

ORGANOGERMANIUM COMPOUNDS

IV. NOVEL PHENYL MIGRATIONS FROM CARBON TO GERMANIUM AND FROM GERMANIUM TO CARBON

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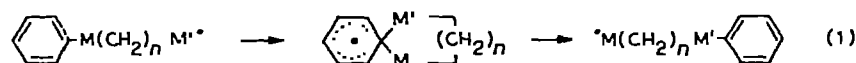
(Received April 25th, 1974)

Summary

Novel radical phenyl migrations from carbon to germanium and from germanium to carbon are described. Both thermal and peroxide-catalyzed reactions of $\text{ArCXY}(\text{CH}_2)_2\text{GeMe}_2\text{H}$ gave the rearranged product, $\text{HCXY}(\text{CH}_2)_2\text{-GeMe}_2\text{Ar}$ ($\text{X} = \text{Y} = \text{Me}$, and $\text{X} = \text{H}$, $\text{Y} = \text{Ph}$). Reduction of $\text{PhMe}_2\text{Ge}(\text{CH}_2)_4\text{Cl}$ with tributylstannane afforded $\text{Ph}(\text{CH}_2)_4\text{GeMe}_2\text{H}$ in low yield. The mechanism of these migrations is discussed and physical properties of 24 new organogermanium compounds are listed.

Introduction

Although migration of the phenyl group is one of the major reaction pathways in carbon-centered radicals [1], no example of such a rearrangement involving other heteroatom-centered radicals except for those from carbon to oxygen [2], from silicon to carbon [3], and from carbon to silicon [4] has been reported. These rearrangements are best interpreted in terms of intramolecular homolytic substitution involving *spiro*-cyclohexadienyl radicals as intermediates (or transition states) (eqn. 1).



Trialkylgermyl radicals are quite inert toward aromatic compounds [4], while silyl radicals can generally enter homolytic aromatic substitution. Therefore, an investigation of the possible migration of a phenyl group either to or from germanium is more interesting than recording a new class of rearrangement

Results

Several (ω -arylalkyl)dimethylgermanes were prepared by partial aralkylation of dimethyldichlorogermane followed by reduction with lithium aluminium hydride. Authentic samples of aryl dimethylalkylgermanes, possible products of rearrangement, were prepared by alkylation of aryl dimethylchlorogermanes. Physical properties and analytical data of these new organogermanium compounds are summarized in Table 1.

