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Photochemistry of Conjugated Polyacetylenes. Photoreaction of 1,4-Diphenyl-1,3-butadiyne with Unsymmetrical Olefins

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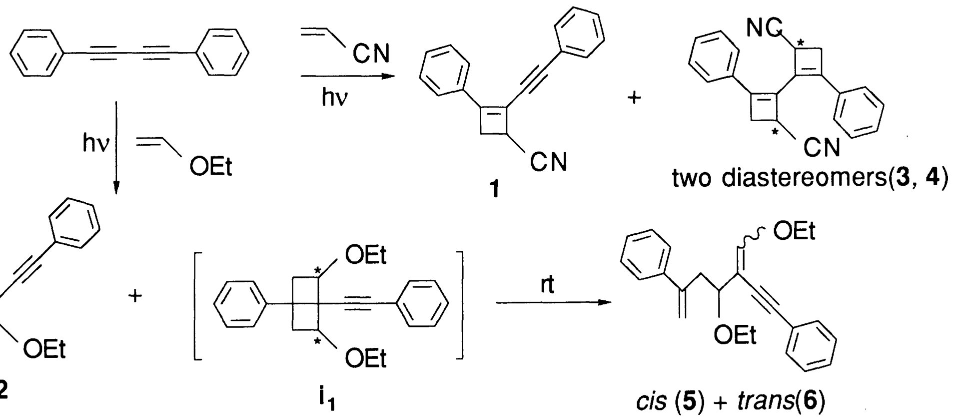
Irradiation of 1,4-diphenyl-1,3-butadiyne (DPB) with unsymmetrical olefins such as acrylonitrile and ethyl vinyl ether yields regiospecific 1:1 and 1:2 photoadducts. The reactive site on the formation of 1:2 photoadducts is different from each other indicating that the reaction proceeds through polar excited states.

We have previously reported an interesting photoreaction of 1,4-diphenyl-1,3-butadiyne (DPB) with an electron deficient olefin, dimethyl fumarate, to yield primary 1:1 and secondary 1:2 photoadducts.[1] One of the 1:2 photoadducts possessed a cyclopropane and an oxirane ring probably formed through an unusual attack of carbonyl C=O double bond by a carbenoid species.

In this investigation, we report a regiospecific photocycloaddition reaction of 1,4-diphenyl-1,3-butadiyne with two unsymmetrical olefins (acrylonitrile, AN and ethyl vinyl ether, EVE). Irradiation (300 nm) of DPB (4 mmol/dm^3) with olefins [2] yields regiospecific 1:1 photoadducts (**1** and **2**) and 1:2 photoadducts (**3**-**6**).[3] Dark yellow and red products, probably polymers, were obtained as the major by-products.



The structure of these adducts was determined by various physical methods, [4] including ^{13}C-NMR spectroscopy, which is vital for the determination of the reaction sites. Photoadducts **1**-**6** do not show the characteristic vibrational fine structure of conjugated polyacetylenes in the UV absorption spectra (Fig. 1) because one of the triple bonds in the conjugated diacetylene is lost.[1,5] The absorption maxima is red shifted in **1**-**4** but blue shifted in **5** and **6**. IR spectra show acetylenic stretching bands with weak intensity in **1**, **2**, **5**, and **6**. Mass spectra of all the photoadducts show M$^+$ peaks, indicating that the photoadducts **1** and **2** are formed by addition of one molecule of olefin while **3**-**6** are formed by addition of two olefin molecules to one

DPB molecule.

The regiochemistry of photoadducts **1**-**4** is determined from the coupling patterns in the ^{1}H-NMR spectra of the hydrogenated products (**1H**-**4H**). If R group is attached to C-2 of cyclobutane ring, the coupling pattern of the proton at C-1 must be a doublet-doublet or a triplet (when two coupling constants are same) while a quartet (when three coupling constants are same), a triplet-doublet, or a multiplet if the R group is attached to C-3 position. The coupling patterns of C1 proton for **1H**, **2H**, **3H**, and **4H** are quartet, triplet-doublet, multiplet and multiplet, respectively indicating that R group is attached to C-3 position in all the photoadducts **1**-**4**.[6] The regiochemistry is also supported by the fragmentation patterns in the mass spectra. All the hydrogenated adducts show the base peak at m/e 104 originated from the fragmentation of cyclobutane ring.

