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Reactions of Ethynylcarbenes Related to Solid-State Polymerization of 1-Phenyl-1,3-butadiyne

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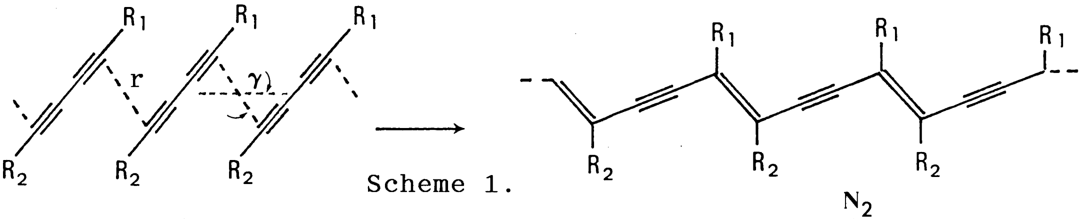
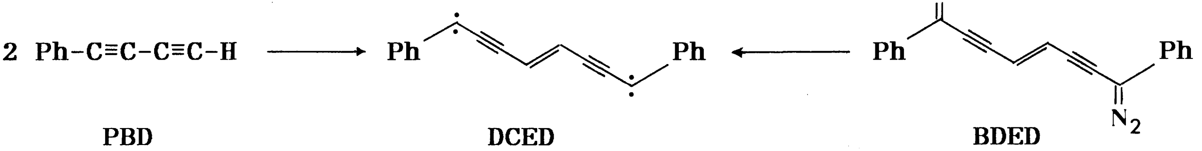
1,8-Diphenyl-1,8-bis(diazo)-octa-4-ene-2,6-diyne was prepared and photolyzed to give 1-phenyl-1,3-butadiyne in high yield. Ethynylphenylcarbene and β-phenylethynylcarbene generated by photolysis in MTHF at 6 K are in equilibrium in which the latter predominates at 90 K.

Topochemical solid-state polymerization of diacetylenes is of interest as a means to construct poly(diacetylenes) having interesting optoelectronic[1)] and magnetic properties.[2)] According to Baughman,[3)] the polymerization reaction takes place when the stacking of the monomer molecules in crystals is regulated as shown in Scheme 1, where r = 3.4 - 4.0 Å and $\gamma \approx 45°$. Ethynylcarbene skeletons are postulated as one of the possible living ends of the oligomeric intermediates in these reactions.[4)] In order to delineate the mechanism of the polymerization of 1-phenyl-1,3-butadiyne **PBD**, one of very few diacetylenes that have the phenyl rings in conjugation with the diacetylene chromophore and yet undergo polymerization, we have generated independently the dicarbenoenediyne **DCED** equivalent to the tail-to-tail-bonded living dimers of the diacetylene (Scheme 2). The molecular stacking capable of such a bonding has actually been found in the crystal of 1-[4-chloro-3-(N-hydroxy-tert-butylamino)-



Scheme 1.



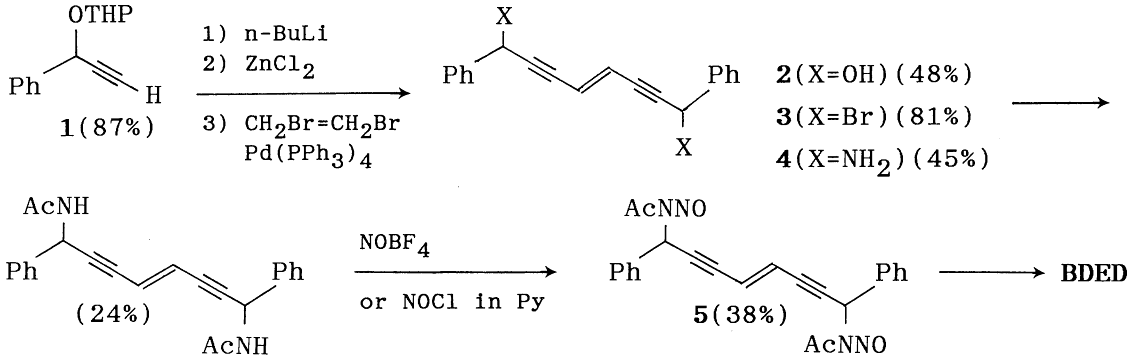
PBD **DCED** **BDED**

Scheme 2.

phenyl]-1,3-butadiyne.$^{2,5)}$ In this work, we prepared the requisite bis-diazo compound **BDED** and studied its photoreactions. Ethynylmonodiazo compounds **ED1** and **ED2** have also been studied as references.

