Triplex, Microwave Induced and Conventional Diels-Alder Reaction of Phenyl-substituted Alkynes with Cyclopentadienes

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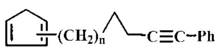
Many reports[1,2] have appeared during the last decade in connection with the mechanism of the triplex cycloaddition reaction. The triplex intramolecular Diels-Alder reaction of alkenylcyclopentadiene and alkenylcyclohexadiene have been studied to compare the photo-adducts with the thermal-adducts and to probe the dependence on tether length between diene and dienophile.

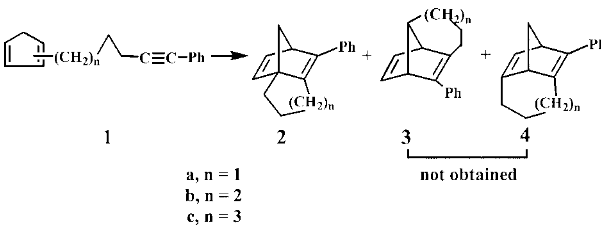
In our previous works[3] on the triplex effect on the reaction of alkenylcyclopentadienes, bridgehead olefin was produced. This bridgehead olefin, however, was not formed in thermal condition. These results lead us to investigate the reaction of alkynylcyclopentadienes (**1**) which might produce a double bridged olefins.



a, n = 1
b, n = 2
c, n = 3

1

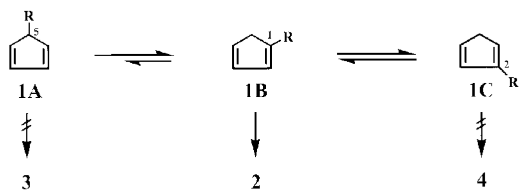
Irradiation[4] of **1** in a DCA-saturated benzene solution at 350 nm produced an adduct **2**. Microwave irradiation[5] of **1** in HMPA solution and conventional heating of HMPA solution of **1** also produced adduct **2** respectively (Eq. (1)).



(1)

Application of ^{13}C-DEPT, H,H-COSY and HETCOR spectral analyses permit the assignment of protons and carbon resonances for **2** (Table 1 for 2a).

It is well established[6] that the 1-, 2- and 5-substituted cyclopentadienes are interrelated by reversible 1,5-hydrogen shift at room temperature. A single adduct derived from 1-substituted isomer was obtained (Eq. (2)).



(2)

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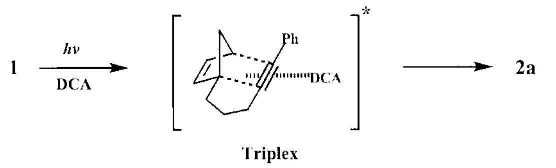
Table 1. Correlation of ^{1}H and ^{13}C resonance of **2a** from HETCOR experiment

^{13}C-NMR δ	Assignment	^{1}H-NMR δ
25.61	C-H_{10}	2.29-2.35 (m, J = 17.2, 7.3, 7.3 Hz, 1H)
		2.56-2.62 (m, J = 17.2, 6.8, 6.8 Hz, 1H)
27.26	C-H_8	1.74-1.95 (m, J = 13.0, 7.6, 7.6 Hz, 1H)
		2.00-2.04 (m, 1H)
29.95	C-H_9	2.05-2.10 (m, 2H)
54.72	C-H_4	4.01 (d, J = 1.5 Hz, 1H)
70.66	q-C_1	
74.70	C-H_7	2.00-2.03 (m, 2H)
124.11		
124.54	C-H_{phenyl}	7.04-7.34 (m, 5H)
127.25		
135.97	q-C_5 or q-C_6	
139.13	q-C_{phenyl}	
140.86	C-H_2	6.54 (d, J = 5.1 Hz, 1H)
145.30	C-H_3	6.80-6.82 (dd, J = 5.1, 3.2 Hz, 1H)
159.02	q-C_5 or q-C_6	

In intramolecular cycloaddition of **1**, the transition states for the adduct **3** from **1A** and **4** from **1C** are less favorable than those for the adduct **2** from **1B**. This unfavorable situation was not overcome by triplex formation (Eq. (3)).



(3)

The low yield of adduct **2c** is presumably due to longer tether length (n=3) which causes diene and dienophile to be further apart.

