ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 93 (1996) 33–37

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

The triplex intramolecular Diels–Alder reaction of phenyl-substituted alkenes with cyclopentadienes

Seung Heui Lee, Hyo Jung Yoon, Woo Ki Chae *

Department of Chemistry Education, Seoul National University, Kwanak-Ku, Shilim-Dong, Seoul 151-742, South Korea

Received 3 April 1995; accepted 22 June 1995

Abstract

The triplex intramolecular Diels–Alder reaction of cyclopentadienes and styrene-like dienophiles that are linked with an alkyl chain was investigated. Sensitized irradiation of alkenylcyclopentadiene with 9,10-dicyanoanthracene leads to a [4+2] adduct without [1,5]-hydrogen shift when the linking chain contains three carbon atoms. If the linking chain contains only two carbon atoms, [1,5]-hydrogen shift occurs prior to cyclization, leading to the formation of a less strained [4+2] adduct.

Keywords: Triplex; Exciplex; Intramolecular Diels–Alder reaction; DCA-sensitizer

1. Introduction

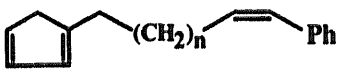
In a recent report on triplex Diels–Alder reactions, Schuster et al. [1] described cyclization reactions of 5-alkenyl-1,3-cyclohexadienes in benzene containing a catalytic amount of 9,10-dicyanoanthracene (DCA).

According to their results, DCA-sensitized irradiation of 5-alkenyl-1,3-cyclohexadienes gives [4+2] adducts without isomerization to 1-alkenyl-1,3-cyclohexadienes prior to intramolecular cyclization. The triplex mechanism was suggested for the cyclization reactions on the basis of no detection of exciplex emission from 5-alkenyl-1,3-cyclohexadiene and DCA.

Thermal intramolecular [4+2] cyclizations of 1-alkenylcyclopentadienes, however, differing from 5-alkenylcyclohexadienes, give two types of tricyclic adducts, A or B, depending on the methylene chain length between the diene and the dienophile [2–5].

A carbon chain length of three ($n=2$) [6] or four ($n=3$) leads specifically to structures of type A, whereas a chain length of two ($n=1$) [7] gives exclusively the tricyclic structure of type B (Scheme 1).

Herein we report a detailed spectroscopic investigation of intramolecular triplex formation and the triplex effect on structures of type A or B from photochemical Diels–Alder reactions of 1-alkenylcyclopentadienes (**1**).



1

a, n=1
b, n=2

2. Experimental details

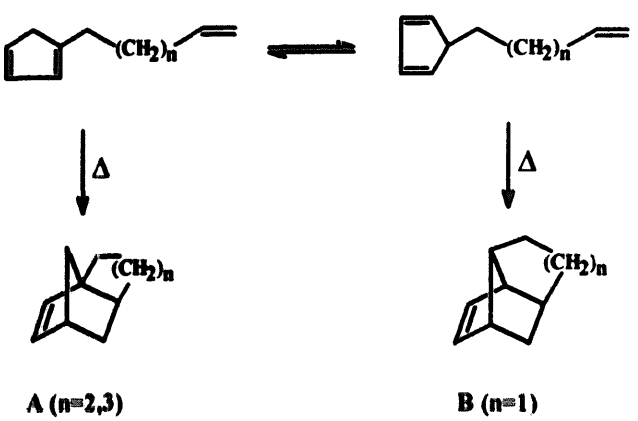
2.1. Materials and general methods

All solvents were freshly distilled and dried before use according to standard procedures. Benzene was shaken with cold concentrated sulphuric acid until the acid layer was colourless and then distilled from sodium. DCA was obtained from Eastman Kodak and used without further purification. All other reagents were used as received unless otherwise specified.

Absorption spectra were measured on a Shimadzu UV-2600 spectrometer. Fluorescence spectra were recorded using a Perkin–Elmer LS-50 spectrofluorometer at an excitation wavelength of 418 nm. Gas chromatography–mass spectrom-

* Corresponding author.

SSDI 1010-6030(95)04143-5



A (n=2,3) B (n=1)

Scheme 1.

etry (GC–MS) measurements were made on a Hewlett–Packard 5980 II gas chromatograph with a Hewlett–Packard 5988 mass spectrometer (EI 70 eV) using an HP-1 (11 m), SPB-5 (30 m) or Ultra-2 (50 m) capillary column. Elemental analysis was performed using a Carlo Erba 1108 instrument. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-80, Varian VXR 200S or Bruker AMX 500 spectrometer and are referenced to tetramethylsilane (TMS). IR spectra were recorded on a Jasco IR-810 instrument.

