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GENERATION AND TRAPPING OF TETRAMETHYLDIGERMENE1)

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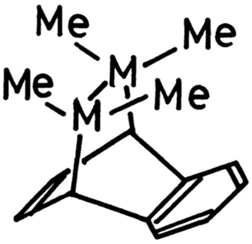
Tetramethyldigermene, generated for the first time by pyrolysis of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo-[2.2.2]octadiene, was successfully trapped by [4+2] cycloaddition with anthracene and 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene.

Contrary to the recent remarkable progress in disilene ($R_2Si=SiR_2$) chemistry,2) there are only a limited number of reports on the germanium-containing multiply bonded species.3) Mazerolles *et al.*4) and Satgè *et al.*5) have studied photolysis of polygermylmercury, in which generation of digermenes or equivalent species is indicated, but obviously much knowledge is required for the chemistry of digermenes. We report here the first successful generation and trapping of tetramethyldigermene.

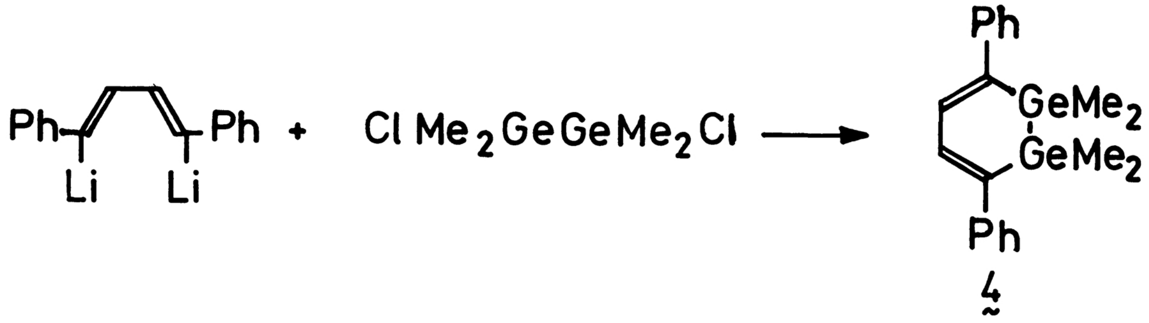
In analogy with tetramethyldisilene, at first a suitable digermene precursor seemed to be 2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (1). Actually, the corresponding disila compound (2) generates tetramethyldisilene successfully either thermally6) of photochemically.7)



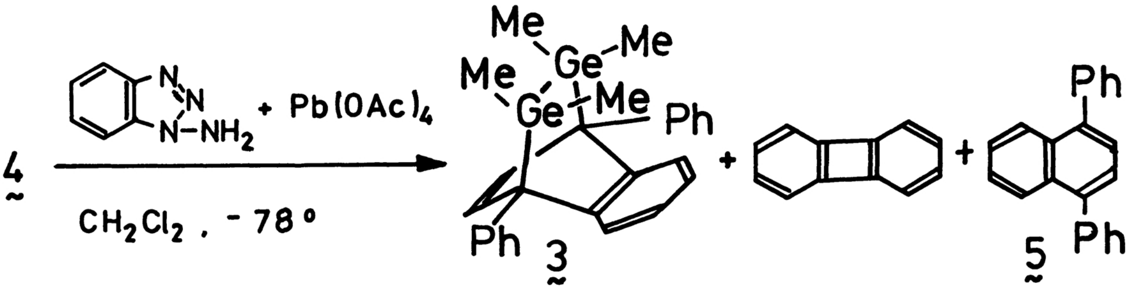
1 : M = Ge
2 : M = Si

Roark and Peddle6) prepared 2 by the reaction of naphthalenide anion radicals with 1,2-dichlotetramethyldisilane. However, all experiments in our hands to react 1,2-dichlorotetramethyldigermane with aromatic anion radicals such as naphthalenide and biphenylide under a variety of conditions resulted in the formation of only polygermane.

Eventually, we have prepared 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (3) as a successful digermene generator. The requisite precursor to 3, 1,1,2,2-tetramethyl-3,6-diphenyl-1,2-digermacyclohexadiene (4), was prepared by the reaction of 1,4-dilithio-1,4-diphenyl-1,3-butadiene with 1,2-dichlorotetramethyldigermane.8)

