REACTIONS OF ORGANOGERMYLENES GENERATED BY PHOTOLYSIS OF 7-GERMANORBORNADIENES AND CYCLOHEXAGERMANES WITH ORGANIC HALIDES AND TRIMETHYLTIN CHLORIDE

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Abstract

Reactions of organogermynes, R_2Ge : ($R=Me$ and iPr), generated by photolysis of 7-germanorbornadienes and cyclohexagermanes with organic halides ($R'X$) were examined by chemical trapping experiments and CIDNP measurements. The organogermynes reacted quantitatively with polyhalomethanes (XCX_3 , $X=Cl, Br$) and benzyl bromide to give the corresponding abstraction products together with polyhaloethanes and bibenzyl, respectively. With trimethyltin chloride the organogermynes afforded effectively the insertion products.

Introduction

The mechanistic study of organogermynes, carbene analogues containing a divalent germanium atom, is currently an active field [1-4]. The concerted and non-concerted radical mechanisms in the thermal and photochemical reactions of organogermynes are discussed by Neumann and co-workers [2, 5, 6], Gaspar and co-workers [7], Egorov and Nefedov [8], Ando and co-workers [9], and our groups [10] using chemical trapping experiments, laser flash photolysis, matrix isolation techniques, and CIDNP techniques. The most used organogermynes in mechanistic study are dimethylgermylene generated thermally and photochemically from 7,7-dimethyl-7-germanorbornadienes [4]. Dodecamethylcyclohexa-germane is also a convenient photochemical precursor of dimethylgermylenes [11]. However, very little is known about the systematic study of the reactivity of organogermynes generated photochemically from different precursors towards organic substrates. In this paper the results of our study of photochemical reactions of organogermynes, R_2Ge : ($R=Me, ^iPr$), generated from 7-germanorbornadienes and cyclohexagermanes with several organic halides ($R'X$) such as polyhalomethanes ($CCl_4, BrCCl_3, CHCl_3, CH_2Cl_2$), benzyl bromide ($PhCH_2Br$), and trimethyltin chloride (Me_3SnCl) by chemical trapping experiments and CIDNP measurements are examined.

Experimental

¹H spectra were recorded with a Varian Unity-Inova 400 MHz NMR and a JEOL JNM-FX 100 MHz NMR. The GC-MS spectra were recorded using a JEOL JMS-DX 303 mass spectrometer. Gas chromatography was done on a Shimadzu GC 8A with 1 m 20% SE30 and 30% Apiezon L columns.

Materials. Dimethyldichlorogermane (Me_2GeCl_2) [12], dimethyldibromogermane (Me_2GeBr_2) [13], diisopropyldichlorogermane (iPr_2GeCl_2) [14], diisopropyldibromogermane (iPr_2GeBr_2) [14], 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene [15], dodecamethylcyclohexagermane [16], and trimethyltin chloride [17], were prepared as described. Carbon tetrachloride (CCl_4), bromotrichloromethane ($BrCCl_3$), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and benzyl bromide are commercially available. Benzene, benzene- d_6 , and cyclohexane- d_{12} were dried over calcium hydride and distilled under argon.

Preparation of 2,3-benzo-7,7-diisopropyl-1,4,5,6-tetraphenyl-7-germanorbornadiene. 2,3-Benzo-7,7-diisopropyl-1,4,5,6-tetraphenyl-7-germanorbornadiene was prepared by the reaction of 1,1-diisopropyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene with benzyne as described in literature [16]. ¹H NMR (δ in C_6D_6) 0.94 (d, $J=7.5$ Hz, 6 H), 1.42 (d, $J=7.5$ Hz, 6 H), 1.52 (sep., $J=7.7$ Hz, 1 H), 2.35 (sep., $J=7.7$ Hz, 1 H), 6.90-7.66 (m, 24 H). MS, m/z 507 (1), 432 (100), 355 (10), 276 (4), 200 (2), 177 (9), 83 (8), 70 (7), 57 (5).