Photolyses were carried out in Pyrex cells with a Rayonet photoreactor equipped with 16 RPR 350 nm broad band lamps.

2.2. *Synthesis of 1-alkenylcyclopentadienes (1)*

2.2.1. *4-Phenyl-(Z)-3-buten-1-ol(3a) and 5-phenyl-(Z)-4-penten-1-ol (3b)*

The procedure of Wenkert et al. [8] was employed for the reaction of 2,3-dihydrofuran (**2a**) and phenylmagnesium bromide without modification. Starting with 14.7 g (0.21 mol) of 2,3-dihydrofuran (**2a**), 10.78 g (0.016 mol) of bis(triphenylphosphine)nickel dichloride ($(tpp)_2NiCl_2$) and 0.2 mol of phenylmagnesium bromide in 300 ml of benzene, 15.0 g (0.12 mol, 60%) of the alcohol **3a** was obtained. ^1H NMR (80 MHz, $CDCl_3$): δ 1.9 (br s, 1H), 2.58 (dq, 2H), 3.70 (t, 2H), 5.68 (dt, 1H), 6.54 (dt, 1H), 7.2–7.4 (m, 5H). IR (neat): 3330, 1610, 1430 cm^{-1}. These spectral data are the same as those of Wenkert et al.

This procedure was repeated with 21.0 g (0.25 mol) of 3,4-dihydropyran (**2b**) to obtain 28.7 g (0.18 mol, 72%) of the alcohol **3b**. ^1H NMR (200 MHz, $CDCl_3$): δ 1.5–1.9 (m, 2H), 2.2–2.5 (m, 2H), 3.5 (t, 2H), 3.6 (br s, 1H), 5.5–5.7 (m, 1H), 6.37 (d, 1H), 7.0–7.4 (m, 5H). IR (neat): 3330, 1610, 1505, 1460 cm^{-1}. These spectral data are the same as those of Wenkert et al.

2.2.2. *1-(4-Phenyl-cis-3-butenyl)cyclopentadiene (1a) and 1-(5-phenyl-cis-4-pentenyl)cyclopentadiene (1b) [9]*

p-Toluenesulphonylchloride (13.8 g, 0.07 mol) was added in small increments to a cold solution (ice bath) of the alcohol **3a** (8.0 g, 0.053 mol) in pyridine and stirring was continued for 24 h at 5 °C.

The white reaction mixture was transferred to a separatory funnel, ice-cold 40% aqueous hydrochloric acid was added and the aqueous layer was extracted with diethyl ether. The combined extracts were washed with water and brine successively and dried over magnesium sulphate. The solvent was removed under reduced pressure to give the tosylate of **3a** as a clean, light yellow oil (8.9 g, 64%).

A 2 M tetrahydrofuran (THF) solution of sodium cyclopentadienylide (13 ml, 0.026 mol) in a three-necked flask was cooled in an ice bath and then 4.0 g (0.013 mol) of the tosylate of **3a** in dry THF was added dropwise. After the addition had been completed, the mixture was allowed to warm to room temperature and stirring was continued for 4 h.

The resulting light brown mixture was transferred to a separatory funnel and extracted with diethyl ether. The combined extracts were washed with brine and dried over magnesium sulphate. The solvent was removed to afford an oil which was purified by silica gel chromatography to obtain 1-(4-phenyl-*cis*-3-butenyl)cyclopentadiene (**1a**) (1.4 g, 60%) and 5-(4-phenyl-*cis*-3-butenyl)cyclopentadiene in trace. The spectral data, especially ^{13}C NMR, show that the compound **1a** exists in equilibrium with 5-(4-phenyl-*cis*-3-butenyl)cyclopentadiene in favour of **1a** at room temperature. ^1H NMR (200 MHz, $CDCl_3$): δ 2.5–2.6 (m, 4H), 2.8–2.9 (dd, 2H), 5.6–6.5 (m, 5H), 7.2–7.3 (s, 5H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 21.466, 22.215, 23.726, 24.506, 34.866, 36.841, 119.904, 120.120, 120.157, 120.605, 121.736, 121.747, 122.266, 122.375, 122.885, 122.959, 124.234, 125.850, 125.878, 126.054, 127.303, 128.262, 131.273, 131.309, 139.914, 142.158. IR (neat): 3050, 3000, 2900, 1618, 1510, 1380 cm^{-1}. GC–MS: *m/e* 196, 165, 152, 117, 91, 79, 51. Anal. Calc. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.72; H, 8.28.