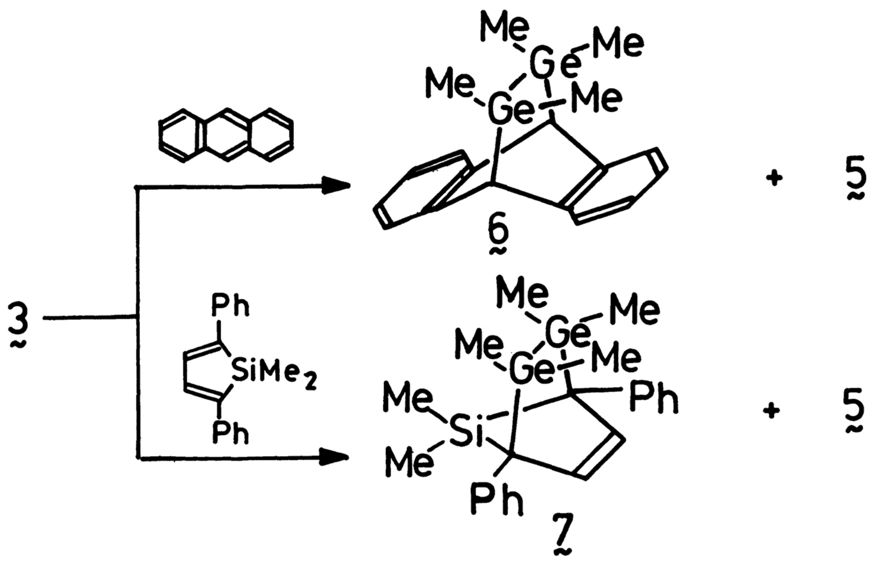


The reaction of 4 with benzyne generated from 1-aminobenzotriazole and lead tetraacetate in dichloromethane at -78°C gave 3.[9] Since 3 is rather thermally unstable, the reaction of 4 with benzyne generated at higher temperature, for example, with benzyne from benzenediazocarboxylate gave 3 only in a trace amount. It is also essential to minimize the contact time with chromatographic materials, since 3 is unstable toward silica gel. Thus flash chromatography (benzene/hexane = 1/8, N_2 pressure) of the crude reaction mixture gave 3 (46%),[9] biphenylene (17%) and 1,4-diphenylnaphthalene (5, 31%).[10]



Pyrolysis of a benzene-d_6 solution of 3 in the presence of equimolar anthracene at 155° for 24 h gave 2,3,5,6-dibenzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (6, 53%) and 5 (86%) together with unreacted 3 (3%). Yields are determined by ^{1}HNMR. The structure of 6 was based on the following spectral properties. ^{1}HNMR (C_6D_6) δ ppm 0.08 (12H, s, GeMe), 3.90 (2H, s, ArCH), 7.0∿7.5 (8H, m, aromatic protons); ^{13}CNMR (C_6D_6) δ ppm 4.90 (GeMe), 43.0 (bridge-head carbons); MS *m/e*(%) M^+ 386 (18), 208 ($Me_2Ge{=}GeMe_2$, 71), 178 (72), 119 (100); High Resolution Mass Found: 386.0167; Calcd for $C_{18}H_{22}Ge_2$: 386.0145.

Similar pyrolysis of 3 in the presence of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene gave 7 (67%) and 5 (70%) together with recovered 3 (13%). The structure of 7 was determined by the following spectroscopic data. ^{1}HNMR (C_6D_6) δ ppm -0.13 (3H, s, SiMe), 0.22 (6H, s, GeMe), 0.46 (6H, s, GeMe), 0.57 (3H, s, SiMe), 6.26 (2H, s, vinyl protons), 6.9∿7.55 (10H, m, Ph); High resolution Mass Found: 470.0521; Calcd for $C_{22}H_{30}SiGe_2$: 470.0539.[11]

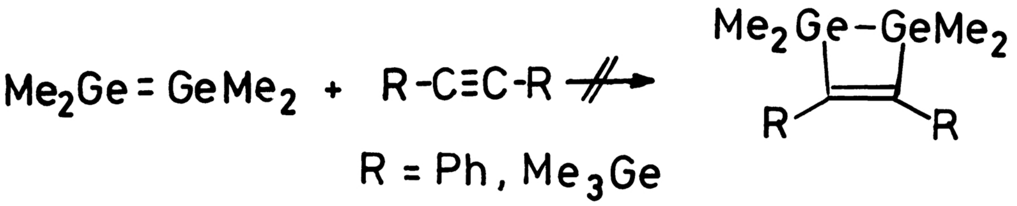


The formation of both 6 and 7 strongly indicates the generation of tetramethyldigermene which can be trapped by the Diels-Alder type reaction, although the direct reaction of 3 to transfer the tetramethyldigermene unit to anthracene and silacyclopentadiene cannot be excluded entirely at this moment.

$$3 \xrightarrow{\Delta} Me_2Ge{=}GeMe_2$$

Tetramethyldisilene reacts with acetylenes such as diphenylacetylene and bis(trimethylsilyl)acetylene to give 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disilacyclobutene and 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobutene, respectively.[12] The latter has been further trasformed into intriguing tetrakis(trimethylsilyl)ethylene and other derivatives.[13,14]

In hopes of obtaining the corresponding digermacyclobutenes, we have investigated the reaction of tetramethyldigermene with diphenylacetylene and bis(trimethylgermyl)acetylene under the same condition described above. However, no expected compound but polymeric materials was obtained.



Further work on digermene chemistry is in progress.

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(8) 4: bp 150°C (0.07 Torr); ^{1}HNMR (CCl_4) δ ppm 0.43 (12H, s), 6.62 (2H, s), 6.96∿7.34 (10H, m); MS *m/e*(%) M^+ 412 (19), 308 (47), 104 (41), 89 (100); High Resolution Mass Found: 412.0260; Calcd for $C_{20}H_{24}Ge_2$: 412.0300.

(9) 3: mp 145∿150°C; ^{1}HNMR (C_6D_6) δ ppm 0.28 (6H, s), 0.44 (6H, s), 6.08 (2H, s), 6.61∿6.85 (4H, m), 7.18∿7.62 (10H, m); ^{13}CNMR (C_6D_6) δ ppm -3.39, -2.22, 52.1, 125.0∿132.6 (six signals), 141.0, 146.1; MS *m/e*(%) M^+ 488 (1), 280 (98), 208 (75); High Resolution Mass Found: 488.0575; Calcd for $C_{26}H_{28}Ge_2$: 488.0612.

(10) This method has been successfully applied to the preparation of the so far elusive 2,3-benzo-1,4-diphenyl-7-silanorbornadiene. H. Sakurai, H. Sakaba, and Y. Nakadaira, *J. Am. Chem. Soc.*, in press.

(11) Both 6 and 7 are extremely unstable on silica gel. Attempts to purify by TLC were in vein.

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