January 1993 Chem. Pharm. Bull. 41(1) 97—107 (1993) 97

Cycloaddition Behavior of Cyclopentadienone toward Allylic Alcohols. Formation of Hydrophthalide Derivatives *via* Internal Addition of Alcohol Group to Bridged Carbonyl of *exo* [4+2]π Cycloadducts

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Received July 27, 1992

The cycloaddition behavior of 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (Ia) toward allylic alcohols (II) was investigated. The *exo* [4+2]π cycloadducts were transformed into hydrophthalide derivatives *via* intramolecular addition of the alcohol group to the strained bridged carbonyl. The *endo* [4+2]π cycloadducts underwent transesterification with the bridgehead methoxycarbonyl group to give the lactone derivatives. The structures of the products were determined on the basis of the ^{1}H- and ^{13}C-NMR spectral data and X-ray analyses. The reactivity of Ia toward allylic alcohols is discussed in terms of frontier molecular orbital (FMO) theory.

Keywords cyclopentadienone; cleavage reaction; stereoselectivity; Diels–Alder reaction; allylic alcohol; X-ray analysis

2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (Ia) is a powerful 4π-source and its cycloaddition behavior toward various dienophiles has been studied systematically.[1] On the other hand, Ia also shows high reactivity toward hydroxylic groups to give 1,4-addition (Michael reaction) products.[2] However, little is known about the cycloaddition of cyclopentadienones with unsaturated alcohols, though we recently examined the cycloaddition of Ia with some allylic alcohols.[3]

Here we wish to discuss the reaction in detail on the basis of the newly obtained data including X-ray analyses of the cycloadducts.

Results

Reactions of Ia with Allyl Alcohol (IIa), Methallyl Alcohol (IIb) and 3-Methyl-3-buten-1-ol (IIc) 2-Propen-1-ol (allyl alcohol) (IIa) reacted with Ia in refluxing chloroform to give three products (IIIa, IVa and IVa′). The elementary analysis data all agreed with the theoretical value for 1 : 1 adducts. In the infrared (IR) spectrum of the main product (IIIa), a characteristic absorption band was observed at 1800 cm^{-1} ascribable to a strained bridged carbonyl of the [4+2]π cycloadduct. The ^{13}C-NMR spectrum of IIIa supported this assignment.

Vicinal carbon–proton couplings have been utilized to assign stereochemistry in a variety of Diels–Alder adducts.[4,5] In the bicyclo[2.2.1]hepten-7-one (norbornene-7-one) system, the coupling between the *endo* methine proton (H_α) and the C_7-carbonyl carbon was readily discernible [J_{CH} = *ca.* 5—9 Hz, dihedral angle ϕ ($O=C_7–C_1–C_6–H$) = 160—170°], whereas the coupling between the carbonyl carbon and the *exo* proton (H_β) is essentially zero ($\phi = 90°$). In the ^{1}H–^{13}C long-range correlation (COSY) spectrum of IIIa, the absence of a correlation between the methine proton (>CH–CH_2OH) and the C_7-carbon indicates that the configuration of the hydroxymethyl group is *endo*.

The IR spectra of the products IVa and IVa′ did not

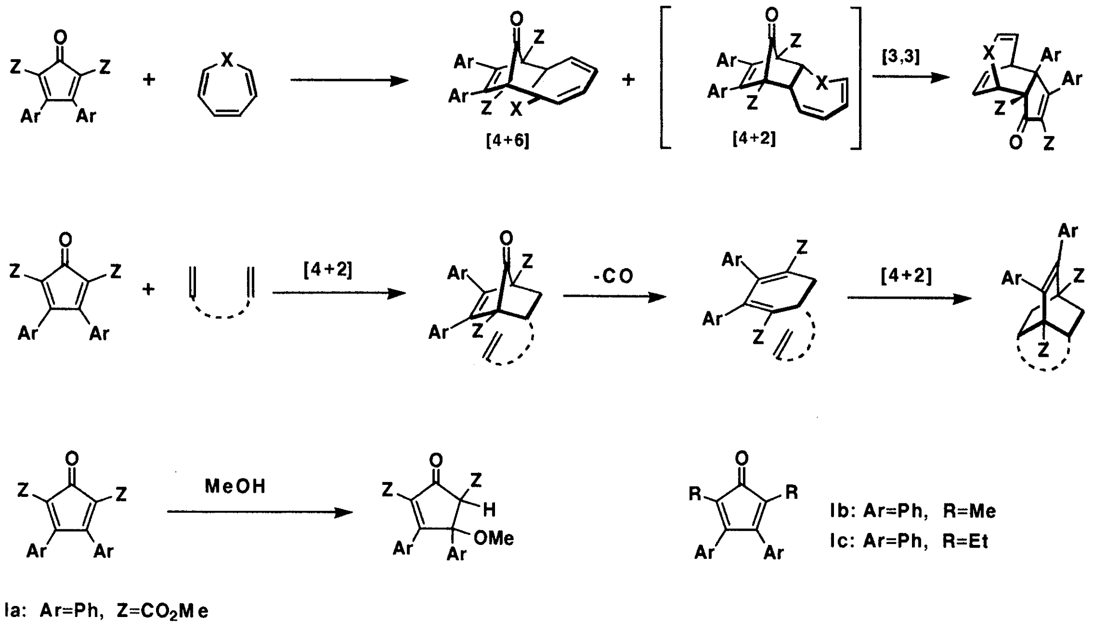

Chart 1

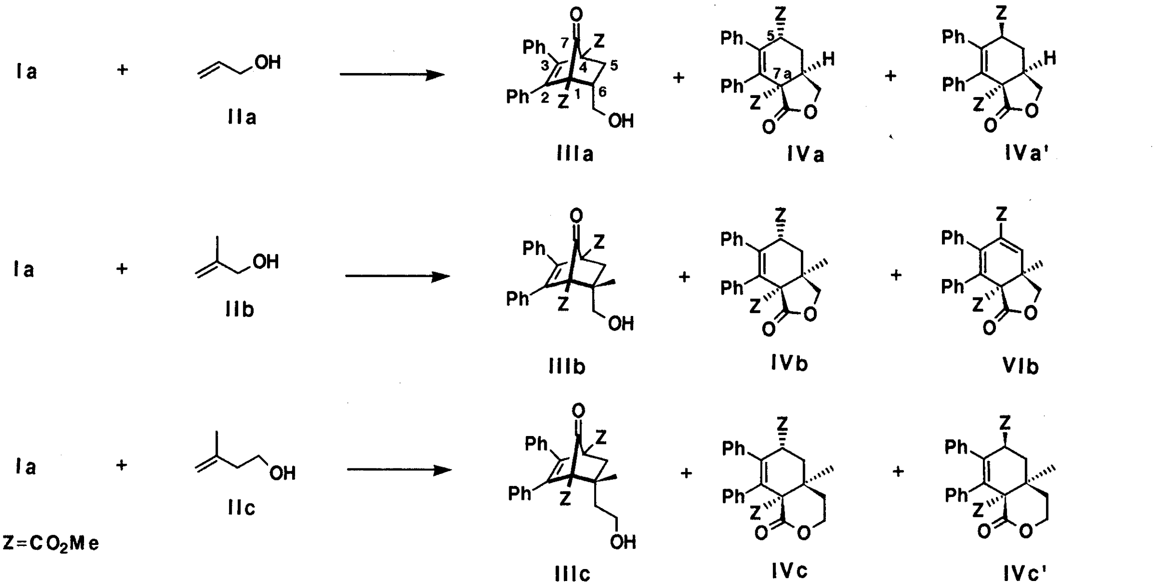

Chart 2

TABLE I. Products from Cycloaddition of Ia and Various Allylic and Homoallylic Alcohols

Diene	Alcohol	Compd.	Time (h)	mp (°C)	Yield (%)
Ia	IIa	IIIa	8[a]	164—166 (dec.)	42
		IVa		130—132	17
		IVa′		Oil	7
	IIb	IIIb	4[a]	113—115 (dec.)	43
		IVb		117—119	11
		VIb		167—168	18
	IIc	IIIc	6[a]	174—175 (dec.)	34
		IVc		Oil	27
		IVc′		171—172	29
	IId	IVd	5[a]	194—195	23
	IIe	IVe	6[a]	266—268	67
	IIf	IVf′	4[a]	134—135	19
	IIg	VIIg	12[a]	193—194 (dec.)	41
	IIh	Vh	20[a]	200—201 (dec.)	37
	IIi	Vi	10[a]	185—186 (dec.)	27
	IIj	Vj	20[a]	151—152 (dec.)	31
	IIk	IIIk	9[b]	172—174 (dec.)	16
	IIm	IIIm	6[a]	Oil	50
Ib	IId	VIIId	30[a]	Oil	55
Ic	IId		24[b]		no

a) $CHCl_3$, reflux. *b*) Toluene, reflux.

show the presence of a strained bridged carbonyl. The ^{1}H-NMR spectral pattern of compound IVa closely resemble that of IVa′, indicating that these compounds are stereoisomers at a carbon carrying a COOMe group. The IR spectra of IVa and IVa′ suggested the presence of five-membered lactone and ester groups. These facts suggest that the bridged carbonyl of the *exo* $[4+2]\pi$ cycloadduct was cleaved and linked with the *exo*-oriented hydroxymethyl group, resulting in a pair of isomeric hydrophthalide derivatives.

The configurations of the ester groups (whether the methoxycarbonyl is *cis* or *trans* with respect to the junction methoxycarbonyl group) were determined by the comparison of the ^{1}H-NMR spectral data with those for IVc and IVc′, whose stereo structure was determined by single crystal X-ray analysis (see below).

