REACTIONS OF CYCLOTRIGERMANE WITH p-BENZOQUINONES: OLIGOMERS AND A NOVEL 1,3-CYCLOADDUCT

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Abstract

Thermolysis of hexamethylcyclotrigermane in the presence of various derivatives of p-benzoquinone are described. A surprising 1,3-cycloadduct was isolated in the case of p-benzoquinone; it is the first example of a 1,3-cycloaddition of a digermene to a quinone followed by a 1,4-H shift. The X-ray crystal structure of the adduct reveals a planar configuration of fused five- and six-membered rings and a deformation of the heterocycle because of the germanium atoms. Two other p-quinones substituted in ortho positions by aromatic cycles (naphthoquinone and anthraquinone) were used to decrease the fraction of the rearranged cycloadduct and thereby to increase the oligomeric forms.

Introduction

Recently we described the reactions of hexamethylcyclotrigermane with various α -diketones¹ and showed that they proceed by a pathway involving radicals to give cyclic and polymeric compounds. The mechanism of the addition of carbonyl compounds such as aldehydes or ketones to disilene or germsilene (generated by photolysis of the corresponding trimetalla compounds) has been determined². These authors also proposed the formation of biradical intermediates which gave disproportionation or ring closure. On the other hand, it has been reported that the photolysis of cyclic organosilanes with phenanthraquinone gave silylene insertion products by a process involving radicals³. We now report reactions of cyclotrigermane with p-benzoquinone, p-naphthoquinone and p-anthraquinone with the objective of determining whether or not they proceed by a similar pathway.

Results and discussion

When 1,4-benzoquinone was allowed to react with hexamethylcyclotrigermane⁴, we obtained a mixture of a linear oligomer **2** having one organogermylene unit, a cyclic oligomer **3**¹ and a surprising 1,3-cycloadduct **4**, the formation of which was mentioned¹ but that was not identified.

Compound **4** could be extracted from the reaction mixture after several recrystallizations from hexane, petroleum ether and ether, and was obtained pure in a 17% yield. In its ¹H and ¹³C NMR spectra, the two mesityl groups are not equivalent, as expected from the different environments of the germanium atoms, one attached to an oxygen atom and the other to a carbon atom of the aromatic ring. The ¹H NMR spectrum of the aromatic system showed the expected coupling interactions of the three non-equivalent protons. An X-ray crystal structure study of compound **4** confirmed its 1,3-cycloadduct structure as shown by the ORTEP diagram in Figure 1. The two five- and six-membered rings are in the same plane, but the heterocycle is highly distorted.

The $C_{56}Ge_1Ge_2$ and $O_1Ge_1Ge_2$ angles are decreased respectively to $87.66(8)^\circ$ and $91.09(6)^\circ$, whereas $C_{51}O_1Ge_2$ and $C_{51}C_{56}Ge_1$ angles are increased to $120.5(2)$ and $117.8(2)$. The bond distance $C_{51}-C_{56}$ ($1.381(3)$ Å) is close to that of the normal $C=C$ double bond⁵, and the corresponding angles $O_1C_{51}C_{56}$ ($122.8(3)^\circ$) and $C_{51}C_{56}Ge_1$ ($117.8(2)^\circ$) are also very near to the values expected for an sp^2 -hybridized C atom. The bond distance Ge_2-O_1 ($1.828(2)$ Å), Ge_1-C_{56} ($1.956(3)$ Å) and Ge_1-Ge_2 ($2.4611(5)$ Å) are consistent with literature values⁶.

The germanium atoms are distorted tetrahedral. The hydroxy hydrogen is disordered over the two possible orientations since both are geometrically suitable. In each case the OH group forms a twelve-membered ring in which there are disordered solvent molecules (hexane in this case) (Figure 2). Selected bond lengths and bond angles are displayed in Table 1, and crystallographic data are given in Table 2.

The same reaction with 1,4-naphthoquinone and anthraquinone, which does not have a hydrogen atom in the ortho position of the quinonic ring, gave only the oligomeric forms **5** and **6** (eq. 2):

Proton NMR measurements indicated a predominant 1:2 composition of quinonic and organogermanium units. In the both cases, minor amounts of the trigermacycloadducts **5a** and **6a**, were detected by mass spectrometry (DCI CH_4 or NH_3) but the digermylated derivative **5b** was found only in the case of the naphthoquinone. Although all these compounds are very soluble in organic solvents, it would be very difficult to extract each macrocycle from the reaction mixture.

