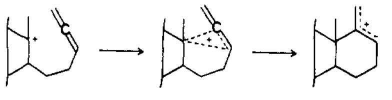
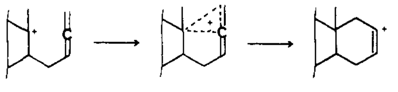
the case of **17** the terminal carbon is unsubstituted[5] and thus conversion to the vinyl cation **5** is favored by electronic factors (and possibly geometric factors). This rationale is useful in that it suggests that substitution of a single methyl group at C-1 in the allenyl cation **1** might lead to preferential formation of five-membered-ring products.[19] Studies to examine this hypothesis are in progress.[20]



2 16 3



1 17 5

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References and Notes

(1) Examples include acetylenes,[2] allenes,[3] and silyl enol ethers.[4]

(2) (a) W. S. Johnson, *Bioorg. Chem.*, **5,** 51 (1976); (b) S. W. Baldwin and J. C. Tomesch, *Synth. Commun.*, **5,** 445 (1975); (c) Tj. Boer-Terpstra, J. Dijkink, H. E. Shoemaker, and W. N. Speckamp, *Tetrahedron Lett.*, 939 (1977), and references cited therein.

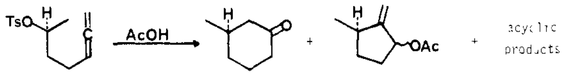
(3) (a) H. T. Hall, Ph.D. Dissertation, Stanford University, 1973. See ref 2a. (b) M. H. Sekera, B.-A. Weissman, and R. G. Bergman, *J. Chem. Soc., Chem. Commun.*, 679 (1973).

(4) S. Hashimoto, A. Itoh, Y. Kitagawa, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **99,** 4193 (1977).

(5) It has been pointed out that, although attack of an electrophile on the central carbon of an allene gives an allyl cation, little of this potential stabilization is realized in the transition state.[3,6]

(6) P. J. Stang, *Prog. Phys. Org. Chem.*, **10,** 205 (1973).

(7) In one previous study on this type of system acetolysis of tosylate i gave predominantly uncyclized products, but both ketone ii (6% yield) and allylic acetate iii (15% yield) were formed: B. Ragonnet, M. Santelli, and M. Bertrand, *Helv. Chim. Acta*, **57,** 557 (1974).



i ii iii

(8) The new compounds prepared in this study were characterized by their spectra (IR, ^1H and ^{13}C NMR) and by elemental composition (combustion analysis or high resolution MS) on the stable compounds.

(9) Cf. M. Gaudemar, *Ann. Chim.* (*Paris*), **1,** 161 (1956).

(10) K. E. Harding and K. A. Parker, *Tetrahedron Lett.*, 1633 (1971).

(11) Only a trace of allenic material could be detected from this reaction although previous preparations of **8** have been reported to contain significant amounts of allene.[12]

(12) K. A. Parker and W. S. Johnson, *J. Am. Chem. Soc.*, **96,** 2556 (1974).

(13) The predominant formation of allenes in the coupling of propargylmagnesium bromide with allyl bromide in THF has been previously noted: L. Miginiac-Groizeleau, *Bull. Chem. Soc. Fr.*, 1449 (1963).

(14) W. S. Johnson and K. E. Harding, *J. Org. Chem.*, **32,** 478 (1967); W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *J. Am. Chem. Soc.*, **87,** 5148 (1965).

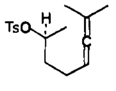
(15) The NMR spectra of the enol formates from cyclization of alcohols **14** and **16** showed that they were isomeric as expected on mechanistic considerations. Thus these procedures could be useful as a means for regiospecific generation of enolates.

(16) The use of $Ac_2O/AcOH/HClO_4$ for cyclizations involving a cyclohexenone functionality as the initiating group was developed in our laboratories: J. L. Cooper and K. E. Harding, *Tetrahedron Lett.*, 3321 (1977).

(17) We recently found that, in some cases, cyclization of cyclohexenones with TFAA/TFA proceeds in higher yields than with $Ac_2O/AcOH/HClO_4$.[16]

(18) G. Modena and U. Tonallato, *Adv. Phys. Org. Chem.*, **9,** 215–225 (1971).