TABLE I
PHYSICAL PROPERTIES AND ANALYTICAL DATA OF NEW ORGANOGERMANIUM COMPOUNDS

Compound	B.p. ($^{\circ}$ C/mmHg)	n_D^{20}	d_4^{20}	Analyses, found	
				(calcd)	(%)
				C	H
Ph(CH ₂) ₁ GeMe ₂ Cl	116.5-117.5/7.5	1.5283	1.2202		
Ph(CH ₂) ₂ GeMe ₂ Cl	135-136/10	1.5263	1.1771		
Ph(CH ₂) ₃ GeMe ₂ Cl	138-140/7.5	1.5218	1.1764		
Ph(CH ₂) ₄ GeMe ₂ Cl	148-150/7.5	1.5175	1.1376		
PhCH(Me)(CH ₂) ₂ GeMe ₂ Cl	105/0.9	1.5215	1.1648		
PhCMe ₂ (CH ₂) ₂ GeMe ₂ Cl	121/4	1.5215	1.1601		
Ph ₂ CH(CH ₂) ₂ GeMe ₂ Cl	143-146/0.6			60.93	6.36
	m p. 61.5-62.5 (in a sealed tube)			(61.22)	(6.35)
<i>p</i> -CH ₃ C ₆ H ₄ CMe ₂ (CH ₂) ₂ GeMe ₂ Cl	130-131/3	1.5227	1.1308		
Ph(CH ₂) ₂ GeMe ₂ H (Ia)	81/6	1.5123	1.1077	57.53	7.77
				(57.52)	(7.72)
Ph(CH ₂) ₃ GeMe ₂ H (Ib)	84-85/3.5	1.5115	1.0717	59.50	8.18
				(59.28)	(8.14)
Ph(CH ₂) ₄ GeMe ₂ H (Ic)	115/9.5	1.5055	1.0592	61.06	8.65
				(60.85)	(8.51)
Ph(CH ₂) ₅ GeMe ₂ H (Id)	116/5.5	1.5049	1.0404	62.57	8.85
				(62.23)	(8.84)
PhCH(Me)(CH ₂) ₂ GeMe ₂ H (Ie)	62/0.5	1.5061	1.0550	61.07	8.49
				(60.85)	(8.51)
PhCMe ₂ (CH ₂) ₂ GeMe ₂ H (If)	123/7	1.5097	1.0575	62.04	8.57
				(62.23)	(8.84)
Ph ₂ CH(CH ₂) ₂ GeMe ₂ H (Ig)	114-115/0.16	1.5603	1.1083	68.41	7.68
				(68.30)	(7.42)
<i>p</i> -CH ₃ C ₆ H ₄ CMe ₂ (CH ₂) ₂ GeMe ₂ H (Ih)	33-85/2	1.5115	1.0458	63.78	9.07
				(63.47)	(9.13)
PhMe ₂ GeEt (IIa)	48/0.8	1.5102	1.0987	57.45	7.75
				(57.52)	(7.72)
PhMe ₂ Ge(<i>n</i> -Pr) (IIb)	70-71/5.5	1.5080	1.0713	59.17	8.09
				(59.28)	(8.14)
PhMe ₂ Ge(<i>n</i> -Bu) (IIc)	70.5-71/1	1.5043	1.0557	60.84	8.46
				(60.85)	(8.51)
PhMe ₂ Ge(<i>n</i> -Am) (IId)	91.5/5	1.5015	1.0292	62.56	9.09
				(62.23)	(8.84)
PhMe ₂ Ge(<i>i</i> -Am) (IIIf)	65-66/2	1.5022	1.0345	62.46	8.72
				(62.23)	(8.84)
PhMe ₂ Ge(CH ₂) ₃ Ph (IIg)	138-139/3	1.5537	1.1077	68.58	7.65
				(68.30)	(7.42)
<i>p</i> -CH ₃ C ₆ H ₄ GeMe ₂ (<i>i</i> -Am) (IIh)	75-76/2	1.5028	1.0183	63.27	9.07
				(63.47)	(9.13)
PhMe ₂ Ge(CH ₂) ₄ Cl (III)	84-85/1	1.1787	1.5276	53.48	7.01
				(53.12)	(7.06)

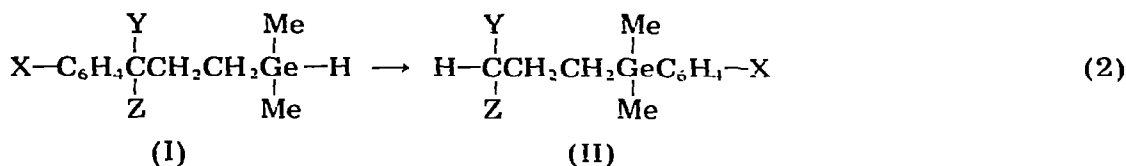
TABLE 2

THERMAL ARYL MIGRATION FROM CARBON TO GERMANIUM AT 320° FOR 24 h^a

Starting germane (mmol)	Products (mmol)			
	Recovered germane	Product	Yield (%)	
If	0.624	0.138	0.155	32.0
	0.483	0.938	0.120	31.7
Ig	0.356	0	0.232	65.1
	0.332	0	0.203	60.9
Ih	0.0544	0	0.0135	24.8

^a Analyzed by GLC*Thermal reaction*

When If, Ig and Ih were heated in an ampule at 320° for 24h, the corresponding arylgermanes, II_f, II_g, and II_h, were obtained in 32.0, 65.1 and 24.8% yield, respectively (eqn. 2). Table 2 lists the results.



(f: X = H, Y = Z = Me; g: X = Y = H, Z = Ph; h: X = *p*-CH₃, Y = Z = Me)

This is the first example of an aryl migration from carbon to germanium. The intramolecular nature of the reaction is supported by the fact that hydrogermanes did not replace an alkyl group from alkylbenzenes, thus phenyl-methylene cleavage did not take place intermolecularly with hydrogermanes. Moreover, an aryl group migrates at the original point attached to carbon as evidenced by the fact that Ih gave II_h exclusively.

