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Pericyclic Reaction of Cyclopentadienones with Nonconjugated Dienes. Formation of Double Diels–Alder Adducts

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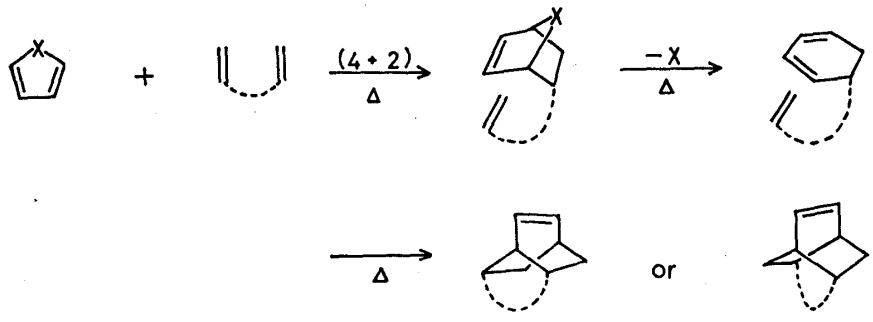
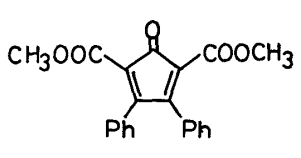
Pericyclic reactions of 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (Ia) with nonconjugated dienes (IIa—g) were investigated. The cyclopentadienone (Ia) reacted readily with IIa—g to give [4+2]π cycloadducts (IIIa—g) that lost carbon monoxide to afford intramolecular double Diels–Alder adducts (Va—g) on heating above the melting points. The structures of these adducts were determined from spectral evidence. The stability of the cycloadducts between twistene and isotwistene type compounds is discussed on the basis of molecular mechanics calculation data.

Keywords——cyclopentadienone; nonconjugated diene; cycloaddition; intramolecular cycloaddition; decarbonylation; double Diels–Alder reaction; MM2; MNDO

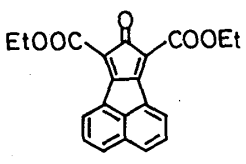
Introduction

Recently, the synthetic applications of inter- and intramolecular Diels–Alder reactions have been expanding rapidly. Kanematsu and one of the authors carried out basic studies of factors influencing stereo-, regio- and pericontrols using cyclopentadienone as a model compound. 2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (Ia) and 2-oxo-1,3-bis(ethoxycarbonyl)-2*H*-cyclopent[*a*]acenaphthylene (Ib) in particular have shown high reactivity toward various dienophiles and can serve as excellent trapping agents for unstable olefinic compounds.[1)]





Ia



Ib

Chart 1

In the reaction of Ib with olefins, the cycloadducts lost carbon monoxide spontaneously to afford tetrasubstituted 1,3-cyclohexadiene drivatives in refluxing benzene. Interestingly, adducts with nonconjugated dienes were transformed into intramolecular double Diels–Alder (DDA) adducts. Molecular mechanics (MM) calculation revealed that the decarbonylation reaction is triggered by strain release in the bicyclo[2.2.1]hepten-7-one (norbornen-7-one) system fused to the acenaphthylene ring.[1b)]

In this connection, we considered that Ia would show a similar reaction behavior under more severe reaction conditions. This paper deals with the pericyclic reaction of Ia with various nonconjugated olefins (IIa—g).

Results

Intermolecular Cycloaddition Reaction of Ia with Nonconjugated Olefins (IIa—g)

Reactions of Ia with excess amounts of olefins (IIa—g) gave 1 : 1 cycloadducts (IIIa—g) in high yields in all cases except IIe (Chart 2). The reaction conditions and properties of the cycloadducts (IIIa—g) are shown in Tables I and II. The infrared (IR) spectra of these cycloadducts commonly showed characteristic bands at 1790—1795 cm^{-1} due to a strained-ring carbonyl group (Table IIa). Careful inspections of the proton nuclear magnetic resonance (^{1}H-NMR) spectra of these cycloadducts revealed that each cycloaddition gave a single product (except in the case of IIg) showing an ABX pattern in the norbornen-7-one moiety attributable to the *endo* cycloadduct (Table IIb). Further confirmation of the stereochemistry of the cycloadducts (X-ray crystallographic analysis) was not achieved because the succeeding decarbonylation reaction of the *endo* and *exo* adducts should give the same decarbonylated product.

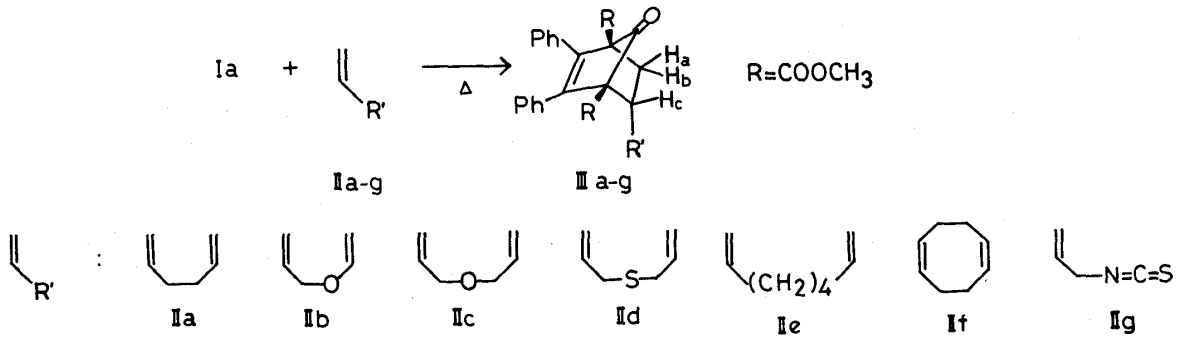


Chart 2

TABLE I. [4+2]π Adducts (III) from the Cycloaddition Reaction of Ia with Nonconjugated Dienes (IIa—g)

