

SYNTHESIS OF SOME FUNCTIONAL GERMANIUM HETEROCYCLES: GERMIRENES AND DERIVATIVES OF GERMACYCLOPENTENE

JOHN V. SCIBELLI and M. DAVID CURTIS

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104 (U.S.A.)

(Received December 23rd, 1971)

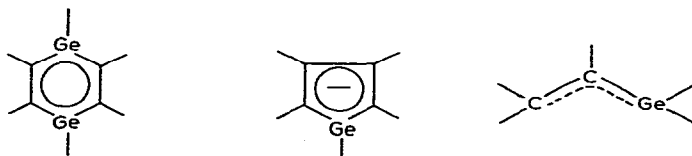
SUMMARY

The germirene, 1,1,4,4-tetraiodo-2,3,5,6-tetramethyl-1,4-digerma-2,5-cyclohexadiene, (VI), was prepared from germanium diiodide and 2-butyne. Reduction with lithium aluminum hydride replaces the iodine with hydrogen. The hydride reacts with mercuric chloride to form *trans*-1,4-dichloro-2,3,5,6-tetramethyl-1,4-digerma-2,5-cyclohexadiene, (VIII), which in turn reacts with carbon tetrachloride to produce 1,1,4,4-tetrachloro-2,3,5,6-tetramethyl-1,4-digerma-2,5-cyclohexadiene, (X). Compound (VIII) reacts with methyl Grignard reagent to give 1,2,3,4,5,6-hexamethyl-1,4-digerma-2,5-cyclohexadiene, (IX). Attempts to form metal carbonyl complexes of (VIII) and (IX) are described.

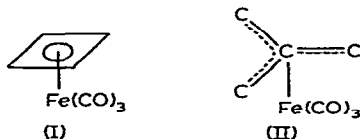
Bromine adds to the double bond of 1,1-dibromo-1-germa-3-cyclopentene to give 1,1,3,4-tetrabromo-1-germacyclopentane which could not be dehydrohalogenated to a functional germacyclopentadiene. 1,1-dimethyl-2-bromo-1-germa-3-cyclopentene was also prepared, but could not be dehydrohalogenated.

INTRODUCTION

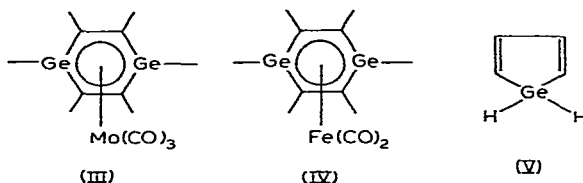
The lack of compounds containing $p_{\pi}-p_{\pi}$ bonds between carbon and germanium is evidence for the extreme instability of such a system. It has been proposed that extended systems, *e.g.*,



might be stabilized by coordination to metal carbonyls^{1,2}. In this connection several unstable π -systems have been stabilized by coordination to transition metal carbonyls, *e.g.*, cyclobutadiene³, (I) and trimethylenemethyl⁴, (II).



In this paper we present the results of our attempts to prepare digermabenzene metal complexes, (III) and (IV), and unsubstituted germole (V).



Digermabenzene complexes were chosen because previous work had led to efficient syntheses of digermacyclohexadienes (germirenes) which appeared to be promising intermediates⁵⁻⁷.

Previous attempts to prepare metal complexes of germoles were apparently hampered by the presence of phenyl substituents on the germole ring^{1,8}, thus our attempt to prepare the unsubstituted compound, (V).

EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were obtained on a Varian Model T-60 spectrometer in benzene-*d*₆ solution. IR spectra were routinely obtained as KBr disks on a Beckman IR-9 spectrophotometer. All reactions and manipulations of solutions were carried out under a nitrogen atmosphere.

