Cycloaddition Behavior of 3,4-Diazacyclopentadienone Dioxides toward Bicyclo[2.2.1]heptadiene Derivatives. X-Ray Analysis of the Cycloadduct and Reaction Pathway

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The cycloaddition behavior of 2,5-disubstituted 3,4-diazacyclopentadienone dioxide **1a-c** toward epoxynaphthalene (**2a**) and norbornadiene (**2b**) was investigated. The structures of the products were determined on the basis of the ¹H- and ¹³C-nmr spectral data and the X-ray analysis data. The stereospecific formation of the *endo-exo* 1,3-dipolar cycloadducts from **2a** indicates that the cycloadduct resulted from the direct 1,3-dipolar cycloaddition. The cycloaddition behavior of **1** toward **2** is discussed on the basis of the PM3-calculated transition-state structures.
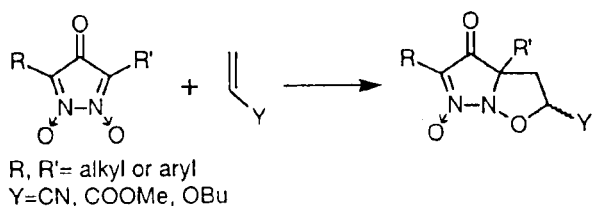
Introduction.

Freeman *et al.*, reported that 3,4-diazacyclopentadienone dioxides **1** underwent cycloaddition to acrylonitrile, methyl acrylate and *n*-butyl vinyl ether to give the 1,3-dipolar cycloadducts [1,2]. However, stereochemistry of the cycloadducts has not been reported. The frontier MO's of **1** calculated by MNDO are closely similar to those of cyclopentadienones, suggesting that **1** would not only act as a 1,3-dipole but also a 1,3-dienone. In this connection, we have communicated a possible reaction pathway based on the X-ray crystal structure of the cycloadduct of **1** and epoxynaphthalene (**2a**) [3].
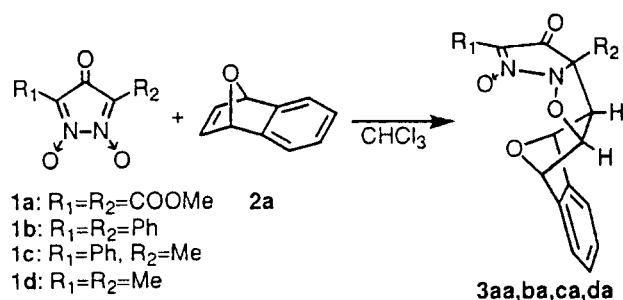
Scheme 1

R, R'= alkyl or aryl
Y=CN, COOMe, OBu

We now discussed the reactions in detail with newly obtained data in order to clarify the character of the reactions.

Results.

Cycloaddition of 2,5-Bis(methoxycarbonyl)-3,4-diazacyclopentadienone Dioxide (**1a**) with Epoxynaphthalene (**2a**).

2,5-Bis(methoxycarbonyl)-3,4-diazacyclopentadienone dioxide (**1a**) reacted with **2a** in chloroform at 40° to give a single product (**3aa**) as pale yellow crystals [3]. The mass spectrum and elemental analysis agreed with the theoreti-

cal value for a 1 : 1 adduct. The IR spectrum of the product (**3aa**) did not show the presence of a strained bridged carbonyl group but two carbonyl absorption bands at 1762 and 1738 cm⁻¹, attributable to nonconjugated and conjugated ester carbonyl groups, respectively. The strongest absorption band at 1570 cm⁻¹ was assigned to the remaining >C=N-O group. In the ¹H-nmr spectrum, the methyl protons of the methoxycarbonyl groups resonate at 3.94 and 3.87 ppm. These facts indicate that **3aa** has an unsymmetrical structure, *i.e.*, a 1,3-dipolar cycloadduct. The ¹³C-nmr spectrum of **3aa** supported this assignment.

Scheme 2

1a: R₁=R₂=COOMe   2a
1b: R₁=R₂=Ph
1c: R₁=Ph, R₂=Me
1d: R₁=R₂=Me

3aa,ba,ca,da

The protons on the bridgehead carbons linked by the ether oxygen appeared as singlets at 5.31 and 5.39 ppm, indicating that **1a** attacked at the *exo*-oriented p-lobes of the ethylenic moiety of **2a**.