Compd.	Temp. (°C)	Time (h)	Solvent	mp (°C)	Yield (%)
IIIa	Reflux	3	$CHCl_3$	114—115	92
IIIb	Reflux	3	$CHCl_3$	127	63
IIIc	Reflux	5	$CHCl_3$	117—118	65
IIId	Reflux	5	$CHCl_3$	126	50
IIIe	r.t.	24	$CHCl_3$	175—177	75
IIIe′[a)]	Reflux	0.17	$CHCl_3$	215	51
IIIf	70	3	Toluene	174—176	89[b)]
IIIg	80	3	Toluene	153—154	63

a) 2 : 1 adduct. *b*) A small amount of 2 : 1 adduct (mp 268.5—269.5 °C) was isolated. Heating a mixture of Ia and an excess amount (10 mol) of IIf without solvent at 70 °C for 5 h gave IIIf in 29% yield. r.t. = room temperature.

TABLE IIa. Analytical and IR Spectral Data for [4+2]π Cycloadducts (IIIa—g)

Compd.	IR (cm^{-1}) C=O[a]		Formula	Analysis (%) Calcd (Found)		
	Ester	Bridge		C	H	N
IIIa	1725	1795	$C_{27}H_{26}O_5$	75.48 (75.61	6.04 6.25)	
IIIb	1725	1795	$C_{26}H_{24}O_6$	74.98 (74.97	5.80 5.82)	
IIIc	1722	1790	$C_{27}H_{26}O_6$	75.68 (75.66	5.65 5.52)	
IIId	1720	1790	$C_{27}H_{26}O_5S$	70.13 (70.12	5.62 5.38)	
IIIe	1728	1790	$C_{29}H_{30}O_5$	75.98 (75.90	6.50 6.68)	
IIIe'[b]	1725	1790	$C_{50}H_{46}O_{10}$	78.01 (78.21	6.31 6.25)	
IIIf	1730	1790	$C_{29}H_{29}O_5$	76.14 (76.04	6.34 6.21)	
IIIg	1720	1790	$C_{24}H_{21}NO_5S$	67.10 (67.25	4.73 4.79	2.96 3.12)

a) KBr. *b*) 2:1 adduct.

TABLE IIb. ^{1}H-NMR Spectral Data for the [4+2]π Cycloadducts (IIIa—g)

Compd.	^{1}H-NMR (in $CDCl_3$) ppm
IIIa	7.26—7.08 (10H, m, 2Ph), 5.84 (1H, m, C–HC=C), 5.07 (1H, dd, J=15.4, 1.5 Hz, =CH), 5.02 (1H, d, J=7.7 Hz, =CH), 3.65, 3.64 (6H, s, 2MeO), 2.97—2.91 (1H, m, Hc), 2.83 (1H, dd, J=12.1, 9.5 Hz, Ha), 2.34—2.08 (4H, m, CH_2CH_2), 1.56 (1H, dd, J=12.1, 5.5 Hz, Hb)
IIIb	7.26—7.10 (10H, m, 2Ph), 5.89 (1H, m, J=17.2, 10.6, 5.5 Hz, C–CH=C), 5.27 (1H, dd, J=17.2, 1.5 Hz, =CH), 5.18 (1H, dd, J=10.6, 1.5 Hz, =CH), 4.94 (1H, dd, J=8.3, 2.9 Hz, Hc), 4.10, 4.18 (2H, dd, J=12.8, 5.5 Hz, O–CH_2–), 3.66, 3.65 (6H, s, 2MeO), 2.96 (1H, dd, J=13.6, 8.3 Hz, Ha), 1.97 (1H, dd, J=13.6, 2.9 Hz, Hb)
IIIc	7.26—7.00 (10H, m, 2Ph), 5.85 (1H, m, C–CH=), 5.25 (1H, d, J=17.2 Hz, =CH), 5.16 (1H, dd, J=10.3, 1.5 Hz, =CH), 3.95 (2H, dd, J=5.5, 1.5 Hz, O–CH_2–C=), 3.83 (1H, dd, J=9.2, 3.3 Hz, C–CH_2–O), 3.77 (1H, dd, J=9.2, 5.9 Hz, C–CH_2–O), 3.61, 3.59 (6H, s, 2MeO), 2.72 (1H, dd, J=12.5, 4.8 Hz, Hb), 2.60 (1H, m, Hc), 2.33 (1H, dd, J=12.5, 10.6 Hz, Ha)
IIId	7.06—7.26 (10H, m, 2Ph), 5.82 (1H, m, C–CH=), 5.18 (1H, d, J=17.2 Hz, =CH), 5.14 (1H, d, J=10.6 Hz, =CH), 3.67, 3.64 (6H, s, 2MeO), 3.09—3.23 (4H, m, CH_2–S–CH_2), 2.91 (1H, m, Hc), 2.27 (1H, t, J=12 Hz, Ha), 1.79 (1H, dd, J=12, 5.5 Hz, Hb)
IIIe	7.4—6.9 (10H, m, 2Ph), 5.0—4.5 (3H, m, CH=CH_2), 3.62, 3.58 (6H, s, 2MeO), 3.4—2.3 (3H, m, Ha, Hb and Hc), 2.1—1.5 (8H, m, –$(CH_2)_4$–)[a]
IIIe'	7.5—6.9 (20H, m, Ar), 3.8 (12H, s, 4MeO), 3.3—2.0 (6H, m, Ha, Hb and Hc), 1.8—1.2 (8H, m, –$(CH_2)_4$–)[a,b]
IIIf	7.20—7.09 (10H, m, 2Ph), 5.84 (2H, m, –CH=CH–), 3.66 (6H, s, 2MeO), 3.07 (2H, dd, J=6.23, 2.94 Hz, >CH–), 2.41—1.88 (8H, m, 4CH_2)
IIIg	(*endo-exo* mixture) 7.06—7.20 (10H, m, 2Ph), 4.28, 4.10, 3.75, 3.50 (2H, m, CH_2NCS), 3.71, 3.652, 3.647, 3.62 (6H, s, 2MeO), 3.33, 2.73 (1H, m, Hc), 2.97, 1.80 (1H, m, Ha), 2.60, 2.48 (1H, m, Hb)[c]