Although If, Ig and Ih gave rearrangement products successfully, no phenyl migration was observed for Ia-Ie.

*Di-*t*-butyl peroxide-catalyzed reaction*

The reaction of hydrogermanes Ia-Ig with di-*t*-butyl peroxide (DTBP) without solvent gave no rearrangement products. Product analysis of a model experiment for trimethylgermane with DTBP (Table 3) revealed that the trimethylgermyl radicals thus generated resulted mainly in the formation of hexamethyldigermene and *t*-butoxytrimethylgermane (eqns. 3-6).



TABLE 3

REACTION OF TRIMETHYLGERMANE WITH DTBP (135°, 20 h)

	Starting material (mmol)		Products ($\times 10^{-1}$ mmol, %) ^a			
	Me ₃ GeH	DTBP	i-PrOGeMe ₃	t-BuOGeMe ₃	Me ₆ Ge ₂	Me ₃ GeOGeMe ₃
run 1	1.30	0.694	0.228 (1.8%)	2.50 (19.2%)	2.62 (40.4%)	0.500 (3.8%)
run 2	1.41	0.725	0.254 (1.8%)	2.35 (16.7%)	2.82 (40.0%)	0.601 (4.3%)

^a Based on starting Me₃GeH.

However, in benzene solution If and Ig gave IIf and IIg, respectively, in the reaction with DTBP at 135°, results being listed in Table 4.

Phenyl migration from germanium to carbon

Radical migration of phenyl from germanium to carbon also occurred when phenyldimethyl(4-chlorobutyl)germane was subjected to reduction with tri-n-butylstannane in the presence of DTBP (eqns. 7 and 8).

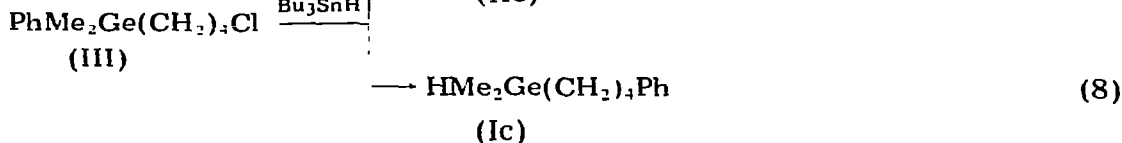
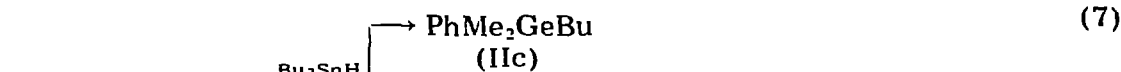


TABLE 4

DTBP-CATALYZED PHENYL MIGRATION IN BENZENE SOLUTION AT 135°

Starting material ($\times 10^{-1}$ mmol)	DTBP	Concentration ^a (mole %)	Product ($\times 10^{-2}$ mmol) (%)		
			Recovered	Product	Yield ^b
<i>If</i>			<i>If</i>	<i>IIf</i>	
5.00	2.65	1	0	1.01	2.0
5.12	2.55	0.1	0.67	2.59	5.1
1.88	1.45	0.01	3.12	0.57	3.7
<i>Ig</i>			<i>Ig</i>	<i>IIg</i>	
4.69	2.69	1	5.68	1.73	4.2
5.15	2.59	0.1	8.34	2.76	6.4
2.44	1.21	0.01	3.60	6.62	31.8

^a Concentration of hydrogermanes. ^b Based on consumed hydrogermane.

