(7) Materials were synthesized using the following literature preparations. I: Meerwein, v. H.; Bodenbenner, K.; Barner, P.; Kunert, F.; Wunderlich, K. *Justus Liebigs Ann. Chem.* **1960,** *632*, 38–55. II: von E. Doering, W.; Saunders, M.; Boyton, H. G.; Earhart, W. H.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* **1958,** *4*, 178–185.

(8) Borch, R. F. *J. Am. Chem. Soc.* **1968,** *90*, 5303–5305.

(9) Determined on a Varian CFT-20 spectrometer operating at 20 MHz for ^{13}C NMR.

(10) The line widths of I are ~35 Hz at 27 °C (except for the methyl resonance which is 16 Hz) and 65 Hz at −180 °C. The line widths of resonances from the C-1 and C-3,5 carbons of II are 80 and 130 Hz, respectively, at 27 °C and 120 and 250 Hz, respectively, at −180 °C. Ring carbons 2 and 6 are not resolved from the resonance due to C-4; thus single-carbon line-width data is not available for these carbons.

(11) Rezvukhin, A. I.; Mamatyuk, V. I.; Koptyug, V. A. *Z. Org. Khim.* **1972,** *8*, 2443.

(12) Fyfe, C. A.; Lyerla, J. R.; Volksen, W.; Yannoni, C. S. *Macromolecules*, in press.

(13) Earl, W; VanderHart, D. L. *Macromolecules*, in press.

(14) Cotton, F. A.; Harris, C. B. *Proc. Natl. Acad. Sci. U.S.A.* **1966,** *65*, 12–15.

(15) Lippmaa, E. T.; Alla, M. A.; Pehk, T. J.; Engelhardt, G. *J. Am. Chem. Soc.* **1978,** *100*, 1929–1931.

(16) Baenziger, N. C.; Nelson, A. D. *J. Am. Chem. Soc.* **1968,** *90*, 6602–6607. The labeling of atoms is incorrect in Table V. The correct labeling shows that the shortest C–Cl distances (ångstroms) are the following: C-1, 4.37; C-2, 3.90; C-3, 3.46; C-4, 3.37; C-5, 3.80; C-6, 3.99.

(17) Spiess, H. W.; Haeberlen, U.; Zimmerman, H. *J. Magn. Reson.* **1977,** *25*, 55–66.

(18) A preliminary account of this work was presented at the 20th Experimental NMR Conference, Asilomar, Calif., Feb. 20, 1979.

J. R. Lyerla, C. S. Yannoni*
IBM Research Laboratory, San Jose, California 95193

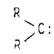
D. Bruck, C. A. Fyfe*
Guelph-Waterloo Centre for Graduate Work in Chemistry
Guelph Campus, Department of Chemistry
University of Guelph, Guelph, Ontario, Canada

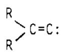
Received March 21, 1979

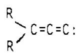
Extended Unsaturated Carbenes.[1]
Generation and Reaction of Allenylidene Carbenes, $(R)_2C{=}C{=}C{=}C{:}$, with Olefins

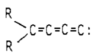
Sir:

Carbenes **1** are well established and highly useful members of the family of reactive intermediates.[2] More recently unsaturated carbenes, consisting of alkylidene **2** and alkenylidene **3** carbenes, have been generated and shown to possess novel properties and chemistry.[3] However, to date no extended unsaturated carbenes beyond **3** have been reported. Such extended unsaturated carbenes would be of interest in their own right in addition to serving as a means of simple entry into cumulene chemistry. In this communication we report the generation and interaction of the next homologous unsaturated carbenes, specifically allenylidene carbenes **4**, with some olefins.