The stereochemistry of the cycloaddition could not be determined on the basis of the spectral data. To get a definitive evidence for the *endo/exo* nature of **3aa**, a single crystal X-ray analysis was undertaken.

Single Crystal X-Ray Analysis of **3aa**.

The crystal structure of **3aa** was solved by the direct

method [4] and refined by the block-diagonal least-squares method [5,6]. The final atomic coordinates are listed in Table 5. The distances and angles are tabulated in Tables 6 and 7, respectively. The molecular structure with numbering sequence used in this study is depicted in Figure 1. As can be seen in Figure 1, **3aa** is the *endo* adduct with respect to the diazacyclopentadienone and *exo* with respect to **2a** (*endo-exo* adduct).

Figure 1. ORTEP Drawing of **3aa** with Number Scheme.

Table 1

Reaction Products 3 from Cycloadditions of **1a-d** with **2a,b**

Dp/1,3-Dipole	Compound	Duration (hours)	Mp(°C)	Yield(%)
2a/				
1a	3aa	4 [a]	169-170 dec	70
1b	3ba	6 [b]	203 dec	76
1c	3ca	5	229-230 dec	46
1d	3da	2 [b]	185-186	73
2b/				
1a	3ab	2[b]	168-169 dec	43
1b	3bb	15[c]	192-194 dec	38
1c	3cb	8	139-141 dec	49 (28) [a]
	3cb'		133-135 dec	(25)
	3'cb		183-184 dec	(47)

[a] Chloroform at 40°C [b] Chloroform reflux [c] Benzene reflux [d] Products ratio in parenthesis.
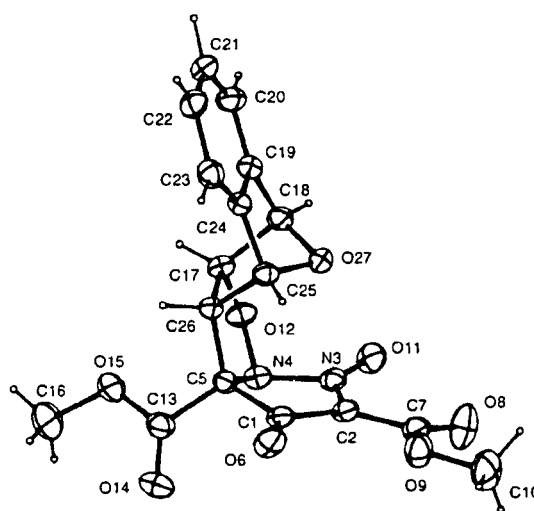
The framework is moderately strained. The bond angles of C1-C5-C26 and C5-C26-C25 are 114.2(2) and 116.2(2)° respectively, which deviate from normal value of 109.5°. These expansions of the angles might be caused by steric repulsion between the bridged oxygen atom and the enone moiety. Non-bonded distance O27...N3 is 2.76Å, which is equal to the van der Waals contact. The sum of the angles around the N3 atom is

Table 2

IR spectral and Analytical Data of Cycloadducts 3

Compound	IR (cm⁻¹) C=O (enone, ester) -C=N-O	MS (m/z)	Formula	Analysis (%) Calcd./Found		
				C	H	N
3aa	1738 1762 1580	374 (M⁺)	$C_{17}H_{14}N_2O_8$	54.55 54.48	3.77 3.61	7.48 7.57
3ab	1738 1760 1568	322 (M⁺)	$C_{14}H_{14}N_2O_7$	52.18 52.06	4.38 4.35	8.70 8.83
3ba	1714 1570	410 (M⁺)	$C_{25}H_{18}N_2O_4$	73.16 72.91	4.42 4.41	6.83 6.80
3bb	1724 1562	358 (M⁺)	$C_{22}H_{18}N_2O_3$	73.73 74.01	5.06 5.05	7.82 7.81
3ca	1714 1568	348 (M⁺)	$C_{20}H_{16}N_2O_4$	68.96 68.73	4.63 4.60	8.04 8.05
3cb	1714 1566	296 (M⁺)	$C_{17}H_{16}N_2O_3$	68.91 69.02	5.78 5.57	9.45 9.44
3cb'	1716 1568		$C_{17}H_{16}N_2O_3$	68.91 68.89	5.78 5.67	9.45 9.49
3'cb	1726 1582	296 (M⁺)	$C_{17}H_{16}N_2O_3$	68.91 68.84	5.78 5.43	9.45 9.47
3da	1718 1580	286 (M⁺)	$C_{15}H_{14}N_2O_4$	62.93 62.90	4.93 4.94	9.79 9.64