a) Taken at 60 MHz. *b*) ^{13}C-NMR (in $CDCl_3$): 191.19 (s, bridged C=O), 167.67 (s, COOMe), 69.38 (s, C–COOMe), 52.18 (q, CH_3), 43.99 (d, >CH–), 25.62 (t, CH_2). *c*) Complex signals due to a mixture of *endo* and *exo* adducts with restricted rotation about the >CH–CH_2NCS bond.

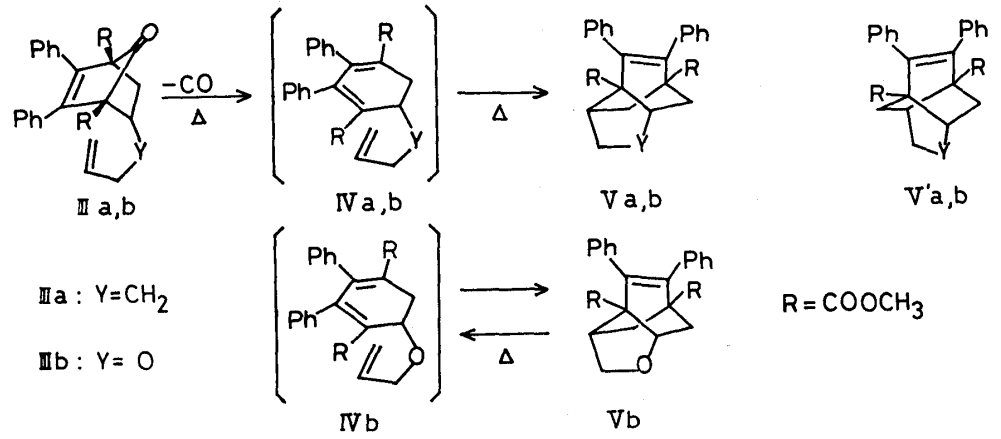


Chart 3

TABLE III. Double Diels–Alder Adducts (V) from Pyrolysis of the [4+2]π Cycloadducts of Ia and Nonconjugated Dienes (IIa—g)

Compd.	Temp. (°C)	Time (h)	mp (°C)	Yield (%)
Va	150	8	177—178	70
Vb	170—120	35	Oil	74[a]
Vc	170	8	185—187[b]	70[a]
Vd	170	8	160—162[b]	68[a]
Ve	220	5	Oil	60[a]
Vf	180	10	227—229	58
Vg	170	8	172—173	40

a) Total yield for the mixture. *b*) Melting point for the isotwistene-type compound.

Thermolysis of the [4+2]π Cycloadduct (IIIa) of Ia and 1,5-Hexadiene (IIa)

Heating IIIa at 170 °C for 8 h gave the decarbonylated product (Va) in 56% yield. The ^{1}H-NMR spectrum of Va indicated the absence of any olefinic proton and the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of Va showed five kinds of sp^3 carbon atoms. These data and elementary analysis indicate that intramolecular cycloaddition had taken place between the 1,3-cyclohexadienyl group and the remaining double bond of the diene to give a DDA adduct (Chart 3). The carbon atoms bearing the methoxycarbonyl groups resonate at 63.37 and 49.59 ppm, suggesting an unsymmetrical isotwistene structure. In the ^{1}H-NMR spectrum, the methine and methylene protons appeared as complex multiplets between 1.30—3.80 ppm. The methoxy signals appeared at 3.13 and 3.19 ppm, supporting an isotwistene structure.

