

STUDIES ON ORGANOGERMANIUM HETEROCYCLES AND RELATED COMPOUNDS

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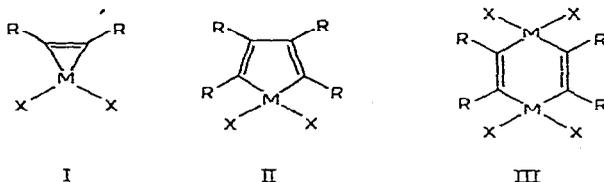
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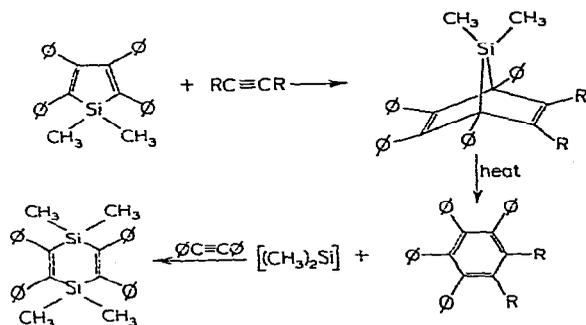
SUMMARY

Attempts to synthesize fluorinated heterocycles containing germanium are described. 1,1-Dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene has been prepared, but did not undergo simple Diels-Alder addition to various acetylenes to give isolable germanorbornadienes. The analogous silicon heterocycle underwent ready addition to hexafluoro-2-butyne to give the trifluoromethyl-substituted silanorbornadiene.

Attention has been given recently to cyclic systems containing germanium or silicon together with some degree of unsaturation (I-III, M=Ge or Si)¹⁻⁴:



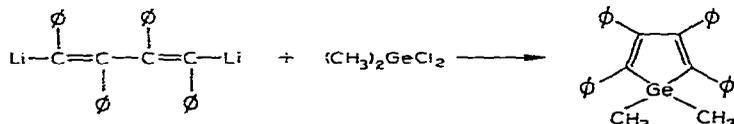
We have studied the reactions of compounds of type II, since the work of Gilman *et al.*⁵ has shown that, for silicon heterocycles, these compounds may be useful intermediates in the production of dimethylsilylene:



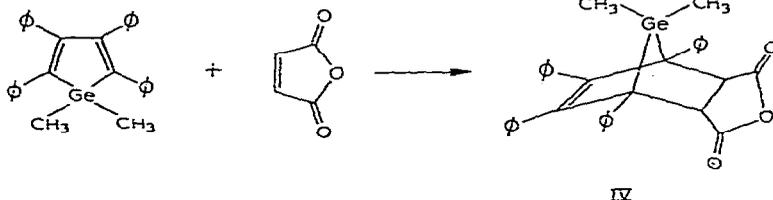
The dimethylsilylene was trapped by reaction with diphenylacetylene, giving a six-membered heterocycle.

