

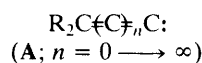
## Generation and Trapping of an Alkatrienylidenecarbene

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Reaction of  $\text{Bu}^t\text{CH}(\text{OMs})\text{C}\equiv\text{C}-\text{C}\equiv\text{CH}$  ( $\text{Ms} = \text{SO}_2\text{Me}$ ) with  $\text{Bu}^t\text{OK}$  and tetramethylethylene or  $\text{Et}_3\text{SiH}$ , in 1,2-dimethoxyethane (glyme) at  $-62^\circ\text{C}$ , results in the respective carbene addition and insertion products.

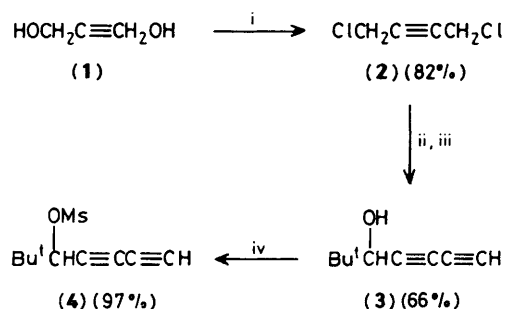
There is considerable current interest and activity<sup>1</sup> in unsaturated carbenes (**1**). Species with 2, 3, 4, and 6 carbons [*i.e.* (**A**), where  $n = 0, 1, 2$ , and 4] have been observed and extensively investigated.<sup>1,2</sup> Yet outside of a single preliminary report by LeNoble and coworkers,<sup>3</sup> nothing is known about the 5 carbon species (**A**;  $n = 3$ ). Herein we report the generation and trapping, *via* addition and insertion, of  $\text{Bu}^t\text{CH}=\text{C}=\text{C}=\text{C}:$ .



6,6-Dimethylhepta-1,3-diyn-5-ol, (**3**), was prepared by a standard literature<sup>3</sup> procedure and converted into its mesylate (**4**) in 97% yield (Scheme 1). Treatment of the diyne sulphonate, (**4**) with  $\text{Bu}^t\text{OK}$  in 1,2-dimethoxyethane (glyme), in the presence of the trapping substrates, at  $-62^\circ\text{C}$ , followed by slow warming to room temperature, results in the formation of carbene (**5**) *via* loss of  $\text{MeSO}_3\text{H}$  (Scheme 2). In the presence of excess tetramethylethylene, a 47% yield of adduct (**6**) was observed with small amounts of impurities.<sup>†</sup> Upon standing at room temperature ( $\sim 3$  days), or slight heating in solution, adduct (**6**) is converted in nearly quantitative yield into a single cyclodimer (**7**). Based upon the spectral data, literature analogies<sup>2,3</sup> and an *X*-ray structure of a closely related dimer,<sup>5</sup> the cyclodimer was assigned the head-to-head dimer structure (**7**). Compound (**7**) is a stable, pale yellow, crystalline solid.

Likewise, in the presence of excess  $\text{Et}_3\text{SiH}$ , an 18% yield of an unstable product is observed, presumably the insertion product (**8**) (Scheme 2) which in the presence of  $\text{Bu}^t\text{OK}$  undergoes a prototropic rearrangement to the diyne (**9**) and the allene (**10**).

<sup>†</sup> Cumulene (**6**) is air-sensitive and relatively unstable. In a refrigerator white, low melting crystals formed. The impurities consisted primarily of dimer (**7**).



**Scheme 1.** Reagents and conditions: i,  $\text{SOCl}_2$ , pyridine; ii, Na, liquid  $\text{NH}_3$ ; iii,  $\text{Bu}^t\text{CHO}$ ; iv,  $\text{MsCl}$  ( $\text{Ms} = \text{SO}_2\text{Me}$ ),  $\text{Et}_3\text{N}$ ,  $0^\circ\text{C}$ .

All structural assignments are based on spectral data.<sup>‡</sup> In particular, cumulenes (**6**) and (**7**) show characteristic infrared