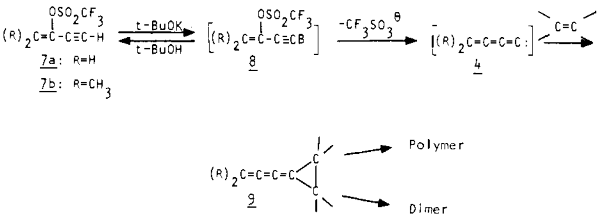

1


2

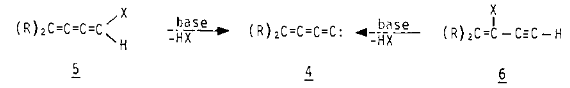

3

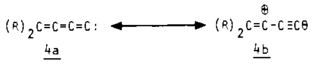

4

Scheme I

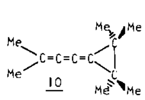


A priori, allenylidene carbenes **4** may be generated using base via α-elimination from an appropriately functionalized cumulene **5** or by γ-elimination from a properly functionalized enyne **6**. These two modes of allenylidene carbene generation are analogous to the generation[3] of alkenylidene carbenes **3** from allenyl and propargyl halides. Since to our knowledge cumulenyl halides **5** are unknown[4] and not readily accessible, we chose triflate functionalized enynes[5] **6** as progenitors of carbene **4**. Reaction of 5.0 mmol of alkynylvinyl triflates[5] **7a** and **7b** with a mixture of excess olefin in 1,2-dimethoxyethane at 0 °C maintained over an argon atmosphere and containing 5.5 mmol of potassium *tert*-butoxide proceeded as shown in Scheme I. Rapid loss of a proton and formation of anion **8** was indicated by reisolation of deuterium incorporated triflate **7b** in deuterated media.[6] Subsequent loss of the triflate ion results in carbene **4** which is a resonance hybrid of the neutral carbene **4a** and the dipolar form **4b**. The contribution of the dipolar form **4b** is presumably minimized by both the relatively high energy of a vinyl cation[7] in comparison with normal carbenium ions and the nonpolar nature of the reaction medium. Carbene **4** is readily trapped by olefins resulting in adduct **9**, whose subsequent fate is strongly dependent upon substituents in both the carbene and the olefin.





Addition of the parent triflate **7a** to tetramethylethylene (TME) results in a polymer most likely via oxygen initiated free radical polymerization of adduct **9**.[8] Using triflate **7b** and TME, the monoadduct **10** is isolated as transparent plates. In


10

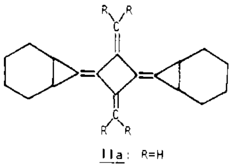

11a: R=H
11b: R=CH$_3$

Table I. Spectral Data for Products **10**, **11a**, and **11b**

compd	mp, °C	mass spectra *m/e* (rel int)	UV[a], λ_{max}, nm (ε)	IR,[b] cm^{-1} (int)	^1H NMR,[c] δ ppm (no., mult)	^{13}C NMR,[d] δ (ppm)
10	58–60	162 (100), M^+	306 sh, (150) 264 (10800) 236 sh, (3900)	2065 (m)	1.17 (12 H, s) 1.80 (6 H, s)	163.5, 121.1, 116.2, 111.7, 30.2 (e), 28.3, 24.6, 21.1
11a	102–104 dec	264 (94), M^+ 165 (100)	256 (1750) 202 (11450)	1900 (m) 1710 (w) 860 (s)	0.63 (2 H, m) 1.19 (8 H, br m) 1.70 (6 H, s)	151.6, 129.7, 118.2, 97.6, 22.8, 21.3, 21.2
11b	114–116 dec	320 (100), M^+	264 (4000) 245 (4000) 207 (19200)	1955 (m) 1710 (w)	0.60 (2 H, m) 1.13 (8 H, br m) 1.70 (6 H, s)	195.3, 103.6, 100.2, 40.1, 21.7, 21.4, 19.4, 16.0

[a] Heptane. [b] 10% CCl_4. [c] CCl_4, internal standard Me_4Si. [d] $CDCl_3$, internal standard Me_4Si, proton decoupled. [e] Impurity.

0002-7863/79/1501-4772$01.00/0

contrast, addition of either triflate **7a** or **7b** to cyclohexene as substrate results in formation of the respective dimers **11a** and **11b** via **9.** Products **10, 11a,** and **11b** were characterized and identified by spectral means as summarized in Table I. These spectral properties are completely consistent with the proposed structures. The medium-intensity 2065-cm^{-1} band and the 264-nm λ_{max} of **10** are indicative of cumulenes.[9] The intense low wavelength absorption (202- and 207-nm λ_{max}, respectively) for both **11a** and **11b** is characteristic of known radialenes as is the weak 1710-cm^{-1} band.[10] The ^{1}H NMR are also consistent with the proposed structures, although they do not differentiate between monomer and dimer.

