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Pericyclic Reactions of 2-Pyrones with Nonconjugated Dienes. Conformational Analysis of the Double Diels–Alder Adducts by Molecular Mechanics Calculation

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Pericyclic reactions of 5-methoxycarbonyl-2-pyrone (Ic) with nonconjugated dienes (IIa—j) were investigated. The diene (Ic) reacted readily with IIa—j to give [4+2]π cycloadducts (IIIa—j) that lost carbon dioxide to afford intramolecular double Diels–Alder (DDA) adducts (V). The structures of these adducts were determined from spectral evidence. The reactivity of the addends and the regiochemistry of the primary adducts are discussed on the basis of modified neglect of diatomic overlap (MNDO) calculation data. The relative stability of the twistene- and isotwistene-type compounds and the conformation of some isotwistene-type compounds are discussed on the basis of the molecular mechanics (MM2) calculation data.

Keywords 2-pyrone; nonconjugated diene; cycloaddition; regiochemistry; decarboxylation; double Diels–Alder reaction; MM2; MNDO

2,5-Bis(methoxycarbonyl)-3,4-diphenyl cyclopentadienone (Ia) and 2-oxo-1,3-bis(ethoxycarbonyl)-2*H*-cyclopenta[*a*]acenaphthylene (Ib) exhibit high reactivity toward various dienophiles including medium-sized-ring conjugated polyenes.[1] In the reaction of Ib with nonconjugated dienes (II) such as 1,5-hexadiene or 1,5-cyclooctadiene, the cycloadducts (III) lost carbon monoxide spontaneously to afford tetrasubstituted 1,3-cyclohexadiene derivatives (IV) which were immediately transformed into intramolecular double Diels–Alder (DDA) adducts (V).

Recently, we reported that the Diels–Alder (DA) adducts of Ia were also transformed into intramolecular DDA adducts without the occurrence of retro-DA reaction upon heating under more severe conditions, and we showed that the pericyclic reaction behavior of Ia towards II can be explained on the basis of molecular orbital (MO) and molecular mechanics (MM, empirical force field) calculation data.[2]

Based on this background and the concept of cyclic conjugation (a modification of the Hückel rule),[3] we considered that 5-methoxycarbonyl-2-pyrone (methyl coumalate) (Ic) would show a similar pericyclic reaction behavior toward inactivated nonconjugated dienes (II) and the resultant DDA adducts would be more suitable model compounds for MM calculation than those derived from Ia,b because the DDA adducts of Ia,b are heavily substituted and the intramolecular crowding may lead to deformation of the parent carbon skeletons.

This paper deals with the pericyclic reaction of Ic with various nonconjugated dienes (IIa—j) containing an ether, thioether or ester group in the chain connecting the two double bonds.

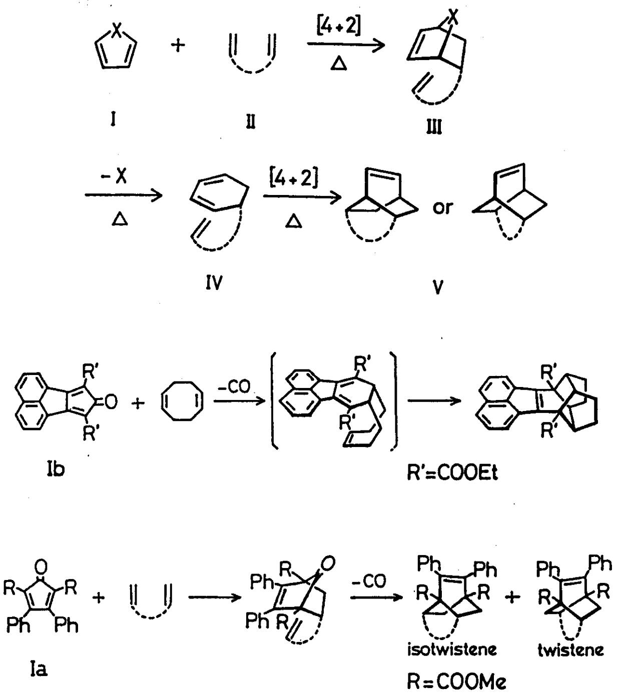


Chart 1

Results

Intermolecular Cycloaddition Reaction of Ic with Nonconjugated Dienes (IIa—j) Reactions of Ic with excess amounts of IIa—j gave 1 : 1 cycloadducts (IIIa—j) in high yields in all cases except IIi (Chart 2). The reaction conditions and properties of the cycloadducts (IIIa—j) are shown in Tables I and II.

In the reaction of Ic with IIa, the DDA adduct was obtained by heating the addends at 100 °C in the presence of *p*-chlorophenol, which acts as a catalytic solvent.[4]

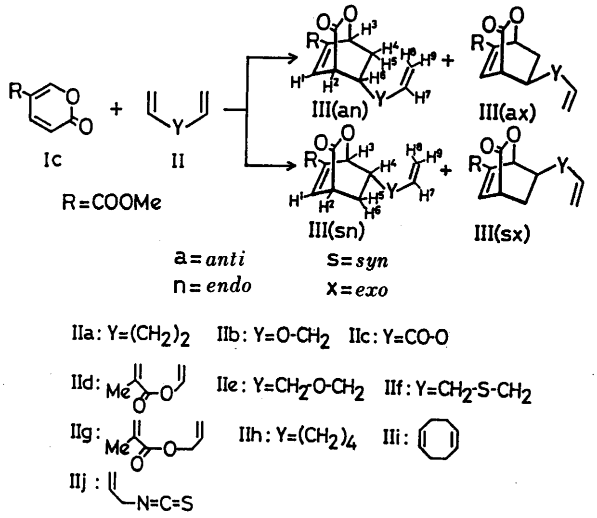


Chart 2

Table I. The Intermolecular DA Reactions of Ic with IIa—j and Yields of the DA Adducts (IIIa—j)

Dienophile	Solvent	Temp. (°C)	Time (h)	Yield (%)$^{a)}$
IIa	No solvent	100$^{c)}$	50	67
	PCP$^{b)}$	100$^{c)}$	54	59$^{d)}$
IIb	No solvent	70$^{c)}$	44	78
IIc	No solvent	70	48	76
IId	No solvent	70	154	87
IIe	No solvent	100$^{c)}$	23	56
	PCP$^{b)}$	70	264	64
	PCP$^{b)}$	100$^{c)}$	23	49
IIf	No solvent	100	41	62
IIg	No solvent	70	205	78
IIh	No solvent	100	69	78
	PCP$^{b)}$	100	17	47
IIi	No solvent	120	31	47$^{d)}$
IIj	No solvent	100$^{c)}$	56	37

a) Total yield of oils. *b)* *p*-Chlorophenol (2 ml) was used with 0.5 g (0.0032 mol) of Ic as a catalytic solvent. *c)* Heated in a sealed tube (stainless steel). *d)* The DDA adduct was produced.

Table II. Ratios of the *anti* to *syn* and of the *anti-endo* to *anti-exo* DA Adducts (III)

Compd.	*anti*	:	*syn*	*anti-endo*	:	*anti-exo*
IIIa	5.4	:	1	1.2	:	1
IIIb	1	:	—	8	:	1
IIIc	4	:	3	1	:	—
IIId$^{a)}$	9.6	:	1	17	:	1
III′d$^{a)}$	1	:	—	1.2	:	1
IIIe	2.9	:	1	2	:	1
IIIf	3.9	:	1	1	:	1
IIIg$^{b)}$	22.9	:	1	9	:	1
III′g$^{b)}$	2.7	:	1	2.2	:	1
IIIh	10	:	1	1.2	:	1
IIIj	1	:	—	3	:	1

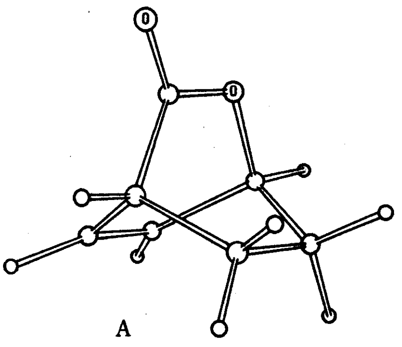
a) IIId : III′d = 1.4 : 1. *b)* IIIg : III′g = 3.2 : 1.

Table III. IR and Mass Spectral Data for the DA Adducts (III)

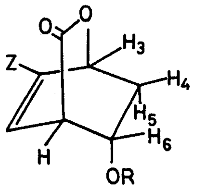
Compd.$^{a)}$	IR (cm^{-1}) C=O		*m*/*z*
	Ester	Bridged lactone	
IIIa (an and ax)	1724	1762	192 (M$^+$ − CO$_2$)
IIIb (an)	1720	1766	238
IIIc (an and sn)	1722	1760	252
IIId (an)	1724	1768	266
III′d (an)	1724	1772	266
III′d (ax)	1722	1774	266
IIIe (an and ax)	1722	1762	253 (M$^+$ + H)
IIIf (an and ax)	1720, 1724	1764	268
IIIg (an)	1730	1768	High MS$^{b)}$
IIIg (ax), III′g (an)	1726	1768	High MS$^{c)}$
III′g (ax and sn)	1722	1768	High MS$^{d)}$
IIIh (an and ax)	1724	1762	High MS$^{e)}$
IIIj (an and ax)	1724	1768	High MS$^{f)}$

a) a, *anti*; s, *syn*; n, *endo*; x, *exo*. *b)* Calcd for $C_{14}H_{16}O_6$: 280.0947. Found: 280.0970. *c)* Calcd for $C_{14}H_{16}O_6$: 280.0947. Found: 280.0948. *d)* Calcd for $C_{14}H_{16}O_6$: 280.0947. Found: 280.0940. *e)* Calcd for $C_{15}H_{20}O_4$: 264.1362. Found: 264.1342. *f)* Calcd for $C_{11}H_{11}NO_4S$: 253.0409. Found: 253.0404.

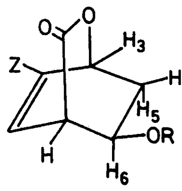
In the case of IIi, the DA cycloadduct (IIIi) could not be isolated even under mild reaction conditions: heating a mixture of Ic and IIi at *ca.* 120 °C without solvent caused decarboxylation followed by intramolecular cycloaddition to give the DDA adduct (Vi) (see also Chart 8).



A



endo IIIb



exo IIIb

Fig. 1. The MNDO Optimized Structure of A

The infrared (IR) spectra of these cycloadducts commonly showed characteristic bands at *ca.* 1765 cm^{-1} due to a strained six-membered lactone carbonyl group (Table III).

The stereochemistry of the cycloadducts (IIIa, e, f, h) was determined by 400 MHz proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The data are summarized in Table IV and the numerals used to identify selected protons for the structure determination are shown in Chart 2.