The formation of trigermylated macrocycles can be explained by an initial homolytic cleavage of one of the germanium-germanium bonds followed by the condensation of the biradical intermediate onto the quinonic species. Such a cleavage of just one Ge-Ge bond to give a trigermylated adduct has previously been observed in the reaction of hexa-*t*-butylcyclotrigermane with iodine⁷. The subsequent release of the dimesityl germylene group by α -monoelectronic elimination [8] should give the biradical di- or mono-metallated intermediates **8** and **9** that rapidly form oligomers **3** and **2** (Scheme 1).

To yield compound **4**, the rearrangement of the biradical intermediate **8** by an elimination of $H^\cdot$ from the aromatic ring seems unlikely. In this case an ionic pathway should be considered. Cyclotrigermanes are well known to generate transient digermene by photolysis or thermolysis^{9,10} and a zwitterionic form **10** can be envisaged (Scheme 2) for the intermediate adduct of the digermene and quinones.

Figure 1: ORTEP drawing of **4**. Hydrogen atoms are omitted for clarity.

Figure 2: Arrangement of units of **4** to form six-membered rings.

Table 1: Selected Bond Lengths (Å) and Bond Angles (deg) of **4**

Bond Lengths			
Ge ₁ Ge ₂	2.461 (5)	Ge ₁ C ₅₆	1.956 (3)
O ₁ Ge ₂	1.828 (2)	Ge ₁ C ₂₁	1.983 (3)
O ₁ C ₅₁	1.374 (3)	C ₅₁ C ₅₆	1.381 (3)
Ge ₂ C ₄₁	1.988 (3)	C ₅₄ O ₂	1.394 (3)
Ge ₂ C ₃₁	1.967 (3)	O ₂ H _{2a}	0.820
Ge ₁ C ₁₁	1.987 (3)	O ₂ H _{2b}	0.820
Bond Angles			
C ₅₁ O ₁ Ge ₂	120.50 (2)	C ₅₆ Ge ₁ C ₁₁	105.94 (11)
C ₅₁ C ₅₆ Ge ₁	117.80 (2)	C ₅₄ O ₂ H _{2b}	109.47
O ₁ Ge ₂ Ge ₁	91.09 (6)	O ₁ Ge ₂ C ₃₁	101.70 (10)
C ₅₆ Ge ₁ Ge ₂	87.66 (8)	C ₃₁ Ge ₂ C ₄₁	109.53 (12)
C ₄₁ Ge ₂ O ₁	103.40 (11)	O ₁ C ₅₁ C ₅₂	116.10 (3)
O ₁ C ₅₁ C ₅₆	122.80 (3)	C ₅₅ C ₅₄ O ₂	119.00 (3)

Then the cycloaddition induced by the germalcation might lead, after migration of a proton, to the expected 1,3-cycloadduct **4**. This is the first example of a cycloaddition reaction between a digermene and a paraquinone.

Scheme 1

Experimental

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Compounds were characterized by the usual analytical techniques: ^1H NMR, A.C.80 or 200 Bruker; ^{13}C { ^1H } NMR, A.C.200 Bruker; IR, Perkin-Elmer 1600 F.T.; Mass spectra, Ribermag R

10 10 (Cl / CH₄), API 100 Perkin-Elmer SCIEX (ES). Elemental analyses were done by the Centre de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse.

Scheme 2

Thermolysis of 1 in presence of parabenzoquinone:

A solution of 1* (0.28 g, 0.3 mmol) and parabenzoquinone (0.11 g, 1 mmol) in 3 mL of benzene was heated at 100°C for 3 d in a Carius tube. The benzene was evaporated in vacuo and the residue extracted with hot hexane. The mixture was filtered. After 2 d at 20°C, brown crystals were formed in the filtrate; they were isolated by decantation and identified as 4: 0.05 g (yield 17 %), mp 160-162 °C. ¹H NMR (C₆D₆) 200 MHz δ : 2.01 (s, 6 H, p-CH₃) and 2.03 (s, 6 H, p-CH₃), 2.30 (s, 12 H, o-CH₃) and 2.44 (s, 12 H, o-CH₃), 3.43 (s, 1 H, OH), 6.57 (s, 4 H, C₆H₂) and 6.60 (s, 4 H, C₆H₂), 6.61 (dd, ⁴J = 3 Hz, ³J = 8.5 Hz, 1 H, C₆H₃), 6.85 (d, ³J = 3 Hz, 1 H, C₆H₃), 6.99 (d, ³J = 8.5 Hz, 1 H, C₆H₃). ¹³C {¹H} NMR (C₆D₆) δ : 20.89 and 20.92 (p-CH₃), 24.58 and 25.56 (o-CH₃), 129.41, 129.49, 136.04, 137.89, 138.66, 138.76, 143.65, 144.23: C₆H₂; 118.85, 118.97, 121.63, 130.32, 148.77, 159.56: C₆H₃. MS (Cl / CH₄): 759 (M + 29), 730 (M), 611 (M- Mes). IR: 3213 cm⁻¹ (ν OH). Anal. calcd for C₄₂H₄₈Ge₂O₂, C₆H₁₄: C, 70.64; H, 7.66. Found: C, 70.44; H, 7.60 %. Crystals suitable for X-ray study were obtained by recrystallization from an ether / petroleum ether mixture (2 / 1). The filtrate when was analyzed by mass spectrometry revealed the presence of 3 (ES MS: = 1415 (M-3CH₃). It was impossible to isolate 3 in pure form. The precipitate was identified as 2 [1].