Table 3

¹H-NMR Spectral Data for the Cycloadducts **3**

Compound	¹H-NMR (in CDCl₃) ppm
3aa	3.87 (3H, s, O-Me), 3.92 (1H, d, J = 6.4, >CH-C-CO-), 3.94 (3H, s, O-Me), 4.99 (1H, d, J = 6.4, N-O-CH<), 5 .31 (1H, br-s, -CH-O-), 5 .39 (1H, br s, CH-O-), 7.22-7.36 (4H, m, aromatic CH)
3ab	1.71 (1H, d, J = 9.9, bridged H), 1.78 (1H, d, J = 9.9, bridged H), 2.92 (1H, dd, J = 6.4, 3.2, >CH-C-CO-), 3 .12 (1H, br-s, bridge-head H), 3.43 (1H, br-s, bridgehead H), 3.90 (3H, s, O-Me), 3.92 (3H, s, O-Me), 4.66 (1H, dd, J = 6.4, 1.9, N-O-CH<), 6.09 (1H, dd, J = 3.3, 5.5, olefinic H), 6 .31 (1H, dd, J = 3 .3, 5.5, olefinic H)
3ba	3.47 (1H, d, J = 6.6, >C-C-CO-), 5.12 (1H, d, J = 6.6, N-O-CH<), 5.44 (1H, s, bridgehead H), 5.51 (1H, s, bridgehead H), 7 .19-7.20 (2H, m, aromatic CH), 7.36-7.57 (8H, m, aromatic CH), 7.72-7.74 (2H, m, aromatic CH), 8.20-8.22 (2H, m, aromatic CH)
3bb	1.34 (1H, d, J = 9.5, bridged H), 1.51 (1H, d, J = 9.5, bridged H), 2.73 (1H, br-s, bridgehead H), 3.02 (1H, br-s, bridgehead H), 3.02 (1H, d, J = 6.2, >CH-C-CO-), 4.77 (1H, d, J = 6.2, N-O-CH<), 6.06 (1H, dd, J = 2.9, 5.9, olefinic H) 6.26 (1H, dd, J = 2.9, 5.9, olefinic H), 7.26-7.48 (6H, m, aromatic CH), 7.86-7.96 (2H, m, aromatic CH), 8.41-8.43 (2H, m, aromatic CH)
3ca	1.68 (3H, s, Me), 2 .87 (1H, d, J = 6.4, >CH-C-CO-), 5.00 (1H, d, J = 6.4, N-O-CH<), 5.25 (1H, s, bridgehead H), 5.35 (1H, s, bridgehead H), 7 .14-7.50 (7H, m, aromatic CH), 8.34-8.37 (2H, m, aromatic CH)
3cb	1.60 (3H, s, Me), 1.81 (1H, d, J = 9.5, bridged H), 2.01 (1H, d, J = 9.5, bridged H), 2.63 (1H, dd, J = 1.5, 6.5, >CH-C-CO-), 2.95 (1H, br-s, J = 1.5, bridgehead H), 3 .11 (1H, br-s, bridgehead H), 4.62 (1H, d, J = 6.5, N-O-CH<), 6.07 (1H, dd, J = 3.3, 5.5, olefinic H), 6.31 (1H, dd, J = 3 .3, 5.5, olefinic H), 7.26-7.51 (3H, m, aromatic CH), 8.42-8.45 (2H, m, aromatic CH)
3cb'	1.09 (1H, J = 10.5, bridged H), 1.56 (1H, d, J = 10.5, bridged H), 1.69 (3H, s, Me), 2.64 (1H, d, J = 7.0, >CH-C-CO-), 2.95 (1H, br-s, bridgehead H), 3.07 (1H, br-s, bridgehead H), 4.99 (1H, d, J = 7.0, N-O-CH<), 6.07-6.09 (1H, m, olefinic H), 6.29-6.32 (1H, m, olefinic H), 7.27-7.72 (3H, m, aromatic CH), 8 .39-8.42 (2H, m, aromatic CH)
3'cb	2.03 (3H, s, Me), 1.32 (1H, d, J = 9.5, bridged H), 1.50 (1H, d, J = 9.5, bridged H), 2.65 (1H, br-s, bridgehead H), 2.91 (1H, d, J = 6.2, >CH-C-CO-), 3.03 (1H, br-s, bridgehead H), 4.73 (1H, d, J = 6.2, N-O-CH<), 6.03 (1H, dd, J = 3.3, 5.5, olefinic H), 6.25 (1H, dd, J = 3.3, 5.5, olefinic H), 7.27-7.43 (3H, m, aromatic CH), 7.79-7.82 (2H, m, aromatic CH)
3da	1.61 (3H, s, Me), 2.02 (3H, s, Me), 2.80 (1H, d, J = 6.6, CH), 4.95 (1H, d, J = 6.6, CH), 5.19 (1H, s, CH), 5.29 (1H, s, CH), 7.17-7.35 (4H, m, aromatic CH)

