Chem. Pharm. Bull. 37(6) 1452—1457 (1989)   Vol. 37, No. 6

Studies on Synthesis of 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene Derivatives. IV.[1] Photoreactions of 5-Substituted-5*H*-dibenzo[*a*,*d*]cycloheptenes with 1,2-Substituted Olefins and the Stereostructures of the Cycloaddition Products

Yasuhiro FUJIWARA,* Motoshige SUMINO, Akira NOZAKI and Masao OKAMOTO*

Kyoto Pharmaceutical University, Misasagi-Nakauchi-cho 5, Yamashina-ku, Kyoto 607, Japan. *Received October 7, 1988*

The photoreactions of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (1a) and its 5-substituted derivatives (1z and 1y) with olefins such as maleates, acrylates and crotonate gave the cycloaddition products (3a—e) in yields of 4—82%. Inversion reactions of the adducts (3b and 3c) with bases were carried out for the purpose of investigating the thermodynamic stability of the cycloadducts and the corresponding isomeric products (3b-*t* and 3c-*t*) were obtained.

The stereostructures of the cycloaddition products and the isomeric products were determined by means of nuclear magnetic resonance (NMR) spectroscopy.

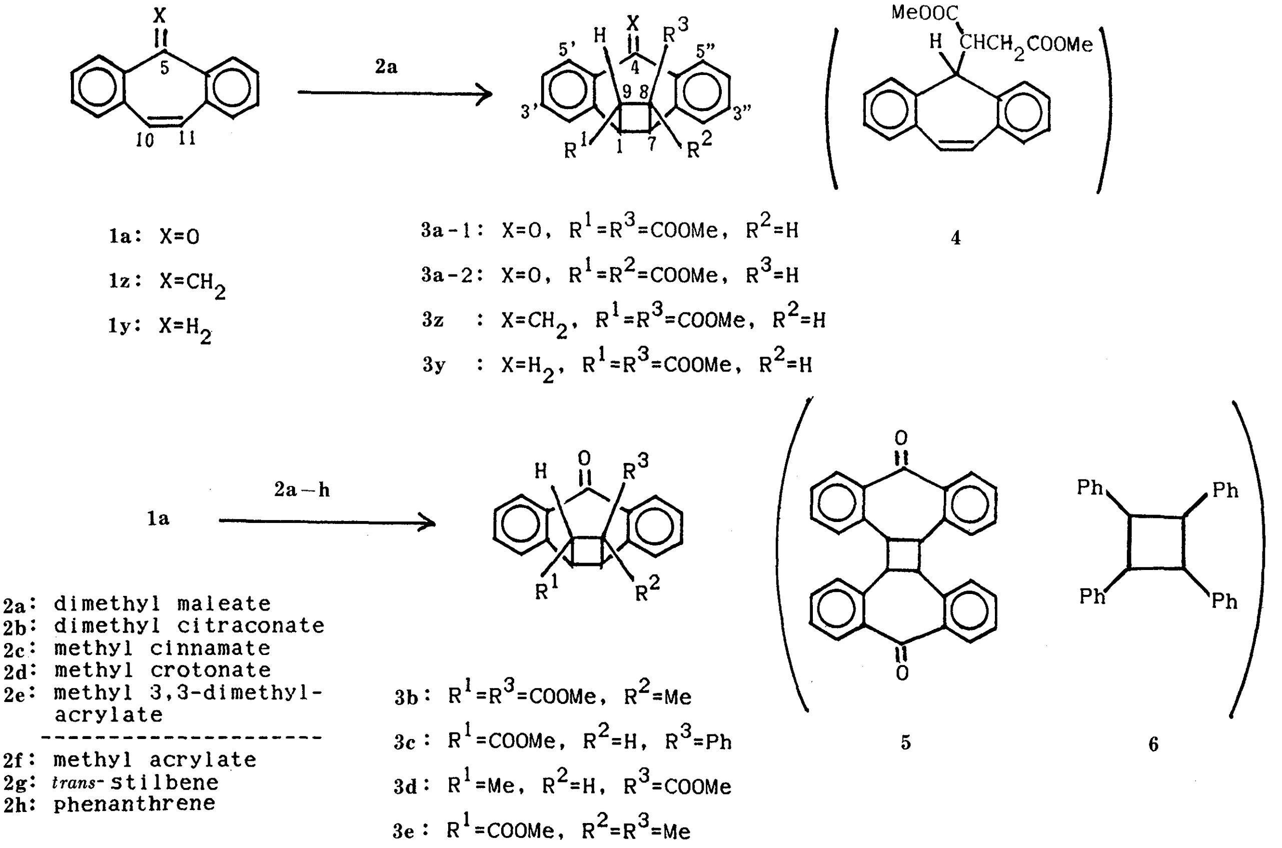
Keywords dibenzobicyclo[5.2.0]nonane derivative; [2+2]photocycloaddition; stereochemistry; two-dimensional NMR; ^1H-^1H NOE; substituent effect

[2+2]Photocycloaddition of phenanthrene[2] or various aromatic nitriles[3] with olefins has been investigated in detail. However, only a few papers have been published on the photocycloaddition of dibenzo[*a*,*d*]cycloheptene derivatives with various olefins.[1,4,5] In preceding papers[1,4] the authors have reported that the photoreaction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**1a**) with dimethyl maleate or dimethyl fumarate gave only the *cis*-cycloadducts, while the reaction with maleic anhydride resulted in the selective formation of the *trans*-cycloadduct.[1,5] In view of the high yield and high stereoselectivity in the former reaction, we undertook to apply the same reaction to substrates having partially analogous structures and olefins.

The present paper deals with photocycloaddition reactions of (a) 5-substituted 5*H*-dibenzo[*a*,*d*]cycloheptenes (**1a**,[4] **1z**, and **1y**) with dimethyl maleate and (b) **1a** with various olefins (**2b**—**h**), inversion reactions of photocycloadducts (**3b** and **3c**) and also the stereochemistry of the adducts (**3b**—**e** and **3b**—**c**-*t*).

The procedure and conditions of photocycloadditon reaction in the preceding paper[4] were applied in the present study. The scheme of the reactions is shown in Chart 1.