(19) Bertrand and coworkers[7] have reported that the system with two methyl groups on the terminal carbon (iv) did give good yields of five-membered-ring products.



iv

(20) This research constitutes a portion of the Ph.D. requirements for J.L.C. and P.M.P.

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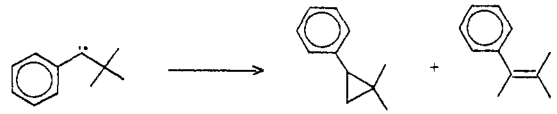
Received September 26, 1977

Gas-Phase Reactions of Phenyltrimethylgermylcarbene. Evidence for Transient Formation of 1,1-Dimethyl-2-phenylgermirane[1]

Sir:

The gas-phase chemistry of phenyl-*tert*-butylcarbene and phenyltrimethylsilylcarbene is now reasonably well worked out.[2] In the *tert*-butylcarbene the normal 1,3-insertion reaction to give the major product, 1,1-dimethyl-2-phenylcyclopropane (**1**) is accompanied by ~15% carbon–carbon insertion to produce trimethylstyrene (**2**).[2] In the silicon case the carbene eschews the usual reactions in favor of addition to the benzene ring to give, ultimately, the silaindan **3**. Minor amounts of products analogous to **1** and **2** can be detected by trapping experiments in the case of the silene and through formation of styrene by extrusion of dimethylsilylene from the silirane.[2] Here we provide a preliminary account of the properties of the analogous germanium-containing carbene and evidence for the formation of a germirane.



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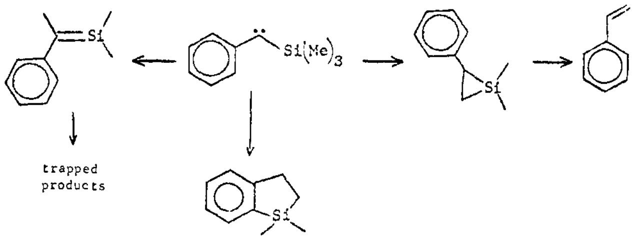
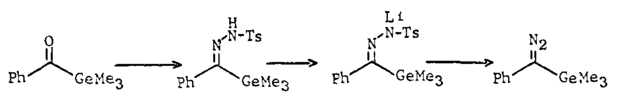


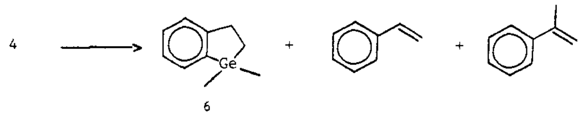
3

Phenyltrimethylgermyl ketone[3] was converted to its tosylhydrazone in good yield by standard procedures. Treatment with butyllithium gave a salt **4** that could be converted on gentle heating under vacuum into the orange diazo compound **5**.



4 5

Flash vacuum pyrolysis of **4** or gas-phase decomposition of **5** in either a vertical quartz tube packed with aged quartz chips or in a conventional Pyrex flow system led to the same set of products, although in slightly different ratios depending upon the method. The best yields were obtained from **4** pyrolyzed at 450 °C under high vacuum. Under these conditions the major product was germaindan **6** (45%) and significant minor products were styrene (15%) and α-methylstyrene (7.5%). Traces of benzyltrimethylgermane and other unidentified products were also found.



6

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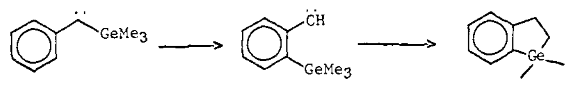
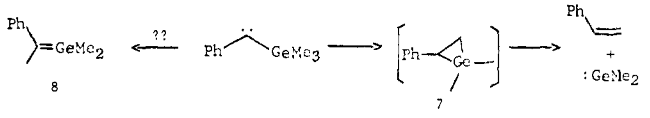
Germaindan **6** is doubtless the product of a carbene-to-carbene rearrangement just as is the analogous silaindan **3**.[2,4]