Table 4

¹³C-NMR Spectral Data for the Cycloadducts **3** [a]

Compound	¹³C-NMR (in CDCl₃) ppm
3aa	183.2 (s), 164.8 (s), 156.2 (s), 143.3 (s) 140.3 (s), 128.3 (d), 128.2 (d), 121.2 (d), 120.6 (d), 115.7 (s), 94.1 (d), 82.1 (s), 81.9 (s), 79.3 (d), 54.4 (q), 53.6 (d), 52.8 (q)
3ab	181.8 (s), 164.8 (s), 156.2 (s), 141.4 (d) 135.4 (d), 115.3 (s), 92.2 (d), 81.2 (s), 57.5 (d), 53.6 (q), 53.0 (q), 45.4 (d), 43.7 (d), 43.5 (t)
3ba	189.6 (s), 144.2 (s), 141.2 (s), 127.4 (d, overlapping carbons), 123.8 (s), 121.3 (d), 120.6 (d), 92.9 (d), 81.5 (d), 80.9 (s), 79.6 (d), 59.2 (d)
3bb	192.2 (s), 141.4 (d), 136.0 (d), 124.2 (s), 91.1 (d), 79.2 (s), 59.0 (d), 44.9 (d), 43.7 (d), 43.4 (t)
3ca	192.7 (s), 144.2 (s), 141.0 (s), 124.2 (s), 93.2 (d), 82.1 (d), 79.8 (d), 76.4 (s), 59.0 (d), 21.4 (q)
3cb	195.0 (s), 141.7 (d), 135.5 (d), 124.3 (s),30.7 (d), 75.3 (s), 56.7 (d), 45.0 (d), 44.8 (t), 42.6 (d), 15.1 (q)
3cb"	193.3 (s), 142.5 (s), 135.6 (d), 94.6 (d), 75.7 (s), 58.7 (d), 45.5 (d), 44.0 (t), 42.6 (d), 23.3 (q)
3 'cb	192.7 (s), 141.7 (d), 135.9 (d), 123.7 (s), 91.2 (d), 80.0 (s), 58.6 (d), 45.0 (d), 43.7 (d), 43.4 (t), 7.5 (q)
3da	193.1 (s), 144.0 (s), 141.0 (s), 127.9 (d), 127.8 (d), 124.2 (s), 121.1 (d), 120.2 (d), 93.4 (d), 82.0 (d), 79.7 (d), 76.9 (s)

about 360°, responsible to sp² hybridization. The C2-N3 and C5-N4 bond lengths are 1.319 and 1.478 Å, respectively. The torsional angle of C1-C2-C7-O8 is 173.5(3)°. These facts suggest that O6, C1, C2, N3 and O11 are roughly coplanar, forming a resonance structure with the p-orbital of the ester carbonyl group.

Cycloaddition of 2,5-Diphenyl, 2-Methyl-5-Phenyl and 3,4-Diazacyclopentadienone Dioxides (1b,c,d) with Epoxynaphthalene (2a).

