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Photochemistry of Phenylpentamethyldigermane

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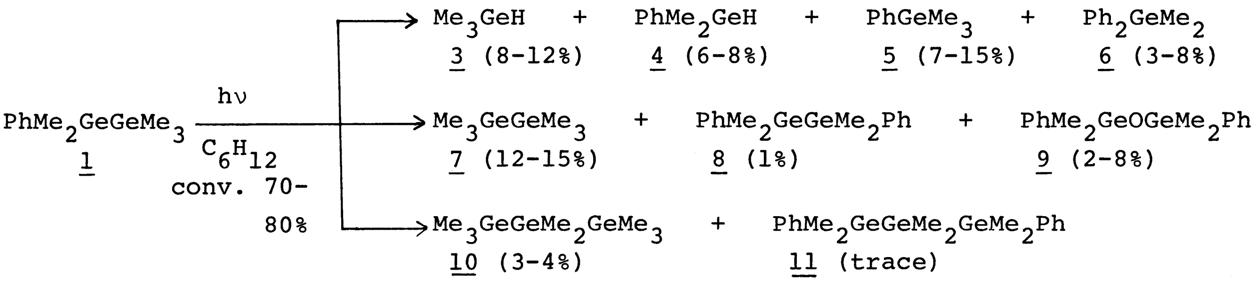
Photolysis of phenylpentamethyldigermane afforded hydrogermanes and digermanes, as main products. These are derived from two germyl radicals generated by photo-induced homolysis of the germanium-germanium bond. Dimethylgermylene is shown to be evolved also on the photolysis.

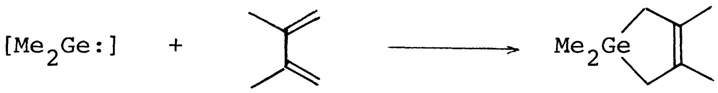
Recently, photochemistry of organosilicon compounds having a σ(Si-Si)-π(C-C) conjugated system has been investigated extensively,[1)] and from the chemistry of group 4B element compounds photochemical behaviors of the germanium analogue is particularly intriguing. Here we report for the first time the photoreaction of phenylpentamethyldigermane (1).[2)] Photolysis of 1 causes homolysis of a germanium-germanium bond which leads to the formation of germyl radicals and a germylene.



Scheme 1.

Irradiation of 1 (0.3-0.07 mmol·dm^{-3}) in cyclohexane with a 110-W low pressure Hg arc lamp at room temperature under Ar atmosphere gave monogermanes 3-6, and digermanes 7-8 together with digermanoxane 9. Interestingly, small amounts of trigermanes 10-11 were also detected in the photolysate. The results are summarized in Scheme 1.[3)] Essentially same results are obtained on the irradiation of 1 in benzene under similar conditions. In addition to hydrogermanes 3 and 4, formation of digermanes 7 and 8 seems indicative of the intermediary of the germyl radicals 12 and 13 generated by homolytic cleavage of the germanium-germanium bond on irradiation. This is further substantiated by the presence of bicyclohexyl in the photo-products detected by means of GC-MS. In agreement with this finding, the photolysis of 1 in cyclohexane containing chloroform gave phenyldimethylchlorogermane (14, 60%) and trimethylchlorogermane (15).[4] Along with dimerization, germyl radicals generated are expected to undergo a similar disproportionation of a silyl radical to give hydrogermanes 3 and 4, and germenes 16 and 17 as depicted in Scheme 2.[5] Germenes are known to react with methanol quite effectively to give methoxylgermanes.[6] However, the photolysis of 1 in benzene containing a large excess of methanol failed to give a detectable amount of the corresponding methoxylgermanes. This implies that hydrogermanes 3 and 4 must be derived from the corresponding germyl radicals 12 and 13 by means of hydrogen-abstraction rather than disproportionation.

On the other hand, occurrence of germane 5 in the photolysate may suggest that dimethylgermylene is evolved on the photolysis. This is supported by the trapping experiment, namely the photolysis of 1 in cyclohexane containing 15 molar excess of 2,3-dimethylbutadiene gave 1,1,3,4-tetramethyl-1-germacyclopenta-3-ene (18, 3%) together with 5 (2.5%).[7] It is noted that in the trapping reaction, hydrogermanes 3 and 4, digermanes 7 and 8, and digermanoxane 9 are produced in expected yields, but, 10 and 11 are not detected even by means of GC-MS. This implies that dimethylgermylene is able to insert a germanium-germanium bond, and formation of unexpected trigermanes 10 and 11 are accounted for by insertion reaction of the germylene into 7 and 8 generated from coupling of trimethylgermyl and phenyldimethylgermyl radicals, respectively. This is readily proved by photolysis of a germylene precursor, 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germa-norbornadiene[7] in the presence of 7. This produces 10 in 7% yield, and constitutes the first example of insertion of the germylene into a germanium-germanium bond. This is in contrast to the behavior of a silylene which undergoes insertion into only activated silicon-silicon bond, such as that of 1,2-disilacyclobutane.[8] 6 is probably originated from 8 by means of photochemical generation of dimethylgermylene.[9] Formation of dimethylgermylene and 5 can be also expalined by 1,2-phenyl shift of 1.[10]