We suggest that styrene owes its appearance to the formation of germirane **7** which extrudes dimethylgermylene,[5] again in analogy to the silicon case.[2] Stable germiranes are not known,[6] although reactions in which they are permissible intermediates have been reported.[4,7] Nevertheless, it is fair to say that no reaction yet described *demands* the intermediacy of a compound containing germanium in a three-membered ring. We believe that the isolation of styrene provides strong evidence for the transient existence of a germirane. Germaindan **6** is a source of neither styrene nor α-methylstyrene, although higher molecular weight products are formed on pyrolysis of **6**.[8]



We have been unable to detect the germene **8** that would be produced by carbon–germanium insertion.[9] Although we have attempted several trapping experiments, the caution warranted by all negative results is most appropriate here.[10]

References and Notes

(1) Support for this work by the National Science Foundation through Grant MPS 74-05690 is gratefully acknowledged. Portions of this work are taken from the A.B. thesis of E.B.N., Princeton University, 1977.

(2) W. Ando, A. Sekiguchi, A. J. Rothschild, R. R. Gallucci, M. Jones, Jr., T. J. Barton, and J. A. Kilgour, *J. Am. Chem. Soc.*, **99**, 7707 (1977).

(3) A. Brook, *J. Am. Chem. Soc.*, **79,** 4373 (1957); K. Yates and F. Agolini, *Can. J. Chem.*, **44,** 2229 (1966); A. G. Brook, *J. Am. Chem. Soc.*, **79,** 4373 (1957).

(4) Anal. Calcd for $C_{10}H_{14}Ge$: C, 58.08; H, 6.82. Found: C, 58.26; H, 6.78. ^1H NMR (δ, CCl_4): 7.37 (m, 4 H), 3.33 (t, 2 H), 1.35 (t, 2 H), 0.02 (s, 6 H). See ref 2 for a comparison with the analogous silicon-containing compound.

(5) For a review of germylenes see J. Satge, M. Massol, and P. Riviere, *J. Organomet. Chem.*, **56**, 1 (1973).

(6) See, however, the last sentence of R. L. Lambert and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972).

(7) D. P. Paquin, R. J. O'Connor, and M. A. Ring, *J. Organomet. Chem.*, **80,** 341 (1974). For a dissenting view see S. P. Kolesnikov, A. I. Ioffe, and O. M. Nefedov, *Bull. Acad. Soc. USSR Chem. Sci.*, **24,** 896 (1975); A. I. Ioffe, L. I. Korzhenevich, S. P. Kolesnikov, and O. M. Nefedov, *ibid.*, **25,** 323 (1976).

(8) Neither photolysis of **5** in a neopentane matrix at −196 °C, followed by quenching with methanol at −30 °C, nor irradiation of benzene/methanol solutions of **5** at room temperature yielded evidence of **7.** In the latter experiment reaction of the carbene with methanol yielded the major product. It is scarcely surprising that in solution intermolecular reaction should be preferred to formation of a germirane.

(9) For a successful trapping of a germene see T. J. Barton, E. A. Kline, and P. M. Garvey, *J. Am. Chem. Soc.*, **95,** 3078 (1973).

(10) We prefer not to comment at this time upon the formation of α-methylstyrene, but it is possible that its appearance and the absence of **8** are connected.

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Hypovalent Radicals. 2.[1] Fluorenylidene Anion Radical—Possible Redox Potentials for the Fluorenylidene/Fluorenylidene Anion Radical Couple

Sir:

The electronic structure of $H_2C^{-}\cdot$ has been examined by ab initio[2] and MINDO/3[3,4] calculations and is in excellent agreement with the estimated experimental structure derived from its photoelectron spectrum;[2a] in the present context, $H_2C^{-}\cdot$ is a σ-anion p radical.[5] MINDO/3 calculations of cyclopentadienylidene anion radical show that the doublet ground state is a carbene π-anion σ radical.[6,7] It was felt that this electronic structure should also apply to the fluorenylidene anion radical ($Fl^{-}\cdot$). Thus, the reactions of and products from $Fl^{-}\cdot$ might then serve as a "standard" to which other carbene anion radicals, e.g., diphenylcarbene anion radical ($Ph_2C^{-}\cdot$),[1] could be compared to gain some structure/reactivity information from their reactions.

