Synthesis and Decomposition Reactions of a 7-Germanorbornadiene

J. G. Zavistoski and J. J. Zuckerman[1]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. *Received April 4, 1968*

Abstract: 1,1-Dimethyl-2,3,4,5-tetraphenylgermole undergoes a Diels–Alder reaction with dimethyl acetylenedicarboxylate to give 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene. The dicarbomethoxy derivative undergoes isomerization slowly at room temperature accompanied by some decomposition and decomposes rapidly without melting at 100°. Pyrolysis in the presence of excess dimethyl acetylenedicarboxylate gave a white solid which yielded 3-carbomethoxy-4,4-dimethyl-4-germa-2,3-dehydro-γ-butyrolactone, 2,2,5,5-tetramethyl-3,4-dicarbomethoxy-2,5-digerma-2,5-dihydrofuran, and an oil from which was isolated a compound identified as either carbotrimethylgermoxydimethylphenylgermane(I) or carbodimethylphenylgermoxytrimethylgermane(II). None of the expected 1,4-digermacyclohexadiene was formed. Cyclohexene is inert during the pyrolysis, but triphenylphosphine gave a germanium–phosphorus polymer. The 7-germanorbornadiene rearranged in benzene–methanol and in methylene dichloride to give a different isomer in each solvent.

In 1964 Gilman announced[2] the discovery of an improved source of the "divalent silicon" intermediates; the precursor was a 7-silanorbornadiene derived as the Diels–Alder adduct of a silacyclopentadiene (silole) with diphenylacetylene or benzyne. These silanorbornadienes were reported to undergo smooth pyrolytic decomposition at 300° with release of the dimethylsilicon moiety and formation of the corresponding aromatic compounds. Pyrolysis in the presence of diphenylacetylene resulted in a 1,4-disilacyclohexadiene; pyrolysis alone gave a dimethylsilane polymer.[3]

This paper describes the results of our study of the synthesis and reactions of the analogous 7-germanorbornadiene ring system.

Experimental Section

Melting points were obtained on a Townson and Mercer Type 5 melting point apparatus and are uncorrected. Elemental analyses and molecular weight determinations were carried out by Galbraith Laboratories, Inc., and by Schwartzkopf Microanalytical Laboratory. An F & M Model 810 gas chromatograph with thermal conductivity detectors was employed with helium as the carrier gas. Solids and liquids were trapped at the exit port in capillary tubing held at room temperature; volatiles at −196° in U-tubes equipped with stopcocks. Separations were carried out in 15-in. 100–200 mesh silica gel (Will Scientific Co.) and 100–200 mesh fluorosil (City Chemical Co.) columns. Nmr spectra were recorded on Varian A-60, A-60A, and HA-100 instruments with tetramethylsilane used as internal standard. Time-averaged spectra were obtained by the use of a Technical Measurements C-1024 computer of average transients. Infrared spectra were recorded on Perkin-Elmer Infracord 137 and 337 instruments with samples as liquid smears or in KBr pellets. Uv and visible spectra were recorded on a Cary 14 spectrometer. Mass spectra were recorded on a Consolidated Engineering Corp. Model 21-103A instrument equipped with a heated inlet system and on Associated Electronics Corp. MS-9 and MS-902 instruments. High-resolution data were obtained from the latter two instruments.

Commercial starting materials were redistilled before use. Diphenylacetylene, initially prepared by bromination of stilbene followed by dehydrobromination and recrystallization from ethanol, was later obtained from Orgmet, Hempstead, N. H. Solvents were dried over $LiAlH_4$ and distilled.

7,7-Dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene was prepared by the method of Gilman.[3] A suspension of 1,1-dimethylsilole[4] (0.008 mole) in phenylacetylene (0.06 mole) was stirred and heated at 100–105° for 10 hr under nitrogen. The reaction mixture was cooled, excess phenylacetylene removed *in vacuo*, and the sticky residue dissolved in boiling petroleum ether and cooled to yield a yellow-white solid.