1,1,4,4-Tetraiodo-2,3,5,6-tetramethyl-1,4-digerma-2,5-cyclohexadiene (VI)

Germanium diiodide was prepared by the method of Foster⁹; GeCl₄ being employed in place of GeI₄. Benzene, ca. 30 ml, and 8 g (0.114 mole) of 2-butyne were distilled, under reduced pressure, into a 100 ml Hoke cylinder which was charged with 12 g (37 mmole) of germanium diiodide. The cylinder was then heated to 170° for 7 h with agitation. Upon cooling to room temperature, unreacted 2-butyne was recovered by distillation. The reaction mixture was dissolved in hot toluene and filtered. The filtrate was concentrated giving a yellow solid. Subsequent recrystallization of the yellow solid gave white crystals of pure (VI); m.p. 273–275°; yield 30–40%. (Found: C, 12.47; H, 1.56; Ge, 18.93; I, 66.69. C₈H₁₂Ge₂I₄ calcd.: C, 12.62; H, 1.58; Ge, 19.15; I, 66.65%.) IR (cm⁻¹): 2950 m, 2920 w, 1630 b, 1432 m, 1379 s, 1148 m, 929 m, 693 s, 463 s, 378 vs, 337 vs.

2,3,5,6-Tetramethyl-1,4-digerma-2,5-cyclohexadiene (VII)

A 200 ml 3-neck flask equipped with a condenser, nitrogen inlet and magnetic stirrer was charged with 2.3 g (3 mmole) of (VI) dissolved in 140 ml of ethyl ether. Lithium aluminum hydride (0.2 g, 6 mmole) was slowly added at 0°. After addition was complete, the mixture was heated to reflux for 1 h, then cooled to room temperature and filtered. The ether was stripped from the filtrate under reduced pressure, and the residue extracted with petroleum ether (b.p. 30–60°) and filtered. The solution was concentrated and cooled in ice giving the hydride, (VII), in quantitative yield. This solid, m.p. 62–63°, can be further purified by sublimation at 50° under reduced pres-

sure. (Found: C, 37.31; H, 6.23; Ge, 56.48. $C_8H_{16}Ge_2$ calcd.: C, 37.50; H, 6.27; Ge, 56.23%.) IR (cm^{-1}): 2947 m, 2880 w, 2020 vs, 1642 b, 1439 b, 1372 m, 1092 s, 873 vs, 738 vs, 698 m, 505 vs, 435 m, 391 s.

trans-1,4-Dichloro-2,3,5,6-tetramethyl-1,4-digerma-2,5-cyclohexadiene (VIII)

The hydride, (VII), was placed in a 100 ml 3-neck flask equipped with a condenser, nitrogen inlet, and magnetic stirrer, and dissolved in 50 ml of ethyl ether. Mercuric chloride, 6 g (22 mmole), was added to the ice-cooled flask. The mixture was then refluxed 1 h and filtered. After removing the ether at reduced pressure, the residue was extracted with petroleum ether (b.p. 30–60°) and filtered. The petroleum ether was stripped at reduced pressure giving the chlorohydride, (VIII), which was purified by sublimation at 75° under reduced pressure (m.p. 94–97°). (Found: C, 29.34; H, 4.13; Cl, 21.57; Ge, 44.80. $C_8H_{14}Cl_2Ge_2$ calcd.: C, 29.41; H, 4.29; Cl, 21.70; Ge, 44.60%.) IR (cm^{-1}): 2920 m, 2850 w, 2075 vs, 1588 w, 1432 s, 1362 w, 923 m, 709 vs, 683 vs, 477 s, 442 w, 380 vs, 358 s, 327 s.

The chlorohydride, (VIII), reacts with carbon tetrachloride at room temperature to give 1,1,4,4-tetrachloro-2,3,5,6-tetramethyl-1,4-digerma-2,5-cyclohexadiene, (X) in quantitative yield, m.p. 134–137°. (Found: C, 25.58; H, 3.27; Cl, 33.79; Ge, 37.28. $C_8H_{12}Cl_4Ge_2$ calcd.: C, 24.29; H, 3.01; Cl, 35.99; Ge, 36.71%.) IR (cm^{-1}): 2932 m, 2861 w, 1431 s, 1368 m, 1255 s, 795 s, 688 s, 369 vs, 331 s.

