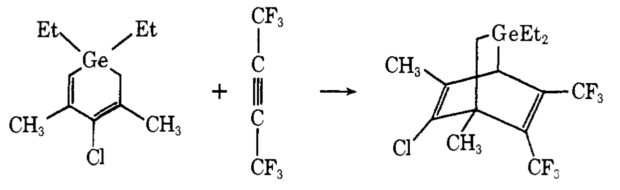
Evidence for a Germanium–Carbon (p–p)π Double Bond

Sir:

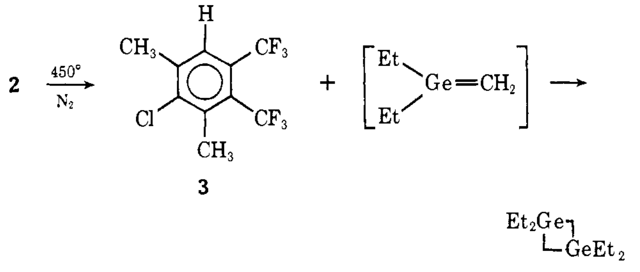
Once thought to be nonexistent,[1] considerable evidence for the transient existence of compounds containing a silicon–carbon,[2] silicon–silicon,[3] or silicon–oxygen[4] (p–p)π double bond has recently accrued. However, we are aware of only one case where (p–p)π bonding between germanium and carbon has been invoked (this in an attempt to explain the much greater acidity of pentaphenylgermole relative to triphenylgermane).[5] A single report has appeared of an attempt to generate a "pure" germanium–carbon (p–p)π double bond, and the route employed, pyrolysis of a germacyclobutane, proved unsuccessful.[6] We report here strong evidence for the intermediacy of a molecule containing a germanium–carbon (p–p)π double bond.

Germacyclohexadiene (**1**)[7] reacted in a sealed tube (overnight at 25° and then 5 hr at 70–80°) with a twofold excess of perfluoro-2-butyne to provide quantitative conversion (by nmr, 80–90% isolated) to the expected Diels–Alder adduct **2**:[8] a colorless, viscous liquid [nmr (CCl_4) δ 0.7 (s, 2 H, CH_2), 0.9–1.2 (m, 10 H, $GeEt_2$), 1.8–1.9 (overlapping Me singlet with Me quartet split by one CF_3, J_{HF} = 2.6 Hz), 3.75 (s, 1 H, bridgehead CH)].[9]



1 **2**

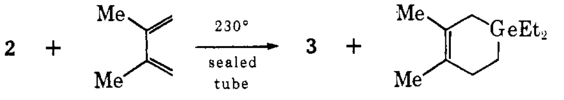
Complete pyrolysis of **2** was conducted in a nitrogen flow system (0.5 Torr, 450°) and the pyrolysate collected at −196°. Analysis of the pyrolysate by gas chromatography revealed only two components and a total absence of **2**. Separation of the two products by preparative gas chromatography afforded pure samples of **3** [50%; nmr (CCl_4) δ 2.45 (s) and 2.55 (d, J = 2.4 Hz) (6 H), 7.48 (br s, 1 H); mass spectrum *m/e* calcd for $C_{10}H_7{}^{35}ClF_6$ 276.0140, found 276.0125][8] and **5** [35%; nmr (CCl_4) δ 0.5 (s, 4 H, ring CH_2),[10] 0.9–1.1 (m, 20 H, Et); *m/e* calcd for $C_{10}H_{24}{}^{74}Ge_2$ 292.0302, found 292.0302][8] as colorless, viscous liquids.



