centration gave the crude product, which was purified by radial preparative layer chromatography (silica gel, 20% EtOAc–hexanes) to give 0.125 g (57%) of *o*-tolualdehyde. This compound was identical with an authentic sample.

Registry No. 1, 20916-85-2; 2, 56635-61-1; 3, 2728-04-3; 4, 103562-84-1; 5a, 103562-85-2; 7, 103562-86-3; 8, 57056-81-2; 9, 103562-87-4; 10, 54887-23-9; 11, 103562-88-5; 12, 103562-89-6; 13, 6161-65-5; 14, 2674-44-4; 15, 5398-11-8; 16, 16859-59-9; 17, 56635-66-6; 18, 103562-93-2; 21, 67023-02-3; 22, 103562-90-9; 23, 6245-57-4; 24, 35598-05-1; 25e, 103562-91-0; 25f, 103590-64-3; *o*-$CH_3C_6H_4CO(CH_2)_3CH_3$, 20359-56-2; *o*-$CH_3(CH_2)_3C_6H_4CO(CH_2)_3CH_3$, 103562-92-1; *N,N,N'*-triethylenediamine, 105-04-4; benzoyl chloride, 98-88-4; *o*-toluic acid, 118-90-1; *n*-propyl iodide, 107-08-4; *o*-anisoyl chloride, 21615-34-9; benzaldehyde, 100-52-7; *o*-methylacetophenone, 577-16-2; *o*-tolualdehyde, 529-20-4; *o*-butylacetophenone, 58632-85-2; *p*-anisoyl chloride, 100-07-2; *N*-methylpiperazine, 109-01-3; *o*-butylbenzaldehyde, 59059-42-6.

Synthetic Applications of the 1-Cyclobutenyltriphenylphosphonium Salt. Synthesis and Reactions of 1,2-Difunctionalized Cyclobutanes

Toru Minami,* Nobuo Harui, and Yuki Taniguchi

Department of Industrial Chemistry, Kyushu Institute of Technology, Sensuicho, Tobata, Kitakyushu 804, Japan

Received February 7, 1986

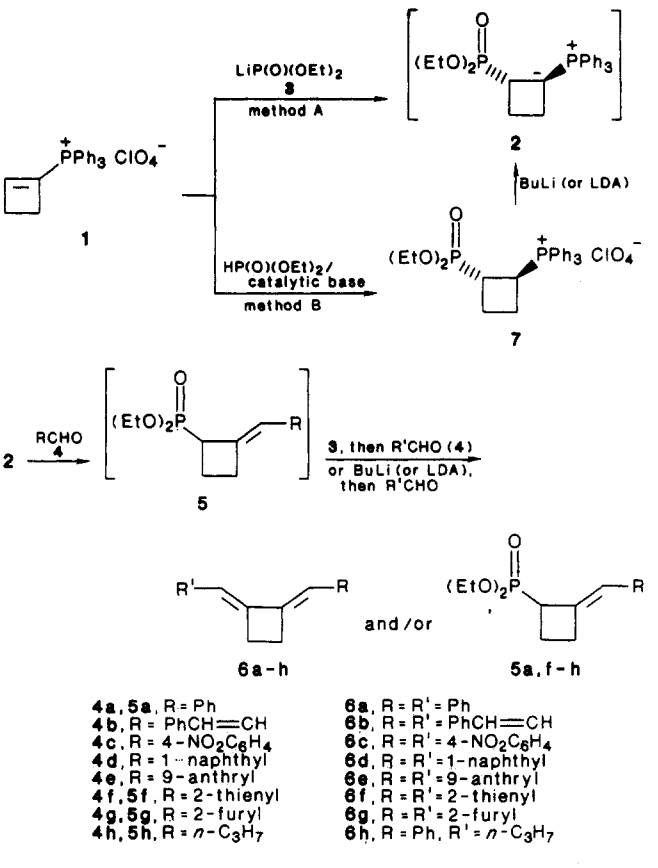
Symmetrical and unsymmetrical 1,2-bis(ylidene)cyclobutanes **6a–g** and **6h** were synthesized in good or moderate yields by the double Wittig reaction of a [2-(diethoxyphosphinyl)cyclobutyl]triphenylphosphonium ylide with aldehydes. The 1,2-bis(ylidene)cyclobutane **6a** readily underwent sequential Diels–Alder reactions with various dienophiles **8a–d** and **15** to give fused bicyclic compounds in good yields. Oxidation and hydrogenation of some 1,2-bis(ylidene)cyclobutanes were studied.

Although the preparation of 1,2-bis(methylene)cyclobutane and its synthetic applications have been well studied,[1] the synthesis of 1,2-bis(ylidene)cyclobutanes and their utilization have been little reported.[2] We have been interested in developing versatile reagents that are applicable to the synthesis of cyclobutanes bearing functionality. We have recently reported preparation of the 1-cyclobutenyltriphenylphosphonium salt **1** and its utilization for the synthesis of functionalized cyclobutanes.[3] In an earlier communication,[4] we described a new synthesis of 1,2-bis(ylidene)cyclobutanes by the reaction of a [2-(diethoxyphosphinyl)cyclobutyl]phosphonium ylide **2** with aromatic aldehydes. In this paper, we report on the reaction of the ylide **2** with various aldehydes and some reactions of the resulting 1,2-bis(ylidene)cyclobutanes.

Results and Discussion

Synthesis of 1,2-Bis(ylidene)cyclobutanes. Since the carbon–carbon double bond of **1** is strongly activated by the phosphonium group,[3a] the salt **1** could be a good Michael acceptor toward diethyl lithiophosphonate (**3**) producing the ylide **2**. So, when the ylide **2**, generated in situ from **1** and 1 equiv of **3** in tetrahydrofuran (THF)–dimethylformamide (DMF) (5:1), was treated with benzaldehyde (**4a**) at room temperature for 24 h, the expected product, diethyl (2-benzylidenecyclobutyl)phosphonate was not obtained, but (*E,E*)-1,2-dibenzylidenecyclobutane (**6a**) was isolated in 50% yield. The reaction using 2 mol equiv of **3** and **4a** to **1**, under similar conditions, led to **6a** in 70% yield.

