Tetrahedron Letters, Vol.32, No.46, pp 6719-6722, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

PHOTOCHEMISTRY OF CONJUGATED POLYACETYLENES: PHOTOREACTION OF 1-PHENYL-1,3-PENTADIYNE WITH SOME OLEFINS

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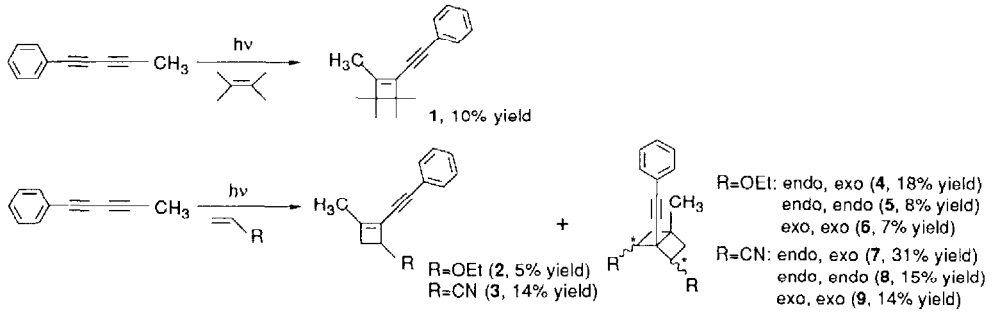
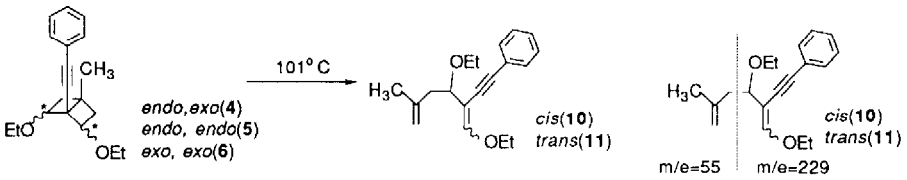
Summary: Photolyses of 1-phenyl-1,3-pentadiyne with various olefins such as 2,3-dimethyl-2-butene, acrylonitrile, and ethyl vinyl ether yield site selective and/or regioselective photoadducts.

We have previously reported the photoreaction of 1,4-diphenyl-1,3-butadiyne with 2,3-dimethyl-2-butene(DMB) to yield cyclobutene, bicyclopropane and bicyclobutene photoadducts.[1] In this investigation, we report a site selective and/or regioselective photoreaction of an unsymmetrical diacetylene, 1-phenyl-1,3-pentadiyne(PPD) with some olefins such as 2,3-dimethyl-2-butene(DMB), acrylonitrile(AN), and ethyl vinyl ether(EVE).

Deaerated DMB solution of PPD(4 mM) was irradiated with 300nm UV light to obtain site specific 1:1 photoadduct(**1**).[3] Irradiation of PPD(4 mM) with unsymmetrical olefins(EVE and AN) in deaerated solutions[2] yields site selective and regioselective [2+2] type 1:1 photoadducts(**2** and **3**) and 1:2 photoadducts(**4-9**).[3] 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 site.



The UV spectra(Figure 1) of these photoproducts do not show the characteristic vibrational fine structure of conjugated polyacetylenes.[5] The absorption maxima were red shifted in **1-3** and blue shifted in **4-9** indicating that the conjugated system is sustained in 1:1 adducts but not in 1:2 adducts. The mass spectra of these photoproducts show molecular ion (M^+) peaks indicating that the photoproducts **1-3** are formed by addition of one olefin molecule, while **4-9** are formed by addition of two olefin molecules to one PPD. The ^{13}C-NMR spectra for all of these adducts show two sp hybridized carbon peaks indicating that one of the carbon-carbon triple bonds remains intact. The existence of ethynyl benzene moiety(120-125 ppm) for all of these adducts indicates that C3-C4 triple bond is the reactive site. The site selective structure of **1-3** was also supported by the methyl substituted sp^2 carbon peaks(156.52, 153.27, and 153.61 ppm, respectively) of the cyclobutene ring. The 1:2 adducts(**4-6**) rearranged to give ring opened 1,5-diene products(**10** and **11**)[6] on warming to 101°C(in methylcyclohexane) indicating that they were bicyclohexyl products.[7]



The regiochemistry of 1:2 adducts(**4-6**) was determined by mass fragmentation patterns of **10** and **11**. The fragments corresponding to the loss of C_4H_7 and $C_{15}H_{17}O_2$ appear at m/e 55 and 229 indicating that the ethoxy groups are attached to the C-2 and C-6 of bicyclohexane products.