Attempted Preparation of 7,7-Dimethyl-1,2,3,4,5-pentaphenyl-7-germanorbornadiene. 1,1-Dimethyl-2,3,4,5-tetraphenylgermole[4] (0.0097 mole) was heated with phenylacetylene (0.097 mole) at 105° for 15 hr under nitrogen with stirring. The reaction vessel was cooled; the addition of petroleum ether precipitated pentaphenylbenzene. No norbornadiene could be isolated. The reaction was repeated with excess phenylacetylene at 90–95° for 12 hr with no change, and at 90–95° for 2 days and at 90–95° for 5 days to give pentaphenylbenzene.

2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene. 1,1-Dimethyl-2,3,4,5-tetraphenylgermole (0.0090 mole) was stirred under nitrogen with dimethyl acetylenedicarboxylate (0.0070 mole) at 0° for 1 hr and at 22° for another hour with no apparent reaction. Gradual warming to 48° resulted in darkening of the reaction mixture. The temperature was quickly lowered to 40° and kept there for 0.5 hr after which the mixture was cooled and washed with cyclohexane (15 cc). Benzene–cyclohexane (1:1, 15 cc) was added; the resulting slurry was filtered, washed with benzene–cyclohexane, dried *in vacuo*, and stored in a sealed container at −20°. The nmr spectrum contained two sharp resonances at τ 9.38 and 9.25, a single sharp resonance at τ 6.38, and a broad aromatic resonance centered about τ 3.05. Proton integration gave a ratio of 1:1:2:7, respectively (calcd 1:1:2:6.7). The infrared spectrum (Figure 1) was very complex. *Anal.* Calcd for $C_{36}H_{32}O_4Ge$: C, 71.94; H, 5.33; Ge, 12.07; mol wt, 600.5. Found: C, 71.88; H, 5.50; Ge, 12.26; mol wt, 588 by osmometry.

Thermolysis of 2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene in the Presence of Dimethyl Acetylenedicarboxylate. The 7-germanorbornadiene was prepared from 1,1-dimethyl-2,3,4,5-tetraphenylgermole (0.035 mole) and excess dimethyl acetylenedicarboxylate (0.35 mole) as described above and the temperature of the reaction mixture raised to 55–60°. A deep red-brown coloration appeared and very rapidly spread through the flask, accompanied by the evolution of heat. The reaction mixture was cooled, and unreacted dimethyl acetylenedicarboxylate was removed *in vacuo*. The resultant viscous, dark-brown residue was distilled at 35–45° *in vacuo* to give a colorless oil (3–4 cc). At 80–150° a white solid collected in the condenser.

---

[1] To whom all inquiries should be addressed at the Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203.

[2] H. Gilman, W. H. Atwell, F. K. Cartledge, and G. L. Schwebke, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[3] H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, 86, 1596, 5584 (1964).

[4] F. C. Leavitt, T. A. Manuel, and F. Johnson, *ibid.*, 81, 3161 (1959); F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, 82, 5099 (1960); our preparation is described by J. G. Zavistoski and J. J. Zuckerman, *J. Organometal. Chem.*, in press.

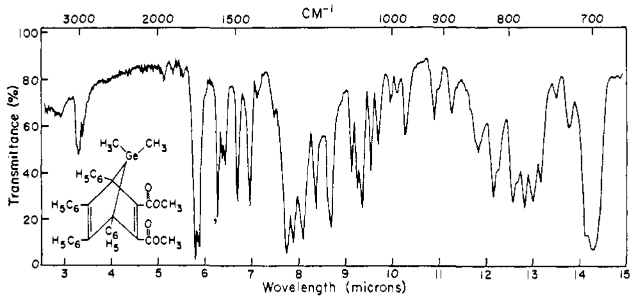


Figure 1. Infrared spectrum of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene.

Carbotrimethylgermoxydimethylphenylgermane(I). Successive 30–40-μl portions of the oil were separated into several components by gas chromatography (6 ft, 10% LAC-728 on 60–80 mesh Chromosorb W, temperature programmed 50–160°) including a white solid (mp 112–113°) whose nmr spectrum in CCl_4 contained two partially resolved resonances separated by 1.3 cps centered at τ 9.8 with the downfield resonance somewhat more intense, no methyl ester resonance, and a rather sharp aromatic resonance at τ 3.0. Proton integration gave a total methylgermanium to aromatic ratio of 2.5:1 (calcd for proposed structure, 3:1). The infrared spectrum contained prominent absorptions at 1740, 1629, 1445, 1262, 1244, 1044, 852, and 800 cm⁻¹. The mass spectrum contained a series of peaks at highest isotope distributions of a digermanium species with the $^{72}Ge_2$ peak at mass 340. The mass spectrum also indicated less abundant P − 15 and P − 30 fragments and an abundant ^{72}Ge fragment of *m/e* 117.