Scheme I



4a, 5a, R = Ph
4b, R = PhCH=CH
4c, R = 4-$NO_2C_6H_4$
4d, R = 1-naphthyl
4e, R = 9-anthryl
4f, 5f, R = 2-thienyl
4g, 5g, R = 2-furyl
4h, 5h, R = *n*-C_3H_7

6a, R = R' = Ph
6b, R = R' = PhCH=CH
6c, R = R' = 4-$NO_2C_6H_4$
6d, R = R' = 1-naphthyl
6e, R = R' = 9-anthryl
6f, R = R' = 2-thienyl
6g, R = R' = 2-furyl
6h, R = Ph, R' = *n*-C_3H_7

These results can be reasonably accounted for by reaction of the phosphonate carbanion, generated from the

(1) See, for examples: (a) Blomquist, A. T.; Verdol, J. A. *J. Am. Chem. Soc.* **1955**, *77*, 1806. (b) Hartzler, H. D.; Benson, R. E. *J. Org. Chem.* **1961**, *26*, 3507. (c) Slobodin, Ya. M.; Khitrov, A. P. *Zh. Obshch. Khim.* **1963**, *33*, 2819; *Chem. Abstr.* **1963**, *60*, 1609e,f. (d) Doering, W. v. E.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 4534. (e) Borden, W. T.; Reich, I. L.; Sharpe, L. A.; Weinberg, R. B.; Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2438. (f) Thummel, R. P.; Nutakul, W. *J. Am. Chem. Soc.* **1978**, *100*, 6171. (g) Thummel, R. P.; Cravey, W. E.; Nutakul, W. *J. Org. Chem.* **1978**, *43*, 2473. (h) Neidlein, R.; Doerr, H. *Liebigs Ann. Chem.* **1980**, 1540.

(2) Davalian, D.; Garratt, P. J.; Koller, W.; Mansuri, M. *J. Org. Chem.* **1980**, *45*, 4183.

(3) (a) Minami, T.; Sako, H.; Ikehira, T.; Hanamoto, T.; Hirao, I. *J. Org. Chem.* **1983**, *48*, 2569. (b) Minami, T.; Hanamoto, T.; Hirao, I. *J. Org. Chem.* **1985**, *50*, 1278.

(4) Minami, T.; Taniguchi, Y.; Hirao, I. *J. Chem. Soc., Chem. Commun.*, **1984**, 1046.

0022-3263/86/1951-3572$01.50/0

Table I. Reaction of the [2-(Diethoxyphosphinyl)cyclobutyl]phosphonium Salt 7 (or the Cyclobutenylphosphonium Salt 1) with Aldehydes 4 in the Presence of Base

entry	aldehydes 4 R	aldehydes 4 R′	method[a]	products (yield,[b] %)
1	Ph	Ph	A	**6a** (70)
2	Ph	Ph	B	**6a** (76), **5a** (5)
3	PhCH=CH	PhCH=CH	A	**6b** (43)
4	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	B	**6c** (45)
5	1-naphthyl	1-naphthyl	B	**6d** (65)
6	9-anthryl	9-anthryl	B	**6e** (47)
7	2-thienyl	2-thienyl	B	**6f** (56), **5f** (12)
8	2-furyl	2-furyl	B	**6g** (75), **5g** (13)
9	Ph	n-C_3H_7	B	**6h** (20),[c] **6a** (15), **5a** (31)
10	n-C_3H_7	n-C_3H_7	B	**5h** (83)

[a] See Experimental section. [b] No attempt to optimize yields has been made. [c] A 3:2 mixture of (1*E*,2*E*)- and (1*E*,2*Z*)-1-benzylidene-2-butylidenecyclobutane.

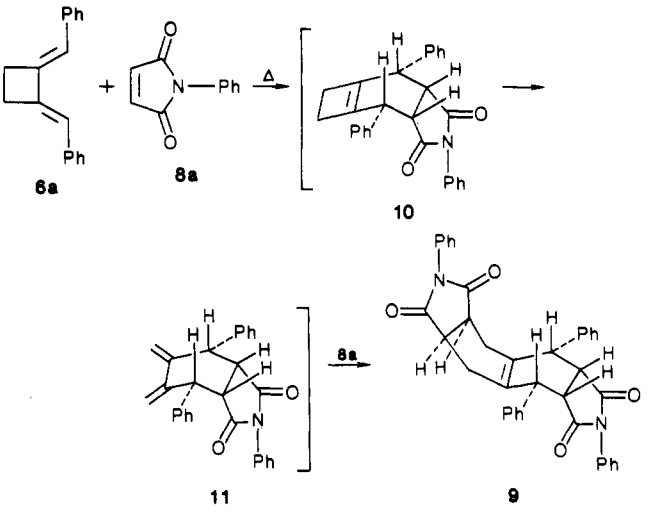
initial Wittig olefination product **5a** and the base **3**, with the second molecule of **4a** to give **6a** (Scheme I).