The photoreaction of **1a**, **1z**,[6] or **1y**[7] with dimethyl maleate (**2a**) gave the corresponding cycloaddition product (**3a**,[4] **3z**, or **3y**) in 82, 23 or 11% yield, respectively. The yields are the ratio (%) to the initially applied **1**. The other



1a: X=O
1z: X=CH_2
1y: X=H_2

3a-1: X=O, R^1=R^3=COOMe, R^2=H
3a-2: X=O, R^1=R^2=COOMe, R^3=H
3z : X=CH_2, R^1=R^3=COOMe, R^2=H
3y : X=H_2, R^1=R^3=COOMe, R^2=H

2a: dimethyl maleate
2b: dimethyl citraconate
2c: methyl cinnamate
2d: methyl crotonate
2e: methyl 3,3-dimethyl-acrylate
2f: methyl acrylate
2g: *trans*-stilbene
2h: phenanthrene

3b: R^1=R^3=COOMe, R^2=Me
3c: R^1=COOMe, R^2=H, R^3=Ph
3d: R^1=Me, R^2=H, R^3=COOMe
3e: R^1=COOMe, R^2=R^3=Me

Chart 1

component of the reaction mixture in the reaction of **1z** with **2a** was unchanged **1z**, and no *exo*-methylene cycloadduct was obtained. The reaction of **1y** with **2a** gave the cycloadduct (**3y**) and the 5-(1,2-bis(methoxycarbonyl))ethyl adduct (**4**), and when the reaction was not carried under a nitrogen atmosphere, **4** was obtained as the only isolable product (yield, 47%).

TABLE I. Reaction Time and Yield of 5*H*-Dibenzo[*a*,*d*]cycloheptenes with Olefins

Starting material	Reagent	Reaction time (h)	Products	Isolated yield (%)
1a[a)]	**2a**[a)]	25	**3a**-1, **3a**-2	75, 7[a)]
1z	**2a**	154	**3z**	23
1y	**2a**	160	**3y**, **4**	11, 23
1a	**2b**	41	**3b**	73
1a	**2c**	24	**3c**	73
1a	**2d**	70	**3d**, **5**	9, 1
1a	**2e**	68	**3e**, **5**	4, 26
1a	**2f**	25	Polymer	—
1a	**2g**	48	**6**	—[b)]
1a	**2h**	48	**5**	61

a) See reference 4. *b*) See experimental section.

The photoreactions of **1a** with various olefins (**2b**—**e**) gave the cycloaddition products (**3b**, **3c**, **3d**, and **3e**) in 73—4% yields (Table I), but in the case of the reactions with **2f**—**h**, only polymers of **2f**, the cyclodimer (**5**)[8)] of **1a** (with **2h**) or the cyclodimer (**6**)[9)] of **2g** were formed. Products in the reaction case (b), other than the compounds shown in Table I, were mainly starting **1a**, and no oxetane derivatives were formed. The reaction time and yield are given in Table I, and physical and spectral data of the photoadducts are summarized in Table II.

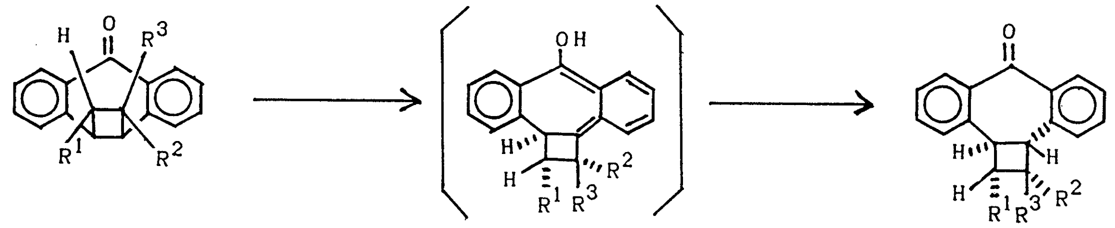
In order to examine the thermodynamic stability of the cycloadducts, reaction of the products (**3b** and **3c**) with base was undertaken. Thus, treatments of **3b** and **3c** with sodium hydride (NaH) or potassium hydroxide (KOH) gave the stereoisomeric products **3b**-*t* (23%) and **3c**-*t* (43%) as main products, respectively. In both cases, no starting materials were remained (Chart 2).

The stereostructures of the photocycloadducts and their isomers were determined by proton nuclear magnetic res-

TABLE II. Physical and Spectral Data for Photoreaction Products (**3z**, **3y**, **3b**—**e**, and **4**) and Their Derivatives (**3b**-*t* and **3c**-*t*)

Compd. No.	mp (°C) (Recryst. solvent)	IR (KBr) cm^{-1} ROCO	IR (KBr) cm^{-1} CO	Formula	Analysis (%) Calcd C	Analysis (%) Calcd H	Analysis (%) Found C	Analysis (%) Found H	MS
3z	115—116 (*n*-Hexane)	1730, 1750		$C_{22}H_{20}O_4$	348.1326[a)]		348.1352		204,[b)] 229, 228, 348 (M$^+$)
3y	142.5—143.5 (EtOH)	1720, 1730		$C_{21}H_{20}O_4$	74.98	5.99	74.84	5.94	192,[b)] 217, 276, 336 (M$^+$)
4	100—101 (EtOH)	1735		$C_{21}H_{20}O_4$	336.1362[a)]		336.1336		191,[b)] 336 (M$^+$)
3b	146—148 (Benzene–*n*-hexane)	1735	1660	$C_{22}H_{20}O_5$	72.51	5.53	72.35	5.26	206,[b)] 305, 364 (M$^+$)
3b-*t*	161—162 (EtOH)	1730	1640	$C_{22}H_{20}O_5$	72.51	5.53	72.49	5.61	193,[b)] 254, 304, 364 (M$^+$)
3c	228.5 (Et_2O)	1730	1655	$C_{25}H_{20}O_3$	81.50	5.47	81.78	5.23	206,[b)] 245, 304, 364, 368 (M$^+$)
3c-*t*	118—119 (EtOH)	1730	1635	$C_{25}H_{20}O_3$	81.50	5.47	81.27	5.68	193,[b)] 206, 231, 308, 368 (M$^+$)
3d	164—165.5 (Et_2O)	1720, 1730	1650	$C_{20}H_{18}O_3$	78.41	5.92	78.52	6.00	206,[b)] 246, 306 (M$^+$)
3e	179—183 ($CHCl_3$)[c)]	1735	1655	$C_{21}H_{20}O_3$	320.1412[a)]		320.1445		206,[b)] 305, 320 (M$^+$)

a) High-resolution MS, M$^+$ (*m*/*z*). *b*) Base peak. *c*) Treatment solvent.