In the reaction of Ic with symmetrical dienophiles (IIa, e, f, h), four stereoisomers (regioisomers and their *endo*/*exo* isomers) are possible. In the *syn* adduct with respect to the –COOMe group, the signals of the H_3 proton attached to the carbon bearing the oxygen atom of the lactone appeared as a weakly split doublet, whereas that of *anti* adduct appeared as a multiplet. In the all cases, the *anti* adducts were produced predominantly (Table II).

Careful inspections of the ^{1}H-NMR spectra of these adducts revealed that each *anti* cycloadduct consists of a mixture of the *exo* and *endo* cycloadducts showing complex overlapped signal patterns of the cyclohexene moiety (Table IV). The configurations and the *exo*/*endo* ratios of the cycloadducts were determined on the basis of the 400 MHz ^{1}H-NMR signals of the H_3, H_4, H_5 and H_6 protons. To determine the precise dihedral angles and coupling constants$^{5)}$ among the H_3, H_4, H_5 and H_6 protons, the stereo structure of a model compound (A), *i.e.*, the cycloadduct of Ic and ethylene, was obtained by MM2 calculation$^{6)}$ followed by MNDO (modified neglect of diatomic overlap) optimization.$^{7)}$

The calculated coupling constants and the observed values for the cycloadducts (*endo* IIIb and *exo* IIIb) of Ic and IIb are listed in Table V. As shown in Table V, the calculated values agreed well with the observed ones. The calculation indicates that the dihedral angles of H_3–C–C–H_4 and H_3–C–C–H_5 are 56.3° and 60.1° respectively. The calculated coupling constant of H_3 with *exo* H_4 (2.3 Hz) is slightly larger than that for *endo* H_5 (1.8 Hz). This

TABLE IV. ^{1}H-NMR Spectral Data for the DA Adducts (III)