TABLE II. IR and Analytical Data of the Products

Compd.	IR (cm^{-1}) C=O			Formula	Analysis (%) Calcd (Found)	
	Ester	Lactone	Bridge		C	H
IIIa	1724		1806	$C_{24}H_{22}O_6$	70.93	5.46
					(70.53	5.57)
IVa	1738	1780		$C_{24}H_{22}O_6$	70.93	5.46
					(70.36	5.34)
IIIb	1736		1800	$C_{25}H_{24}O_6$	71.42	5.75
					(71.48	5.91)
IVb	1738	1788		$C_{25}H_{24}O_6$	High MS[a]	
VIb	1724	1776		$C_{25}H_{22}O_6$	71.76	5.30
	1748				(71.09	5.35)
IIIc	1736		1794	$C_{26}H_{26}O_6$	71.87	6.03
					(72.16	6.01)
IVc	1738	1738		$C_{26}H_{26}O_6$	High MS[b]	
IVc′	1736	1736		$C_{26}H_{26}O_6$	71.87	6.03
					(71.35	6.15)
IVd	1722	1786		$C_{30}H_{26}O_6$	74.67	5.43
					(74.44	5.42)
VIIId			1768	$C_{28}H_{26}O_2$	High MS[c]	
IVe	1740	1776		$C_{24}H_{20}O_6$	71.27	4.49
					(70.78	4.85)
IVf′	1736	1736		$C_{28}H_{28}O_6$	High MS[d]	
VIIg	1730	1770	1790	$C_{24}H_{20}O_5$	74.21	5.19
					(74.47	5.21)
Vh	1738	1764	1800	$C_{29}H_{28}O_5$	76.30	6.18
					(75.97	6.16)
Vi	1730	1770	1790	$C_{25}H_{22}O_5$	74.61	5.51
					(74.43	5.36)
Vj	1732	1774	1814	$C_{30}H_{30}O_5$	76.57	6.43
					(76.26	6.36)
IIIk	1732		1796	$C_{31}H_{34}O_6$	74.09	6.82
					(73.87	6.94)
IIIm	1738		1800	$C_{30}H_{26}O_6$	High MS[e]	

a) Calcd for $C_{25}H_{24}O_6$: 420.1557. Found: 420.1573. *b*) Calcd for $C_{26}H_{26}O_6$: 434.1712. Found: 434.1729. *c*) Calcd for $C_{28}H_{26}O_2$: 394.1955. Found: 395.1933. *d*) Calcd for $C_{28}H_{28}O_6$: 460.1909. Found: 460.1886. *e*) Calcd for $C_{30}H_{26}O_6$: 482.5328. Found: 482.5310.

In the ^{1}H-NMR spectra of the cleaved products obtained in this study, there is a characteristic spectral feature which can provides a clue for clarification of the *cis*/*trans* nature

TABLE III. The ^{1}H-NMR Spectral Data of the Products

Compd.	^{1}H-NMR (in CDCl$_3$) ppm
IIIa	7.26—7.08 (10H, m, two Ph), 3.72 (2H, m, O–CH$_2$–), 3.67, 3.63 (6H, both s, two MeO), 3.20 [1H, m, >CH– (*exo*)], 2.81 [1H, dd, *J*=10.26, 12.46 Hz, >CH–$\underline{\mathrm{H}}$ (*exo*)], 1.41 [1H, dd, *J*=5.86, 12.46 Hz, >CH–$\underline{\mathrm{H}}$ (*endo*)]
IVa	7.29—6.93 (10H, m, two Ph), 4.37, 3.68 (2H, m, O–CH$_2$–), 4.10 (1H, dd, *J*=2.20, 9.52 Hz, >CH–COO–), 3.69, 3.61 (6H, both s, two MeO), 3.37 (1H, m, >CH–), 2.42, 2.10 (2H, m, –CH$_2$–)
IVa′	7.29—6.93 (10H, m, two Ph), 4.35 (1H, dd, *J*=5.13, 9.53 Hz, O–CH$_2$–), 4.18 (1H, dd, *J*=1.47, 8.06 Hz, >CH–COO–), 3.92 (1H, dd, *J*=5.13, 10.99 Hz, O–CH$_2$–), 3.42, 3.33 (6H, both s, two MeO), 3.18 (1H, m, >CH–), 2.34 (1H, m, >CH–$\underline{\mathrm{H}}$), 2.22 (1H, m, >CH–$\underline{\mathrm{H}}$)
IIIb	7.26—7.08 (10H, m, two Ph), 3.89 (1H, d, *J*=11.63 Hz, O–CH$_2$–), 3.68, 3.62 (6H, both s, two MeO), 3.46 (1H, d, *J*=11.36 Hz, O–CH$_2$–), 2.38 [1H, d, *J*=12.83 Hz, >CH–$\underline{\mathrm{H}}$ (*exo*)], 1.69 [1H, d, *J*=12.83 Hz, >CH–$\underline{\mathrm{H}}$ (*endo*)], 1.44 (3H, s, Me)
IVb	7.08—6.84 (10H, m, two Ph), 4.38 (1H, d, *J*=8.79 Hz, O–CH$_2$–), 3.99 (1H, d, *J*=8.79 Hz, O–CH$_2$–), 3.88, 3.40 (6H, both s, two MeO), 3.85 (1H, dd, *J*=6.59, 10.26 Hz, >CH–COO–), 2.48 (1H, dd, *J*=10.26, 14.65 Hz, >CH–$\underline{\mathrm{H}}$), 2.12 (1H, dd, *J*=6.59, 13.92 Hz, >CH–$\underline{\mathrm{H}}$), 1.26 (3H, s, Me)
VIb	7.09—6.92 (10H, m, two Ph), 6.44 (1H, s, =CH–), 4.44 (1H, d, *J*=8.80 Hz, O–CH$_2$–), 4.20 (1H, d, *J*=8.80 Hz, O–CH$_2$–), 3.39, 3.33 (6H, both s, two MeO), 1.31 (3H, s, Me)
IIIc	7.26—7.00 (10H, m, two Ph), 3.81 (2H, m, O–CH$_2$–), 3.63, 3.60 (6H, both s, two MeO), 2.39, 1.82 (2H, m, –CH$_2$–), 2.38 [1H, d, *J*=12.46, >CH–$\underline{\mathrm{H}}$ (*exo*)], 2.14 [1H, d, *J*=12.46, >CH–$\underline{\mathrm{H}}$ (*endo*)], 1.35 (3H, s, Me)
IVc	7.36—6.94 (10H, m, two Ph), 4.47 (2H, m, O–CH$_2$–), 3.86, 3.39 (6H, both s, two MeO), 3.84 (1H, dd, *J*=7.33, 10.26 Hz, >CH–COO–), 2.59 (1H, m, O–CH$_2$C$\underline{\mathrm{H}}_2$), 2.21 (1H, dd, 10.26, 13.92 Hz, >CH–$\underline{\mathrm{H}}$), 2.00 (1H, dd, *J*=7.33, 13.92 Hz, >CH–$\underline{\mathrm{H}}$), 1.67 (1H, m, O–CH$_2$C$\underline{\mathrm{H}}_2$), 1.37 (3H, s, Me)
IVc′	7.07—6.96 (10H, m, two Ph), 4.53—4.38 (2H, m, O–CH$_2$–), 3.94 (1H, dd, *J*=6.96, 10.63 Hz, >CH–COO–), 3.37, 3.22 (6H, both s, two MeO), 2.26 (1H, dd, *J*=10.63, 13.55 Hz, >CH–$\underline{\mathrm{H}}$), 2.05—1.91 (3H, m, >CH–$\underline{\mathrm{H}}$ and –CH$_2$), 1.55 (3H, s, Me)
IVd	7.39—6.96 (15H, m, three Ph), 4.06 (2H, m, O–CH$_2$–), 3.96 (1H, d, *J*=9.53 Hz, >CH–COO–), 3.42, 3.07 (6H, both s, two MeO), 3.38 (2H, m, >CH– and Ph–CH<)
VIIId	7.38—6.25 (15H, m, three Ph), 3.77 (2H, m, O–CH$_2$–), 3.16 [1H, d, *J*=6.60 Hz, >CH–$\underline{\mathrm{H}}$ (*exo*)], 2.56 [1H, dd, 6.60, 11.73 Hz, >CH–$\underline{\mathrm{H}}$ (*endo*)], 1.36, 1.20 (6H, both s, two Me)
IVe	7.13—6.93 (10H, m, two Ph), 4.51—4.43 (2H, m, O–CH$_2$ and O–CH$_2$), 4.37—4.26 (2H, m, O–CH$_2$ and O–CH$_2$), 3.81 (1H, d, *J*=8.06 Hz, >CH–COO–), 3.73 (3H, s, MeO), 3.48 (1H, m, –CH<), 3.32 (1H, m, –CH<)
IVf′	7.06—6.96 (10H, m, two Ph), 5.83—5.74 (1H, m, =CH–), 5.16—5.12 (2H, m, =CH$_2$), 4.18 (1H, m, >CH–O), 3.86 (1H, dd, *J*=6.60, 10.99 Hz, >CH–COO–), 3.34, 3.14 (6H, both s, two MeO), 3.17 (1H, m, >CH–), 2.41—2.33 (3H, m, –CH$_2$– and >CH–$\underline{\mathrm{H}}$), 2.17 (1H, ddd, *J*=3.66, 6.60, 13.92 Hz, >CH–$\underline{\mathrm{H}}$), 1.97 (1H, ddd, *J*=2.93, 10.99, 13.92 Hz, >CH–$\underline{\mathrm{H}}$), 1.50 (1H, ddd, *J*=3.66, 10.73, 14.65 Hz, >CH–$\underline{\mathrm{H}}$)
VIIg	7.40—7.03 (10H, m, two Ph), 4.66 (1H, dd, *J*=8.06, 9.53 Hz, O–CH$_2$–), 4.10 (1H, dd, *J*=9.52, 10.26 Hz, O–CH$_2$–), 3.55 (3H, s, MeO), 2.98 [1H, m, >C$\underline{\mathrm{H}}$–Me (*endo*)], 2.44 [1H, m, >CH– (*exo*)], 1.47 (3H, d, *J*=6.59 Hz, Me)
Vh	7.37—7.09 (10H, m, two Ph), 4.91 (1H, m, O–CH<), 3.44 (3H, s, MeO), 2.47 [1H, d, *J*=9.16 Hz, >CH– (*endo*)], 2.11 (1H, d, *J*=15.02 Hz, >CH–$\underline{\mathrm{H}}$), 1.96 (1H, m, >CH–$\underline{\mathrm{H}}$), 1.68, 1.02, 1.01 (9H, s, 3-Me), 1.46 (1H, d, *J*=15.02 Hz, >CH–$\underline{\mathrm{H}}$), 1.17 (1H, >CH–$\underline{\mathrm{H}}$)
Vi	7.32—7.08 (10H, m, two Ph), 4.48 (1H, dd, *J*=8.79, 9.89 Hz, O–CH$_2$), 4.24 (1H, dd, *J*=9.89, 10.62 Hz, O–CH$_2$), 3.46 (3H, s, MeO), 2.60 [1H, dd, *J*=8.79, 10.62 Hz, >CH– (*endo*)], 1.56, 1.42 (6H, both s, two Me)
Vj	7.35—7.07 (10H, m, two Ph), 5.11 (1H, m, =CH–), 4.41 (1H, dd, *J*=8.80, 9.89 Hz, O–CH$_2$–), 4.19 (1H, dd, *J*=9.89, 10.63 Hz, O–CH$_2$–), 3.43 (3H, s, MeO), 2.67 [1H, dd, *J*=8.79, 10.62 Hz, >CH– (*endo*)], 2.43, 2.17, 1.93, 1.52 (4H, m, –CH$_2$–CH$_2$–), 1.70, 1.62, 1.38 (9H, s, three Me)
IIIk	7.19—7.04 (10H, m, two Ph), 5.85 (1H, m, =CH–), 5.18 (1H, dd, *J*=7.33, 17.22 Hz, =CH–$\underline{\mathrm{H}}$), 5.06 (1H, dd, *J*=7.33, 17.22 Hz, =CH–$\underline{\mathrm{H}}$), 3.63, 3.57 (6H, both s, two MeO), 2.46 [1H, m, >CH (*exo*)], 1.81, 1.69, 1.58 (4H, m, –CH$_2$–CH$_2$–), 1.39, 1.37, 1.26 (9H, s, three Me)
IIIm	7.25–6.82 (14H, m, aromatic H), 3.69—3.65 (6H, both s, two MeO), 3.42 (1H, br d, 13.92 Hz, >CH$_2$), 2.72 [1H, m, >CH–$\underline{\mathrm{H}}$ (*exo*)], 2.52 [1H, dd, *J*=3.66, 12.46 Hz, >CH– (*exo*)], 2.44 (1H, dd, *J*=11.36, 13.92 Hz, >CH$_2$), 2.21 [1H, dd, *J*=10.26, 12.46 Hz, >CH– (*endo*)]