DCA fluorescence was quenched by cyclopentadiene and phenylacetylene, which correspond to the diene and dienophile respectively in 1. Figure 1 shows the fluorescence of DCA in benzene solution containing increasing concentration of phenylacetylene. Quenching rate obtained by Stern-Volmer technique is 5.6×10^{7} $M^{-1}s^{-1}$. The broad and weak structureless emission with a maximum at 550 nm was assigned to the DCA-phenylacetylene exciplex. However, the exciplex emission of DCA with the compound 1 under any condition was not detected. This result implies that exciplex is formed in the case of **1** but the high concentration of diene quenches the exciplex emission forming the triplex.

Table 2. The product distribution for the reaction of 1 under triplex, MWI, and thermal condition

Reaction condition	Reaction time	Product distribution (%)		
		2a	**2b**	**2c**
DCA (Triplex)	10-20 h	30	0	0
MWI	3-5 min	37	71	8
Thermal	1-2 h	74	66	6

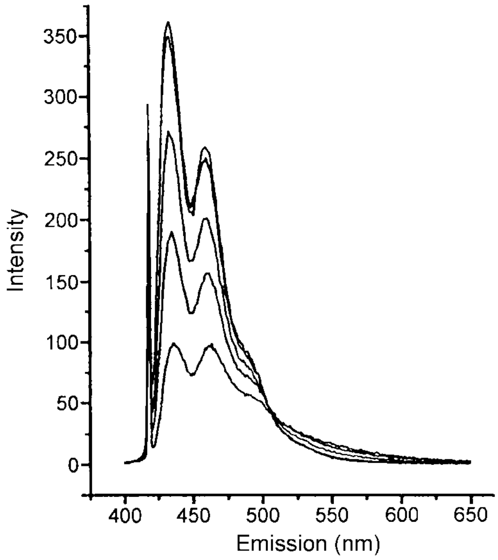


Figure 1. Quenching of DCA fluorescence with phenylacetylene.

Since the triplex Diels-Alder reaction occurs only in non-polar solvents where dissociation of the intermediary exciplex to radical ions is energetically unfavorable, cation radical mechanism for [2+4]adduct was excluded without further study of solvent effects.

In the sensitized irradiation of **1b** and **1c**, the adducts **2b** and **2c** were not obtained probably due to inefficient triplex formation.

Microwave irradiation did not show any non-thermal effect on the reaction, however, the reaction time was decreased to 3-5 min. to obtain maximum yield of products. This short reaction time is ascribed to fast heating upon microwave irradiation as compared to conventional heating system.

In conclusion, DCA-sensitized reaction of **1**, the triplex formation did not overcome longer tether length (**2b** and **2c**) and MWI reaction did not show any non-thermal effect.