Compd.[a]	^{1}H-NMR ($CDCl_3$) δ ppm[b]
IIIa (an)	7.27 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=1.8$ Hz, H_1), 5.68—5.80 (1H, m, H_7),[c] 5.60—5.70 (1H, m, H_3),[c] 5.03 (1H, br, H_8),[c] 4.99 (1H, br, H_9),[c] 3.81 (3H, s, OMe), 3.67 (1H, dd, $J_{2,1}=6.2$, $J_{2,6}=2.5$ Hz, H_2), 2.48 (1H, ddd, $J_{4,5}=13.6$, $J_{4,6}=9.2$, $J_{4,3}=4.0$ Hz, H_4), 2.19—2.29 (1H, m, H_6), 2.04—2.14 (2H, m, methylene), 1.25—1.43 (2H, m, methylene), 1.26 (1H, dd, $J_{5,4}=13.6$, $J_{5,6}=5.1$ Hz, H_5)
IIIa (ax)	7.40 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 5.68—8.80 (1H, m, H_7),[c] 5.60—5.70 (1H, m, H_3),[c] 5.03 (1H, br, H_8),[c] 4.99 (1H, br, H_9),[c] 3.80 (3H, s, OMe), 3.54 (1H, dd, $J_{2,1}=6.6$, $J_{2,6}=2.2$ Hz, H_2), 2.04—2.18 (2H, m, methylene), 1.94 (1H, ddd, $J_{5,4}=12.5$, $J_{5,6}=9.5$, $J_{5,3}=1.8$ Hz, H_5), 1.86 (1H, m, H_6), 1.76 (1H, ddd, $J_{4,5}=12.5$, $J_{4,6}=4.4$, $J_{4,3}=4.0$ Hz, H_4), 1.41—1.67 (2H, m, methylene)
IIIb (an)	7.24 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=1.8$ Hz, H_1), 5.84 (1H, m, H_7), 5.70 (1H, ddd, $J_{3,4}=3.7$, $J_{3,1}$ and $J_{3,5}=1.8$ Hz, H_3), 5.27 (1H, dd, $J_{8,7}=17.2$, $J_{8,9}=1.5$ Hz, H_8), 5.21 (1H, dd, $J_{9,7}=10.3$, $J_{9,8}=1.5$ Hz, H_9), 4.07—4.16 (2H, m, H_2 and H_6),[c] 3.95—4.02 (2H, m, methylene), 3.82 (3H, s, OMe), 2.64 (1H, ddd, $J_{4,5}=14.3$, $J_{4,6}=7.7$, $J_{4,3}=3.7$ Hz, H_4), 1.64 (1H, ddd, $J_{5,4}=14.3$, $J_{5,3}$ and $J_{5,6}=1.8$ Hz, H_5)
IIIb (ax)	7.24 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=1.5$ Hz, H_1), 5.88 (1H, m, H_7), 5.63—5.66 (1H, m, H_3), 5.28 (1H, dd, $J_{8,7}=17.2$, $J_{8,9}=1.5$ Hz, H_8), 5.20 (1H, dd, $J_{9,7}=10.3$, $J_{9,8}=1.5$ Hz, H_9), 4.13 (1H, dd, $J=12.8$, $J=5.5$ Hz, methylene), 4.00 (1H, dd, $J=12.8$, 5.9 Hz, methylene), 3.96 (1H, dd, $J_{2,1}=6.6$, $J_{2,6}=3.3$ Hz, H_2), 3.89 (1H, ddd, $J_{6,5}=8.0$, $J_{6,4}=3.7$, 3.3 Hz, H_6), 3.80 (3H, s, OMe), 2.12 (1H, ddd, $J_{5,4}=13.9$, $J_{5,6}=8.0$, $J_{5,3}=1.8$ Hz, H_5), 2.09 (1H, ddd, $J_{4,5}=13.9$, $J_{4,3}$ and $J_{4,6}=3.7$ Hz, H_4)
IIIc (an)	7.33 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=2.0$ Hz, H_1), 7.19 (1H, dd, $J_{7,8}=13.9$, $J_{7,9}=6.2$ Hz, H_7), 5.76—5.79 (1H, m, H_3), 4.96 (1H, dd, $J_{8,7}=13.9$, $J_{8,9}=1.8$ Hz, H_8), 4.67 (1H, dd, $J_{9,7}=6.2$, $J_{9,8}=1.8$ Hz, H_9), 4.10 (1H, dd, $J_{2,1}=6.2$, $J_{2,6}=2.9$ Hz, H_2), 3.81 (3H, s, OMe), 3.26 (1H, ddd, $J_{6,4}=10.3$, $J_{6,5}=4.0$, $J_{6,2}=2.9$ Hz, H_6), 2.64 (1H, ddd, $J_{4,5}=13.9$, $J_{4,6}=10.3$, $J_{4,3}=4.0$ Hz, H_4), 2.11 (1H, ddd, $J_{5,4}=13.9$, $J_{5,6}=4.0$, $J_{5,3}=1.5$ Hz, H_5)
IIIc (sn)	7.46 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 7.14 (1H, dd, $J_{7,8}=13.9$, $J_{7,9}=6.2$ Hz, H_7), 5.96 (1H, dd, $J_{3,4}=3.7$, $J_{3,1}=2.2$ Hz, H_3), 4.98 (1H, dd, $J_{8,7}=13.9$, $J_{8,9}=1.8$ Hz, H_8), 4.66 (1H, dd, $J_{9,7}=6.2$, $J_{9,8}=1.8$ Hz, H_9), 3.79 (3H, s, OMe), 3.74 (1H, ddd, $J_{2,1}=6.6$, $J_{2,5}=3.0$, $J_{2,6}=2.6$ Hz, H_2), 3.52 (1H, ddd, $J_{4,5}=9.5$, $J_{4,6}=5.9$, $J_{4,3}=3.7$ Hz, H_4), 2.34 (1H, ddd, $J_{5,6}=13.2$, $J_{5,4}=9.5$, $J_{5,2}=3.0$ Hz, H_5), 1.99 (1H, ddd, $J_{6,5}=13.2$, $J_{6,4}=5.9$, $J_{6,2}=2.6$ Hz, H_6)
IIId (an)	7.37 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=2.0$ Hz, H_1), 7.17 (1H, dd, $J_{7,8}=13.9$, $J_{7,9}=6.2$ Hz, H_7), 5.69 (1H, ddd, $J_{3,4}=3.7$, $J_{3,1}=2.0$, $J_{3,5}=1.8$ Hz, H_3), 4.96 (1H, dd, $J_{8,7}=13.9$, $J_{8,9}=1.8$ Hz, H_8), 4.68 (1H, dd, $J_{9,7}=6.2$, $J_{9,8}=1.8$ Hz, H_9), 3.90 (1H, d, $J_{2,1}=6.2$ Hz, H_2), 3.80 (3H, s, OMe), 2.51 (1H, dd, $J_{5,4}=14.3$, $J_{5,3}=1.84$ Hz, H_5), 2.16 (1H, dd, $J_{4,5}=14.3$, $J_{4,3}=3.7$ Hz, H_4), 1.54 (3H, s, Me)
III′d (an)	7.28 (1H, dd, $J_{1,2}=6.0$, $J_{1,3}=2.0$ Hz, H_1), 6.01 (1H, br, H_8), 5.76 (1H, ddd, $J_{3,4}=3.7$, $J_{3,1}=2.0$, $J_{3,5}=1.5$ Hz, H_3), 5.61 (1H, qd, $J_{9,Me}$ and $J_{9,8}=1.5$ Hz, H_9), 5.33—5.37 (1H, m, H_6), 4.13 (1H, dd, $J_{2,1}=6.0$, $J_{2,6}=3.5$ Hz, H_2), 3.85 (3H, s, OMe), 2.84 (1H, ddd, $J_{4,5}=15.02$, $J_{4,6}=8.1$, $J_{4,3}=3.7$ Hz, H_4), 1.89 (3H, dd, $J_{Me,9}=1.5$, $J_{Me,8}=0.7$ Hz, Me), 1.70 (1H, ddd, $J_{5,4}=15.0$, $J_{5,3}$ and $J_{5,6}=1.5$ Hz, H_5)
III′d (ax)	7.30 (1H, dd, $J_{1,2}=6.7$, $J_{1,3}=2.6$ Hz, H_1), 6.14 (1H, br, H_8), 5.70—5.73 (1H, m, H_3), 5.64 (1H, br, H_9), 5.12 (1H, ddd, $J_{6,5}=9.2$, $J_{6,2}$ and $J_{6,4}=3.3$ Hz, H_6), 3.94 (1H, dd, $J_{2,1}=6.7$, $J_{2,6}=3.3$ Hz, H_2), 3.83 (3H, s, OMe), 2.33 (1H, ddd, $J_{5,4}=14.7$, $J_{5,6}=9.2$, $J_{5,3}=1.5$ Hz, H_5), 2.14 (1H, ddd, $J_{4,5}=14.7$, $J_{4,3}=3.7$, $J_{4,6}=3.3$ Hz, H_4), 1.93 (3H, br, Me)
IIIe (an)	7.26 (1H, dd, $J_{1,2}=6.3$, $J_{1,3}=2.2$ Hz, H_1), 5.79—5.93 (1H, m, H_7),[c] 5.65—5.68 (1H, m, H_3),[c] 5.15—5.30 (2H, m, H_8 and H_9),[c] 3.90—3.97 (2H, m, O-CH_2),[c] 3.87 (1H, dd, $J_{2,1}=6.2$, $J_{2,6}=2.6$ Hz, H_2), 3.81 (3H, s, OMe), 3.26 (1H, dd, $J=9.0$, 5.5 Hz, CH_2-O), 3.07 (1H, t, $J=9.0$ Hz, CH_2-O), 2.50—2.59 (1H, m, H_6), 2.44 (1H, ddd, $J_{4,5}=13.6$, $J_{4,6}=9.5$, $J_{4,3}=4.0$ Hz, H_4), 1.21 (1H, dd, $J_{5,4}=13,6$, $J_{5,6}=4.0$ Hz, H_5)
IIIe (ax)	7.41 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 5.79—5.93 (1H, m, H_7 overlap), 5.65—5.68 (1H, m, H_3),[c] 5.15—5.30 (2H, m, H_8 and H_9),[c] 3.86—4.04 (2H, m, O-CH_2),[c] 3.80 (3H, s, OMe), 3.77—3.81 (1H, m, H_2),[c] 3.53 (1H, dd, $J=9.5$, 5.9 Hz, CH_2-O), 3.33 (1H, dd, $J=9.5$, 8.8 Hz, CH_2-O), 2.08—2.15 (1H, m, H_6), 1.89 (1H, ddd, $J_{5,4}=13.9$, $J_{5,6}=10.3$, $J_{5,3}=1.8$ Hz, H_5), 1.79 (1H, ddd, $J_{4,5}=13.9$, $J_{4,6}=5.9$, $J_{4,3}=3.7$ Hz, H_3)
IIIf (an)	7.26 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=2.2$ Hz, H_1), 5.69—5.82 (1H, m, H_7),[c] 5.64—5.68 (1H, m, H_3),[c] 5.06—5.13 (2H, m, H_8 and H_9),[c] 3.90 (1H, dd, $J_{2,1}=6.2$, $J_{2,6}=1.8$ Hz, H_2), 3.82 (3H, s, OMe), 3.13 (2H, m, S-CH_2),[c] 2.50—2.56 (1H, m, H_4),[c] 2.38—2.47 (1H, m, H_6), 2.35 (1H, dd, $J=13.2$, 7.0 Hz, CH_2-S), 2.27 (1H, dd, $J=13.2$, 8 Hz, CH_2-S), 1.38 (1H, ddd, $J_{5,4}=13.6$, $J_{5,6}=2.2$, $J_{5,3}=1.5$ Hz, H_5)
IIIf (ax)	7.41 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 5.69—5.82 (1H, m, H_7),[c] 5.64—5.68 (1H, m, H_3),[c] 5.06—5.13 (2H, m, H_8 and H_9), 3.82 (3H, s, OMe), 3.76 (1H, dd, $J_{2,1}=6.6$, $J_{2,6}=1.8$ Hz, H_2), 3.13 (2H, m, S-CH_2),[c] 2.52—2.56 (2H, m, S-CH_2),[c] 1.97—2.02 (2H, m, H_5 and H_6),[c] 1.87 (1H, dd, $J_{4,5}=8.1$, $J_{4,3}=3.7$ Hz, H_4)
IIIg (an)	7.35 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=2.2$ Hz, H_1), 5.87 (1H, ddt, $J_{7,8}=17.2$, $J_{7,9}=10.3$, $J_{7,CH_2}=5.9$ Hz, H_7), 5.66 (1H, ddd, $J_{3,4}=3.7$, $J_{3,1}=2.2$, $J_{3,5}=1.8$ Hz, H_3), 5.30 (1H, dd, $J_{8,7}=17.2$, $J_{8,9}=1.4$ Hz, H_8), 5.27 (1H, dd, $J_{9,7}=10.3$, $J_{9,8}=1.4$ Hz, H_9), 4.56—4.62 (2H, m, O-CH_2), 3.87 (1H, d, $J_{2,1}=6.2$ Hz, H_2), 3.79 (3H, s, OMe), 2.50 (1H, dd, $J_{5,4}=14.3$, $J_{5,3}=1.8$ Hz, H_5), 2.12 (1H, dd, $J_{4,5}=14.3$, $J_{4,3}=3.7$ Hz, H_4), 1.50 (3H, s, Me)
IIIg (ax)	7.34 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 5.91 (1H, ddt, $J_{7,8}=17.2$, $J_{7,9}=10.3$, $J=5.9$ Hz, H_7), 5.68 (1H, ddd, $J_{3,4}=4.0$, $J_{3,1}=2.2$, $J_{3,5}=1.8$ Hz, H_3), 5.35 (1H, dd, $J_{8,7}=17.2$, $J_{8,9}=1.4$ Hz, H_8), 5.27 (1H, dd, $J_{9,7}=10.26$, $J_{9,8}=1.4$ Hz, H_9), 4.58—4.70 (2H, m, O-CH_2), 3.83 (3H, s, OMe), 3.77—3.86 (1H, m, H_2),[c] 3.02 (1H, dd, $J_{4,5}=13.9$, $J_{4,3}=4.0$ Hz, H_4), 1.51—1.56 (1H, m, H_5),[c] 1.27 (3H, s, Me)
III′g (an)	7.29 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=1.8$ Hz, H_1), 6.13 (1H, s, H_8), 5.70 (1H, ddd, $J_{3,4}=4.0$, $J_{3,1}$ and $J_{3,5}=1.8$ Hz, H_3), 5.63 (1H, s, H_9), 4.02 (1H, dd, $J=11.4$, 5.50 Hz, CH_2-O), 3.82 (3H, s, OMe), 3.77—3.86 (2H, m, H_2 and CH_2-O),[c] 2.63—2.68 (1H, m, H_6), 2.52 (1H, ddd, $J_{4,5}=13.6$, $J_{4,6}=9.0$, $J_{4,3}=4.0$ Hz, H_3), 1.94 (3H, s, Me), 1.31 (1H, ddd, $J_{5,4}=13.6$, $J_{5,6}=2.9$, $J_{5,3}=1.8$ Hz, H_5)
III′g (ax)	7.44 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 6.15 (1H, s, H_8), 5.71—5.67 (1H, m, H_3), 5.62 (1H, s, H_9), 4.33 (1H, dd, $J=11.7$, 5.0 Hz, CH-O), 4.08 (1H, dd, $J=11.7$, 7.3 Hz, CH_2-O), 3.81 (3H, s, OMe), 3.65—3.73 (1H, m, H_2),[c] 2.23—2.30 (1H, m, H_6),[c] 1.95 (3H, s, Me), 1.93—1.98 (2H, m, H_4 and H_5)[c]
III′g (sn)	7.46 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.5$ Hz, H_1), 6.13 (1H, s, H_8), 5.72 (1H, dd, $J_{3,4}=3.3$, $J_{3,1}=2.5$ Hz, H_3), 5.63 (1H, s, H_9), 4.08 (1H, m, CH_2-O),[c] 3.78 (3H, s, OMe), 3.65—3.73 (2H, m, H_2 and CH_2-O),[c] 2.85—2.94 (1H, m, H_5), 2.23—2.30 (1H, m, H_4),[c] 1.95 (3H, s, Me), 1.18 (1H, ddd, $J_{6,5}=12.8$, $J_{6,4}=5.7$, $J_{6,2}=2.5$ Hz, H_6)
IIIh (an)	7.25 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=1.8$ Hz, H_1), 5.71—5.82 (1H, m, H_7),[c] 5.64—5.65 (1H, m, H_3),[c] 4.93—5.02 (2H, m, H_8 and H_9),[c] 3.81 (3H, s, OMe), 3.66 (1H, dd, $J_{2,1}=6.2$, $J_{2,6}=2.5$ Hz, H_2), 2.53 (1H, ddd, $J_{4,5}=13.6$, $J_{4,6}=9.2$, $J_{4,3}=4.4$ Hz, H_4), 2.16—2.23 (1H, m, H_6), 2.00—2.06 (2H, m, methylene), 1.18—1.51 (7H, m, H_5 and methylene)[c]
IIIh (ax)	7.40 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 5.71—5.82 (1H, m, H_7),[c] 5.64—5.65 (1H, m, H_3),[c] 4.93—5.02 (2H, m, H_8 and H_9),[c] 3.80 (3H, s, OMe), 3.54 (1H, dd, $J_{2,1}=6.6$, $J_{2,6}=1.8$ Hz, H_2), 2.00—2.06 (2H, m, methylene),[c] 1.93 (1H, ddd, $J_{5,4}=12.5$, $J_{5,6}=9.2$, $J_{5,3}=1.5$ Hz, H_5), 1.65—1.79 (2H, m, H_4 and H_6),[c] 1.18—1.51 (6H, m, methylene)
IIIj (an)	7.29 (1H, dd, $J_{1,2}=6.2$, $J_{1,3}=1.8$ Hz, H_1), 5.69—5.73 (1H, m, H_3),[c] 3.83 (3H, s, OMe), 3.79—3.83 (1H, m, H_2),[c] 3.46 (1H, dd, $J=14.3$, 5.9 Hz, CH_2-N), 3.33 (1H, dd, $J=14.3$, 8 Hz, CH_2-N), 2.59—2.66 (1H, m, H_6), 2.56 (1H, ddd, $J_{4,5}=13.6$, $J_{4,6}=9.2$, $J_{4,3}=4.0$ Hz, H_4), 1.31 (1H, ddd, $J_{5,4}=13.6$, $J_{5,6}=3.7$, $J_{5,3}=1.1$ Hz, H_5)

Table IV. (continued)

Compd.[a]	^{1}H-NMR ($CDCl_3$) δ ppm[b]
IIIj (ax)	7.42 (1H, dd, $J_{1,2}=6.6$, $J_{1,3}=2.2$ Hz, H_1), 5.69—5.73 (1H, m, H_3),[c] 3.82 (3H, s, OMe), 3.73 (1H, dd, $J_{2,1}=6.6$, $J_{2,6}=2.2$ Hz, H_2), 3.68 (1H, dd, $J=14.3$, 6.6 Hz, CH_2-N), 3.54 (1H, dd, $J=14.3$, 8.4 Hz, CH_2-N), 2.20—2.30 (1H, m, H_6), 2.04 (1H, ddd, $J_{5,4}=13.9$, $J_{5,6}=10.3$, $J_{5,3}=1.5$ Hz, H_5), 1.81 (1H, ddd, $J_{4,5}=13.9$, $J_{4,6}=5.5$, $J_{4,3}=3.7$ Hz, H_4)

a) a, *anti*; s, *syn*; n, *endo*; x, *exo*. *b)* See Chart 2 for the proton numbering. *c)* Overlapped with the other signals.

