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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Strained Ring Compounds of Silicon and Germanium

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To cite this Article Weidenbruch, Manfred , Schäfer, Annemarie , Grimm, Fred-Thomas and Thom, Karl-Ludwig(1989) 'Strained Ring Compounds of Silicon and Germanium', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 41: 1, 229 — 234

To link to this Article: DOI: 10.1080/10426508908039710

URL: <http://dx.doi.org/10.1080/10426508908039710>

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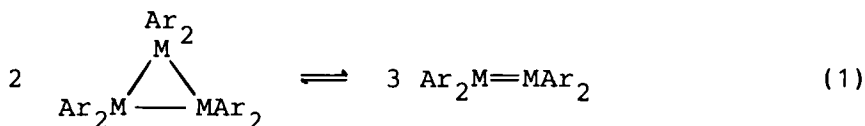
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STRAINED RING COMPOUNDS OF SILICON AND GERMANIUM

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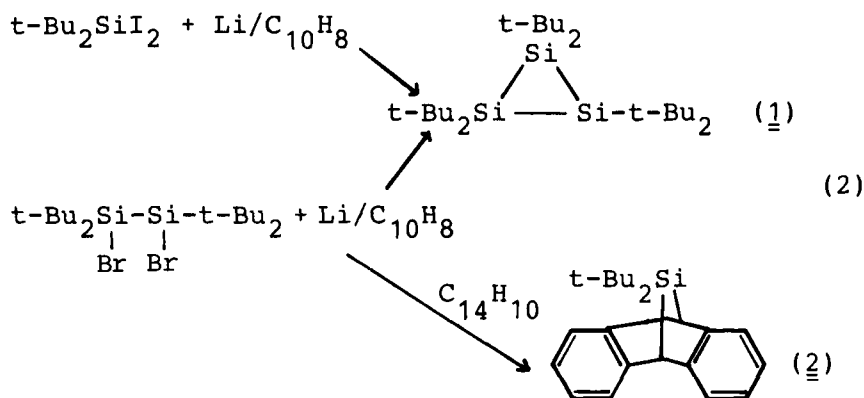
Abstract Several three- and four-membered rings of silicon and germanium have been obtained by reductive halogen elimination from dihalosilanes or -germanes, respectively. Among these rings hexa-tert-butylcyclotrisilane and -cyclotrigermane reveal the largest M-M bond lengths within these series of compounds. The chemical behaviour of the cyclotrisilane skeleton is characterized by two paths which can be classified according to the number of Si-Si bond cleavages. In the "dark" one Si-Si bond is cleaved leading to open-chained trisilanes or to ring insertion products. Photolysis of hexa-tert-butylcyclotrisilane proceeds by cleavage of two Si-Si bonds giving di-tert-butylsilylene and tetra-tert-butylidisilene which can be trapped by various multiply bonded compounds. These trapping reactions lead to several types of small or medium-sized novel silacycles.

The first homoatomic three-membered cycles of silicon^{1a}, germanium^{1b}, and tin^{1c} were prepared by Masamune et al. and subsequently photolytically converted into the corresponding dimetallenes¹ (Eq. (1)).



M = Si, Ge, Sn; Ar = 2,6-Dialkylphenyl

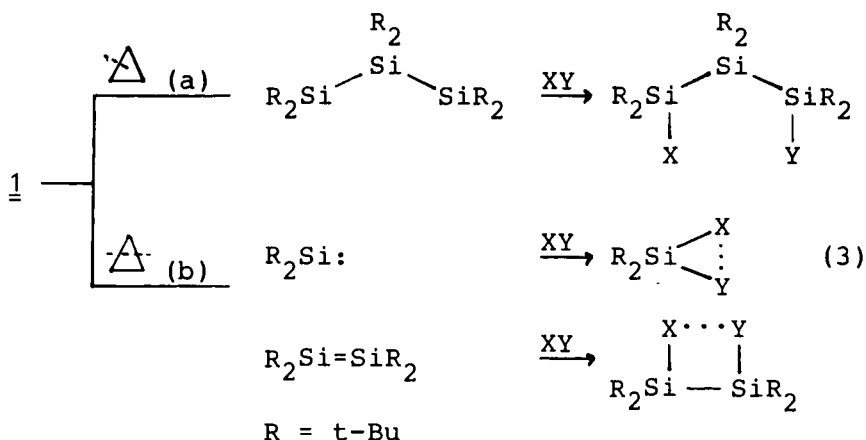
Earlier attempts to obtain hexa-tert-butylcyclo-trisilane (1), the most strained among these cycles, gave only acyclic compounds². However, in 1984 we succeeded in the preparation of 1 by halogen abstraction from di-tert-butylldiiodosilane or from 1,2-dibromo-1,1,2,2-tetra-tert-butylldisilane, respectively³. The formation of 1 presumably occurs via di-tert-butylsilylene which can be trapped by anthracene to give the 7-silabicyclo[2.2.1]heptadiene (2)⁶ (Eq. (2)).



