexenyl, 4-pentenylsilyl, and 4-pentenylgermyl radicals are summarized in Table 2. 5-Hexenyl radicals afford the cyclization product III almost exclusively. On the other hand, 4-pentenylsilyl and 4-pentenylgermyl radicals afford cyclization product II predominantly. The ratio of the cyclization products II to III increases in the order $C \ll Si < Ge$.

TABLE 1

RING CLOSURE REACTIONS OF ω-ALKENYLDIMETHYLGERMANES [a]



$Me_2HGe(CH_2)_nCH{=}CH_2 \rightarrow \overbrace{(CH_2)_{n+2}GeMe_2}^{} + (CH_2)_n\underset{CMe}{\frown}GeMe_2$

(I) (II) (III)

(n = 2—5)

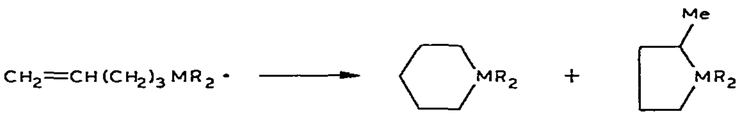
Starting materials (mmol)			Products (mmol)				Yields (%) [b]
I	C_6H_6	initiators	II	III	II/III	I	
n = 2		*AIBN*					
1.092	10.92	0.154	trace	0	—	0.731	—
1.092	32.76	0.154	trace	0	—	0.915	—
1.092	109.2	0.143	0.007	0	—	0.794	2.3
		BPO					
1.092	10.92	0.106	0.031	0	—	0.321	4.0
1.092	32.76	0.096	0.123	0	—	0.299	15.5
1.092	109.2	0.078	0.112	0	—	0.449	17.4
n = 3		*AIBN*					
0.382	3.82	0.041	0.095	0.005	19.0	0.175	48.3
0.382	38.2	0.041	0.042	trace	—	0.330	70.6
		BPO					
0.382	3.82	0.041	0.149	0.009	16.6	0.043	46.6
0.382	38.2	0.041	0.042	trace	—	0.330	80.8
n = 4		*AIBN*					
1.022	10.00	0.147	0.107	0.019	5.6	0.379	19.6
1.022	30.14	0.147	0.108	0.016	6.8	0.577	27.9
1.022	100.1	0.147	0.029	trace	—	0.857	17.6
		BPC					
1.022	10.00	0.147	0.164	0.048	3.4	0.352	31.6
1.022	30.14	0.147	0.249	0.066	3.8	0.340	46.2
1.022	100.1	0.147	0.201	0.051	3.9	0.743	90.3
n = 5		*AIBN*					
0.573	5.73	0.122	0	0	—	0.527	—
0.573	17.19	0.183	0.007	0	—	0.465	6.5
0.573	57.3	0.160	0.008	0	—	0.528	17.8
		BPO					
0.573	5.73	0.103	0.018	0	—	0.109	3.9
0.573	17.19	0.110	0.027	0	—	0.111	5.8
0.573	57.3	0.110	0.041	0	—	0.244	12.5

[a] The reactions of compounds I were carried out using AIBN at 42°C for 15 h and BPO at 80°C for 20 h.

[b] The yields of cyclization products were based on the concentrations of consumed hydrogermanes.

TABLE 2

THE RATIOS OF THE CYCLIZATION PRODUCTS II TO III IN $CH_2{=}CH(CH_2)_3MR_2^{\bullet}$ (M = C, Si, and Ge)



(II) (III)

M	II/III	References
C (R = Me, Me)	~20/~80	4
Si (R = Me, Ph)	~85/~15	3
Ge (R = Me, Me)	~95/~5	this work