of the two COOMe groups. Selected ^{1}H-NMR data are given in Table V. The molecular model of each isomer tells us that the *trans* products have magnetically equivalent COOMe groups (equatorial–equatorial), whereas in the *cis* products, the two COOMe groups are nonequivalent, one lying far from the shielding zone of the adjacent phenyl ring (axial–equatorial). The anisotropic influence on the allylic methine proton in the *cis* and *trans* isomers is opposite to that on the COOMe groups: the allylic methine proton of IVa resonates at 4.10 ppm whereas that of IVa′ resonates at 4.18 ppm. From these facts, we can safely say that the two COOMe groups take *cis* configuration with respect to each other in IVa and *trans* configuration in IVa′.

In the reaction of Ia with 2-methylallyl (methallyl) alcohol (IIb), similar behavior was observed. The primary cycloadduct (IIIb) was obtained in 43% yield. The *endo* nature of IIIb was determined on the basis of the ^{1}H–^{13}C COSY spectral behavior as mentioned above. The cleaved products (IVb and VIb) are considered to be derived from the *exo* [4+2]π cycloadducts. The configuration of the COOMe groups of IVb was determined to be *cis* from the ^{1}H-NMR spectral behavior as described above. The methyl groups resonate at 3.40 and 3.88 ppm, respectively. The higher-field methyl signal is assignable to the angular COOMe, which is closer to the benzene ring than the lower one. This assignment is supported by the fact that the allylic proton appeared at 3.85 ppm, higher field than those of the *trans* isomers. Compound VIb is assumed to be the dehydrogenation product of the *trans* cleaved product (IVb′). The MS and ^{1}H-NMR spectrum of VIb support this assignment. In the presence of a radical inhibitor, *i.e.*, hydroquinone, the yield of VIb was decreased, suggesting that a radical may intervene in the cleavage reaction.

Next, we studied the reaction behavior of a homoallylic alcohol. In the reaction of Ia with 3-methyl-3-buten-1-ol (IIc), the primary [4+2]π cycloadduct (IIIc) and two kinds

Table IV. The ^{13}C-NMR Spectral Data of the Products

Compd.	^{13}C-NMR (in $CDCl_3$) ppm
IIIa	190.2, 169.9, 167.1 (s, C=O), 68.5, 64.6 (s, $>\underline{C}$–CO), 64.2 (t, O–CH_2–), 52.9, 52.4 (q, MeO), 39.5 (d, >CH–), 29.8 (t, –CH_2–)
IVa	172.9, 171.9, 169.4 (s, C=O), 69.8 (t, O–CH_2–), 60.8 (s, $>\underline{C}$–CO), 53.0, 51.8 (q, MeO), 47.2 (d, $>\underline{C}$H–CO), 40.1 (d, >CH–), 27.2 (t, –CH_2–)
IIIb	189.5, 169.7, 167.5 (s, C=O), 72.3, 64.0 (s, $>\underline{C}$–CO), 68.3 (t, O–CH_2–), 52.7, 52.3 (q, MeO), 44.1 (s, >C<), 39.0 (t, –CH_2–), 21.1 (q, Me)
IVb	172.8, 169.7, 168.0 (s, C=O), 73.0 (t, O–CH_2–), 62.9 (s, $>\underline{C}$–CO), 52.8, 52.0 (q, MeO), 45.5 (d, $>\underline{C}$–CO), 42.1 (s, >C<), 30.2 (t, –CH_2–), 24.1 (q, Me)
VIb	173.0, 167.5, 166.8 (s, C=O), 136.4 (d, =CH–), 76.5 (t, O–CH_2–), 52.6, 51.8 (q, MeO), 47.2 (s, >C<), 18.2 (q, Me)
IIIc	190.9, 167.9, 167.4 (s, C=O), 72.0, 64.2 (s, $>\underline{C}$–CO), 59.1 (t, O–CH_2–), 52.2, 51.7 (q, MeO), 41.8, 41.0 (t, –CH_2–), 22.9 (q, Me)
IVc	173.1, 169.2, 166.8 (s, C=O), 65.9 (s, $>\underline{C}$–CO), 65.7 (t, O–CH_2–), 52.7, 51.9 (q, MeO), 46.0 (d, $>\underline{C}$H–CO), 35.7 (t, –CH_2–), 25.9 (q, Me)
IVc′	173.2, 169.5, 168.8 (s, C=O), 65.7 (s, $>\underline{C}$–CO), 65.0 (t, O–CH_2–), 52.1, 52.0 (q, MeO), 46.9 (d, $>\underline{C}$H–CO), 37.0, 34.1 (t, –CH_2–), 23.5 (q, Me)
IVd	171.9, 171.5, 169.3 (s, C=O), 67.4 (t, O–CH_2–), 62.3 (s, $>\underline{C}$–CO), 55.5 (d, $>\underline{C}$H–CO), 53.1, 51.5 (q, MeO), 45.3, 43.5 (d, >CH–)
VIIId	206.3 (s, C=O), 62.0 (t, O–CH_2–), 60.0, 55.0 (s, >C<), 51.1, 50.3 (d, >CH–), 11.1, 9.6 (q, Me)
IVe	173.4, 170.1, 168.5 (s, C=O), 67.8, 66.1 (t, O–CH_2–), 58.9 (s, $>\underline{C}$–CO), 53.4 (q, MeO), 42.7 (d, $>\underline{C}$H–CO), 42.7, 32.5 (d, >CH–)
IVf′	172.8, 169.8, 169.6 (s, C=O), 131.4 (d, =CH–), 118.7 (t, =CH_2), 75.4 (d, >CH–O), 61.6 (s, $>\underline{C}$–CO), 52.5, 51.7 (q, MeO), 48.8 (d, $>\underline{C}$H–CO), 39.8, 33.8, 32.4 (t, –CH_2–), 33.4 (d, >CH–)
VIIg	188.7, 167.3, 167.2 (s, C=O), 71.1, 66.0 (s, $>\underline{C}$–CO), 70.3 (t, O–CH_2–), 52.4 (q, MeO), 49.9, 38.0 (d, >CH–), 18.9 (q, Me)
Vh	189.3, 167.3, 167.0 (s, C=O), 77.1 (d, >CH–O), 64.8 (s, $>\underline{C}$–CO), 51.9 (q, MeO), 50.3 (d, >CH–), 47.2, 40.1 (t, –CH_2–), 42.5, 32.4 (s, >C<), 32.3, 29.6, 25.2 (q, Me)
Vi	188.5, 167.9, 167.0 (s, C=O), 74.0, 65.3 (s, $>\underline{C}$–CO), 67.6 (t, O–CH_2–), 52.5 (d, >CH–), 52.2 (q, MeO), 41.1 (s, >C<), 28.6, 21.6 (q, Me)
Vj	187.9, 167.6, 166.8 (s, C=O), 123.0 (d, =CH–), 74.8, 65.0 (s, $>\underline{C}$–CO), 67.9 (t, O–CH_2–), 52.0 (q, MeO), 50.3 (d, >CH–), 44.3 (s, >C<), 39.5, 22.7 (t, –CH_2–), 25.7, 18.1, 17.8 (q, Me)
IIIk	191.6, 168.2, 167.3 (s, C=O), 144.7 (d, =CH–), 111.9 (t, =CH_2), 73.1, 71.8, 62.9 (s, $>\underline{C}$–CO, $>\underline{C}$–OH), 52.1, 51.6 (q, MeO), 49.8 (d, >CH–), 43.7 (s, >C<), 42.2, 23.5 (t, –CH_2–), 28.6, 27.9, 20.0 (q, Me)
IIIm	191.5, 168.5, 168.0 (s, C=O), 68.2, 64.0 (s, >C<), 52.6, 52.4 (q, MeO), 38.9 (d, >CH–), 34.1, 33.1 (t, –CH_2–)

Table V. Chemical Shifts of the Methoxycarbonyl Groups and the Allylic Methine Protons in Some Cleaved Products of the *exo* Cycloadducts

Compound	Chemical shift (ppm)					
	C_{7a}-COOMe		C_5-COOMe		C_5-H	
IVa cis	3.61		3.69		4.10	
trans		3.42		3.33		4.18
IVb *cis*	3.40		3.88		3.85	
IVc *cis*	3.39		3.86		3.84	
trans		3.37		3.22		3.94
IVf′ *trans*		3.34		3.14		3.86

of the cleaved products (IVc and IVc′) were obtained.