In the present work, we have extended this work to include analogous ger-

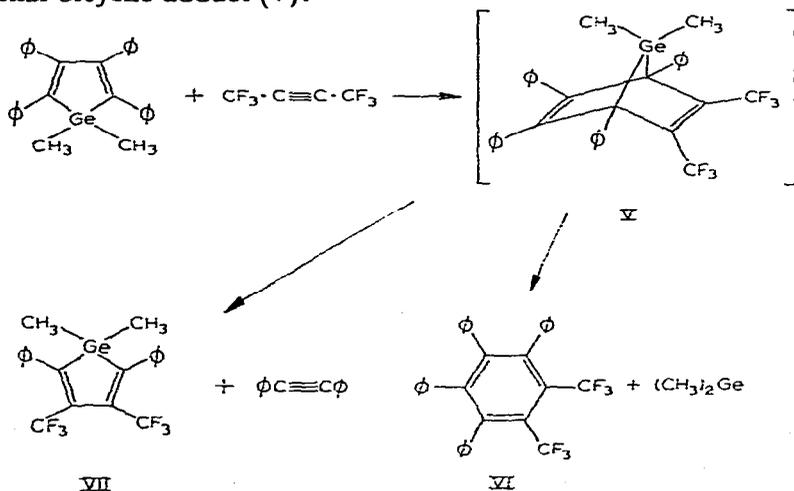
manium compounds and their reaction with hexafluoro-2-butyne. Leavitt *et al.*⁶ have reported a general route from diphenylacetylene to compounds of structure II ($R = C_6H_5$) and claim that it is applicable when $M = Ge$, although they did not give specific characterization of any germanium compound except a bicyclic spiro derivative. We have found that their method, which involves the dimerization of the diphenylacetylene in the presence of lithium followed by reaction of the resulting 1,4-dilithiotetraphenylbutadiene with the appropriate metal halide, has to be modified slightly to give the desired 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene (II, $R = C_6H_5$, $X = CH_3$; this compound will be abbreviated hereafter to "the germole"). However, the resulting germole was readily isolated as an air-stable greenish-yellow solid.



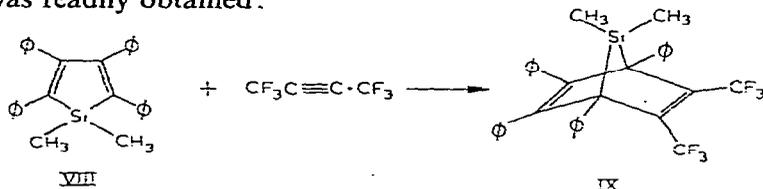
As a test of the germole's ability to undergo Diels-Alder additions of the type found for the analogous silicon compounds, its reaction with maleic anhydride was studied. Ready addition to give the expected norbornene adduct (IV) occurred:



Attempts to prepare 7-germanorbornadiene adducts by similar addition reactions with acetylenes were less successful. Reaction with hexafluorobutyne occurred readily, and a white crystalline product, m.p. 201–202° was isolated. This did not contain germanium, however, and was readily identified as bis(trifluoromethyl)tetraphenylbenzene (VI), presumably arising from elimination of dimethylgermene from the initial bicyclic adduct (V):

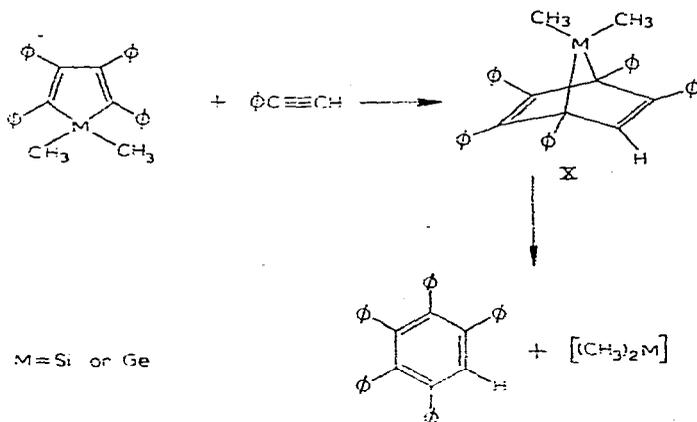


Although the reaction was carried out in the presence of excess hexafluorobutyne, no trace could be found of any compound resulting from its reaction with a dimethylgermene fragment. After removal of compound VI from the reaction products a brown, resinous material was present which could not be purified. On gentle heating, it evolved diphenylacetylene and left a further amorphous residue which was identified as 1,1-dimethyl-2,5-diphenyl-3,4-bis(trifluoromethyl)-1-germacyclopentadiene (VII). This compound also may be readily visualized as a decomposition product of the initial adduct (V), which was presumably present in the resinous reaction product. When the reaction of the analogous silole (VIII) with hexafluorobutyne was attempted, the results were more clear-cut and the 1:1 bicyclic adduct (IX) was readily obtained:



This silanorbomadiene compound was very stable, but decomposed on heating *in vacuo* to 300° to give a brown polymeric material and dimethyldifluorosilane in 70% yield. The latter compound was surprising, since, by analogy with earlier work⁵ or reactions of the similar germanium compound, one would have expected dimethylsilylene to be evolved.