Table V. Coupling Constants for the Parent Compound (A) and IIIb

H_x-H_y	Coupling constants (Hz)		
	Calcd[a] A	Observed	
		endo-IIIb	*exo*-IIIb
H_3-H_4	2.3 (3.1)[b]	3.7	3.7
H_3-H_5	1.8 (2.4)	1.8	1.8
H_4-H_5	—	14.3	13.9
H_4-*endo* H_6	1.6 (2.2)	—	3.7
H_4-*exo* H_6	8.2 (10)	7.7	—
H_5-*endo* H_6	8.2 (10)	—	8.0
H_5-*exo* H_6	1.6 (2.3)	1.8	—

a) Based on the Karplus rule[5a] using the MNDO-optimized structure. *b)* Values in parentheses were calculated based on the Williamson–Johnson rule.[5b]

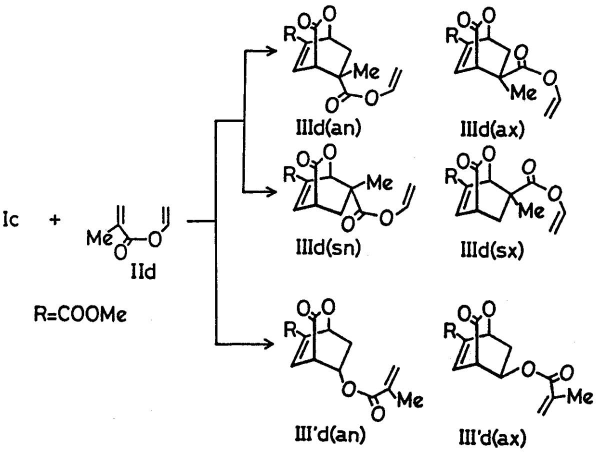


Chart 3

trend is also observed in structurally similar compounds.[8]

In bicyclo[2.2.2]octenes, it has been reported that the configuration of the protons can be determined from the difference of their ^{1}H-NMR chemical shifts, which is associated with a long-range shielding effect of the C=C double bond.[8,9] In our cases, the signal due to the *endo* H_6 proton of the *exo* adduct clearly appeared at a higher magnetic field than that due to the *exo* H_6 proton of the *endo* adduct. For the cycloadduct (IIIb) of Ic with IIb, these facts indicate the main product of IIIb to be the *endo* cycloadduct.

Similarly, the configurations of the cycloadducts (IIIa—j) were determined on the basis of the ^{1}H-NMR spectral data (see Table IV). However, further rigorous confirmation of the stereochemistry of the cycloadducts by single crystal X-ray analysis was not achieved because the succeeding decarboxylation reaction of the *endo* and *exo* [4+2] cycloadducts should give the same decarboxylated product.

In the reaction of vinyl acrylate (IIc), *endo* cycloadducts were produced exclusively in the *anti*:*syn* ratio of 4:3. The cycloaddition occurred at the acrylic moiety. In the case of allyl vinyl ether (IIb), the vinyl moiety was attacked exclusively and the *anti* cycloadducts were produced in the *endo*:*exo* ratio of 8:1.

Cycloaddition of allyl methacrylate (IIg) led to a mixture of cycloadducts in which Ic reacted with two reaction sites, *i.e.* the allyl and methacryl moieties. The *syn*/*anti* and *endo*/*exo* ratios were estimated from the ^{1}H-NMR spectral

Table VI. Reaction Conditions for DDA Reaction of Ic with II

Compd.[a]	Temp. (°C)	Time (h)	mp (°C)	Yield (%)
Va (a and s)	180[b]	16	164—169[c]	50
Vb (a)	180[b]	7	162—164[c]	68
Vc (a and s)	170[b,d]	26.5	97—122[e]	67
Vd (a)	180[b,d]	5	Oil	90
Ve (a and s)	160[b]	11.5	85— 91[e,f]	47
Vf (a)	180[b]	14.5	104—106	19
IVg (a)	180[b,d]	7	Oil	69
IVh (a)	180[b,d]	4	Oil	80
Vi	120	31	Oil	47
IVj (a)	180[b,d]	5	Oil	82

a) a, *anti*; s, *syn*. *b)* In sealed tube (benzene). *c)* Melting point of VI. *d)* Pyrolysis of the corresponding DA adduct (III). *e)* Mixture of V (a) and V (s). *f)* The melting point of VIe (a) and VIe (s) is 189—194 °C.

Table VII. Analytical and IR Spectral Data for DDA Adducts (V)

Compd.[a]	IR (cm^{-1}) C=O (ester)	Formula	Analysis Calcd (Found)	
			C	H
Va (a and s)	1712	$C_{12}H_{16}O_2$	—	—
VIa (a)	1670[b]	$C_{11}H_{14}O_2$	74.13 (73.93	7.92 7.81)
Vb (a)	1712	$C_{11}H_{14}O_3$	—	—
VIb (a)	1696[b]	$C_{10}H_{12}O_3$	66.65 (66.64	6.71 6.73)
Vc (a)	1770[c] 1712	$C_{11}H_{12}O_4$	63.45 (63.40	5.81 6.05)
Vd (a)	1776[c] 1714	$C_{12}H_{14}O_4$	High MS[d]	
Ve (a and s)	1714	$C_{12}H_{16}O_3$	—	—
VIe (a and s)	1670[b]	$C_{11}H_{14}O_3$	68.02 (68.24	7.26 7.10)
Vf (a)	1714	$C_{12}H_{14}O_2S$	64.25 (63.96	7.19 6.98)
IVg (a)	1724	$C_{13}H_{16}O_4$	High MS[e]	
IVh (a)	1724	$C_{14}H_{20}O_2$	High MS[f]	
Vi	1716	$C_{14}H_{18}O_2$	—	—
VIi	1670[b]	$C_{13}H_{16}O_2$	76.44 (76.54	7.89 7.85)
IVj (a)	1720[g]	$C_{10}H_{11}NO_2S$	High MS[h]	

a) a, *anti*; s, *syn*. *b)* Carboxylic acid. *c)* Lactone. *d)* Calcd for $C_{12}H_{14}O_4$: 222.0892. Found: 222.0891. *e)* Calcd for $C_{13}H_{16}O_4$: 236.1049. Found: 236.1055. *f)* Calcd for $C_{14}H_{20}O_2$: 220.1463. Found: 220.1452. *g)* 2096 cm^{-1} (-N=C=S). *h)* Calcd for $C_{10}H_{11}NO_2S$: 209.0511. Found: 209.0495.

data.

Allyl isothiocyanate (IIj) reacted with Ic at 100 °C to give the *anti* cycloadduct as an *endo–exo* mixture.

Thermolysis of the [4+2]π Cycloadduct (IIIa) of Ic and 1,5-Hexadiene (IIa) Heating a mixture of Ic and IIa in benzene at 180 °C in a sealed tube for 16 h gave the DDA adduct (Va) as an oil in 50% yield. The IR spectrum of Va exhibited an unstrained conjugated ester carbonyl band at $1712\,cm^{-1}$. The ^{13}C-NMR spectrum of Va showed five kinds of sp^3 carbon atoms: C_1 (C_{3a}), C_2 (C_3) and C_4 (C_8) resonate at 29.87, 37.98 and 32.12 ppm respectively. This suggests that the product has a mirror symmetry with regard to a plane through the C_5, C_6, C_7 and C_{7a} atoms, indicative of an isotwistene structure. The ^1H-NMR spectrum of Va indicated the presence of an olefinic proton (C_7-H) ascribable to the trisubstituted olefin (–CH=C–COOMe), which coupled with C_{7a}-H and also weakly coupled with C_5-H.

The ^1H- and ^{13}C-NMR spectra of the product showed the presence of the regioisomer (*syn* Va). The formation ratio (*syn*/*anti*) was estimated to be 3/20 from the peak-area integration data of C_7-H.

Hydrolysis of Va with alcoholic NaOH followed by treatment with HCl afforded the corresponding free carboxylic acid and recrystallization from *n*-hexane–benzene gave the *anti* cycloadduct (*anti* VIa) in a pure state. The IR spectrum of VIa exhibited a characteristic broad band in the vicinity of $2952\,cm^{-1}$ due to carboxylic OH groups and a conjugated carbonyl absorption at $1670\,cm^{-1}$ (–CH=C–COOH). The ^1H- and ^{13}C-NMR spectra of VIa showed closely similar spectral patterns to those of Va. The C_7-H of VIa resonates at 7.45 ppm, 0.18 ppm lower field than that of Va.

These data and elementary analysis indicate that intramolecular cycloaddition had taken place between the 1,3-cyclohexadienyl moiety of the decarboxylated DA adduct and the remaining double bond of the nonconjugated diene (IIa) to give a isotwistene-type DDA cycloadduct (Chart 4).

When the reaction of Ic with IIa was carried out in the presence of phenolic compounds such as *p*-chlorophenol, smooth decarboxylation occurred to give Va.

TABLE VIII. ^1H-NMR Spectral Data for the DDA Adducts (V)