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References

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3. (a) Yoon, H. J.; Chae, W. K. *Tetrahedron Lett.* **1997**, *38*, 5169. (b) Lee, S. H.; Yoon, H. J.; Chae, W. K. *J. Photochemistry and Photobiology (A)* **1996**, *93*, 33.
4. A solution of 0.5-1 g of 1 in 200 mL of DCA-saturated benzene was transferred into ten Pyrex tubes and degassed with purified nitrogen. The samples were irradiated with 16-RPR-350 nm lamps for 10-15 hours.
5. A domestic microwave oven which produces 2450 MHz radiation (700W) was used for irradiation.
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7. **1a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.83-1.92 (m, 2H), 2.43-2.50 (m, 2H), 2.57-2.64 (m, 2H), 2.94-3.00 (m, 2H), 6.10-6.47 (m, 3H), 7.28-7.45 (m, 5H); ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 19.54, 28.29, 29.09, 29.34, 30.23, 41.73, 81.35, 90.36, 124.38, 126.91, 127.30, 127.94, 128.60, 131.15, 131.96, 132.87, 134.29, 135.03, 149.20; IR (neat) 3058, 2939, 2900, 2360 cm^{-1}; HRMS Calcd. for $C_{16}H_{16}$: 208.1253 Found 208.1252; Anal. Calcd. for $C_{16}H_{16}$: C, 92.34: H, 7.66. Found C, 91.91: H, 7.94.
1b: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61-1.74 (m, 4H), 2.38-2.45 (m, 4H), 2.88-2.95 (m, 2H), 6.02-6.46 (m, 3H), 7.23-7.40 (m, 5H); ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 19.30, 28.04, 28.45, 28.88, 29.34, 30.21, 41.24, 43.21, 80.70, 80.75, 90.15, 90.22, 124.07, 126.51, 127.47, 128.17, 130.53, 131.54, 132.43, 133.73, 134.68, 146.83, 149.52; IR (neat) 3058, 2936, 2860, 2231 cm^{-1}; HRMS Calcd. for $C_{17}H_{18}$: 222.1409 Found 222.1404; Anal. Calcd. for $C_{17}H_{18}$: C, 91.83: H, 8.17. Found C, 91.91: H, 8.09.
1c: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.50-1.64 (m, 6H), 2.38-2.43 (m, 4H), 2.88-2.95 (m, 2H), 6.01-6.45 (m, 3H), 7.24-7.40 (m, 5H); ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 19.77, 28.78, 29.03, 29.07, 29.64, 30.11, 30.97, 41.61, 43.64, 81.06, 90.69, 90.74, 124.52, 126.26, 126.72, 127.83, 128.55, 130.81, 131.93, 132.83, 134.03, 135.16, 147.52, 150.27; IR (neat) 3058, 3033, 2933, 2858, 2234 cm^{-1}; HRMS Calcd. for $C_{18}H_{20}$: 236.1565 Found 236.1560; Anal. Calcd. for $C_{18}H_{20}$: C, 91.47: H, 8.53. Found C, 91.87: H, 8.13.
2a: ^{1}H NMR and ^{13}C NMR are in Table 1. IR (neat) 3059, 2963, 2929, 2855, 1490, 1442 cm^{-1}. HRMS Calcd. for $C_{16}H_{16}$: 208.1253 Found 208.1250.
2b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43-1.46 (m, 2H), 1.63-1.70 (m, *J* = 13, 13, 5, 3 Hz, 1H), 1.82-1.86 (m, 2H), 1.93-1.94 (dd, *J* = 5.8, 1.6 Hz, 1H), 1.96-1.97 (dd, *J* = 5.8, 1.7 Hz, 1H), 1.96-1.98 (m, 1H), 2.15-2.19 (m, *J* = 13, 5.0, 3.0, 1 Hz, 1H), 2.96-3.01 (m, *J* = 17, 4, 2, 2 Hz, 1H), 3.74-3.76 (m, *J* = 4.5, 1.7, 1.0 Hz, 1H), 6.81-6.82 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.67-6.69 (dd, *J* = 5.0, 0.7 Hz, 1H), 7.14-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 23.91, 24.50, 27.16, 30.17, 52.94, 61.12, 74.30, 125.74, 126.21, 128.19, 137.86, 142.68, 144.37, 145.64, 149.17; IR (neat) 3054, 3018, 2926, 2855, 1493, 1443 cm^{-1}; HRMS Calcd. for $C_{17}H_{18}$: 222.1409 Found 222.1405; Anal. Calcd. for $C_{17}H_{18}$: C, 91.83: H, 8.17. Found C, 91.89: H, 8.11.
2c: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.43-1.50 (m, 1H), 1.50-1.60 (m, 1H), 1.54-1.62 (m, 1H), 1.81-1.85 (m, 3H), 1.85-1.90 (m, 1H), 2.01-2.03 (dd, *J* = 6.1, 4.7 Hz, 2H), 2.10-2.15 (m, 1H), 2.17-2.18 (dd, *J* = 5.7, 1.5 Hz, 1H), 2.62-2.67 (dd, *J* = 14.2, 7.8 Hz, 1H), 3.60-3.61 (m, 1H), 6.58-6.59 (d, *J* = 5.0 Hz, 1H), 6.96-6.98 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.17-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 26.47, 29.25, 29.32, 32.13, 32.74, 53.91, 67.18, 74.01, 125.81, 125.96, 128.11, 137.86, 143.15, 145.51, 147.48, 153.47; IR (neat) 3058, 3018, 2923, 2849, 1449 cm^{-1}; HRMS Calcd. for $C_{18}H_{20}$: 236.1565 Found 236.1563.