Next, we studied on cycloaddition of 2,5-diphenyl-3,4-diazacyclopentadienone dioxide (**1b**) with **2a**. The reac-

tion proceeded in refluxing chloroform to give only the 1,3-dipolar cycloadduct. The ¹H-nmr spectral pattern of compound (**3ba**) closely resembles that of **3aa**. The methine proton adjacent to the junction phenyl group resonates at 3.47 ppm, which is higher field than that of **3aa** (3.92 ppm), presumably due to ring current effect of the phenyl group, indicating that **3ba** is also the *endo-exo* cycloadduct.

The cycloaddition of 2-methyl-5-phenyl-3,4-diazacyclopentadienone dioxide (**1c**) with **2a** gave a sole product (**3ca**). The junction methyl protons resonate at 1.68 ppm and coupled with the *cis*-oriented methine pro-

ton in the NOE spectrum. These facts indicate that **3ca** is the *endo-exo* cycloadduct which is derived from site-selective cycloaddition of **1c** to the 1,3-dipole moiety bearing a methyl group.

Table 5

Atomic Coodinates [a] of **3aa** with Estimated standard

Deviation in Parenthesis

Atom	x/a	y/b	z/c	B [b]
C1	5717 (2)	-295 (2)	6727 (2)	2.81 (6)
C2	6060 (2)	-343 (2)	7850 (2)	2.75 (6)
N3	6828 (2)	476 (2)	8004 (2)	2.80 (5)
N4	7254 (2)	913 (2)	6957 (2)	2.81 (5)
C5	6359 (2)	734 (2)	6189 (2)	2.65 (6)
O6	5033 (2)	-886 (2)	6277 (2)	3.91 (5)
C7	5654 (2)	-1052 (3)	8773 (2)	3.23 (7)
O8	6067 (2)	-1083 (3)	9638 (2)	5.63 (7)
O9	4789 (2)	-1652 (2)	8487 (2)	4.34 (6)
C10	4314 (3)	-2400 (4)	9334 (3)	5.68 (11)
O11	7291 (2)	841 (2)	8813 (2)	3.79 (5)
O12	7487 (1)	2189 (2)	7021 (2)	3.04 (4)
C13	6854 (3)	294 (3)	5142 (2)	3.40 (7)
O14	6926 (3)	-768 (2)	4867 (2)	5.85 (8)
O15	7228 (2)	1279 (2)	4634 (2)	4.33 (6)
C16	7766 (4)	1047 (5)	3637 (4)	7.11 (14)
C17	6594 (2)	2936 (2)	6654 (2)	2.64 (6)
C18	5964 (2)	3454 (3)	7595 (2)	2.77 (6)
C19	5153 (2)	4318 (2)	7105 (3)	2.68 (6)
C20	5041 (3)	5605 (3)	7053 (3)	3.51 (8)
C21	4156 (3)	6070 (3)	6517 (2)	3.71 (8)
C22	3442 (3)	5278 (3)	6013 (2)	3.70 (8)
C23	3588 (2)	3974 (3)	6031 (2)	3.31 (7)
C24	4434 (2)	3519 (2)	6603 (2)	2.52 (6)
C25	4841 (2)	2207 (2)	6830 (2)	2.62 (6)
C26	5802 (2)	2026 (2)	6108 (2)	2.40 (6)
O27	5347 (2)	2370 (2)	7877 (1)	2.81 (4)

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

2,5-Dimethyl-3,4-diazacyclopentadienone dioxide (**1d**) reacted with **2a** gave the cycloadduct **3da**. The structure was determined by comparison of the ¹H-nmr spectral data with those of **3ca**. The chemical shifts of the junction methyl group and two methines at ring juncture are close to those observed in **3ca**, suggesting that the *endo-exo* cycloadduct was produced exclusively.

Cycloaddition of 2,5-Disubstituted-3,4-diazacyclopentadienone Dioxide (**1a,b,c**) with Norbornadiene (**2b**).

The 1,3-dipole having electron-deficient substituents **1a** reacted with **2b** in refluxing chloroform to give the cycloadduct **3ab**. On the other hand, diphenyl substituted 1,3-dipole **1b** reacted with **2b** in refluxing benzene to give

only the cycloadduct **3bb**. The cycloaddition behavior of 2-methyl-5-phenyl substituted 1,3-dipole **1c** is quite different from the other cases, giving four 1 : 1 cycloadducts derived from combination of *endo/exo* and site selectivities. Of those, isolated products are the *endo* and *-exo* isomers, **3cb** and **3cb'**, derived from attack at the methyl nitrone moiety and the *exo* isomer **3'cb** from attack at the phenyl nitrone moiety [8].