1,2,3,4,5,6-Hexamethyl-1,4-digerma-2,5-cyclohexadiene (IX)

An ethyl ether solution of (VIII) (7 g, 22.4 mmole) was titrated with 2 M methylmagnesium iodide in ethyl ether to a pale pink endpoint using 1,10 phenanthroline as the indicator¹⁰. The ether was stripped and the residue suspended in petroleum ether (b.p. 30–60°) and the mixture filtered. The solvent was stripped from the filtrate giving a gummy oil. Sublimation under reduced pressure at 65° gave the desired product, (IX), m.p. 48–50°, in 50% yield. (Found: C, 40.85; H, 6.82; Ge, 49.70. $C_{10}H_{20}Ge_2$ calcd.: C, 42.10; H, 7.01; Ge, 50.89%.) IR (cm^{-1}): 2910 s, 2850 m, 1995 vs, 1432 m, 1408 m, 1363 (sh), 839 vs, 786 vs, 711 vs, 657 vs, 577 s, 468 m, 429 m, 381 s, 320 s.

Reaction of (IX) with $(CH_3CN)_3Mo(CO)_3$

A 1.1 g (4 mmole) sample of $(CH_3CN)_3Mo(CO)_3$, prepared by the method of Tate *et al.*¹¹, was combined with 0.8 g (2.8 mmole) of (IX) in n-hexane and refluxed 6 h under a nitrogen atmosphere. The solution was filtered giving a tan metal carbonyl polymer of undetermined composition, and a pale yellow filtrate. The solvent was stripped under reduced pressure and the unreacted (IX) recovered by sublimation.

A similar procedure employing THF as solvent gave identical results.

Reaction of (IX) with $Fe_2(CO)_9$

A 100 ml 3-neck flask was charged with 1.0 g (3 mmole) of $Fe_2(CO)_9$, 0.75 g (3 mmole) of (IX) and 50 ml ethyl ether. The solution was refluxed 2 h with magnetic stirring and then filtered. The ether was replaced by ethanol to give a viscous red liquid which could not be induced to crystallize. Attempts to purify this liquid by chromatography on a Florisil column led to decomposition. A portion of the liquid was distilled (short path) at 150° under reduced pressure to give a small amount of

red liquid which could not be adequately characterized. Decomposition of the material was noted during distillation.

Reaction of (VIII) with $\text{Na}_2\text{Fe}(\text{CO})_4$

$\text{Na}_2\text{Fe}(\text{CO})_4$ ¹², 0.64 g (3 mmole), was combined with 1.0 g (3 mmole) of (VIII) in n-hexane and refluxed 2 h. The solution was filtered giving the expected sodium chloride and a reddish filtrate. Removal of the solvent under reduced pressure gave an oil which could not be adequately characterized.

1,1,3,4-Tetrabromo-1-germacyclopentane (XII)

Germanium dibromide and 1,1-dibromo-1-germa-3-cyclopentene (XI) were prepared by the method of Curtis and Wolber¹³.

Bromine, 11.4 g (0.7 mole), dissolved in ca. 15 ml of carbon tetrachloride was added dropwise with stirring to an ice-cooled solution of 20.0 g (0.7 mole) of 1,1-dibromo-1-germa-3-cyclopentene, (XI), in carbon tetrachloride. After decoloration of the bromine was complete the solvent was stripped under reduced pressure. Recrystallization of the crude yellow solid from petroleum ether (b.p. 30–60°) gave 20 g (65% yield) of the pure white product, (XII), m.p. 70.5–71.5°. (Found: C, 10.96; H, 1.41; Br, 71.80. $\text{C}_4\text{H}_6\text{Br}_4\text{Ge}$ calcd.: C, 10.76; H, 1.41; Br, 71.60%.)

Iodine failed to react with the germacyclopentene, (XI), even after refluxing in carbon tetrachloride for 24 h.

Attempts to dehydrohalogenate (XII)

Method 1. A 5.0 g (11 mmole) sample of (XII) was treated with 3.42 g (22 mmole) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU, Aldrich) at room temperature under a nitrogen atmosphere. Immediately upon addition of the DBU a black tar formed from which no monomeric products could be obtained.

Method 2. A 100 ml 3-neck flask equipped with a constant pressure dropping funnel, nitrogen inlet and a Vigreux column attached to a dry ice-cooled flask was charged with 3.42 g (22 mmole) of DBU and ca. 30 ml of hexadecane. The system was evacuated to a pressure of 10^{-2} mmHg and the solution heated to 80° so as to "flash out" the monomeric product. A hexadecane solution of (XII) (5.0 g, 11 mmole) was added dropwise with stirring. Again a black tar appearing to be polymeric in nature was formed.

