Thus, we reach the reasonable conclusion that interchanging the hydroxy and carboxy groups of I/II or III/IV does not create within the lactone pairs significant energy differences which could complicate comparisons of the hydroxy acids.

Acid-catalyzed lactonizations of hydroxy acids I, II, III, and IV have relative rates of 1, 1.2, 36, and 22, respectively (Table I).[21] The faster rates found for III and IV probably originate from steric acceleration of the type detected by Bunnett[22] in the lactonization of 3-substituted 2-(hydroxymethyl)benzoic acids. The crucial observation, however, is that I and II lactonize at nearly identical rates despite the 10° difference in alignment between the hydroxy and carboxy groups.[23] Similarly, III and IV display virtually no rate dependence on orientation within the confines of a 9° variation. We have thus demonstrated experimentally for the first time that *an angular displacement of a few degrees is not kinetically significant*.[24] Orbital steering theory, predicated upon a sensitive relationship between rate and small angle changes, seems indefensible in light of our results.

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(21) Second-order rate constants for lactonization, determined spectrophotometrically at 25.0 °C in 0.2–10 N HCl, were extrapolated to zero ionic strength. The resulting uncertainty in the rate constants (perhaps ±50%) has no bearing on the main conclusions of this paper.

(22) J. F. Bunnett and C. F. Hauser, *J. Am. Chem. Soc.*, **87**, 2214 (1965).

(23) It is likely but unproven that hydroxy addition to the carbonyl is the rate-determining step in the lactonizations. Obviously, the observed rate constant is a function of the addition rate whether formation *or* collapse of the tetrahedral intermediate is rate determining.

(24) Alternatively, one might conclude that the angles of 70° and 80° for I and II in Table I bracket an optimal lactonization angle near 75°. This seems unlikely since it would require a *different* optimal angle for III and IV (one near 81°). Furthermore, 75° is smaller than the optimal angle suggested by recent X-ray work: W. B. Schweizer, G. Procter, M. Kaftory, and J. D. Dunitz, *Helv. Chim. Acta*, **61**, 2783 (1978). Unfortunately, it is experimentally impossible to secure more than a two-point plot of k_{obsd} vs. angle while still obeying the stipulations listed in the third paragraph of this article.

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Extended Unsaturated Carbenes.[1] Generation and Trapping of an Alkatetraenylidenecarabene, $(R)_2C{=}C{=}C{=}C{=}C{=}C{:}$[2]

Sir:

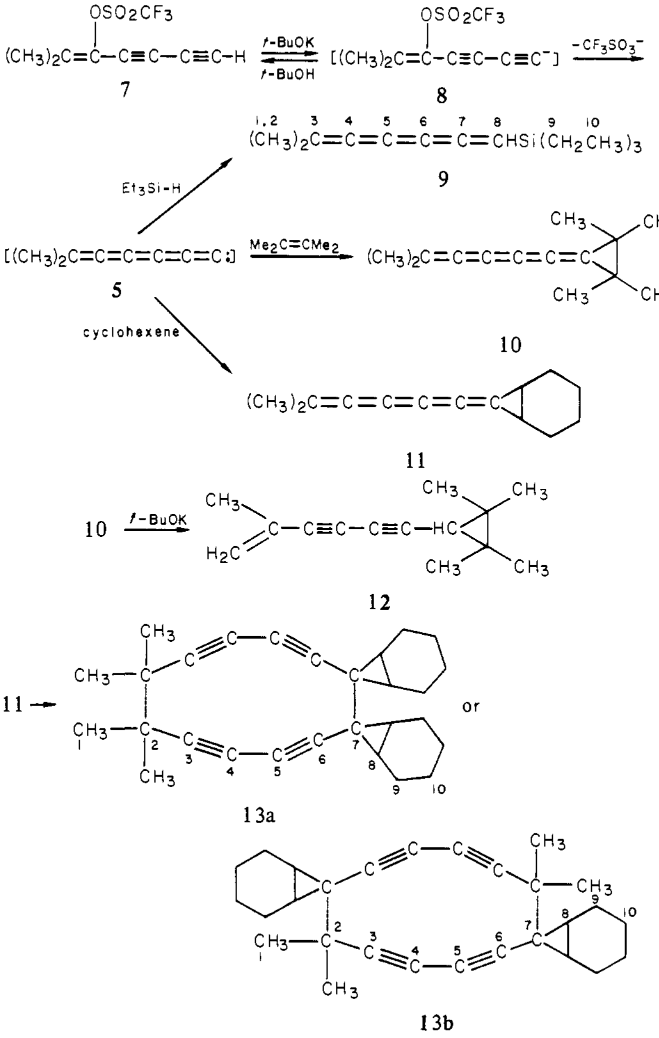
To date, the first three members of the homologous unsaturated carbenes (**1**), namely, alkylidenecarbenes[3] (**2**), alkenylidenecarbenes[3] (**3**), and alkadienylidenecarbenes[1] (**4**) have been observed