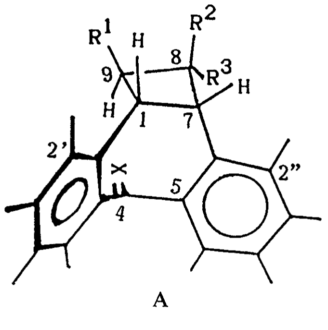


3b: $R^1=R^3=COOMe$, $R^2=Me$

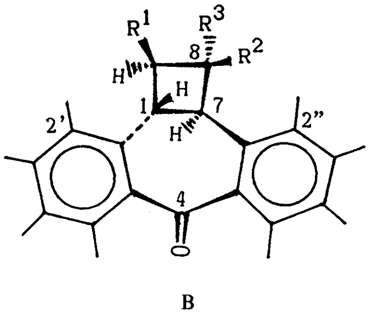
3c: $R^1=COOMe$, $R^2=H$, $R^3=Ph$

3b-*t*: $R^1=R^3=COOMe$, $R^2=Me$

3c-*t*: $R^1=COOMe$, $R^2=H$, $R^3=Ph$



A



B

Chart 2

TABLE III. Assigned ^{1}H Signals for Photocycloadducts (**3z**, **3y**, and **3b**—**e**) and Their Derivatives (**3b**-*t* and **3c**-t) in $CDCl_3$

Compd. No.	Chemical shift[a] (δ)								
	H(2′)	H(2″)	H(1)	H(7)	H(8)	H(9)	$COOC\underline{H}_3$(8)	$COOC\underline{H}_3$(9)	Other H
3z	7.14	6.99	4.03	4.24	3.80	4.62	3.23	3.63	5.52 (= <H) 5.60 (= <H)
3y	7.11	6.97	4.18	4.36	3.99	4.38	3.27	3.71	3.59 (H(4) ex[b]) 4.89 (H(4) en[b])
3b	7.33	7.07	4.405	3.93		4.18	3.15	3.63	1.63 ($C\underline{H}_3$(8))
3b-*t*	7.165	7.315	4.12	3.825		4.025	3.76	3.86	1.40 ($C\underline{H}_3$(8))
3c	7.32	6.58	4.26	4.47	4.23	3.855		3.54	6.82 (Ph$\underline{H}$(2,5))
3c-*t*	7.37	7.195	3.90	3.90	4.14	3.47		3.81	7.39 (Ph$\underline{H}$(2,5))
3c-*t*[c]	7.45	7.22	3.84	3.94	4.08	3.55		3.77	7.53 (Ph$\underline{H}$(2,5))
3d	7.16	7.06	3.38	4.43	3.21	3.12	3.205		1.07 ($C\underline{H}_3$(9))
3e	7.32	7.01	4.435	3.71		3.07		3.62	0.62 ($C\underline{H}_3$(8) en[b]) 1.35 ($C\underline{H}_3$(8) ex[b])

Numbering of the proton-bearing carbons is shown in Chart 1. *a*) Given in ppm relative to internal TMS, ±0.001 ppm. *b*) en, *endo*; ex, *exo*. *c*) In acetone-d_6.

onance (^{1}H-NMR) spectroscopy (correlation spectroscopy (COSY) for long-range coupling detection[10]) and ^{1}H–^{1}H nuclear Overhauser effect (NOE)[11]). That is, assignments of H(2′), H(2″) on benzene rings and H(1), H(7) in cyclobutane derivatives were undertaken by detection of the long-range couplings (≤1.0 Hz) between H(1) and H(2′) and between H(7) and H(2″), since a similar approach was used for analogous compounds in the previous reports.[1,4]) Since the long-range couplings (≤1.0 Hz) between H(1) and H(2′) and between H(7) and H(2″) for the newly obtained cycloadducts were clearly observed in the COSY and/or ^{1}H–{^{1}H} NMR spectra (not shown), the assignments of H(2′), H(2″), H(1), and H(7) were confirmed. Assignments of the other protons in the benzene and cyclobutane rings were obtained from ^{1}H–^{1}H coupling networks by ordinary COSY and/or ^{1}H–{^{1}H) NMR experiments.

In this way, ^{1}H assignments of all the cyclobutane derivatives were straightforwardly obtained and the assigned protons relevant to stereochemical analyses are shown in Table III.

To obtain information concerning the configuration and the conformation of these cyclobutane derivatives in solution, ^{1}H–^{1}H NOE[11]) experiments were carried out. The intensity (%) of NOEs between protons of the cycloadducts is given in Table IV.

As shown in Table IV, since large NOEs between the methyl resonance (δ 1.63) and H(1), and between the methyl resonance and H(7) in **3b** were observed, the methyl group, H(1), and H(7) on the cyclobutane ring can be considered to take *cis* configuration with respect to each other, and since irradiation at the resonances due to H(1) and H(7) produced large NOEs for H(2′) and H(2″) in the benzene rings, respectively, the distances between H(1) and H(2′) and between H(7) and H(2″) can be considered to be very short. Moreover, the methyl signal of *endo*-methoxycarbonyl[4]) attached to C(8) was observed at δ 3.15. The connectivity between C(8) and $COOCH_3$ (8) was established by low-power irradiation at both methoxy methyl (δ 3.15) and methyl (δ 1.63) resonances in ^{13}C–{^{1}H} NMR experiments, that is, the carbon signal ($\underline{C}OO$– (8)) was effectively decoupled by each of the irradiations. On the other hand, the methyl group at C(8) on the cyclobutane ring of **3b**-*t* can be considered to take a *cis* re-

TABLE IV. ^{1}H–^{1}H NOE Values of the Photocycloadducts (**3z**, **3y**, and **3b**—**e**) and Their Derivatives (**3b**-*t* and **3c**-*t*) in $CDCl_3$ at 25 °C