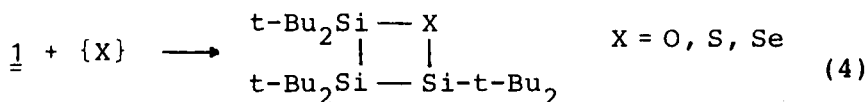
1 exhibits the largest Si-Si bonds yet found in a silacycle. The analogously substituted cyclo-trigermene reveals a nearly identical molecular structure of D_3 -symmetry⁴. Reducing the steric congestion of 1 by replacement of one tert-butyl group per silicon atom by the less bulky cyclohexyl or isopropyl groups leads either to the three- or to the four-membered homoatomic cycles depending on the reaction conditions employed⁵.

The reactivity of 1 has been studied in greater details. Its chemical behaviour can be classified according to the number of Si-Si bond cleavages (Eq. (3)).

In the "dark" the reaction of 1 with oxygen, sulfur, and grey selenium follows route (a) yielding the

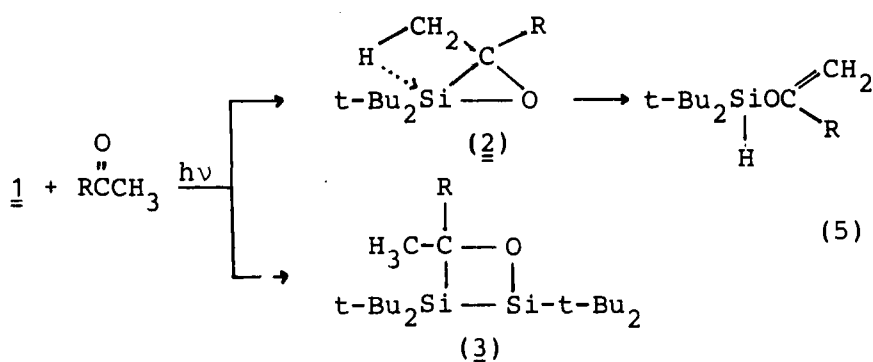


ring-extended oxa-, thia- and selenatrisiletanes⁶ (Eq. (4)). The photochemically or catalytically induced reactions follow route (b) with simultaneous formation of

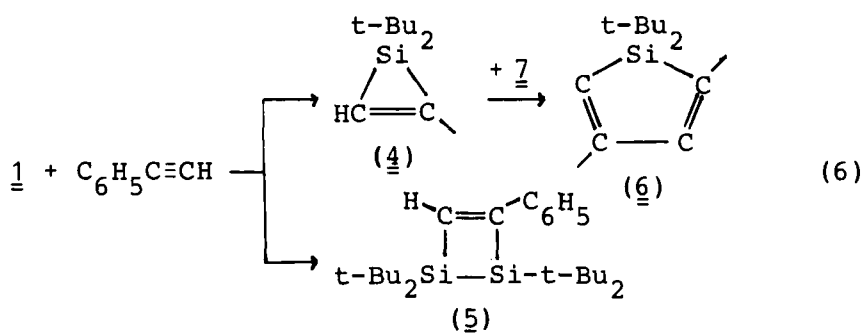


silylene and disilene as cleavage products. Photolysis of 1 in the presence of ketones leads to the addition products of both intermediates across the CO double bond giving the oxasiliranes (2) and the oxadisiletanes (3). Whereas 2 cannot be isolated, the compounds 3 are stable in the solid state. In solution, however, the addition products formed from the enolizable ketones acetone or acetophenone rearrange to the acyclic silanyl or disilanyl enol ethers, respectively⁷ (Eq. (5)).