Matrix isolation of 7-germanorbornadienes at 77 K. The 7,7-diisopropyl-7-germanorbornadiene (**3**) (30 mg) was dissolved in 3-methylpentane (3-MP) (5 ml) and sealed *in vacuo* in a quartz cell connected to a Pyrex tube. The cell was introduced into an Oxford cryostat. The sample was cooled to 77 K and irradiated with a 110-W low-pressure Hg arc lamp. The UV spectra were recorded on a Shimadzu UV2200 spectrometer.

Photochemical reactions of 7-germanorbornadienes with organic halides and trimethyltin chloride. As a representative example, the photochemical reaction of 7,7-dimethyl-7-germanorbornadiene (**1**) with carbon tetrachloride (CCl_4) is described. A degassed sealed Pyrex tube containing a dry benzene (5 ml) solution of **1** (0.05 mmol) and CCl_4 (0.2-0.5 mmol) was irradiated with a high-pressure Hg arc lamp (450 W) for 35 min at 0 °C. NMR, GC, and GC-MS analysis of the resulting mixture showed Me_2GeCl_2 (0.05

mmol, 100%), 1,2,3,4-tetraphenylnaphthalene (0.05 mmol, 100%), and hexachloroethane, Cl_6C_2 (0.03 mmol, 57%). $\text{Me}_3\text{SnGeMe}_2\text{Cl}$: ^1H NMR (δ in C_6D_6) 0.27 (s, 9 H), 0.76 (s, 6 H). MS, m/z 302 (M^+). $\text{Me}_3\text{SnGe}^i\text{Pr}_2\text{Cl}$: ^1H NMR (δ in C_6D_6) 0.38 (s, 9 H), 0.93 (d, $J=7.5$ Hz, 6 H), 1.42 (d, $J=7.5$ Hz, 6 H), 1.53 (sep., $J=7.5$ Hz, 1 H), 2.35 (sept., $J=7.5$ Hz, 1 H). MS, m/z 356 (M^+).

Photochemical reactions of dodecamethylcyclohexagermane with organic halides. As a representative example, the photochemical reaction of dodecamethylcyclohexagermane (**3**) with CCl_4 is described. A degassed sealed quartz tube containing a dry benzene (5 ml) of **3** (0.05 mmol) and CCl_4 (0.5 mmol) was irradiated with a low-pressure Hg arc lamp (110 W) for 1 h at room temperature. NMR, GC, and GC-MS analysis of the resulting mixture showed Me_2GeCl_2 (0.05 mmol, 100%), decamethylcyclopentagermane (0.04 mmol, 80%), Cl_6C_2 (0.02 mmol, 39%), and unidentified products.

^1H CIDNP measurements of the photolysis of 7,7-diisopropyl-7-germabenzonorbornadiene with benzyl bromide. A cyclohexane- d_{12} (0.5 ml) solution of 7,7-diisopropyl-7-germabenzonorbornadiene (**2**) (60 mg) and benzyl bromide (19 mg) was deoxygenated in a 5 mm quartz NMR tube by bubbling pure argon gas for 10 min before irradiation. NMR spectra were measured before and after irradiation. The details of the CIDNP apparatus and measurements have been published elsewhere [18]. The 500-W high pressure Hg arc lamp light was focussed onto the NMR detecting region of a sample cell through a water filter and quartz lenses. The sampling and the irradiation time were controlled by a DG 535 pulse generator (Stanford Research Systems, Inc) with an electrical shutter. The irradiation period was 7 s prior to the applied RF pulse. The total interval including the signal sampling was 8 s. Usually, the signal was accumulated 4-8 times.

Results and Discussion

Electronic Absorption Spectra of Organogermynes. Germynes were generated by UV photolysis at 254 nm of 7-germanorbornadienes (**1**, **2**) or dodecamethylcyclohexagermane (**3**).