Compd. No.	Irradiated[a]	Observed (%)[b]
3z	H(7)	H(2″) (21.0), H(8) (20.0), H(1) (9.0)
	H(1)	H(2′) (18.0), H(7) (10.0), H(8) (2.1)
	H(8)	H(7) (9.0), H(1) (3.4)
3y	H(2″)	H(7) (19.0)
	H(4)en[c]	H(4)ex[c] (30.0), H(9) (28.0)
	H(9,7)	H(2″) (17.0), H(4)en[c] (13.5), H(8) (21.0), H(1) (11.0)
	H(1)	H(2′) (20.0)
	H(4)ex[c]	H(4)en[c] (29.0)
3b	H(1)	H(2′) (21.0), H(7) (12.0)
	H(7)	H(2″) (22.0), H(1) (10.0)
	CH_3(8)	H(7) (11.5), H(1) (8.5), H(9) (3.5)
3b-*t*	H(2′)	H(9) (17.0)
	H(7)	H(9) (6.6)
	H(9)	H(2′) (14.0), H(7) (10.0)
	CH_3(8)	H(2″) (21.0), H(1) (25.0), H(9) (4.5)
3c	H(9)	PhH(2,5) (13.0)
	H(1,8)	H(2′) (19.0), H(7) (16.0), PhH(2,5) (7.8)
	H(7)	H(2″) (19.0), H(1,8) (8.9)[d]
	PhH(2,5)	H(9) (29.0), H(8) (11.0)
	H(2′)	H(1) (15.0)
	H(2″)	H(7) (15.0)
3c-*t*	H(9)	H(2′)+PhH(2,5) (7.7),[f] H(7) (14.0), H(8) (3.5)
	H(1,7)	H(8) (12.5), H(9) (12.0), PhH(2,5) (6.9)
	H(8)	H(1) (18.0), H(2″) (11.5), PhH(2,5) (4.2), H(9) (2.5)
	H(2″)	H(8) (13.5), H(7) (3.0)
3c-*t*[e]	H(9)	H(2′) (15.0), H(7) (7.8), H(8) (3.0), PhH(2,5) (3.8)
	H(1)	H(8) (8.6), H(2′) (2.2)
	H(7)	H(9) (12.0), H(2″) (6.7), PhH(2,5) (5.8)
	H(8)	H(2″) (10.0), H(1) (10.0), PhH(2,5) (5.8), H(9) (4.5)
	H(2″)	H(8) (13.0)
3d	H(7)	H(2″) (21.0), H(8) (14.5), H(1) (10.0)
	H(1)	H(2′) (22.0), H(8) (16.0), H(7) (11.5)
	CH_3(9)	H(9) (25.0), H(8) (13.0), H(1) (7.5), H(7) (−5.6)[g]
3e	H(1)	H(2′) (20.0), H(7) (9.5), H(9) (3.3)
	H(7)	H(2″) (16.0), H(8) (6.3)
	CH_3(8)en[c]	H(9) (26.0), H(2″) (4.6)
	CH_3(8)ex[c]	H(7) (11.0), H(1) (10.0)

a) Decoupling power ($\gamma H_2/2\pi$): 2.8—4.0 Hz. *b*) Ratio of the intensity of a signal to that of the irradiated large-negative one in the difference spectra. *c*) en, *endo*; ex, *exo*. *d*) Average value of NOE enhancement of H(1) and H(8). *e*) In acetone-d_6. *f*) Average value of NOE enhancement of PhH(2,5) and H(2′). *g*) See reference 12.

lationship with respect to H(1) and also to be spatially very close to H(2′′), since irradiation at the resonance (δ 1.40) due to the methyl protons produced large NOEs for both H(1) and H(2′′). Moreover, based on the NOEs between H(9) (δ 4.025) and H(2′) and between H(9) and H(7), H(9) can be considered to be spatially close to H(2′) and also to take *cis* configuration with respect to H(7), which resides in a 1,3-relationship with respect to H(9).

Taking into consideration stereomodels based on the NOE results, the configuration and conformation should be A form for **3b** and B form for **3b**-*t* as shown in Chart 2. Similarly, based on the NOE results in Table IV, the other photocycloadducts (**3c**—**e**, **3z**, and **3y**) were concluded to take A form, and **3c**-*t* to take B form.

The mass spectra (MS) of all the cycloadducts (**3z**, **3y**, or **3b**—**e**) showed a fragment ion peak (*m/z* 204, 192, or 206) of the molecule (**1**) as the base peak (not shown, see Table II).

From the experimental results mentioned above, the characteristic features of the photoreactions may be summarized as follows:

(1) In the reactions of case (a): The yield of the reaction of **1a** with dimethyl maleate[4)] even at a short reaction time is very much higher than those in the reactions of **1z** and **1y**.

(2) In the reactions of case (b): Reactivity of the olefins (**2a**—**h**) with **1a** for cycloadduct formation is higher in the cases of 1,2-bis(methoxycarbonyl)- (**2a** and **2b**) and 1-methoxycarbonyl-2-phenyl (**2c**) olefins than in the case of methylated monomethoxycarbonyl olefins (**2d**—**e**), and no photocycloadducts of **1a** with the other olefins (**2f**—**h**) are obtained.

(3) Each of the photocycloadducts (**3z**, **3y** and **3a**—**e**) takes *cis* configuration at the ring juncture between the seven- and four-membered rings.

(4) Isomerizations of **3b** and **3c** with bases give the *trans* isomers at the ring juncture (**3b**-*t* and **3c**-*t*).

(5) The MS data including the previous data[4)] indicate that the ion peak resulting from loss of the olefin by retro-photoreaction-type cleavage is the base peak in all the photocycloaddition products. On the other hand, the ion peak resulting from loss of the olefin and CH fragments or loss of the substituent(s) on the cyclobutane ring is the base peak in the isomerized compounds.

A possible interpretation of the characteristics (1), (2) and (3) is as follows. The stereoselectivity and the yields in the cycloadduct formations (**1a** with **2a**,[4)] **2b** or **2c**) are very similar to those reported by Farid *et al.*[2,13)] and Caldwell *et al.*[3a)] These similarities would suggest that the photocycloadditions in the present case took place *via* a similar reaction route involving intermediates in an excited state, so called exciplexes,[2b,3a,14)] to give the sterically hindered 1 : 1 cycloadducts. The experimental data showed that the cycloadducts were formed effectively in high yield when a carbonyl group was present in **1** and a 1,2-bis(dimethoxycarbonyl) or 1-methoxycarbonyl-2-phenyl group in **2**. Therefore, it appears that the substituents of