α-Phenylpropargyl alcohol was protected as a THP ether **1**, treated with n-butyllithium, and then coupled with 1,2-dibromoethylene in the presence of $ZnCl_2$ and a Pd(0) catalyst to give the enediynediol **2** (Scheme 3). This was transformed into dibromo compound **3** and then to diamine **4**. N-acetylation followed by N-nitrosation gave bis(N-nitrosoacetamide) **5**. Addition of a saturated solution of NaOH in methanol to **5** in ether at - 20 °C gave **BDED** in good yield; λ_{max} (ether) 367, 373, 390 (ϵ = 25000), 480 (sh), 500 (ϵ = 300), 540(sh) nm; IR(PVC film) 2046, 2196 cm^{-1}. It was extremely labile and started to decompose at ca. -5 °C. The decomposition was followed by the uv absorptions that showed an isosbestic point at 450 nm and found to be complete in ca. 6 h at 0 °C. Therefore **BDED** was used directly after concentrating the filtrate of the reaction mixture.

ED1 and **ED2** were prepared similarly by the action of a base to the corresponding N-nitroso-N-acetamides. All new compounds gave satisfactory elemental analyses and NMR and IR spectral data.



Scheme 3.

When a solution of **BDED** in MTHF was irradiated (λ > 540 nm) at 4.2 K, absorptions due to the starting material disappeared rapidly with instantaneous grow-in of absorptions at ca. 260 nm with vibrational fine structure, suggesting an efficient formation of a phenyldiacetylene chromophore. **PBD** was actually obtained in good yield (70%) when **BDED** was irradiated (λ >540 nm) both in fluid solution at ambient temperature and in solid solution at cryogenic temperatures. When the photolysis was monitored by EPR (9.443 GHz) spectroscopy, a pair of broad plus and minus signals in a derivative mode with a separation of ca. 110 G grew in at g = 2. A randomly oriented triplet biradical with a very small zero-field splitting (zfs) parameter D is suggested to be responsible for the signals. These signals disappeared on continued irradiation or by elevating the temperature in the dark to 40 K. Then two sets of weak signals characteristic of unoriented ethynylmonocarbenes appeared ($|D| = 0.367$, $|E| = 0.004$ and $|D| = 0.430$, $|E| = 0.002$ cm^{-1}) and their intensity soon leveled off on continued irradiation. These are considered to be side products derived from monodiazo compounds present presumably as impurities in the starting **BDED**. In IR spectra obtained by irradiation at 15 K of a poly(vinyl chloride) film impregnated with **BDED** was observed an absorption at 3300 cm^{-1} characteristic of C-H stretching of terminal acetylenic bonds as soon as the irradiation was started.

Photolysis of diazo compound **ED1** was monitored both by EPR spectra in MTHF glass and IR absorptions in nitrogen matrix at cryogenic temperatures. The formation of the corresponding ethynylcarbene **EC1** was confirmed by its EPR fine structures characteristic of an ethynylcarbene (Fig. 1). The spectrum pattern changed only slightly but not appreciably after annealing at 90 K followed by a remeasurement at 6 K. The magnetic fields of the Z, XY and low-field Z transitions gave g = 2.003 and zfs values of $|D| = 0.543$ and $|E| = 0.003$ cm^{-1} that are in good agreement with those (D = 0.541 and E = 0.0035 cm^{-1}) in the literature.[6] Similarly **ED2** gave EPR fine structures consisting mostly of **EC2** ($|D| = 0.526$ and $|E| = 0.010$) and a small amount of **EC1**. Interestingly, the spectrum obtained after annealing this sample at 90 K was different from the original one but quite similar to that of **EC1**, showing that **EC2** underwent thermal rearrangement into **EC1**.