The primary cycloadduct (IIIc) was determined to be the *endo* [4+2]π cycloadduct on the basis of its ^{1}H–^{13}C COSY spectral behavior.

Compounds IVc and IVc′, having a six-membered lactone, are considered to be derived from the *exo* [4+2]π cycloadduct.

Reactions of Ia with Cinnamyl Alcohol (IId), (2*Z*)-2-Butene-1,4-diol (IIe) and 1-Allyl-3-buten-1-ol (IIf) (2*E*)-3-Phenylpropen-1-ol (cinnamyl alcohol) (IId) reacted with Ia in refluxing chloroform to give the cleaved product (IVd). The ^{13}C-NMR spectal data supported the formation of IVd. The methyl protons of the angular COOMe group resonate at 3.42 ppm and the other methyl protons resonate at 3.07 ppm. The latter is considerably higher than has been observed in other cases. This may be due to the shielding effect of the *cis* oriented phenyl group. In the reaction, as a secondary orbital interaction[6] between the phenyl group of IId and Ia is operative, the phenyl group takes an *endo* orientation in the primary [4+2]π cycloadduct, obliging the hydroxymethyl group to take an *exo* orientation.

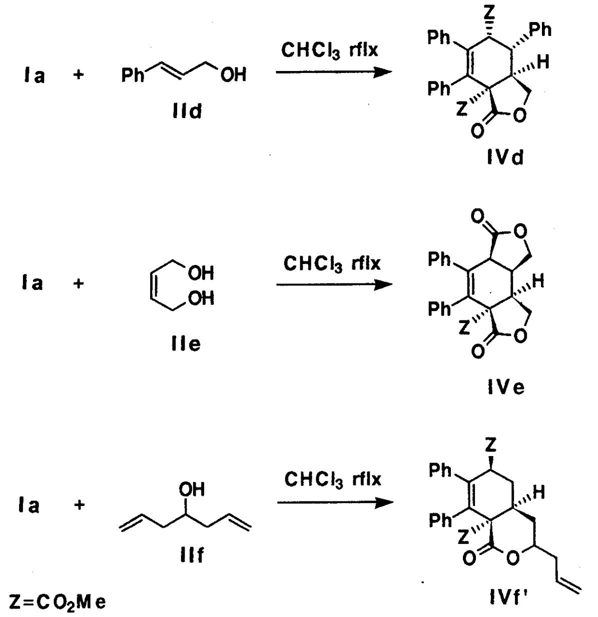

Chart 3

In the reaction of Ia with (2*Z*)-2-butene-1,4-diol (IIe), the bislactone derivative (IVe) was produced in 67% yield, indicating the *exo* addition to be predominant. Taking *cis* configuration of the dienophile into consideration, the structure of IVe could be unequivocally determined to be as depicted in Chart 3, with the two lactone groups in *cis* disposition. The additional lactone was considered to be formed by transesterification of the COOMe group with the *cis*-oriented hydroxymethyl function.

Another type of secondary homoallylic alcohol (IIf) afforded the *trans*-type cleaved product (IVf′). The spectral feature of IVf′ are similar to those of IVc′. The dimethoxycarbonyl groups resonate at 3.34 and 3.14 ppm and the allylic methine proton appears at 3.86 ppm, having a splitting pattern ($J=6.6$, 11 Hz) consistent with that observed in IVc′.

Reactions of Ia with Crotyl Alcohol (IIg), Isophorol (IIh), 3,3-Dimethylallyl Alcohol (IIi), Geraniol (IIj), Linalool (IIk) and 2-Allylphenol (IIm) The product (VIIg) of the reaction of Ia with IIg is unstable and gradually transformed to an unidentified compound during chromatography on slica gel. The IR and ^{13}C-NMR spectra of the crude product indicated the presence of three types of carbonyl groups, *i.e.*, bridged ketone, five-membered lactone and ester, suggesting that the *endo*-oriented hydroxymethyl group had undergone transesterification with COOMe to give an energetically unstable *trans*-type five-membered lactone.

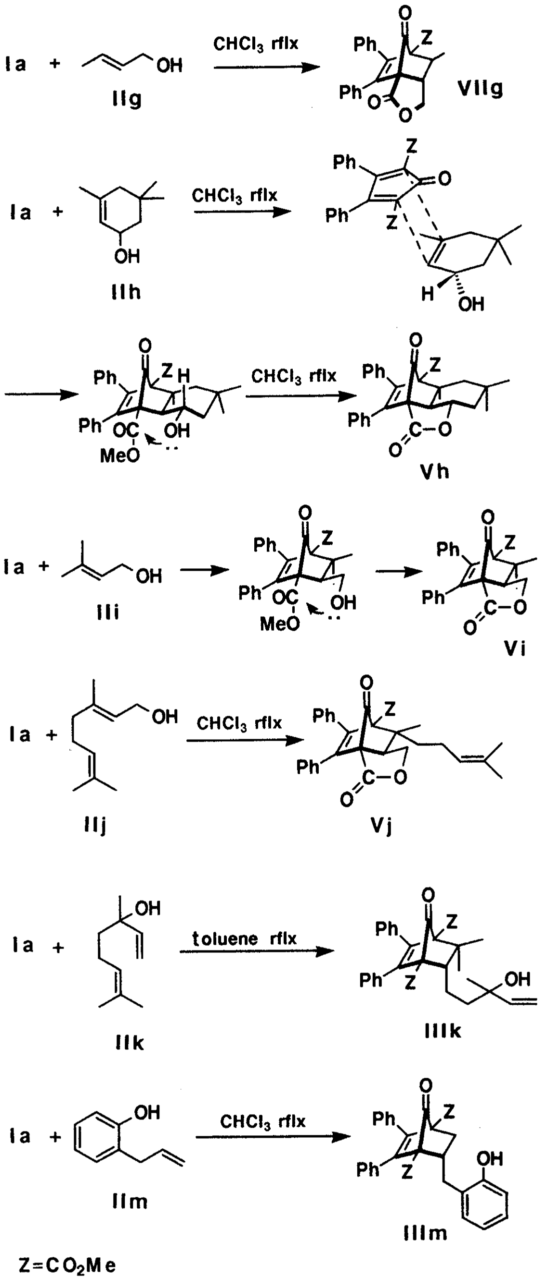

Chart 4

Allylic alcohols (IIh—j) reacted with Ia to give the primary [4+2]π cycloadducts as isolable products. Each of the [4+2]π cycloadducts has a lactone group formed by transesterification of the COOMe group with the hydroxymethyl group. The *exo*/*endo* nature of the cycloadducts was determined on the basis of the ^{1}H–^{13}C COSY spectral data (see Chart 4). In the reaction with 3,5,5-trimethyl-2-cyclohexenol (isophorol) (IIh), the [4+2]π cycloadduct (Vh) was produced. The ^{1}H–^{13}C COSY spectrum showed the presence of coupling between the bridged junction proton (*endo*) and the carbonyl carbon [Hα-C(7)], indicating that Vh is the *exo* adduct, in which the cyclohexane ring takes *exo* orientation. The coupling constant ($J=9$ Hz) between >CH– and >CH–O implies that the two protons are diaxial (*trans*-coplanar).

3,3-Dimethylallyl alcohol (IIi) reacted with Ia to give the [4+2]π cycloadduct (Vi), in which the *exo*-oriented hydroxymethyl group is linked with the COOMe group, in 27% yield. In the case of geraniol (IIj), the [4+2]π cycloadduct (Vj) was obtained, *i.e.*, the allylic alcohol moiety reacted with Ia. The ^{1}H–^{13}C COSY spectral data of Vi and Vj suggest that each of the lactone moieties is *exo*-oriented. The single crystal X-ray analysis of Vj indicates that the 4,4-dimethyl-3-butenyl moiety is *endo*-oriented, and the *exo*-oriented hydroxymethyl group reacted with the COOMe group to form the lactone derivative.

Linalool (IIk) did not react at the allylic alcohol moiety but reacted at the dimethylallyl moiety to give IIIk.