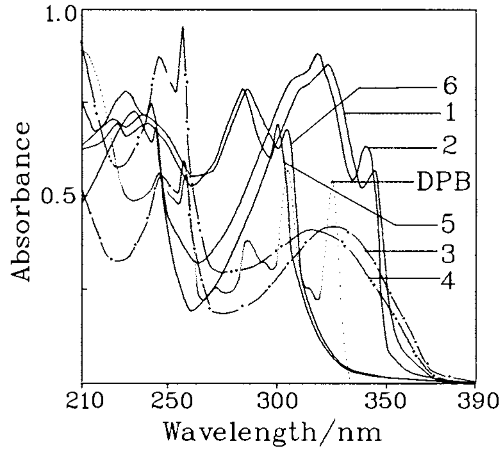
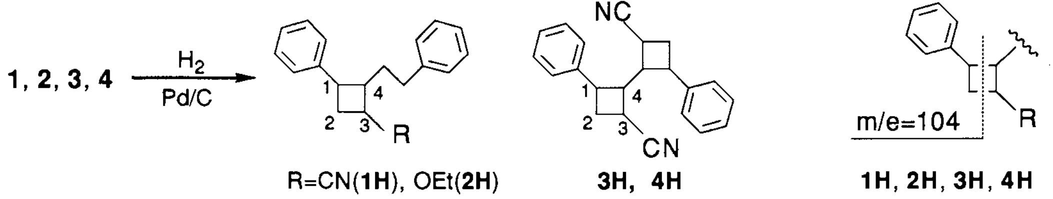


Fig. 1. UV absorption spectra of DPB and 1−6.



In the photoreaction of phenyl-1,3-pentadiyne with EVE, three stereoisomeric bicyclic[2.2.0.]hexane photoadducts which undergo thermal rearrangement to give ring opened 1,5-diene products were obtained.[7] These 1,5-diene products have a structure very similar to **5** and **6** strongly supporting the intermediate i_1 to give **5** and **6**.

In the photolysis of DPB with EVE, 1:1 photoadduct **2** is initially formed and extended irradiation of the solution results in decrease of **2** and formation of 1:2 adducts (**5** and **6**) indicating that 1:2 adducts are formed as secondary photoadducts from 1:1 adducts (Fig. 2). Photolysis of pure **2** with EVE results in the formation of 1:2 adducts strongly supporting that **2** is the primary and **5** and **6** are the secondary photoadducts. Similar results (Fig. 2) are obtained from the photolysis of DPB with AN but the 1:2 adducts

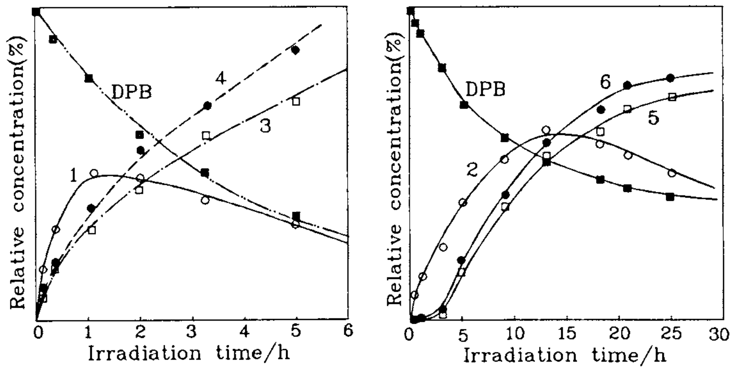


Fig. 2. Kinetics of the photoreactions. The concentration change of each compound was monitored against irradiation time.

