

GERMATHIIRANE INTERMEDIATE FROM THE REACTION OF GERMYLENE
WITH THIOKETONES

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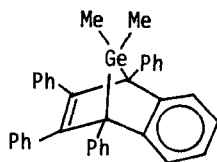
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Summary: Digermadithiolane was obtained from the reaction of dimethylgermylene and thioketones via germathirane intermediate. In the gas phase reaction digermathietane was obtained, probably by the [2+2] cycloaddition of tetramethyldigermene with thioketone.

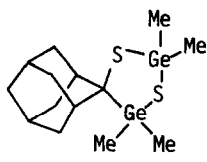
Recently renewed activities in small ring systems of cyclosilane concern the nature of silicon bonding resulting from strain structure, and we have been successful in the isolation and characterization of sterically protected silaoxirane and silathirane¹⁾.

In attempt to gain the definitive evidence for silicon analogues germa-cyclopropane with heteroatom²⁾, we studied the reaction of dimethylgermylene with thioketone, providing for the first time germathirane intermediate.

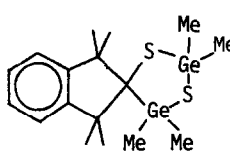
Dimethylgermylene generated by thermolysis of 7-germanorbornadiene 1³⁾ (1 mmol) reacted smoothly with adamantanethione (2 mmol) or 1,1,3,3-tetramethyl-2-indanethione (2 mmol) in benzene at 70°C to give digermadithiolane 2⁴⁾ (38%) and adamantylideneadamantane (4%) or digermadithiolane 3⁵⁾ (11%) respectively, along with 1,2,3,4-tetraphenylnaphthalene. The most economical mechanistic rationalization for the formation of 2 and 3 is addition of germylene to thioketone to form germathirane 4, elimination of sulfur to form germathione 5, and the insertion of 5 into 4. Thus, above results provided a first example of the formation of germathirane in the reaction of germylene and thioketone, which reacts with germathione to give the ring expansion products, although the insertion of germathione into thirane have been known⁶⁾.



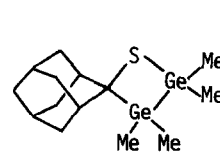
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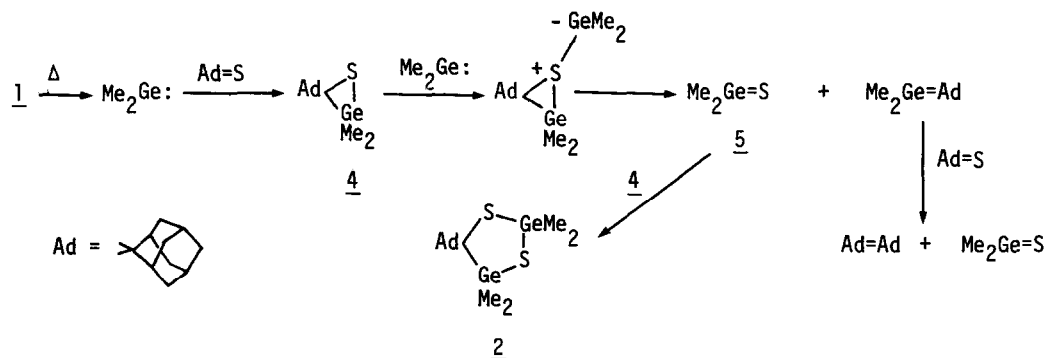
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3



4



Although germylene is known to polymerize significantly under the reaction conditions, we studied the flow copolyrolysis with adamantanethione in gas chromatochamber at 250°C. Digermadithiolane 2 was obtained along with a surprising third product, digermathietane 6⁷⁾ in 50-60% yield. The yield of 6 was maximum at equal mole ratio of 1 and adamantanethione, but decreased with increasing of concentration of thioketone. Thus, it is reasonable to suggest that germylene dimerizes at first to form digermene followed by [2+2] cycloaddition with thioketone. Another conceivable route is germylene insertion into germathirane intermediate, but this path is not likely for three membered ring compounds from the reaction of carbene analogy⁸⁾.

References and Notes

- 1) (a) W. Ando, M. Ikeno and A. Sekiguchi, *J. Am. Chem. Soc.*, 1978, 100, 3613; (b) W. Ando, Y. Hamada, A. Sekiguchi and K. Ueno, *Tetrahedron Lett.*, 1982, 23, 5323; (c) W. Ando, Y. Hamada, A. Sekiguchi and K. Ueno, *Tetrahedron Lett.*, 24, 4033.
- 2) P. Riviere, M. Riviere-Baudet and J. Satge, *J. Organomet. Chem.*, 1975, 96, C7.
- 3) M. Schriewer and W. P. Neumann, *J. Am. Chem. Soc.*, 1983, 105, 897.
- 4) ¹H-NMR (CCl_4, δ) 0.72(s,6H), 0.82(s,6H), 1.33-2.87(m,14H). Mass (m/e) 406 (M^+).
- 5) mp. 144.5-145.5°C. ¹H-NMR (CCl_4, δ) 0.78(s,6H), 0.92(s,6H), 1.56(s,12H), 7.20(s,4H). Mass (m/e) 444(M^+). Elemental Analysis; Calcd for $\text{C}_{17}\text{H}_{28}\text{S}_2\text{Ge}_2$: C,46.22, H,6.38. Found: C,46.23, H,6.40.
- 6) J. Barrau, M. Bouchaut, H. Lavayssiere, G. Dousse and J. Satge, *J. Organomet. Chem.*, 1983, 243, 281.
- 7) ¹H-NMR (CCl_4, δ) 0.60(s,6H), 0.70(s,6H), 1.20-2.60(m,14H). Mass (m/e) 374 (M^+). Compound 6 is very air sensitive, but thermally stable. The insertion of sulfur into Ge-Ge bond was found in the reaction of 6 and S_8 in benzene at 80°C.
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