Method 3. To a carbon tetrachloride solution of (XII) (5.0 g, 11 mmole) cooled to –20° under a nitrogen atmosphere was added a carbon tetrachloride solution of DBU (3.4 g, 22 mmole) at –20° with stirring. Once again only a black tar, indicative of polymeric decomposition products, was formed.

Attempts employing other bases, such as diisopropylethyl amine, triethylamine, and potassium tert-butoxide gave similar results. The weaker base 2,6-lutidine failed to react with the tetrabromide, (XII).

1,1-Dimethyl-1-germa-3-cyclopentene (XIII)

This compound was prepared in 40% yield by the method of Mironov and Gar¹⁴, b.p. 116–118°.

Attempted bromination of (XIII)

The identical procedure as given for the bromination of the dibromide, (XI),

was followed. Removal of solvent under reduced pressure gave a colorless liquid which was identified as dimethyldibromogermane, b.p. 68–70°/20 mmHg (lit.¹⁵ 153°/746 mmHg). No addition products were obtained.

Cleavage to dimethyldichlorogermane was the only reaction observed when (XIII) was allowed to react with chlorine.

α-Bromination of (XIII) with N-bromosuccinimide

A 300 ml 3-neck flask equipped with mechanical stirrer, reflux condenser and nitrogen inlet was charged with 6.7 g (43 mmole) of (XIII), 7.7 g (43 mmole) of *N*-bromosuccinimide and 150 ml of carbon tetrachloride. Benzoyl peroxide (trace) was added as an initiator and the mixture refluxed 3 h. Upon cooling to room temperature the mixture was filtered giving 4.3 g (100% of theoretical) succinimide, m.p. 122–124 and a colorless filtrate. Removal of solvent, followed by vacuum distillation gave 7.0 g (70% yield) of 1,1-dimethyl-2-bromo-1-germa-3-cyclopentene, (XIV). The mass spectrum exhibited a parent ion peak at *m/e* 236. Peaks at *m/e* 221 and 157 corresponding to loss of methyl and bromine from the parent were also observed. The isotopic distribution pattern as well as fragmentation scheme were as expected¹⁶.

Attempts to brominate the dibromide, (XI), with *N*-bromosuccinimide were unsuccessful. The stoichiometric amount of succinimide was obtained, however only a tar could be isolated from the filtrate. Likewise, germanium dibromide reacted exothermically with 1-chlorobutadiene to give a dark orange tar from which 2-chloro-1-germa-3-cyclopentene could not be isolated.

Attempted 1,4 elimination of (XIV)

The methods already described for dehydrohalogenation of (XII) were tried. In all cases a tar formed immediately upon combination of the reagents. In no case could a monomeric product be isolated.

Determination of dipole moment of (VIII)

Dielectric constants were determined with a Wissenschaftlich-Technische Werkstätten Dipolmeter model DMO1. Refractive indices were determined with a Bausch and Lomb refractometer at the sodium-D line. Solutions of (VIII) in cyclohexane (purified by distillation from lithium aluminium hydride under nitrogen) were prepared with weight fractions between 10^{-3} and 2×10^{-2} , maintaining a nitrogen atmosphere. The data were treated according to the method of Hedstrand¹⁷, giving a dipole moment of 0 ± 0.05 D.

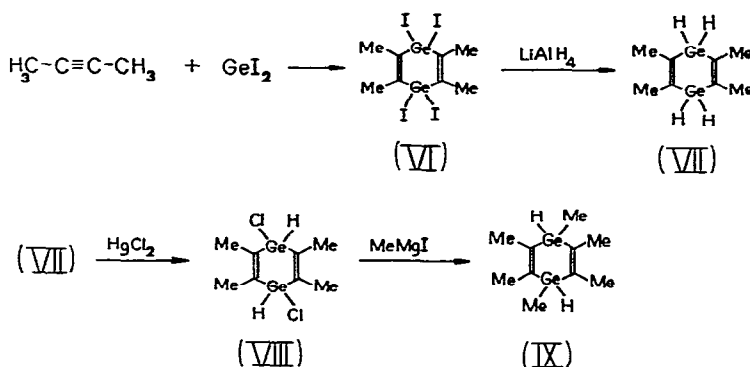
RESULTS AND DISCUSSION

The overall synthetic route to the methylhydride (IX) is shown in Scheme 1.