Treatment of **2** with cinnamaldehyde (**4b**) similarly led to (*E*,*E*)-1,2-dicinnamylidenecyclobutane (**6b**) in 43% yield. However, this one-pot synthesis (method A) cannot be effectively applied to reactive aromatic aldehydes such as *p*-nitrobenzaldehyde (**4c**) due to byproduct formation.[5] In order to correct this disadvantage, we have separately prepared the [2-(diethoxyphosphinyl)cyclobutyl]triphenylphosphonium salt **7** by the reaction of **1** with diethyl phosphonate in the presence of a catalytic amount of base. The ylide **2**, prepared from **7** and 1 equiv of butyllithium [or lithium diisopropylamide (LDA)], was allowed to react with **4c**, followed by treatment with 1 equiv of butyllithium (or LDA) and subsequent reaction with a second equivalent of **4c** to give the desired **6c** in 45% yield. Accordingly, this two-step method (B) was employed by using **7** and 1-naphthaldehyde (**4d**), 9-anthraldehyde (**4e**), 2-thiophenecarboxaldehyde (**4f**), and furfural (**4g**) to produce the corresponding bis(ylidene)cyclobutanes **6d–g** in 47–75% yields together with monoolefination products **5a,f,g** (see Table I). The synthetic methods for bis(ylidene)cyclobutanes are limited in scope, however. For the reaction to proceed well, R in **4** must be an aromatic group. When R = n-C_3H_7 (**4h**), diethyl (2-*n*-butylidenecyclobutyl)phosphonate (**5h**) was obtained as the sole product in 83% yield. None of the expected di-*n*-butylidenecyclobutane was produced. To synthesize the unsymmetrical bis(ylidene)cyclobutanes, **2** was reacted with **4a** in THF at room temperature for 10 h followed by sequential treatment with 1.1 equiv of LDA at −78 °C for 1 h and 1 equiv of **4h** at room temperature for 10 h to afford the desired 1-benzylidene-2-propylidenecyclobutane (**6h**) in 20% yield along with **5a** (31%) and **6a** (15%).

Diels–Alder Reactions of 1,2-Bis(ylidene)cyclobutanes. Treatment of the diene **6a** with *N*-phenylmaleimide (**8a**) in toluene at 150 °C for 30 h in a sealed tube afforded exclusively the 1:2 adduct **9** in 74% yield. Structural assignment of **9** was based on its ^1H NMR spectrum[6] ($CDCl_3$), which showed methylene (br s, 4 H) at δ 2.47, methine (m, 6 H) at δ 3.10–4.20, phenyl (dd, J = 2.65 Hz, J = 6.05 Hz, 2 H) at δ 5.95–6.25, and the other phenyl protons (m, 18 H) at δ 6.90–7.70. The structure was further confirmed by the ^{13}C NMR spectrum (see Table III). As shown in Scheme II, the formation of **9** can be explained by the Diels–Alder reaction of **6a** with **8a**, ring opening to the diene **11**, and the Diels–Alder reaction of **11** with a second molecule of **8a** from the anti direction. Addition from the syn direction would be hindered by steric repulsion between **8a** and the phenyl groups in the initially formed 1:1 Diels–Alder adduct **11**.

In contrast, the reaction of **6a** with dimethyl (**8b**) or diethyl maleate (**8c**) and diethyl fumarate (**8d**) afforded mixtures of the anti and syn 1:2 adducts **12a,b–14a,b** in 45–83% yields (eq 1). As shown in Table II, the major products **12a** and **13a** were assigned as the anti 1:2 adducts rather than the syn 1:2 adducts on the basis of their ^{13}C spectra (see Table III) and mechanistic grounds as above. The reaction of **6a** with dimethyl acetylenedicarboxylate (**15**) gave only tetramethyl 1,4-diphenylnaphthalene-2,3,6,7-tetracarboxylate (**16**) (45%), which was produced via dehydrogenation of the corresponding 1:2 adduct (Scheme III). The compound **16** was alternatively synthesized in 58% yield by the reaction of **12** with excess *N*-bromosuccinimide (NBS) in carbon tetrachloride, followed by treatment of the resulting bromide with triethylamine.

Scheme II



Scheme III

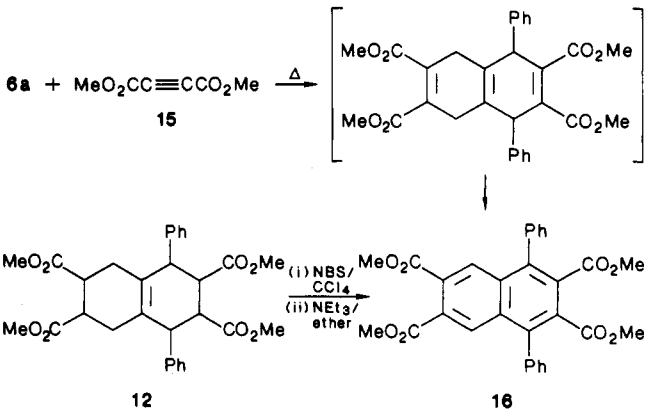


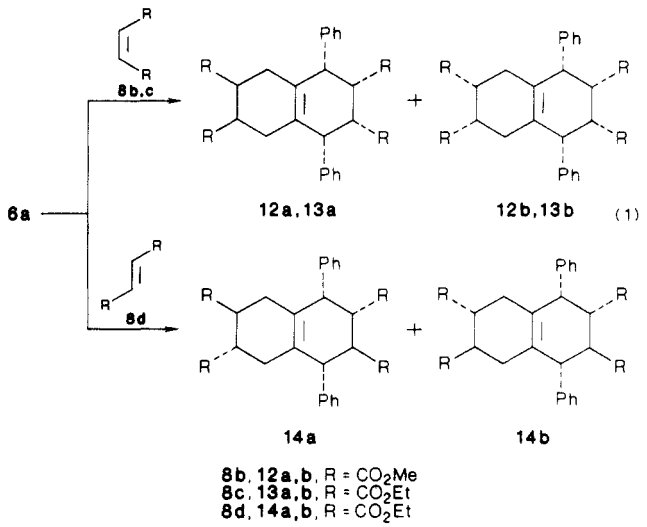
Table II. Diels–Alder Adducts of 6a to Olefins 8a–d[a]

olefins	products	% yield (ratio[b])
8a	**9**	74
8b	**12a + 12b**	72 (4:1)
8c	**13a + 13b**	45 (7:3)
8d	**14a + 14b**	83 (1:1)

[a] The reaction was carried out at 150 °C for 30 h in a sealed tube. [b] Determined by the ^{13}C NMR data of the mixture.

