Generation and Trapping of an Alkatrienylidenecarbene

Peter J. Stang* and Alan E. Learned
Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112, U.S.A.

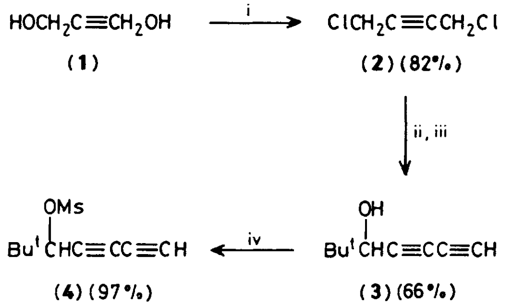
Reaction of Bu^{t}CH(OMs)C≡C–C≡CH (Ms = SO_2Me) with Bu^{t}OK and tetramethylethylene or Et_3SiH, in 1,2-dimethoxyethane (glyme) at −62 °C, results in the respective carbene addition and insertion products.

There is considerable current interest and activity[1] 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.[1,2] Yet outside of a single preliminary report by LeNoble and coworkers,[3] nothing is known about the 5 carbon species (**A**; n = 3). Herein we report the generation and trapping, *via* addition and insertion, of Bu^{t}CH=C=C=C=C:.

$$R_2C\!\left(C\right)_{n}\!C:$$
$$(\mathbf{A};\ n = 0 \longrightarrow \infty)$$

6,6-Dimethylhepta-1,3-diyn-5-ol, (**3**), was prepared by a standard literature[3] procedure and converted into its mesylate (**4**) in 97% yield (Scheme 1). Treatment of the diyne sulphonate, (**4**) with Bu^{t}OK in 1,2-dimethoxyethane (glyme), in the presence of the trapping substrates, at −62 °C, followed by slow warming to room temperature, results in the formation of carbene (**5**) *via* loss of $MeSO_3H$ (Scheme 2). In the presence of excess tetramethylethylene, a 47% yield of adduct (**6**) was observed with small amounts of impurities.† Upon standing at room temperature (~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[2,3] and an X-ray structure of a closely related dimer,[5] 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 Et_3SiH, an 18% yield of an unstable product is observed, presumably the insertion product (**8**) (Scheme 2) which in the presence of Bu^{t}OK undergoes a prototropic rearrangement to the diyne (**9**) and the allene (**10**).



Scheme 1. *Reagents and conditions:* i, $SOCl_2$, pyridine; ii, Na, liquid NH_3; iii, Bu^{t}CHO; iv, MsCl (Ms = SO_2Me), Et_3N, 0 °C.

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

---

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

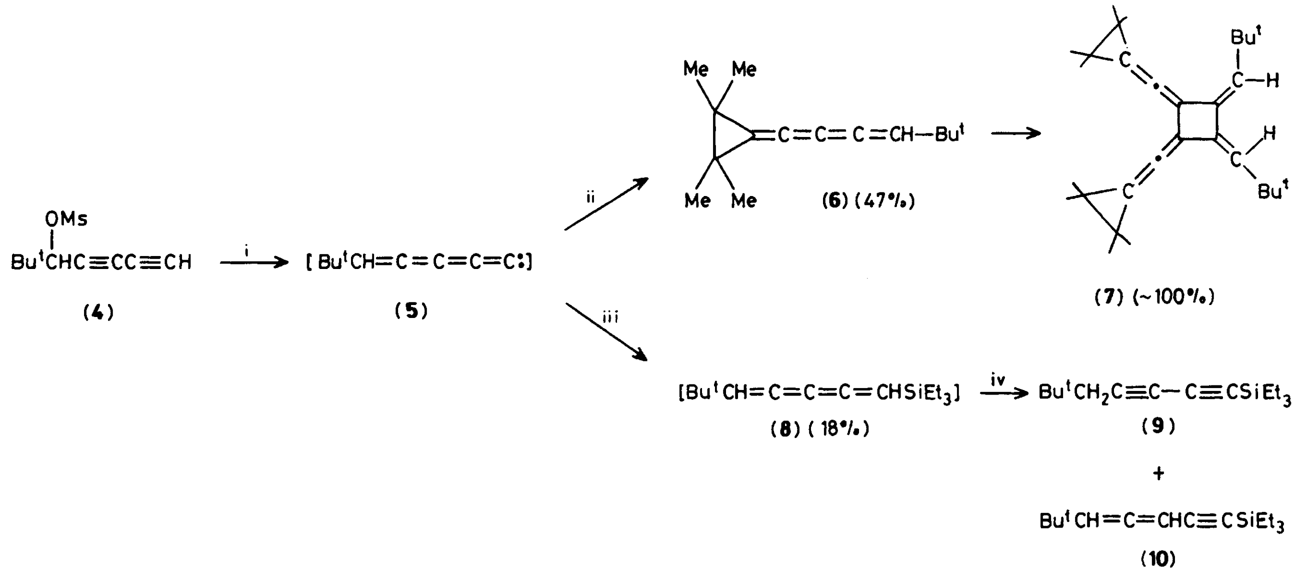
‡ *Spectral data* for (**4**): i.r. (neat): 3265, 2965, 2210, 2060, 1360, 1140, 925 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): δ 0.99 (s, 9), 2.32 (s, 1), 3.05 (s, 3), 4.79 (s, 1); ^{13}C n.m.r. ($CDCl_3$): δ 25.13, 36.30, 38.84, 66.44, 70.24, 70.30, 72.81, 79.19.

(**6**): I.r. (neat): 2940, 2920, 2060, 1560, 1455, 1105 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): δ 1.11 (s, 9), 1.29 (s, 6), 1.31 (s, 6), 5.42 (s, 1); ^{13}C n.m.r. ($CDCl_3$): δ 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 °C, *m/z* (chemical ionisation), 404 (M^+, 100%); i.r. (KBr): 2940, 2920, 1985, 1440, 1375, 1360, 1100, 805 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): δ 1.10 (s, 18), 1.26 (s, 12), 1.28 (s, 12), 5.64 (s, 2); ^{13}C n.m.r. ($CDCl_3$): δ 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 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): δ 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}C n.m.r. ($CDCl_3$): δ 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 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): δ 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}C n.m.r. ($CDCl_3$): δ 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^{t}OK, glyme, −62 to 25 °C, −Me$_3$SO$_3$H; ii, Me$_2$C=CMe$_2$; iii, Et$_3$SiH; iv, Bu^{t}OK.

absorption at 2060 and 1995 cm^{-1}, respectively, whereas the rearranged diyne (**9**) shows two triple bond absorptions at 2215 and 2100 cm^{-1}. Likewise, the ^{13}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 facia* evidence for carbene (**5**), as do the rearranged silane insertion products (**9**) and (**10**). Hence, our studies, along with LeNoble's,[3] 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.

Financial support by the NSF (CHE-84-19099) is gratefully acknowledged.

Received, 27th August 1987; Com. 1268

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.