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)

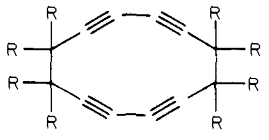
[a] 9 and **12** in hexane, 13 in EtOH. [b] 9 and **12** neat, **13** 10% in CCl_4. [c] CCl_4, internal Me_4Si. [d] $CDCl_3$, proton decoupled.

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 **1** + $h\nu$ → **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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(1) Demuth, M.; Bender, C. O.; Braslavsky, S. E.; Görner, H.; Burger, U.; Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1979**, *62*, 847–851.

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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.

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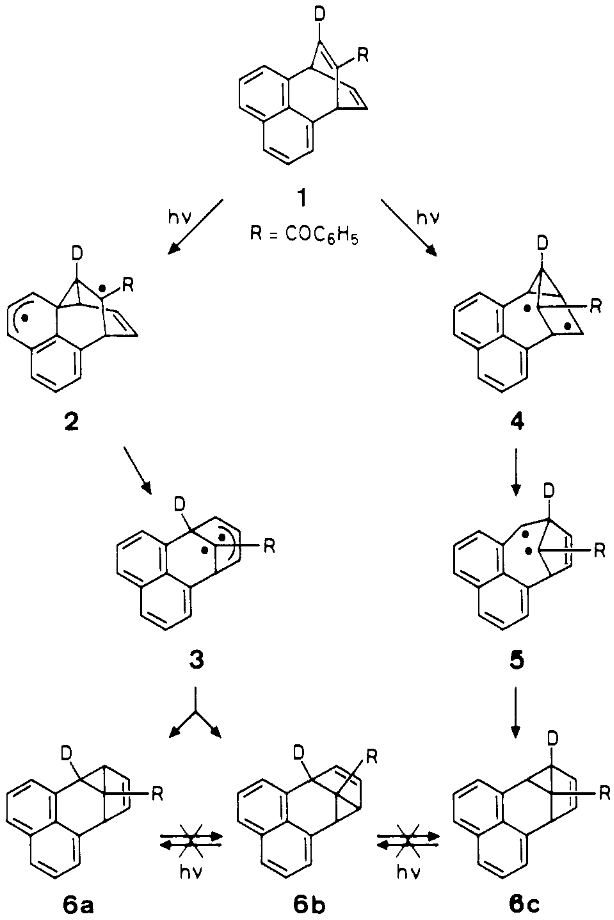
Scheme I. Reaction Paths Proposed for the Photorearrangement **1** → **6a-c**[1]



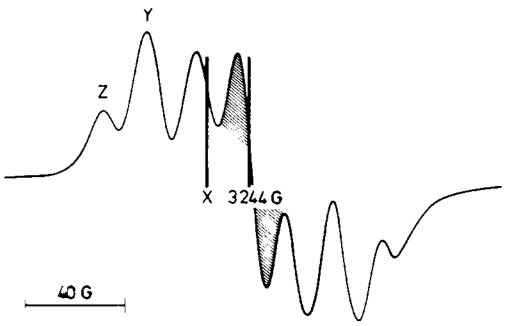


Figure 1. Long-lived component of the ESR spectrum, recorded in the dark after irradiation of **1** at >340 nm in 2-methyltetrahydrofuran matrix at 77 K. The shaded portion corresponds to radical byproducts.

and $E' = 4$ G ($E = 0.0004$ cm^{-1}). A $\Delta m = 2$ transition was not observed even under high gain and modulation adjustment.

The parameters of the short-lived component of the ESR spectrum are characteristic of an electronically excited and randomly oriented aromatic triplet state,[5] which can be attributed to the naphthalene of **1** (T_1).[6]

The persistent spectrum (Figure 1) has all the characteristics expected of a randomly oriented ground-state triplet biradical.[7,8] The lack of a half-field signal ($\Delta m = 2$) is in accord with the small zero-field parameter, characteristic of a weak interaction between the radical centers.

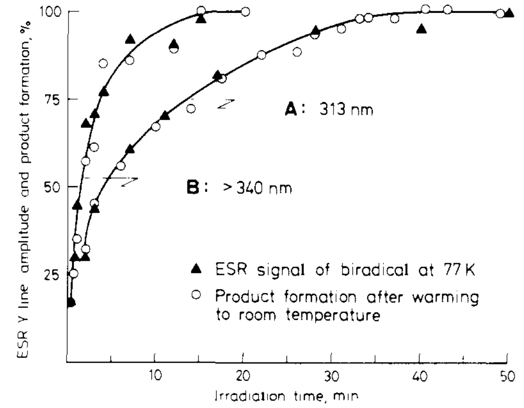


Figure 2. Comparison of long-lived ESR signal intensity and formation of product **6** as a function of irradiation time. (A) Excitation at 313 nm; (B) Excitation at >340 nm. (○) Amplitude of ESR Y line; (▲) product **6** formation after the ESR sample was warmed to room temperature. Maxima of ESR intensity and product formation taken as 100%. Note that the diagram is not normalized for light intensities of the two excitation wavelengths.

