

## Novel Cyclization of a Copper Carbenoid: the First Synthesis of a [5]Radialene (Pentamethylenecyclopentane) Derivative

Masahiko Iyoda,<sup>\*a</sup> Hiroyuki Otani,<sup>a</sup> Masaji Oda,<sup>a</sup> Yasushi Kai,<sup>b</sup> Yoshiko Baba,<sup>b</sup> and Nobutami Kasai<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

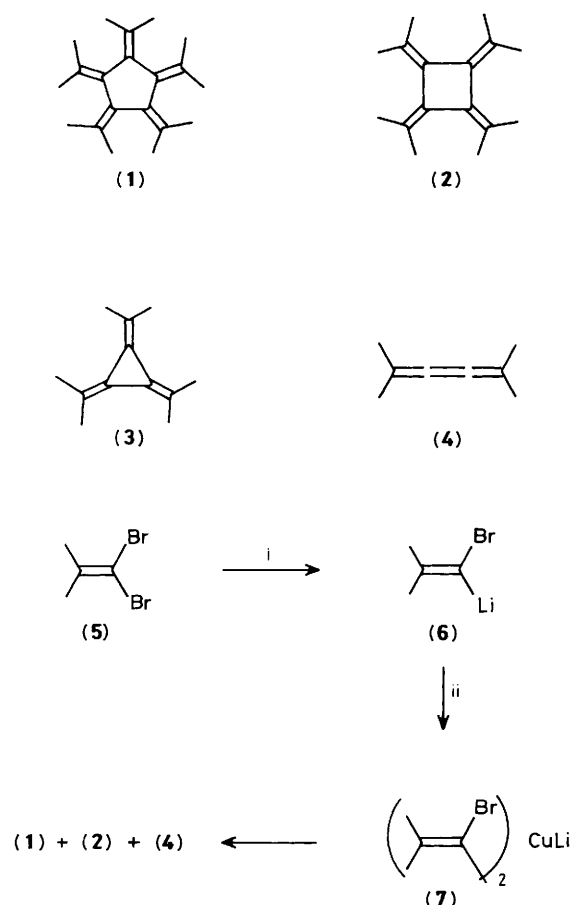
<sup>b</sup> Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

Reaction of 1,1-dibromo-2-methylpropene with butyl-lithium at  $-100^{\circ}\text{C}$ , followed by treatment with a copper(I) complex produces the ate-type complex of the corresponding copper carbenoid, which cyclizes upon warming to afford decamethyl[5]radialene together with octamethyl[4]radialene; the structure of decamethyl[5]radialene has been established by X-ray analysis.

Although many radialenes (polymethylenecycloalkanes) have already been synthesized, [5]radialene remains elusive and its chemistry is unexplored. Recently, we reported the unusual cyclization of an ate-type complex of a copper carbenoid to produce octaphenyl[4]radialene.<sup>1</sup> Since this cyclization proceeds formally as a cyclo-oligomerization of methylenecarbene, we expected that the reaction could be used for the synthesis of odd-membered radialenes. We report here a

one-pot synthesis of decamethyl[5]radialene (**1**), the first [5]radialene derivative, together with octamethyl[4]radialene (**2**).

The lithium carbenoid (**6**), derived from 1,1-dibromo-2-methylpropene (**5**), is known to produce 2,5-dimethylhexa-2,3,4-triene (**4**), and isopropylidencarbene generated from (**6**) adds to (**4**), under suitable conditions, to yield hexamethyl[3]radialene (**3**).<sup>2</sup> However, the thermal reaction of the



**Scheme 1.** Reagents: i, Bu<sup>n</sup>Li, -100 °C; ii, Cu<sup>I</sup>, -100 °C.

corresponding copper carbenoid afforded apparently different results.

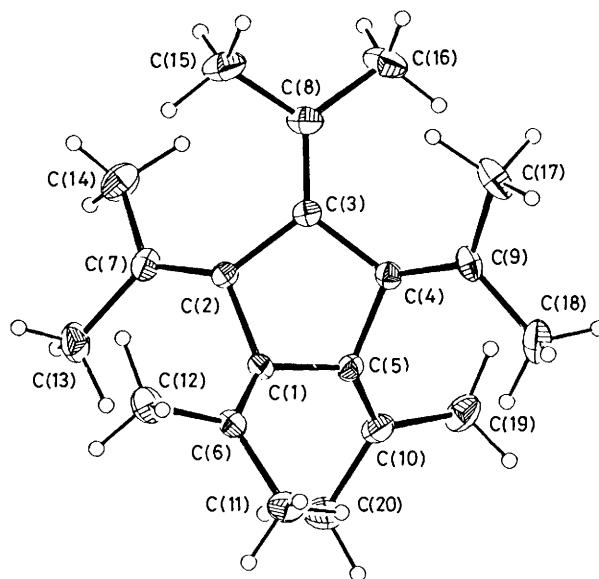
The lithium carbenoid (6), generated from (5) by the action of BuLi (1 equiv.) at -100 °C in tetrahydrofuran (THF), was treated with a Cu<sup>I</sup> complex (0.5 equiv.) at -100 °C to produce the ate-type complex (7) (Scheme 1). When the reaction mixture was stirred at -80 °C for 2 h and then warmed to room temperature, decamethyl[5]radialene (1) and octamethyl[4]radialene (2) were formed in the yields shown in Table 1. The ratio of (1) : (2) depended on the Cu<sup>I</sup> complex employed, and CuI·PBu<sub>3</sub> gave the best results, producing (1) in 32% and (2) in 23% yield. CuBr·SMe<sub>2</sub> and CuCN were also effective but CuI resulted in the formation of a complex mixture containing neither (1) nor (2). Considerable amounts of (4) were formed in all reactions but this decomposed during isolation of the products owing to its air-sensitivity. Although the structure and the state of aggregation of the ate-type complex (7) are still uncertain, *i.e.*, the composition of (7) merely indicates the stoichiometry of the reagents, oligomerization of the ate-type complex (7) plays an important role in the formation of radialenes (1) and (2), and the thermal reaction of the copper carbenoid which was prepared from CuI·PBu<sub>3</sub> (2 equiv.) and (6) (1 equiv.) gave fair amounts of (4) with (1) in 12% and (2) in 4% yield. Additionally, thermal reactions of (7) did not afford hexamethyl[3]radialene (3), suggesting that the coupling of (7) resulted in the formation of radialenes (1) and (2).