Thermolysis of the [4+2]π Cycloadduct (IIIb) of Ia and Allyl Vinyl Ether (IIb)

Heating IIIb at 170 °C gave a mixture of the decarbonylated 1 : 1 adduct (IVb) and the DDA adduct (Vb) (Chart 3). NMR monitoring of the reaction mixture revealed that Vb is in rapid equilibrium with IVb at the temperature required for the decarbonylation. The relative amounts of the Vb and IVb forms were determined at various temperatures (Table V). At *ca.* 155 °C, the populations of Vb and IVb are approximately equal, and as the temperature is increased, IVb becomes the preferred form. The DDA adduct, Vb could not be isolated in a pure state but was obtained in 92% pure form after equilibration of the mixture at 120 °C.

TABLE IVa. Analytical and IR Spectral Data for DDA Adducts (Va—g)

Compd.	IR (cm^{-1})[a] $\nu_{C=O}$	Formula	Analysis (%) Calcd (Found)		
			C	H	N
Va	1725	$C_{26}H_{26}O_4$	77.61 (77.42	6.46 6.19)	
Vb	1720	$C_{25}H_{24}O_5$	74.25 (74.01	5.49 5.65)	
Vc	1720	$C_{26}H_{26}O_5$	74.62 (74.38	6.62 6.61)	
Vd	1730	$C_{26}H_{26}O_4S$	71.86 (72.01	6.03 6.29)	
Ve	1720	$C_{29}H_{30}O_4$	78.11 (77.60	7.02 7.01)	
Vf	1735	$C_{28}H_{28}O_4$	78.48 (78.09	6.59 6.49)	
Vg[b]	1720	$C_{24}H_{21}NO_4S$	68.72 (69.01	5.05 5.04	3.34 3.30)

a) KBr. *b*) MS *m/z*: 419 (M^+).

TABLE IVb. ^{1}H-NMR Data for DDA Adducts (Va—g)

Compd.	^{1}H-NMR (in $CDCl_3$) ppm
Va	7.10—6.85 (10H, m, 2Ph), 3.13, 3.19 (6H, s, 2MeO), 2.758 (1H, d, J=10 Hz, >CH–), 2.43 (1H, t, J=10, 10 Hz, >CH–H), 1.95 (1H, d, J=10 Hz, >CH–H), 1.68—1.59 (4H, m, $-CH_2CH_2-$)
Vb	7.20 (10H, m, 2Ph), 3.8—3.4 (2H, m, O–CH_2–), 3.22 (6H, s, 2MeO), 3.0—1.8 (6H, m, aliphatic protons)
Vc	7.10—6.87 (10H, m, 2Ph), 3.74, 3.56 (2H, ABq, J=11.4 Hz, $-OCH_2-$), 3.23, 3.17 (6H, s, 2MeO), 2.48 (1H, t, J=12, 12 Hz, >CH–H), 2.41 (1H, d, J=12 Hz, >CH–H), 2.06 (1H, d, J=12 Hz, >CH–)
Vd	7.08—6.86 (10H, m, 2Ph), 3.24, 3.14 (6H, s, 2MeO), 3.06, 2.79 (2H, ABq, J=12 Hz, S–CH_2–), 2.41—2.23 (3H, m, >CH– and $-CH_2-$)
Ve (mixture)	7.4—6.9 (10H, m, 2Ph), 4.05—3.1 (8H, m, methylenes), 3.52, 3.42, 3.39 (6H, s, 2MeO), 3.0—1.3 (6H, m, methylene and methine)
Vf	7.22—6.73 (10H, m, 2Ph), 3.05 (6H, s, 2MeO), 2.74—2.48 (4H, br s, >CH–), 2.12—1.57 (8H, m, $-CH_2CH_2-$)
Vg	7.69—7.02 (10H, m, 2Ph), 3.65 (2H, ABq, $-CH_2N-$), 2.49 (1H, d, J=12 Hz, >CH–), 2.42 (1H, d, J=12 Hz, >CH–H), 2.06 (1H, d, J=12 Hz, >CH–H)

TABLE IVc. ^{13}C-NMR Data for DDA Adducts (Va, c, d, f, g)

Compd.	^{13}C-NMR (in $CDCl_3$) ppm
Va	174.60, 173.90 (s, C=O), 63.37, 49.59 (s, C–CO), 51.40 (q, O–CH_3), 42.04 (t, $-CH_2CH_2-$), 38.59 (d, >CH–), 30.86 (t, $>CH_2$)
Vc	174.68, 173.25 (s, C=O), 69.10 (t, CH_2–O), 53.83 (s, 2C–CO), 51.37, 50.33 (q, CH_3), 34.82 (d, >CH–), 33.55 (t, $>CH_2$)
Vd	174.69, 172.84 (s, C=O), 54.60, 50.44 (s, 2C–CO), 51.38, 51.26 (q, OCH_3), 33.62 (t, CH_2–S), 31.71 (d, >CH–), 29.58 (t, $>CH_2$)
Vf	175.58 (s, C=O), 63.14 (s, 2C–CO), 51.90 (q, O–CH_3), 44.90 (d, >CH–),[a] 25.75 (t, $>CH_2$)[a]
Vg	174.19, 172.76 (s, C=O), 144.25 (s, C=S), 69.09 (t, CH_2–N), 53.89, 50.41 (s, C–CO), 51.49, 51.40 (q, O–CH_3), 34.97 (t, $>CH_2$), 33.69 (d, >CH–)

a) Broadened signals, presumably due to restricted rotation about the C–COOMe bonds.

