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REACTION OF GERMYLENE WITH THIOKETENES: SYNTHESIS OF ALKYLIDENEDIGERMATHIETANES

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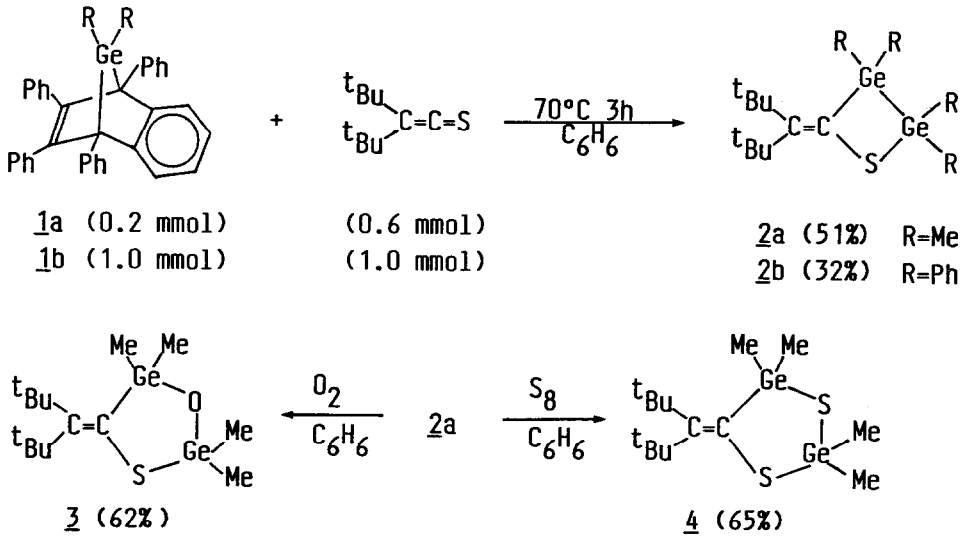
Summary: In the reaction of dimethyl- or diphenylgermylene with di-tert-butylthioketene alkylidenedigermathietanes were obtained, probably via alkylidenegermathiiranes. The exact structure of alkylidenedigermathietane 2b was confirmed by X-ray crystal analysis.

In recent years, interest in the chemistry of small ring compounds has remarkably increased because of its unique properties resulting from high strain energy. Introduction of exomethylene to three membered ring skelton increases strain energy and isomerize via trimethylenemethane analogues.[1] In contrast to rather extensive studies of alkylidenecyclopropanes and their heterocyclic analogues, there is no report on the chemistry of germanium analogues. Recently, we have shown that the reaction of germylene with thioketone gives isolable germathiirane.[2] Now, in the hope of the direct synthesis of alkylidenegermathiiranes, we studied the reaction of germylene with di-tert-butylthioketene.

Thermolysis of 7,7-dimethyl- or 7,7-diphenyl-7-germanorbornadiene 1a,b[3] and di-tert-butylthioketene[4] in benzene at 70°C produced alkylidenedigermathietanes 2a[5] or 2b mainly along with 1,2,3,4-tetraphenylnapthalene. 2a could be isolated by preparative GLC, but it is very air sensitive and easily oxidized to form 3[6]. Elemental sulfur also reacts with 2a to yield 4[7]. 2b could be purified by flash chromatography and it is very stable in the atmosphere of oxygen or moisture in contrast to lability of 2a toward oxygen.



The ^{1}H-NMR, ^{13}C-NMR, mass spectroscopy, and elemental analysis of 2b prove its structure. (^{1}H-NMR($CDCl_3$,δ) 1.15(s,9H), 1.74(s,9H), 7.30-7.87(m,20H). ^{13}C-NMR ($CDCl_3$,δ) 32.41(q), 33.29(q), 41.27(s), 41.68(s), 128.11(d), 128.46(d), 128.98 (d), 132.69(s), 134.21(d), 134.62(d), 136.91(s), 139.67(s), 161.98(s). Mass m/e 626(M^+). Elemental analysis; Calcd for $C_{34}H_{38}Ge_2S$: C,65.45, H,6.14. Found: C,65.53, H,6.27.)