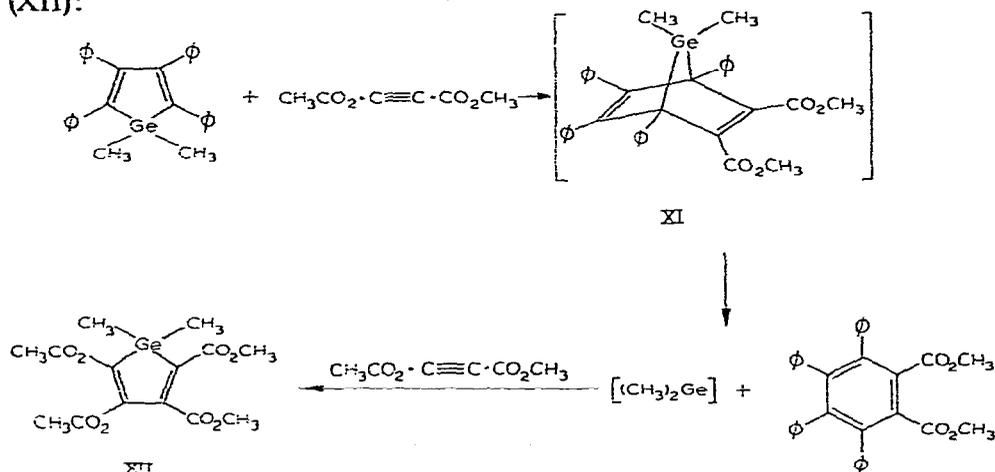
In investigating the reactions of 1,1-dimethyltetraphenylsilole (II, R = C₆H₅, X = CH₃), Gilman and coworkers⁵ found that it added very readily across phenylacetylene to give the expected silanorbomadiene (X, M = Si) which gave good yield of dimethylsilene on pyrolysis, the other product being pentaphenylbenzene:



Although the analogous reaction sequence with the germole has been briefly reported by Nefedov and coworkers⁷, we were not able to isolate the germanobornadiene adduct (X, M = Ge). Reaction occurred rapidly under mild conditions (110°), but the main product was pentaphenylbenzene, the germanium being incorporated into a polymeric residue which was not characterized.

A very similar result was found when the germole interacted with dimethyl acetylenedicarboxylate, CH₃O₂C·C≡C·CO₂CH₃. Although the silole is known⁵

to give a stable silanorbornadiene, the reaction of the germole did not give an adduct. Instead, the main product identified was dimethyl tetraphenylphthalate, arising, as did the pentaphenylbenzene in the previous reaction, through the decomposition of the germanorbornadiene (XI). The dimethylgermene fragment apparently reacted with further acetylene to give a compound identified as a five-membered heterocycle (XII):



The formation of this last compound is of interest, in view of the recent report by Atwell and Weyenberg⁴ that no silacyclopentadiene is formed in the reaction of dimethylsilylene with diphenylacetylene. The authors interpreted that result as indicating that a diradical, formed by the cleavage of a silacyclopropene ring, is not an intermediate in that reaction. The difference we find with the germanium compound may be due to the readier formation of the intermediate diradical, $(\text{CH}_3)_2\text{GeC}(\text{CO}_2\text{CH}_3)=\dot{\text{C}}(\text{CO}_2\text{CH}_3)$, either through cleavage of the germacyclopropene or through addition of dimethylgermanium to the acetylene. The latter process is considered unlikely for dimethylsilylene because of its singlet nature⁶.