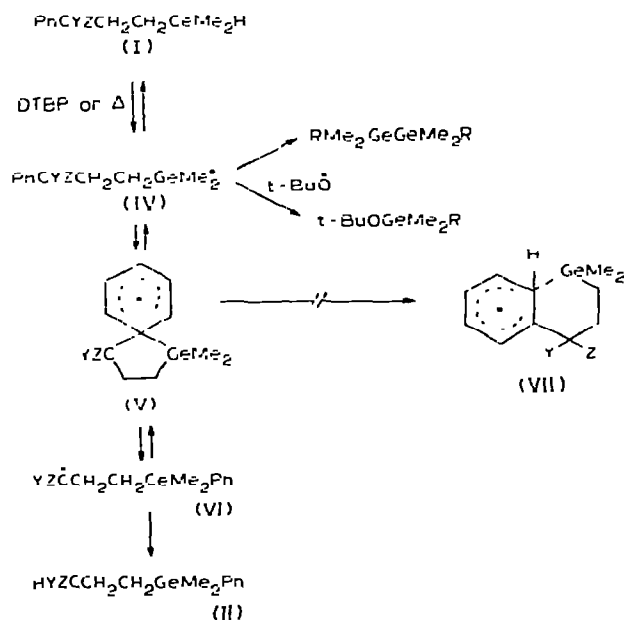
Although simple reduction giving phenyldimethylbutylgermane predominates over rearrangement (IIc/Ic = ca. 20 by GLC), formation of Ic demonstrates conclusively phenyl migration from germanium to carbon.

Discussion

Alkyl- and halo-germanium hydrides display great reactivity toward unsaturated compounds. Thus, addition reactions of germanes occur thermally in high yields without any catalyst. Moreover, both inhibition by free-radical scavengers and acceleration by free-radical initiators or by UV irradiation demonstrate the free-radical nature of these thermal reactions [5]. Uncatalyzed thermal reduction of organic halides with germanes has been also reported to be a homolytic reaction [6]. Therefore it is reasonable to assume that thermal phenyl migration involves a free germyl radical such as IV.

Involvement of IV in phenyl migration is indicated more clearly in the DTBP-catalyzed reactions. The data fit Scheme 1.

SCHEME 1



The retention of the *para* substituent in the product as seen in the rearrangement of Ih to IIh is in agreement with this scheme, which is analogous to the similar phenyl migration in silyl radicals [4]. However, several different features can be pointed out for the present case.

It is reasonable that the rearrangement to VI is observed only for those compounds in which Y and Z are CH₃ or Z is Ph, because the rearranged radicals are stabilized by two methyl groups or by a phenyl group. The migratory aptitude of germyl radicals is, however, less than that of the corresponding silyl radicals. Thus, substitution of one methyl group at the benzylic position

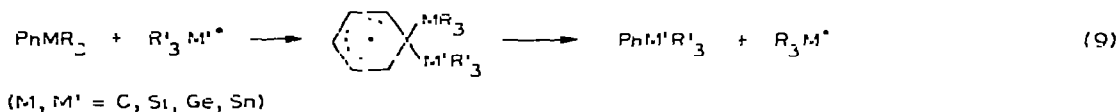
in I was not enough to drive the rearrangement in both thermal and DTBP-catalyzed reactions.

Contrary to the case of silyl radicals, no cyclized product was obtained from V. This fact reflects probably both the reluctance of germyl radicals to aromatic substitution and the efficient trapping of intermediate radicals by the more reactive germyl hydride.

Dimerization of germyl radicals and coupling with a t-butoxy radical also are important pathways. Although we did not examine the formation of digermanes from each hydrogermane Ia-Ih, a model experiment indicated that hexamethyldigermane was the most dominant product in the reaction of trimethylgermane with DTBP.

In dilute solutions, however, rearrangement can compete with dimerization and coupling. Thus, the extent of rearrangement depended on the concentration of hydrogermanes. As seen in Table 4, the rearrangement product from Ig was obtained in higher yield in more dilute solution in accord with this explanation, although the trend is not clear for If. Seemingly the latter discrepancy arose from the short kinetic chain length due to the poor migratory aptitude of If.

Finally, it is noteworthy that 1,5-phenyl shifts from germanium to carbon also took place. Therefore, radical phenyl migrations are generally reversible between germanium and carbon. The extent (or direction) of rearrangement should depend on the reactivity of both the germyl and the carbonyl radicals. It is one of the interesting problems in free-radical chemistry to investigate the relative reactivities of not only rearrangement (intramolecular ipso-substitution shown in eqn. 1) but also intermolecular ipso-substitution (eqn. 9). We will discuss structure and reactivity for such reactions in a forthcoming publication.