Previous^{5,6} methods of preparing digermacyclohexadienes had to be modified to give high yields of the methyl substituted germirene, (VI). Especially important was the reaction temperature and the rigorous exclusion of traces of water. The tetraiodide, (VI), is an air-stable, white solid which reacts immediately with water to give a gummy hydroxide, which can be converted to the oxide upon heating.

Reduction of (VI) with lithium aluminum hydride gave the tetrahydride, (VII). The hydride, (VII), decomposed during work-up when the excess lithium aluminum

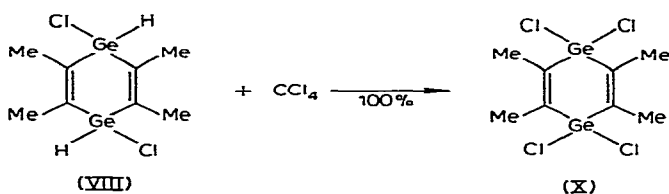
SCHEME 1



hydride was destroyed with aqueous solutions of hydrochloric acid, ammonium chloride or sodium hydroxide. Hence, the ether was removed under vacuum and the product extracted from the excess lithium aluminum hydride with pentane. The tetrahydride, (VII), is slightly air sensitive but can be stored indefinitely under a dry nitrogen atmosphere. The IR spectrum of (VII) exhibited an intense peak at 2020 cm^{-1} attributable to the Ge-H stretch. In the NMR, two singlets at $\delta 4.33 \text{ ppm}$ and 1.77 ppm (area ratio 1/3) were observed corresponding to the Ge-H and methyl protons, respectively.

When (VII) was combined with mercuric chloride¹⁸ one hydrogen on each germanium was replaced by chloride giving the chlorohydride, (VIII). It was hoped that this reaction would proceed by a concerted mechanism giving chlorides *cis* with respect to the plane of the ring. A *cis* configuration would be necessary for subsequent complexation to metal carbonyl moieties. The Ge-H stretch of (VIII) was observed in the IR at 2075 cm^{-1} . This shift to higher frequency upon substitution of chlorine for hydrogen is consistent with expectations^{19,20}, and the observation of only one IR band eliminates a structure in which both chlorines are on the same germanium atom. The NMR spectrum of (VIII) consisted of two singlets, indicative of only one isomer, at $\delta 5.45 \text{ ppm}$ and 1.77 ppm (area ratio 1/6) corresponding to the Ge-H and methyl protons, respectively. Again the shift in position of the Ge-H signal upon substitution of chlorine for hydrogen is expected²¹.

It is interesting to note that the tetrachloride, (X), is not formed when (VIII) is refluxed with mercuric chloride but is obtained in quantitative yield when (VIII) is dissolved in carbon tetrachloride at room temperature.



The methylhydride, (IX), is obtained by titrating (VIII) with a methyl Grignard reagent. In this way, an excess of Grignard reagent was avoided, simplifying work-up

considerably. The Ge-H stretch of (IX) was found at 1995 cm^{-1} ; the expected shift again being observed. The NMR spectrum consisted of a quartet ($J = 3\text{ Hz}$) at $\delta\ 4.40\text{ ppm}$, a singlet at 1.77 ppm and a doublet at 0.30 ppm ($J = 3\text{ Hz}$) in an area ratio of 1/6/3 corresponding to Ge-H, C-CH₃ and Ge-CH₃ protons respectively.