Discussion

The addition of ω-alkenylgermyl radicals to carbon—carbon double bonds should occur intramolecularly or intermolecularly to give cyclic radicals or linear radicals, respectively. The addition of organogermyl radicals to olefins is shown to be an irreversible process under these conditions [5], therefore, it would seem reasonable to assume that two cyclic radicals were formed irreversibly. The primary (germacycloalkyl)methyl radicals produced by addition of organogermyl radicals to the β carbon of carbon—carbon double bonds give cyclization products III by abstraction of hydrogen of hydrogermanes I. On the other hand, the secondary germacycloalkyl radicals produced by addition of organogermyl radicals to the α carbon of carbon—carbon double bonds give cyclization products II after hydrogen abstraction. The secondary germacycloalkyl radicals are obviously more stable than the primary (germacycloalkyl)-methyl radicals. Furthermore, in addition to the stability of the product radicals, the geometric restraints on disfavored ring closure in the case of carbon radicals may be bypassed because of the large atomic radii and bond distances in germanium compounds [6]. Therefore, ω-alkenyldimethylgermyl radicals give cyclization products II predominantly.

Intermolecular addition of organogermyl radicals to carbon—carbon double bonds may proceed with increasing reaction temperatures and increasing concentrations of the hydrogermanes effectively.

Experimental

Physical properties and analytical data of the organogermanium compounds obtained are listed in Table 3.

Preparation of ω-alkenyldimethylchlorogermanes

As a representative example, the preparation of 4-pentenyldimethylchlorogermane is described.

A Grignard reagent was prepared from 4-pentenylchloride (13.6 g, 0.13 mol) and magnesium (3.2 g, 0.13 mol) in 100 ml of THF. To dimethyldichlorogermane (22.0 g, 0.13 mol) in 200 ml of ether was added the Grignard reagent over a period of 1 h. The reaction mixture was stirred under reflux for 3 h. After filtration of the mixture to remove salt, the solvent and then the product were distilled. Fractionation gave 4-pentenyldimethylchlorogermane (16.6 g, 0.08 mol, 61.8% yield), b.p. 82—84°C/24 mmHg; NMR * (δ, in CCl_4) 0.76 (s, 6H), 1.19—2.35 (m, 6H), 4.91—5.25 (m, 2H), 5.60—6.12 (m, 1H); IR (cm^{-1}, neat) 1240 (ν(Ge—Me)), 1650 (ν(C=C)).

For other chlorogermanes, yields (%), NMR (δ in CCl_4), and IR (cm^{-1}, neat) are indicated. 3-Butenyldimethylchlorogermane, 38.8; 0.77 (s, 6H), 1.13—2.83 (m, 4H), 4.83—5.30 (m, 2H), 5.50—6.63 (m, 1H); 1240 (ν(Ge—Me)), 1640 (ν(C=C)). 5-Hexenyldimethylchlorogermane, 48.4; 0.75 (s, 6H), 1.08—2.45 (m, 8H), 4.42—5.18 (m, 2H), 5.38—6.35 (m, 1H); 1240 (ν(Ge—Me)), 1640

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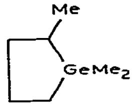
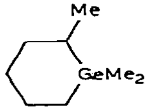
* NMR spectra were recorded on a Varian FT-80A.

TABLE 3

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF ORGANOGERMANIUM COMPOUNDS

Compound	B.p. (°C/mmHg)	n_D^{20}	Analyses (Found (calcd.) (%))	
			C	H
$CH_2{=}CH(CH_2)_2GeMe_2Cl$	69—71/72	1.4625		
$CH_2{=}CH(CH_2)_3GeMe_2Cl$	82—84/24	1.4555		
$CH_2{=}CH(CH_2)_4GeMe_2Cl$	108/20	1.4769		
$CH_2{=}CH(CH_2)_5GeMe_2Cl$	125/50	1.4700		
$CH_2{=}CH(CH_2)_2GeMe_2H$	95—97	1.4320	45.51 (45.39)	8.91 (8.89)
$CH_2{=}CH(CH_2)_3GeMe_2H$	70/90	1.4450	48.96 (48.66)	9.50 (9.33)
$CH_2{=}CH(CH_2)_4GeMe_2H$	83/75	1.4511	51.45 (51.43)	9.59 (9.71)
$CH_2{=}CH(CH_2)_5GeMe_2H$	84/25	1.4506	53.70 (53.82)	9.93 (10.04)
	117	1.4450	45.60 (45.39)	9.03 (8.89)
	53/35	1.4551	48.84 (48.66)	9.53 (9.33)
	70/85	1.4592	48.76 (48.66)	9.30 (9.33)
	53—54/17	1.4521	51.74 (51.43)	9.68 (9.71)
	65/25	1.4550	51.69 (51.43)	9.65 (9.71)