Irradiation of a cyclohexane solution of 7,7-diisopropyl-7-germanorbornadiene (**2**) and 2,3-dimethyl-1,3-butadiene with a high-pressure Hg arc lamp at 0 °C produced 1,1-diisopropyl-3,4-dimethyl-1-germacyclopent-3-ene in 89% yield. The formation of 1-germacyclopent-3-ene can be rationalized by the reaction of diisopropylgermylene with 2,3-dimethyl-1,3-butadiene [4].

Irradiation of **2** in 3-MP at 77 K for 10 min led to a yellow coloration of the glass and to an absorption at 450 nm. When the 3-MP glass was melted, the 450-nm maximum rapidly diminished. UV spectra of dimethylgermylene generated by photolysis of **1** and **3** in 3-MP at 77 K have been reported to be at 420 nm [19] and 450 nm [16], respectively.

Chemical Trappings. Photochemical reactions of organogermynes, $\text{R}_2\text{Ge}:$ ($\text{R}=\text{Me}$ and ^iPr) with several organic halides ($\text{R}'\text{X}$) were examined. The results are summarized in Tables 1 and 2.

On irradiation of benzene solutions of 7-germabenzonorbornadienes (**1** and **2**) containing organic halides ($\text{R}'\text{X}$) such as XCCl_3 ($\text{X}=\text{Cl}$, Br) and PhCH_2Br with a high-pressure Hg arc lamp through a Pyrex filter at 0 °C for 35 min - 1 h, dihalogermanes (R_2GeX_2), 1,2,3,4-tetraphenylnaphthalene, and coupling products ($\text{R}'\text{-R}'$) were formed in high yields as shown in Table 1. Similarly, benzene solutions of dodecamethylcyclohexagermane (**3**) containing $\text{R}'\text{X}$ (CCl_4 , BrCCl_3 , PhCH_2Br) were irradiated with a low pressure Hg arc lamp at room temperature for 1-1.5 h to give quantitatively R_2GeX_2 together with decamethylcyclopentagermane, $\text{R}'\text{-R}'$, and unidentified products as shown in Table 1. The yields of the products in Table 1 are almost independent of the concentrations of $\text{R}'\text{X}$ (2.5-10 eq. for **1-3**), solvent used (benzene or cyclohexane), and the irradiation times (1-2 h).

Prolonged irradiation of **3** led to increased yields of Me_2GeCl_2 , octamethylcyclotetragermane, and 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,3,4,5-tetragermacyclopentane. With CHCl_3 and CH_2Cl_2 organogermynes

generated from 1-3 could not afford abstraction products, probably due to the relatively strong bond dissociation energy of C-Cl.

The formation of R_2GeX_2 ($R=Me, ^iPr$) may be the result of a stepwise halogen abstraction from organic halides by organogermynes as shown in the silicon cases [20]. The radical ($R^\cdot$) generated by abstraction of organogermynes from $R'X$ dimerizes to $R'-R'$. The radical nature of the intermediate is confirmed by the formation of R_2GeX_2 and $R'-R'$.

The formation of $CCl_3\cdot$ - CCl_3 obtained when $R_2Ge:$ reacts with $BrCCl_3$ reflects the bond dissociation energy of germanium-halogens: $Ge-Br < Ge-Cl$. ($BrCl_2C$) $_2$ could not be detected by GC-MS. Neumann and co-workers have reported the formation of Me_2GeCl_2 only with $XCCl_3$, and Me_2GeBr_2 and $PhCH_2(GeMe_2)Br$ with $PhCH_2Br$ by the reaction of $Me_2Ge:$ generated photochemically from 1 [5]. However, we could not detect $PhCH_2(GeMe_2)Br$ under our experimental conditions by NMR and GC-MS.