Dimethyl maleate (or its fumarate isomer) was identified by its mass spectrum as were dimethyl chloro- and dimethyl bromomaleates (or their fumarate isomers) as impurities.

3-Carbomethoxy-4,4-dimethyl-4-germa-2,3-dehydro-γ-butyrolactone. The white solid residue was dissolved in chloroform and 10–20-μl samples were separated into several components by gas chromatography (6 ft, 10% SE-30 column with 60–80 mesh Chromosorb W packing, temperature programmed 50–170°) including a white solid, mp 127–128°, which was the major component (yield 25%). The nmr spectrum (Figure 2) contained three sharp resonances at τ 2.89, 6.18, and 9.13 in a 1:3:6 ratio. The mass spectrum showed a monogermanium molecular ion at 230 (^{72}Ge). The spectrum also (see Figure 3) contained P − 15, P − 31, P − 59, and P − 74 fragments, but no germanium-containing fragment at *m/e* 117. The uv spectrum contained an absorption at 2150 Å (log E_{max} = 4.0). A CCl_4 solution decolorized bromine. The infrared spectrum contained prominent absorption bands at 1740, 1640, 1595, 1410, 1280, 1055, 910, 840, and 709 cm⁻¹. *Anal.* Calcd for $C_7H_{10}O_4Ge$: C, 35.5; H, 4.35; Ge, 31.8; mol wt, 230.5. Found: C, 36.06; H, 4.30; Ge, 31.83; mol wt, 225.

2,2,5,5-Tetramethyl-3,4-dicarbomethoxy-2,5-digerma-2,5-dihydrofuran. The next eluent was a white solid (mp 53–54°) whose nmr spectrum contained only two sharp resonances at τ 6.26 and 9.43 in the integrated ratio 1:2. The mass spectrum contained a digermanium molecular ion at *m/e* 366 ($^{74}Ge_2$). An exact mass of 365.9516 was obtained from high-resolution analysis (calcd for $C_{10}H_{18}O_5{}^{74}Ge_2$, 365.9574). The spectrum also contained P − 15, P − 31, P − 59, and an abundant digermanium fragment at mass $^{74}Ge_2$ of 225.

Another eluent decomposed partially on the chromatographic column. The mass spectrum indicated polygermanium-containing fragments to at least *m/e* 690.

Triphenylphosphine Reaction with 2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene. To triphenylphosphine (0.0090 mole) and benzaldehyde (0.020 mole) in stirred refluxing benzene (10cc) under nitrogen was added a slurry of germanorbornadiene (0.0067 mole) in benzene (50 cc), and refluxing was continued for 0.5 hr. Benzene was distilled, and the pale yellow-white solid residue (mp 210–255°) was filtered under nitrogen and dried *in vacuo*. The nmr spectrum of the soluble portion in deuteriochloroform contained strong resonances in the aromatic and carbomethoxy regions, but only very weak resonances in the methylgermanium region. None of the ir spectra of the sublimation fractions of the residue contained absorption bands in the 1700- or 1195-cm⁻¹ ($\nu_{P=O}$ of triphenylphosphine oxide) regions.

Thermolysis of 2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene in the Presence of Cyclohexene. The 7-germanorbornadiene prepared as above (0.022 mole) was stirred in refluxing cyclohexene (50 cc) (which had been washed with four portions of a dilute acidified ferrous sulfate solution, dried over calcium sulfate, and distilled *in vacuo*) for 0.5 hr under nitrogen during which time the slurry developed a yellow color. After cooling, the solution was evaporated to dryness *in vacuo* to yield a distillate of cyclohexene and a residue containing dimethyl tetraphenylphthalate. Slow sublimation of the residue at 110–120° *in vacuo* gave a pale yellow solid whose nmr spectrum in deuteriochloroform showed weak resonances in the aromatic and carbomethoxy regions and several resonances in the methylgermanium region. Glpc (2 ft, 10% SE-30 on 60–80 mesh Chromosorb W, temperature programmed 50–180°) gave several components, the most abundant of which were studied by nmr spectroscopy with the aid of a computer of average transients. With one exception the samples contained resonances in the methylgermanium region. None, however, contained resonances in the τ 7–9 region (methylene protons). 1,1-Dimethyl-2,3,4,5-tetraphenylgermole and dimethyl tetraphenylphthalate were the last to be eluted from the chromatographic column and were also the two most abundant.