(ν(C=C)). 6-Heptenyldimethylchlorogermane, 63.0; 0.65 (s, 6H), 0.99—2.37 (m, 10H), 4.72—5.12 (m, 2H), 5.36—5.87 (m, 1H); 1240 (ν(Ge—Me)), 1640 (ν(C=C)).

Preparation of ω-alkenyldimethylgermanes

As a representative example, the preparation of 4-pentenyldimethylgermane is described.

To a solution of lithium aluminum hydride (2.3 g, 0.06 mol) in 100 ml of ether was added 4-pentenyldimethylchlorogermane (11.5 g, 0.06 mol). The reaction mixture was stirred with reflux for 3 h. After hydrolysis, organic substances were extracted with ether and the extract was dried over calcium chloride. Fractional distillation gave 4-pentenyldimethylgermane (3.4 g, 0.02 mol, 33.3% yield), b.p. 70°C/90 mmHg; NMR (δ in CCl_4) 0.25 (d, J 3.8 Hz, 6H), 0.66—2.38 (m, 6H), 3.74—4.00 (m, 1H), 4.71—5.27 (m, 2H), 5.40—6.00 (m, 1H); IR (cm^{-1}, neat) 1240 (ν(Ge—Me)), 1640 (ν(C=C)), 2020 (ν(Ge—H)).

For other hydrogermanes, yields (%), NMR (δ in CCl_4), and IR (cm^{-1}, neat) are indicated. 3-Butenyldimethylgermane, 67.4; 0.20 (d, J 3.9 Hz, 6H), 0.57—1.33 (m, 4H), 3.65—4.02 (m, 1H), 4.73—5.14 (m, 2H), 5.49—6.05 (m, 1H); 1240 (ν(Ge—Me)), 1640 (ν(C=C)), 2050 (ν(Ge—H)). 5-Hexenyldimethylgermane, 31.2; 0.25 (d, J 3.8 Hz, 6H), 0.59—2.48 (m, 8H), 3.68—4.00 (m, 1H), 4.53—5.27 (m, 2H), 5.37—6.20 (m, 1H); 1240 (ν(Ge—Me)), 1640 (ν(C=C)), 2050 (ν(Ge—H)). 6-Heptenyldimethylgermane, 52.0; 0.18 (d, J 3.5 Hz, 6H), 0.56—2.35 (m, 10H), 3.74—4.00 (m, 1H), 4.76—5.18 (m, 2H), 5.48—6.15 (m, 1H); 1240 (ν(Ge—Me)), 1640 (ν(C=C)), 2050 (ν(Ge—H)).

Preparation of germacycloalkanes

As a representative example, the preparation of 1,1-dimethyl-1-germacyclohexane is described.

