Carbene–Carbene Rearrangement in 2-Propynylidenes

Masaki Noro, Noboru Koga, and Hiizu Iwamura*

Department of Chemistry, Faculty of Science
The University of Tokyo
7-3-1 Hongo, Tokyo 113, Japan

Received February 8, 1993

Ethynylcarbenes are key reactive intermediates in various reactions such as topochemically controlled solid-state polymerization of some 1,3-butadiyne derivatives[1] and formation of a variety of bicyclic ring compounds containing ethynyl group.[2] Recently 1-phenyl-2-propynylidene (**1**) was found by EPR spectroscopy to undergo rearrangement to 3-phenyl-2-propynylidene (**2**).[3] While this carbene–carbene rearrangement (eq 1) is considered to be trivial and even was represented as a resonance hybrid of the parent propynylidene (H in place of Ph in eq 1) in an earlier computational work,[4] we wished to disclose the scope of these rearrangements and studied 1,5-diphenylpenta-2,4-diynylidene by means of X-band (ν = 9.417 GHz) EPR spectroscopy.

(1)

The corresponding diazo compound **D** was prepared by the coupling of 3-amino-3-phenylpropyne[3a] with phenylethynyl bromide in the presence of Cu(I) hydroxyamine hydrochloride, followed by conversion of the amino group to the diazo group via an *N*-nitrosoacetamide. An analytically pure sample of **D**[5] was freshly made by chromatography on basic alumina (activity V, *n*-pentane elution) prior to each EPR measurement. Photolysis of **D** in frozen 2-methyltetrahydrofuran (MTHF) or isopentane containing a small amount of *n*-pentane at 10 K was carried out in an EPR cavity. When **D** in MTHF was irradiated ($\lambda > 460$ nm) at 10 K, signals characteristic of a triplet carbene appeared at 179.6, 522.0, 549.0, and 853.0 mT, corresponding to H_{-z}, H_x, H_y and H_z transitions, respectively, from which zero-field splitting (zfs) parameters have been obtained as $|D/hc| = 0.482$ and $|E/hc| = 0.007$ cm^{-1}. As the temperature was raised to 70 K after the photolysis, these triplet signals decreased their intensity reversibly in accordance with the Curie law. In the temperature range 70–80 K, however, the spectrum changed gradually to a set of other signals at 201.7, 540, and 870.0 mT, corresponding to H_{-z}, $H_x \simeq H_y$, and H_z transitions due to another triplet as shown in Figure 1, giving $|D/hc| = 0.497$ and $|E/hc| < 0.0001$ cm^{-1}.

When the observed zfs data are compared with those of **1** ($|D/hc| = 0.526$ and $|E/hc| = 0.010$ cm^{-1}) and **2** ($|D/hc| = 0.543$ and $|E/hc| = 0.003$ cm^{-1}),[3a] the spectral changes are interpreted in terms of the initial formation of 1,5-diphenylpenta-2,4-diynylidene **C1** followed by a carbene–carbene rearrangement of **C1** to bis(phenylethynyl)carbene **C2** at 70–80 K (Scheme I). No appreciable change in the EPR spectrum of **C1** was observed when subsequent irradiation was performed at 48 K with the shorter-wavelength light of $\lambda > 420$, 380, and 340 nm, showing that the observed rearrangement was not photochemical but thermal.

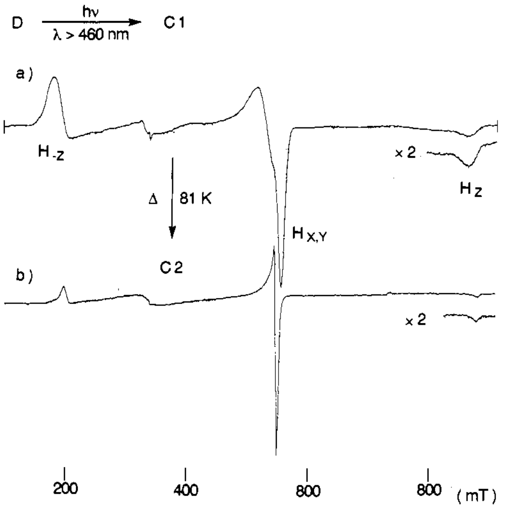
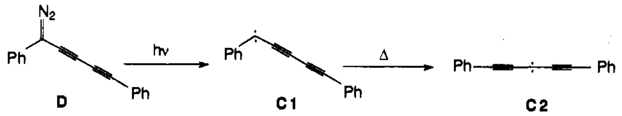


Figure 1. X-band EPR spectra due to (a) **C1** obtained by photolysis of **D** in MTHF matrix at 10 K and (b) **C2** after subsequent heating up to 81 K and recooling to 10 K.