The apparent difference in stability between the 7-germanorbornadiene ring system, which we were unable to isolate, and the readily prepared 7-silanorbornadiene and 7-germanorbornene may be due to the slightly larger size of the germanium atom. The difference between the two is quite small, e.g. the C-Si bond length is 1.89 Å in tetramethylsilane⁹ compared with 1.98 Å for the C-Ge bond in tetramethylgermane¹⁰, but this may be sufficient to distort the ring system to the point where elimination of dimethylgermene or other fragments may more readily occur.

EXPERIMENTAL

General techniques

Volatile materials were manipulated using conventional vacuum techniques and separated by fractional condensation. Reactions were carried out in sealed, previously evacuated, Pyrex Carius tubes. VPC separations were carried out in a Perkin-Elmer model 154 instrument on a dinonyl phthalate column. Molecular weights were determined by Regnault's method in the gas phase or with a Mechrolab model 301A vapour pressure osmometer. Products were identified by their infrared

spectra (gas phase, unless otherwise noted) recorded on Beckman IR-5A or IR-10 spectrophotometers. NMR spectra were recorded on Varian model A-60 or DP-60 instruments using 60 Mcps and 56.4 Mcps for proton and fluorine respectively. Unless otherwise noted, chemical shifts are referred to tetramethylsilane (internal) for protons and trichlorofluoromethane (internal) for fluorine. Microanalyses were performed by Dr. A. Bernhardt Laboratories, Mulheim, Germany. Throughout, the abbreviation "pet. ether" refers to petroleum ether, boiling range 60–80°.

Preparation of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene (germole)

1,4-Dilithiotetraphenylbutadiene was prepared by the method of Leavitt *et al.*⁶ In a typical reaction, freshly cut lithium metal (0.75 g, 108 mmole) in dry diethyl ether (120 ml) was stirred with diphenylacetylene (20 g, 112 mmole) in a closed flask for 12 h, by which time virtually all the lithium had disappeared. A further 250 ml of ether was then added, followed by dropwise addition of dimethyldichlorogermane (20 g, 108 mmole) in ether (50 ml). Immediate reaction was apparent and the mixture was stirred for 1 h, then the ether removed *in vacuo*. The residual solid was extracted with methylene chloride to remove lithium chloride, giving a yellow solution. The procedure used by Leavitt *et al.* in analogous reactions involved the addition of methanol at this point, but in our experience this led to the precipitation of tetraphenylbutadiene. Instead, we found it satisfactory to remove the methylene chloride by evaporation, then wash the remaining solid with small portions of cold pet. ether. The residual bright greenish-yellow solid was 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene of satisfactory purity, m.p. 179–181°. An analytical sample, prepared by recrystallization from pet. ether, had the same m.p. (Found: C, 78.9; H, 5.53; mol. wt., 467. C₃₀H₂₆Ge calcd.: C, 78.4; H, 5.66%; mol. wt., 459).

The proton NMR spectrum showed a sharp singlet at 0.67 ppm, assigned to (CH₃)₂Ge<, and a multiplet centred on 6.9 ppm, assigned to aromatic protons, the integrated aromatic/aliphatic intensity ratio being 3.35 (calcd.: 3.33). The infrared spectrum of the compound (KBr disc) showed the following principal absorptions: 3080 w, 3070 w, 3020 w, 2980 w, 2900 w, 1595 m, 1575 m, 1486 m, 1440 m, 1415 w, 1295 m, 1270 w, 1230 w, 1180 w, 1155 w, 1085 w, 1075 m, 1050 w, 1025 m, 975 w, 960 w, 910 m, 825 m, 782 s, 735 m, 705 s, 695 s, 600 m, 580 w, 560 m, 520 w cm⁻¹.