Crystal and Experimental Data for 4:

The structure was solved by direct methods using SHELXS96 (Sheldrick, 1996) and difmap synthesis using SHELXL96 (Sheldrick, 1996). All non-hydrogen atoms are anisotropic, and hydrogen atoms are isotropic. Hydrogen atoms were calculated at idealized positions using a riding model with different C—H distances for each type of hydrogen.

The isotropic displacement factors, U-iso, were adjusted to 50 % higher value of the bonded carbon atom (methyl) and 20 % higher (others). The hydroxy hydrogen was calculated and it is disordered over the two possible orientations since both are geometrically suitable. In each case, the OH group forms a six-membered ring through H-bonds. This ring formation results in the construction of a channel in which there are disordered solvent molecules. The location of these molecules in the channel was precluded by the high degree of disorder. The PLATON program CALC SQUEEZE was used to subtract the solvent contribution from the observed data. The identity of the solvent (hexane) was deduced from NMR and elemental analyses. This attribution also agrees with the geometry of the channels. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 135142, deposit@ccdc.cam.ac.uk.

Thermolysis of 1 in the presence of p-naphthoquinone:

A solution of 1 (0.28 g, 0.3 mmol) and p-naphthoquinone (0.07 g, 0.45 mmol) in 1.5 mL of benzene was heated at 100°C for 16 h in a Carius tube. The benzene was evaporated in vacuo and the residue (highly soluble in common solvents) was analyzed and identified as a mixture of oligomeric forms 5: ¹H NMR (CDCl₃) δ : 1.92-2.65 (m, 18 H, p-CH₃ and o-CH₃), 6.63 (s, 8 H, C₆H₂), 6.80-7.35 (m, 6 H, C₁₀H₆). Mass spectra showed the presence of 5a and 5b: MS (Cl / CH₄): 5a: 1090 (M), 5b: 780 (M).

Table 2: Data for the X-ray crystal structure analysis of 4

Crystal size (mm)	0.14 x 0.14 x 0.08
formula	C ₄₂ H ₄₈ Ge ₂ O ₂ , C ₆ H ₁₄
Fw	816.20
Crystal color / shape	Colourless / block
Crystal System	Trigonal
Space Group	R -3
a (Å)	36.483 (9)
b (Å)	36.483 (9)
c (Å)	17.583 (5)
β (°)	90
V (Å ³)	20268 (8)
Z	18
dc (g cm ⁻³)	1.204
μ (mm ⁻¹)	1.869
λ (Å)	1.54056
F(000)	6840
θ range (°)	2.42 to 69.90
No reflections measured	41656
No independant reflections (R _{int})	8562
Trans. range	0.57 to 0.90
h range	-45 to 45
k range	-44 to 44
l range	-21 to 21
R ₁ (obs / all data)	0.0353 / 0.0668
WR ₂ (obs / all data)	0.0640 / 0.0688
No parameters	428
No of restraints	0

Thermolysis of 1 in the presence of p-anthraquinone:

A solution of 1 (0.28 g, 0.3 mmol) and *p*-anthraquinone (0.09 g, 0.45 mmol) in 1.5 mL of benzene was heated at 100°C for 3 d in a Carius tube. The benzene was evaporated in vacuo and the residue (highly soluble in common solvents) was analyzed and identified as a mixture of oligomeric forms 6: ¹H NMR (CDCl₃) δ: 1.85-2.85 (m, 18 H, *p*-CH₃ and *o*-CH₃), 6.80 (s, 8 H, C₆H₂), 7.50-8.54 (m, 8 H, C₁₄H₈). Mass spectra showed the presence of 6a: MS (Cl / CH₄): 1141 (M + 1).

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