$$\underset{\mathbf{1},\ n\,=\,0-\infty}{R_2C{\neq}C{\neq}_nC{:}} \qquad \underset{\mathbf{2}}{R_2C{=}C{:}} \qquad \underset{\mathbf{3}}{R_2C{=}C{=}C{:}} \qquad \underset{\mathbf{4}}{R_2C{=}C{=}C{=}C{:}}$$

and their properties and chemistry explored. In this communication, we report the generation and trapping of the six-carbon homologue (**1**, *n* = 4), specifically 5-methyl-1,2,3,4-hexatetraenylidenecarbene (**5**), a member of the alkatetraenylidenecarbene (**6**) family.

$$\underset{\mathbf{5}}{(CH_3)_2C{=}C{=}C{=}C{=}C{=}C{:}} \qquad \underset{\mathbf{6}}{(R)_2C{=}C{=}C{=}C{=}C{=}C{:}}$$

Scheme I



In analogy to the generation[1] of **4** via a γ elimination from 1-ethynylvinyl triflate, carbene **5** was obtained from 1-butadiynylvinyl triflate (**7**) prepared in 70% overall yield in a three-step process from $(CH_3)_2CHCOCl$ and $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$.[4]

Reaction of 2.4 mmol of butadiynylvinyl triflate (**7**) and 3.0 mmol of freshly sublimed *t*-BuOK in a mixture of excess trap (36 mmol) and 1,2-dimethoxyethane at 0 °C over an argon atmosphere proceeded as shown in Scheme I. Rapid deprotonation and equilibrium formation of anion **8** were indicated by reisolation of deuterium-incorporated triflate **7** in deuterated media. Subsequent slow loss of the triflate ion results in carbene **5** that may be trapped by silane or olefins. "Insertion" of carbene **5** into triethylsilane results, after column chromatography on silica gel, in 10% isolated yield of the novel substituted cumulene[5] **9**. Addition to tetramethylethylene gave 41% of enediyne **12**, presumably via base-catalyzed isomerization of the initially formed adduct **10**.[6] Trapping with cyclohexene results in a 31% isolated yield of the cyclyne **13**, the result of either a (symmetry forbidden) cycloaddition or some kind of a free-radical dimerization of initial adduct **11**. Compounds **9**, **12**, and **13** were characterized and identified by spectral means as summarized in Table I. These

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(1) Paper 12 in a series on unsaturated carbenes. Paper 11: Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1979**, *101*, 4772–4773.

(2) Presented at the 180th National Meeting of the American Chemical Society, San Francisco, August 1980.

(3) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405. Hartzler, H. D. In "Carbenes"; Moss, R. A.; Jones, M., Eds.; Wiley-Interscience: New York, 1975; Vol. II, Chapter 2, pp 43–100.

(4) Stang, P. J; Ladika, M. *Synthesis*, in press.