The most characteristic and useful spectral features of **10, 11a,** and **11b** are exhibited by the mass spectra and ^{13}C NMR data. For both **10** and **11b**, the respective molecular ions are the base peaks and, for **11a**, the molecular ion has an intensity of 94%. The ^{13}C spectrum of **10** is in accord with those of analogous cumulenes[11] and the spectra of dimers **11a** and **11b** are characteristic of similar alkylidenecyclopropanes[12] and in harmony with expectations[13] for such hydrocarbons.

In summary, we have discovered a simple highly efficient means of allenylidene carbene **4** generation. These species readily add to olefins to give highly oxygen sensitive cumulenes and their dimers. At present, we are examining the possibility that allenylidene carbenes **4** are similar in nature to the related unsaturated carbenes **2** and **3** which are found to be electrophilic and possess a singlet ground state.[14] This question, as well as the chemistry of these novel unsaturated reactive intermediates, will be the subject of future reports.

Acknowledgment. This research was supported by the National Science Foundation (CHE78-03596).

References and Notes

(1) Paper 11 in a series on unsaturated carbenes. Paper 10: Stang, P. J.; Bjork, J. A. *J. Chem. Soc., Chem. Commun.* **1978,** 1057–1058.

(2) For reviews and pertinent references see: "Carbenes", Jones, M., Jr.; Moss, R. A., Eds.; Wiley-Interscience: New York, 1973 and 1975; Vols. I and II. Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. Hine, J. "Divalent Carbon"; Ronald Press: New York, 1964.

(3) For reviews and leading references see: Stang, P. J. *Chem. Rev.* **1978,** *78*, 383–405. Stang, P. J. *Acc. Chem. Res.* **1978,** *11*, 107–114. Hartzler, H. D. In "Carbenes", Vol II, Moss, R. A., Jones, M, Eds., Jr.; Wiley-Interscience: New York, 1975; Chapter 2, pp 43–100.

(4) Fischer, H. In "The Chemistry of Alkenes", Patai, S., Ed.; Wiley-Interscience: London, 1964; Chapter 13, pp 1025–1160. Murray, M. In "Methoden der Organischen Chemie", Müller, E., Ed.; G. Thieme: Stuttgart, 1977; Vol. V/2a, pp 963–1076.

(5) Stang, P. J.; Fisk, T. E. *Synthesis*, in press.

(6) A referee has pointed out that deuterium incorporation does not prove that anion **8** lies on the reaction coordinate leading to carbene **4.** It has been shown (Shiner, V. J., Jr.; Wilson, J. W. *J. Am. Chem. Soc.* **1962,** *84*, 2402–2408) that initial proton loss from propargyl halide systems is rapid and reversible and the rate-determining step is loss of halide ion to give carbene **3.** Owing to the close similarity between this system and ours and the available solvolysis rate data for vinyl triflates (see ref 7), we feel that this is the most likely path to carbene **4.**

(7) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

(8) GLC monitoring of the reaction mixture indicates the rapid disappearance of starting triflate **7a** and the appearance of a new peak with a retention time expected for a 1:1 adduct which disappears upon workup and formation of polymer.

(9) Ball, W. J.; Landor, S. R.; Punja, N. J. *J. Chem. Soc. C* **1967**, 194–197.

(10) Heilbronner, E. *Theoret. Chim. Acta* **1966,** *4*, 64–68. Griffin, G. W.; Peterson, L. I. *J. Am. Chem. Soc.* **1963,** *85*, 2268–2273.

(11) Van Dongen, J. P. C. M.; de Bie, M. J. A.; Steur, R. *Tetrahedron Lett.* **1973,** 1371–1374.

(12) Pasto, D. J.; Borchardt, J. K. *J. Org. Chem.* **1976,** *41*, 1061–1063.