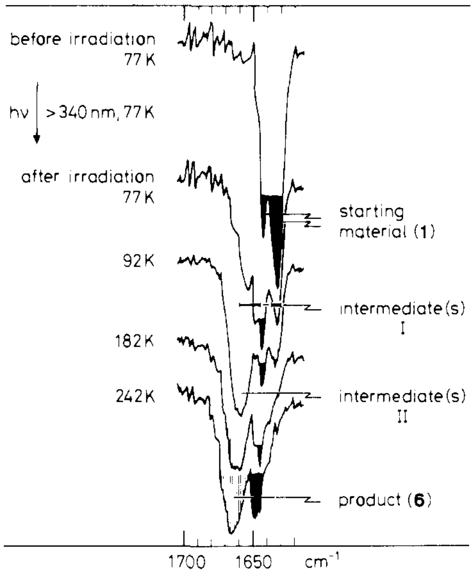


Figure 3. IR spectra recorded at 77 K before irradiation of **1** and after irradiation of **1** for 30 min during warming up from 77 to 242 K. Solvent 2-methyltetrahydrofuran, λ(excitation) >340 nm. Note that the band shapes of **1** (dark portions) and **6** (shaded) at 242 K are the same as those of the respective reference samples at this temperature. Only one frozen-out rotamer of **1** appears at 77–182 K after irradiation,[11] and the buildup of **6** begins to show at 182 K.

We assign the biradical spectrum to an intermediate (or intermediates; see below) in the rearrangement **1** → **6a–c**. No ESR signal was found upon irradiation of **6** at either wavelength in MTHF at 77 K. The Y-line amplitude[9] of the long-lived signal reached maximum intensity after ~35-min irradiation at 313 nm and after ~15-min irradiation at >340 nm. Since the signal intensity did not decrease in the dark after irradiation, a comparison with product formation is meaningful. The amount of **6** formed was measured by GLC after the ESR samples were warmed to room temperature. Normalizing maximum product formation and ESR signal saturation to 100% enabled the relative increases in product formation and ESR signal intensity with time to be compared (Figure 2). The close fit of the two curves for both excitation wavelengths is compatible with the role of the biradical as a precursor to **6**. The possibility that the biradical is an intermediate leading to another product (rather than to **6**) can be eliminated. For a line width of 12 G (Y line), a minimum steady-state concentration of ca. 10^{-5} M is required for detection

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(5) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772.

(6) Note that **1** has a naphthalene-like phosphorescence at 77 K: Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1975**, *58*, 397–415. For the ESR parameters of triplet naphthalene, see ref 7.

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(9) The Y line was chosen in view of its large amplitude, symmetric shape, and independence from the zero-field monoradical absorption.

of any ESR signal with our equipment.[4] Yet, no products other than **1** and **6** were found by GLC, under conditions where a product concentration $\geq 5 \times 10^{-7}$ M could have been detected.[10]

An IR investigation showed the consecutive appearance of new frequencies (I, 1634 and 1648–1655 cm^{-1}; II, 1660 cm^{-1}) upon irradiation for 30 min at 77 K and warming in the dark to 92 K, before the formation of product **6** (ν_{CO} = 1665 cm^{-1}) (Figure 3).[11] A three-step sequence is thus established which can be accommodated by the proposed reaction scheme. Both the long-lived ESR component and the transient IR bands I are observable only below 92 K, i.e., they may well arise from the primary metastable photoproduct(s), either **2** alone or a mixture of **2** and **4**[12] (note that the ratio (**6a** + **b**)/**6c** is ~5:1 at 77 K[1]). If so, then the IR band II could be due to **3** (and possibly **5**). The IR frequencies I and II are suggested to be those of the α-keto (oxallyl) radical groups, although we are not aware of appropriate reference data.

The observed D value of 0.0054 cm^{-1} is considerably smaller than any of the D values reported previously for triplet biradicals. Our assignment to the extensively delocalized biradical **2** appears acceptable, however, in light of the spread of D from 0.01–0.03 cm^{-1} for partly delocalized biradicals[14] to 0.08 cm^{-1} for the localized 1,3-cyclopenta diyl.[15]

The transition from intermediate **2** to **3** when the temperature is raised to 92 K should be accompanied by the development of a new ESR spectrum which then should persist until ~180 K. However, no resolved signal was observed when measurements were carried out at 92 K with a flow cavity. Although it cannot be ruled out that this result was merely due to inhomogeneity caused by the nitrogen flow, the assignment of structure **3** to the species responsible to the IR band II must therefore remain tentative. Still, it appears more plausible than the alternative that the IR change between 77 and 92 K is associated with a rotation of the benzoyl group in **2** from out of conjugation into conjugation with the radical center. If this were the case, one might expect a shift to lower rather than higher IR frequency (as is observed in Figure 3). Furthermore, the benzoyl rotamers of **1** are frozen out at ca. 200 K, and oxallyl rotamers (as in **2**–**5**) are likely to have a higher barrier.