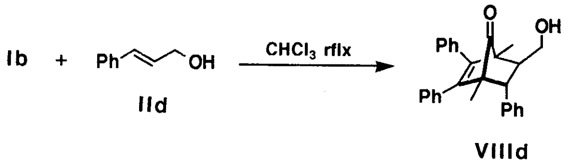

Chart 5

Table VI. Crystal Data and Intensity Measurements

Compd.	IVc′	Vj
Formula	$C_{26}H_{26}O_6$	$C_{30}H_{30}O_5$
Molecular weight	434.5	470.6
Crystal system	Triclinic	Triclinic
Lattice parameters		
a (Å)	14.445 (20)	11.693 (11)
b (Å)	15.928 (21)	11.807 (11)
c (Å)	11.221 (15)	9.660 (12)
α (°)	67.45 (9)	89.88 (9)
β (°)	115.10 (10)	110.04 (8)
γ (°)	114.54 (9)	90.49 (8)
V (Å^3)	2242 (6)	1253 (2)
Space group	$P\bar{1}$	$P\bar{1}$
Z value	4	2
D_c (gcm^{-3})	1.288	1.248
D_m (gcm^{-3})	1.286	1.245
Solvent	Ethanol–acetone	
Radiation	MoK_α radiation ($\lambda=0.7107$ Å)	
	40 kV–25 mA	35 kV–15 mA
No. of reflections		
Collected	4219 ($2\theta<55°$)	4309 ($2\theta<60°$)
Used for refinement ($F_O>3.0\sigma F$, $2\theta<55°$)	2897	3194
R value	0.060	0.060

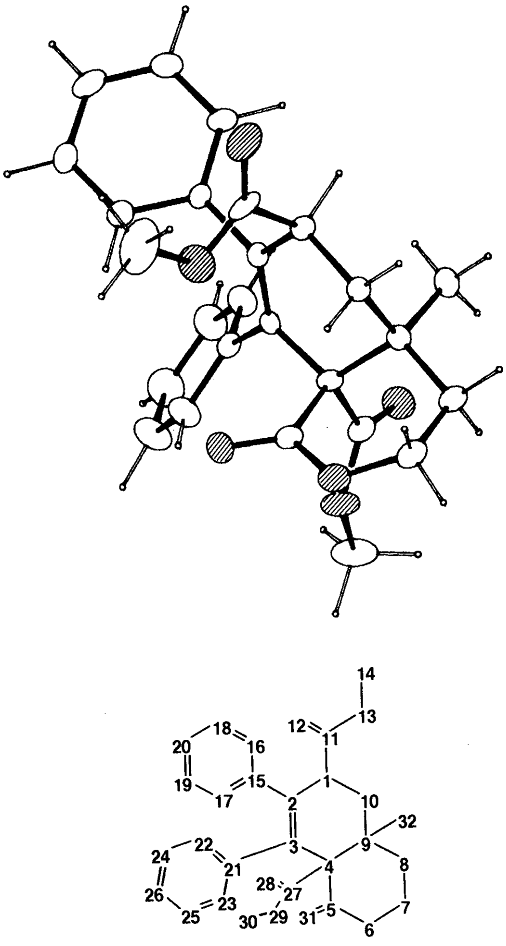

Fig. 1. Crystal Structure of IVc′

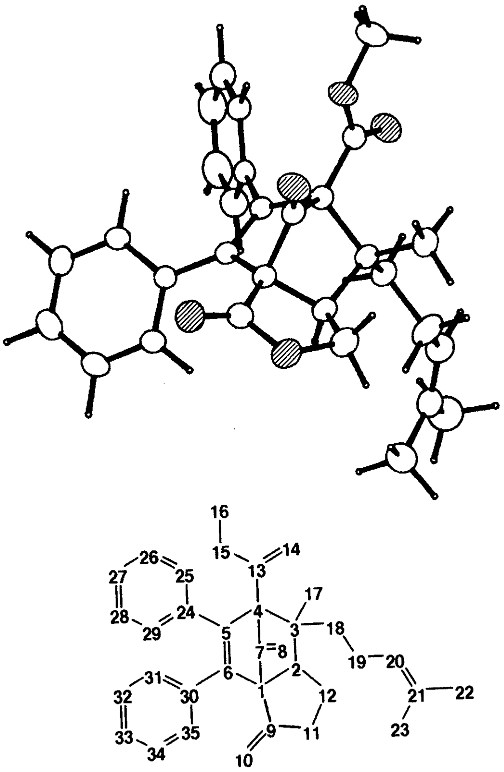

Fig. 2. Crystal Structure of Vj

Table VII. Fractional Atomic Coordinates[a] and Isotropic Temperature Factors (B) of IVc′ for Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	B[b]
C01	5916 (4)	7505 (4)	10799 (5)	3.24 (23)
C02	5252 (4)	7340 (4)	9497 (5)	2.92 (23)
C03	5542 (4)	7869 (4)	8480 (5)	2.85 (22)
C04	6577 (4)	8698 (4)	8576 (5)	2.66 (22)
C05	6325 (5)	9615 (4)	8338 (5)	3.66 (25)
O06	7145 (3)	10379 (3)	8681 (4)	4.88 (19)
C07	8148 (5)	10298 (5)	9667 (6)	5.37 (30)
C08	8412 (5)	9413 (5)	9921 (5)	4.55 (28)
C09	7443 (4)	8528 (4)	9893 (5)	3.35 (24)
C10	6896 (4)	8381 (4)	10819 (5)	3.56 (24)
C11	5210 (5)	7609 (5)	11356 (5)	5.17 (29)
O12	5059 (4)	7079 (5)	12317 (5)	8.77 (29)
O13	4772 (5)	8292 (4)	10644 (5)	7.46 (29)
C14	4090 (8)	8455 (9)	11098 (11)	10.83 (69)
C15	4238 (4)	6523 (4)	9484 (5)	3.08 (23)
C16	4281 (5)	5626 (4)	10230 (6)	4.03 (26)
C17	3253 (5)	6654 (4)	8773 (6)	4.30 (26)
C18	3338 (6)	4883 (5)	10263 (6)	5.08 (32)
C19	2309 (5)	5906 (5)	8824 (6)	5.35 (31)
C20	2348 (5)	5023 (5)	9556 (6)	4.98 (29)
C21	4927 (4)	7637 (4)	7234 (5)	3.10 (23)
C22	4816 (5)	6789 (4)	7078 (6)	4.18 (28)
C23	4519 (6)	8303 (5)	6180 (6)	5.25 (31)
C24	4308 (6)	6594 (6)	5902 (7)	6.00 (36)
C25	4022 (6)	8112 (5)	5027 (6)	6.33 (35)
C26	3922 (6)	7271 (6)	4889 (6)	6.61 (37)
C27	7006 (5)	8842 (4)	7524 (5)	3.87 (25)
O28	7296 (4)	8263 (3)	7474 (4)	5.28 (22)
O29	6958 (4)	9655 (3)	6682 (4)	5.53 (22)
C30	7177 (8)	9779 (6)	5549 (7)	7.60 (45)
O31	5448 (3)	9712 (3)	7817 (4)	4.77 (19)
C32	7803 (5)	7664 (5)	10203 (5)	4.33 (28)
C01′	905 (4)	2499 (4)	12615 (5)	3.33 (24)
C02′	247 (4)	2342 (4)	13410 (4)	2.86 (22)
C03′	545 (4)	2863 (4)	14202 (4)	2.63 (21)
C04′	1575 (4)	3706 (4)	14300 (5)	3.11 (23)
C05′	1332 (5)	4628 (4)	13375 (5)	3.48 (24)
O06′	2148 (3)	5379 (3)	13077 (4)	4.79 (18)
C07′	3149 (5)	5308 (5)	13185 (6)	4.92 (30)
C08′	3410 (5)	4422 (5)	14073 (6)	4.31 (27)
C09′	2443 (4)	3536 (4)	14025 (5)	3.47 (25)
C10′	1897 (4)	3378 (4)	12696 (5)	3.34 (25)
C11′	201 (5)	2612 (5)	11247 (6)	4.98 (31)
O12′	56 (4)	2085 (4)	10667 (5)	8.25 (30)
O13′	−216 (4)	3309 (4)	10834 (4)	7.07 (25)
C14′	−899 (8)	3453 (8)	9542 (7)	10.92 (51)
C15′	−754 (4)	1521 (4)	13240 (4)	2.86 (21)
C16′	−1753 (5)	1653 (5)	12814 (6)	4.58 (28)
C17′	−725 (5)	620 (4)	13424 (5)	4.00 (26)
C18′	−2692 (5)	903 (5)	12584 (6)	5.16 (31)
C19′	−1666 (5)	−114 (5)	13187 (6)	4.70 (29)
C20′	−2639 (5)	21 (5)	12778 (6)	5.04 (29)
C21′	−80 (4)	2648 (4)	15041 (5)	3.34 (23)
C22′	−176 (5)	1793 (5)	15944 (6)	4.69 (30)
C23′	−477 (6)	3303 (5)	15041 (6)	5.13 (33)
C24′	−675 (6)	1587 (5)	16812 (6)	5.82 (34)
C25′	−973 (7)	3100 (6)	15909 (8)	6.81 (43)
C26′	−1076 (6)	2231 (6)	16782 (7)	6.58 (38)
C27′	2003 (5)	3845 (4)	15627 (5)	3.75 (25)
O28′	2296 (4)	3265 (3)	16559 (3)	5.22 (20)
O29′	1957 (4)	4657 (3)	15624 (4)	5.39 (21)
C30′	2156 (8)	4785 (6)	16831 (7)	7.55 (44)
O31′	453 (3)	4711 (3)	12927 (4)	4.62 (18)
C32′	2796 (5)	2661 (5)	14927 (5)	4.38 (28)

[a] Positional parameters are multiplied by 10^4. [b] Thermal parameters are given by the equivalent temperature factors (Å^2).

Table VIII. Bond Distances (Å) of IVc′ for Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Molecule 1		Molecule 2	
C01–C02	1.529 (8)	C01′–C02′	1.520 (11)
C01–C10	1.519 (7)	C01′–C10′	1.530 (7)
C01–C11	1.532 (12)	C01′–C11′	1.530 (8)
C02–C03	1.333 (8)	C02′–C03′	1.334 (10)
C02–C15	1.501 (7)	C02′–C15′	1.492 (7)
C03–C04	1.524 (7)	C03′–C04′	1.530 (7)
C03–C21	1.502 (8)	C03′–C21′	1.498 (10)
C04–C05	1.543 (11)	C04′–C05′	1.542 (8)
C04–C09	1.571 (7)	C04′–C09′	1.571 (12)
C04–C27	1.555 (11)	C04′–C27′	1.541 (9)
C05–O06	1.353 (7)	C05′–O06′	1.346 (7)
C05–O31	1.199 (8)	C05′–O31′	1.193 (8)
O06–C07	1.457 (8)	O06′–C07′	1.443 (10)
C07–C08	1.495 (12)	C07′–C08′	1.494 (9)
C08–C09	1.518 (8)	C08′–C09′	1.518 (8)
C09–C10	1.536 (11)	C09′–C10′	1.544 (9)
C09–C32	1.529 (11)	C09′–C32′	1.533 (9)
C11–O12	1.201 (8)	C11′–O12′	1.198 (12)
C11–O13	1.311 (10)	C11′–O13′	1.310 (11)
O13–C14	1.461 (19)	O13′–C14′	1.451 (8)
C15–C16	1.380 (8)	C15′–C16′	1.388 (10)
C15–C17	1.372 (9)	C15′–C17′	1.382 (10)
C16–C18	1.388 (9)	C16′–C18′	1.390 (8)
C17–C19	1.395 (8)	C17′–C19′	1.380 (8)
C18–C20	1.382 (10)	C18′–C20′	1.361 (12)
C19–C20	1.356 (10)	C19′–C20′	1.358 (12)
C21–C22	1.371 (11)	C21′–C22′	1.382 (8)
C21–C23	1.401 (8)	C21′–C23′	1.383 (13)
C22–C24	1.400 (11)	C22′–C24′	1.391 (13)
C23–C25	1.372 (10)	C23′–C25′	1.391 (15)
C24–C26	1.377 (10)	C24′–C26′	1.355 (16)
C25–C26	1.354 (14)	C25′–C26′	1.381 (10)
C27–O28	1.191 (11)	C27′–O28′	1.199 (7)
C27–O29	1.316 (7)	C27′–O29′	1.321 (10)
O29–C30	1.473 (12)	O29′–C30′	1.456 (11)

