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Photochemical Intramolecular Diels-Alder Reactions of 1-Substituted Cyclopentadienes by Triplex Formation

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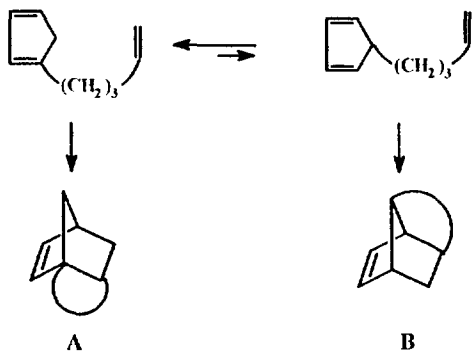
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In recent report, Schuster¹ *et al.* investigated the triplex Diels-Alder reaction to overcome [2+2] dimerization of diene to dienophile. According to Schuster's results, DCA (9,10-dicyanoanthracene)-sensitized irradiation of 5-alkenyl-1,3-cyclohexadiene gives [4+2] adduct without isomerization to 1-alkenyl-1,3-cyclohexadiene prior to cyclization. 1-Substituted cyclopentadienes,² however, differing from 5-alkenylcyclohexadienes, [1,5]-hydrogen transfer is possible prior to cyclization producing two types of tricyclic adduct A and B (Scheme 1).

In this report, we wish to discuss spectroscopic implication of intramolecular triplex and the triplex effect on the product distribution from cyclization of the substituted cyclopentadienes 1 and 2.

1-(1,5-Dimethyl-4-hexenyl)cyclopentadiene (**1**) and 1-(5-Phenyl-*cis*-4-pentenyl)cyclopentadiene (**2**) were synthesized according to the reports by Fallis³ and Wenkert⁴ respectively.

Irradiation of DCA-saturated benzene solution of **1** and **2** at 350 nm give [4+2] adducts **3** and **5** as major products (eq. 1). The structures of **3** and **5** were identified by ¹H and ¹³C NMR spectroscopy.⁵ A consideration of ¹³C DEPT



Scheme 1.

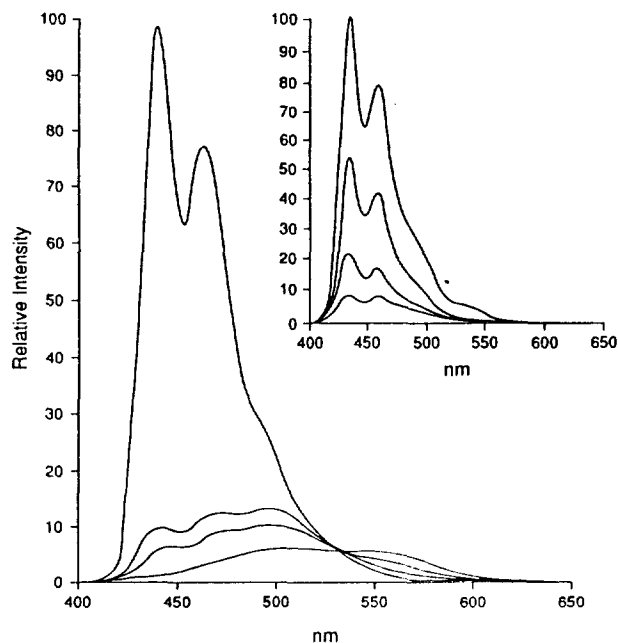
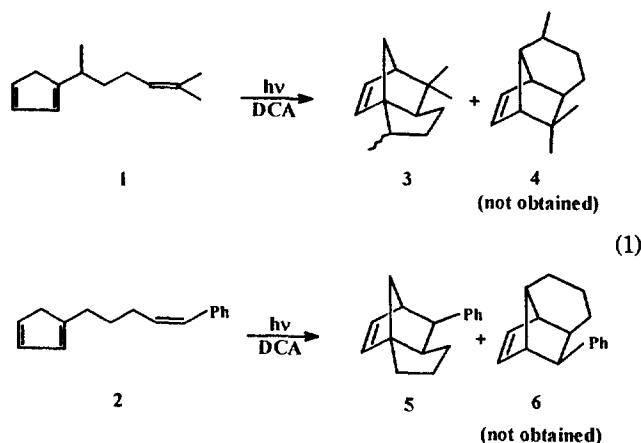


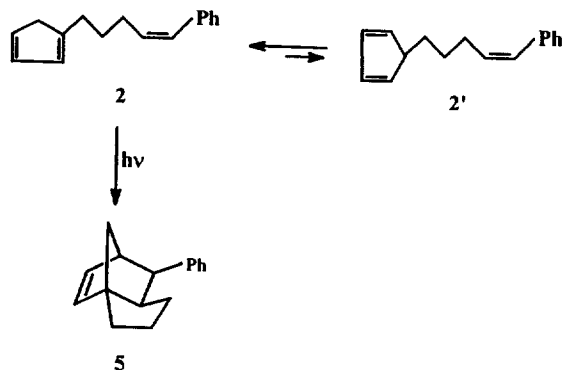
Figure 1. Fluorescence spectra of DCA with increasing concentration of *trans*- β -methylstyrene in benzene. Insert: quenching of the DCA fluorescence with cyclopentadiene.

spectrum of **5** permits discrimination of the compound **5** and **6**. One of the minor products formed in DCA-sensitized reactions of **1** and **2** seems to be [2+2] adduct by comparison with the major product obtained in the benzophenone-sensitized reactions. However, detailed identification procedures of these products were not performed.