Compd.[a]	^1H-NMR ($CDCl_3$) δ ppm
Va (a)[b]	7.27 (1H, dd, $J_{7,7a}=7.0$, $J_{7,5}=1.8$ Hz, C_7-H), 3.74 (3H, s, OMe), 3.03—3.04 (1H, br, C_5-H), 2.57 (1H, ddd, $J_{7a,7}=7.0$, $J_{7a,1}$ and $J_{7a,3a}=4$ Hz, C_{7a}-H), 1.86—1.89 (4H, m, C_1-H, C_{3a}-H, C_2-H and C_3-H),[c] 1.47—1.54 (4H, m, C_2-H, C_3-H, C_4-H and C_8-H),[c] 1.21 (2H, dd, $J_{4,4}$ and $J_{8,8}=12.5$, $J_{4,5}$ and $J_{8,5}=2.5$ Hz, C_4-H and C_8-H)
VIa (a)[b]	7.45 (1H, dd, $J_{7,7a}=7.0$, $J_{7,5}=1.8$ Hz, C_7-H), 3.03—3.04 (1H, br, C_5-H), 2.60 (1H, ddd, $J_{7a,7}=7.0$, $J_{7a,1}$ and $J_{7a,3a}=4$ Hz, C_{7a}-H), 1.81—1.94 (4H, m, C_1-H, C_{3a}-H, C_2-H and C_3-H),[c] 1.49—1.55 (4H, m, C_2-H, C_3-H, C_4-H and C_8-H),[c] 1.22 (2H, dd, $J_{4,4}$ and $J_{8,8}=12.8$, $J_{4,5}$ and $J_{8,5}=2.6$ Hz, C_4-H and C_8-H)
Vb (a)[d]	7.13 (1H, dd, $J_{4,3a}=6.6$, $J_{4,6}=1.8$ Hz, C_4-H), 4.09 (1H, dd, $J_{7a,7}=7$, $J_{7a,3a}=5.5$ Hz, C_{7a}-H), 3.84 (1H, dd, $J_{gem}=7.7$, $J_{2,3}=4.0$ Hz, C_2-H), 3.76 (3H, s, OMe), 3.65 (1H, d, $J_{gem}=7.7$ Hz, C_2-H), 3.15—3.17 (1H, br, C_6-H), 3.10 (1H, ddd, $J_{3a,4}=6.6$, $J_{3a,7a}=5.5$, $J_{3a,3}=3.67$ Hz, C_{3a}-H), 2.19 (1H, m, C_3-H), 1.62 (1H, m, C_8-H), 1.56 (1H, dd, $J_{7,7}=13.9$, $J_{7,6}=4.0$ Hz, C_7=H), 1.50 (1H, ddd, $J_{gem}=12.8$, $J_{8,3}=3.0$, $J_{8,6}=2.2$ Hz, C_8-H), 1.39 (1H, m, C_7-H)
VIb (a)[d]	7.28 (1H, dd, $J_{4,3a}=7.0$, $J_{4,6}=1.8$ Hz, C_4-H), 4.15 (1H, dd, $J_{7a,7}=6.6$, $J_{7a,3a}=5.5$ Hz, C_{7a}-H), 3.87 (1H, dd, $J_{gem}=7.7$, $J_{2,3}=4.0$ Hz, C_2-H), 3.70 (1H, d, $J_{gem}=7.7$ Hz, C_2-H), 3.12—3.16 (2H, m, C_{3a}-H and C_6-H),[c] 2.22 (1H, m, C_3-H), 1.65 (1H, m, C_8-H), 1.60 (1H, dd, $J_{gem}=13.9$, $J_{7,6}=3.5$ Hz, C_7-H), 1.53 (1H, ddd, $J_{gem}=13.0$, $J_{8,3}$ and $J_{8,6}=2.6$ Hz, C_8-H), 1.41 (1H, m, C_7-H)
Vc (a)[e]	7.08 (1H, dd, $J_{7,7a}=6.6$, $J_{7,5}=1.5$ Hz, C_7-H), 4.57 (1H, dd, $J_{1,8}=7.3$, $J_{1,7a}=4.8$ Hz, C_1-H), 3.79 (3H, s, OMe), 3.73 (1H, ddd, $J_{7a,7}=6.6$, $J_{7a,1}=4.8$, $J_{7a,3a}=4.4$ Hz, C_{7a}-H), 3.46 (1H, br, C_5-H), 2.36 (1H, ddd, $J_{3a,4}=11.0$ and 1.47, $J_{3a,7a}=4.4$ Hz, C_{3a}-H), 2.02 (1H, ddd, $J_{4,4}=13.9$, $J_{4,5}=3.3$, $J_{4,3a}=1.5$ Hz, C_4-H), 1.87 (1H, dd, $J_{gem}=14.7$, $J_{8,5}=3.3$ Hz, C_8-H), 1.57 (1H, m, C_4-H), 1.49 (1H, m, C_8-H)
Vd (a)[e]	7.08 (1H, dd, $J_{7,7a}=7.0$, $J_{7,5}=1.5$ Hz, C_7-H), 4.53 (1H, dd, $J_{1,8}=7.3$, $J_{1,7a}=5.5$ Hz, C_1-H), 3.80 (3H, s, OMe), 3.38—3.42 (2H, m, C_5-H and C_{7a}-H),[c] 2.10 (1H, dd, $J_{gem}=13.9$, $J_{4,5}=3.3$ Hz, C_4-H), 1.81 (1H, dd, $J_{gem}=14.7$, $J_{8,5}=3.0$ Hz, C_8-H), 1.44 (1H, m, C_8-H), 1.11 (1H, ddd, $J_{gem}=13.9$, $J_{4,5}$ and $J_{4,8}=2.6$ Hz, C_4-H), 1.82 (3H, s, Me)
Ve (a)[f]	7.34 (1H, d, $J_{5,4}=7.0$ Hz, C_5-H), 3.73—3.78 (2H, m, C_1H_2-O-C_3H_2),[c] 3.76 (3H, s, OMe), 3.43 (2H, d, $J_{gem}=11.0$ Hz, C_1H_2-O-C_3H_2), 3.17 (1H, br, C_7-H), 2.50 (1H, br, C_{4a}-H), 1.49—1.62 (6H, m, C_4-H, C_{8a}-H, C_8-H and C_9-H)
VIe (a)[f]	7.50 (1H, dd, $J_{5,4a}=7.0$, $J_{5,7}=1.8$ Hz, C_5-H), 3.77—3.82 (2H, m, C_1H_2-O-C_3H_2), 3.46 (2H, d, $J_{gem}=11.0$ Hz, C_1H_2-O-C_3H_2), 3.17—3.18 (1H, br, C_7-H), 2.54 (1H, dd, $J_{4a,5}=7.0$, $J_{4a,4}=2.2$ Hz, C_{4a}-H), 1.51—1.64 (6H, m, C_4-H, C_{8a}-H, C_8-H and C_9-H)
Vf (a)[f]	7.36 (1H, dd, $J_{5,4a}=7.0$, $J_{5,7}=1.8$ Hz, C_5-H), 3.76 (3H, s, OMe), 3.17 (1H, br, C_7-H), 2.84 (2H, dd, $J_{gem}=13.9$, $J_{1,8a}$ and $J_{3,4}=2.0$ Hz, C_1H_2-S-C_3H_2), 2.33 (2H, dd, $J_{gem}=13.9$, $J_{1,8a}$ and $J_{3,4}=3.0$ Hz, C_1H_2-S-C_3H_2), 2.24 (1H, ddd, $J_{4a,5}=7.0$, $J_{4a,4}$ and $J_{4a,8}=2.6$ Hz, C_{4a}-H), 1.76—1.87 (2H, m, C_4-H and C_{8a}-H),[c] 1.74—1.81 (2H, m, C_8-H and C_9-H),[c] 1.40—1.48 (2H, m, C_8-H and C_9-H)
IVg (a)[g]	6.92 (1H, ddd, $J_{3,4}=5.1$, $J_{3,5}=4.0$, $J_{3,1}=1.5$ Hz, H_3), 6.42 (1H, dd, $J_{1,2}=9.9$, $J_{1,3}=1.5$ Hz, H_1), 5.95 (1H, d, $J_{2,1}=9.9$ Hz, H_2), 5.85—5.96 (1H, m, H_7), 5.30 (1H, dd, $J_{8,7}=17.2$, $J_{8,9}=1.5$ Hz, H_8), 5.23 (1H, dd, $J_{9,7}=10.6$, $J_{9,8}=1.5$ Hz, H_9), 4.61 (2H, d, $J=5.5$ Hz, O-CH_2), 3.77 (3H, s, OMe), 2.98 (1H, dd, $J_{5,4}=9.1$, $J_{5,3}=4.0$ Hz, H_5), 2.43 (1H, dd, $J_{4,5}=9.0$, $J_{4,3}=5.1$ Hz, H_4), 1.29 (3H, s, Me)
IVh (a)[g]	6.89 (1H, dd, $J_{3,5}=5.1$, $J_{3,4}=4.4$ Hz, H_3), 6.33 (1H, d, $J_{1,2}=10.3$ Hz, H_1), 5.81 (1H, dd, $J_{2,1}=10.3$, $J_{2,6}=3.5$ Hz, H_2), 5.74—5.85 (1H, m, H_7), 4.99 (1H, m, H_8), 4.94 (1H, m, H_8), 3.76 (3H, s, OMe), 2.44 (1H, ddd, $J_{5.4}=17.6$, $J_{5,6}=8.4$, $J_{5,3}=5.1$ Hz, H_5), 2.23—2.34 (1H, m, H_6), 2.13 (1H, ddd, $J_{4,5}=17.6$, $J_{4,6}=11.36$, $J_{4,3}=4.4$ Hz, H_4), 2.02—2.08 (2H, m, methylene), 1.30—1.47 (6H, m, methylene)
Vi[h]	7.31 (1H, dd, $J_{7,7a}=7.0$, $J_{7,5}=1.8$ Hz, C_7-H), 3.76 (3H, Me), 2.86 (1H, br, C_5-H), 2.39 (1H, ddd, $J_{7a,7}=7.0$, $J_{7a,1}$ and $J_{7a,3a}=2.9$ Hz, C_{7a}-H), 1.72—1.81 (8H, m, C_1-H, C_{3a}-H, C_4-H, C_8-H, C_2-H, C_3-H, C_9-H and C_{10}-H),[c] 1.51—1.60 (4H, m, C_2-H, C_3-H, C_9-H and C_{10}-H)[c]
VIi[h]	7.50 (1H, dd, $J_{7,7a}=7.0$, $J_{7,5}=1.8$ Hz, C_7-H), 2.85 (1H, br, C_5-H), 2.43 (1H, ddd, $J_{7a,7}=7.0$, $J_{7a,1}$ and $J_{7a,3a}=2.93$ Hz, C_{7a}-H), 1.74—1.86 (8H, m, C_1-H, C_{3a}-H, C_4-H, C_8-H, C_2-H, C_3-H, C_9-H and C_{10}-H),[c] 1.51—1.60 (4H, m, C_2-H, C_3-H, C_9-H, C_{10}-H)[c]
IVj (a)[g]	6.92 (1H, ddd, $J_{3,4}=4.8$, $J_{3,5}=4.4$, $J_{3,1}=1.5$ Hz, H_3), 6.52(1H, ddd, $J_{1,2}=9.9$, $J_{1,3}$ and $J_{1,6}=1.5$ Hz, H_1), 5.79 (1H, dd, $J_{2,1}=9.9$, $J_{2,6}=4.0$ Hz, H_2), 3.78 (3H, s, OMe), 3.59 (1H, dd, $J=13.9$, $J_{CH_2,6}=6.2$ Hz, CH_2-N), 3.45 (1H, dd, $J=13.9$, $J_{CH_2,6}=6.5$ Hz, CH_2-N), 2.67—2.77 (1H, m, H_6), 2.56 (1H, ddd, $J_{5,4}=18.8$, $J_{5,6}=8.4$, $J_{5,3}=4.4$ Hz, H_5), 2.42 (1H, ddd, $J_{4,5}=18.8$, $J_{4,6}=9.2$, $J_{4,3}=4.8$ Hz, H_4)

a) a, *anti*; s, *syn*. *b)* See Chart 4 for the carbon atom numbering. *c)* Overlapped with the other protons. *d)* See Chart 5 for the carbon atom numbering. *e)* See Chart 6 for the carbon atom numbering. *f)* See Chart 7 for the carbon atom numbering. *g)* See Chart 9 for the proton numbering. *h)* See Chart 8 for the carbon atom numbering.