TABLE V. Equilibrium between IVb and Vb at Various Temperatures[a)]

Temp. (°C)	Time (h)	IVb : Vb
170	0.92	2.3 1
160	1.5	1.4 1
150	4	1 1.9
140	7.5	1 10.8
120	35	1 11.5

a) Followed by measuring the peak area of COOMe signals of VIb and Vb in the ^{1}H-NMR spectra.

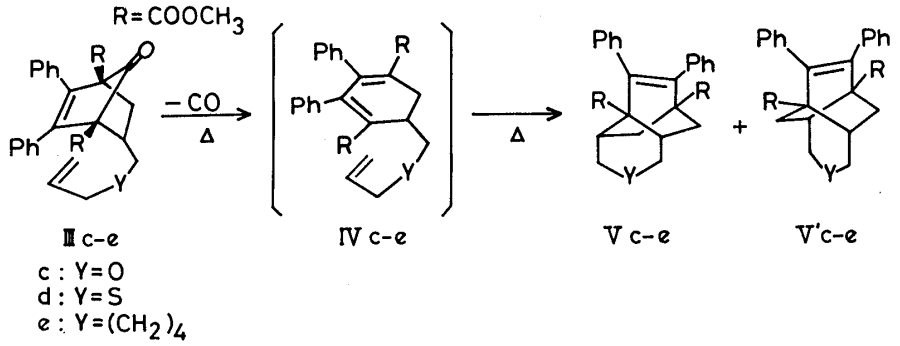


Chart 4

Thermolysis of the [4+2]π Cycloadducts (IIIc—e) of Ia and the Diallyl Ether (IIc), Sulfide (IId) and 1,7-Octadiene (IIe)

Heating IIIc at 170 °C afforded a colorless oil. In the ^{1}H-NMR spectrum of the product, the methoxy groups appeared as three peaks (3.69, 3.5 and 3.4 ppm). Inspection of their chemical shifts and relative intensities indicated that the product consists of isotwistene and twistene forms (Vc and V'c).

The isotwistene-type compound was isolated as a crystalline form after the mixture had been kept at a temperature below 10 °C in a refrigerator for several months. This indicates that equilibration of the two possible isomeric structures occurs slowly even at low temperature, and the isotwistene-type compound predominates at equilibrium.

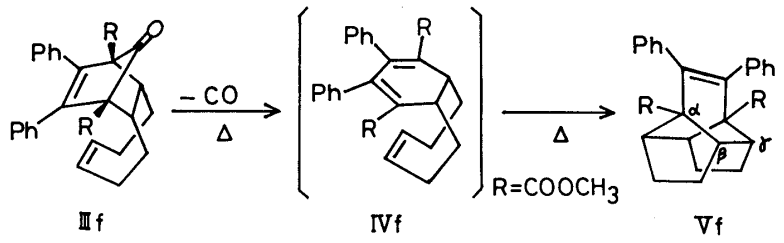
The structure of Vc was established by 400 MHz ^{1}H-NMR spectral analysis. The ^{1}H-NMR spectrum of Vc showed the signals of the methylene protons adjacent to the ether oxygen atom as an AB quartet (geminal coupling) which did not couple with the vicinal methine proton. To be precise, the higher-field doublet appeared as a broadened doublet as compared with the low-field one, indicating that the former very weakly coupled with the vicinal methine proton. The Karplus[2)] rule based on the dihedral angles calculated by MM calculation (Allinger's MM2)[3)] on the parent molecule of Vc suggests that the coupling constants among the methylene protons and the methine proton should be about 0 and 7.2 Hz, respectively. A decrease in the coupling constant between the methylene and the methine protons may be attributed to increased electronegativity of the methylene carbon ($-CH_2-O-$).[4)]

The coupling constants between the three protons on the bicyclo[2,2,2]octene moiety were evaluated by first-order analysis assuming it to be an ABX system (see Table IVb).

The cycloadduct IIId or IIIe showed similar reaction behavior (Chart 4).

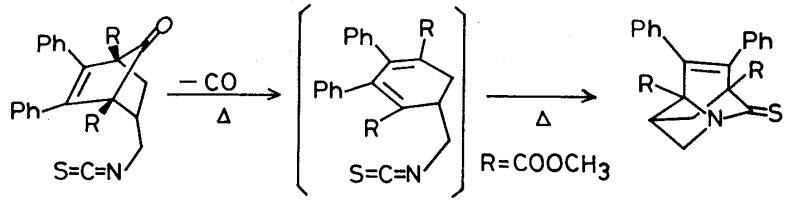
Thermolysis of the [4+2]π Cycloadduct (IIIf) of Ia and 1,5-Cyclooctadiene (IIf)

Heating IIIf at 170 °C produced Vf in 58% yield (Chart 5). The ^{13}C-NMR spectrum showed three types of sp^3 carbon atoms (25.8, 44.9 and 63.1 ppm) (Table IVc). In the ^{1}H-



IIIf IVf Vf

Chart 5



IIIg IVg Vg

Chart 6

NMR spectrum, the methine proton appeared as a broad singlet at 2.74—2.48 ppm and the olefinic protons ascribable to the intermediary IVf were not observed.