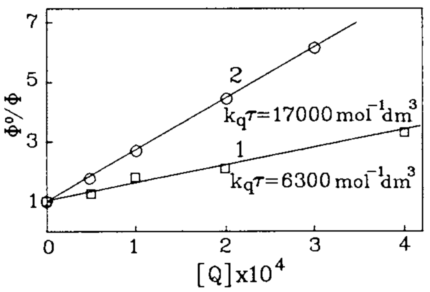
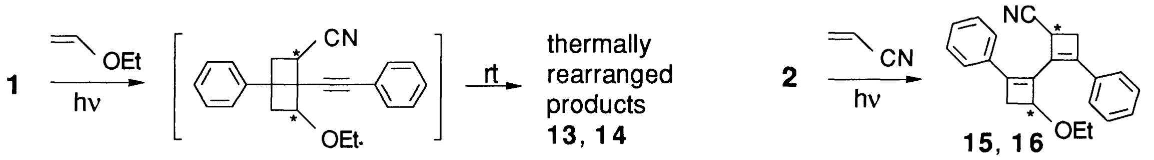


Fig. 3. Stern−Volmer plots on the formation of 1(DPB/AN 1:1 adduct, Q: azulene) and 2(DPB/EVE 1:1 adduct, Q: 9,10-diphenylanthracene).

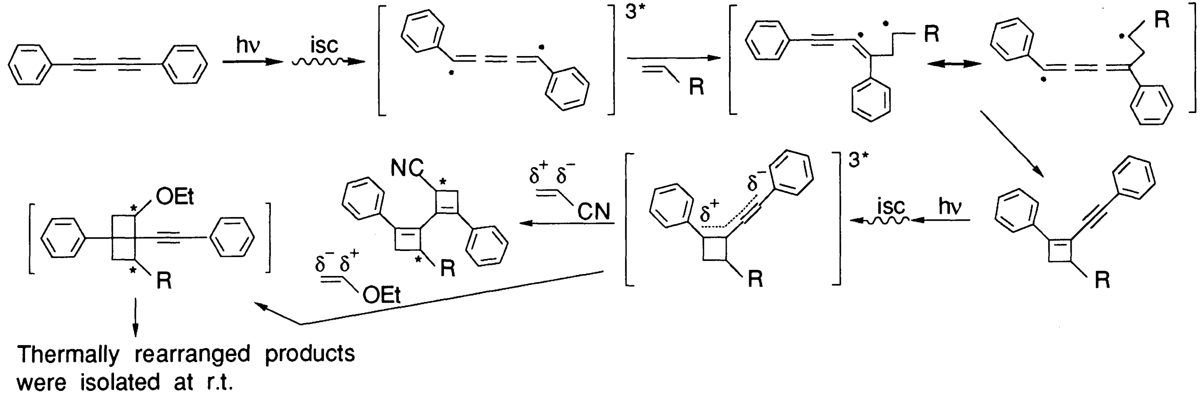
(**3**-**4**) are also obtained at the initial stage suggesting that some different pathway(s) exist in the formation of 1:2 adducts. Detailed kinetic study for this pathway is under investigation. The photoreaction of DPB with olefins to give 1:1 adducts is efficiently quenched by triplet quenchers (azulene; E_t=129.3 kJ/mol, 9,10-diphenylanthracene; E_t=174.9 kJ/mol)[8] as the quantum yields decrease linearly with increasing quencher concentration yielding large $k_q\tau$ values (of 6300 for **1** and 17000 $mol^{-1}dm^3$ for **2**, respectively) indicating that the photoreaction proceeds *via* the triplet excited state of DPB (Fig. 3). The photoreaction to give 1:1 adducts is also efficiently quenched by oxygen, supporting the triplet reaction mechanism.

