

H, 3.41; N, 4.73. Found: C, 36.48; H, 2.91; N, 4.75.

**Conversion of 5 to 4d.** A mixture of 220 mg (5.23 mmol) of cyanamide, 1.48 g (5.00 mmol) of 5, and 691 mg (5.00 mmol) of anhydrous, powdered  $K_2CO_3$  in 15 mL of THF was heated at reflux for 19 h. The reaction mixture was cooled to room temperature and filtered. The solid collected was washed with acetone, and the combined filtrates were evaporated at reduced pressure to give an oil, which solidified upon trituration with  $Et_2O$ . The solid was collected, washed with  $Et_2O$ , and suspended in 2.6 mL of 2 N HCl. After the suspension was stirred for 1 h, the solid was collected by filtration and dried under vacuum at room temperature to afford 1.00 g (69%) of 4d as a white solid, mp 117-119 °C, which was identical with a sample prepared as described above by IR and  $^1H$  NMR.<sup>13</sup>

**Registry No.** 1a, 104667-72-3; 1b, 104667-74-5; 1c, 104667-75-6; 1d, 104692-77-5; 1e, 104667-73-4; 1f, 99453-15-3; 1g·HCl, 99453-18-6; 1h, 104667-78-9; 2, 10191-60-3; 3a, 98-10-2; 3b, 88-19-7; 3c, 70-55-3; 3d, 6961-82-6; 3e, 1869-24-5; 3f, 5455-59-4; 3g, 7720-45-8; 3h, 105536-22-9; 4a, 104692-80-0; 4b, 104667-66-5; 4c, 104667-67-6; 4d, 104667-65-4; 4e, 104667-64-3; 4f, 99453-14-2; 4g, 99453-16-4; 4h, 104667-70-1; 5, 84346-43-0; cyanamide, 420-04-2.

**Supplementary Material Available:** Details of reaction scale and stoichiometry and characterization data (physical properties, IR and NMR spectral data, and elemental analyses) for 1 and 4 (4 pages). Ordering information is given on any current masthead page.

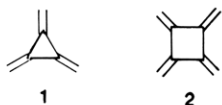
### X-ray Structure of a Novel [4]Radialene from the Cyclodimerization of an Unsaturated Carbene Derived Pentatetraene<sup>1</sup>

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As a consequence of both their considerable strain energy and possible cyclic delocalization via cross conjugation radialenes represent an inherently interesting class of hydrocarbons.<sup>2</sup> Although both [3]radialene (1) and [4]-radialene (2) and a few substituted derivatives are known,<sup>2</sup>



we are not aware of any X-ray data on this unusual class of hydrocarbons. Hence, we wish to report the first single-crystal X-ray structure of a novel substituted [4]radialene.

As we reported<sup>3</sup> recently, trapping of carbene 4 with  $Me_2C=CMe_2$  results in a 47% yield of cumulene 5, which upon standing at room temperature for several days or heating for a few hours undergoes cyclodimerization to 6 in quantitative yield as shown in Scheme I. Dimer 6 is a stable pale yellow crystalline compound that presumably formed via a thermal  $[2\pi\alpha + 2\pi\sigma]$  cycloaddition analogous to the known<sup>4</sup> dimerizations of ketenes and allenes.

An ORTEP of 6 is given in Figure 1, and the relevant crystal data, bond distances, and bond angles are in Tables

(1) Abstracted from the Ph.D. Dissertation of A. E. Learned, The University of Utah, 1987.

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(3) Stang, P. J.; Learned, A. E. *J. Chem. Soc., Chem. Commun.* 1988, 301.

(4) Landor, S. R. *The Chemistry of Allenes*; Academic: New York, 1982; Vol. 3.

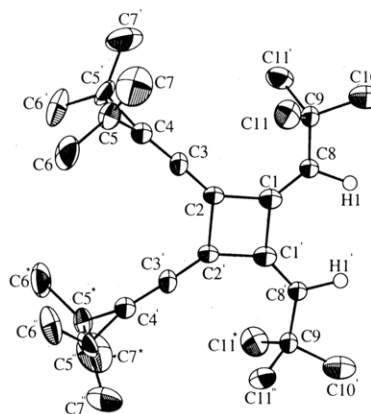


Figure 1.