Thermolysis of the [4+2]π Cycloadduct (IIIg) of Ia and Allyl Isothiocyanate (IIg)

Heating IIIg above its melting point caused evolution of CO gas to afford decarbonylated 1:1 adduct (Vg) in 40% yield. The IR spectrum of Vg did not show an isothiocyanate (–N=C=S) absorption band in the vicinity of 2230 cm^{-1} but showed a strong thiocarbonyl (C=S) absorption band at 1100 cm^{-1}. The ^{13}C-NMR spectrum of IVg showed five kinds of sp^3 carbon atoms, supporting the proposed structure of the DDA adduct.

Discussion

The initial stage of the reaction falls into the category of an inverse-type reaction in Sustmann's classification[5] for cycloadditions, in which the dominant interaction is the one between the LUMO (lowest unoccupied molecular orbital) of the cyclopentadienone and the HOMO (highest occupied molecular orbital) of the nonconjugated diene. The high reactivity of Ia as a 4π-acceptor in reactions with olefins derives from its low-lying LUMO and antiaromatic character.

In the reaction with allyl isothiocyanate (IIg), Ia did not react with the isothiocyanate moiety but reacted with the allyl moiety. This reaction behavior can be accounted for by considering the second highest occupied molecular orbital (NHOMO), lying 0.76 eV lower than the HOMO[6] (Table VI). The degenerate HOMO's of IIg have a nodal property at the C atom of the N=C=S group. This is very unfavorable for a concerted cycloaddition.

The second stage of the reaction, decarbonylation, must be triggered by strain release of the norbornen-7-one moiety assisted by the favorable electronic interactions. The strain in the parent norbornen-7-one system was estimated to be about 26 kcal/mol by the MM2 calculation.[7] The decarbonylation is considered to compete with the retro-Diels–Alder reaction as shown in Chart 7. However, the retro-Diels–Alder reaction could not be observed in all cases.

The Mulliken bond orders[8] for a structurally similar molecule, *endo*-tricyclo-[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one, based on the MINDO/3 approximation[9] indicate that there

TABLE VI. FMO Energy Level and Coefficients for Allyl Isothiocyanate and Cyclopentadienone

Compound		Allyl isothiocyanate[a]						Cyclopentadienone[c]		
Orbital levels (eV)		−10.605 (NHOMO)	−9.997[b]	−9.820 (HOMO)	0.063[b]	0.443 (LUMO)	0.693		−9.710 (HOMO)	−0.918 (LUMO)
Coefficients	C_3	−0.676		0.095		0.601	−0.384	O	0.0	−0.393
	C_2	−0.677		0.078		−0.548	0.380	C_1	0.0	0.377
	N	0.063	−0.459[b]	0.479	−0.306[b]	−0.238	−0.439	C_2	−0.565	0.423
	C	−0.047	0.101[b]	−0.022	0.723[b]	0.390	0.651	C_3	−0.427	−0.414
	S	−0.160	0.833[b]	−0.842	−0.377[b]	−0.178	−0.288	C_4	0.425	−0.417
								C_5	0.564	0.424

a) Heat of formation (ΔH_f), 50.321 kcal/mol. *b*) In-plane orbital. The MNDO calculation indicated that allyl isothiocyanate has nearly degenerate HOMO's (−9.997 and −9.820 eV) and LUMO's (0.063 and 0.443 eV), and attachment of the allyl group stabilizes the in-plane orbital. *c*) Heat of formation (ΔH_f), 9.761 kcal/mol.