A di-Grignard reagent was prepared from 1,5-dibromopentane (14.0 g, 0.06 mol) and magnesium (3.6 g, 0.15 mol) in 100 ml of THF. To dimethyldichlorogermane (10 g, 0.06 mol) dissolved in 200 ml of ether was added the di-Grignard reagent over a period of 30 min. The reaction mixture was stirred with reflux for 4 h. After hydrolysis, organic substances were extracted with ether and the extract was dried over calcium chloride. Fractional distillation gave 1,1-dimethyl-1-germacyclohexane (5.2 g, 0.03 mol, 50% yield), b.p. 70°C/85 mmHg; NMR (δ in CCl_4) 0.17 (s, 6H), 0.66—2.04 (m, 10H); IR (cm^{-1}, neat) 1230 (ν(Ge—Me)). For other germacycloalkanes, yield (%), NMR (δ in CCl_4), and IR (cm^{-1}, neat) are indicated. 1,1-Dimethyl-1-germacyclopentane, 26.6; 0.16 (s, 6H), 0.60—1.83 (m, 8H); 1240 (ν(Ge—Me)). 1,1-Dimethyl-2-methyl-1-germacyclopentane, 24.0; 0.19 (s, 3H), 0.25 (s, 3H), 0.63—2.47 (m, 9H), 3.50—4.16 (m, 1H); 1240 (ν(Ge—Me)). 1,1-Dimethyl-2-methyl-1-germacyclohexane, 21.2; 0.11, 0.15, 0.20, 0.28 (s, 6H), 0.50—2.44 (m, 11H), 3.36—3.92 (m, 1H); 1240 (ν(Ge—Me)). 1,1-Dimethyl-1-germacycloheptane, 23.4; 0.16 (s, 6H), 0.72—1.99 (m, 12H); 1240 (ν(Ge—Me)). 1,1-Dimethyl-1-germacyclooctane *, 0.14 (s, 6H), 0.77—1.05 (m, 4H), 1.10—1.81 (m, 8H); 1240 (ν(Ge—Me)).

Ring closure reactions

A hydrogermane, radical initiator, and benzene were placed in a Pyrex glass tube. The tube was sealed after degassing and was immersed in a constant temperature bath and kept at 42°C for AIBN and 80°C for BPO. The reaction mixture was analyzed by GLC (Shimazu GC 6A with SE30 20% 2 m or Apiezon L 30% 2 m). The amounts of products were determined by an internal-standard method. Each product was separated by preparative GLC and the structure was verified by comparing the retention time on GLC and NMR, IR and mass spectra with those of authentic samples except for 1,1-dimethyl-1-germacyclooctane. 1,1-Dimethyl-1-germacyclooctane was identified by careful examination of the NMR, IR, and mass spectra.

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* NMR spectra were recorded on a Varian FT-80A.

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References

1 (a) M. Lesbre, P. Mazerolles, and J. Satgé, The Organic Compounds of Germanium, Chapter 4, John Wiley & Sons, New York, 1971; (b) H. Sakurai, in Jay K. Kochi (Ed.), Free Radicals Vol. II, Chapter 25, John Wiley & Sons, New York, 1973; (c) H. Sakurai, Proc. IIIrd Intern. Conf. Organometal. Coordin. Chem. Germanium, Tin, and Lead, Dortmund, 1980, J. Organometal. Chem. Library, 12 (1981) 267—291.

2 For examples; (a) M. Julia, Acc. Chem. Res., 4 (1971) 386; (b) J.W. Wilt, in Jay K. Kochi (Ed.), Free Radicals, Vol. I, Chapter 8, John Wiley & Sons, New York, 1973; (c) A.L.J. Beckwith and K.U. Ingold, in P. de Mayo (Ed.), Rearrangements in Ground and Excited States, Vol. I, Chapter 4, Academic Press, New York, 1980.

3 H. Sakurai, T. Hirose, and A. Hosomi, Abstr., 26th Ann. Meeting Chem. Soc. Japan, Vol. III, 1972, p. 1001.

4 C. Walling and A. Cioffari, J. Am. Chem. Soc., 94 (1972) 6059.

5 S.W. Bennett, C. Eaborn, R.A. Jackson, and R. Pearce, J. Organometal. Chem., 16 (1968) P17.

6 J.E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman, and R.C. Tomas, Chem. Commun., (1976) 736.