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Photochemical Isomerization of 1-Germa-2,4-cyclohexadienes

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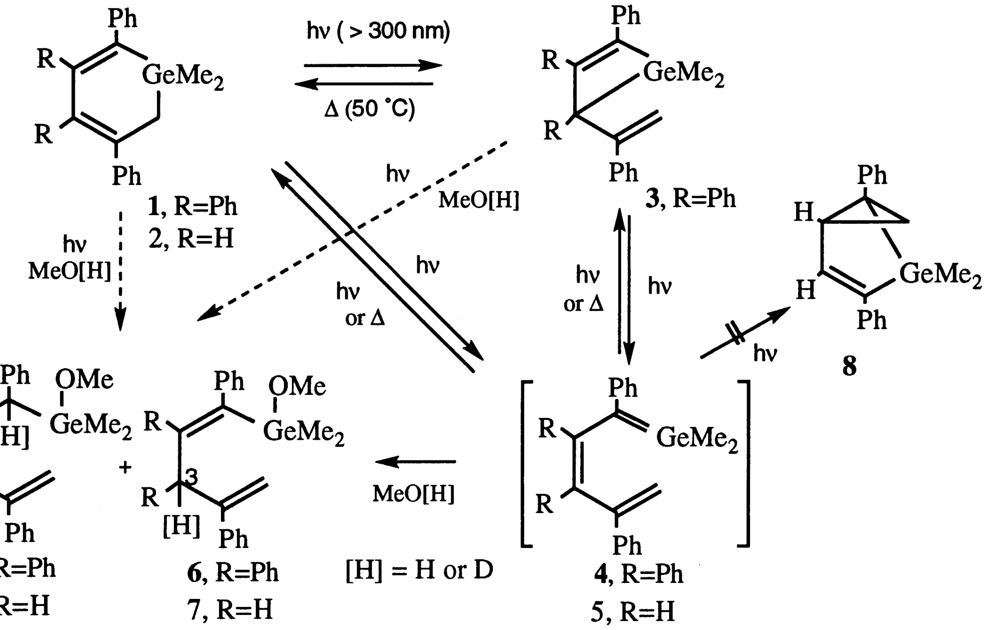
Tetraphenylgermacyclohexadiene photochemically isomerized to the 4-vinylgermacyclobutene. In contrast, diphenylgermacyclohexadiene remained unchanged on irradiation in benzene, but in the presence of methanol it was converted to the methoxygermane probably through the 1-germahexatriene intermediate.

Photochemical isomerization of 1,3-cyclohexadienes and hexatrienes has been one of the most fundamental topics of organic photochemistry.[1)] Silicon analogs of the 1,3-cyclohexadienes, 1-sila-2,4-disilacyclohexadienes have been reported to undergo photochemical isomerization to give a 4-vinylsilacyclobutene or a silabicyclo[3.1.0]hexa-3-ene depending on the number of phenyl substituents on the cyclic diene part.[2)] We describe herein the first photochemical conversions of two germanium analogs of 1,3-cyclohexadiene, namely 2,3,4,5-tetraphenyl- and 2,4-diphenyl-germa-2,4-cyclohexadienes **1** and **2**.[3,4)]

On irradiation of a degassed C_6D_6 solution of **1** in an NMR tube with a 450-W high pressure Hg arc lamp with a Pyrex filter, two types of NMR signals newly appeared; two singlets due to the Ge-Me groups at δ 0.38 and 0.62 and two doublets at δ 5.53 and 5.71 which are characteristic for those of terminal methylene protons.[5)] After irradiation for 10 min, all signals assignable to **1** were displaced by those new signals and this indicates

Scheme



that on irradiation **1** was quantitatively isomerized to 4-vinylgermacyclobutene **3**. Then, the irradiation of **3** formed in C_6D_6 containing excess amounts of methanol at 0 °C for 15 min gave a mixture composed of **1**, **3** and a methoxygermane in ca. 1:1:2 ratio. The structure for the methoxygermane was assigned to either **6** or **6'** on the basis of its NMR spectra.[6] Interestingly, on heating in benzene containing excess amounts of methanol at 45 °C for 5 min **3** reverted to **1** quantitatively without formation of **6** (**6'**). On the other hand, **1** in C_6D_6 containing methanol was irradiated for 1 min to give **6** (**6'**) in 70% yield accompanied by a trace amount of **3**. Since the germanium-carbon double bonded species are known to be highly reactive toward alcohol,[7] the formation of methoxygermane **6** (**6'**) could be rationalized by intermediary of **4**.[2,8] However, the results indicate that thermal isomerization of **3** to **1** may not proceed via **4** in contrast to the case of the silicon analog.[2]