The above procedure was repeated with 24 g (0.036 mol) of the tosylate of **3b** and 0.1 mol of sodium cyclopentadienylide to obtain 14 g (88%) of 1-(5-phenyl-*cis*-4-pentenyl)cyclopentadiene (**1b**) and 5-(5-phenyl-*cis*-4-pentenyl)cyclopentadiene in trace. The spectral data, especially ^{13}C NMR, show that the compound **1b** exists in equilibrium with 5-(5-phenyl-*cis*-4-pentenyl)cyclopentadiene in favour of **1b** at room temperature. ^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). ^{13}C NMR (500 MHz, $CDCl_3$): δ 28.676, 28.776, 29.505, 29.826, 30.398, 30.690, 41.615, 43.644, 126.499, 126.826, 126.857, 126.954, 128.468, 128.499, 129.138, 129.259, 129.536, 129.584, 130.824, 132.838, 132.981, 133.066, 134.029, 135.078, 138.126, 138.155, 147.134, 149.750. IR (neat): 3060, 3020, 2930, 1590, 1490, 1440, 1360 cm^{-1}. GC–MS: *m/e* 210, 181,

167, 144, 130, 115, 91, 77, 65. Anal. Calc. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.18; H, 8.82.

2.3. General procedures for preparation of authentic tricylic compounds (4b, 5a) [6]

Purified tri-*n*-butylamine (3–4 ml) was added to a three-necked flask under nitrogen and the flask was placed in a silicone oil bath maintained at 200 °C. A solution of the triene **1a** or **1b** (2–3 mmol) in tri-*n*-butylamine was added dropwise to the hot solvent with stirring over a period of 1 h. The cooled solution was poured into ice-cold aqueous hydrochloric acid and extracted with diethyl ether. The combined ether extracts were washed with cold, dilute hydrochloric acid and dried over magnesium sulphate. The solvent was removed and the residual yellow oil was chromatographed on silica gel with *n*-hexane to afford the tricyclic compounds **4b** and **5a**.

6-Phenyltricyclo[5.2.1.$0^{1,5}$]dec-8-ene (**4b**). ^{1}H 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. IR (neat): 3050, 3010, 2950, 2850, 1600, 1490, 1450 cm^{-1}. GC–MS: *m/e* 210, 181, 167, 149, 130, 119, 91, 65, 39. Anal. Calc. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.18; H, 8.66.

2-Phenyltricyclo[4.3.0.$0^{3,7}$]non-4-ene (**5a**). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.1–1.6 (m, 4H), 2.15 (s, 1H), 2.35 (s, 1H), 2.75 (d, 1H), 2.8 (s, 1H), 2.97 (s, 1H), 5.95 (m, 1H), 6.35 (m, 1H), 7.1–7.4 (m, 5H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 21.165, 29.257, 38.964, 47.323, 49.180, 54.846, 62.817, 125.204, 127.776, 128.043, 129.766, 139.860, 143.015. IR (neat): 3060, 3030, 2950, 2870, 1720, 1680, 1600, 1495, 1460, 1450 cm^{-1}. GC–MS: *m/e* 196, 165, 152, 130, 115, 91, 77, 51.

2.4. Photochemistry of 1-alkenylcyclopentadienes (1)

2.4.1. DCA-sensitized irradiation of 1-(4-phenyl-cis-3-butenyl)cyclopentadiene (1a)

A solution of 530 mg of **1a** in 60 ml of DCA-saturated benzene was transferred into five Pyrex tubes and degassed with nitrogen. The samples were irradiated with 16 RPR 350 nm lamps for 42 h. The solvent was then evaporated in vacuo to give a pale yellow liquid. Silica gel chromatography gave 20 mg (5.7%) of **5a**, 180 mg of recovered **1a** and some isomeric products in trace. The spectral data are the same as those for authentic [4+2] adduct. ^{13}C DEPT (200 MHz, $CDCl_3$) of **5a**: δ21.165 (CH_2), 29.257 (CH_2), 38.964 (CH), 47.323 (CH), 49.180 (CH), 54.846 (CH), 62.817 (CH), 125.204 (CH), 127.776 (CH), 128.043 (CH), 129.766 (CH), 139.860 (CH), 143.015 (C).