TABLE V. ^{13}C-NMR Chemical Shifts of the Cyclobutane Derivatives in $CDCl_3$

Carbon$^{a)}$	Compounds							
	3z	**3y**	**3b**	**3b**-*t*	**3c**	**3c**-*t*	**3d**	**3e**
1	43.06	42.80	39.58	41.45	43.18	45.75$^{b)}$	48.61	39.66
2(1′)	134.73$^{c)}$	136.65$^{c)}$	136.89	139.69$^{c)}$	136.97$^{c)}$	142.91$^{c)}$	137.98	137.57$^{c)}$
3(6′)	140.51$^{c)}$	138.57$^{c)}$	141.87	140.50$^{c)}$	142.07$^{c)}$	137.34	142.00	141.82$^{c)}$
4	151.47	40.91	199.83	194.95	200.79	192.70	200.05	201.15
$=CH_2$	119.59							
5(6′′)	142.58$^{c)}$	139.62$^{c)}$	140.04	136.87$^{c)}$	139.53$^{c)}$	137.66$^{c)}$	139.72	139.79$^{c)}$
6(1′′)	133.75	135.42$^{c)}$	135.53	140.29$^{c)}$	136.54$^{c)}$	143.17$^{c)}$	136.28	138.42$^{c)}$
7	45.29	43.14	55.11	49.36	50.99	47.46$^{b)}$	47.49	54.13
8	45.62	44.62	51.78	49.43	48.18	46.12	50.44	43.13
CO	170.32$^{c)}$	171.85	171.62$^{c)}$	174.85$^{c)}$			170.59	
OCH_3	51.24	51.50	51.82	52.08			51.21	
CH_3 en$^{d)}$								25.41
CH_3 ex$^{d)}$			19.84					25.59
Ph-C					127.66$^{e)}$	126.93$^{f,b)}$		
					127.93$^{f)}$	127.29$^{g)}$		
					126.68$^{g)}$	128.82$^{e,b)}$		
					136.41$^{h,c)}$	140.78$^{h)}$		
9	43.63	43.38	49.92	45.46	49.64	49.40	41.80	55.68
CO	173.74	174.15	171.47$^{c)}$	170.64$^{c)}$	173.06	173.79		172.15
OCH_3	51.86	52.10	51.63	52.85	51.88	52.29		51.43
CH_3							19.10	
2′	129.39	130.46	130.29	122.52	129.95	124.64	129.63	130.16
3′	127.81$^{i)}$	126.53$^{i)}$	131.87	132.09	131.76	132.90	131.47	131.82
4′	127.64$^{i)}$	127.62$^{j)}$	127.75$^{i)}$	127.03	127.99	126.99	127.29$^{i)}$	127.56
5′	128.61	129.22	128.84	130.65	128.65	132.19	128.88	128.49
2′′	129.90	132.16	132.04	127.36	132.37	124.23	131.89	131.71
3′′	127.92$^{i)}$	126.86$^{i)}$	131.98	132.64	132.17	132.78	132.05	132.26
4′′	127.64$^{i)}$	127.85$^{j)}$	127.96$^{i)}$	127.17	126.72	126.99	127.61$^{i)}$	127.07
5′′	129.34	129.50	129.21	132.30	129.44	132.07	129.52	129.46

Chemical shifts are given in ppm relative to internal $^{13}\underline{C}H_3Si(CH_3)_3$, ±0.015 ppm. Assignments of protonated carbons were made from CH COSY spectra together with consideration of ^1H–^1H coupling networks. *a*) Numbering is shown in Chart 1. *b*) Assignments were confirmed by comparing with the assigned ^{13}C shifts with the same NMR techniques in acetone-d_6 solutions. *c*) Assignments were confirmed by ^{13}C–$\{^1H\}$ NMR experiments. *d*) en, *endo*; ex, *exo*. *e*) PhC(2,6). *f*) PhC(3,5). *g*) PhC(4). *h*) PhC(1). *i,j*) Assignments may be interchanged.

both **1** and **2** in the cycloaddition reaction play important roles for stabilization of the intermediate in the exited state.

The unexpected formation of **4** is very interesting, but we do not yet have enough experimental data to propose a reaction process.

In conclusion, the reactions of **1a** with **2b**—**c** gave photocycloadducts in high isolated yields. Isomerization of each adduct (**3b**—**c**) gave the corresponding isomeric adduct (**3b**-*t* and **3c**-*t*). Based on the NOE data, the stereostructures were shown to be *cis* at the ring juncture between the seven- and four-membered rings for the photocycloadducts (**3b**—**e**) and *trans* for the isomerized products (**3b**—**c**-*t*). The configuration of the other substituents on the cyclobutane ring and the conformations were also established (Charts 1 and 2).

Experimental

All melting points were measured with a Yanagimoto hot-stage apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu IR-420 spectrophotometer. MS were obtained on a Hitachi M-80 mass spectrometer with a direct inlet system operating at an ionization energy of 20 eV. Elementary analyses were carried out with a Yanagimoto microdetermining apparatus. For preparative thin-layer chromatography (PTLC), silica gel (Merck, Kieselgel 60PF$_{254}$) was used as an adsorbent.

All the ^{13}C (75.4 MHz)- and ^{1}H (300.0 MHz) NMR spectra were obtained on a Varian XL-300 spectrometer using a 5 mm broad-band probe and operating in a pulse Fourier transform mode with quadrature detection. The software used to obtain two-dimensional NMR spectra was from Varian Instruments, version 6.1D. All spectra were recorded for chloroform-d_1 ($CDCl_3$) and acetone-d_6 solutions which contained 10—30 mg of samples in 0.6 ml of solvent, which included tetramethylsilane (TMS) as an internal reference.

The ^{1}H–^{1}H NOE experiments were performed by a method described elsewhere.4) The COSY experiments for long-range coupling determination were performed using the reported pulse sequence.10) The delay used for long-range coupling detection was 0.18—0.3 s. The spectra were processed by using a pseudo-echo function15) as a weighting function. ^{1}H–^{1}H Coupling networks of the cyclobutane derivatives were conformed by ^{1}H–{^{1}H} NMR and/or ordinary COSY16) experiments. The correlation between ^{1}H and ^{13}C in NMR spectrometry of cyclobutane derivatives was determined by CH COSY experiments.4,16) Some of the quaternary carbon in the derivatives were assigned by low-power selective ^{13}C–{^{1}H} NMR4) experiments. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

A General Method for Photoreaction of 5*H*-Dibenzo[*a*,*d*]cycloheptenes with Olefins A solution of substrate (1 mmol) and an excess amount of olefin (7—15 mmol) in dioxane (5.1 ml) was externally irradiated with a 100 watt high-pressure Hg lamp under N_2 in a quartz or Pyrex vessel for the time indicated in Table I. After removal of the solvent, excess olefin and the other components by distillation *in vacuo*, the residue was purified by the method described later. The physical and spectral data of the products are summarized in Table II and the ^{13}C- and ^{1}H-NMR data of the cyclobutane derivatives are given in Tables V and VI.

3z: Purified by PTLC on silica gel with chloroform ($CHCl_3$) as the eluent and recrystallized from the solvent listed in Table II to give **3z** as pale yellow prisms.

3y and **4**: Isolated by PTLC on silica gel with $CHCl_3$ as the eluent and each purified by recrystallization from the solvent listed in Table II.