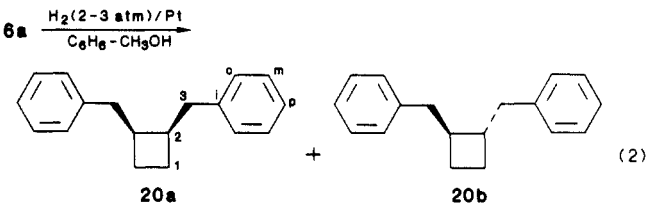
(5) Byproducts are mainly composed of the adduct of diethyl phosphonate to **4c**.

(6) Although we cannot exclude the stereoisomeric syn form, we favor this less on mechanistic grounds.



The cycloaddition of singlet oxygen to the diene **6a** was also examined. Treatment of a methylene chloride solution of **6a** with singlet oxygen,[7] followed by the reaction with triethyl phosphite, led to 2-benzylidenecyclobutyl phenyl ketone (**17**) (35%) and 1,2-dibenzoylcyclobutane (**18**) (5%) together with recovered **6a** (31%). This result suggests formation of the 1,4-cycloadduct **19** (Scheme IV).

We have studied the catalytic hydrogenation of the dienes **6a,g**. Hydrogenation of the diene **6a** in benzene–methanol over a platinum catalyst at low hydrogen pressure (2–3 atm) afforded a mixture of two stereoisomers, *cis*- (**20a**) and *trans*-1,2-dibenzylcyclobutanes (**20b**) (total yield 74%) in a 2.6:1 ratio (eq 2). The structural assign-

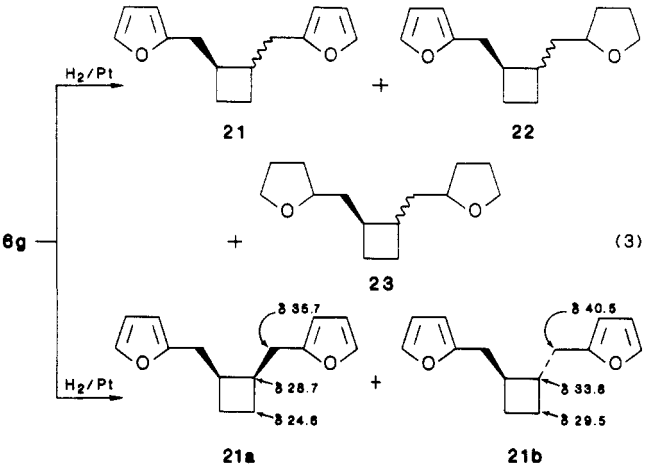


ments for **20a** and **20b** are based on their NMR spectra.[8] In contrast, we found that hydrogenation of **6g** under similar conditions produced a mixture of products including 1,2-bis(2-furylmethyl)cyclobutane (**21**), 1-(2-furylmethyl)-2-(2-tetrahydrofurylmethyl)cyclobutane (**22**), and 1,2-bis(2-tetrahydrofurylmethyl)cyclobutane (**23**) in 10–33% yields (eq 3). Similar treatment over a palladium catalyst led to a 3:1 mixture of the cis isomer **21a** and the trans isomer **21b** in 54% yield.

In summary, we found that the (2-phosphinylcyclobutyl)phosphonium salt **7** is a versatile reagent for the synthesis of 1,2-bis(ylidene)cyclobutanes, which are useful for the construction of fused bicyclic ring systems and also for the preparation of functionalized cyclobutanes.

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-FX-60 in $CDCl_3$ operating at 60 and 15.04 MHz with Me_4Si as an internal standard. IR spectra were recorded with a Shimazu IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are uncorrected.



[2-(Diethoxyphosphinyl)cyclobutyl]triphenylphosphonium Perchlorate (7). To a solution containing cyclobutenyltriphenylphosphonium perchlorate (1)[3a] (8.30 g, 20 mmol) and diethyl phosphonate (3.86 g, 28 mmol) in dry THF/DMF (10/1, 55 mL) was added *n*-butyllithium (2 mmol), and the solution was stirred at room temperature for 10 h. After the reaction mixture was neutralized with 10% aqueous HCl, the solvent was evaporated. The residue was recrystallized from CH_2Cl_2/ether to give **7**: 10.83 g (98%); mp 186–186.5 °C; IR (KBr) 1440, 1230, 1100, 1015 cm^{-1}; ^1H NMR δ 1.28 (t, 6 H, Me), 1.90–3.50 (m, 5 H, CH_2 and CH), 3.80–4.40 (quint, 4 H, OCH_2), 4.40–5.0 (br, 1 H, CH), 7.73–7.83 (m, 15 H, Ph).

Anal. Calcd for $C_{26}H_{31}O_7P_2Cl$: C, 56.48; H, 5.65. Found: C, 56.43; H, 5.69.

General Procedure for the Synthesis of 1,2-Bis(ylidene)cyclobutanes 6 and/or (2-Ylidenecyclobutyl)phosphonates 5. Method A. To the phosphonium ylide **2**, generated in situ from the phosphonium salt **1** (2.07 g, 5 mmol) and diethyl lithiophosphonate (**3**) (10 mmol) in THF/DMF (5/1, 30 mL), were added aldehydes **4** (10.5 mmol), and the reaction mixture was stirred at room temperature for 24 h. After evaporation of the sovlent in vacuo, the residue was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4, and evaporated. The resulting solid was chromatographed on preparative TLC (silica gel, Wakogel B-5F, benzene) to give samples **6**.