Table 6

Interatomic Distances (Å) and Their Estimated
Standard Deviations of **3aa**

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C1	-C2	1.450 (4)	C1	-C5	1.527 (4)
C1	-O6	1.200 (4)	C2	-N3	1.319 (4)
C2	-C7	1.474 (4)	N3	-N4	1.493 (3)
N3	-O11	1.215 (3)	N4	-C5	1.478 (4)
N4	-O12	1.386 (3)	C5	-C13	1.531 (4)
C5	-C26	1.544 (4)	C7	-O8	1.183 (4)
C7	-O9	1.314 (4)	O9	-C10	1.459 (5)
O12	-C17	1.450 (3)	C13	-O14	1.180 (4)
C13	-O15	1.315 (4)	O15	-C16	1.450 (5)
C17	-C18	1.535 (4)	C17	-C26	1.541 (4)
C18	-C19	1.498 (4)	C18	-O27	1.440 (3)
C19	-C20	1.372 (4)	C19	-C24	1.384 (4)
C20	-C21	1.385 (5)	C21	-C22	1.376 (5)
C22	-C23	1.394 (5)	C23	-C24	1.363 (4)
C24	-C25	1.508 (4)	C2	-C26	1.548 (4)
C25	-O27	1.445 (3)			

The structures of the cycloadducts obtained were detemined on the basis of the stereochemistry of **3cb'**, which was established to be the *endo-exo* cycloadduct by inspection of the NOE effect between the junction methyl and methine protons. The *endo* nature of **3cb'** is also deduced from the up-field shift (1.09 ppm) of a bridged methine proton signal, resulting from the ring current effect of the phenyl group on the nitrone moiety.
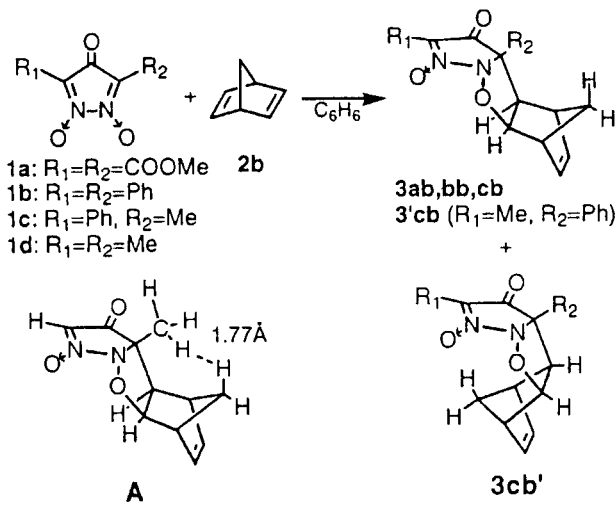
Scheme 3

1a: R₁=R₂=COOMe   2b
1b: R₁=R₂=Ph
1c: R₁=Ph, R₂=Me
1d: R₁=R₂=Me

3ab,bb,cb
3'cb (R₁=Me, R₂=Ph)

A

3cb'