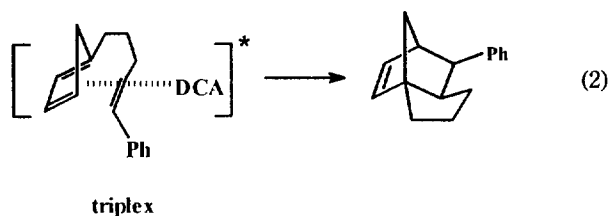
For a spectroscopic implication of the triplex formation, the DCA fluorescence was quenched by *trans*- β -methylstyrene and cyclopentadiene which are parts of the diene and dienophile in compound **2**. Figure 1 shows the fluorescence of DCA in benzene solutions containing increasing concentration of *trans*- β -methylstyrene. The broad, structureless emission with a maximum at 550 nm is assigned to the DCA-*trans*- β -methylstyrene exciplex.

However, the exciplex emission of the trienes **1** and **2** under any conditions were not detected. These results imply that exciplexes are formed in the case of these trienes but the concentration ratio of diene to dienophile is always 1



Scheme 2.

to 1 in these trienes, diene or dienophile might quench the emission of exciplex forming the triplex (eq. 2).



In a thermal intramolecular [2+4] cyclization of 1-alkenylcyclopentadienes, three carbon chain length between diene and dienophile leads specifically to structure of type A (Scheme 1 and eq. 1). On extending the results of thermal [2+4] cyclization to the triene 1 and 2, we hoped that the cycloadduct obtained from the triplex Diels-Alder reaction could be different from the thermal adduct. Our results, however, shows that the triplex condition does not change the product distribution of [2+4] cyclization. Presumably the starting triene 2 exists in equilibrium with 2' in favor of 2, which leads to type A adduct, 5 (Scheme 2).

Since the triplex cyclization of 1 and 2 did not produce the product of type B (Scheme 1), the triplex effect of two carbon chain length between diene and dienophile on [4+2] cyclizations is under investigation.

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- Spectral data for 2: ^1H NMR (200 MHz, CDCl_3) δ 1.6-1.8 (m, 2H), 2.4 (m, 4H), 2.8-2.9 (dd, 2H), 5.8-6.2 (m, 3H), 6.4 (m, 2H), 7.1-7.3 (m, 5H); IR (neat) 3060, 3020, 2930, 1590, 1490, 1440, 1360 cm^{-1} ; MS m/e 210, 181, 167, 144,

130, 115, 91, 77, 65; Anal. Calcd. for $\text{C}_{16}\text{H}_{18}$: C, 91.37; H, 8.63. Found: C, 91.18; H, 8.82.

Spectral data for 5: ^1H NMR (200 MHz, CDCl_3) δ 0.5-0.8 (m, 1H), 1.3-1.5 (m, 2H), 1.65-2.15 (m, 6H), 2.9 (d, 1H), 3.12 (br s, 1H), 6.23 (d, 2H), 7.1-7.3 (m, 5H); ^{13}C NMR (200 MHz, CDCl_3) δ 26.517, 27.092, 28.650, 46.492, 47.773, 49.637, 50.983, 63.118, 125.103, 127.913, 127.932, 137.652, 142.566, 144.379; ^{13}C DEPT δ 26.517 (CH_2), 27.092 (CH_2), 28.650 (CH_2), 49.637 (CH_2), 46.492 (CH), 47.773 (CH), 50.983 (CH), 125.103 (CH), 127.913 (CH), 127.932 (CH), 137.652 (CH), 142.566 (CH), 63.118 (C), 144.379 (C); IR (neat) 3050, 3010, 2950, 2850, 1600, 1490, 1450 cm^{-1} ; MS m/e 210, 181, 167, 149, 130, 119, 91, 65, 39; Anal. Calcd. for $\text{C}_{16}\text{H}_{18}$: C, 91.37; H, 8.63. Found: C, 91.18; H, 8.66. Spectral data for 3: reference No. 3.

Syntheses and Spectroscopic Characterization of Octabromotetrakis(2,6-difluorophenyl)-21-thiaporphyrin and Tetrabromotetrakis(2,6-difluorophenyl)-21,23-dithiaporphyrin

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Non-planar porphyrin compounds are of current interest, because conformational distortion influences electronic and redox properties of the porphyrin ligand in a protein. Domed and ruffled porphyrin conformation has been observed in the X-ray crystal structure of nickel-containing cofactor F430, bacterochlorophylls, chlorins and many other hemoproteins.¹ Porphyrin model compounds with distorted structures have been recently synthesized and their structures are determined by X-ray and NMR spectroscopic techniques.^{2,3} The peripherally crowded porphyrin such as octaphenyl-, octaalkyl-, tetracycloalkenyl-substituted meso-tetraphenylporphyrin are severely nonplanar.⁴⁻⁶ Also β -pyrrole bromination of tetraphenylporphyrin (TPP), tetrakis(2,6-dichlorophenyl)porphyrin, tetrastemylporphyrin and tetrakis(pentafluorophenyl)porphyrin causes severe distortion of the porphyrin to a saddle shape.⁷ ^1H NMR study confirms that the conformational distortion is maintained in solution.³ Herein we report syntheses and spectroscopic characterization of β -carbon brominated compounds of tetrakis(2,6-difluorophenyl)-21-thiaporphyrin (F_8STPP) and tetrakis(2,6-difluorophenyl)-21,23-dithiaporphyrin ($\text{F}_8\text{S}_2\text{TPP}$).

Halogenated thia- and dithiaporphyrin derivatives were synthesized as shown in Scheme 1. Reaction of dithiophene and 2,6-difluorobenzaldehyde in THF solution produced 2,5-bis[(2,6-difluorophenyl)hydroxymethyl]thiophene (BDHT).⁸ Condensation of BDHT with 2 mol of 2,6-difluorobenzaldehyde and 3 mol of pyrrole in the presence of $\text{BF}_3 \cdot \text{OEt}_2$, followed by oxidation with *p*-chloranil gives a mixture