Method B. After the phosphonium ylide **2**, generated from **7** (5.53 g, 10 mmol) and *n*-butyllithium (11 mmol) in THF (30 mL) at 0 °C for 1 h, was reacted with aldehydes **4** (12 mmol) at room temperature for 6 h, the mixture was cooled to −75 °C, and LDA (12 mmol) was added while the mixture was stirred at this temperature for 1 h. To this were then added aldehydes **4** (12 mmol), and the mixture was allowed to warm to room temperature and to stir for 10 h. After similar workup, the residue was chromatographed on preparative TLC (silica gel, benzene and benzene/methanol) to give samples **6** and/or **5**. The yields of the products are summarized in Table I.

(*E*,*E*)-1,2-Dibenzylidenecyclobutane (6a): mp 140 °C (lit.[2] mp 114–115 °C); IR (KBr) 1485, 1445 cm^{-1}; ^1H NMR δ 3.15 (s, 4 H, CH_2), 6.64 (s, 2 H, olefinic H), 7.31 (br s, 10 H, Ph); ^{13}C NMR δ 30.8, 117.6, 126.7, 127.9, 128.6, 137.5, 143.8; MS, *m*/*z* 232 (M^+).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.03; H, 7.20.

(*E*,*E*)-1,2-Dicinnamylidenecyclobutane (6b): mp 167–169 °C; IR (KBr) 1475, 1430, 1260 cm^{-1}; ^1H NMR δ 2.83 (s, 4 H, CH_2), 6.20–6.90 (m, 6 H, olefinic H), 7.05–7.55 (m, 10 H, Ph); ^{13}C NMR δ 26.3, 119.5, 125.5, 126.4, 127.4, 128.7, 131.8, 137.8, 144.8; HRMS, *m*/*z* calcd for $C_{22}H_{20}$ 284.1587, found 284.1590.

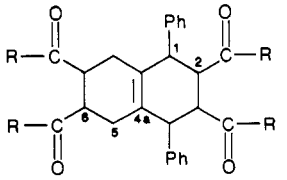
(*E*,*E*)-1,2-Bis(4-nitrobenzylidene)cyclobutane (6c): mp 244–246 °C; IR (KBr) 1585, 1500, 1330 cm^{-1}; ^1H NMR δ 3.25 (s, 4 H, CH_2), 6.78 (s, 2 H, olefinic H), 7.46 (d, *J* = 8.97 Hz, 4 H, Ph), 8.20 (d, *J* = 8.97 Hz, 4 H, Ph); ^{13}C NMR δ 31.0, 117.9, 124.1, 128.3, 139.9, 143.2, 147.7; HRMS, *m*/*z* cald for $C_{18}H_{14}N_2O_4$ 322.0953, found 322.0927.

(*E*,*E*)-1,2-Bis(di-1-naphthylmethylene)cyclobutane (6d): mp 167.5–168 °C; IR (KBr) 1580, 1500 cm^{-1}; ^1H NMR δ 3.01 (s, 4 H, CH_2), 7.31–8.25 (m, 16 H, olefinic and Ar H); ^{13}C NMR δ 30.5, 113.9, 123.8, 124.9, 125.5, 125.7, 126.0, 127.3, 128.7, 131.6,

(7) For a review, see: Denny, R. W.; Nickon, A. *Organic Reactions*; Wiley: New York, 1973; Vol. 20, Chapter 2, p 133.

(8) We assigned the cis structure **20a** based on the following ^{13}C NMR data for **20a** and **20b**. **20a**: ^{13}C NMR δ 24.4 (C-1), 36.5 (C-2), 38.9 (C-3), 125.7 (C-p), 128.3 (C-o), 128.7 (C-m), 141.5 (C-i). **20b**: ^{13}C NMR δ 25.1 (C-1), 42.2 (C-2), 43.4 (C-3), 125.7 (C-p), 128.3 (C-o), 128.7 (C-m), 141.0 (C-i).

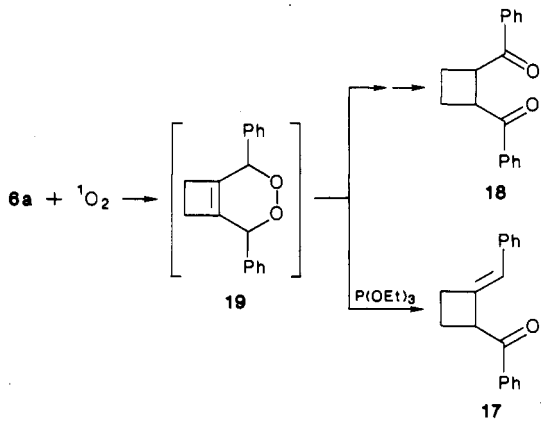
Table III. ^{13}C NMR Data of Compounds 9 and 12–14



compd	^{13}C chemical shifts,[a] ppm					
	C-1	C-2	C-5	C-6	C-4a	C=O
9	40.5	45.3	29.9	43.7	*b*	174.4, 178.5
12a	40.5	47.2	30.1	46.3	142.0	171.5, 173.2
12b	40.1	48.0	30.1	46.0	140.6	172.0, 172.7
13a	40.6	47.4	30.2	46.5	142.3	171.1, 172.8
13b	40.3	48.1	30.2	45.9	140.9	171.8, 172.4
14	40.5	46.6	28.6	45.7	140.1	171.4, 173.4
	40.9	47.7	30.4	45.9	141.0	174.0, 174.4
	41.7		31.4			
	42.2		31.8			

[a] Chemical shifts for $CDCl_3$ solutions with respect to Me_4Si. [b] The resonance was obscured by overlapping with other peaks.

Scheme IV



133.4, 133.9, 145.2; HRMS, *m/z* calcd for $C_{26}H_{20}$ 332.1564, found 332.1557.