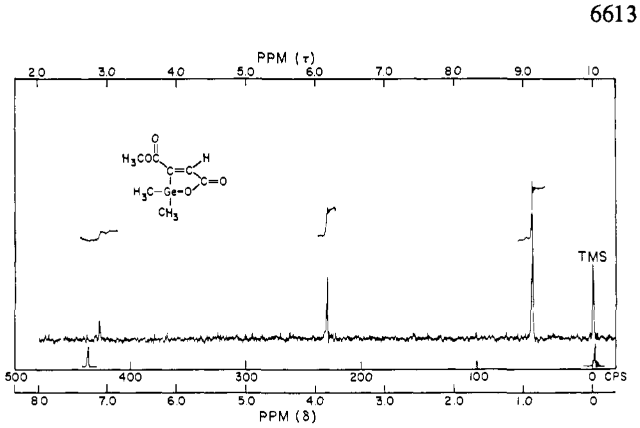


Figure 2. Nmr spectrum of 3-carbomethoxy-4,4-dimethyl-4-germa-2,3-dehydro-γ-butyrolactone.

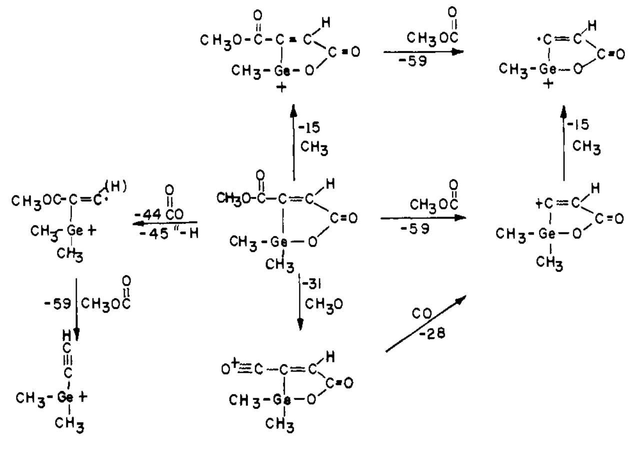


Figure 3. Proposed fragmentation pattern from the mass spectrum of 3-carbomethoxy-4,4-dimethyl-4-germa-2,3-dehydro-γ-butyrolactone.

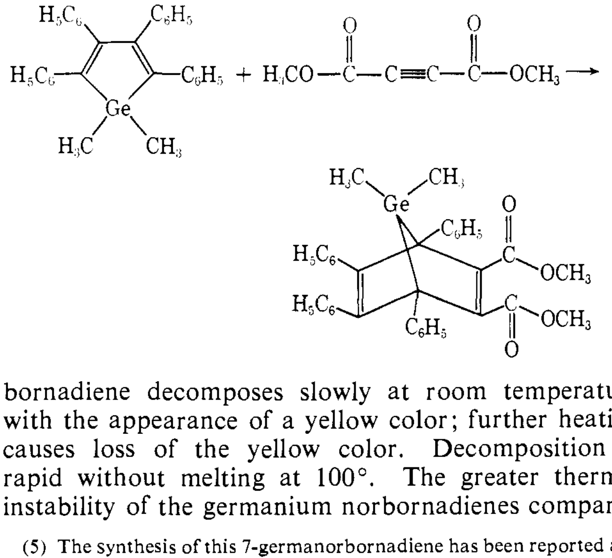
Rearrangement of 2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene in Benzene–Methanol. A solution of the 7-germanorbornadiene in benzene (0.002 *M*) slowly turned yellow, and the course of the change was followed by nmr. Methanol (0.15 cc) was added with shaking. Successive spectra revealed the progress of the rearrangement. The original germanorbornadiene methyl resonances disappeared while new resonances appeared at τ 6.22, 6.67, 9.25, and 10.21. When the solution was heated to boiling the color quickly disappeared and the nmr spectrum was that of dimethyl tetraphenylphthalate with a broad envelope of methylgermanium resonances centered about τ 9.6. Bromine in CCl_4 was added to a dilute CCl_4 solution of the bright yellow rearrangement product until the yellow color disappeared. The solution was evaporated to dryness *in vacuo* to yield dimethyldibromogermane which was identified by its nmr and mass spectra. Dimethyl tetraphenylphthalate remained.