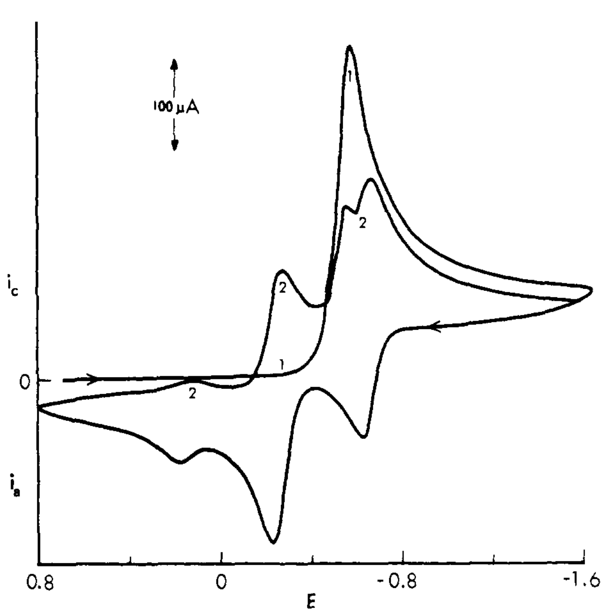

Figure 1. Cyclic voltammogram of 5×10^{-3} M FlN_2 in DMF-(n-Bu)$_4$-$N^{+}ClO_4^{-}$ at a scan rate of 0.2 V/s: working electrode, 0.25-cm^2 planar Pt button; reference electrode, Cd(Hg)/$CdCl_2$, KCl (saturated) in DMF (−0.75 V vs. SCE). The numbers 1 and 2 denote first and second cycles, respectively.

The cyclic voltammetric reduction of 9-diazofluorene (FlN_2) at a platinum electrode in DMF-(n-Bu)$_4N^{+}ClO_4^{-}$ shows a cathodic wave near −0.60 V vs. Cd(Hg)/$CdCl_2$ (Figure 1). Although the 9-diazofluorene anion radical ($FlN_2^{-}\cdot$) is too short-lived to give an anodic wave on the reverse, positive-going sweep, three reversible couples do arise which are seen on this and all subsequent cycles near +0.16, −0.24, and −0.64 V. The normalized peak heights for the most positive couple are kinetically controlled and decrease in magnitude with either an increase in the concentration of FlN_2 or a decrease in the cyclic voltammetric scan rate. The two remaining processes are also kinetically controlled and were ascertained from product studies of exhaustively electrolyzed solutions and by comparison with an authentic sample to arise from the stepwise reduction of fluorenone azine [($Fl{=}N$-)$_2$] to its dianion. Exhaustive, controlled-potential electrolysis of FlN_2 at any potential in the range from −0.8 to −2.0 V afforded ($Fl{=}N$-)$_2$ in high yield (91 ± 7%).[8] Fluorenone was observed as a minor product when electrolysis was effected in the presence of adventitious amounts of oxygen; neither fluorene nor any dimeric product was detected by gas chromatography in other than trace amount (<0.5%).

The identities of the transient species which give rise to the most positive redox couple in Figure 1 and the observed kinetic behavior are even more interesting. The possibility that a solvent- or electrolyte-derived intermediate was the unidentified electroactive component was eliminated when similar cyclic voltammetric behavior was observed for FlN_2 in solvent-electrolyte systems of CH_3CN-(n-Bu)$_4N^{+}ClO_4^{-}$, DMF-$LiClO_4$, and $(CH_3)_4N^{+}PF_6^{-}$ in DMF and CH_3CN. In addition, cyclic voltammetric examination of ($Fl{=}N$-)$_2$ and other plausible products (fluorene, fluorenone, 9-aminofluorene, 9,9′-bifluorenyl, and 9,9′-bifluorenylidene) showed that none of these compounds gave a reversible redox couple near 0.16

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