From these data it appeared that only one of the two possible isomers, *cis* or *trans*, was present. In order to ascertain which isomer was present, the dipole moment of (VIII) was determined. The chlorohydride, (VIII), was chosen for this study due to its stability by comparison to the methylhydride, (IX), and the larger separation between the theoretical dipole moments for its two isomers. A moment of $0 \pm 0.05\text{ D}$ was obtained in cyclohexane solvent, thus indicating that (VIII) has the *trans*-configuration. A simultaneous displacement of both hydrogens by mercuric chloride would undoubtedly give the *cis*-isomer. Thus the two chlorides must add independently and a mixture of isomers might be expected. Addition of the first chloride must create a considerable steric barrier to the contiguous approach of a second molecule of mercuric chloride, thus leading to exclusive formation of the *trans*-isomer.

It has been shown²² that substitution reactions of germanium chlorides parallel those of similar silicon chlorides which proceed with complete inversion of configuration²³. In view of this and the NMR evidence, it seems certain that the methylhydride, (IX), has the same stereochemistry as the chlorohydride.

Although we expected complexation reactions to proceed readily only with the *cis*-isomers of (VIII) and (IX), we deemed it worthwhile to determine if metal carbonyl complexes could be obtained from the *trans*-isomers.

King has shown²⁴ that tris(acetonitrile)molybdenum tricarbonyl reacts with compounds having π systems to give arene molybdenum tricarbonyl complexes. Most of the reactions reported by King are simple displacement reactions, although cyclopentadiene is reduced to cyclopentadienide by the acetonitrile complex. Pentaphenylgermole^{1,25} is also reduced by tris(acetonitrile)molybdenum tricarbonyl. In contrast, compound (IX) failed to react with $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$ under a variety of conditions. At elevated temperatures, the molybdenum carbonyl complex appeared to decompose to an insoluble, polymeric carbonyl which did not contain the germirene ligand. The hydride, (IX), could be recovered in near quantitative yield by sublimation.

The oxidation-reduction reaction between $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$ and cyclopentadiene or pentaphenylgermole may be thought of as a reaction between a metal and an acid. The high reactivity of the cyclopentadiene and the germole may be attributed to their relatively high acidities¹. The $\text{p}K$ of (IX) is probably close to 23^1 which is apparently too low to permit reaction with the molybdenum carbonyl complex.

The methyl hydride, (IX), did react with diiron enneacarbonyl to give viscous red oils which decomposed on attempted purification. The chlorohydride, (VIII), and disodium tetracarbonylferrate(-2) reacted to give sodium chloride and a red gum, which appeared to be polymeric but could not be adequately characterized. In light of the *trans* structure, derived from the dipole moment, formation of polymeric products is expected.

The addition of bromine to 1,1-dibromo-1-germa-3-cyclopentene, (XI), proceeds readily to give 1,1,3,4-tetrabromo-1-germacyclopentane, (XII), presumably with the 3,4-bromines *trans*. The NMR spectrum of this compound is shown in Fig. 1.

The spectrum consists of multiplets at $\delta\ 4.9\text{ ppm}$ and 2.6 ppm (area ratio 1/2)

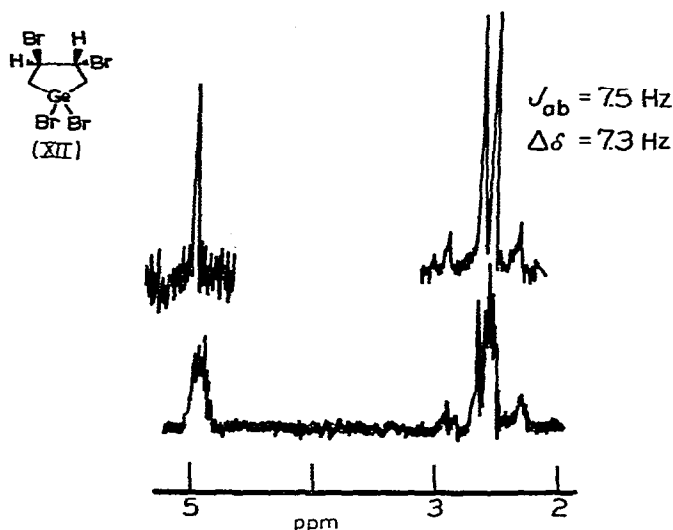


Fig. 1. 60 MHz spectrum of (XII).

which upon decoupling collapse respectively to a singlet and an AB quartet, $J(AB) = 7.5$ Hz, $\Delta\delta(AB) = 7.3$ Hz.