Nuclear Overhauser effect(NOE) provided substantial evidence for the regiochemistry of 1:2 photoproducts(**4-9**). Saturation of methyl protons in these photoadducts(**4-9**) gives a larger intensity enhancement of the methylene protons(H_B and H_C) than H_A and irradiation of H_A gives a larger NOE effect for methylene protons than methyl protons (Table 1). The ^{1}H- and ^{13}C-NMR spectra[4] of 1:2 adducts **5**, **6**, **8**, and **9** show symmetrical patterns in the bicyclic ring and **4** and **7** are unsysmmetrical.[4] Three diastereomers (by two chiral centers and one puckered bicyclohexane ring) can exist for each set of photoadducts **4-6** and **7-9**. Adducts **4** and **7** are determined to be *endo,exo* products from their unsymmetric structure deduced from their ^{1}H-and ^{13}C-NMR spectra. The other products(**5**, **6**, **8**, and **9**) are determined to be *endo,endo* and *exo,exo* bicyclic stereoisomers. The stereochemisty of **5**, **6**, **8**, and **9** is assigned by NOE studies provided substantial support for orientation of ethoxy and nitrile group (Table 1).

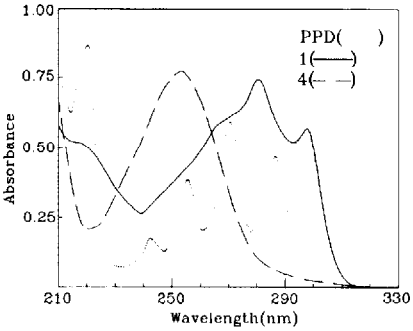
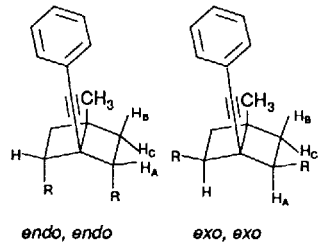


Figure 1. UV absorbance spectra of PPD (2.7×10^{-5}M), 1(5.1×10^{-5}M), and 4(5.0×10^{-5} M). UV spectra of the other 1:1 and 1:2 photoadducts are very similar to those of 1 and 4, respectively.[4]

Saturation of methyl protons(1.26 ppm) in adduct **8** gives an intensity enhancement(1.1%) of H_A, while saturation of H_A gives 1.1% enhancement of methyl proton intensity. On the other hand, saturation of methyl protons of adduct **9** does not give intensity enhancement of H_A and saturation of H_A does not give an enhancement of methyl protons indicating that adduct **8** is *endo,endo* and **9** is *exo,exo* product, respectively. The NOE studies for **5** and **6** also give smiliar results as shown in Table 1, indicating that adduct **5** is *endo,endo* and **6** is *exo,exo* product.



Adducts	Satd. region	Enhancement (%)			
		H_A	H_B	H_C	CH_3
5	CH_3	1.6	2.4	—	—
	H_A	—	4.7	1.0	0.7
6	CH_3	—	1.9	—	—
	H_A	—	0.9	4.3	—
8	CH_3	1.1	2.0(H_B and H_C)[a]		—
	H_A	—	5.0(H_B and H_C)[a]		1.1
9	CH_3	—	2.1	—	—
	H_A	—	—	4.4	—

Table 1. Results of NOE studies on **5**, **6**, **8**, and **9**.
a; The methylene protons(H_B and H_C) of **8** are not resolved in the ^{1}H-NMR.