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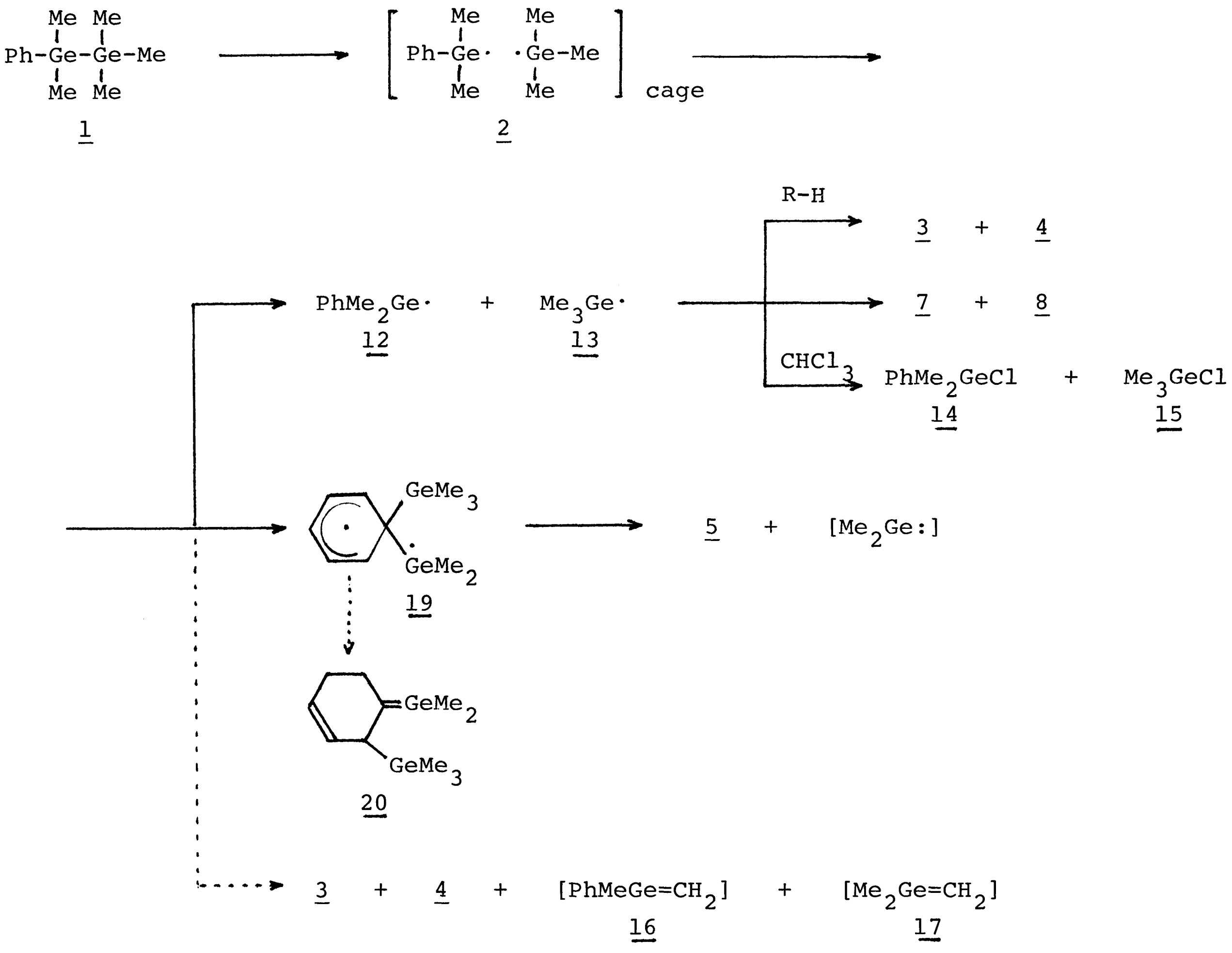
The origin of oxygen of 9 is unclear at this moment. In spite of efforts of minimizing moisture and air, 9 was still obtained in appreciable amounts.

These results described above can be rationalized on the basis of analogous reaction mechanism proposed for the photolysis of aryldisilanes as shown in Scheme 2.[1e] In contrast to the case of aryldisilanes, a formal 1,3-germyl migration to 20 is no longer a major course of reaction path in the photolysis of 1. The trapping product of 20 is not detected even on the photolysis of 1 in benzene containing methanol. Instead, more pronounced formation of radical coupling and abstraction products are noted in the germanium analogue. The differences in the photolysis between these two series may be ascribed to the differences in reactivities of



Scheme 2.[11]

the corresponding radical intermediates. The disproportionation of group 4B element-centered radicals proceeds more effectively for silyl radicals than germyl radicals. π-Bonding of carbon must be formed more effectively with a silicon atom than with a germanium atom.[12,13] The ipso-substitution of silyl radicals occurs more readily than that of germyl radicals.[14] The bond dissociation energy of germanium-carbon bond is less than that of a silicon-carbon bond.[15] On addition of a germyl radical to the benzene ring, loss of the resonance energy can not be compensated with gain of σ bond formation with a ring carbon atom. The ipso-substitution by a germyl radical does not occur smoothly as the case of a silyl radical.

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3) All new photo-products are identified by comparison with their physicochemical properties with those prepared independently.

4) Since the retention time of 15 on GLC was partially overlapped with that of the solvent employed. The yield of 15 produced could not be estimated.

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9) 6 could be prepared also by addition of phenyldimethylgermyl radical to benzene followed by loss of hydrogen. However, no deuterium was incorporated into 6 on the irradiation in C_6D_6.

10) We thank the refree for constructive criticism on this point.

11) Laser flash photolysis (λ=266 nm, pulse width 5 ns, power 10 mJ per pulse) of 1 in cyclohexane at 293 K gave three transient absorption bands; 320, 370, and 420 nm. The absorption of 320 nm observed was assigned to phenyldimethylgermyl radical and that of 420 nm observed was tentatively assigned to dimethylgermylene. The absorption of 370 nm is unclear at this moment. Similar results for phenylpentamethyldisilane were obtained. K. Mochida and M. Wakasa, unpublished results.

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