It is interesting to note that bromine or chlorine cleaved the ring of 1,1-dimethyl-1-germa-3-cyclopentene, (XIII), to give Me_2GeX_2 ($X = \text{Br}, \text{Cl}$). Reaction of (XIII) with *N*-bromosuccinimide gave 1,1-dimethyl-2-bromo-1-germa-3-cyclopentene, (XIV). A similar bromination attempt with the dibromide, (XI), was unsuccessful, again emphasizing the remarkable difference in chemistry of these two compounds. Attempts to dehydrohalogenate (XII) and (XIV) under a variety of conditions gave polymeric tars. From this study it is evident that dehydrobromination of the bromine-substituted germacyclopentanes or germacyclopentenenes will not give unsubstituted germole.

ACKNOWLEDGEMENTS

The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work (grant 4858-AC3). One of the authors (J.V.S.) is also grateful for a Sun Oil Company summer fellowship, administered by the Department of Chemistry. The mass spectrometer was purchased with the aid of the National Science Foundation, grant GP-8345.

REFERENCES

- 1 M. D. Curtis, *J. Amer. Chem. Soc.*, **91** (1969) 6011.
- 2 R. C. Job and M. D. Curtis, submitted for publication.
- 3 J. D. Fitzpatrick, L. Watts, G. F. Emerson and R. Petit, *J. Amer. Chem. Soc.*, **87** (1965) 3254.
- 4 G. F. Emerson, K. Erlich, W. P. Giering and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **88** (1966) 3172.
- 5 M. E. Volpin, V. G. Dulova, Yu. T. Struchkov, N. K. Bokiy and D. N. Kursanov, *J. Organometal. Chem.*, **8** (1967) 87.
- 6 M. E. Volpin, Yu. T. Struchkov, L. V. Vilkov, V. S. Mastuykov, V. G. Dulova and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1963) 2067.

- 7 F. Johnson and R. S. Gohlke, *Tetrahedron Lett.*, 26 (1962) 1291.
 - 8 B. F. Hallam and P. C. Pauson, *J. Chem. Soc.*, (1956) 3030, and S. McVey and P. C. Pauson, *J. Chem. Soc.*, (1965) 4312.
 - 9 L. S. Foster, *Inorg. Syn.*, 3 (1950) 63.
 - 10 S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, 9 (1967) 165.
 - 11 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1 (1962) 433.
 - 12 R. B. King, *J. Amer. Chem. Soc.*, 83 (1961) 3604; J. Takats, private communication.
 - 13 M. D. Curtis and P. Wolber, *Inorg. Chem.*, 11 (1972) 431.
 - 14 V. F. Mironov and T. K. Gar, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1963) 578; *Dokl. Akad. Nauk SSSR*, 152, 5 (1963).
 - 15 V. A. Ponomarenko and G. Ya. Vzenkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1957) 994.
 - 16 A. M. Duffield, C. Djerassi, P. Mazerolles, J. Dubac and G. Manuel, *J. Organometal. Chem.*, 12 (1968) 123.
 - 17 G. Hedestrand, *Z. Phys. Chem. B*, 2 (1929) 428.
 - 18 H. H. Anderson, *J. Amer. Chem. Soc.*, 82 (1962) 3016.
 - 19 R. Mathis, J. Satgé and F. Mathis, *Spectrochim. Acta*, 18 (1962) 1463.
 - 20 R. Mathis, N. Constant, J. Satgé and F. Mathis, *Spectrochim. Acta*, 20 (1964) 515.
 - 21 M. L. Maddox, S. L. Stafford and H. D. Kaesz, *Advan. Organometal. Chem.*, 3 (1965) 1.
 - 22 A. G. Brook and G. J. D. Peddle, *J. Amer. Chem. Soc.*, 85 (1963) 2338.
 - 23 L. Sommers, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill N.Y., 1st ed., 1965, p. 76-94.
 - 24 R. B. King, *Inorg. Chem.*, 5 (1966) 1837.
 - 25 J. V. Scibelli and M. D. Curtis, unpublished results.
- J. Organometal. Chem.*, 40 (1972)