Experimental

Preparation of (ω -arylalkyl)dimethylchlorogermanes

As a representative example, the preparation of (2-phenylethyl)dimethylchlorogermane is described.

A Grignard reagent was prepared from 2-phenyl-1-chloroethane (7.0 g, 50 mmol) and magnesium (1.2 g, 50 mmol) in 20 ml of diethyl ether. To dimethyldichlorogermane (8.0 g, 46 mmol) dissolved in ether (100 ml) was added the Grignard reagent diluted to 150 ml by ether over a period of 1 h. After filtration of the mixture to remove salt, the solvent and then the product were distilled. Fractionation gave pure Ia (6.7 g, 27.4 mmol, 59.7%), b.p. 116.5-117.5°/7.5 mmHg; NMR* (δ , CCl₄) 0.57 (s, 6H), 1.52 (t, 2H, *J* 8Hz), 2.92 (t, 2H, *J* 8Hz), 7.3 (s, 5H).

For other chlorogermanes, yield (%) and NMR (δ , CCl₄), are indicated. (3-phenylpropyl)dimethylchlorogermane, 42.1; 0.64 (s, 6H) 0.9-2.4 (m, 4H), 2.69

* NMR spectra were taken on a Varian T 60. Chemical shifts are expressed as δ (ppm).

(t, 2H, J 8Hz), 7.26 (s, 5H). (4-Phenylbutyl)dimethylchlorogermane, 49.7; 0.63 (s, 6H), 0.94-1.98 (m, 6H), 2.45-2.85 (m, 2H), 7.24 (s, 5H). (5-Phenylpentyl)dimethylchlorogermane, 36.5; 0.63 (s, 6H), 0.92-1.95 (m, 8H), 2.45-2.8 (m, 2H), 7.22 (s, 5H). (3-Phenylbutyl)dimethylchlorogermane, 59.5; 0.58 (s, 6H), 0.6-1.18 (m, 2H), 1.28 (d, 3H, J 6.8Hz) 1.54-2.1 (m, 2H), 2.64 (q, 1H, J 6.8Hz), 7.2 (s, 5H). (3-Phenyl-3-methyl-butyl)dimethylchlorogermane, 53.0; 0.55 (s, 6H), 0.55-1.05 (m, 2H), 1.3(s, 6H), 1.6-2.12(m, 2H), 7.26(s, 5H). (3,3-Diphenyl-propyl)dimethylchlorogermane, 36.2; 0.62 (s, 6H), 0.75-1.4 (m, 2H), 2.0-2.3 (m, 2H), 3.6-4.0 (m, 1H), 7.25 (s, 10H). [3-(*p*-Methylphenyl)-3-methylbutyl]-dimethylchlorogermane, 41.7; 0.56 (s, 6H), 0.56-1.04 (m, 2H), 1.27 (s, 6H), 1.55-2.0 (m, 2H), 2.30 (s, 3H), 7.15 (s, 4H).

Preparation of (ω -aryllalkyl)dimethylhydrogermanes

To a solution of lithium aluminium hydride (1.3 g, 34 mmol) in 30 ml of ether was added (2-phenylethyl)dimethylchlorogermane (6.0 g, 24.7 mmol). After hydrolysis, organic substances were extracted with ether and the extract was dried on anhydrous sodium sulfate. Pure Ia was fractionated through a short column, b.p. 81°/6mmHg. Yield was 3.9 g (18.8 mmol, 76.5%). NMR (δ , CCl₄) 0.2 (d, 6H, J 3.6Hz), 1.0-1.4 (t, 2H, J 8Hz), 2.75 (t, 2H, J 8Hz), 3.9 (sep., 1H, J 3.6Hz), 7.23 (s, 5H).