The palladium-salt catalyzed reactions of 1 follow the same mechanism as proposed for the photochemically induced ring cleavage. Trapping of the cleavage products by phenylacetylene (7) should give the silacyclopropene (4) and the 1,2-disilacyclobutene (5). Whereas 5 can be

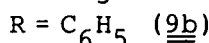
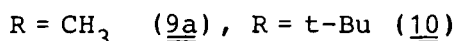
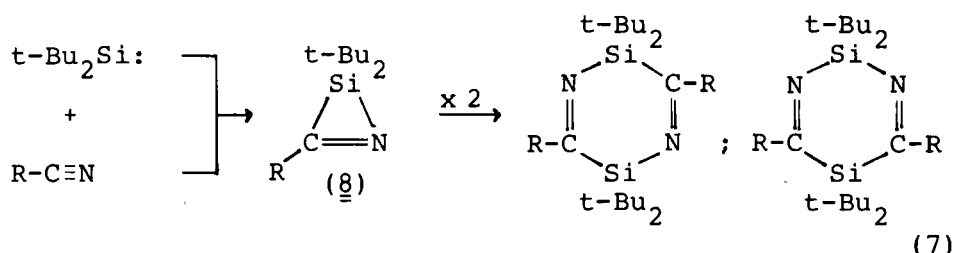


isolated, 4 undergoes a further two atom insertion reaction yielding the silol (6)⁷ (Eq. (6)).

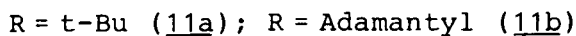
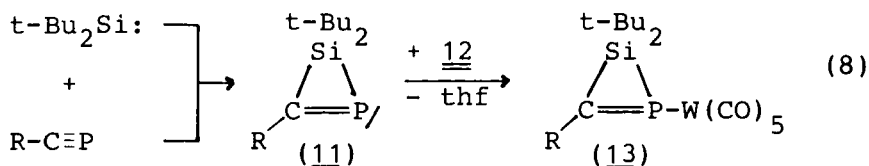


According to the different stabilities of the resulting compounds in several cases only the silylene or the disilene addition product can be isolated from the reaction mixture. Photolysis of 1 in the presence of nitriles is thought to proceed by a [2+1] addition of the silylene across the CN triple bond yielding the unstable rings (8) which dimerize to give the diazadisilacyclohexadienes (9) and (10)⁸ (Eq. (7)).

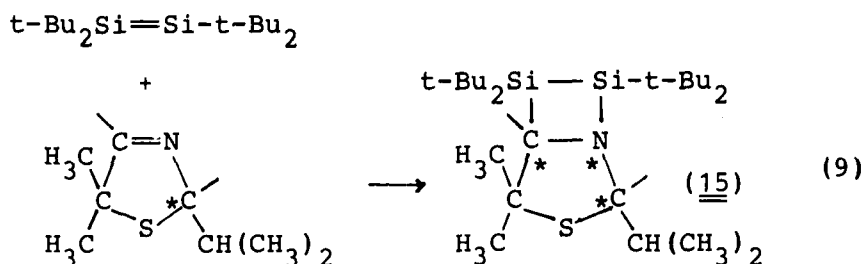
In solution, 9a rearranges within two days by a twofold hydrogen transfer from the methyl carbon atoms to the nitrogen atoms leading to a new heterocyclic compound containing two exocyclic CC double bonds⁸.



The suggested formation of the intermediate 8 by silylene addition to nitriles is indirectly confirmed by an analogous reaction of 1 with phospho-alkynes. Due to the larger P=C bond in this case the silylene addition products are isolable as oily liquids. The phosphasilirenes (11) react with the tungsten complex $\text{W(CO)}_5(\text{thf})$ (12) by replacement of tetrahydrofuran (thf) giving the phosphane complex (13)⁹ (Eq. (8)).



Hitherto only one case is known where the disilene addition product is more stable as the corresponding silylene adduct. Photolysis of 1 in the presence of racemic 3-thiazoline proceeds diastereoselectively by disilene addition to the CN double bond yielding the azadisilacyclobutane derivative (14)¹⁰ (Eq. (9)).



Acknowledgments Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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