Reaction of the germole with maleic anhydride

The germole (2.5 g, 5.3 mmole) and maleic anhydride (0.5 g, 5.1 mmole) in benzene (10 ml) were heated to 75° for 12 h in a sealed tube. A white solid separated on cooling and was purified by recrystallization from benzene to give the 1 : 1 adduct, 7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride. (Found: C, 73.8; H, 5.02. C₃₄H₂₈GeO₃ calcd.: C, 73.5; H, 5.03%.)

The proton NMR spectrum of the adduct gave sharp absorptions at 1.02, 1.37 and 5.08 ppm and an aromatic multiplet centred on 7.4 ppm. The first two peaks are assigned to the methyl groups on germanium (which are now non-equivalent) and the third peak to the hydrogen atoms at the 2,3 positions. The integrated aromatic/aliphatic intensity ratio was 2.42 (calcd.: 2.50). Principal infrared absorption peaks (KBr disc) were at 3078 w, 3040 w, 1860 m, 1785 s, 1600 m, 1585 w, 1500 m, 1450 m, 1260 m, 1240 m, 1220 s, 1160 w, 1110 w, 1080 m, 1070 m, 1035 m, 985 w, 970 m,

930 s, 875 w, 845 m, 800 m, 780 m, 775 m, 765 m, 720 m, 710 s, 625 m, 600 m, 570 m, 545 m cm^{-1} .

Reaction of the germole with hexafluorobutyne

Germole (4.0 g, 8.2 mmole) and hexafluoro-2-butyne (7.6 g, 47 mmole) were heated to 190° in a sealed tube (100 ml) for 5 h. On cooling, needle-like crystals and brown resinous material were visible in the tube and unreacted butyne (5.4 g, 33 mmole) was recovered as the only volatile product. The residue in the reaction tube was extracted with cold pet. ether, leaving a white solid which was recrystallized from pet. ether to give a product identified as bis(trifluoromethyl)tetraphenylbenzene, m.p. 201–202°. (Found: C, 74.2; H, 4.01; F, 21.9. $\text{C}_{32}\text{H}_{20}\text{F}_6$ calcd.: C, 74.1; H, 3.86; F, 22.0%.)

The pet. ether soluble fraction was recovered as a dark yellow resinous material on removal of solvent *in vacuo*. Its proton NMR spectrum showed absorptions at 0.72 and 0.78 ppm, indicating that methyl groups attached to germanium were in two different environments, together with aromatic multiplet absorption centred on 7.3 ppm. On attempting to sublime the resin by heating to 75° *in vacuo*, diphenylacetylene sublimed out to leave a further resinous material identified as 1,1-dimethyl-2,5-diphenyl-3,4-bis(trifluoromethyl)-1-germacyclopentadiene. (Found: C, 54.8; H, 4.07; F, 26.2, mol. wt., 457. $\text{C}_{20}\text{H}_{16}\text{F}_6\text{Ge}$ calcd.: C, 54.3; H, 3.62; F, 25.7%; mol. wt., 443.)

The proton NMR spectrum now showed only a single methyl absorption, at 0.67 ppm, together with an aromatic multiplet centred on 7.12 ppm. Infrared absorptions were present at 3088 w, 3060 w, 3028 w, 1760 w, 1715 w, 1680 w, 1610 m, 1575 w, 1495 m, 1445 m, 1415 w, 1370 w, 1340 m, 1245 vs, 1160 vs, 1070 m, 1025 w, 910 w, 840 m, 815 m, 790 m, 755 s, 695 s, 685 s, 620 w, 590 w, 575 w, 535 w, 505 w cm^{-1} .

The reaction of the germole with the butyne was repeated several times, using lower temperatures or using benzene as a solvent, but no difference was observed in the nature of the products.

Reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (silole) with hexafluorobutyne

The silole was prepared in a manner similar to that used for the germole, using the procedure of Gilman *et al.*⁴. Silole (1.25 g, 3.0 mmole) in benzene (10 ml) was heated to 115° for 24 h with hexafluoro-2-butyne (4.9 g, 30 mmole). After removal of unreacted butyne and solvent, a cream-coloured residue remained which was recrystallized from pet. ether to give white crystals of 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene, m.p. 143–145°. (Found: C, 71.3; H, 4.50; F, 19.1. $\text{C}_{34}\text{H}_{26}\text{F}_6\text{Si}$ calcd.: C, 71.0; H, 4.51; F, 19.8%.)