4: ^{1}H-NMR ($CDCl_3$) δ: 1.95 (1H, dd, J=16.9, 3.8 Hz, H(5-(2)), 2.62 (1H, dd, J=16.9, 11.0 Hz, H(5-(2)), 3.21 (3H, s, $\mathrm{OC\underline{H}_3}$)(5-(1)), 3.50 (3H, s, $\mathrm{OC\underline{H}_3}$(5-(2)), 3.55 (1H, ddd, J=11.5, 11.0, 3.8 Hz, H(5-(1)), 4.06 (1H, d,

TABLE VI. ^{1}H-NMR Spectral Data for Photocycloadducts (**3z**, **3y**, and **3b**—**e**) and Their Derivatives (**3b**-*t* and **3c**-*t*) in $CDCl_3$

Compd.	Chemical shift$^{a)}$ (δ), coupling constant (J, Hz$^{b)}$), and assignment
3z	3.23 (3H, s, OMe(8)), 3.80 (3H, s, OMe(9)), 3.80 (1H, t-like, J=10.2, 9.8, H(8)), 4.03 (1H, dd, J=10.7, 9.8, H(1)), 4.24 (1H, t-like, d, J=9.8, 9.8, 0.8, H(7)), 4.62 (1H, t-like, d, J=10.7, 10.2, 0.8, H(9)), 5.52 (1H, d, J=1.7, =CH(4)), 5.60 (1H, d, J=1.7, =CH(4)), 6.99 (1H, m, H(2′′)), 7.14 (1H, m, H(2′)), 7.16—7.23 (4H, m, H(3′,3′′,4′,4′′)), 7.26 (1H, m, H(5′)), 7.34 (1H, m, H(5′′))
3y	3.27 (3H, s, OMe(8)), 3.59 (1H, d, J=15.0, H(4)*exo*), 3.71 (3H, s, OMe(9)), 3.99 (1H, dd, J=11.2, 8.7, H(8)), 4.18 (1H, t-like, J=10.5, 9.9, H(1)), 4.36 (1H, t-like, J=11.2, 10.5, H(7)), 4.38 (1H, t-like, J=9.9, 8.7, H(9)), 4.89 (1H, d, J=15.0, H(4)*endo*), 6.97 (1H, m, H(2′′)), 7.06—7.15 (4H, m, H(3′,3′′,4′,4′′)), 7.11 (1H, m, H(2′)), 7.17 (1H, m, H(5′)), 7.20 (1H, m, H(5′′))
3b	1.63 (3H, s, Me(8)), 3.15 (3H, s, OMe(8)), 3.63 (3H, s, OMe(9)), 3.92 (1H, ddd, J=9.8, 0.9, 0.6, H(7)), 4.18 (1H, dd, J=11.4, 0.9, H(9)), 4.41 (1H, dd, J=11.4, 9.8, H(1)), 7.07 (1H, ddd, J=7.5, 1.4, 0.6, H(2′′)), 7.32 (1H, t-like, d, J=7.5, 7.5, 1.5, H(4′)), 7.32 (1H, t-like, d, J=7.5, 7.7, 1.6, H(4′′)), 7.33 (1H, dm, J=7.5, H(2′)), 7.42 (2H, t-like, d, J=7.5, 7.5, 1.5, H(3′,3′′)), 7.56 (1H, dd, J=7.5, 1.5, H(5′)), 7.72 (1H, dd, J=7.7, 1.6, H(5′′))
3b-*t*	1.40 (3H, s, Me(8)), 3.76 (3H, s, OMe(8)), 3.82 (1H, ddd, J=11.6, 0.9, 1.1, H(7)), 3.86 (3H, s, OMe(9)), 4.025 (1H, d, J=10.4, H(9)), 4.12 (1H, t-like, dd, J=11.6, 10.4, 0.9, 0.8, H(1)), 7.16 (1H, ddd, J=7.5, 1.3, 0.8, H(2′)), 7.31 (1H, ddd, J=7.5, 1.3, 1.1, H(2′′)), 7.32 (1H, t-like, m, J=7.5, 7.8, H(4′)), 7.39 (2H, t-like, m, J=7.5, 8.0, H(4′′)), 7.48 (1H, t-like, d, J=7.5, 7.5, 1.3, H(3′)), 7.51 (1H, t-like, d, J=7.5, 7.5, 1.5, H(3′′)), 7.56 (1H, dd, J=7.8, 1.3, H(5′)), 8.305 (1H, dd, J=8.0, 1.5, H(5′′))
3c	3.54 (3H, s, OMe(9)), 3.86 (1H, t-like, d, J=10.9, 10.7, 0.7, H(9)), 4.23 (1H, dd, J=10.9, 8.8, H(8)), 4.26 (1H, dd, J=10.7, 8.8, H(1)), 4.47 (1H, t-like, J=8.8, 8.8, H(7)), 6.58 (1H, dd, J=7.4, 1.7, H(2′′)), 6.83 (2H, dm, J=7.7, PhH(2,6)), 7.02 (1H, m, PhH(4)), 7.03 (2H, m, PhH(3,5)), 7.05 (1H, t-like, d, J=7.4, 7.4, 2.0, H(3′′)), 7.09 (1H, t-like, d, J=7.4, 7.3, 1.7, H(4′′)), 7.32 (1H, ddm, J=7.4, 1.3, H(2′)), 7.33 (1H, t-like, d, J=7.4, 7.4, 1.5, H(4′)), 7.43 (1H, t-like, d, J=7.4, 7.4, 1.6, H(3′)), 7.58 (1H, dd, J=7.5, 1.6, H(5′)), 7.71 (1H, dd, J=7.3, 2.0, H(5′′))
3c-*t*	3.47 (1H, m, H(9)), 3.81 (3H, s, OMe(9)), 3.90 (2H, m, H(1,7)), 4.14 (1H, m, H(8)), 7.195 (1H, dddm, J=7.4, 1.5, 0.9, H(2′′)), 7.28 (1H, m, PhH(4)), 7.32—7.41 (6H, m, PhH(2,3,5,6), H(4′,4′′)), 7.37 (1H, dm, J=7.4, H(2′), 7.455 (1H, t-like, d, J=7.5, 7.4, 1.5, H(3′′)), 7.53 (1H, t-like, d, J=7.4, 7.4, 1.4, H(3′)), 8.18 (1H, dd, J=7.7, 1.5, H(5′′)), 8.23 (1H, dd, J=7.5, 1.4, H(5′))
3c-*t*$^{c)}$	3.55 (1H, t-like, J=9.4, 9.3, H(9)), 3.77 (3H, s, OMe(9)), 3.84 (1H, t-, t-like, J=10.9, 9.3, 1.0, 1.0, H(1)), 3.945 (1H, t-, t-like, J=10.9, 9.7, 1.0, 1.0, H(7)), 4.08 (1H, t-like, J=9.7, 9.4, H(8)), 7.205 (1H, d, t-like, J=7.5, 1.5, 1.0, H(2′′)), 7.28 (1H, t-like, m, J=7.2, 7.2, PhH(4)), 7.38 (2H, t-like, m, J=7.2, 7.6, PhH(2,5)), 7.38 (1H, m, H(4′′)), 7.41 (1H, t-like, m, J=7.9, 7.5, H(4′)), 7.45 (1H, d, t-like, J=7.5, 1.5, 1.0, H(2′)), 7.52 (1H, t-like, d, J=7.5, 7.5, 1.5, H(3′′)), 7.53 (2H, dm, J=7.6, PhH(2,6)), 7.59 (1H, t-like, d, J=7.5, 7.5, 1.5, H(3′)), 8.10 (1H, dd, J=7.9, 1.5, H(5′′)), 8.16 (1H, dd, J=7.9, 1.5, H(5′))
3d	1.07 (3H, d, J=6.0, Me(9)), 3.12 (1H, ddq, J=10.8, 10.0, 6.0, H(9)), 3.205 (3H, s, OMe(8)), 3.21 (1H, t-like, J=10.0, 9.1, H(8)), 3.38 (1H, dd, J=10.8, 8.7, H(1)), 4.43 (1H, t-like, d, J=9.1, 8.7, 0.7, H(7)), 7.06 (1H, ddd, J=7.6, 1.5, 0.7, H(2′′)), 7.16 (1H, dd, J=7.4, 1.5, H(2′)), 7.30 (1H, t-like, d, J=7.5, 7.4, H(4′)), 7.30 (1H, t-like, d, J=7.5, 7.7, 1.5, H(4′′)), 7.39 (1H, t-like, d, J=7.4, 7.5, 1.5, H(3′)), 7.41 (1H, t-like, d, J=7.5, 7.6, 1.6, H(3′′)), 7.53 (1H, dd, J=7.5, 1.5, H(5′)), 7.77 (1H, dd, J=7.7, 1.6, H(5′′))
3e	0.62 (3H, s, Me(8)*endo*), 1.35 (3H, s, Me(8)*exo*), 3.06 (1H, dd, J=11.2, 0.8, H(9)), 3.62 (3H, s, OMe(9)), 3.71 (1H, ddd, J=9.8, 0.8, 0.5, H(7)), 4.345 (1H, dd, J=11.2, 9.8, H(1)), 7.01 (1H, ddd, J=7.5, 1.4, 0.5, H(2′′)), 7.28 (1H, t-like, d, J=7.5, 7.4, 1.4, H(4′)), 7.32 (1H, dd, J=7.5, 1.5, H(2′)), 7.33 (H, t-like, d, J=7.5, 7.7, 1.4, H(4′′)), 7.40 (1H, t-like, d, J=7.5, 7.5, 1.5, H(3′)), 7.45 (1H, t-like, d, J=7.5, 7.5, 1.6, H(3′′)), 7.58 (1H, dd, J=7.5, 1.5, H(5′)), 7.77 (1H, dd, J=7.7, 1.6, H(5′′))