(13) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. Levi, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

(14) Experimental: ref 3. Theoretical: Kenney, J. W., III; Simons, J.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1978,** *100*, 6930–6936. Apeloig, Y.; Schreiber, R. *Tetrahedron Lett.* **1978,** 4555–4558. Dykstra, C. E.; Parsons, C. H.; Oates, C. L. *J. Am. Chem. Soc.* **1979,** *101*, 1962–1965.

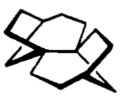
Peter J. Stang,* Thomas E. Fisk
Chemistry Department, The University of Utah
Salt Lake City, Utah 84112

Received April 24, 1979

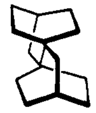
Twofold Cation-Olefin Cyclization. Synthesis of *syn*-[3.2.1]^2- and [2.2.2]^{2}Geminane

Sir:

A large number of topologically fascinating molecules constructed of repeating alicyclic units are possible. Of these, only the homologous series comprised of adamantane,[1] diamantane,[2] triamantane,[3] and the tetramantanes[4] has received significant attention. This is a consequence not only of their relationship to the diamond lattice,[5] but also because of their relative thermodynamic stability and consequent ready availability by Lewis acid catalyzed cationic rearrangement of many isomeric precursors.[6] Since this synthetic approach is not extrapolatable to ring systems having different topographies, the absence of molecules from the latter group can be traced chiefly to an existing lack of viable synthetic methodology.[7,8] In this communication, we outline a new approach within this field of research which is founded on the concept of twofold cation-olefin cyclization, and is both efficient and simple. The present contribution describes the synthesis of novel hydrocarbons **1** and **2** which, for convenience, have been colloquially named *syn*-[3.2.1]^{2}geminane and [2.2.2]^{2}geminane, respectively.[9,10]



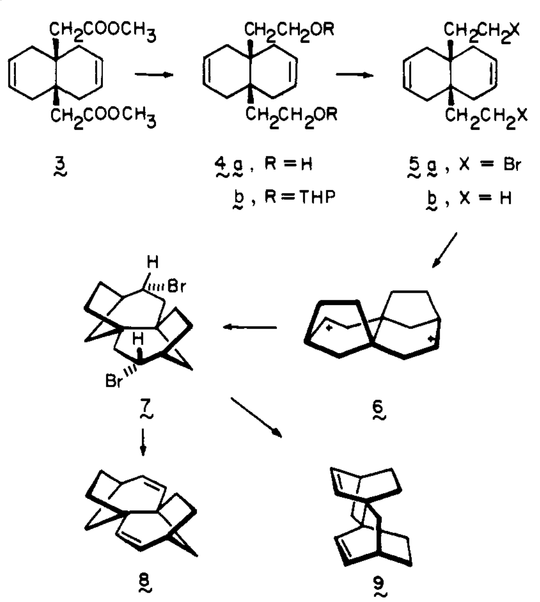
1



2

The molecular frameworks of **1** and **2** are formally constructed of pairs of bicyclo[3.2.1]octane and bicyclo[2.2.2]octane ring systems, respectively, which have been fused symmetrically across a common C_1–C_2 bond. This innovation delivers a C_2 symmetric structure for **1** and a still more symmetric (C_{2h}) molecule in the case of **2.**

Reduction of known diester **3**[11] with lithium aluminum hydride in refluxing tetrahydrofuran afforded diol **4a** (98%), mp 152–153 °C,[12] which was subsequently converted to the bistetrahydropyranyloxy derivative **4b** (100%). Treatment of **4b** with triphenylphosphine dibromide in dichloromethane at room temperature for 20 h led directly[13] to dibromide **5a** (67%): mp 133.5–134.5 °C; ^{1}H NMR (δ, $CDCl_3$) 5.46 (narrow m, 4 H), 3.28 (t, J = 7 Hz, 4 H), 1.98 (pseudosinglet, 8 H), 1.97 (t, J = 7 Hz, 4 H). For subsequent comparison purposes and to further substantiate that **5a** had formed without rearrangement, the dibromide was reduced with sodium in liquid



0002-7863/79/1501-4773$01.00/0