The proton NMR spectrum showed singlet absorptions at 0.47 and 0.61 ppm associated with methyl groups on silicon in two environments, and an aromatic multiplet centred on 6.89 ppm. The integrated aromatic/aliphatic intensity ratio was 3.38 (calcd.: 3.33). Infrared absorptions (KBr disc) were present at 3080 w, 3060 w, 3025 w, 1600 m, 1585 m, 1570 m, 1495 m, 1290 s, 1270 m, 1255 m, 1240 s, 1170 vs, 1140 vs, 1100 m, 1080 m, 1040 m, 1015 m, 1000 m, 985 m, 915 m, 880 m, 845 m, 825 m, 795 m, 750 m, 700 s, 670 m, 610 m, 570 m, 545 m cm^{-1} .

Thermal decomposition of 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene

The 7-silanorbornadiene (0.25 g, 0.43 mmole) was kept at 300° in a sealed, evacuated tube (20 ml) for 3 h, by which time a brown resinous material had formed. Examination of volatile products showed a trace of silicon tetrafluoride and dimethyldifluorosilane (0.03 g, 0.3 mmole) as the only products. The latter compound was identified from its infrared spectrum and molecular weight (Found: 94; Calcd.: 96).

Pyrolysis in the presence of diphenylacetylene also gave dimethyldifluorosilane as the only identifiable product.

Reaction of the germole with phenylacetylene

The germole (1.0 g, 2.2 mmole) and phenylacetylene (2.0 g, 19 mmole) were heated to 120° for 12 h in a sealed, evacuated tube (20 ml). Excess phenylacetylene was removed *in vacuo* and the solid reaction products extracted with pet. ether to leave a residue which was recrystallized from benzene/pet. ether to give 0.80 g of a cream solid, identified as pentaphenylbenzene (m.p. 248–249°; Lit.¹¹ m.p. 251°). (Found: C, 93.9; H, 6.12. C₃₆H₂₆ calcd.: C, 94.3; H, 5.71%.)

The pet. ether soluble portion of the reaction product was a yellow resinous material which was not characterized.

Reaction of the germole with dimethylacetylenedicarboxylate

The germole (1.9 g, 4.1 mmole) and dimethylacetylenedicarboxylate (3.0 g, 21 mmole) were heated to 75° for 15 min in a sealed evacuated tube (50 ml), by which time reaction was apparent. Extraction of the contents of the tube with benzene, followed by addition of pet. ether and concentration, gave a light red precipitate (2.25 g) and a red solution. The precipitate was recrystallized from benzene/pet. ether to give cream crystals identified as dimethyltetraphenylphthalate (m.p. 259–260°; Lit. m.p. 259–261°). (Found: C, 82.6; H, 5.39. C₃₄H₂₆O₄ calcd.: C, 82.0; H, 5.20%.)

The red solution obtained above was further concentrated and filtered, then solvents removed to give a dark red resinous material which was involatile *in vacuo*. It could not be obtained in a crystalline form, but analytical data were consistent with formulation as 1,1-dimethyl-2,3,4,5-tetrakis(carbomethoxy)-1-germacyclopentadiene. (Found: C, 45.4; H, 4.80. C₁₄H₁₈GeO₈ calcd.: C, 44.8; H, 4.81%.)

The proton NMR spectrum showed rather broad absorptions at 0.98 and 4.18 ppm (ref.: external TMS) assigned to (CH₃)₂Ge< and CH₃CO₂- respectively. The methoxy/methyl integrated ratio was found to be 2.07 (calcd.: 2.0).

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