2.4.2. DCA-sensitized irradiation of 1-(5-phenyl-cis-4-pentenyl)cyclopentadiene (1b)

A solution of 230 mg of **1b** in 23 ml of DCA-saturated benzene was transferred into two Pyrex tubes and purged with nitrogen. The samples were irradiated with 16 RPR 350 nm lamps for 5 h. The solvent was then evaporated in vacuo to give a pale yellow liquid. Silica gel chromatography gave 43 mg (27%) of **4b**, 68 mg of recovered **1b** and other isomeric products in trace. The spectral data are the same as those for authentic [4+2] adduct. ^{13}C DEPT (200 MHz, $CDCl_3$) of **4b**: 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).

2.4.3. Quenching experiments

For quenching of the DCA fluorescence, the concentration of DCA in benzene solutions containing varying amounts of *trans*-β-methylstyrene was maintained constant (2.1×10^{-6} M). The fluorescence quenching of DCA with *trans*-β-methylstyrene was measured by excitation at 418 nm while monitoring the intensity of emission at 435 nm. The maximum quencher concentration was 2 M.

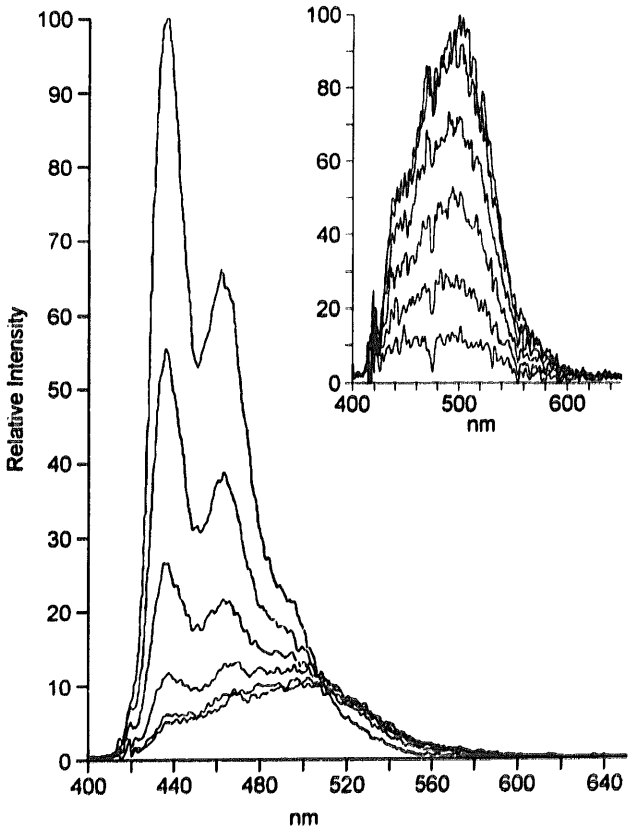


Fig. 1. Fluorescence spectra of benzene solutions of DCA with increasing concentrations of *trans*-β-methylstyrene. Inset: quenching of exciplex emission by cyclopentadiene.

The exciplex (DCA–*trans*-β-methylstyrene) emission was quenched with increasing amounts of cyclopentadiene and the maximum quencher concentration was 2 M (see Fig. 1, inset).

3. Results and discussion

3.1. Preparation of 1-alkenylcyclopentadienes (1)

The route for the preparation of **1a** (1-(4-phenyl-*cis*-3-butenyl)cyclopentadiene) and **1b** (1-(5-phenyl-*cis*-4-pentenyl)cyclopentadiene) is shown in Scheme 2.

In the ring-opening reactions of dihydrofuran (**2a**) and dihydropyran (**2b**), the catalyst $(tpp)_2NiCl_2$ plays an important role [8] in the synthesis of the (*Z*)-alcohols **3**.

These alcohols were treated with tosyl chloride, and cyclopentadiene derivatives were obtained from the reaction of the tosylate with cyclopentadienyl anion in THF [9].