Table IX. ^{13}C-NMR Spectral Data for the DDA Adducts (V)

Compd.[a]	^{13}C-NMR ($CDCl_3$) δ ppm
Va (a)[b]	165.33 (s, C=O), 143.05 (d, C_7), 139.13 (s, C_6), 51.34 (q, OMe), 43.47 (d, C_5), 37.98 (t, C_2 and C_3), 35.61 (d, C_{7a}), 32.12 (t, C_4 and C_8), 29.87 (d, C_1 and C_{3a})
VIa (a)[b]	170.17 (s, C=O), 146.21 (d, C_7), 138.60 (s, C_6), 43.70 (d, C_5), 37.87 (t, C_2 and C_3), 35.62 (d, C_{7a}), 32.13 (t, C_4 and C_8), 28.06 (d, C_1 and C_{3a})
Vb (a)[c]	164.78 (s, C=O), 141.01 (s, C_5), 138.55 (d, C_4), 74.95 (d, C_{7a}), 74.13 (t, C_2), 51.61 (q, OMe), 42.50 (d, C_6), 38.31 (t, C_7), 35.82 (d, C_{3a}), 35.31 (t, C_8), 27.38 (d, C_3)
VIb (a)[c]	168.88 (s, C=O), 141.03 (d, C_4), 140.68 (s, C_5), 75.05 (d, C_{7a}), 74.07 (t, C_2), 42.68 (d, C_6), 38.13 (t, C_7), 35.82 (d, C_{3a}), 35.21 (t, C_4), 27.11 (d, C_3)
Vc (a)[d]	179.96 (s, C=O lactone), 164.06 (s, C=O ester), 142.65 (s, C_6), 135.40 (d, C_7), 76.87 (d, C_1), 51.91 (q, OMe), 40.92 (d, C_5), 37.10 (d, C_{7a}), 33.49 (t, C_8), 30.66 (d, C_{3a}), 29.72 (t, C_4)
Vd (a)[d]	181.60 (s, C=O lactone), 164.12 (s, C=O ester), 142.35 (s, C_6), 135.46 (d, C_7), 75.14 (d, C_1), 51.94 (q, OMe), 46.90 (d, C_5), 41.93 (s, C_{3a}), 37.55 (t, C_8), 32.66 (t, C_4), 30.45 (d, C_{7a}), 20.70 (q, Me)
Ve (a)[e]	165.31 (s, C=O), 144.79 (d, C_5), 139.02 (s, C_6), 70.35 (t, C_1 and C_3), 51.10 (q, OMe), 36.90 (d, C_7), 30.77 (d, C_{4a}), 30.40 (t, C_8 and C_9), 30.31 (d, C_4 and C_{8a})
VIe (a)[e]	169.93 (s, C=O), 147.49 (d, C_5), 138.87 (s, C_6), 70.44 (t, C_1 and C_3), 37.29 (d, C_7), 31.13 (d, C_{4a}), 30.49 (t, C_8 and C_9), 30.31 (d, C_4 and C_{8a})
Vf (a)[e]	165.56 (s, C=O), 146.51 (d, C_5), 138.78 (s, C_6), 51.35 (q, OMe), 38.69 (d, C_{4a} and C_7), 31.77 (t, C_1 and C_3), 29.31 (t, C_8 and C_9), 28.61 (d, C_4 and C_{8a})
Vi[f]	165.79 (s, C=O), 142.99 (d, C_7), 133.79 (s, C_6), 51.37 (q, OMe), 44.02 (d, C_{7a}), 41.41 (d, C_5), 40.83 (d, C_1, C_{3a} or C_4, C_8), 40.19 (d, C_1, C_{3a} or C_4, C_8), 26.05 (t, C_2, C_3 or C_9, C_{10}), 25.74 (t, C_2, C_3 or C_9, C_{10})
VIi[f]	170.44 (s, C=O), 146.00 (d, C_7), 133.28 (s, C_6), 44.30 (d, C_{7a}), 41.09 (d, C_5), 40.94 (d, C_1, C_{3a} or C_4, C_8), 40.18 (d, C_1, C_{3a} or C_4, C_8), 26.06 (t, C_2, C_3 or C_9, C_{10}), 25.73 (t, C_2, C_3 or C_9, C_{10})

a) a, *anti*. *b*) See Chart 4 for the carbon atom numbering. *c*) See Chart 5 for the carbon atom numbering. *d*) See Chart 6 for the carbon atom numbering. *e*) See Chart 7 for the carbon atom numbering. *f*) See Chart 8 for the carbon atom numbering.

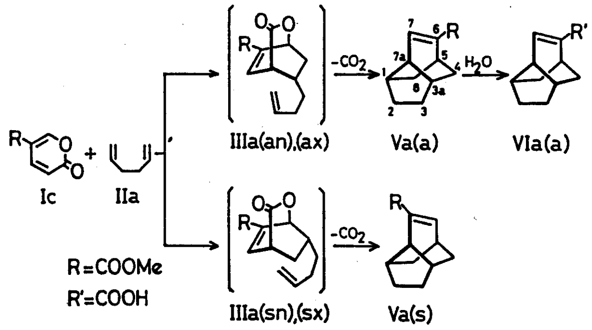


Chart 4

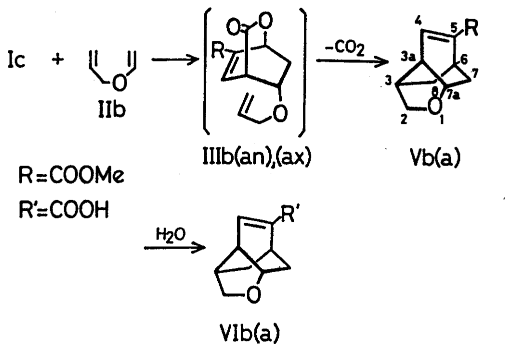


Chart 5

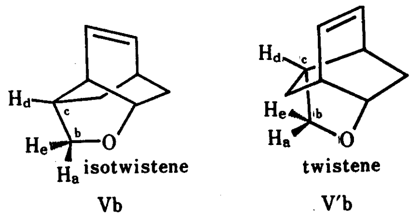


Fig. 2. The MM2 Calculation Models of Vb and V′b

Thermolysis of the [4+2]π Cycloadduct (IIIb) of Ic and Allyl Vinyl Ether (IIb) Heating a mixture of Ic and IIb in benzene at 180 °C in a sealed tube for 7 h gave a DDA adduct mixture (Vb) as an oil (Chart 5). The two-dimensional proton–proton chemical shift correlation (^{1}H-COSY) spectrum of the product indicated the presence of a weak coupling between C_3-H (methine) and C_{3a}-H, suggesting Vb to have the isotwistene structure. The corresponding free carboxylic acid (VIb) was obtained in a pure state by hydrolysis.

The signals of the methylene protons (C_2-H) adjacent to the ether oxygen atom appeared as a distorted AB quartet (geminal coupling) in which one of the protons again coupled with C_3-H to show a doublet of doublets.

To ascertain the difference of the splitting patterns between the twistene (V′b) and isotwistene (Vb) type compounds, we evaluated the coupling constants between the CH_2-O methylene and the adjacent methine proton on the basis of the dihedral angles of the MM2 optimized structures of the parent molecules of Vb and V′b (see Fig. 2 and Table X). As shown in Table X, in the case of Vb, one of the CH_2-O protons should give a doublet signal ($J_{vic}=0.0$ and $J_{gem}=8.0$ Hz) and the other, a doublet of doublets. On the other hand, in the case of V′b, the signals of both protons should appear as doublets of doublets. The observed pattern is consistent with the former case, supporting the isotwistene structure.

It is worth noting that the dihedral angle for V′b calculated by MNDO seems to be unreliable because of the presence of abnormally long bond lengths (see the discussion).

Thermolysis of the [4+2]π Cycloadducts (IIIc, d) of Ic and Vinyl Acrylate (IIc) and Vinyl Methacrylate (IId) Heating a mixture of Ic and IIc in benzene at 170 °C in a sealed tube did not give the DDA adduct but caused an intermolecular DA reaction to give a polymerization pro-

Table X. Calculated Heats of Formation (ΔH_f) and Dihedral Angles by MM2 and MNDO Methods and Coupling Constants Based on the Karplus and William–Johnson Rules for the Possible DDA Adducts of 5-Methoxycarbonyl-2-pyrone (Ic) and Allyl Vinyl Ether

Calcd values	MM2	MNDO	J_{obs} (Hz)
Isotwistene-type (Vb)			
ΔH_f	−19.5	−21.2	
Dihedral angle, coupling constant (J, J')[a)]			
H_e–C_b–C_c–H_d	36.1 (5.3, 6.5)	29.9 (6.1, 7.5)	4.03
H_a–C_b–C_c–H_d	85.8 (0.2, 0.1)	89.7 (0.3, 0.0)	0.0
Twistene-type (V′b)			
ΔH_f	−11.5	−1.4	
Dihedral angle, coupling constant (J, J')[a)]			
H_a–C_b–C_c–H_d	70.5 (0.7, 1.1)	64.5 (1.3, 1.9)	
H_e–C_b–C_c–H_d	48.9 (3.4, 4.3)	53.5 (2.7, 3.5)	

a) J: Coupling constant calculated by means of the Karplus rule.[5a)] J': Coupling constant calculated by means of the Williamson–Johnson rule.[5b)]

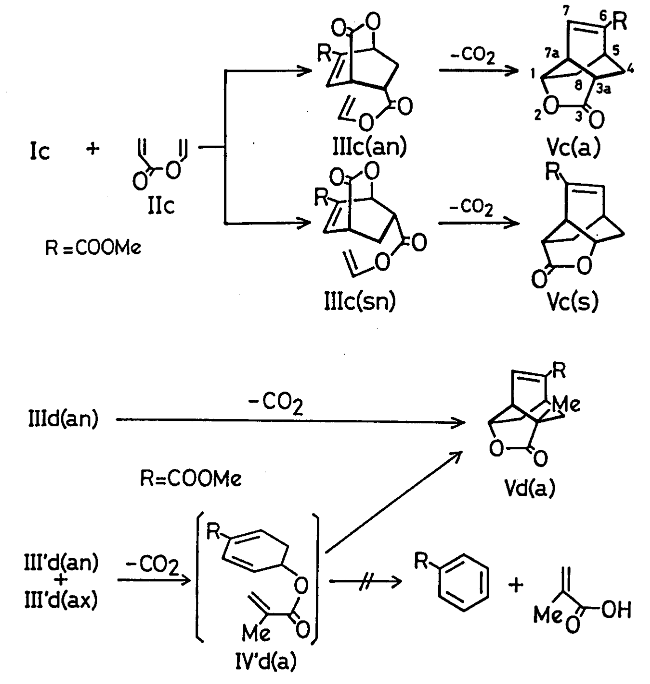


Chart 6

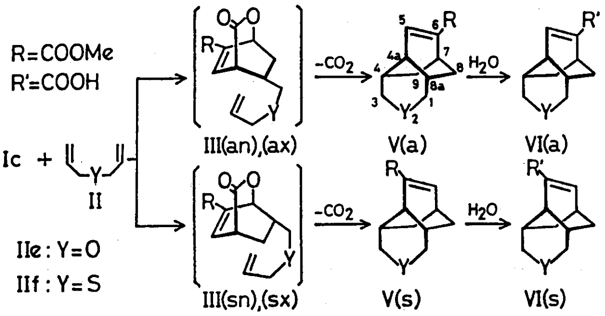


Chart 7

duct. On the other hand, heating a diluted benzene solution of IIIc in a sealed tube at 170 °C for 26.5 h gave a crystalline product which showed a wide melting range (mp 97—122 °C), suggesting the presence of a large amount of the regioisomer (*syn* Vc). The *syn*/*anti* ratio of the DDA adduct (Vc) was estimated to be 3/4 based on the ^{1}H-NMR spectral data.