(5) For reviews on cumulenes, see: 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.; Georg Thieme Verlag: Stuttgart, 1977; Vol. V/2a, pp 963–1076.

(6) Direct evidence for adduct **10** comes from the observation of a small close second spot on the TLC of product **12** and an additional band at 2050 cm^{-1} in the IR strongly characteristic of cumulenes.[1,5]

(7) Karich, G.; Jochims, J. C. *Chem. Ber.* **1977**, *110*, 2680–2694. Bertsch, K.; Karich, G.; Jochims, J. C. *Ibid.* **1977**, *110*, 3304–3313. Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527–4531.

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Table I. Summary of Spectral Data for Compounds 9, 12, and 13

compd	mass spectra, m/e (rel int)	UV^a λ_{max}, nm (ϵ)	IR,^{b} cm^{-1} (int)	^{1}H NMR,^{c} δ	^{13}C NMR,^{d} δ
9	218 (18, M$^+$), 189 (54), 161 (86), 133 (100)	226 (7300), 239 (5940), 251 (6900), 268 sh (8420), 300 (22 000), 318 (20 900), 368 (175), 398 (53)	2190 (w), 2140 (s), 2045 (s), 1615 (m), 730 (s)	0.3–1.5 (15 H, m, Si–CH_2CH_3), 2.04 (6 H, s, CH_3), 5.27 (1 H, br s, CH)	166.04 (C-4), 150.35 (C-7), 122.01 (C-5), 103.66 (C-6), 94.57 (C-3), 81.81 (C-8), 24.59, 24.45 (C-1, C-2), 7.26 (C-10), 4.33 (C-9)
12	186 (51, M$^+$), 171 (18), 156 (29), 141 (52), 83 (100)	215.5 (42 300), 219 (41 300), 243 (5370), 256 (8470), 270.5 (11 100), 287 (8290)	3080 (w), 2215 (s), 2130 (w), 1603 (m), 898 (s)	0.97 (1 H, s, cyclopropyl), 1.18 (12 H, s, CH_3), 1.92 (3 H, m, CH_3), 5.40 (2 H, m, $C=CH_2$)	
13	368 (25, M$^+$), 353 (33), 339 (17), 325 (38), 311 (24), 297 (59), 283 (60), 269 (81), 255 (100)	244 (2210), 257.5 (2190), 272.5 (1540)	3080 (w), 2215 (s), 2140 (w)	0.83 (4 H, m, cyclopropyl), 1.26 (12 H, s, CH_3), 1.10–1.55 (8 H, m, cyclohexane), 1.55–2.00 (8 H, m, cyclohexane)	95.80 (C-3), 88.47 (C-6), 75.30 (C-4), 69.86 (C-5), 42.15 (C-2), 29.46 (C-7), 23.41 (C-1), 20.98, 20.30, 19.69 (C-8, C-9, C-10)

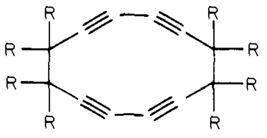
^{a} 9 and 12 in hexane, 13 in EtOH. ^{b} 9 and 12 neat, 13 10% in CCl_4. ^{c} CCl_4, internal Me_4Si. ^{d} $CDCl_3$, proton decoupled.

spectral properties are fully consistent with the proposed structures and the available literature analogies. In particular, all three compounds gave good molecular ions and easily recognized fragment ions in the mass spectrometer.