Rearrangement of 2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene in Methylene Chloride. A methylene dichloride solution of the germanorbornadiene was prepared and studied by successive nmr spectra. A yellow color appeared while the original germanorbornadiene resonances grew less intense and new resonances appeared in the methylgermanium region at τ 9.6 (broad band), 9.28, and 9.13, and at τ 6.76 and 6.52 in the carbomethoxy region. The aromatic region became greatly altered. After approximately 9 hr the reaction was complete. Integration of these five new resonances (excluding the aromatic region) gave a ratio of 3:1:1:1:4, respectively, while the original 7-germanorbornadiene had given rise to three methyl resonances in the ratio 1:1:2 reading downfield (dimethylgermanium protons nonequivalent), and the pure rearrangement product gave four equal methyl resonances (both the carbomethoxy and methylgermanium group protons nonequivalent). The decomposition product would be expected to add two additional methyl resonances of intensity m to give the integrated ratio m:1:1:1:1:m. In the case of this isomer there is apparent overlap of two signals to give a pattern of m:1:1:1:(1 + m). The resonance at τ 6.52 and the pattern in the aromatic region were characteristic of dimethyl tetraphenylphthalate. The spectrum in the τ 6.52 region was recorded at 100 Mc, but no splitting of the resonance was observed. The solution was evaporated to dryness and the yellow residue redissolved in carbon tetrachloride, but the spectrum did not change. The visible spectrum showed a maximum at 4060 Å. During chromatography on silica gel with benzene-methylene chloride (3:1 then 1:1) as eluent, the yellow band faded to colorless and dimethyl tetraphenylphthalate formed. The column chromatograph was repeated in the dark with identical results.

Results and Discussion

In contrast to the straightforward preparation of the thermally stable 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene,[3] we find that the conditions necessary to promote the Diels-Alder reaction between phenylacetylene and 1,1-dimethyl-2,3,4,5-tetraphenylgermole are also sufficient to decompose the resulting 7-germanorbornadiene.[5]

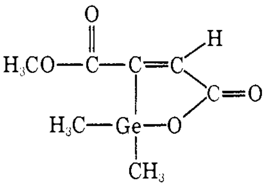
2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene was prepared in 77% yield under mild conditions as the Diels-Alder adduct of 1,1-dimethyl-2,3,4,5-tetraphenylgermole and dimethyl acetylenedicarboxylate (eq 1). This 7-germanorbornadiene decomposes slowly at room temperature with the appearance of a yellow color; further heating causes loss of the yellow color. Decomposition is rapid without melting at 100°. The greater thermal instability of the germanium norbornadienes compared with their silicon analogs permitted study of their decomposition reactions under much milder conditions than those employed by Gilman, *et al.*[3]



(1)

Pyrolysis of 7-silanorbornadienes in the presence of acetylenes was proposed to proceed *via* a divalent silicon intermediate to give 1,4-disilacyclohexadienes. However, pyrolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene at 300° in the presence of diphenylacetylene took place in an anomalous manner without the formation of disilacyclohexadiene. No products of this reaction were identified.[3] We find that the analogous reaction of the germanium norbornadiene sets in at 50° and proceeds rapidly and exothermically with gentle heating to 60° in dimethyl acetylenedicarboxylate. An oil and a white solid were isolated on distillation at 35–45° (<1 mm), along with a residue of dimethyl tetraphenylphthalate. No 1,4-digermacyclohexadiene was found.

The white solid from vacuum distillation was separated into its components by glpc. The major component (25% yield) decolorized bromine and showed a monogermanium molecular ion at mass 230 (^{72}Ge) in its mass spectrum (calcd for $C_7H_{10}O_4{}^{72}Ge$, 230). The nmr spectrum (see Figure 2) contained resonances in the methylgermanium and carbomethoxy region and at τ 2.97 in an integrated ratio of 6:3:1. The ir spectrum contained two absorptions in the carbonyl region; the uv spectrum contained an ethylenic absorption at 2150 Å (log E_{max} = 4.0). On this basis, and from microanalytical and molecular weight data, we propose the structure 3-carbomethoxy-4,4-dimethyl-4-germa-2,3-dehydro-γ-butyrolactone.