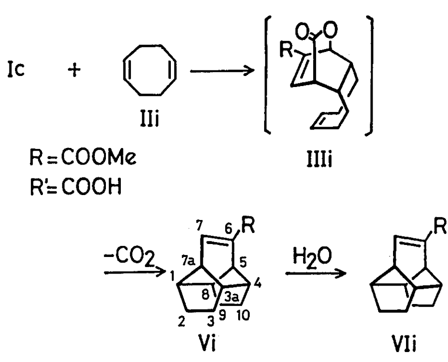


Chart 8

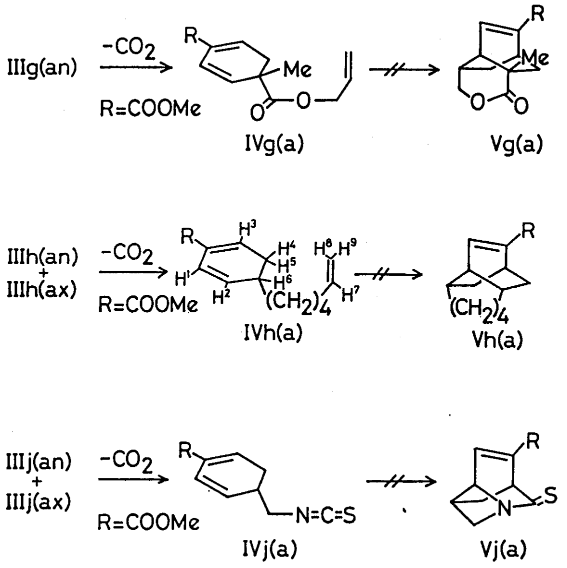


Chart 9

The IR spectrum of Vc showed the strained five-membered lactone absorption at 1770 cm^{-1}. The ^{1}H-COSY spectrum of the product indicated the C_{7a}-H proton to be strongly coupled with the C_1-H, C_{3a}-H and C_7-H methine protons, supporting the isotwistene structure.

The cycloadduct IIId showed similar reaction behavior to give *anti* Vd (Chart 6).

Thermolysis of the [4+2]π Cycloadducts (IIIe, f) of Ic and Diallyl Ether (IIe) and Diallyl Sulfide (IIf) Heating a mixture of Ic and IIe in benzene at 160 °C in a sealed tube for 11.5 h afforded a crystalline product, mp 85—91 °C in 47% yield. Inspection of the chemical shifts and relative intensities indicated the product to consist of *syn* and *anti* forms (*syn* Ve and *anti* Ve) with the predominant formation of the *anti* DDA adduct. The pure *anti* DDA adduct (Ve) was obtained by conversion to the carboxylic acid (VIe).

In the case of IIf, similar treatment carried out at 180 °C for 14.5 h gave a crystalline product (Vf), mp 104—106 °C, in 19% yield. The ^{1}H- and ^{13}C-NMR spectra indicated the absence of the regio isomer.

Thermolysis of the [4+2]π Cycloadduct (IIIi) of Ic and 1,5-Cyclooctadiene (IIi) Heating a mixture of Ic and IIi at 120 °C produced Vi as an oil in 47% yield (Chart 8). The ^{13}C-NMR spectrum showed six sp^3 carbon atoms (44.02, 41.41, 40.83, 40.19, 26.05 and 25.74 ppm), reflecting the presence of a mirror plane of symmetry (Table IX). In the ^{1}H-NMR spectrum, the methine proton appeared as a broad singlet at 2.84—2.39 ppm and olefinic protons ascribable to the intermediary IIIi or IVi were not observed.

Thermolysis of the [4+2]π Cycloadduct (IIIg, h, j) of Ic and Allyl Methacrylate (IIg), 1,7-Octadiene (IIh) and Allyl Isothiocyanate (IIj) Heating the DA adduct of IIg and Ic gave the decarboxylated 1 : 1 adduct (IVg). Heating a benzene solution of the cycloadduct (IIIh) of Ic and IIh in a sealed tube caused evolution of CO_2 gas to afford the decarboxylated 1 : 1 adduct (IVh) in 47% yield. The ^1H-NMR spectrum of the product showed the presence of the vinyl olefinic protons. In the case of IIj, the IR spectrum of the crude product showed an isothiocyanate (–N=C=S) absorption band in the vicinity of 2230 cm^{-1}. These results suggest that the intramolecular cycloaddition did not occur, in sharp contrast to the results for the cycloadducts of Ia and IIh and IIj.10)

Discussion

The degree of cyclic electron delocalization depends on the mode of donor-acceptor arrangements of the component systems as well as orbital phase continuity requirements and a concept of continuity–discontinuity of cyclic conjugation has been successfully employed in predicting the electronic properties of unknown molecules.3) According to the cyclic conjugation theory, the cyclic conjugation in 5-methoxycarbonyl-2-pyrone (Ic) is discontinuous since the donors and the acceptors are alternately arranged. So Ic is predicted to have non-aromatic or non-antiaromatic character showing, moderate cycloaddition reactivity toward inactivated nonconjugated dienes such as 1,5-cyclooctadiene. On the other hand, in 5-methyl-2-pyrone (Id), the cyclic conjugation is continuous and the orbital phase continuity requirements are satisfied suggesting that Id will show low reactivity toward the nonconjugated dienes due to a high degree of electron delocalization (aromatic character). Therefore, we chose the 5-methoxycarbonyl derivative as a cheletropic 4π-synthon.

To ascertain the cycloaddition behavior of Ic toward II, we performed MNDO calculations on Ic and some nonconjugated dienes. In the case of Ic, the corresponding carboxylic acid (coumalic acid) was used as a calculation model and optimized assuming a planar structure (Fig. 3).

As shown in Fig. 3, the initial stage of the reaction of Ic with nonconjugated dienes except vinyl acrylate falls into the category of an inverse-type reaction in Sustmann's classification11) for cycloadditions, in which the dominant interaction is the one between the LUMO (lowest unoccupied molecular orbital) of Ic and the HOMO (highest occupied molecular orbital) of the nonconjugated diene (II). In comparison with antiaromatic cyclopentadienones such as Ia, the low reactivity of Ic as a 4π-acceptor toward olefins is considered to arise from its higher-lying LUMO than cyclopentadienone and non-antiaromatic character.3)

With regard to regioselectivity in the reaction of Ic with nonconjugated dienes (Fig. 3), the observed selectivity is considered to result from steric repulsion between the methoxycarbonyl substituent of 2-pyrone and the remaining double-bond moiety of the nonconjugated dienes. For example, there is little difference in the eigenvectors of the double bond of 1,5-hexadiene, indicating that the eigenvectors do not play a leading role in determination of the regiochemistry.

In the reaction with vinyl acrylate (IIc), Ic did not react with the $CH_2=CH–O–$ moiety but reacted with the $CH_2=CH–CO–$ moiety. This reaction behavior could not be accounted for in terms of a simple qualitative FMO treatment based on the MNDO calculation data. The perturbation calculation12) for a neutral-type reaction including the adjacent orbitals and the secondary orbital interaction indicated that the stabilization energy for attack at the $CH_2=CH–CO–$ moiety is larger than the energy for attack at the $CH_2=CH–O–$ moiety. This prediction is consistent with the experimental result, indicating that the secondary orbital interaction should not be unduly underestimated. The predominant formation of *endo* IIIc can be explained by considering the normal-type interaction between the LUMO of IIc and the HOMO of Ic to be a main contributor. The second highest occupied molecular orbital (NHOMO) of IIc has a nodal property at the C atom of the carbonyl group. This is very unfavorable for secondary interaction.

The second stage of the reaction, decarboxylation, is considered to be a retro DA reaction of cycloadducts of 1,3-cyclohexadienes and O=C=O assisted by the favorable electronic interactions and strain release of the bicyclo[2.2.2]octene system. The strain in the parent bicyclo[2.2.2]octane system was estimated to be *ca.* 8.9 kcal/mol by the MM2 calculation. The decarboxylation is considered to compete with the retro DA reaction (formation