3.2. Photochemistry of cyclopentadiene derivatives (1)

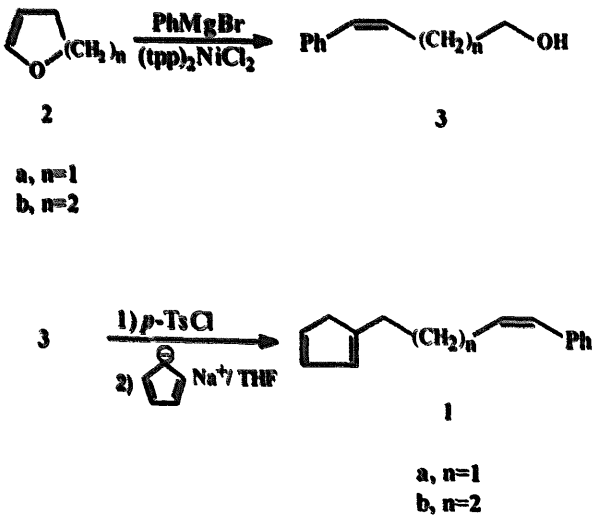
Irradiation of a DCA-saturated benzene solution of **1a** at 350 nm gives a [4+2] adduct and a trace amount of other products which were shown by GC–MS to be isomeric with the starting material (Eq. (1)).

(1)

1a **4a** **5a**

not obtained

The major adduct from the DCA-sensitized photoreaction is formed exclusively when **1a** is heated in tri-*n*-butylamine at 200 °C. The products from both thermal and photosensitized reactions were isolated by column chromatography and



2 **3**

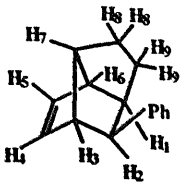
a, n=1
b, n=2

1

a, n=1
b, n=2

Scheme 2.

Table 1
Correlation of ^1H and ^{13}C resonances of **5a** from HETCOR experiment



5a

^{13}C NMR δ	Assignment	^1H NMR δ
21.165, 29.257	$C-H_8$, $C-H_9$	1.1–1.6 (m, 4H)
38.964	$C-H_1$	2.15 (s, 1H)
62.817	$C-H_7$	2.35 (s, 1H)
49.180	$C-H_2$	2.75 (s, 1H)
54.846	$C-H_6$	2.80 (s, 1H)
47.323	$C-H_1$	2.97 (d, 1H)
129.766	$C-H_5$	5.95 (q, 1H)
139.860	$C-H_4$	6.35 (q, 1H)
125.204, 127.776, 128.043, 143.015	$C-H_{phenyl}$	7.1–7.4 (m, 5H)

shown to be the intramolecular [4+2] cycloaddition product **5a** by various spectral methods.

The structure of **5a** was analyzed by ^1H and ^{13}C NMR spectroscopy. Application of COSY and HETCOR (Table 1) spectral techniques permits the assignment of the proton and carbon resonances for the compound **5a**. In particular, consideration of its ^{13}C DEPT spectrum permits discrimination of the compounds **4a** and **5a**.

One of the minor products formed in the DCA-sensitized reaction of **1a** seems to be a [2+2] adduct by comparison with the major product obtained in the benzophenone-sensitized reaction, since the cyclization products from the benzophenone-sensitized irradiation are known to be [2+2] adducts. However, detailed identification procedures for these minor products were not performed.

The pentenyl-substituted cyclopentadiene **1b** was irradiated to probe the significance of the chain length between the diene and the dienophile in the intramolecular triplex Diels–Alder reaction.

Irradiation of **1b** in a benzene solution containing DCA sensitizer gives a [4+2] cycloadduct and a trace amount of several isomeric compounds. One of the products was identified as the tricyclic [4+2] adduct **4b** by comparison of its NMR spectrum with that of the cycloadduct formed in the thermal intramolecular Diels–Alder reaction of **1b** (Eq. (2)).

(2)

1b **4b** **5b**

not obtained

The result that the tricyclic compound **5b** is not obtained from DCA-sensitized irradiation of **1b** indicates that [1,5]-hydrogen transfer does not occur prior to intramolecular cyclization.

3.3. Quenching of sensitizer and exciplex emission

Both the diene and the dienophile are usually effective quenchers of cyanorene excited singlet states. For a detailed spectroscopic investigation of triplex formation, the DCA fluorescence was quenched by cyclopentadiene and *trans*-β-methylstyrene, which correspond to the diene and dienophile parts respectively in the triene **1**. Fig. 1 shows the fluorescence of DCA in benzene solutions containing increasing concentrations of *trans*-β-methylstyrene. The broad, structureless emission with a maximum at 500 nm is assigned to the DCA–*trans*-β-methylstyrene exciplex.