A fragmentation pattern for the proposed structure in shown in Figure 3. In the nmr spectrum the unusually large downfield shift of the ethylenic proton can be rationalized in terms of the diamagnetic deshielding arising from the adjacent ene-carbonyl system. The presence of the single, sharp methylgermanium resonance serves to rule out rigid ring conformations with the ring oxygen out of the plane (the four atoms directly attached to the ethylenic system must be coplanar like those of the in-ring =CC(=O)O– system). Thus the ring system must either be planar or undergoing a tortional motion rapid compared with nmr lifetimes.[6] The structure proposed contains the elements of methyl acetylenedicarboxylate and $Ge(CH_3)_2$.

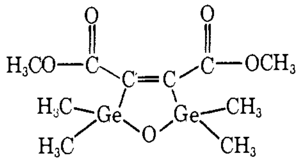
The second most abundant fraction from the white solid was subjected to high-resolution mass spectral analysis. A polyisotopic molecular ion was found which contained a series of strong peaks at highest mass at 366 (365.9516 relative to $^{74}Ge_2$; calcd for $C_{10}H_{18}O_5{}^{74}Ge_2$, 365.9574) corresponding to the 13 possible

---

(5) The synthesis of this 7-germanorbornadiene has been reported at a meeting (O. M. Nefedov and T. Székely, Abstracts, International Symposium on Organosilicon Chemistry, Prague, 1965) and discussed in a review (O. M. Nefedov and M. N. Manakov, *Angew. Chem. Intern. Ed. Engl.*, 5, 1021 (1966)). It is said to pyrolyze to give a dimethylgermanium polymer and to pyrolyze in the presence of ethylene to give cyclic organogermanium compounds. The preparation and physical properties have not yet been published.

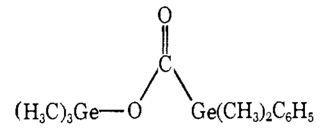
(6) In the only structural study we are able to find of the parent organic analog, 2,5-dihydrofuran, the author's electron-diffraction data were found to fit an assumed planar model: J. Y. Beach, *J. Chem. Phys.*, 9, 54 (1941).

mass distributions of a digermanium ion.[7] The mass spectrum also contained P − 15 (loss of CH_3), P − 31 (loss of CH_3O), and P − 59 (loss of $COOCH_3$) fragments and an abundant digermanium fragment at 225 ($^{74}Ge_2$), probably containing the structure $(CH_3)_2GeOGe(CH_3)_2$. The nmr spectrum contained only two resonances, one each in the carboxymethyl and methylgermanium regions in an integrated ratio of 2:1. On this basis we are led to the structure

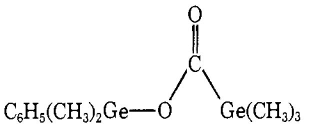


2,2,5,5-tetramethyl-3,4-dicarbomethoxy-2,5-digerma-2,5-dihydrofuran, which contains the elements of dimethyl acetylenedicarboxylate, two dimethylgermanium moieties and oxygen. The presence of single sharp resonance for the methyl protons in the carbomethoxy groups and on the germanium atoms serves to rule out rigid ring conformations where the ring oxygen is out of the plane formed by the atoms directly attached to the ethylenic carbons or conformations where the carbomethoxy groups are not free to rotate. Thus the ring system must either be planar or undergoing a tortional motion about the germanium atoms rapid with respect to nmr lifetimes.