The oxygen effects on the formation of 1:1 adducts with olefins to give 1:2 adducts were studied. The quantum yields of **3**, **4**, **5**, and **6** decreased to 20, 17, 19, and 15%, respectively in aerated solutions indicating that all of these 1:2 adducts are produced *via* the triplet excited states of 1:1 adducts.

The attack site of 1:1 adducts (**1**, **2**) by olefins to give 1:2 adducts (**3**, **4** and $\mathbf{i}_1$) is dependent on the electron density of olefinds, i.e., the triple bond for AN but the double bond for EVE, indicating that the triplet excited state of 1:1 photoadducts may have a polar character. Irradiation of 1:1 adduct **1** with EVE (400 $mmol/dm^3$) in THF gives different 1:2 adducts from that of **2** and AN (400 $mmol/dm^3$).[9]



From these results, a plausible reaction mechanism involving a polar triplet structure as shown in the following scheme is proposed.



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References

1) S. J. Lee and S. C. Shim, *Tetrahedron Lett.*, **31**, 6197 (1990).
2) [AN]= 400 $mmol/dm^3$ in THF and [EVE]= 800 $mmol/dm^3$ in n-hexane.
3) **1**; 1-(phenylethynyl)-2-phenyl-4-cyanocyclobutene, 14% yield,
2; 1-(phenylethynyl)-2-phenyl-4-ethoxycyclobutene, 5% yield,
3;1,1'-(2,2'-diphenyl-4,4'-*anti*-dicyano)dicyclobutene, 15% yield,
4;1,1'-(2,2'-diphenyl-4,4'-*syn*-dicyano)dicyclobutene, 14% yield,
5; 1,3-diethoxy-2-phenylethynyl-5-phenyl-(*cis*-1),5-hexadiene, 9% yield,

6; 1,3-diethoxy-2-phenyl-ethynyl-5-phenyl-(*trans*-1),5-hexadiene, 8% yield.

4) **1**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.66-7.36 (m, 10H), 3.78 (dd, 1H), 3.18 (dd, 1H), 3.02 (dd, 1H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 149.77, 132.83, 131.74, 129.78, 129.04, 128.56, 128.42, 125.84, 122.10, 119.08, 113.87, 96.30, 82.73, 32.28, 28.61 ppm; MS (70 eV), m/e 255 (M$^+$); UV (MeOH) λ_{max} 340 nm. **2**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.73-7.32 (m, 10H), 4.65 (dd, 1H), 3.87 (m, 1H), 3.72 (m, 1H), 3.05 (dd, 1H), 2.70 (dd, 1H), 1.32(t, 3H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 148.77, 134.07, 131.60, 129.13, 128.44, 128.38, 128.35, 126.34, 123.25, 120.92, 95.82, 84.46, 74.99, 63.92, 35.76, 15.55 ppm; MS (70 eV), m/e 274 (M$^+$); UV (n-hexane) λ_{max} 343 nm. **3**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.30-7.10 (m, 10H), 3.96 (t, 2H), 3.26 (d, 4H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 144.64, 132.92, 129.47, 128.10, 127.25, 125.63, 119.35, 32.37, 26.04 ppm; MS (70 eV), m/e 308 (M$^+$); UV (MeOH) λ_{max} 325, nm. **4**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.31-7.23 (m, 10H), 3.87 (dd, 2H), 3.35 (dd, 2H) 3.17 (dd, 2H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 145.40, 132.83, 128.59, 128.40, 126.94, 125.92, 119.32, 32.55, 26.93 ppm; MS (70 eV), m/e 308 (M$^+$); UV (MeOH) λ_{max} 315 nm. **5**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.22-7.46 (m, 10H), 6.67 (s, 1H), 5.32 (br s, 1H), 5.21 (br s, 1H), 4.49 (dd, 1H), 3.79 (m, 2H), 3.57 (m, 1H), 3.31 (m, 1H), 3.01 (dd, 1H), 2.91 (dd, 1H), 1.16 (t, 3H), 1.15 (t, 3H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 154.13, 144.91, 141.47, 131.27, 128.11, 128.02, 127.30, 127.11, 126.33, 124.25, 114.56, 103.22, 88.97, 86.29, 71.71, 69.00, 63.45, 39.94, 15.25, 15.16 ppm; MS (70 eV), m/e 346 (M$^+$); UV (n-hexane) λ_{max} 311 nm. **6**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.26-7.50 (m, 10H), 6.24 (s, 1H), 5.32 (br s, 1H), 5.22 (br s, 1H), 3.93 (q, 2H), 3.66 (t, 1H), 3.56 (m, 2H), 3.20 (m, 2H), 3.01 (d, 2H), 1.31 (t, 3H), 1.14 (t, 3H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 152.84, 144.82, 141.19, 131.53, 128.23, 128.06, 127.61, 127.27, 126.37, 123.95, 115.41, 100.54, 95.13, 83.59, 78.08, 69.08, 63.37, 41.20, 15.19 ppm; MS (70 eV), m/e 346 (M$^+$); UV (n-hexane) λ_{max} 313 nm.