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.39; H, 6.30.

***(E,E)*-1,2-Bis(9-anthrylmethylene)cyclobutane (6e)**: mp 233–235 °C; IR (KBr) 1618 cm^{-1}; ^1H NMR δ 2.40 (s, 4 H, CH_2), 7.26 (s, 2 H, olefinic H), 7.71–8.40 (m, 18 H, Ar H); HRMS, *m/z* calcd for $C_{34}H_{25}$ 432.1878, found 432.1878.

***(E,E)*-1,2-Bis(2-thienylmethylene)cyclobutane (6f)**: mp 135–137 °C; IR (KBr) 1615, 1500 cm^{-1}; ^1H NMR δ 2.95 (s, 4 H, CH_2), 6.81 (s, 2 H, olefinic H), 6.94–7.01 (m, 4 H), 7.17–7.27 (m, 2 H); ^{13}C NMR δ 29.4, 111.8, 125.3, 125.9, 127.3, 141.3, 141.9; MS, *m/z* 244 (M^+).

Anal. Calcd for $C_{14}H_{12}S_2$: C, 68.84; H, 4.95. Found: C, 68.51; H, 5.00.

Diethyl [2-(2-thienylmethylene)cyclobutyl]phosphonate (5f): oil; IR (neat) 1655, 1440, 1220, 1020 cm^{-1}; ^1H NMR δ 1.46 (t, 6 H, Me), 2.05–3.71 (br m, 5 H, CH_2 and CH), 3.91–4.39 (quint, 4 H, OCH_2), 6.55–6.73 (m, 1 H, olefinic H), 6.91–7.55 (m, 3 H); HRMS, *m/z* calcd for $C_{13}H_{19}O_3PS$ 286.0792, found 286.0784.

***(E,E)*-1,2-Bis(2-furylmethylene)cyclobutane (6g)**: oil; IR (neat) 1590, 1480 cm^{-1}; ^1H NMR δ 2.90 (s, 4 H, CH_2), 6.16 (s, 2 H, olefinic H), 6.29–6.34 (m, 4 H), 7.28–7.31 (m, 2 H); ^{13}C NMR δ 29.6, 106.8, 108.3, 111.7, 141.6, 142.0, 153.7; HRMS, *m/z* calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0829.

Diethyl [2-(2-furylmethylene)cyclobutyl]phosphonate (5g): oil; IR (neat) 1640, 1450, 1220, 1020 cm^{-1}; ^1H NMR δ 1.33 (t, 6 H, Me), 2.09–3.75 (br m, 5 H, CH_2 and CH), 3.90–4.39 (quint, 4 H, OCH_2), 6.11 (br, 1 H, olefinic H), 6.19–6.40 (m, 2 H), 7.34–7.38 (m, 1 H); HRMS, *m/z* calcd for $C_{13}H_{19}O_4P$ 270.1022, found 270.1039.

Diethyl (2-butylidenecyclobutyl)phosphonate (5h): oil; IR (neat) 1625, 1460, 1220, 1030 cm^{-1}; ^1H NMR δ 0.93–1.36 (m, 11 H, CH_2 and Me), 1.94–3.89 (br, 7 H, $=CHCH_2$ and cyclobutyl CH_2 and CH), 3.90–4.40 (quint, 4 H, OCH_2), 5.17–5.30 (br, 1 H, olefinic H); HRMS, *m/z* calcd for $C_{12}H_{23}O_3P$ 246.1486, found 246.1436.

(1*E*,2*E*)- and (1*E*,2*Z*)-1-Benzylidene-2-butylidenecyclobutane (6h) and Diethyl (2-Benzylidenecyclobutyl)phosphonate (5a). The reaction was carried out according to method B by using the salt **7** (2.76 g, 5 mmol), benzaldehyde (**4a**) (0.58 g, 5.47 mmol), and butyraldehyde (**4h**) (0.47 g, 6.50 mmol) to produce a 0.20 g (20%) of a 3:2 mixture of (1*E*,2*E*)- and (1*E*,2*Z*)-**6h**, whose ratio was determined by its ^{13}C NMR spectrum, along with **6a** (0.17 g, 15%) and **5a** (0.44 g, 31%). The compound **6h** had the following properties: oil; IR (neat) 1600, 1500 cm^{-1}; ^1H NMR δ 0.80–1.14 (m, 3 H, Me), 1.25–2.45 (m, 4 H, $=CHCH_2CH_2$), 2.76 and 2.80 (br, 4 H, cyclobutyl CH_2), 5.08–6.44 (m, 2 H, olefinic H), 7.22 (s, 5 H, Ph); ^{13}C NMR δ 14.0, 22.8, 23.0, 27.2, 28.5, 29.0, 116.3, 119.0, 121.7, 124.6, 126.1, 126.3, 127.6, 128.4, 137.9, 138.1, 140.3, 141.9, 143.1, 143.9; HRMS, *m/z* calcd for $C_{15}H_{18}$ 198.1409, found 198.1409.

Compound **5a** had the following properties: oil; IR (neat) 1598, 1450, 1220, 1020 cm^{-1}; ^1H NMR δ 1.32 and 1.33 (t, J = 7.03 Hz, 6 H, Me), 2.14–3.83 (m, 5 H, CH_2 and CH), 3.90–4.39 (quint, 4 H, OCH_2), 6.30–6.42 (br, 1 H, olefinic H), 7.23 (s, 5 H, Ph); HRMS, *m/z* calcd for $C_{15}H_{21}O_3P$ 280.1229, found 280.1241.