The single crystal X-ray diffraction study for 2b is also consistent with the proposed structure. The crystal of 2b are triclinic and space group $P\bar{1}$ with cell dimensions a=11.355(1), b=14.511(1), c=19.070(3), α=93.76(1), β=90.38(2), γ=101.66(1); V=3070.0(5)Å^3 (Z=4).[8] Intensity data were collected on a four circle diffractometer with Mo Kα radiation using ω-2θ scans. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically to R=0.088 for 5427 observed reflections ($|F|>3\sigma|F|$, $3<\theta<55°$). Figure 1 shows ORTEP diagrams for 2b.

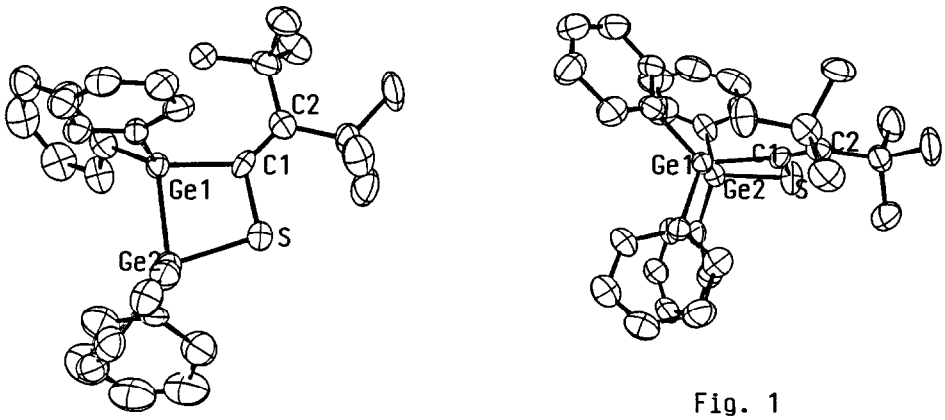
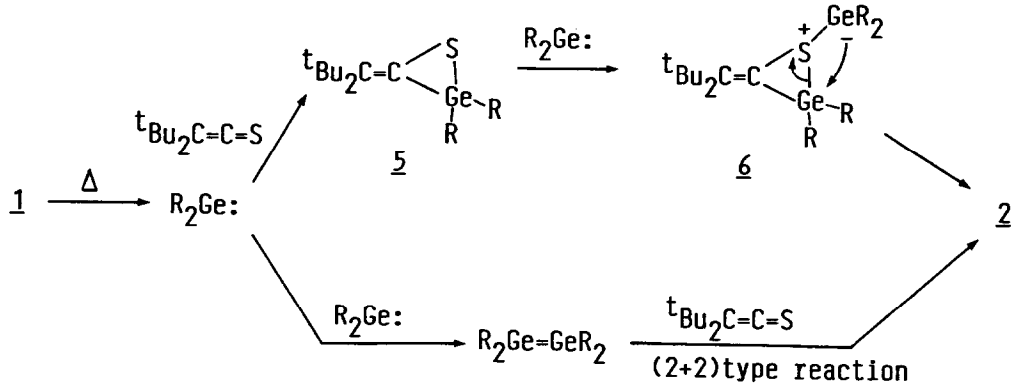