5) S. C. Shim, T. S. Lee, and S. J. Lee, *J. Org. Chem.*, **55**, 4544 (1990).

6) **1H**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.35-6.95 (m, 10H), 3.75 (q, 1H), 3.30 (q, 1H), 2.97-2.60 (m, 3H), 2.45 (m, 1H), 2.20 (m, 1H), 1.82 (m, 1H), 1.65 (m, 1H); MS (70 eV), m/e 261 (M$^+$). **2H**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.35-6.89 (m, 10H), 3.97 (q, 1H), 3.58 (td, 1H), 3.47 (m, 2H), 2.64 (m, 1H), 2.50 (m, 1H), 2.39-2.28 (m, 3H), 1.50-1.26 (m, 2H), 1.23 (t, 3H); MS (70 eV), m/e 280 (M$^+$). **3H**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.50-7.20 (m, 10H), 4.10 (m, 1H), 3.70 (m, 1H), 3.40 (m, 1H), 3.00 (m, 1H), 2.70-2.30 (m, 6H); MS (70 eV), m/e 312 (M$^+$). **4H**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.60-7.30 (m, 10H), 3.85 (m, 2H), 3.35 (m, 2H), 2.80-2.36 (m, 6H); MS (70 eV), m/e 312 (M$^+$).

7) J. H. Kwon, S. J. Lee, and S. C. Shim, *Tetrahedron Letters*, submitted (1991).

8) S. L. Murov, " Handbook of Photochemistry," Marcel Dekker Inc., New York, (1973).

9) **13**(*trans*); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.51-7.25 (m, 10H), 5.62 (s, 1H), 5.32 (br s,1H), 5.13 (br s, 1H), 3.88 (m, 1H), 3.40 (m, 1H), 3.17 (m, 1H), 3.02 (dd, 2H), 2.71 (dd, 1H), 1.05 (t, 3H); MS (70 eV), m/e 327 (M$^+$); UV (MeOH) λ_{max} 309, 294 nm. **14**(*cis*); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.45-7.25 (m, 10H), 6.36 (s, 1H), 5.39 (br s, 1H), 5.23 (br s, 1H), 3.91 (q, 2H), 3.19-3.10 (m, 2H), 2.94 (dd, 1H), 1.25 (t, 3H); MS (70 eV), m/e 327 (M$^+$); UV (MeOH) λ_{max} 302, 284 nm. **15**; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.37-7.12 (m, 10H), 4.69 (m, 1H), 3.77 (m, 1H), 3.61 (m, 2H), 3.26 (dd, 1H), 3.08 (m, 2H), 2.73 (m,1H), 1.23 (t, 3H); MS (70 eV), m/e 327 (M$^+$); UV (MeOH) λ_{max} 320, 257, 249 nm. **16**; formed very small amount; MS (70 eV), m/e 327 (M$^+$); UV (MeOH) λ_{max} 324, 256, 248 nm.

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