In the photolysis(Figure 2) of PPD with EVE and AN, the 1:1 photoadduct **2**(3) is initially formed and prolonged irradiation of the solution results in the formation of 1:2 photoadducts **4-6**(**7-9**) suggesting that 1:1 photoadduct is the primary photoproduct and 1:2 photoadducts are the secondary photoproducts.

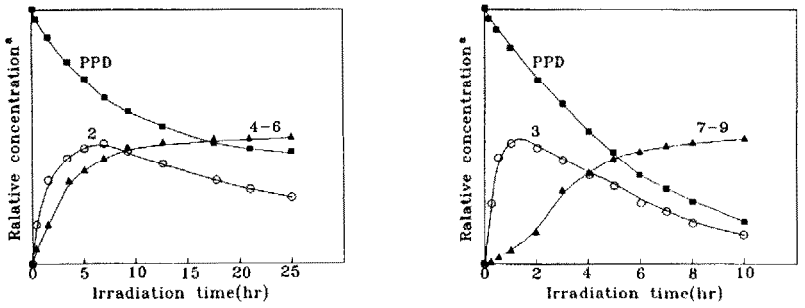


Figure 2. Kinetics of the photoreactions.
a; The concentration change of each compound was monitored against irradiation time.

Irradiation of pure **2**(**3**) with EVE(AN) in deaerated n-hexane(THF) solution results in the formation of **4-6**(**7-9**) strongly supporting that 1:2 photoadducts are formed as the secondary photoproducts from 1:1 photoadducts and regiochemistry of 1:1 photoadducts is deduced from the regiochemistry of 1:2 adducts(**4-9**). The mechanistic studies for the reaction are in progress in this laboratory.

Acknowledgements; This investigation was supported by the Korea Science and Engineering Foundation and OCRC-KOSEF.

References and Notes

1. S. C. Shim, T. S. Lee, and S. J. Lee, *J. Org. Chem.* **1990**, 15 (55), 4544.
2. (a) c(EVE)= 400mM in *n*-hexane. (b) c(AN)= 400mM in THF.
3. **1**: 1-(phenylethynyl)-2-methyl-3,3,4,4-tetramethylcyclobutene.
   2: 1-(phenylethynyl)-2-methyl-4-ethoxycyclobutene.
   3: 1-(phenylethynyl)-2-methyl-4-cyanocyclobutene.
   4: 2,6-*endo,exo*-diethoxy-1-(phenylethynyl)-4-methylbicyclo[2.2.0.]hexane.
   5: 2,6-*endo,endo*-diethoxy-1-(phenylethynyl)-4-methylbicyclo[2.2.0.]hexane.
   6: 2,6-*exo,exo*-diethoxy-1-(phenylethynyl)-4-methylbicyclo[2.2.0.]hexane.
   7: 2,6-*endo,exo*-dicyano-1-(phenylethynyl)-4-methylbicyclo[2.2.0.]hexane.
   8: 2,6-*endo,endo*-dicyano-1-(phenylethynyl)-4-methylbicyclo[2.2.0.]hexane.
   9: 2,6-*exo,exo*-dicyano-1-(phenylethynyl)-4-methylbicyclo[2.2.0.]hexane.
4. All the photoadducts are oily.

   1: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.27-7.45(5H, m), 1.71(3H, s), 1.13(6H, s), 1.05(6H, s); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 156.52, 131.50, 128.18, 127.76, 126.01, 123.76, 92.90, 82.03, 48.54, 47.17, 22.20, 21.34, 10.72; **IR**(NaCl) 2948, 2862, 2194, 1595, 1489, 1446, 1368, 756, 690 cm^{-1}; **UV**(MeOH) λ–max 298 and 288 nm; **MS**(70eV), m/e 224(M^+, 4.0), 139(M^+-$C_9H_7^+$, 100); **HRMS**, m/e 224.1553, calcd for $C_{17}H_{20}$ 224.1565.