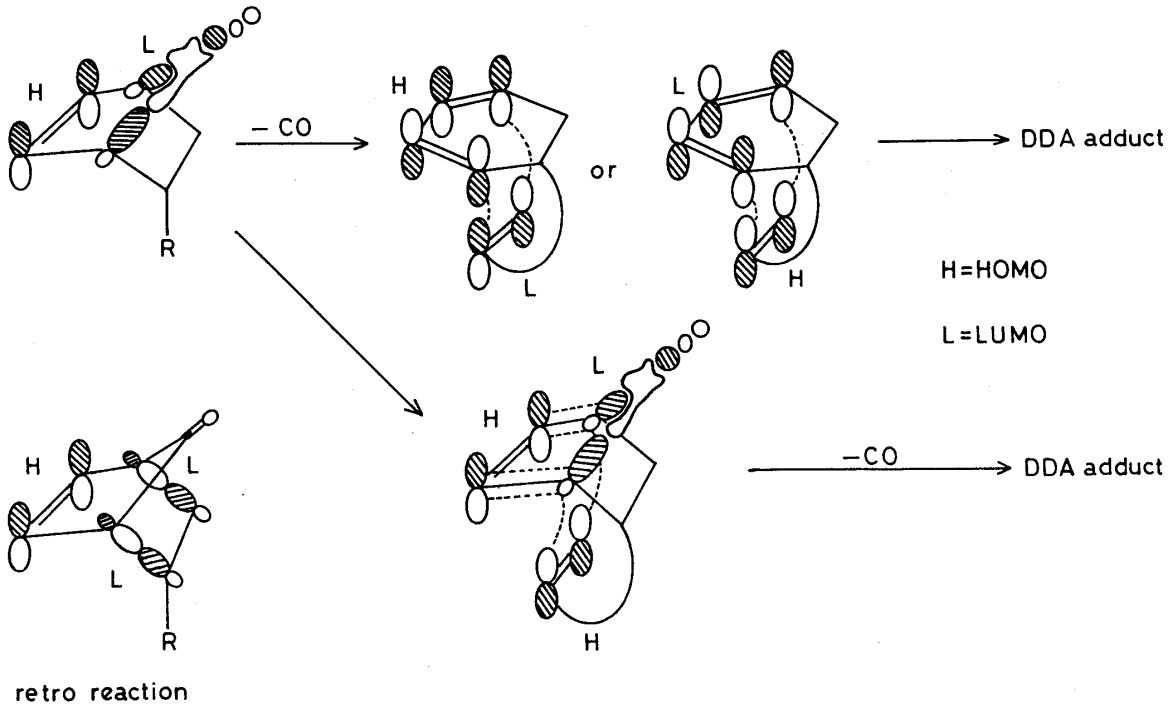


Chart 7

is a significant through-space interaction between the ketonic bridged bond and the double bond of the stilbene moiety, indicating that the interaction might play an important role in stabilization of the transition state. The frontier molecular orbital (FMO) view[10] on the facile decarbonylation of the primary [4+2]π adducts (III) is that the interaction of the LUMO of the ketonic bridged bond with the HOMO of the double bond is assisted by the electronegative methoxycarbonyl groups, as shown in Chart 7.

The third step (intramolecular cycloaddition) is considered to fall into the category of an inverse-type reaction in Sustmann's classification for cycloadditions, in which the 1,4-bis(methoxycarbonyl)-2,3-diphenylcyclohexadienyl moiety behaves as a 4π-acceptor.

The second- and third-step reactions are considered to be inseparable because the decarbonylation rates[11] were affected by the presence of the remaining double bond of the nonconjugated diene. The intramolecular cycloaddition may be explained in terms of a

TABLE VII. Energies for the DDA Adducts Calculated by the MM2 Method

Calcd value	(V'a)	Va	(V'b)	Vb	(V'c)	Vc	(V'e)	Ve	Vf
Energy (kcal)									
Steric energy	34.706	28.678	36.836	28.869	39.424	33.295	36.597	31.357	47.675
Compression	2.098	1.235	2.073	1.135	1.796	1.549	1.664	1.591	2.282
Bending	6.439	5.646	7.204	5.906	9.441	4.734	7.245	3.970	15.190
Stretch-bond	−0.293	−0.195	−0.135	−0.076	0.232	0.181	0.184	0.108	−0.253
Van der Waals	13.418	8.014	14.694	8.462	14.841	12.509	13.379	11.493	10.879
Torsion	12.910	13.846	12.629	13.053	12.858	14.084	13.991	14.060	19.443
ΔH_f	15.69	9.66	−11.53	−19.50	−12.92	−19.05	11.17	5.93	22.40[d]
Rel ΔH_f	0.0	−6.03[a]	0.0	−7.97[b]	0.0	−6.13	0.0	−5.24	—
Strain energy	30.17	24.14	29.07	21.10	31.45	25.32	31.40	26.16	41.79
Bond length (Å)									
C_α–C_β (C_3–C_4)[c]	1.5599	1.5442			1.5535	1.5405	1.551	1.542	1.5461[e]
C_β–C_γ (C_4–C_9)[c]	1.5453	1.5489			1.5457	1.5522	1.546	1.553	1.5609[e]

a) Rel ΔH_f by MMI method, −3.46 kcal/mol. *b*) Rel ΔH_f by MMI method, −5.56 kcal/mol. *c*) See Chart 5 and Fig. 1 for the atom numbering. *d*) MNDO calculated heat of formation (ΔH_f), 27.1 kcal/mol. *e*) MNDO calculated bond length for C_α–C_β, 1.5824 Å; C_β–C_γ, 1.5788 Å.