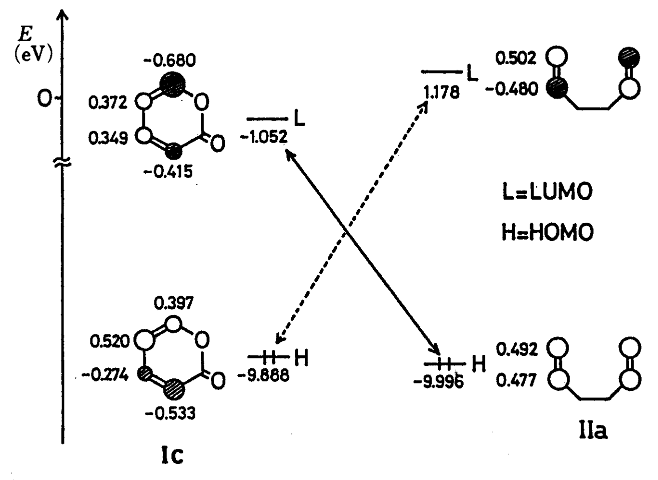


Fig. 3. The MNDO Energy Levels and Coefficients of Ic and IIa

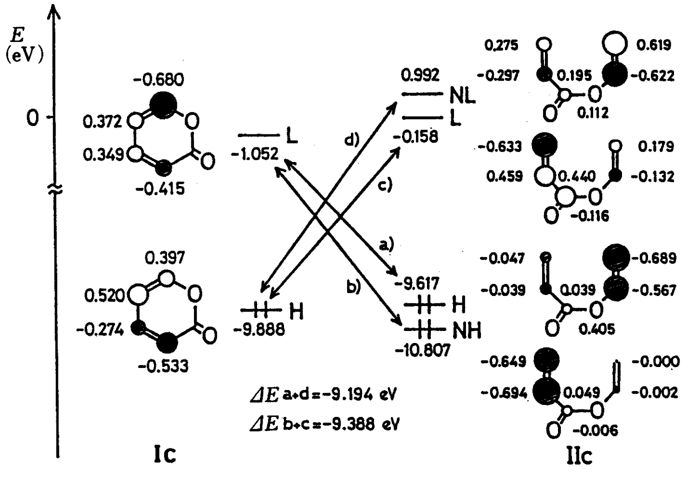


Fig. 4. The FMO Interaction Energies of Ic and IIc

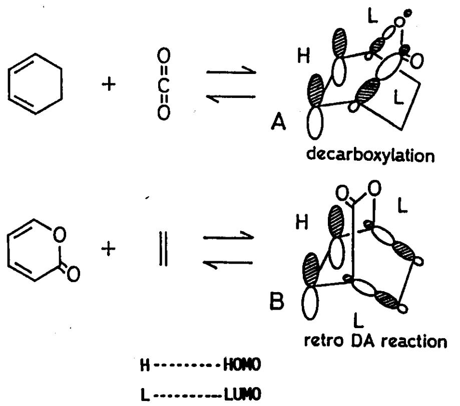


Chart 10

TABLE XI. Energies and Geometries for the Conformational Isomers of the DDA Adducts of Diallyl Ether and Diallyl Sulfide Calculated by the MM2 Method

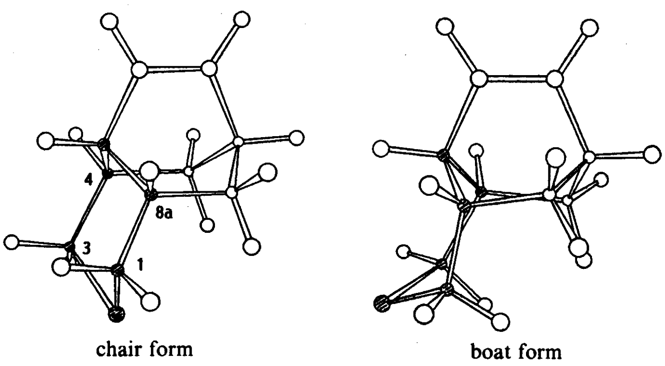
Calcd. values	Compound V			
	Ve (X=–O–)		Vf (X=–S–)	
	Boat	Chair	Boat	Chair
Energy (kcal)				
Steric	33.3	26.5	29.8	22.9
ΔH_f	−19.1	−25.9	20.1	13.2
Strain	25.3	18.5	25.4	18.5
Nonbonded distance (Å)				
C_3–C_{8a}	2.75	2.85	2.90	3.05
C_1–C_4	2.91	2.85	3.12	3.05

of I and II), as shown in Chart 10. However, the retro-DA reaction could not be observed in all cases. The decarboxylation interaction can be interpreted in terms of the cyclic three-system interaction[13] in which the presence of low-lying σ-LUMO's becomes quite favorable for the interaction among the LUMO's of the two σ bonds and the HOMO of the π bond [π-HOMO (diene moiety), σ-LUMO (C–OCO bond), σ-LUMO (C–CO bond)]. This mechanism is supported by the fact that the decarboxylation was accelerated by the lowering in energy of the σ-LUMO's by hydrogen bonding to the carbonyl function.[14]

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

In the previous paper, we described the MM2 calculation data of the parent molecules of several DDA adducts and discussed the relative stabilities between the twistene- and isotwistene-type compounds on the basis of the heats of formation. In this study, we carried out MM2 and MNDO calculations on some DDA adducts. The calculation data are summarized in Tables X and XI.

For the DDA adducts of Vb and V'b, both the MM2 and MNDO calculations indicate that the isotwistene-type compound Vb is thermodynamically more stable than the twistene-type compound V'b. The MNDO-calculated heat of formation (ΔH_f, −21.2 kcal/mol) of the isotwistene-type compound Vb is in good agreement with that (−19.5 kcal/mol) calculated by the MM method (see Table X). However, the MNDO-calculated heat of formation (−1.4 kcal/mol) of the twistene-type compound V'b is considerably higher than that (−11.5 kcal/mol) calculated by the MM2 method. In the MNDO optimized structure of the twistene-type compound V'b, there appeared an abnormally long σ bond (>1.61 Å), which was calculated to be 1.56 Å by MM2. This fact can probably be attributed to the known tendency of MNDO to overestimate repulsive interactions between atoms.



chair form boat form

Fig. 5. The MM2 Optimized Structures for Vf

See Chart 7 for the atomic numbering.

The MM2 optimized structure of the DDA adduct (Vf) of Ic and diallyl sulfide (IIf) is interesting. Two conformational isomers due to chair–boat inversion of the six-membered ring containing the sulfur atom were calculated without interconversion during optimization. The chair form of the isotwistene-type compound, Vf, is *ca.* 7 kcal/mol more stable than the boat form. This structural feature was also found in the DDA adduct (Ve) of diallyl ether (IIe). Interestingly, in the less stable boat form, the MM2-optimized structure of the DDA adduct (Ve) does not have mirror plane symmetry due to the distortion of the six-membered ring. For example, the ring of Vf was distorted considerably: the interatomic distance between C_3 and C_{8a} is 0.22 Å shorter than the one between C_1 and C_4 whereas the chair form has the same value (see Fig. 5).

The ^{1}H-NMR spectrum of Ve 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 (precisely speaking, the higher-field doublet appeared as a broadened doublet). Inspection of the dihedral angles calculated by MM2 revealed that the observed J values are well reflected in the chair conformation as compared with the boat one.

Finally, mention should be made of short C–H···H–C contacts in the DDA adduct Vi (or VIi) of 1,5-cyclooctadiene. In highly crowded molecules, the presence of short C–H···H–C contacts has aroused considerable attention and a number of compounds has been examined by MM methods.[15] The MM2 calculation on the parent molecule of Vi showed that Vi involves a very close intramolecular nonbonded H···H contact (2.06 Å). Taking into consideration the known tendency that MM methods overestimate such close nonbonded distances by about 0.1 Å, the actual value in question is estimated to be *ca.* 1.96 Å. The interaction energy due to short H/H contacts is 2.12 kcal/mol.

Because the MM parameters for the acrylic acid moiety are not available, the detailed structure of Vi was obtained by the MO method using MNDO structure optimization.

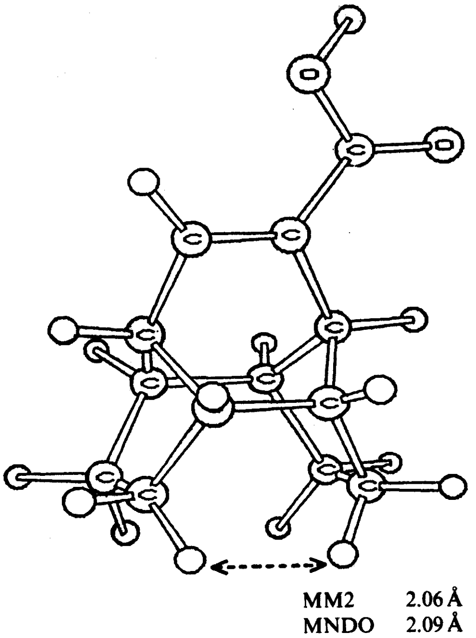


Fig. 6. The MNDO Optimized Structure of Vi and the Short C–H···H–C Contacts

See Chart 8 for the atomic numbering.

The MNDO calculations were performed on the conformational isomers of Vi. The calculated structures are depicted in Fig. 6. The heats of formation indicate that the transoid structure is 0.22 kcal/mol more stable than the cisoid one. This result agrees well with conformations observed in the X-ray structures of conjugated acids such as cinnamic acid.[16] The MNDO calculations furnished linear C_2–H···H–C_9 (C_3–H···H–C_{10}) contacts of 2.09 Å, close to the MM2 value. Experimental data on Vi appear to be desirable for comparison.[17]

In conclusion, all the pericyclic reaction behaviors involved in this study can be explained in terms of FMO theory.[18] The DDA adducts isolated are isotwistene-type compounds and the product distributions are thermodynamically controlled. The analysis of the ^{1}H-NMR and MM calculation data of the DDA adducts indicates that the isotwistene-type compounds from 1,5-hexadiene analogues have symmetrical structure and conformationally fixed chair-form and that the DDA adduct of 1,5-cyclooctadiene has very short H/H contacts.

Experimental

All melting points are uncorrected. NMR spectra were taken with Hitachi R-600 (60 MHz) and JEOL GX-400 (400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR) spectrometers for 5—10% (w/v) solutions with tetramethylsilane (TMS) 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 (MS) and high-resolution MS were taken with a JEOL JMS-DX-300 spectrometer operating at an ionization potential of 75 eV.

MNDO and MMPI calculations were performed on a FACOM M-360 computer in the Computer Center of Kumamoto University. MM2 calculations were performed on a Fujitsu FM-16β (CPU 80286) personal computer using the program locally modified for MS-DOS FORTRAN.

Cycloaddition of 5-Methoxycarbonyl-2-pyrone (Ic) with Non-conjugated Dienes (IIa—j). General Procedure of Cycloaddition A solution of Ic and an excess amount of a diene in benzene was heated at 100—120 °C until a thin layer chromatography (TLC) spot of Ic could not be recognized. After cooling, the solvent was evaporated off under reduced pressure. The residue was purified by chromatography on silica gel. The DA adduct was isolated as a mixture of the stereoisomers and its formation ratio was determined by 400 MHz ^{1}H-NMR spectroscopy. Identification of the DA adduct was achieved by transformation to the DDA adduct. The results are summarized in Tables I—IV.

In this operation, the reaction mixture was placed in a sealed tube and heated at 170 °C to give the DDA adduct.

Thermolysis of the [4+2]π Cycloadduct (IIIa—j). Formation of DDA Adducts (Va—c, j) The [4+2]π adducts were heated at 170 °C to give oils with evolution of CO_2 gas. The oils were purified by chromatography on silica gel with *n*-hexane–benzene. The results are summarized in Tables VI—IX.

Hydrolysis of the DDA Adduct A solution of V in EtOH containing an equimolar amount of NaOH was refluxed for 5 h. After evaporation of EtOH, the residue was treated with water and acidified with 10% HCl. The organic substance was extracted with $CHCl_3$. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel. The solid was recrystallized from benzene–hexane to give a pure sample. The results are included in Tables VI—IX.

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