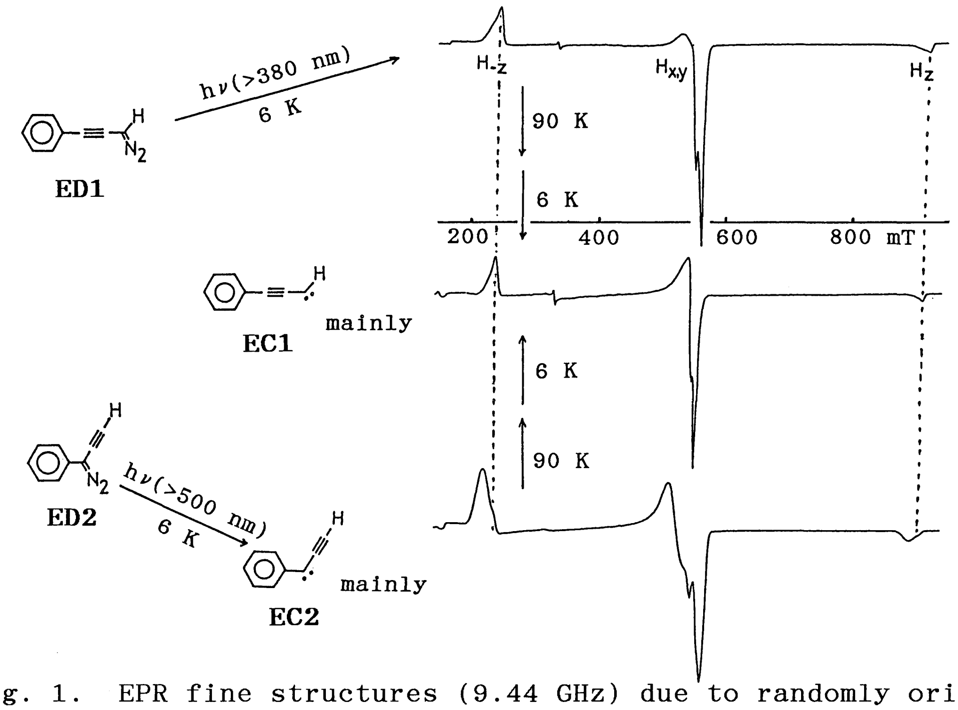
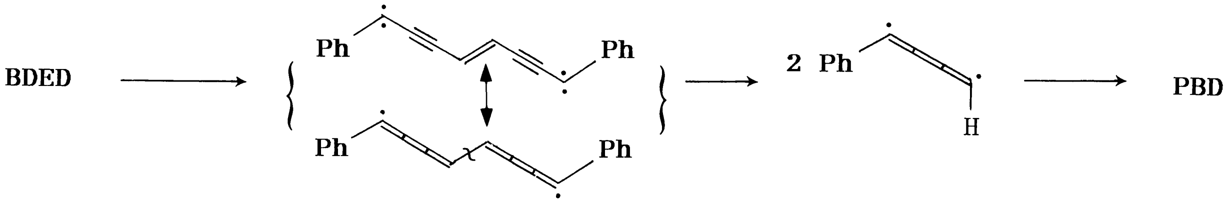


Fig. 1. EPR fine structures (9.44 GHz) due to randomly oriented ethynylcarbenes **EC1** and **EC2** in MTHF.

Neither intermediate triplet monocarbene nor quintet **DCED** was detected. No products were obtained deriving from an external trapping of the carbene centers of **DCED**. All the spectroscopic evidence at cryogenic temperatures points to an extremely facile photolytic reaction of the ene bond even at these temperatures. The carbene-carbene rearrangement observed here shows that the ethynylcarbenes are more stable when a phenyl substituent is far from the carbenic center and suggests that the dicarbenes are better represented by structure **DCED'**. Then the observed cleavage at the C-C bond that was originally the ene bond can be readily understood (Scheme 4). In Bergman reactions of enediynes, there is no precedents for the cleavage at the ene moiety. This is probably due to the lack of a single-bond character in the Z-ene moiety in the precursors and the presence of a strong driving force due to aromatic stabilization in the products.

The reaction of **BDED** observed here corresponds to depolymerization of intermediate dimer **DCED** of **PBD**. Its formation must be reversible. The 1,1'-bridged dimeric dicarbene is estimated to be longer lived than the 4,4'-dimer. The topochemical requirement for successful solid-state polymerizations must be rather severe. Only when the third molecule of **PBD** is appropriately situated with respect to the carbenic center of **DCED** in crystals and there are not much translational and vibrotational motions necessary, the reaction should start in a forward direction and constitute a propagation reaction.



DCED' Scheme 4.

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