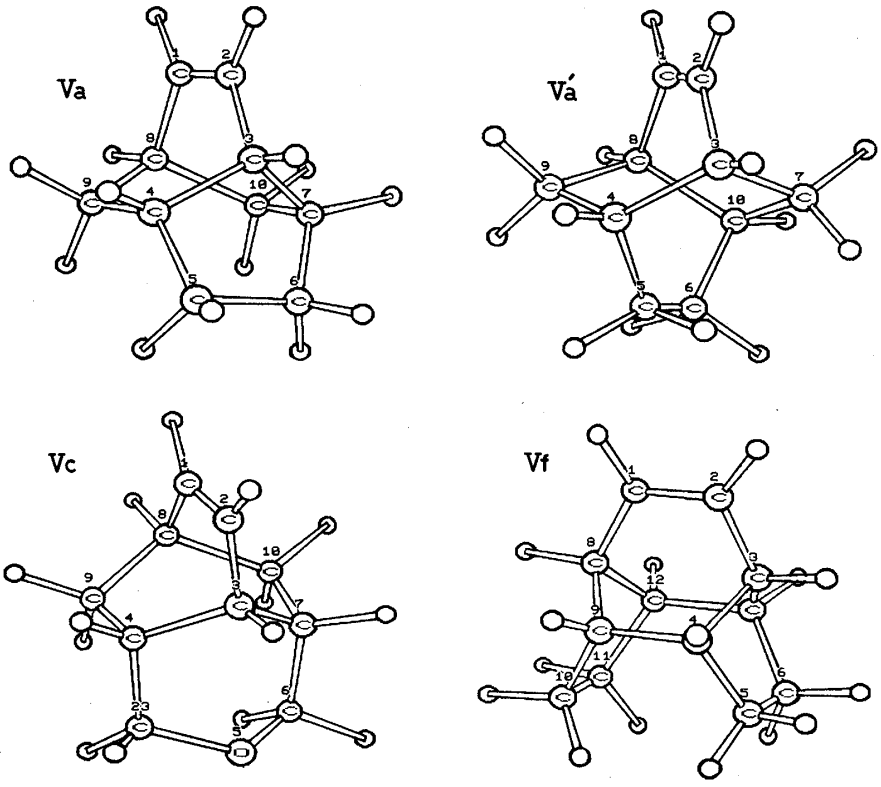


Fig. 1. The MM2 Optimized Structures for Va, V'a, Vc and Vf

transition state in which the *p* atomic orbitals of the remaining double bond of the nonconjugated diene partially overlap with growing *p* atomic orbitals arising from C–CO bond scission (see Chart 7).

The compounds involved in this study seem to be very suitable for MM calculation. Detailed sructural information about the DDA adducts and the relative stabilities of some DDA adducts was obtained by means of MM calculations based on Allinger's MM2 method. For simplicity, the MM2 calculations were carried out on the parent molecules. The

calculation data are summarized in Table VII and the calculated structures for Va, V′a, Vc and Vf are depicted in Fig. 1.

To assess the agreement between the result of the MM method and that of the MO method, we also performed an MNDO (modified neglect of diatomic overlap) semiempirical self-consistent field (SCF)-MO calculation[12] on the DDA adduct of 1,5-cyclooctadiene (IIf) and Ia. The heat of formation calculated by MNDO is in good agreement with that calculated by the MM method. The results are included in Table VII.

For the DDA adducts (Va and V′a), the MM calculations indicate that the heat of formation (ΔH_f) of the isotwistene-type compound, Va is 6.03 kcal/mol, a much smaller energy than that of the twistene-type compound, V′a, indicating V′a to be thermodynamically less stable. The isotwistene-type compound, Vb, obtained from the reaction of allyl vinyl ether (IIb) and Ia, is 7.97 kcal/mol more stable than the twistene-type compound, V′b. As regards steric energy, van der Waals energies (1,4-interaction) are operative in the destabilization of the twistene-type compounds. On the other hand, in the cases of Vc and Ve the bending energy is the main contributor to steric energy.

The calculated strain energy of the DDA adduct (Vf) of 1,5-cyclooctadiene (IIf) and Ia is 41.79 kcal/mol, considerably higher than that of the DDA adduct (Va) derived from 1,5-hexadiene (IIa) and Ia. At a first glance, we thought that the adduct might easily undergo retro-Diels–Alder reaction to give the cyclohexadiene derivative (IVf) owing to its high degree of strain energy. Contrary to this expectation, however, the retro-Diels–Alder reaction could not be observed on heating. The observed stability may be due to the localization of the strain energy at the C_β–C_γ bond rather than the C_α–C_β bond which ought to be cleaved by retro-Diels–Alder reaction. This is consistent with the MM-calculated bond lengths (see Chart 5).

In conclusion, all the pericyclic reaction behaviors involved in this study can be explained in terms of FMO theory. The DDA adducts isolated are isotwistene-type compounds and the product distributions are thermodynamically controlled. The analysis of the formation reaction of DDA adducts indicates that force field (molecular mechanics) calculations are helpful in interpreting the observed thermodynamic stability.

Experimental

All melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were taken with Hitachi R-600 and GX-400 (400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR) spectrometers for *ca.* 10% (w/v) solution with tetramethylsilane (TMS) as an internal standard; chemical shifts are expressed in δ values. IR spectra were recorded on a JASCO IR-G infrared spectrophotometer equipped with a grating. Mass spectra (MS) were taken with a JEOL JMS-01SG double-focussing spectrometer operating at an ionization potential of 75 eV. High-performance liquid chromatographic (HPLC) analyses were performed on a JASCO FAMILIC 100N chromatograph equipped with an ultraviolet (UV) detector and a column of Fine Pak SIL C12.

Molecular orbital calculations were performed on a FACOM M-382 computer in the Computer Center of Kyushu University.

Molecular mechanics calculations (MMI and MMPI) were performed on a FACOM M-360 computer in the Computer Center of Kumamoto University. MM2 calculations were performed on a FUJITSU FM-16β (FD-type) computer using the program locally modified for MS-DOS FORTRAN.

Cycloaddition of 2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (Ia) with Nonconjugated Dienes (IIa—g). General Procedure of Cycloaddition——A solution of Ia and an excess amount of a diene in chloroform was heated at a given temperature until the red color had faded away. The solvent was evaporated off under reduced pressure. The residue was purifid by recrystallization from *n*-hexane. The results are summarized in Tables I and II.

Thermolyses of the [4+2]π Cycloadduct (IIIa—g). Formation of DDA Adducts (Va—g)——The [4+2]π adducts were heated at 170 °C to give oils with evolution of CO gas. The oils were purified by chromatography on silica gel with *n*-hexane–benzene. The results are summarized in Tables III and IV.

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