3 **5**

The formation of 1,1,3,3-tetraethyl-1,3-digermacyclobutane (**5**) strongly argues for the intermediacy of 2-ethyl-2-germabutene (**4**), a compound containing the germanium–carbon (p–p)π double bond. Formation of 1,3-disilacyclobutanes from various thermal precursors has often been cited as evidence for silaalkene intermediates. Indeed the gas-phase thermal decomposition of the silabicyclo[2.2.2]octadiene system proceeds in a fashion exactly analogous to that described here for **2**.[2f]

Although trapping of **4** with anything other than itself has proven much more difficult than in the case of silaalkenes, we have been successful in one case. The copyrolysis of **2** and an excess of 2,3-dimethylbutadiene (sealed tube, 230°, 20 min) cleanly afforded the Diels–Alder adduct **6**[8] [59%; nmr ($DCCl_3$) δ 0.50–1.15 (m, 12 H, CH_2GeEt_2), 1.36 (br s, 2 H, $GeCH_2$), 1.73 (br s, 6 H, CH_3), 2.0–2.25 (br t, 2 H, CH_2); mass spectrum *m/e* calcd for $C_{11}H_{22}{}^{74}Ge$ 228.09334, found 228.09214]. This same product is formed, albeit in lower yield, in the flow gas-phase copyrolysis.



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[1] W. E. Dasent, "Nonexistent Compounds," Marcel Dekker, New York, N. Y., 1965.

[2] (a) N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov, and V. I. Zavyalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3, 584 (1966); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (c) R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, *J. Organometal. Chem.*, **34**, 53 (1972); (d) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 882 (1971); (e) T. J. Barton and C. L. McIntosh, *Chem. Commun.*, 861 (1972); (f) T. J. Barton and E. A. Kline, *J. Organometal. Chem.*, **42**, C21 (1972); (g) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7926 (1972); (h) P. Boudjouk and L. H. Sommer, *Chem. Commun.*, 54 (1973).

[3] D. N. Roark and G. J. D. Peddle, *J. Amer. Chem. Soc.*, **94**, 5837 (1972).

[4] L. E. Gusel'nikov, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **6**, 84 (1971); I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971). Copyrolysis of 1,1-dimethylsilacyclobutane and benzaldehyde affords good yields of styrene, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane; T. J. Barton and E. A. Kline, unpublished observation. We believe that this results from the cycloaddition of $Me_2Si{=}CH_2$ to the carbonyl group to form an unstable silaoxetane which thermally decomposed to styrene and $Me_2Si{=}O$ which undergoes cyclic oligomerization. A similar reaction with heptanal has recently been mentioned in the literature: ref 2h, footnote 5. A single attempt to perform an analogous reaction with **2** and benzaldehyde was unsuccessful in our hands.

[5] M. D. Curtis, *J. Amer. Chem. Soc.*, **91**, 6011 (1969).

[6] N. S. Nametkin, *et al.*, *Dokl. Akad. Nauk SSSR*, **194**, 1096 (1970). Although no germanium-containing products were found which could be attributed to the intervention of a "germaalkene," the formation of ethylene leaves open the question whether such a species is involved in at least part of this thermal decompositon.

[7] D. Seyferth, *et al.*, *J. Amer. Chem. Soc.*, **92**, 657 (1970).

[8] Satisfactory (±0.2%) analyses for C and H were obtained for compounds **2** (also Cl), **3** (also Cl), **5**, and **6**.

[9] The spectral information on **2** does not totally exclude certain isomeric structures, some of which could conceivably thermally extrude **4**. The likelihood that this combination took a course other than the 2 + 4 addition is small in our opinion. A detailed discussion of this point will be included in the complete paper.

[10] The chemical shift of the ring-methylene protons of **5** is quite similar to the value of δ 0.64 for the only reported analogous ring system, 1,1,3,3-tetramethyl-1,3-digermacyclobutane: V. F. Mironov, T. K. Gar, and S. A. Mikhailyants, *Dokl. Akad. Nauk SSSR*, **188** (1), 120 (1969).

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A Mechanism for Electrophilic Nitration

Sir:

Although electrophilic aromatic nitration has received an overwhelming amount of attention, little agreement about its mechanistic details has thus far