### Scheme I

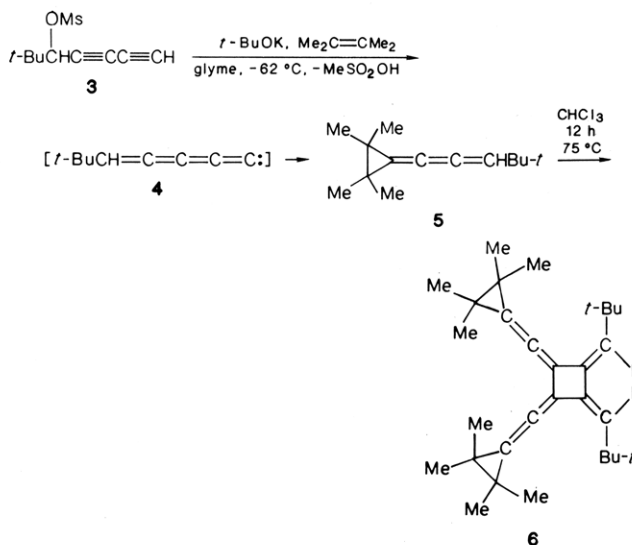


Table I. Summary of Crystallographic Data

molecular formula	$C_{30}H_{44}$
molecular weight	404.69
crystal system	tetragonal
space group	$P4_2/m$ (113)
cell dimensions, Å	
a	10.792 (5)
b	10.792 (4)
c	12.022 (5)
volume, Å <sup>3</sup>	1400.1
z	2
d(calcd), g/cm <sup>3</sup>	0.960
crystal dimensions, mm	0.27 × 0.25 × 0.21
diffractometer	Syntex P1
radiations, Å	(Mo $K\alpha$ ) 0.71073
data collection method	$2\theta:\theta$
scan speed, deg/min	(variable) 2.5-8.0
reflections measured	659, $h(0,14)$ , $k(0,14)$ , $l(0,18)$
scan range	$K_{\alpha 1} -1.0$ to $K_{\alpha 2} +1.0$
$2\theta$ , deg	2.0-48.0
total bkgd. time/scan time	0.5
no. of reflections between std.	98
total unique data	557
obsd data, $I > 3\sigma I$	227
abs coeff ( $\mu$ ), cm <sup>-1</sup>	0.496
no. of variables	51
R (averaging)	0.027, 0.025
max shift/error	0.0
R(F)	7.51
$R_w(F)$	7.72
goodness of fit	1.914
max diff Fourier peak, e/Å <sup>3</sup>	0.52

I-III, respectively. The molecule resides on a mirror symmetry so that the carbon atoms  $C_1, C_2, C_3, C_4, C_8, C_9,$

Table II. Bond Distances (in Angstroms)

atom 1	atom 2	distance <sup>a</sup>
C1	C1'	1.596 (5)
C1	C2	1.50 (2)
C1	C8	1.30 (2)
C2	C2'	1.624 (5)
C2	C3	1.29 (2)
C3	C4	1.31 (2)
C4	C5	1.45 (2)
C5	C5'	1.54 (1)
C5	C6	1.54 (2)
C5	C7	1.48 (2)
C8	C9	1.435 (2)
C9	C10	1.52 (2)
C9	C11'	1.515 (8)
C9	C11	1.51 (2)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Bond Angles (in Degrees)

atom 1	atom 2	atom 3	angle <sup>a</sup>
C1'	C1	C2	90.5 (6)
C1'	C1	C8	134.0 (10)
C2	C1	C8	135.6 (8)
C1	C1'	C2'	90.5 (7)
C1	C1'	C8'	133.9 (7)
C1	C2	C2'	89.5 (5)
C1	C2	C3	141.1 (7)
C2'	C2	C3	129.0 (10)
C1'	C2'	C2	89.5 (6)
C2	C2'	C3'	129.4 (6)
C2	C3	C4	178.0 (10)
C3	C4	C5	147.9 (6)
C3	C4	C5'	147.9 (3)
C5	C4	C5'	64.2 (8)
C1	C8	C9	130.0 (10)
C8	C9	C10	110.0 (10)
C8	C9	C11'	112.0 (5)
C8	C9	C11	112.0 (8)
C4	C5	C5'	57.9 (6)
C4	C5	C6	119.0 (10)
C4	C5	C7	118.0 (10)
C5'	C5	C6	119.0 (10)
C5'	C5	C7	122.0 (10)
C6	C5	C7	112.0 (10)
C4	C5'	C5	57.9 (5)
C4	C5'	C6'	118.7 (3)
C4	C5'	C7'	118.1 (5)
C5	C5'	C6'	118.6 (5)
C5	C5'	C7'	121.9 (5)
C10	C9	C11'	108.4 (4)
C10	C9	C11	108.4 (7)
C11'	C9	C11	106 (1)

