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Bridgehead Olefins from Triplex Intramolecular Diels-Alder Reaction of Phenyl-Substituted Dienophiles with Cyclopentadienes

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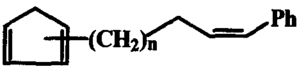
Abstract : Sensitized irradiation of alkenylcyclopentadiene (**1b**, **1c**) with 9,10-dicyanoanthracene (DCA) produced anti-Bredt [2+4] tricyclic adducts (**3b**, **3c**) which were not obtained in thermal condition. These bridgehead olefins were considered as a further support for the existence of a triplex intermediate in DCA-sensitized intramolecular Diels-Alder reaction. © 1997 Elsevier Science Ltd.

Alkenylcyclopentadienes have been used extensively for the formation of Diels-Alder adducts as precursor to natural products.[1] However, intramolecular Diels-Alder reaction involving cyclopentadiene with chain attached C-2 has not been reported up to 1989, even though the corresponding reaction of acyclic diene is known.[2] In 1989, Grubbs[3] *et al.* reported that intramolecular Diels-Alder reaction of α,β-unsaturated ester attached to cyclopentadiene produced a bridgehead olefin as a minor product (6%). Fallis'[4] work on the total synthesis of longifolene via an intramolecular Diels-Alder strategy, the bridgehead olefins were not obtained because of constrained nature of the dienophile. To our knowledge this type of skeletal structure has not been reported since Grubbs' report.

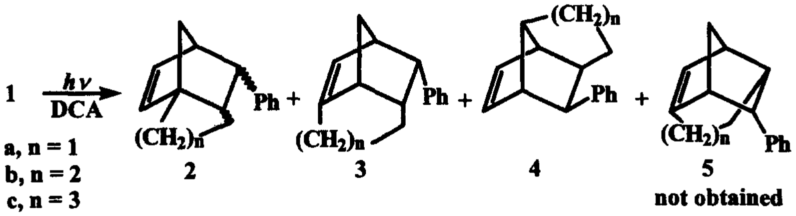
Since Schuster[5] and other workers[6] introduced a triplex intermediate into the discussion of sensitized cycloaddition, the triplex intramolecular Diels-Alder reaction of alkenylcyclopentadienes(**1**) has been studied [7] to compare the photo-adduct with the thermal-adduct and to probe the dependence on tether length between diene and dienophile. In our previous work[7] on the triplex effect on the reaction of **1a** and **1b**, the product distributions were same as those of thermal reaction and adducts which have a bridgehead double bond were not found.



1

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

Sensitized irradiation of **1c** with 9,10-dicyanoanthracene (DCA), however, produced anti-Bredt adduct (**3c**) and this result lead us to reinvestigate the reaction of **1a** and **1b**. Herein we wish to discuss the mechanism for the formation of the bridgehead olefins which further support the triplex formation from **1**. Irradiation[8] of **1c** in a DCA-saturated benzene solution at 350 nm produced [2+4] adduct **2c** (7.5%) and anti-Bredt adduct **3c** (13%) (Scheme 1).



Scheme 1

Irradiation of **1b** in the same reaction condition as **1c** produced **2b** (8%) and bridgehead olefin **3b** (12%) which was not found in our previous work.[7] Irradiation of **1a** produced **4a** (6%) only. The structure of **2** and **3** were analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy.[9] Application of ^{13}C-DEPT, H,H-COSY and HETCOR spectral techniques permit the assignment of the protons and carbon resonances for **2** and **3**. Figure 1 and 2 shows the proton assignments of **2c** and **3b** respectively.

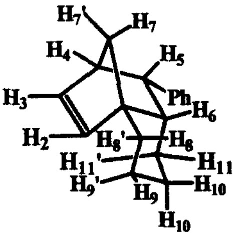


Figure 1. Proton assignments[9] of 2c

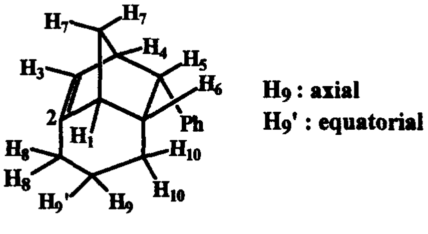
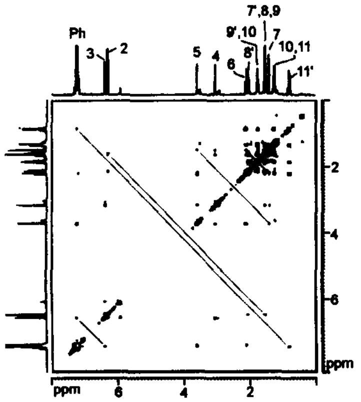


Figure 2. Proton assignments[9] of 3b

Compound **2c** was formed by endo addition due to π-π interaction between diene and phenyl group. This endo approach was confirmed by NOESY spectrum of **2c** (Figure 3). In NOESY spectrum of **2c**, H_7 couples to H_5 and H_6 but not to phenyl hydrogens. H_7' couples to H_2 but not to H_5. Phenyl hydrogens couples to H_3 and H_{11}' (Figure 3). H_{11}'(axial) in **2c** is extremely shielded (0.847 ppm) presumably due to ring-current effect by phenyl group in proximity. H_9(axial) in **3b** is also shielded (0.63 - 0.68 ppm)[9] for the same reason.