Diels–Alder Reactions of Diene 6a with Dienophiles 8a–d. General Procedure. A mixture of the diene **6a** (0.232 g, 1 mmol) and a dienophile (3 mmol or a large excess) either in toluene or neat was heated at 150 °C for 30 h in a glass tube. The reaction mixture was chromatographed on preparative TLC (silica gel, ether) to give a pure adduct. Isolation of stereoisomers was unsuccessful. The yields and ^{13}C NMR data of the adducts are summarized in Tables II and III, respectively.

***anti*-Octahydronaphthalene-2,3,6,7-tetracarboximide 9**: mp 160–162 °C; IR (KBr) 1710, 1380 cm^{-1}; MS, *m/z* 578 (M^+).

Anal. Calcd for $C_{38}H_{30}O_4N_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 79.18; H, 5.40; N, 4.45.

***anti*- and *syn*-Tetramethyl octahydronaphthalene-2,3,6,7-tetracarboxylate (12a and 12b)**: oil; IR (neat) 1730, 1170 cm^{-1}; ^1H NMR δ 1.90–2.50 (br, 4 H, CH_2), 2.80–4.00 (m, 18 H, CH and Me), 7.27 (s, 10 H, Ph); HRMS, *m/z* calcd for $C_{30}H_{32}O_8$ 520.2097, found 520.2131.

Anal. Calcd for $C_{30}H_{32}O_8$: C, 69.21; H, 6.20. Found: C, 69.27; H, 6.20.

***anti*- and *syn*-Tetraethyl octahydronaphthalene-2,3,6,7-tetracarboxylate (13a and 13b)**: oil; IR (neat) 1730, 1175 cm^{-1}; ^1H NMR δ 0.7–1.35 (m, 12 H, Me), 1.90–2.45 (br, 4 H, CH_2), 2.75–4.30 (m, 14 H, CH and OCH_2), 7.28 (s, 10 H, Ph); HRMS, *m/z* calcd for $C_{34}H_{40}O_8$ 576.2724, found 576.2748.

Tetraethyl octahydronaphthalene-2,3,6,7-tetracarboxylate (14a,b): oil; IR (neat) 1730, 1180 cm^{-1}; ^1H NMR δ 0.79 (t, J = 7.14 Hz, 3 H, Me), 1.15 (t, J = 6.96 Hz, 6 H, Me), 1.18 (t, J = 6.96 Hz, 3 H, Me), 1.75–2.35 (br, 4 H, CH_2), 2.55–4.30 (m, 14 H, CH and OCH_2), 7.28 (s, 10 H, Ph); HRMS, *m/z* calcd for $C_{34}H_{40}O_8$ 576.2724, found 576.2702.

Anal. Calcd for $C_{34}H_{40}O_8$: C, 70.81; H, 6.99. Found: C, 70.91; H, 7.03.

Tetramethyl 1,4-Diphenylnaphthalene-2,3,6,7-tetracarboxylate (16). (A) Reaction of 6a with Dimethyl Acetylenedicarboxylate (15). The reaction was carried out as described above by using **6a** (23 mg, 0.1 mmol) and **15** (142 mg, 1 mmol). After removal of excess **15** in vacuo, the residue was chromatographed on preparative TLC (silica gel) with ether/hexane (7/3) as the eluent to give 23 mg (45%) of **16**: mp 61 °C; IR (KBr) 1730, 1285, 1137 cm^{-1}; ^1H NMR δ 3.51 (s, 6 H, Me), 3.84 (s, 6 H, Me), 7.0–7.60 (m, 10 H, Ph), 8.06 (s, 2 H, naphthyl H); ^{13}C NMR δ 52.4, 52.8, 128.4, 128.8, 129.1, 129.9, 131.3, 133.0, 136.3, 139.7, 167.5, 168.0; HRMS, m/z calcd for $C_{30}H_{24}O_8$ 512.1471, found 512.1476.

(B) Synthesis via 12. A solution of **12** (4:1 mixture of **12a** and **12b**) (70 mg, 0.14 mmol) and NBS (170 mg, 0.96 mmol) in CCl_4 (5 mL) containing catalytic amounts of dibenzoyl peroxide was heated at reflux for 6 h. After removal of succinimide by filtration the filtrate was concentrated in vacuo. To a solution of the residue in ether (10 mL) was added triethylamine (0.7 mL) and the mixture was refluxed for 5 h. After removal of triethylamine hydrobromide by filtration, the filtrate was evaporated. The residue was chromatographed on preparative TLC (silica gel, ether/hexane) to give **16** (40 mg, 58%).

Reaction of 6a with Singlet Oxygen. To a solution of a 1:1 adduct[7] of 0.34 g (1.1 mmol) of triphenyl phosphite and ozone in CH_2Cl_2 (2 mL) at −75 °C was added a solution of **6a** (0.16 g, 0.69 mmol) in CH_2Cl_2 (5 mL). The mixture was allowed to warm to −35 °C, stirred at this temperature for 2 h, and allowed to stand at room temperature overnight. Then, triethyl phosphite (0.115 g, 0.69 mmol) was added to the reaction mixture, followed by heating at reflux for 2 h. After the usual workup, the residue was chromatographed on preparative TLC (silica gel, benzene) to give **17** (60 mg, 35%), **18** (10 mg, 5%), and recovered **6a** (50 mg, 31%).

Compound **17** had the following properties: oil; IR (neat) 1675, 1595, 1450 cm^{-1}; ^1H NMR δ 2.03–3.06 (br m, 4 H, CH_2), 4.84–5.09 (br, 1 H, CH), 6.35–6.39 (br m, 1 H, olefinic H), 7.10–8.01 (m, 10 H, Ph); ^{13}C NMR δ 25.0, 30.8, 52.0, 124.7, 126.5, 127.3, 128.4, 128.5, 128.7, 133.1, 136.0, 136.9, 138.7, 198.3; HRMS, m/z calcd for $C_{18}H_{16}O$ 248.1201, found 248.1187.