Table IX. Bond Angles (°) of IVc′ for Non-hydrogen Atoms with Their Estimated Standard Deviation in Parentheses

Molecule 1		Molecule 2	
C02–C01–C10	113.9 (5)	C02′–C01′–C10′	114.2 (6)
C02–C01–C11	109.3 (5)	C02′–C01′–C11′	109.2 (5)
C10–C01–C11	108.4 (6)	C10′–C01′–C11′	107.9 (4)
C01–C02–C03	123.5 (5)	C01′–C02′–C03′	123.7 (5)
C01–C02–C15	113.0 (5)	C01′–C02′–C15′	112.8 (6)
C03–C02–C15	123.5 (5)	C03′–C02′–C15′	123.4 (6)
C02–C03–C04	120.0 (5)	C02′–C03′–C04′	120.0 (6)
C02–C03–C21	122.3 (5)	C02′–C03′–C21′	122.6 (5)
C04–C03–C21	117.5 (5)	C04′–C03′–C21′	117.4 (6)
C03–C04–C05	109.0 (6)	C03′–C04′–C05′	110.3 (4)
C03–C04–C09	112.2 (4)	C03′–C04′–C09′	111.8 (6)
C03–C04–C27	108.2 (5)	C03′–C04′–C27′	107.8 (5)
C05–C04–C09	108.8 (5)	C05′–C04′–C09′	108.9 (5)
C05–C04–C27	107.6 (5)	C05′–C04′–C27′	107.5 (6)
C09–C04–C27	110.9 (5)	C09′–C04′–C27′	110.5 (5)
C04–C05–O06	118.6 (6)	C04′–C05′–O06′	118.8 (5)
C04–C05–O31	124.0 (5)	C04′–C05′–O31′	122.8 (5)
O06–C05–O31	117.3 (7)	O06′–C05′–O31′	118.5 (5)
C05–O06–C07	123.0 (5)	C05′–O06′–C07′	124.2 (5)
O06–C07–C08	115.1 (6)	O06′–C07′–C08′	115.0 (6)
C07–C08–C09	113.0 (6)	C07′–C08′–C09′	113.4 (5)
C04–C09–C08	108.2 (4)	C04′–C09′–C08′	108.4 (6)
C04–C09–C10	104.6 (5)	C04′–C09′–C10′	104.8 (5)
C04–C09–C32	113.6 (6)	C04′–C09′–C32′	114.0 (5)
C08–C09–C10	111.4 (6)	C08′–C09′–C10′	111.2 (5)
C08–C09–C32	108.8 (6)	C08′–C09′–C32′	109.6 (5)
C10–C09–C32	110.3 (5)	C10′–C09′–C32′	108.9 (6)
C01–C10–C09	112.4 (6)	C01′–C10′–C09′	112.3 (5)
C01–C11–O12	121.6 (8)	C01′–C11′–O12′	121.0 (7)
C01–C11–O13	112.6 (6)	C01′–C11′–O13′	112.9 (7)
O12–C11–O13	125.7 (9)	O12′–C11′–O13′	126.1 (6)
C11–O13–C14	116.9 (7)	C11′–O13′–C14′	115.8 (8)
C02–C15–C16	120.1 (5)	C02′–C15′–C16′	120.9 (6)
C02–C15–C17	121.3 (5)	C02′–C15′–C17′	121.3 (6)
C16–C15–C17	118.6 (5)	C16′–C15′–C17′	117.7 (5)
C15–C16–C18	119.9 (6)	C15′–C16′–C18′	121.2 (7)
C15–C17–C19	121.0 (6)	C15′–C17′–C19′	120.2 (7)
C16–C18–C20	121.2 (6)	C16′–C18′–C20′	119.9 (7)
C17–C19–C20	120.5 (6)	C17′–C19′–C20′	121.6 (7)
C18–C20–C19	118.8 (6)	C18′–C20′–C19′	119.4 (6)
C03–C21–C22	120.7 (5)	C03′–C21′–C22′	118.8 (7)
C03–C21–C23	121.2 (6)	C03′–C21′–C23′	123.0 (5)
C22–C21–C23	118.0 (6)	C22′–C21′–C23′	117.9 (7)
C21–C22–C24	121.0 (6)	C21′–C22′–C24′	121.3 (8)
C21–C23–C25	120.9 (8)	C21′–C23′–C25′	121.0 (6)
C22–C24–C26	119.1 (9)	C22′–C24′–C26′	119.9 (7)
C23–C25–C26	120.3 (7)	C23′–C25′–C26′	119.6 (11)
C24–C26–C25	120.7 (7)	C24′–C26′–C25′	120.3 (10)
C04–C27–O28	123.3 (5)	C04′–C27′–O28′	124.1 (7)
C04–C27–O29	111.7 (7)	C04′–C27′–O29′	112.1 (5)
O28–C27–O29	124.9 (7)	O28′–C27′–O29′	123.7 (6)
C27–O29–C30	115.2 (7)	C27′–O29′–C30′	116.7 (5)

2-Allylphenol reacted with Ia to give only the *endo* $[4+2]\pi$ cycloadduct (IIIm), which did not undergo any transformation reactions.

Reaction of 2,5-Dimethyl- and 2,5-Diethyl-3,4-diphenylcyclopentadienone (Ib and Ic) with Cinnamyl Alcohol (IId) To compare the cycloaddition reactivity of Ia with those of 2,5-dialkyl-substituted cyclopentadienones, the dimethyl- and diethyl derivatives (Ib and Ic) were allowed to react with IId. The cyclopentadienone Ib reacted with IId in refluxing toluene for 30 h to afford the $[4+2]\pi$ cycloadduct (VIIId) in 55% yield (see Chart 5). In contrast, the diethyl derivative (Ic) did not give any cycloadduct. The structure of VIIId was determined by comparison of the spectral data[1c)] with those of III.

X-Ray Crystallographic Structure Determination of the Reaction Products In order to obtain definitive evidence for the stereostructures of the products obtained in this study, we performed X-ray crystallographic analyses on typical products, *i.e.*, the cleaved product IVc′ and the $[4+2]\pi$ cycloadduct Vj, derived from the cycloaddition reactions of Ia with 3-methylbuten-3-ol (IIc) and geraniol (IIj), respectively.

The single crystals were obtained by slow evaporation of the solvents (see Table VI). The structures were solved by the direct method using the program MULTAN.[7)] Block-diagonal least squares refinements[8)] converged the *R* factors to 0.06 and 0.06, respectively. Fractional atomic coordinates and their bond lengths and angles for IVc′ are given in Tables VII, VIII and IX, respectively and those for Vj, in Tables X, XI and XII, respectively. The computer-generated (ORTEP)[9)] drawings and the numbering systems used in this paper are shown in Figs. 1 and 2.

Crystal Structure of IVc′ The observed structure involves *trans*-oriented MeOCO– groups. The methyl protons of the MeOCO– groups are located in the effective shielding zone. The atoms C(1), C(2), C(3) and C(4) are almost planar. The dihedral angles of C(3)–C(2)–C(1)–C(10) and C(2)–C(3)–C(4)–C(9) are 5.3° and 29.9°, respectively. The *cis*-fused lactone adopts chair form. The C(4)–C(9) bond length of 1.571 Å is moderately elongated from the normal value. This elongation might be caused by steric conjestion around the tetrahedral carbons (see Fig. 1). The methyl protons of the MeOCO– group adjacent to the lactone moiety resonate at lower field than opposite-side methoxy group, presumably due to the difference in anisotropic effect of the ring current of the vicinal phenyl groups.

TABLE X. Fractional Atomic Coordinates[a] and Isotropic Temperature Factors (*B*) of Vj for Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*[b]
C1	739 (2)	7602 (2)	5214 (3)	3.36 (7)
C2	1790 (3)	8366 (2)	5152 (3)	3.64 (8)
C3	2856 (2)	7541 (2)	5222 (3)	3.50 (7)
C4	2279 (2)	6347 (2)	5433 (3)	3.21 (7)
C5	1963 (2)	6326 (2)	6845 (3)	3.08 (7)
C6	1039 (2)	7039 (2)	6705 (3)	3.25 (7)
C7	972 (2)	6558 (2)	4364 (3)	3.49 (7)
O8	336 (2)	6134 (2)	3259 (2)	5.01 (6)
C9	−393 (3)	8249 (2)	4420 (3)	3.96 (8)
O10	−1409 (2)	8119 (2)	4415 (3)	5.51 (7)
O11	−115 (2)	9075 (2)	3618 (2)	5.13 (7)
C12	1165 (3)	9037 (3)	3747 (4)	5.16 (10)
C13	3010 (3)	5357 (2)	5244 (3)	3.60 (8)
O14	4085 (2)	5270 (2)	5868 (3)	5.18 (7)
O15	2328 (2)	4569 (2)	4344 (2)	4.47 (6)
C16	2972 (3)	3574 (3)	4149 (4)	5.68 (12)
C17	3137 (3)	7485 (3)	3791 (3)	4.64 (9)
C18	4000 (3)	7855 (3)	6531 (3)	3.99 (8)
C19	4558 (3)	8999 (3)	6333 (4)	5.61 (11)
C20	5621 (3)	9328 (3)	7659 (4)	5.23 (10)
C21	5765 (3)	10259 (3)	8457 (4)	5.26 (11)
C22	6904 (4)	10467 (4)	9766 (5)	7.17 (14)
C23	4850 (4)	11184 (4)	8201 (5)	7.04 (15)
C24	2598 (2)	5604 (2)	8145 (3)	3.28 (7)
C25	2598 (3)	4436 (3)	7993 (3)	4.09 (9)
C26	3189 (3)	3779 (3)	9228 (4)	5.51 (12)
C27	3765 (3)	4272 (4)	10570 (4)	6.30 (12)
C28	3761 (3)	5425 (4)	10726 (4)	5.90 (11)
C29	3187 (3)	6091 (3)	9510 (3)	4.52 (9)
C30	419 (2)	7277 (2)	7760 (3)	3.08 (7)
C31	110 (3)	6415 (2)	8548 (3)	4.13 (9)
C32	−448 (3)	6642 (3)	9547 (4)	5.20 (11)
C33	−733 (3)	7739 (3)	9788 (4)	5.07 (10)
C34	−458 (3)	8603 (3)	8996 (4)	4.78 (10)
C35	120 (3)	8378 (2)	7997 (3)	4.06 (9)

a) Positional parameters are multiplied by 10^4. *b*) Thermal parameters are given by the equivalent temperature factors (Å^2).