Scheme I



The irradiation ($\lambda > 460$ nm) of **D** in frozen isopentane/*n*-pentane at 10 K gave rise to an EPR spectrum consisting of a ca. 1:1 mixture of carbenes **C1** and **C2** under similar conditions, and the rearrangement was observed in the temperature range 54–67 K. The rearrangement is suggested to be medium-controlled and more facile in isopentane/*n*-pentane than in MTHF, a trend often seen in unimolecular bond reorganization.[6] The intrinsic barrier to the rearrangement is concluded to be lower than 133 cal/mol.

The shift of the carbene center away from the position α to the phenyl ring to the centeral carbon is similar to the rearrangement from **1** to **2**.[3] We note that the $|D|$ values of the carbene species which is governed by the dipolar interaction between the σ and π spins at the carbene center are increased by the rearrangement in both cases. At the same time, the $|E|$ values are decreased. A most interesting finding is that the $|E|$ value of **C2** is close to 0, suggesting that bis(phenylethynyl)carbene **C2** has axial symmetry and therefore assumes almost linear configuration.[7] **C2** and its analogs (*t*-Bu and TMS in place of Ph) have been generated by α-elimination of the corresponding propargyl bromide[8a] and thermal decomposition of the lithium salts of the tosylhydrazones,[8b] respectively, and shown to give mixtures of the products due to dimerization of **C1**/**C1** and **C1**/**C2** in addition to **C2**/**C2**. Reactivity of **C1** should not be mistaken for its greater abundance relative to **C2**, which is now concluded to be thermodynamically more stable of the two forms.

Acknowledgment. This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 03102003) from the Ministry of Education, Science and Culture, Japan.

---

(1) Sixl, H.; Neumann, W.; Huber, R.; Denner, V.; Sigmund, E. *Phys. Rev. B* **1985**, *31*, 142. Gross, H.; Sixl, H. *Chem. Phys. Lett.* **1982**, *91*, 262.

(2) (a) Selvarajan, R.; Boyer, J. H. *J. Org. Chem.* **1971**, *36*, 1679. (b) Padwa, A.; Gareau, Y.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 983.

(3) (a) Koga, N.; Matstumura, M.; Noro, M.; Iwamura, H. *Chem. Lett.* **1991**, 1357. (b) DePinto, J. T.; McMahon, R. J. *Abstracts*; 11th IUPAC Conference on Physical Organic Chemistry, Ithaca, NY, August 2–7, 1992; B-6.

(4) (a) Maier, G.; Reisenauer, H. P.; Schwab, W.; Carsky, P.; Spirko, V.; Hess, B. A., Jr.; Schaad, L. J. *J. Chem. Phys.* **1989**, *91*, 4763. (b) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wassserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378.

(5) A deep-red oil: IR (KBr discs) 2142, 2203 (νC$\equiv$C), and 2044 (νC$=$N$=$N) cm^{-1}.

(6) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240.

(7) Ab initio calculations for propynylidene indicate that the potential energy surface with respect to C–H bending is nearly flat (DeFrees, D. J.; McLean, A. D. *Astrophys. J.* **1986**, *308*, L31). For other linear carbene derivatives, see: (a) Bernheim, R. A.; Kempf, R. J.; Humeer, P. W.; Skell, P. S. *Astrophys. J.* **1964**, *41*, 1156. (b) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196.

(8) (a) Hori, Y.; Noda, K.; Kobayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1969**, *40*, 3563. (b) Hauptmann, H. *Tetrahedron* **1976**, *32*, 1293.

0002-7863/93/1515-4916$04.00/0