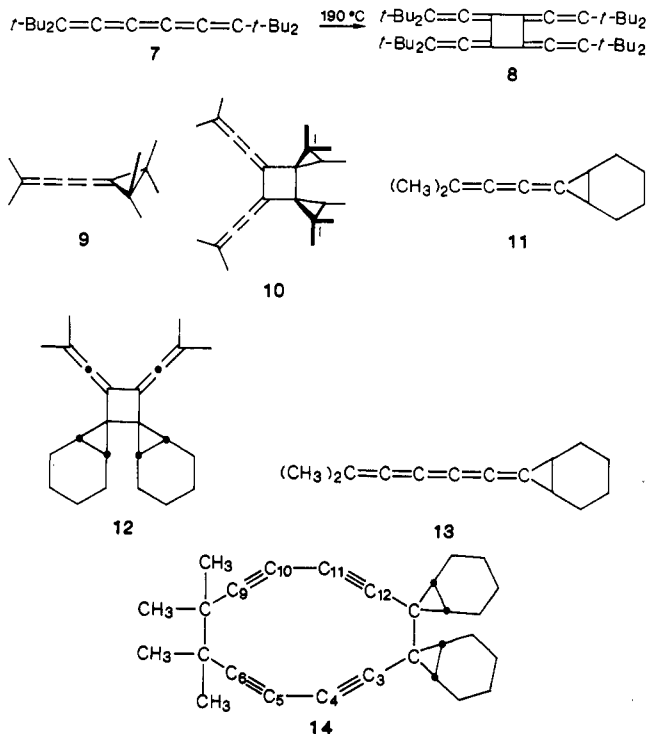
<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

and C<sub>10</sub> are on special positions.

Perusal of the data in Tables II and III reveals some interesting aspects of the structure of **6**. Whereas saturated cyclobutane rings are normally puckered, the ring in **6** is, as predicted, planar. The internal bond angles of the ring are close to the expected 90°. The bond lengths of the cyclobutane ring in **6** are particularly interesting. Two of the bonds are about 1.50 Å or about 0.007 Å shorter than the usual C<sub>sp<sup>2</sup></sub>-C<sub>sp<sup>3</sup></sub> length<sup>5</sup> of 1.507 Å, whereas the other two bonds at 1.596 and 1.624 Å are considerably longer. The olefinic double bonds at about 1.30 Å are normal as are the two sets of allenic bonds, compared to the 1.305 Å bond length<sup>6</sup> in symmetrically substituted allenes. The remainder of the structural features of **6** are within ex-

pected normal ranges and are therefore unexceptional.

Carbene-derived cumulene cyclodimers have been previously observed. Specifically, Hartzler<sup>7</sup> reported dimer **8** from tetra-*tert*-butylhexapentaene **7**. Le Noble<sup>8</sup> and co-workers reported **10** from **9** and we<sup>9</sup> reported **12** from **11** and **14** from **13**. What is not yet clear is what exactly



controls the mode of cyclodimerizations and why seemingly similar cumulenes such as hexapentaenes **7** and **13** and pentatetraenes such as **5** and **9** result in such different cyclodimers. Differential electron density distributions<sup>10</sup> in the various cumulenes might account for these results.

### Experimental Section

Cumulene<sup>1,3</sup> **5** (0.191 g, 0.95 mol) was dissolved in 2 mL of CDCl<sub>3</sub> and was placed in a sealed tube under argon. After 12 h of heating at 75 °C NMR indicated the quantitative conversion of **5** into **6**. The CDCl<sub>3</sub> was removed under reduced pressure, and the residue was recrystallized from degassed pentane to give 0.19 g, ~100%, of pale yellow crystals of **6**: mp 205–207 °C dec; UV (*n*-hexane) 237 (ε 28 700), 224 (29 200), 217 (22 000), 198 nm (25 000); mass spectrum (CI), *m/z* (relative intensity) 404 (M<sup>+</sup>, 100), 347 (13), 57 (56); IR (KBr) 2940, 2920, 1985, 1440, 1375, 1360, 1100, 870, 805 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.10 (s, 18), 1.26 (s, 12), 1.28 (s, 12), 5.64 (s, 2); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 178.7, 138.2, 126.2, 111.0, 102.5, 32.3, 32.0, 29.8, 22.1, 21.1. Anal. Calcd C<sub>30</sub>H<sub>44</sub>: C, 89.03; H, 10.96. Found C, 89.25, H, 10.80. Structure determination was carried out on a suitable single crystal with a Syntex P1 diffractometer, and the data are summarized in Tables I–III.

**Acknowledgment.** We are grateful to the NSF (CHE 84-19099) for financial support.

**Supplementary Material Available:** A listing of atomic coordinates and displacement parameters (3 pages); a listing of structure factors (3 pages). Ordering information is given on any current masthead page.

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(8) Basak, S.; Srivastava, S.; Le Noble, W. J. *J. Org. Chem.* 1987, 52, 5095. Le Noble, W. J.; Basak, S.; Srivastava, S. *J. Am. Chem. Soc.* 1981, 103, 4638.

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