A Novel Silanediyl–Germanediyl (Silylene–Germylene) Exchange in 1,1-Dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene

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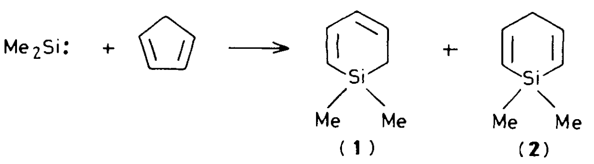
Photochemically generated dimethylsilanediyl reacts with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene to bring about a silanediyl–germanediyl exchange.

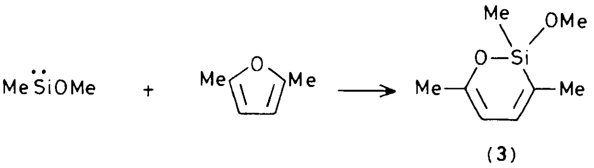
The reactions of dimethylsilanediyl with cyclic dienes have been the subject of several investigations.[1—6] For example, thermally generated dimethylsilanediyl reacts with cyclopentadiene[3] to cause ring expansion and the formation of products (**1**) and (**2**), reaction (1). Similarly, methoxy(methyl)silanediyl reacts with 2,5-dimethylfuran to give the ring expanded product, (**3**), in low yield,[4] reaction (2).

However, recent work by Sakurai, Kobayashi, and Nakadira[6] has shown that ring expansion does not take place when the cyclic diene being used as a substrate is a 1-silacyclopentadiene. In this instance a silanediyl–silanediyl exchange is the dominant reaction. This prompted us to report our finding that photochemically generated dimethylsilanediyl reacts with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene[7] (**6**) and brings about a silanediyl–germanediyl exchange.

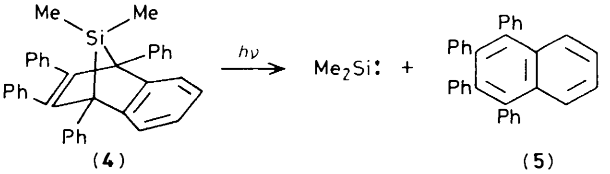
Dimethylsilanediyl was generated by photolysis of (**4**), (1 ×



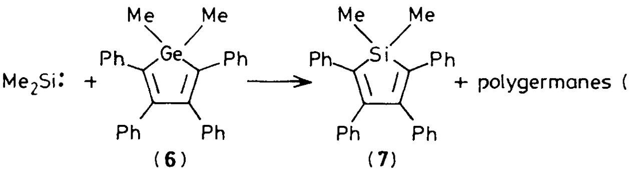
(1)



(2)



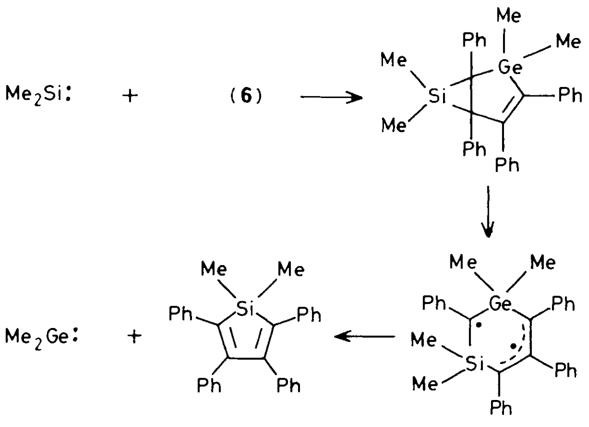
(3)



(4)

10^{-2} M) at 300 nm and 25 °C in benzene as solvent.[8] When the germole (**6**) (1×10^{-2} M) was present a silanediyl–germanediyl exchange took place giving (**5**), (**7**), and polygermanes as the major products, reactions (3) and (4). Yields were quantitative at 25% conversion of (**4**). All of the products, with the exception of the polygermanes, were identified by g.c.–mass spectroscopy and by comparison with authentic samples.[7–9] The polygermanes were characterised by g.c.–mass spectroscopy alone and the major product contained at least four dimethylgermanediyl units. Similar results were obtained when dodecamethylcyclohexasilane [c-$(Me_2Si)_6$] was used as the photochemical source of the silanediyl,[10] reaction (5).

$$\text{c-}(Me_2Si)_6 \xrightarrow{h\nu} \text{c-}(Me_2Si)_5 + Me_2Si: \qquad (5)$$



(6)

We presume that the rather unusual silanediyl–germanediyl exchange involves initial formation of a vinylcyclopropane which subsequently rearranges and extrudes dimethylgermanediyl, reaction (6).

Interestingly, vinylcyclopropane formation has been proposed for all of the reported reactions of silanediyls with cyclic dienes. However, the products of reactions (1), (2), and (6) show that each decomposes by a unique route.

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