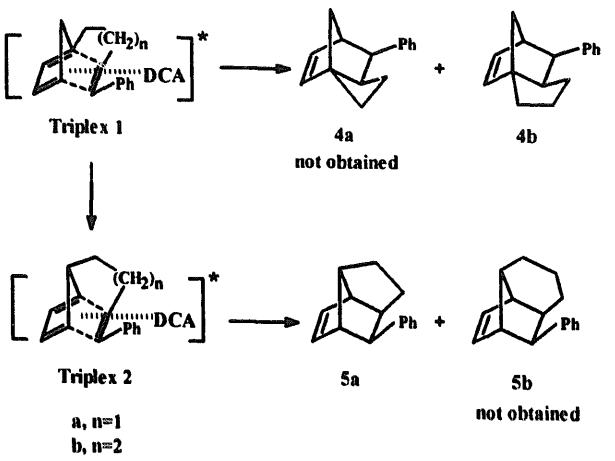
The exciplex formed from DCA and the dienophile can be shown to react with the diene, because the intensity of emission from the DCA–*trans*-β-methylstyrene exciplex is reduced as the concentration of cyclopentadiene is increased (Fig. 1, inset). Capture of the exciplex by the cyclopentadiene must involve a triplex with an unsymmetrical (acceptor–donor–donor) structure [10–13].

However, no exciplex emission from the trienes **1a** and **1b** was detected under any condition. This result might imply that exciplexes are formed in the case of these trienes but that the high local concentration of dienes quenches the exciplex emission, forming the triplexes [1].

3.4. Triplex effect on product of type A or B depending on carbon chain length

The application of the thermal intramolecular Diels–Alder reaction to alkenyl-1,3-cyclopentadienes has been reported previously [2–7]. A related synthesis and carbon chain length application were reported by Snowden [2] and Brieger and Anderson [7].

By extending their results to the trienes **1**, we hoped that the cycloadduct obtained from the triplex Diels–Alder reaction would be different from the adduct produced in the thermal reaction. Our results, however, show that the triplex condition did not change the chain length effect on the [4+2] product distribution. Presumably the triplex **1a** isomerizes to the triplex **2a** prior to cyclization to give the less strained



Scheme 3.

adduct **5a** instead of **4a**. In contrast, the triplex **1b** produces **4b** without isomerization to the triplex **2b**, since the product **4b** is much less strained than **4a** (Scheme 3).

Acknowledgements

This work was financially supported in part by the Korea Science and Engineering Foundation (911-0302-022-2) and the Basic Science Research Institute Program (1993).

References

[1] G.B. Schuster, I. Wölfle and S. Chan, *J. Org. Chem., 56* (1991) 7313.
[2] R.L. Snowden, *Tetrahedron Lett., 22* (1981) 97.
[3] D.W. Landry, *Tetrahedron, 39* (1983) 2761.
[4] G. Brieger and J.N. Bennett, *Chem. Rev., 80* (1980) 63.
[5] O. Wallquist, M. Rey and A.S. Dreiding, *Helv. Chim. Acta, 66* (1983) 1891.
[6] E.J. Corey and R.S. Glass, *J. Am. Chem. Soc., 89* (1967) 2600.
[7] G. Brieger and D.R. Anderson, *J. Org. Chem., 36* (1971) 243.
[8] E. Wenkert, E.L. Michelotti, C.S. Swindell and M. Tingoli, *J. Org. Chem., 49* (1984) 4894.
[9] E.G. Breitholle and A.G. Fallis, *J. Org. Chem., 43* (1978) 1964.
[10] N. Akbulut, D. Hartsough, J. Kim and G.B. Schuster, *J. Org. Chem., 54* (1989) 2549.
[11] G.C. Calhoun and G.B. Schuster, *J. Am. Chem. Soc., 108* (1986) 8021.
[12] M. Itoh, N. Takita and M. Matsumoto, *J. Am. Chem. Soc., 101* (1979) 7363.
[13] R.A. Caldwell, D. Creed and H. Ohta, *J. Am. Chem. Soc., 97* (1975) 3246.