For other hydrogermanes, yield (%) and NMR (δ , CCl₄) are shown. Ib, 72.4; 0.2 (d, 6H, J 3.6Hz), 0.6-1.12 (m, 2H), 1.45-2.04 (m, 2H), 2.66 (t, 2H, J 8Hz), 3.91 (sep., 1H, J 3.6 Hz), 7.25 (s, 5H). Ic, 64.5; 0.2 (d, 6H, J 3.6Hz), 0.58-2.0 (m, 6H), 2.45-2.85 (m, 2H), 3.88 (sep., 1H, J 3.6Hz), 7.22 (s, 5H). Id, 70.5; 0.2 (d, 6H, J 3.6Hz), 0.58-1.95 (m, 8H), 2.4-2.8 (m, 2H), 3.87 (sep., 1H, J 3.6Hz), 7.24 (s, 5H). Ie, 76.3; 0.16 (d, 6H, J 3.6Hz), 0.35-0.97 (m, 2H), 1.24 (d, 3H, J 6.8Hz), 1.4-1.87 (m, 2H), 2.61 (q, 1H, J 6.8Hz), 3.73 (sep., 1H, J 3.6Hz), 7.2 (s, 5H). If, 78.0; 0.13 (d, 6H, J 3.6Hz), 0.33-0.75 (m, 2H), 1.3 (s, 6H), 1.51-1.9 (m, 2H), 3.77 (sep., 1H, J 3.6Hz), 7.13 (s, 5H). Ig, 77.5; 0.2 (d, 6H, J 3.6Hz), 0.6-1.05 (m, 2H), 1.95-2.4 (m, 2H), 3.5-4.3 (m, 1H), 7.3 (s, 10H). Ih, 88; 0.17 (d, 6H, J 3.6Hz), 0.25-0.7 (m, 2H), 1.23 (s, 6H), 1.4-1.8 (m, 2H), 2.3 (s, 3H), 3.73 (sep., 1H, J 3.6Hz), 7.08 (s, 4H).

Preparation of (aryl)(dimethyl)(alkyl)germanes

These compounds were prepared from aryldimethylchlorogermane and an appropriate Grignard reagent in 75-85% yield.

Preparation of phenyl(4-chlorobutyl)dimethylgermane (III)

In a two-necked 20 ml flask were placed 4-chloro-1-butene (0.9 g, 10 mmol) and phenyldimethylgermane (1.8 g, 10 mmol). A catalytic amount of chloroplatinic acid dissolved in isopropyl alcohol was added to the mixture with stirring. The mixture was heated at 30-40° for 3h and then distilled under reduced pressure. Pure III was obtained as an oil. Yield 2.0 g (7.4 mmol, 74%). NMR (δ , CCl₄) 0.34 (s, 6H), 0.53-1.2 (m, 2H), 1.2-1.94 (m, 4H), 3.44 (t, 2H, J 6Hz), 7.2-7.45 (m, 5H).

Thermal reaction

A sample (ca. 2 g) of I was placed in a small Pyrex glass tube and the tube

was sealed after degassing. It was then immersed in a salt-bath kept at 320°. After 24 h, the reaction mixture was analyzed by GLC (a Hitachi model 063 with a 2 m column of 30% Apiezon L). The amounts of the 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 and IR and NMR spectra with those of authentic samples.

Thermolysis of Ia-Ie gave no rearranged product (by GLC) and was not examined further. If, Ig and Ih gave rearranged products, the results of analysis being listed in Table 2.

DTBP-catalyzed reaction

A hydrogermane and DTBP, which were distilled before use, were placed in a Pyrex glass tube. The tube was sealed after degassing and was immersed in a constant temperature bath kept at 135°. The products were analyzed similarly as described above.

Reaction of III with n-tributylstannane

A mixture of III (0.136 g, 0.501 mmol), tri-n-butylstannane (0.087 g, 0.501 mmol) and DTBP (0.038 g, 0.258 mmol) was dissolved in 5 ml of benzene and was placed in a sealed tube. The mixture was kept at 135° for 20 h and the products were analyzed by GLC. n-Butyldimethylphenylgermane (IIc) and (4-phenylbutyl)dimethylgermane (Ic) were identified by GLC (30% Apiezon L and 10% polyethyleneglycol) with approximate relative area of 20/1.

Acknowledgment

The research was supported in part by the Grant-in-aid (No. 8304 and 68304) of the Ministry of Education. We also thank the Mitsubishi Metal Corporation for a generous gift of germanium dioxide.

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* A 1/1 mixture of NaNO₃ and KNO₃ with a thermostatted electric heater.