The first sizable component eluted from the oil by glpc was a white solid (mp 112–113°) in an estimated yield of 10% which we identify as $C_{12}H_{20}O_2Ge_2$ and assign as either carbotrimethylgermoxydimethylphenylgermane (I) or carbodimethylphenylgermoxytrimethylgermane (II) by means of its mass spectrum



I

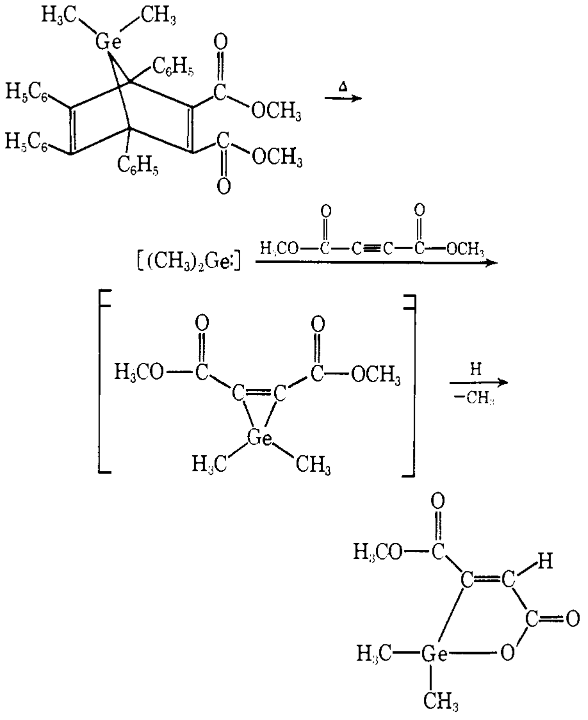


II

which contained a series of strong peaks at highest mass corresponding to a digermanium molecular ion at mass 340 ($^{72}Ge_2$) (calcd for $C_{12}H_{20}O_2{}^{72}Ge_2$, 340). The mass spectrum also contained less abundant P − 16, P − 30, and P − 76 (loss of phenyl) fragments and an abundant ^{72}Ge fragment of mass 117 which would correspond to the $(CH_3)_3Ge$ structure. The nmr spectrum in CCl_4 contained two partially resolved methylgermanium resonances separated by 1.3 cps centered at τ 9.8 with the downfield resonance *ca.* one-third more intense, no methyl ester resonance, and a rather sharp aromatic resonance at τ 3.0. Integration of this very dilute solution gave the methylgermanium:aromatic proton ratio as 2.5:1 (calcd 3:1). The infrared spectrum contained ester absorptions (cm^{-1}) at 1740 and 1262, methylgermanium at 1244, phenylgermanium at 1440 and 1045, a broad germanium–oxygen at 852, and the usual absorption pattern for a monosubstituted benzene.

It is difficult to differentiate between structures I and II on the basis of our spectral evidence unless we assume that the resonance arising from the $(CH_3)_3GeO$ system should be found downfield from the $(CH_3)_3Ge$-$C(=O)$- signal on simple electronegativity grounds. There seems at present no compelling reason to make such an assumption, but it is true, however, that the $-COOCH_3$ structure is part of the original acetylene molecule, and the insertion of a $Ge(CH_3)_2$ moiety into this OCH_3 bond would lead to structure I.

Of the three germanium-containing compounds found from this reaction, only the major product can be rationalized on the basis of a dimethylgermanium intermediate (eq 2). Normal carbene insertion into



(2)

the double bond would be expected to produce a three-membered "germirene" structure. On ring opening, however, the formation of the Ge–O bond apparently competes successfully with the usual dimerization to the 1,4-digermacyclohexadiene.[8] The origin of the two other organogermanium products remains obscure. The complexity of the reaction paths places doubt on the formation of these compounds directly from a dimethylgermanium intermediate.[9]

Organic carbenes react with phosphines to form phosphonium ylides which then undergo the Wittig reaction with carbonyl compounds. A germanium analog of the phosphine dihalomethylenes, $(C_6H_5)_3P \cdot GeI_2$, has been prepared,[10] but pyrolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene in a refluxing benzene solution of triphenylphosphine and benzaldehyde gave no triphe-

---

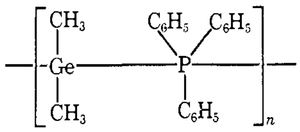
[7] A. Carrick and F. Glockling, *J. Chem. Soc., A*, 623 (1966).