a) Given in ppm relative to internal TMS, ±0.001 ppm. *b*) Average error ±0.12 Hz. *c*) In acetone-d_6.

$J=11.5$ Hz, H(5)), 6.94 (1H, d, $J=11.9$ Hz, H(10 or 11)), 7.01 (1H, d, $J=11.9$ Hz, H(11 or 10)), 7.18 (1H, m, H(4 or 6)), 7.28—7.31 (5H, m, H(2, 3, 7, 8 and 6 or 4)), 7.33 (2H, m, H(1,9)). ^{13}C-NMR ($CDCl_3$) δ: 35.50 (C(5-(2)), 40.09 (C-5-(1)), 51.41 (O$\underline{C}H_3$(5-(1)), 51.66 (O$\underline{C}H_3$(5-(2)), 56.99 (C(5)), 126.97, 127.18, 128.58, 128.78, 129.70 (C(4 or 6), 129.74 (C(1 or 9)), 129.94 (C(9 or 1)), 130.34 (C(10 or 11)), 130.66 (C(6 or 4)), 131.55 (C(11 or 10)), 134.07 (C(9a or 11a)), 134.40 (C(11a or 9a)), 136.79 (C(4a or 5a)), 137.68 (C(5a or 4a)), 171.97 ($\underline{C}=O$(5-(2))), 174.77 ($\underline{C}=O$(5-(1))).

3b: Recrystallized from *n*-hexane–benzene. Colorless prisms.

3c: Recrystallized from ether (Et_2O). Colorless needles.

3d: Recrystallized from Et_2O–*n*-hexane to give **5** (1% yield), mp 250—252 °C (lit.,[8a] 237—238.5 °C, 251 °C[8b]). The mother liquor was concentrated to give **3d** as pale yellow prisms.

3e: Recrystallized from Et_2O to give **5** (26% yield). The mother liquor was evaporated off and the residue was purified by PTLC with $CHCl_3$ as the eluent to give **3e** as a pale yellow amorphous solid.

6 (Reaction of **1a** with **2g**): In the reaction of **1a** (500 mg) and **2g** (3.2 g), the residue was purified by PTLC on silica gel with $CHCl_3$ as the eluent and the product was recrystallized from Et_2O to give **6** (49 mg), mp 156—158 °C (lit.,[9] 163 °C) and the starting material **1a** (452 mg).

Reaction of 3b with NaH NaH (50%, 60 mg, washed with *n*-hexane) was added to a stirred solution of **3b** (400 mg) in anhydrous dimethylformamide (3 ml) and the mixture was stirred at 80 °C for 25 min. The resulting solution was poured into ice-water (15 ml), then the precipitate was collected by filtration. The filtrate was acidified with 10% hydrochloric acid (HCl) and extracted with Et_2O. The extract was washed with aqueous saturated NaCl solution and dried over Na_2SO_4. The concentrated ethereal solution was treated with diazomethane (CH_2N_2)–Et_2O and the reaction mixture was concentrated. The residual solid and the above precipitate were combined and purified by PTLC with $CHCl_3$ as the eluent. Recrystallization from ethanol (EtOH) gave 93 mg (23%) of **3b-*t*** as colorless needles, mp 161—162 °C. The physical and spectral data are summarized in Table II and the ^{13}C- and ^{1}H-NMR data are listed in Tables V and VI.