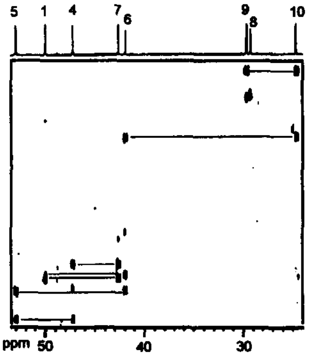


Figure 3. NOESY spectrum of 2c

Figure 4. INADEQUATE spectrum of 3b

Bridgehead olefin **5b** is mechanistically possible, however, this olefin was not obtained in both thermal and photochemical reactions probably due to the restricted geometry imposed by the short tether length. Consideration of COSY and INADEQUATE spectrum of **3b** permits discrimination of **3b** and **5b** (Figure 4).

In INADEQUATE spectrum of **3b**, C-10 is connected to C-6 but not to C-5. Through the structural identification of the products, it was found that there were no *cis-trans* isomerizations of dienophiles during the irradiation.

It is well established[2,4] that the 1-, 2- and 5-alkenylcyclopentadienes are interrelated by reversible 1,5-hydrogen shift at room temperature. In thermal Diels-Alder reaction of **1**, single adducts derived from either the 1- or 5-substituted isomer were obtained (Scheme 2).

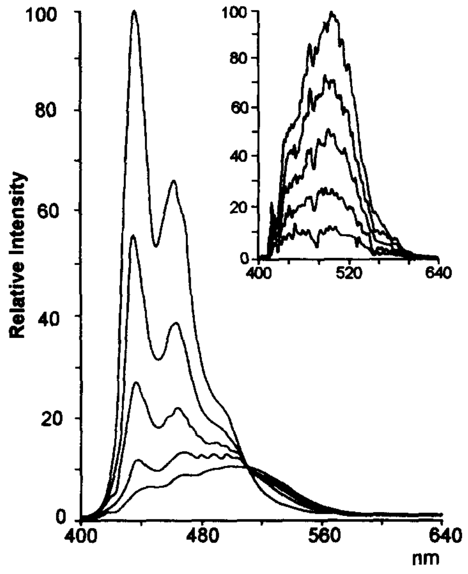
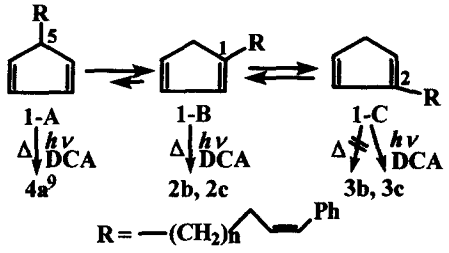
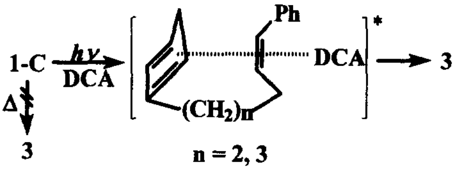


Figure 5. Quenching of DCA fluorescence (Insert : Quenching of exciplex emission)



Scheme 2



Scheme 3

In thermal reaction of **1-C** with short tether length (n=1, 2, 3), the transition states for the adduct **3** are less favorable than those for the adduct **2** from **1-B**. In DCA-sensitized reaction, however, this unfavorable situation for the product 3 (n=2, 3) could be overcome by triplex formation (Scheme 3).

DCA fluorescence was quenched by cyclopentadiene and *trans-β*-methylstyrene, which correspond to the diene and the dienophile respectively in the triene **1**. Figure 5 shows the fluorescence of DCA in benzene solutions containing increasing concentrations of *trans-β*-methylstyrene. Quenching rate obtained by Stern-Volmer technique is $7.7 \times 10^8\ M^{-1}s^{-1}$. The broad, structureless emission with a maximum at 500 nm was assigned to the DCA-*trans-β*-methylstyrene exciplex. This emission at 500 nm was successively quenched by increasing concentrations of cyclopentadiene (Figure 5, insert). Quenching of the exciplex emission by cyclopentadiene might involve a triplex formation. However, no exciplex emission from DCA and the triene **1** was detected under any condition though DCA fluorescence was quenched by triene **1** with a rate of $6 \times 10^9\ M^{-1}s^{-1}$. These results imply that exciplexes are formed in the case of these trienes but that the high concentration of dienes quenches the exciplex emission forming the triplexes.[5f] Since the triplex Diels-Alder reaction occurs only in nonpolar solvents where dissociation of the intermediary exciplex to radical ions is energetically unfavorable,[5f] cation radical mechanism for the formation of [2+4] adducts was excluded without further study of the solvent effects.