Crystal Structure of Vj The structure of Vj was established to be the $[4+2]\pi$ cycloadduct in which the allylic alcohol moiety reacted as a dienophile and the *exo*-oriented hydroxymethyl group linked with the bridgehead MeOCO– group to form a five-membered lactone ring. The framework of the bicyclo[2.2.1]hepten-7-one moiety is considerably strained. The C(1)–C(7)–C(4) angle is 95.3°, in accordance with the characteristic IR absorption at 1814 cm^{-1} and ^{13}C-NMR peak at 187.9 ppm. The C(4)–C(5)–C(6) and C(1)–C(6)–C(5) angles of 109.5° and 106.9° deviate from the normal sp^2 carbon angle of 120°. The lactone ring adopts an envelope structure in which the atoms C(2), C(1), C(9) and O(11) are nearly planar. The C(1)–C(9)–O(10) angle is 130.0° in accordance with the IR absorption band at 1774 cm^{-1} due to five-membered lactone ring.

An interesting feature is the presence of a very long bond, [C(3)–C(4) 1.600(4) Å]. The C3 and C4 carbons are tertiary ones, so the steric repulsion may be serious. However, MM2 calculation could not reproduce this elongation, indicating that MM2 calculation is not suitable for strained or overcrowded systems like the present one.[10a] An electronic factor is considered to be account for the elongation.[10b]

TABLE XI. Bond Distances (Å) of Vj for Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

C1–C2	1.536 (4)	C1–C6	1.514 (4)	C1–C7	1.559 (4)
C1–C9	1.498 (4)	C2–C3	1.571 (4)	C2–C12	1.526 (5)
C3–C4	1.600 (4)	C3–C17	1.528 (5)	C3–C18	1.536 (4)
C4–C5	1.531 (5)	C4–C7	1.546 (4)	C4–C13	1.502 (4)
C5–C6	1.345 (4)	C5–C24	1.491 (4)	C6–C30	1.468 (5)
C7–O8	1.181 (3)	C9–O10	1.194 (4)	C9–O11	1.350 (4)
O11–C12	1.460 (5)	C13–O14	1.199 (4)	C13–O15	1.331 (4)
O15–C16	1.447 (5)	C18–C19	1.534 (5)	C19–C20	1.497 (5)
C20–C21	1.319 (5)	C21–C22	1.508 (5)	C21–C23	1.495 (6)
C24–C25	1.387 (4)	C24–C29	1.385 (4)	C25–C26	1.394 (5)
C26–C27	1.368 (6)	C27–C28	1.371 (6)	C28–C29	1.383 (5)
C30–C31	1.388 (5)	C30–C35	1.389 (4)	C31–C32	1.365 (6)
C32–C33	1.380 (5)	C33–C34	1.374 (5)	C34–C35	1.382 (6)

TABLE XII. Bond Angles (°) of Vj for Non-hydrogen Atoms with Their Estimated Standard Deviation in Parentheses

C2–C1–C6	111.3 (2)	C2–C1–C7	98.8 (3)	C2–C1–C9	105.0 (2)
C6–C1–C7	97.4 (2)	C6–C1–C9	126.2 (3)	C7–C1–C9	115.0 (2)
C1–C2–C3	105.6 (2)	C1–C2–C12	101.0 (2)	C3–C2–C12	119.8 (3)
C2–C3–C4	101.1 (2)	C2–C3–C17	113.8 (2)	C2–C3–C18	110.0 (2)
C4–C3–C17	107.7 (2)	C4–C3–C18	112.9 (2)	C17–C3–C18	111.0 (3)
C3–C4–C5	111.4 (2)	C3–C4–C7	97.5 (2)	C3–C4–C13	112.9 (3)
C5–C4–C7	96.5 (2)	C5–C4–C13	114.8 (2)	C7–C4–C13	121.6 (2)
C4–C5–C6	109.5 (2)	C4–C5–C24	123.7 (3)	C6–C5–C24	126.8 (3)
C1–C6–C5	106.9 (3)	C1–C6–C30	124.4 (2)	C5–C6–C30	128.8 (3)
C1–C7–C4	95.3 (2)	C1–C7–O8	129.8 (3)	C4–C7–O8	134.8 (3)
C1–C9–O10	130.0 (3)	C1–C9–O11	108.7 (3)	O10–C9–O11	121.3 (3)
C9–O11–C12	111.4 (2)	C2–C12–O11	105.2 (3)	C4–C13–O14	123.7 (3)
C4–C13–O15	112.7 (2)	O14–C13–O15	123.6 (3)	C13–O15–C16	115.5 (2)
C3–C18–C19	113.0 (3)	C18–C19–C20	112.3 (3)	C19–C20–C21	127.9 (3)
C20–C21–C22	121.3 (3)	C20–C21–C23	125.2 (3)	C22–C21–C23	113.5 (4)
C5–C24–C25	120.0 (2)	C5–C24–C29	120.4 (3)	C25–C24–C29	119.6 (3)
C24–C25–C26	118.8 (3)	C25–C26–C27	120.9 (3)	C26–C27–C28	120.4 (3)
C27–C28–C29	119.5 (3)	C24–C29–C28	120.7 (3)	C6–C30–C31	121.4 (3)
C6–C30–C35	120.8 (3)	C31–C30–C35	117.9 (3)	C30–C31–C32	121.1 (3)
C31–C32–C33	120.7 (4)	C32–C33–C34	119.1 (4)	C33–C34–C35	120.4 (3)
C30–C35–C34	120.8 (3)				

Discussion

The cyclopentadienone (Ia) showed high cycloaddition reactivity toward various olefinic alcohols (II), although the dienophiles used are not activated by introduction of electron-withdrawing or electron-releasing substituents on the parent ethylene moiety and the transition states are not stabilized by nonbonded interactions such as secondary orbital interactions.[6] The modified neglect of diatomic overlap (MNDO) calculations[11] indicate that the HOMO energy level (−10.00 eV) of allyl alcohol is slightly lower than that of propene (−9.967 eV), suggesting that the dienophilic reactivity of olefinic alcohols is almost the same as that of the parent olefins. The MNDO calculation indicates that the remarkably high cycloaddition reactivity of Ia arises from an extremely low-lying LUMO energy level (−1.683 eV)[12] of Ia, due not only to the electron-withdrawing effect of the COOMe groups but also to compression of the frontier molecular orbital (FMO) energy levels by the two phenyl groups (see Table XIII).

In the transition state, the absence of the secondary orbital interaction is reflected in the low *endo* slectivity,[1c] resulting in formation of considerable amounts of *exo* adducts, which in turn readily transformed into mixtures of isomeric hydrophthalide derivatives (IV).

The *exo*-oriented hydroxy group attacks the bridged carbonyl carbon to cause cleavage of the strained ketonic bond, resulting in formation of allylic radicals stabilized by the two phenyl groups. The resultant hydrogen radical may approach the vacant *p*-orbital from the α or β site to give the two stereoisomers of the hydrophthalide derivatives (Chart 6). Whether the *exo* adducts transform to hydrophthalide derivatives or lactone derivatives is considered to depend upon the presence of steric interferences by the vicinal alkyl groups.

As regards the formation pathway of V, compound V might result from intramolecular cycloaddition of 2-alkenoxycarbonyl-5-methoxycarbonyl-3,4-diphenylcyclopentadienone (A) formed from transesterification of Ia with a large excess of 2-alkenol. However, we can rule out this possibility because we could not observe the presence of any alcoholysis product when the reaction was carried out in alcoholic solvents (see Chart 7).

In general, the *endo* adducts were isolated without further transformation to lactone derivatives. However, an exception was observed in the case of crotyl alcohol. The *endo* adduct underwent transesterification to give the unstable *trans* lactone derivative, which was gradually transformed to an unidentified compound. The *endo* lactone is considered to be less stable than the *exo* one due to ring strain of the twisted five-membered lactone condensed with

TABLE XIII. FMO Energy Level and Coefficients for Allyl Alcohol (IIa), Cyclopentadienone (CP) and 2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (Ia)

		IIa		Propene		CP[b]		Ia	
Orbital levels (eV)		−10.00 (HOMO)	1.018 (LUMO)	−9.967 (HOMO)	1.117 (LUMO)	−9.710 (HOMO)	−0.918 (LUMO)	−10.34[c] (HOMO)	−1.673 (LUMO)
Coefficients	O					0.0	−0.393	0.0	−0.335
	C1					0.0	0.377	0.0	0.291
	C2	0.668	0.703	0.689	−0.707	−0.565	0.423	−0.498	0.417
	C3	0.642	−0.672	0.668	0.675	−0.427	−0.414	−0.367	−0.429
	C4					0.425	−0.417	0.352	−0.429
	C5					0.564	0.424	0.483	0.416

a) Heat of formation (ΔH_f), −37.41 kcal/mol. *b*) ΔH_f, 9.761 kcal/mol. *c*) The HOMO (−9.675 eV) does not have any coefficients on the cyclopentadienone ring but is localized in the diphenyl moieties. ΔH_f, −101.95 kcal/mol. Dipole moment, 4.168 debye. The optimized structure of the cyclopentadienone ring is as follows: $O{=}C_1$, 1.216 Å; C_1–C_2, 1.516 Å; C_2–C_3, 1,372 Å; C_3–C_4 1.517 Å.