The intense UV absorptions at 300 and 318 nm and the strong infrared bands at 2045 and 2140 cm^{-1} are highly characteristic of hexapentaenes[7] and hence in accord with the proposed cumulene **9**, as is its proton NMR. The most definitive spectral feature of cumulene **9** is its ^{13}C NMR and the low-field absorptions between 81 and 166 ppm due to the six unsaturated carbons characteristic of such sp-hybridized cumulene carbons.[7,8]

The identity of **12** is unambiguously established by its ^{1}H NMR and confirmed by its UV and IR absorption typical of such diynes.[9]

The structure of dimer **13** is established by its molecular ion at m/e 368 and its ^{13}C NMR with four distinct acetylenic carbons in the 69–96-ppm range, as well as by its UV and IR absorption, all in excellent agreement with known cyclyne analogues **14**[10] and **15**.[11] Unfortunately, neither the spectral data nor the mode of formation allow a distinction between the two possible cyclodimers, **13a** or **13b**. However, the fact that only ten signals were observed in the ^{13}C NMR and that only a single sharp spot is seen on TLC strongly suggests that only one of the two possible dimers of **13** is actually formed.



14, R = H
15, R = CH_3

In summary, we have established that highly unsaturated extended carbenes (**6**) may be readily generated and trapped, albeit in only modest yields. Insertion of **5** into Et_3SiH gives previously unknown[5] novel silicon-functionalized cumulene **9** whereas addition to olefins results in rearranged ene–diyne **12** or an unusual dimer, namely, cyclyne **13**. The full scope of alkatetraenylidenecarbene generation as well as the nature and chemistry of these reactive intermediates are under active investigation.

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ESR and IR Evidence for Intermediates in the Di-π-methane Photorearrangement of a Naphthobarrelene-Like Compound after Low-Temperature UV Irradiation

Sir:

We previously reported on the photorearrangement of the bicyclo[3.2.2]nonanaphthalene **1** to give three isomeric semibullvalene-like products **6a–c**.[1] A similar rearrangement also occurs, in a reversible fashion, in a thermal ground state process.[2] It was proposed that the di-π-methane photorearrangement **1** → **6a–c** proceeds along reaction paths which evolve from two primary photochemical processes, namely naphthyl–vinyl (→**2**) and vinyl–vinyl bonding (→**4**). Evidence for competition between several paths and the involvement of a transient ($\tau \sim 1.5 \times 10^{-8}$ s at 280–350 K) in addition to excited triplet **1** was presented.[1]

We now present direct proof of the existence of two discrete intermediates in the transformation $\mathbf{1} + h\nu \rightarrow \mathbf{6a{-}c}$ obtained by low-temperature ESR and IR spectroscopy. Irradiations were carried out in 2-methyltetrahydrofuran (MTHF)[3] matrixes with 313- and >340-nm light at 77 K.[4] Continuous irradiation at either excitation wavelength gave two ESR spectra. A transient spectrum showed a strong $\Delta m = 2$ transition at 1764 G and a $\Delta m = 1$ portion (XYZ pattern) with $D' = 800$ G ($D = 0.075$ cm^{-1}) and $E' = 66$ G ($E = 0.0065$ cm^{-1}). In addition, a partially line-resolved signal dominated at 3244 G ($=H_0$). Unlike the other signals, the latter persisted when irradiation was discontinued, without a decrease in intensity over a period of several hours. The persistent central signal could be resolved into the spectrum given in Figure 1. The zero-field parameters are $D' = 58$ G ($D = 0.0054$ cm^{-1})

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[3] In the sequence hexafluorobenzene, ether/isopentane/ethanol (5:5:2), and MTHF, the ESR signal resolution increased markedly.

[4] Light source: SP-1000 W high-pressure Hg lamp (Philips Richtstrahler combined with liquid filter solutions [313 nm, 0.567 g of K_2CrO_4 and 2.056 g of Na_2CO_3 in 1 L of distilled H_2O; >340 nm, 750 g of NaBr and 8 g of $Pb(NO_3)_2$ in 1 L of H_2O]. Varian E9 ESR spectrometer: sensitivity 5 × 10^{10} of ΔH spins, spectra of samples [(1.0–6.6) × 10^{-2} M **1**] placed in a liquid nitrogen cooled Dewar were recorded at 9.05-GHz microwave frequency. Perkin-Elmer 580 IR spectrometer: 10^{-1} M **1**, 25-μm path length.