Diphenyl derivative **2** in degassed C_6D_6 in an NMR tube was irradiated under similar conditions for 45 h, but any noticeable spectral change was not recognized. However, irradiation of **2** for 10 min in C_6D_6 containing methanol readily gave **7** and **7'** in 10 and 39%, respectively.[9] These results indicate that 1-germahexatriene **5** should be generated and trapped efficiently by methanol. In the absence of methanol, **5** should revert thermally quite efficiently to the starting diene **2**. In contrast to the silicon analog,[2] the corresponding 2-germabicyclo[3.1.0]hexa-3-ene **8** was not detected in the photoproducts, the reason for which is not certain at this moment. Direct photochemical methanolysis of **1** and **2** leading to the corresponding methoxygermanes may be less probable but conceivable as the other possible reaction paths (Scheme).

1-Germa-2,4-cyclohexadienes **1** and **2** show their UV maxima at the same wavelength (330 nm), but the intensity of the maxima is much stronger for **2**. This implies that the germacyclohexadiene ring of **1** may be more sterically strained, and this may cause **1** to be more photochemically labile in benzene.

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References

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2) Y. Nakadaira, S. Kanouchi, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 5621 (1974).
3) **1**: mp 136-142 °C; MS m/z 474 (M^+, ^{74}Ge); ^{1}HNMR (C_6D_6) δ 0.36 (s, 6H), 2.33 (s, 2H), 6.95 (m, 20H); UV (cyclohexane) λ_{max} 330 nm (ε 7760).
4) **2**: an oil: MS m/z 322 (M^+, ^{74}Ge); ^{1}HNMR (C_6D_6) δ 0.40 (s, 6H), 2.02 (d, J=1.8 Hz, 2H), 6.46 (dt, J=6.7 and 1.8 Hz, 1H), 6.92 (d, J=6.7 Hz, 1H), 7.3 (m, 10H); UV (cyclohexane) λ_{max} 330 nm (ε 21000).
5) **3**: MS m/z 474 (M^+, ^{74}Ge); ^{1}HNMR (C_6D_6) δ 0.38 (s, 3H), 0.62 (s, 3H), 5.53 (d, J=0.8 Hz, 1H), 5.71(d, J=0.8 Hz, 1H), 7.1 (m, 20H).
6) **6** (**6'**): MS m/z 475 (M^+-OMe, ^{74}Ge), 371 (M^+-$GeMe_2OMe$, 100%); ^{1}HNMR (C_6D_6) δ 0.28 (s, 3H), 0.37 (s, 3H), 3.36 (s, 3H), 4.66 (s, 1H), 5.34 (d, J<0.1 Hz, 1H), 5.77 (d, J>0.1 Hz, 1H). The signal at δ 4.66 was missing on irradiation in the presence of methanol-d_1 .
7) J. Satgé, *Adv. Organomet. Chem.*, **21**, 241 (1982).
8) The structure **6** having a hydrogen at C_3 suggests that the direct photo-induced methanolysis of **3** may be another possible route to **6** as indicated in Scheme.
9) **7**: MS m/z 354 (M^+, ^{74}Ge);^{1}HNMR (C_6D_6) δ 0.29 (s, 6H), 3.39 (s, 3H), 3.28 (d, J=7.0 Hz, 2H), 5.13 (q, J=1.6 Hz, 1H), 5.37 (dt, J=1.6 and 0.8 Hz), 6.18 (t, J=7.0 Hz, 1H), 7.19 (m, 10H). **7'**: MS m/z 354 (M^+, ^{74}Ge); ^{1}HNMR (C_6D_6) δ 0.18 (s, 3H), 0.21 (s, 3H), 3.33 (s, 3H), 3.88 (d, J=12.3 Hz, 1H), 5.31 (dd, J=2.0 and 2.1 Hz, 1H), 5.50 (dd, J=2.0 and -1Hz, 1H), 6.14 (dd, J=12.3 and 11.3 Hz, 1H), 6.26 (ddd, J=11.6, 2.0, and -1 Hz, 1H), 7.19 (m, 10H). On the NMR spectra of **7** and **7'** obtained on irradiation in the presence of methanol-d_1, the signal at δ 3.28 was reduced to one-half, and that at δ 3.88 was almost missing.

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