In conclusion, DCA-sensitized reaction of the triene **1**, the triplex formation was proposed based upon that the emission of exciplex (dienophile-------DCA) was quenched by cyclopentadiene, and the formation of anti-Bredt adduct was thought to be a further support for the triplex formation.

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8. A solution of 1~2g 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 ~ 20 hours.
9. **1b**, **2b** and **4a**: spectral data and elemental analysis are in reference 7. **2b** is an exo adduct confirmed by NOESY spectrum.
   1c : ^{1}H NMR ($CDCl_3$, 200 MHz) 1.26 ~ 1.62 (4H, m), 2.38 ~ 2.46 (4H, m), 2.94 (2H, dd. J=20 Hz, 1,3 Hz), 5.7 (1H, m), 6.17~6.47 (4H, m), 7.25 ~ 7.58 (5H, m) ; ^{13}C NMR ($CDCl_3$, 200 MHz) 28.417, 29.055, 29.332, 29.637, 30.294, 41.195, 43.183, 125.844, 126.420, 128.076, 128.786, 130.506, 132.047, 132.935, 134.702, 137.723, 147.047, 149.840 (**1c** exists in equilibrium with 2-substituted cyclopentadiene at room temperature) ; IR ($CHCl_3$) 2920, 1600, 1490, 1360 cm-1 ; HRMS (EI+) Calcd. for $C_{17}H_{20}$: 224.1566 found 224.1563.
   2c : ^{1}H NMR ($CDCl_3$, 500 MHz) 0.847 (1H, qd, J = 13 Hz, 3 Hz, H_{11}'), 1.275 ~ 1.300 (1H, m, H_{11}), 1.281 ~1.301 (1H, m, H_{10}), 1.574 ~ 1.593 (1H, m, H_{10}), 1.458 (1H, d, J = 7.8 Hz, H_7), 1.573 ~ 1.593 (1H, m, H_7'), 1.560 ~ 1.593 (1H, m, H_9), 1.796 ~ 1.810 (1H, m, H_9'), 1.573 ~ 1.593 (1H, m, H_8), 2.075 ~ 2.123 (1H, m, H_8'), 3.077 ~ 3.099 (1H, m, H_4), 2.124 ~ 2.150 (1H, m, H_6), 3.634 (1H, dd, J = 10 Hz, 3 Hz, H_5), 6.407 (1H, dd, J = 6 Hz, 3 Hz, H_3), 6.317 (1H, d, J = 5.9 Hz, H_2), 7.183 ~ 7.263 (5H, m) : ^{13}C NMR ($CDCl_3$, 500 MHz) 23.757 (CH_2), 27.322 (CH_2), 28.390 (CH_2), 31.249 (CH_2), 49.268 (CH), 50.383 (CH), 50.663 (CH), 54.914 (C), 56.002 (CH_2), 136.408 (CH), 137.772 (CH), 125.581 (CH), 127.460 (CH), 129.674 (CH), 142.740 (C) : HRMS (EI+) Calcd. for $C_{17}H_{20}$: 224.1566 found 224.1554.
   3b : ^{1}H NMR ($CDCl_3$, 300 MHz) 0.63 ~ 0.68 (1H, m, H_9, axial), 1.18 ~ 1.25 (1H, m, H_{10}), 1.35 ~ 1.40 (1H, m H_{10}), 1.32 ~ 1.33 (2H, m, $2H_7$), 1.45 ~ 1.52 (1H, m, H_9', equatorial), 2.11 ~ 2.17 (1H, m, H_8), 2.23 ~ 2.25 (1H, m, H_8), 2.82 ~ 2.84 (1H, s, H_1), 2.91 ~ 2.92 (1H, m, H_6), 3.30 (1H, broad s, H_4), 3.50 (1H, d, J = 8.79 Hz, H_5), 5.94 (1H, s, H_3), 7.05 ~ 7.38 (5H, m) : ^{13}C NMR ($CDCl_3$, 500 MHz) 24.746 (CH_2), 29.371 (CH_2), 29.740 (CH_2), 42.085 (CH), 42.724 (CH_2), 47.345 (CH), 50.095 (CH), 53.110 (CH), 127.759 (CH), 142.734 (C), 125.125 (CH), 127.640 (CH), 128.825 (CH), 148.898 (C) : HRMS (EI+) Calcd. for $C_{16}H_{18}$: 210.1409 found 210.1394.

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