Compound **18** had the following properties: oil; IR (neat) 1675, 1595, 1450 cm^{-1}; ^1H NMR δ 2.29–2.43 (m, 4 H, CH_2), 4.26–4.70 (m, 2 H, CH), 7.26–8.04 (m, 10 H, Ph); ^{13}C NMR δ 23.0, 42.5, 128.7, 133.3, 135.3, 199.6; HRMS, m/z calcd for $C_{18}H_{16}O_2$ 264.1149, found 264.1144.

Hydrogenation of 6a. The hydrogenation of **6a** (0.232 g, 1.0 mmol) was accomplished in 6 h in benzene/methanol (2/1, 15 mL) over Pt (PtO_2, 20 mg) at 2–3 atm of hydrogen pressure to afford 0.175 g (74%) of a 2.6:1 mixture of **20a** and **20b**. Samples of each were purified by preparative TLC (silica gel, hexane).

Product **20a** had the following properties: oil; IR (neat) 1600, 1495, 1450 cm^{-1}; ^1H NMR δ 1.40–2.28 (br, 4 H, CH_2), 2.28–3.08 (br, 2 H, CH), 2.79 (s, 4 H, PhCH_2), 7.20 (s, 10 H, Ph); HRMS, m/z calcd for $C_{18}H_{20}$ 236.1564, found 236.1533.

Product **20b** had the following properties: oil; IR (neat) 1600, 1495, 1450 cm^{-1}; ^1H NMR δ 1.28–2.28 (br, 4 H, CH_2), 2.28–3.00 (br, 2 H, CH), 2.77 (s, 4 H, PhCH_2), 7.18 (s, 10 H, Ph); HRMS, m/z calcd for $C_{18}H_{20}$ 236.1564, found 236.1581.

Hydrogenation of 6f. (A) Over a Platinum Catalyst. The hydrogenation of **6f** (0.42 g, 2.0 mmol) was similarly accomplished over Pt to give a mixture of **21** (42 mg, 10%), **22** (144 mg, 33%), and **23** (84 mg, 19%). Purified samples of each were composed of cis and trans isomers and had the following properties.

21: oil; IR (neat) 1595, 1505 cm^{-1}; ^1H NMR δ 1.48–2.27 (m, 4 H, cyclobutyl CH_2), 2.40–3.12 (br, 2 H, CH), 2.78 (s, 4 H, CH_2), 5.90–5.95 (m, 2 H), 6.21–6.29 (m, 2 H), 7.12–7.29 (m, 2 H).

22: oil; IR (neat) 1595, 1505, 1060 cm^{-1}; ^1H NMR δ 1.63–2.18 (m, 10 H, CH_2), 2.18–3.20 (br, 2 H, CH), 2.71 (s, 2 H, CH_2), 3.62–3.91 (m, 3 H, OCH_2 and OCH), 5.90–5.95 (m, 1 H), 6.20–6.29 (m, 1 H), 7.24–7.28 (m, 1 H); HRMS, m/z calcd for $C_{14}H_{20}O_2$ 220.1480, found 220.1464.

23: oil; IR (neat) 1460, 1065 cm^{-1}; ^1H NMR δ 1.40–2.20 (m, 16 H, CH_2), 2.20–3.20 (br, 2 H, CH), 3.20–4.20 (m, 6 H, OCH_2 and OCH); HRMS, m/z calcd for $C_{14}H_{24}O_2$ 224.1775, found 224.1759.

(B) Over a Palladium Catalyst. The hydrogenation of **6f** (0.21 g, 1.0 mmol) was similarly accomplished over Pd–C (10%, 20 mg) to give a 0.117 g (54%) yield of a 3:1 mixture of **21a** and **21b**, whose ratio was determined from the ^{13}C NMR spectra of the mixture.

The cis isomer **21a** had the following properties: ^{13}C NMR δ 24.6, 28.7, 35.7, 104.9, 110.0, 140.7, 155.1; HRMS, m/z calcd for $C_{14}H_{16}O_2$ 216.1151, found 216.1185.

The trans isomer **21b** had the following property: ^{13}C NMR δ 29.5, 33.8 40.5, 104.9, 110.0, 140.7, 154.8.

Acknowledgment. We are grateful for financial support of this work by a Grant-in-Aid for Scientific Research (60550596) from the Japan Ministry of Education, Science and Culture.

Registry No. **1**, 86046-73-3; **3**, 72726-66-0; **4a**, 100-52-7; **4b**, 104-55-2; **4c**, 555-16-8; **4d**, 66-77-3; **4e**, 642-31-9; **4f**, 98-03-3; **4g**, 98-01-1; **4h**, 123-72-8; **5a**, 103532-52-1; **5f**, 103532-53-2; **5g**, 103532-54-3; **5h**, 103532-58-7; **6a**, 94618-65-2; **6b**, 94618-66-3; **6c**, 103532-55-4; **6d**, 103532-56-5; **6e**, 103532-57-6; **6f**, 103532-50-9; **6g**, 103532-51-0; (*E*,*E*)-**6h**, 103532-59-8; (*E*,*Z*)-**6h**, 103532-60-1; **7**, 103532-49-6; **8a**, 941-69-5; **8b**, 624-48-6; **8c**, 141-05-9; **8d**, 623-91-6; **9**, 103617-35-2; **12a**, 103562-42-1; **12b**, 103532-62-3; **13a**, 103562-41-0; **13b**, 103532-63-4; **14a**, 103532-61-2; **14b**, 103532-64-5; **15**, 762-42-5; **16**, 94632-94-7; **17**, 103532-65-6; **18**, 70014-01-6; **20a**, 103532-66-7; **20b**, 103532-67-8; *cis*-**21**, 103532-68-9; *trans*-**21**, 103532-71-4; **22**, 103532-69-0; **23**, 103532-70-3; $HP(O)(OEt)_2$, 762-04-9.