Octamethyl[4]radialene (2) obtained in these reactions had spectral data identical with those of the compound formed by nickel-catalysed dimerization of (4).<sup>3</sup> Decamethyl[5]radialene

**Table 1.** Thermal reaction of the copper carbenoid (7).

Cu <sup>I</sup> complex	% Yield <sup>a</sup>	
	(1)	(2)
CuI·PBu <sub>3</sub>	32	23
CuBr·SMe <sub>2</sub> <sup>b</sup>	14	30
CuCN	20	13
CuI	0	0

<sup>a</sup> The yields are for products isolated after chromatographic separation. <sup>b</sup> In the presence of excess of dimethyl sulphide.



**Figure 1.** X-Ray structure of (1).

(1) exhibited characteristic spectra reflecting its highly symmetrical structure in solution: colourless prisms, m.p. 100–101 °C, C<sub>20</sub>H<sub>30</sub> (*M*<sup>+</sup> 270.2340, calc. 270.2346); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 1.68 (s); <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>) δ 138.6, 122.6, and 24.2; *m/z* (75 eV) 270 (*M*<sup>+</sup>, 56%), 256 (21), and 255 (100); u.v. λ<sub>max</sub>. (log ε, cyclohexane) 230 (4.610), 236sh (4.587), and 284sh (3.776) nm.

The molecular structure of (1), determined by X-ray diffraction, is shown in Figure 1.† The molecule has approximate C<sub>2</sub> symmetry with a 2-fold axis passing through the mid-point of the C(1)–C(5) bond and the C(3) and C(8)

† *Crystal data* for (1): C<sub>20</sub>H<sub>30</sub>, *M*, 270.5, triclinic, space group *P* $\bar{1}$ , *a* = 10.470(3), *b* = 10.551(3), *c* = 9.621(3) Å, α = 106.26(3), β = 116.89(2), γ = 81.95(3)°; *U* = 909.9(5) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 0.99 g cm<sup>-3</sup>. Diffraction intensities were measured on a Rigaku four-circle diffractometer with graphite monochromatized Mo-K<sub>α</sub> radiation using a crystal with dimensions of 0.2 × 0.3 × 0.4 mm<sup>3</sup>. A total of 4177 reflections were collected to 2θ = 55°, of which 2263 had |*F*<sub>0</sub>| > 3σ(*F*<sub>0</sub>) and were used in the refinement. The intensity data were corrected for Lorentz and polarization effects but not for absorption [μ(Mo-K<sub>α</sub>) 0.59 cm<sup>-1</sup>]. The structure was solved by direct methods (MULTAN-78)<sup>4</sup> and refined by full-matrix least-squares (XRAY SYSTEM).<sup>5</sup> All the hydrogen atoms were located on the difference Fourier maps and included isotropically in the refinement together with the anisotropic non-hydrogen atoms. The weighting scheme used was *w* = [σ<sup>2</sup>(*F*<sub>o</sub>) + 0.003(*F*<sub>o</sub>)<sup>2</sup>]<sup>-1</sup>. The final *R* index was 0.08. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

atoms. The five-membered ring adopts a half-chair conformation. The intra-ring torsion angle around the C(1)–C(5) bond is  $47.3^\circ$ , while those around C(2)–C(3) and C(3)–C(4) are  $16.1^\circ$  and  $13.6^\circ$ , respectively. The nonbonded atomic distances between the neighbouring methyl carbon atoms are in the range  $3.011$  [C(16)  $\cdots$  C(17)] to  $3.395$  Å [C(11)  $\cdots$  C(20)], which are much shorter than the van der Waals contact of  $4.0$  Å. The mean distances of endo- and exo-cyclic carbon–carbon bonds are  $1.496$  Å and  $1.349$  Å.

Received, 23rd June 1986; Com. 868

### References

- 1 M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba, and N. Kasai, *J. Am. Chem. Soc.*, in the press.
  - 2 H. D. Hartzler, *J. Am. Chem. Soc.*, 1964, **86**, 526; G. Köbrich, W. E. Breckoff, H. Heinemann, and A. Akhtar, *J. Organomet. Chem.*, 1965, **3**, 492; G. Köbrich and H. Heinemann, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 594; G. Köbrich, H. Heinemann, and W. Zündorf, *Tetrahedron*, 1967, **23**, 565.
  - 3 M. Iyoda, S. Tanaka, M. Nose, and M. Oda, *J. Chem. Soc., Chem. Commun.*, 1983, 1058; also see, L. Stehling and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 496.
  - 4 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 'MULTAN-78: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,' University of York, England, and Louvain, Belgium, 1978.
  - 5 J. M. Stewart, XRAY SYSTEM, Report TR-446, Computer Science Centre, University of Maryland, Maryland, 1976.
-