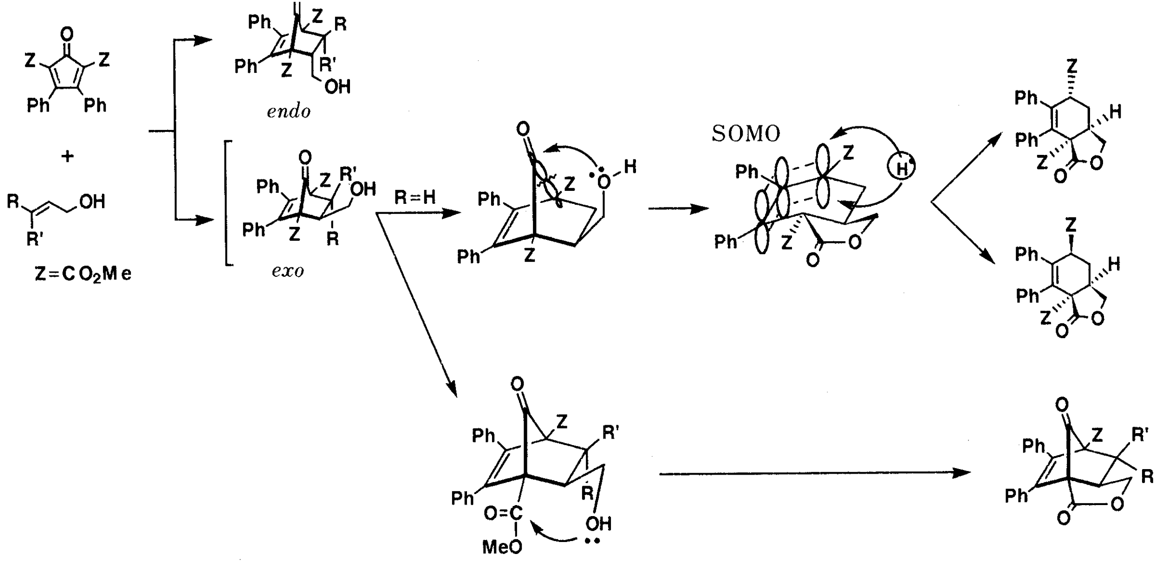

Chart 6

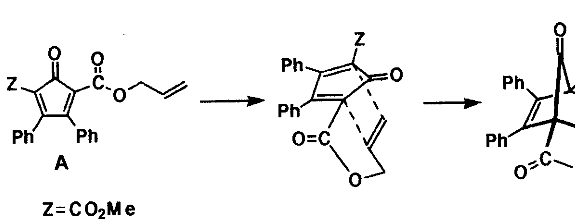

Chart 7

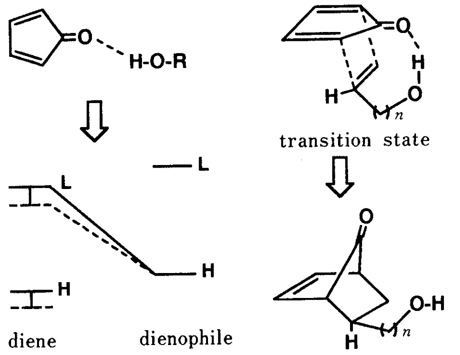

Fig. 3. Possible Role of the Hydrogen Bonding in the Cycloaddition of Ia with Unsaturated Alcohols

the rigid bicyclo[2.2.1]heptenone system.

In connection with the cycloaddition reactivity and stereoselectivity of Ia, a possible role of hydrogen bonding between the carbonyl oxygen of Ia and the hydroxy group of II should be mentioned. In the present reaction system, hydrogen bonding effects on the reactivity and stereoselectivity are considered to be operative. The MNDO-PM3 calculations imply that hydrogen bonding between allyl alcohol (IIa) and the carbonyl oxygen of cyclopentadienone (CP) lowers the LUMO energy level of CP by *ca.* 0.3 eV, and the reaction system is stabilized by *ca.* 4 kcal/mol in heat of formation (ΔH_f) as comparison with the sum of ΔH_f (IIa) and ΔH_f (CP). In such a situation, the *exo* selectivity is expected to be increased. The predominant formation of the *exo* adduct in the reaction of Ia with IIe may be arisen from the enhanced hydrogen-bonding capability due to the bifunctional hydroxy groups.13)

Further work is in progress on the probable mechanism of the cleavage reaction.

Experimental

All melting point are uncorrected. Nuclear magnetic resonance spectra were taken with Hitachi R-600 (60 MHz ^{1}H-NMR) and JEOL GX-400 (400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR) spectrometers for 5—10% (w/v) solutions with tetramethylsilane as an internal standard. Chemical shifts are given as δ values (ppm): s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; br, broad; m, multiplet. IR spectra were recorded on a Hitachi 270-30 infrared spectrophotometer. Mass spectra and high-resolution mass spectra were taken with a JEOL JMS-DX-300 spectrometer operating at an ionization potential of 75 eV.

MNDO calculations were performed on a FACOM M-780 computer in the Computer Center of Kumamoto University and on a Fujitsu S4/2 workstation.

Materials 2,5-Dimethoxycarbonyl-3,4-diphenylcyclopentadienone (Ia),14) 2,5-dimethyl-3,4-diphenylcyclopentadienone (Ib),14) and 2,5-diethyl-3,4-diphenylcyclopentadienone (Ic)15) were prepared according to the established methods. Olefinic alcohols are commercially available.

Cycloaddition of 2,5-Dimethoxycarbonyl-3,4-diphenylcyclopentadienone (Ia) with Unsaturated Alcohols (IIa—k). General Procedure of Cycloaddition A solution of Ia and an excess amount of an olefinic alcohol in chloroform was heated at 20—60°C until Ia was no longer detectable by TLC. After cooling, the solvent was evaporated off under reduced pressure. The residue was purified by recrystallization or by chromatography on silica gel. The product was isolated as a mixture of the stereoisomers and its formation ratio was determined by 400 MHz ^{1}H-NMR spectroscopy. The results are summarized in Tables I, II, III and IV.

X-Ray Crystallographic Study. Compound IVc′ A single crystal of IVc′ was prepared by slow evaporation of ethanol–acetone solution. The density was measured by flotation in an aqueous potassium iodide solution. The cell constants were obtained from least-squares refinement of the 2θ angle of 20 reflections. The triclinic space group was determined to be $P\bar{1}$ (No. 2) from the number of molecules per unit cell ($Z=4$) and was later confirmed in the course of the structure refinement. Intensity data were collected on Rigaku AFC-6 automated diffractometer with graphite monochromated MoK_α radiation and by using the 2θ–ω scan mode to a limit of $2\theta=55°$. Crystal stability was monitored by recording two standard reflections after measurement of every 100 reflections, and no decay was observed. A total 4219 independent reflections were measured, and after Lorentz and polarization corrections were applied, 2897 were treated as observed ($F_O>3\sigma F$, $2\theta<55°$). No correction was applied for absorption. The data are summarized in Table VI.

An overall temperature factor obtained from a Wilson plot did not give the correct solution. Therefore, the value of 5.0 Å was used to calculate the normalized structure factor. An E map calculated with 500 signed E's ($E>1.34$), which gave a combined figure of merit of 1.895, revealed the position of 60 of the nonhydrogen atoms.

The position of the remaining four atoms of methoxy groups could not found from a difference Fourier map. The atom were located on reasonable positions by using HYCO80. In the course of refining, their thermal parameters did not diverge. All hydrogens were placed in calculated positions. Keeping the vibrational amplitudes for hydrogen fixed (B(H)$=B$(C)$+1.0$) and refining with thermal parameters for all the C, O atoms resulted in a final R factor of 0.060. The weighting schemes used were $w=1.0$ for $F_O<30.0$, and $w=900/F_O^2$ for $F_O>30.0$ for the observed reflections.

Compound Vj A single crystal of Vj was prepared by slow evaporation of ethanol–acetone solution. Determination of the cell constants and collection of the intensity data were carried out in almost the same manner as in the case of IVc′. The cell constants are given in Table VI.

A total of 4309 independent reflections were measured, and after Lorentz and polarization corrections were applied, 3194 were treated as observed ($F_O>3\sigma F$, $2\theta<55°$). No correction was applied for absorption. The data are summarized in Table VI.

An overall temperature factor of 3.55 Å^2 was obtained from a Wilson's plot and used to calculate normalized structure factors (E). The structure was solved by the direct method using the MULTAN78 series of programs. An E map calculated with 500 signed E's ($E>1.49$), which gave a combined figure of merit of 2.456, revealed the positions of all the expected nonhydrogen atoms. Refinements were carried out by the block-diagonal least-squares method. Several further cycles for the nonhydrogen atoms converged the R factor to 0.11. The positions of hydrogens bonded to carbon atoms were calculated by using the program HYCO80. After adding the hydrogens, keeping their vibrational amplitudes fixed (B(H)$=B$(C)$+1.0$), and refining, we obtained a final R of 0.060. In final refinements, the following weights were used for the observed reflections: $w=1.0$ for $F_O<10.0$, and $w=100/F_O^2$ for $F_O>10.0$.

All calculations were performed on the FACOM M-360 computer in the Computer Center of Kumamoto University with the Universal Crystallographic Computation Program (UNICS III).6)

Acknowledgment The authors thank the members of the Analytical Center of this Faculty for the spectral measurements. Thanks are also due to Mr. T. Aoki and Miss K. Tanaka for technical assistance.

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