Reaction of 3c with KOH A mixture of **3c** (500 mg), KOH (1.0 g), EtOH (8 ml), and water (2 ml) was heated under reflux for 4 h. After removal of the solvent by evaporation *in vacuo*, the residue was dissolved in a small amount of water and acidified with 10% HCl. The precipitate was extracted with Et_2O. The extract was washed with aqueous saturated NaCl solution, dried over Na_2SO_4, and concentrated. The remaining ethereal solution was treated with CH_2N_2–Et_2O and the resulting solution was kept standing for 2 h to give 217 mg (43%) of a solid. Recrystallization of the solid from EtOH gave **3c-*t*** as colorless needles, mp 118—119 °C. The physical and spectral data are summarized in Table II and the ^{13}C- and ^{1}H-NMR data are listed in Tables V and VI.

5-Methylene-5*H*-dibenzo[*a,d*]cycloheptene (1z) Methyltriphenylphosphonium iodide (885 mg, 2.19 mmol) was added portionwise to a solution of 1.55 N *n*-butyl lithium (BuLi, 1.4 ml, 2.19 mmol) in anhydrous Et_2O (10 ml) under a nitrogen atmosphere over 2 h. A solution of **1a** (300 mg, 1.46 mmol) in anhydrous Et_2O (10 ml) was added dropwise to the resulting ylide solution and the mixture was heated under reflux for 5 h. After cooling, the resulting precipitate was filtered off and washed several times with petroleum ether. The combined filtrate was evaporated *in vacuo*. The residual mass was purified by PTLC on silica gel with $CHCl_3$ as the eluent. Recrystallization from *n*-hexane gave **1z** (234 mg, 75%) as white plates, mp 117—118 °C (lit.,[6] 119—120 °C).

5*H*-Dibenzo[*a,d*]cycloheptene (1y) A mixture of **1a** (500 mg, 2.43 mmol) and aluminum triisopropoxide (1.43 g, 7.0 mmol) was heated to 250 °C for 10 min. The reaction mixture was cooled to room temperature, treated with 12 N HCl (14 ml) in H_2O (30 ml), and shaken for 15 min. The remaining solid was collected and dried. Recrystallization from methanol (MeOH) gave **1y** (234 mg, 50%) as white plates, mp 130.5—132.5 °C (lit.,[7] mp 130—133 °C).

Acknowledgment The authors wish to express their gratitude to Dr. Yoshio Sumida of this University for measurement of the mass spectra and also to the members of the Elemental Analysis Room of Nippon Shinyaku Co., Ltd. Thanks are also due to Miss Kaoru Nakayama, Miss Hiroko Inoue, and Mr. Yasushi Watanabe for technical assistance.

References and Notes

1) Part III: Y. Fujiwara and M. Okamoto, *Chem. Pharm. Bull.*, **37**, 267 (1989).
2) *a*) S. Farid, J. C. Doty and J. L. R. Williams, *J. Chem. Soc., Chem. Commun.*, **1972**, 711; S. Farid, S. E. Hartman, J. C. Doty and J. L. R. Williams, *J. Am. Chem. Soc.*, **97**, 3697 (1975); *b*) J. L. R. Williams, S. Y. Farid, J. C. Doty, R. C. Daly, D. P. Specht, R. Searle, D. G. Borden, H. J. Chang and P. A. Martic, *Pure Appl. Chem.*, **49**, 523 (1977).
3) *a*) R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, **96**, 2994 (1974); R. A. Caldwell, N. I. Ghali, C. K. Chien, D. DeMarco and L. Smith, *ibid.*, **100**, 2857 (1978); R. A. Caldwell, K. Mizuno, P. E. Hansen, L. P. Vo, M. Frentrup and C. D. Ho, *ibid.*, **103**, 7263 (1981); *b*) K. Mizuno, C. Pac and H. Sakurai, *ibid.*, **96**, 2993 (1974); R. A. Caldwell and T. S. Maw, *J. Photochem.*, **11**, 165 (1979); *c*) C. Pac, T. Sugioka, K. Mizuno and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **46**, 238 (1973); K. Mizuno C. Pac and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, **1974**, 648; M. Yamada, C. Pac and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **53**, 502 (1980); *d*) T. S. Cantrell, *J. Am. Chem. Soc.*, **94**, 5929 (1972).
4) M. Okamoto, Y. Fujiwara, T. Oka and Y. Uemura, *Chem. Pharm. Bull.*, **36**, 521 (1988).
5) Syntex Corp., Brit. Patent 1428481 (Cl. CO7CD, A61K) [(*Chem. Abstr.*, **85**, 46267*a* (1976)].
6) A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, **73**, 1673 (1951); T. W. Cutshall and P. W. Rabideau, *Can . J. Chem.*, **50**, 2364 (1972).
7) T. W. Campbell, R. Ginsig and H. Schmid, *Helv. Chim. Acta*, **36**, 1489 (1953); K. E. Eichstadt, J. C. Reepmeyer, R. B. Cook, P. G. Riley, D. P. Davis and R. A. Wiley, *J. Med. Chem.*, **19**, 47 (1976).
8) *a*) W. Tochtermann, G. Schnabel and A. Manschreck, *Justus Liebigs Ann. Chem.*, **705**, 169 (1967); *b*) Y. Asscher, P. Lindley, A. Rotman and I. Agranat, *Chem. Pharm. Bull.*, **33**, 4847 (1985).
9) G. Ciamician and P. Silber, *Chem. Ber.*, **35**, 4128 (1902); J. D. Fulton and J. D. Dunitz, *Nature* (London), **160**, 161 (1947).
10) A. Bax and R. Freeman, *J. Magn. Reson.*, **44**, 542 (1981).
11) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect, Chemical Applications," Academic Press, New York, 1971.
12) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect, Chemical Applications," Academic Press, New York, 1971, Chapter 3.
13) It has been reported that the photoreaction of phenanthrene with cinnamate esters proceeds in a stereoselective manner to give sterically hindered *cis* cycloadducts having an *endo* phenyl group to the phenanthrene moiety as major products (*ca.* 90%), and the high stereoselectivity of the addition strongly suggests the intermediacy of sandwich exciplexes.[2b]
14) S. L. Mattes and S. Farid, *Acc. Chem. Res.*, **15**, 80 (1982), and references cited therein.
15) A. Box, R. Freeman and G. A. Morris, *J. Magn. Reson.*, **43**, 333 (1981); Y. Kuroda, Y. Fujiwara, M. Saito and T. Shingu, *Chem. Pharm. Bull.*, **36**, 849 (1988).
16) A. Box, "Two-dimensional NMR in Liquids," D. Reidel Publishing Co., Dordrecht, Holland, 1982, Chapter 2.