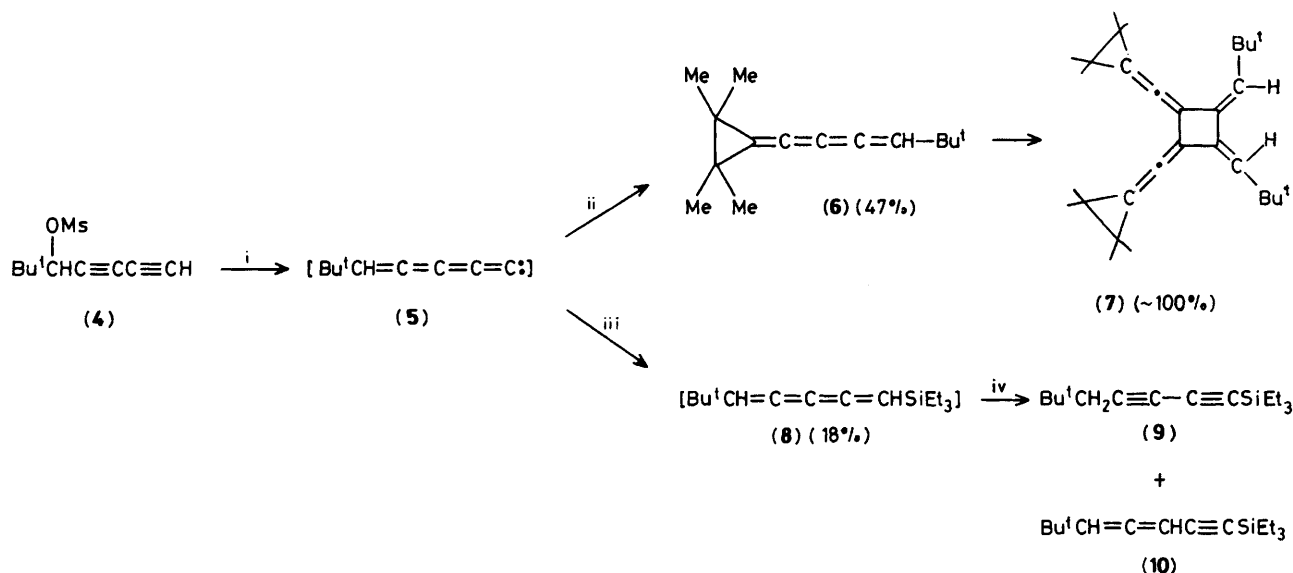
<sup>‡</sup> *Spectral data for (4)*: i.r. (neat): 3265, 2965, 2210, 2060, 1360, 1140, 925  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  0.99 (s, 9), 2.32 (s, 1), 3.05 (s, 3), 4.79 (s, 1);  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  25.13, 36.30, 38.84, 66.44, 70.24, 70.30, 72.81, 79.19.

(**6**): i.r. (neat): 2940, 2920, 2060, 1560, 1455, 1105  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  1.11 (s, 9), 1.29 (s, 6), 1.31 (s, 6), 5.42 (s, 1);  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  21.34, 21.45, 30.16, 32.67, 34.27, 108.54, 124.83, 126.13, 157.23, 166.77.

(**7**): M.U. 205— $207^\circ\text{C}$ ,  $m/z$  (chemical ionisation), 404 ( $M^+$ , 100%); i.r. (KBr): 2940, 2920, 1985, 1440, 1375, 1360, 1100, 805  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  1.10 (s, 18), 1.26 (s, 12), 1.28 (s, 12), 5.64 (s, 2);  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  21.15, 22.09, 29.85, 31.97, 32.35, 102.50, 110.96, 126.25, 138.25, 178.75.

(**9**): i.r. (neat): 2945, 2905, 2215, 2100, 1460, 1260, 1175, 1010, 810  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  0.60 (q,  $J$  8.1 Hz, 6), 0.97 (t,  $J$  8.1 Hz, 9), 0.98 (s, 9), 2.14 (s, 2);  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  4.22, 7.37, 29.06, 31.65, 34.27, 67.04, 77.95, 80.81, 89.44.

(**10**): i.r. (neat): 2950, 2905, 2150, 1945, 1455, 1000, 720, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  0.59 (q,  $J$  8.1 Hz, 6), 0.97 (t,  $J$  8.1 Hz, 9), 1.05 (s, 9), 5.36 (d,  $J$  6.6 Hz, 1), 5.41 (d,  $J$  6.6 Hz, 1);  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  4.39, 7.42, 29.94, 32.56, 77.42, 91.92, 99.77, 104.65, 210.67.



**Scheme 2.** Reagents and conditions: i, Bu<sup>t</sup>OK, glyme, -62 to 25 °C, -Me<sub>3</sub>SO<sub>3</sub>H; ii, Me<sub>2</sub>C=CMe<sub>2</sub>; iii, Et<sub>3</sub>SiH; iv, Bu<sup>t</sup>OK.

absorption at 2060 and 1995 cm<sup>-1</sup>, respectively, whereas the rearranged diyne (9) shows two triple bond absorptions at 2215 and 2100 cm<sup>-1</sup>. Likewise, the <sup>13</sup>C n.m.r. spectra show unique signals characteristic of the various products. Specifically, there are five cumulenic carbon signals for (6) and three such signals (and two olefinic ones) for dimer (7), whereas diyne (9) shows four acetylenic signals, and (10) has both acetylenic and allenic carbon absorptions.

Adduct (6) provides *prima facie* evidence for carbene (5), as do the rearranged silane insertion products (9) and (10). Hence, our studies, along with LeNoble's,<sup>3</sup> firmly establish the five carbon reactive intermediate, (5), as a member of the family of extended unsaturated carbenes, and thereby provide a rather conspicuous missing link in the series.

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## References

- 1 P. J. Stang, *Acc. Chem. Res.*, 1982, **15**, 348.
- 2 P. J. Stang and M. Ladika, *J. Am. Chem. Soc.*, 1981, **103**, 6437; P. J. Stang and M. R. White, *ibid.*, p. 5429; P. J. Stang and T. E. Fisk, *ibid.*, 1980, **102**, 6813.
- 3 W. J. LeNoble, S. Basak, and S. Srivastava, *J. Am. Chem. Soc.*, 1981, **103**, 4638.
- 4 J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 1993.
- 5 M. Kaftory, I. Agmon, M. Ladika, and P. J. Stang, *J. Am. Chem. Soc.*, 1987, **109**, 782.