[8] R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963); F. Johnson and R. S. Gohlke, *Tetrahedron Letters*, 1291 (1962); F. Johnson, R. S. Gohlke, and W. A. Nasatavicus, *J. Organometal. Chem.*, **3**, 233 (1965); M. E. Volpin, Ya. T. Struchkov, L. V. Vilkov, V. S. Mastyukov, V. G. Dulova, and D. N. Kursanov, *Izv. Akad. Nauk, Ser. Khim.*, 1909 (1963); M. E. Volpin, V. G. Dulova, Ya. T. Struckov, N. K. Bokiy, and D. N. Kursanov, *J. Organometal. Chem.*, **8**, 87 (1967); N. G. Bokiy, G. N. Zakharova, and Ya. T. Struchkov, *Zh. Struct. Khim.*, **8**, 501 (1967).

[9] In the organic series bicycloheptadiene formed as the Diels–Alder adduct of tetraphenylcyclopentadienone and diphenylacetylene releases carbon monoxide on thermolysis (W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934)), but other bicycloheptadienes undergo a reverse Diels–Alder reaction or isomerization (W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); J. Diekmann, *ibid.*, **28**, 2880 (1963)).

[10] R. B. King, *Inorg. Chem.*, **2**, 199 (1963).

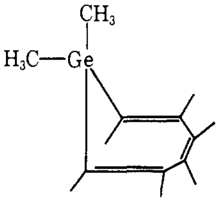
nylphosphine oxide. An insoluble Ge- and P-containing waxy material was isolated whose ir spectrum contained absorptions due to methylgermanium groups, phenyl groups, and a likely Ge–P bond at 830 cm^{-1}. This material is probably a polymer with a Ge–P backbond structure



If a phosphorus–germanium ylide had formed, its polymerization predominates over the Wittig reaction with benzaldehyde.

Pyrolysis of the 7-germanorbornadiene was also carried out in the presence of cyclohexene, a useful trap for carbene intermediates. Analysis by nmr of the product mixture separated by glpc using a computer of average transients failed to detect methylene resonances in any of the organogermanium products. A reverse Diels–Alder reaction had occurred to a small extent to form 1,1-dimethyl-2,3,4,5-tetraphenylgermole, but no reaction with cyclohexene had taken place. No reaction was observed with either ethylene or nitric oxide.

A yellow color appeared when 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene was dissolved in benzene. Gilman, *et al.*, have described the rearrangement of the analogous 7,7-diphenyl-7-silanorbornadiene in benzene–ethanol or on treatment with basic alumina to give a yellow compound for which they tentatively proposed a silacycloheptatriene structure.[3,11] The 7-germanorbornadiene also rearranges in benzene–methanol to give a yellow solid which takes up bromine to yield dimethyldibromogermane and dimethyl tetraphenylphthalate. Some decomposition to the phthalate accompanies the isomerization. Column chromatography of the yellow isomer results in further decomposition. The nmr spectrum of the isomer shows the nonequivalence of the two methylgermanium groups, with one methyl resonance at τ 10.21. The abnormally large diamagnetic shielding needed to produce such a high shift could be rationalized on the basis of a germacycloheptatriene structure with the germanium atom out of the plane of the six carbons, in which the



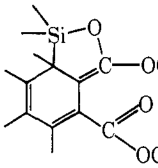
endo-methylgermanium would be more affected by the triene system of the ring.[12]

The 7-germanorbornadiene rearranges at a moderate rate in methylene chloride with *ca.* 58% decomposition to a dimethylgermanium polymer and dimethyl tetraphenylphthalate. Although this yellow isomer also contains two nonequivalent methylgermanium groups and two nonequivalent carbomethoxy groups, it is clear that it is different from the benzene–methanol rearrangement product as shown by comparison of their nmr spectra (*e.g.*, the absence of the methylgermanium resonance at τ 10.21 in the latter). Both these isomers resist hydrogenation in ethyl acetate using a PtO_2 catalyst.

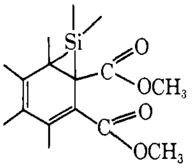
Acknowledgments. This investigation was supported by National Science Foundation Grant GP-5025 and by the Advanced Research Projects Agency. The authors are indebted to the Department of Chemistry, Harvard University, for the use of their MS-9 mass spectrometer and to Drs. G. O. Dudek and J. Wright for their kind assistance.

---

(11) Two other possible isomeric structures were considered



and



the latter in view of the formal analogy with the cycloheptatriene–norcaradiene equilibrium.

(12) The organic analog of the bridge compound, bicyclo[2.2.1]-heptadiene, undergoes thermal isomerization to cycloheptatriene: W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).