   2: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.19-7.39 (5H, m), 4.41(1H, m), 3.67(1H, m), 3.56(1H, m), 2.58(1H, m), 2.36(1H, m), 1.85(3H, dd), 1.28(3H, t); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 153.27, 131.49, 128.22, 128.09, 124.03, 123.37, 92.81, 82.52, 75.58, 63.89, 39..77, 29.68, 16.06,15.49; **IR**(NaCl) 2974, 2919, 2200, 1489, 1442, 1113, 757, 691 cm^{-1}; **UV**(MeOH) λmax 294 and 277 nm; **MS**(70eV), m/e 212(M^+, 51.7), 139(M^+-C_6H_{13}, 100), 115($C_9H_7^+$, 78.9); **HRMS**, m/e 212.1219, calcd for $C_{15}H_{16}O$ 212.1201.

   3: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.29-7.47 (5H, m), 3.62(1H, m), 2.83(1H, m), 2.71(1H, m), 1.91(3H, dd); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 153.61, 131.65, 128.72, 128.32, 122.27, 119.39, 117,65, 93.43, 80.70, 36.11, 29.14, 16.15; **IR**(NaCl) 2930, 2236, 2203, 1489,1437,1319, 758, 691 cm^{-1}; **UV**(n-hexane) λmax

292 and 276 nm; **MS**(70eV), m/e 193(M^+, 13.6), 165(M^+-CH_2N, 17.5), 140(M^+-AN, 55.6), 139(M^+-ANH, 100); **HRMS**, m/e 193.0908, calcd for $C_{14}H_{11}N$ 193.0891.

4: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.25-7.45(5H, m), 4.44(1H, dd), 4.17(1H, dd), 3.78(1H, m), 3.64(1H, m), 3.47(2H, m), 2.46(1H, dd), 2.26(1H, dd), 2.13(1H, dd), 2.04 (1H, dd), 1.20-1.32(9H, m); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 131.62, 128.10, 127.54, 124.09, 87.48, 87.41, 72.75, 70.15, 64.74, 63.90, 51.37, 43.84, 39.23, 33.88, 22.06, 15.20, 15.15; **IR**(NaCl) 2972, 2879, 2216, 1442, 1371,1343, 1174, 1114, 756, 692 cm^{-1}; **UV**(MeOH) λmax 253 nm; **MS**(70eV), m/e 284(M^+, 0.6), 229(M^+-C_4H_7, 18.2), 115($C_9H_7^+$, 100), 29($C_2H_5^+$, 88.8); **HRMS**, m/e 284.1778, calcd for $C_{19}H_{24}O_2$ 284.1776.

5: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.26-7.43(5H, m), 4.27(2H, dd), 3.67(2H, m), 3.49(2H, m), 2.41(2H, dd), 2.29(2H, dd), 1.23(6H, t), 1.20(3H, s); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 131.63, 128.11, 127.45, 124.33, 88.78, 84.45, 76.65, 64.87, 52.66, 40.82, 38.90, 23.56,15.24; **IR**(NaCl) 2973, 2868, 2211, 1443, 1375, 1185, 1141, 1094, 756, 692 cm^{-1}; **UV**(MeOH) λmax 252 nm; **MS**(70eV), m/e 284(M^+, 0.6), 229(M^+-C_4H_7, 19.1), 115($C_9H_7^+$, 100), 29($C_2H_5^+$, 82.0); **HRMS**, m/e 284.1780, calcd for $C_{19}H_{24}O_2$ 284.1776.

6: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.26-7.45(5H, m), 3.94(2H, dd), 3.86(2H, m), 3.48(2H, m), 2.41(2H, dd), 1.98(2H, dd), 1.33(3H, s), 1.27(6H, t); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 131.56, 128.18, 127.59, 123.96, 91.50, 86.04, 76.46, 65.02, 48.03, 41.28, 35.33, 22.05,15.17; **IR**(NaCl) 2972, 2866, 2218, 1490,1442, 1340, 1164, 1164, 11177, 757, 692 cm^{-1}; **UV**(MeOH) λmax 254 nm; **MS**(70eV), m/e 284(M^+, 0.5), 229(M^+-C_4H_7, 7.9), 115($C_9H_7^+$, 85.7), 29($C_2H_5^+$, 100); **HRMS**, m/e 284.1793, calcd for $C_{19}H_{24}O_2$ 284.1776.