In conclusion, we note that, for the first time in di-π-methane photochemistry, direct evidence for the intervention of a biradical intermediate (or a category of biradical intermediates) and strong support for a second intermediate have been obtained. This result confirms the postulated[16] stepwise mechanism for the photorearrangement of barrelenes. Furthermore, it corroborated the conclusions previously drawn[13] from the rearrangement of independently generated biradical intermediates of the type now observed directly.

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[10] Glass capillary GLC column; OV 101, 70 ft. Components >0.05% were detectable, i.e., 5×10^{-6} M at a total concentration of 10^{-2} M. A further factor of ten derives from the minimum ESR signal detectability for a 10% amplitude in the plot of Figure 2, safely assuming a maximum biradical concentration of 10^{-2} M for 100% signal amplitude.

[11] The IR experiment also reveals the striking fact that of the two rotamers of **1** which are frozen out at 77 K the major component (ν_{CO} = 1633 cm^{-1}) photoreacts preferentially while the minor component (ν_{CO} = 1644 cm^{-1}) remains largely unchanged (accounting for ca. 30% recovered **1** after 2-h irradiation at 77 K). We note that the residual IR band at around 1647 cm^{-1} (242 K) exactly corresponds to the carbonyl band of **1** under these conditions. This remarkable influence of excited-state geometry, as reflected by the ground-state conformation, on the photoreactivity at 77 K is currently under further investigation. At room temperature, a similar effect is not observed (Φ_{366} for product formation = 1.0[1]).

[12] The intermediate **4** is structurally similar to a triplet biradical which has been generated by diazo decomposition and shown to preferentially afford the di-π-methane product of 2,3-naphthobarrelene.[13]

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Effect of Through-Bond Interaction on Terminal Methylene Rotation in the Tetramethylene Diradical

Sir:

How the ease of terminal methylene rotation in tetramethylene (butane-1,4-diyl) depends upon the conformation about the central C–C bond remains a major unanswered question in the study of this diradical.[1] The pioneering investigation by Hoffmann and co-workers[2] of the potential surface for the singlet diradical revealed small barriers to terminal methylene rotation in the gauche conformation about the central C–C bond but large barriers in the trans conformation. In the latter conformation, the strong perference found for the 90,90 geometry at the terminal methylene groups (Figure 1) was traced to the stabilizing interaction between the formally nonbonding atomic orbitals (AO's) on these carbons and the orbitals of the central C–C bond. As a result of this "through-bond coupling" between the AO's on the terminal carbons in the 90,90 geometry of the trans diradical, Hoffmann's EH calculations found the 90,90 geometry to be favored over 0,90 and 0,0 by, respectively, 12.7 and 13.4 kcal/mol. From INDO calculations, Stephenson and Gibson[3] obtained values of 45.0 and 46.7 kcal/mol for these energy differences.

Both of the above calculations are flawed by the use of one-configuration wave functions to represent singlet diradicals. In order to reduce the contribution of high-energy ionic terms to the wave function for a homosymmetric singlet diradical, a two-configuration wave function is required.[4] For instance, if the closely spaced $7a_g$ and $6b_u$ molecular orbitals (MO's) at the 90,90 tetramethylene geometry are denoted as S and A, corresponding to the symmetry behavior of each with respect to the twofold axis, the wave function for the lowest singlet state takes the form of eq 1.

$$^1A_g = c_1|\ldots A^2\rangle - c_2|\ldots S^2\rangle \qquad (1)$$

In eq 1, $c_1 > c_2$ since A lies below S in energy. The origin of this energy difference is that the interactions in A between the AO's on the terminal carbons and the orbitals of the central C–C linkage are bonding while in S these interactions are antibonding.[2] Consequently, the presence of $|\ldots S^2\rangle$ in the two-configuration ^1A_g wave function might be expected to reduce the net bonding between the AO's on the terminal carbons and the orbitals of the central C–C bond, thus lowering the energy difference between 90,90 and both 0,90 and 0,0.

The 90,90 geometry of *trans*-tetramethylene is a true intermediate on the STO-3G CI surface calculated by Segal for the singlet diradical.[5] However, Segal did not compute the energies of the 0,90 and 0,0 geometries. In order to determine whether

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[1] For recent reviews of tetramethylene chemistry, see: Borden, W. T. *React. Intermed.* **1980**, in press. Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; p 311.

[2] Hoffmann, R.; Swaminathan, S.; Odell, B. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091.

[3] Stephenson, L. M.; Gibson, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 4599.

[4] See, for instance: Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

[5] Segal, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 7892.