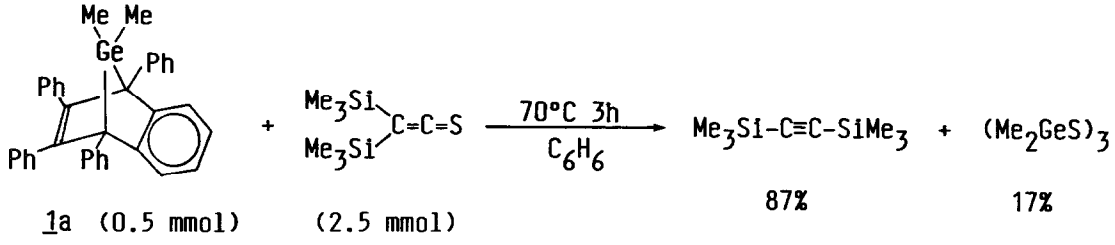
Fig. 1

The four membered ring consisting of Ge(1), Ge(2), S, C(1) has a puckered structure in which the dihedral angle formed by plane Ge(1), Ge(2), S and plane Ge(1), S, C(1) is average 15.4° in two molecules. The bond angle of C(1)-Ge(1)-Ge(2), Ge(1)-Ge(2)-S, Ge(1)-C(1)-S, and C(1)-S-Ge(2) are 85.6(4), 78.7(2), 99.3(7), and 94.8(5)°,respectively. The bond lengths of Ge(1)-Ge(2) (2.406(2)), Ge(1)-C(1)(2.020(15)), Ge(2)-S(2.242(6)), and C(1)-S(1.847(16)Å) in the ring are consistent with those of single bonds, and C(1)-C(2)(1.31(2)Å) with the double bond length.

Product 2 appears to be derived from either alkylidenegermathiirane 5 followed by ylide 6 formation and migration or (2+2) type reaction of thioketene with digermene. But latter one seems to be unlikely, because in our conditions germylene generated gently and the concentration of germylene is too low to dimerize to form digermene.

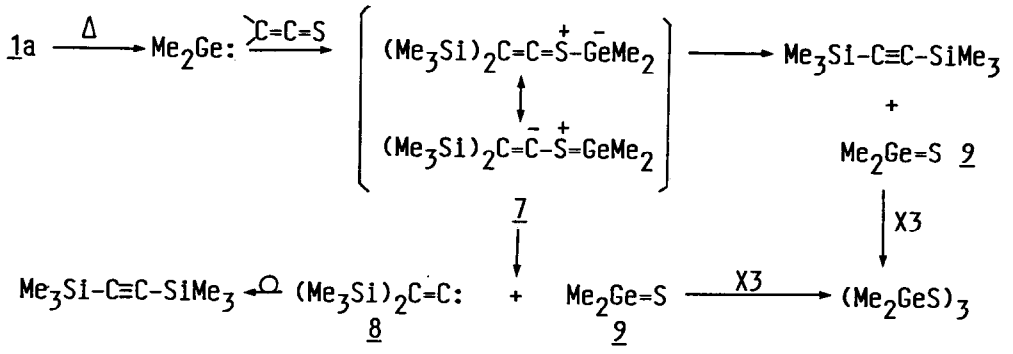


In the reaction of germylene with bis(trimethylsilyl)thioketene[9] bis(trimethylsilyl)acetylene (87%) and $(Me_2GeS)_3$ (17%) were obtained, along with 1,2,3,4-tetraphenylnapthalene. Digermathietane or germathiirane were not formed in this reaction.



1a (0.5 mmol) (2.5 mmol)

These products imply addition of germylene to thioketene to give germylthiocarbonylylide intermediate 7 which decomposes directly to acetylene and germathione. Alternatively, 7 decomposes to alkylidene carbene 8 and germathione 9, followed by silyl migration.



References and Notes

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5) 2a purified by GLC was contaminated by a small amount of 3.
2a ^{1}H-NMR($CDCl_3$,δ) 0.72(s,6H), 0.77(s,6H), 1.21(s,9H), 1.53(s,9H).
Mass m/e 378(M^+).

6) 3 ^{1}H-NMR($CDCl_3$,δ) 0.70(s,6H), 0.77(s,6H), 1.36(s,9H), 1.63(s,9H).
Mass m/e 394(M^+).

7) 4 ^{1}H-NMR($CDCl_3$,δ) 0.90(s,12H), 1.40(s,9H), 1.62(s,9H).
Mass m/e 410(M^+).

8) The asymmetric unit contains two crystallographically independent molecules, and they were quite similar in conformation, bond angles, and bond lengths. The bond angles and lengths of one molecule are given in the text, and those of the anothers are as follows. The bond angle; C(1)-Ge(1)-Ge(2): 84.5(5), Ge(1)-Ge(2)-S:78.3(2), Ge(1)-C(1)-S:100.2(8), C(1)-S-Ge(2):94.6(6)°. The bond lengths; Ge(1)-Ge(2):2.408(3), Ge(1)-C(1):2.018(17), Ge(2)-S:2.240(6) C(1)-S:1.807(18), C(1)-C(2):1.36(2)Å.

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