7: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.29-7.50(5H, m), 3.89(1H, dd), 3.59(1H, dd), 2.58(1H, dd), 2.41-2.47(3H, m), 1.28(3H, s); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 131.76, 128.80, 128.16, 121.51, 118.68, 118.14, 91.75, 82.75, 45.48, 43.89, 37.34, 35.24, 28.81, 27.89, 21.36; **IR**(NaCl) 2953, 2238, 1491, 1440, 1068, 759, 692 cm^{-1}; **UV**(MeOH) λmax 249 nm; **MS**(70eV), m/e 246(M^+, 11.4), 231(M^+-CH_3, 50.9), 204(M^+-C_2H_2N, 91.4), 55($C_4H_7^+$, 100); **HRMS**, m/e 246.1131, calcd for $C_{17}H_{14}N_2$ 246.1157.

8: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.28-7.41 (5H, m), 3.69(2H, dd), 2.51-2.61(4H, m), 1.26(3H, s); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 131.63, 128.90, 128.31, 121.46, 116.58, 88.91, 85.38, 46.74, 40.48, 36.45, 27.64, 20.27; IR(NaCl) 2952, 2237, 1444, 1070, 760, 692 cm^{-1}; **UV**(MeOH) λmax 248 nm; **MS**(70eV), m/e 246(M^+, 5.6), 231(M^+-CH_3, 37.5), 204(M^+-C_2H_2N, 72.1), 55($C_4H_7^+$, 100); **HRMS**, m/e 246.1152, calcd for $C_{17}H_{14}N_2$ 246.1157.

9: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.29-7.56(5H, m), 3.45(2H, dd), 2.58(2H, dd), 2.37(2H, dd), 1.36(3H, s); ^{13}**C-NMR**(75MHz, $CDCl_3$) δ 132.02, 128.87, 128.21, 121.71, 118.89, 93.63, 81.30, 46.04, 45.11, 36.37, 31.09, 22.47; **IR**(NaCl) 2953, 2241, 1490,1443, 1070, 759, 693 cm^{-1}; **UV**(MeOH) λmax 249 nm; **MS**(70eV), m/e 246(M^+, 1.6), 231(M^+-CH_3, 10.7), 204(M^+-C_2H_2N, 17.4), 55($C_4H_7^+$, 89.6); **HRMS**, m/e 246.1141, calcd for $C_{17}H_{14}N_2$ 246.1157.

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6. **10**: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.25-7.43(5H, m), 6.73(1H, s), 4.81(1H, s), 4.78(1H, s), 4.57(1H, dd), 3.93(2H, q), 3.61(1H, m), 3.40(1H, m), 2.49(2H, m), 1.78(3H, s), 1.28(3H, t), 1.22(3H, t) ; **IR**(NaCl) 2923, 2852, 2201, 1639, 1490, 1201, 1087, 756, 691 cm^{-1}; **UV**(n-hexane) λmax 302, 286 nm; **MS**(70eV), m/e 284(M^+, 5.8), 229(M^+-C_4H_9, 17.5), 115($C_9H_7^+$, 48.3), 29($C_2H_5^+$, 100).

11: ^{1}**H-NMR**(300MHz, $CDCl_3$) δ 7.26-7.49(5H, m), 6.48(1H, s), 4.81(2H,br s), 4.01(2H, q), 3.78(1H, t), 3.64(1H, m), 3.32(1H, m), 2.51(2H, d), 1.78(3H, s), 1.35(3H,t), 1.21(3H, t); **IR**(NaCl) 2921, 2852, 2208, 1695, 1451, 1233, 757, 696 cm^{-1}; **UV**(n-hexane) λmax 300, 283 nm; **MS**(70eV), m/e 284(M^+, 4.5), 229(M^+-C_4H_9, 18.5), 115($C_9H_7^+$, 47.0), 29($C_2H_5^+$, 100).

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(Received in Japan 5 August 1991)