Table 1. Reactions of Organogermynes, $R_2Ge:$ ($R=Me, ^iPr$) and Organic halides

Precursor	$R'X$	Conditions	Products (Yield/%) ^{a)} R_2GeX_2 $R'-R'$
1	CCl_4	$h\nu > 300$ nm, 35 min	100 57.0
2	"	$h\nu > 300$ nm, 1 h	100 39.0
3	"	$h\nu < 300$ nm, 1 h	100 39.0
1	$BrCCl_3$	$h\nu > 300$ nm, 1 h	65.0 ($X=Br$) 57.0 ($R=CCl_3$) 2.0 ($X=Cl$)
2	"	$h\nu > 300$ nm, 1 h	87.0 ($X=Br$) 58.0 ($R=CCl_3$) 9.0 ($X=Cl$)
3	"	$h\nu < 300$ nm, 1.5 h	60.0 ($X=Br$) 52.0 ($R=CCl_3$) 40.0 ($X=Cl$)
1	$PhCH_2Br$	$h\nu > 300$ nm, 1 h	100 36.0
2	"	$h\nu > 300$ nm, 1 h	94.0 16.0
3	"	$h\nu < 300$ nm, 1.5 h	99.0 53.0

^{a)} NMR yields. ^{b)} A trace amount of $PhCH_2(Ge^iPr_2)Br$ by NMR.

On the other hand, by photolysis of 1-3 with trimethyltin chloride (Me_3SnCl) in benzene, the insertion product of organogermynes into the Sn-Cl bond, $Me_3Sn-GeR_2Cl$, was formed in high yields. No abstraction products of $R_2Ge:$ were detected.

¹H CIDNP Measurements. Using the pulse technique, CIDNP effects could be observed at room temperature in the reaction of 7-germanornadienes (2) with benzyl bromide under various conditions. During continuous UV irradiation for 7 s (4-8 scans), the intensities of the NMR signals due to 2 and benzyl bromide were similar to those obtained in the case of 1. ¹H CIDNP signals have been observed in the reactions of 1 with CCl_4 , $BrCCl_3$, benzyl bromide, and Me_3SnCl [2, 5, 21].

Table 2. Reactions of Organogermynes, $R_2Ge:$ ($R=Me, ^iPr$) and Trimethyltin Chloride

Precursor	Conditions	(Yield/%) ^{a)} of $Me_3Sn(GeR_2)Cl$
1	$h\nu > 300$ nm, 1 h	95.0
2	$h\nu > 300$ nm, 1 h	92.0
3	$h\nu < 300$ nm, 1 h	82.0

^{a)} NMR yields.

Reaction Mechanism. From these chemical trapping experiments and ¹H CIDNP measurements previously reported and examined in this study, we propose scheme 1 as one possible reaction pathway under these experimental conditions.

With polyhalomethanes ($XCCl_3$), benzyl bromide, and Me_3SnCl , ¹H CIDNP signals have been observed by Neumann's and Egorov's groups [2, 5, 21]. Confirming CIDNP evidence has been gained from insertion of $R_2Ge:$ into the C-X bonds of $XCCl_3$, benzyl bromide, and Me_3SnCl . The insertion here is a radical abstraction-recombination procedure. However, no insertion products of $R_2Ge:$ into C-X bonds of $XCCl_3$ and benzyl bromide were formed under these experimental conditions as shown in Table 1. The ratio of yields of R_2GeX_2 vs. $R'-R'$ is roughly 1.8-2.6 for CCl_4 , 1.2-1.9 for $BrCCl_3$, and 1.9-5.9 for $PhCH_2Br$. These product ratios may be explained both by the abstraction-recombination process and by the two-step radical abstraction process with free $R_2Ge:$. Thus, organogermynes $R_2Ge:$ abstract a halogen from $R'X$ to give a halogermynyl (R_2XGe) and an organic radical ($R^\cdot$). R_2XGe abstracts furthermore a halogen from organic halides to produce a dihalogermane (R_2GeX_2) and R' . The radical $R^\cdot$ generated by abstraction of $R_2Ge:$ from $R'X$ dimerizes to $R'-R'$.

Scheme 1.

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