Table 7
Bond Angles(°) and Their Estimated standard
Deviations of **3aa**

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C2	-C1	-C5	107.0 (2)	C2	-C1	-O6	128.8 (3)
C5	-C1	-O6	124.1 (3)	C1	-C2	-N3	108.7 (2)
C1	-C2	-C7	131.3 (3)	N3	-C2	-C7	119.8 (3)
C2	-N3	-N4	111.3 (2)	C2	-N3	-O11	132.2 (2)
N4	-N3	-O11	116.1 (2)	N3	-N4	-C5	103.2 (2)
N3	-N4	-O12	109.5 (2)	C5	-N4	-O12	108.8 (2)
C1	-C5	-N4	102.9 (2)	C1	-C5	-C13	113.0 (2)
C1	-C5	-C26	114.2 (2)	N4	-C5	-C13	104.9 (2)
N4	-C5	-C26	106.0 (2)	C13	-C5	-C26	114.2 (2)
C2	-C7	-O8	124.2 (3)	C2	-C7	-O9	110.3 (3)
O8	-C7	-O9	125.6 (3)	C7	-O9	-C10	115.4 (3)
N4	-O12	-C17	110.5 (2)	C5	-C13	-O14	124.9 (3)
C5	-C13	-O15	109.1 (3)	O14	-C13	-O15	125.9 (3)
C13	-O15	-C16	117.3 (3)	O12	-C12	-C18	112.3 (2)
O12	-C17	-C26	107.2 (2)	C18	-C17	-C26	102.0 (2)
C17	-C18	-C19	106.3 (2)	C17	-C18	-O27	101.5 (2)
C19	-C18	-O27	102.2 (2)	C18	-C19	-C20	134.2 (3)
C18	-C19	-C24	104.5 (2)	C20	-C19	-C24	121.3 (3)
C19	-C20	-C21	117.3 (3)	C20	-C21	-C22	121.5 (3)
C21	-C22	-C23	120.6 (3)	C22	-C23	-C24	117.6 (3)
C19	-C24	-C23	121.6 (3)	C19	-C24	-C25	105.0 (2)
C23	-C24	-C25	133.4 (3)	C24	-C25	-C26	106.2 (2)
C24	-C25	-O27	101.6 (2)	C26	-C25	-O27	101.1 (2)
C5	-C26	-Cl7	103.3 (2)	C5	-C26	-C25	116.2 (2)
Cl7	-C26	-C25	100.8 (2)				

The ^{1}H-nmr spectrum of **3cb** is closely similar to that of **3cb'** except for the chemical shift of the bridged methylene. The NOE experiment showed that the junction methyl protons coupled with a bridgehead methine proton and a bridged methylene proton. These facts indicate that **3cb** is the *exo-exo* cycloadduct, in which the low-field shift (2.01 ppm) of the bridged methylene maybe due to steric interference between the bridged methylene and junction methyl groups. The MNDO-PM3 optimized structure of the model cycloadduct (A) of 2-methyl-3,4-diazacyclopentadienone dioxide (**1e**) and **2b** indicates the presence of very short contact between the methyl and methylene protons. The calculated distance is *ca.* 1.77Å and the distance between the relevant carbons is 3.23Å. In the ^{13}C-nmr spectrum, the steric compression [7] produced the upfield shift of the junction methyl carbon (15.1 ppm) as comparison with those of **3ca** and **3cb'** (21.4 and 23.3ppm).

The cycloadduct **3'cb** is assigned to the *exo-exo* cycloadduct formed from attack of **2b** at the phenyl nitrone moiety. The ^{1}H-nmr spectral feature of **3'cb** closely resembles with that of the *exo-exo* cycloadduct **3bb** of the diphenyl dioxides **1b** and **2b**. The bridged

methylene protons resonate at 1.32 ppm for **3'cb** and 1.34 ppm for **3bb**, which is effectively shielded by the junction phenyl group.

Taking into consideration the ^{1}H-nmr spectral features mensioned above, the structure of **3ab** can be determined to be the *exo-exo* cycloadduct. The bridged methylene protons resonate at considerably lower field (1.78 ppm) as observed in **3cb**, attributable to the steric repulsion with the junction methoxycarbonyl group.

The ^{1}H-nmr and ^{13}C-nmr spectral data of the cycloadducts isolated are summarized in Tables 3 and 4.

Molecular Orbital Calculations.

The MNDO-PM3 [9] method was used for the semiempirical MO calculations using the MOPAC [10] (version 6.02) molecular orbital package which was locally modified for a Fujitsu S-4/2 engineering workstation. The *endo-exo* and *exo-exo* transition states (TS1 and TS2) for the model reaction of 2-methyl-3,4-diazacyclopentadienone dioxide (**1e**) with **1a** and the *endo-exo* and *exo-exo* transition stated (TS3 and TS4) for the reaction of **1e** with norbornadiene (**2b**) were located using the SADDLE routine [11] implemented in MOPAC and refined with the NLLSQ [12] or the TS [13] routines.

Discussion.

Cyclopentadienones and diazacyclopentadienones show high cycloaddition reactivity toward various dienophiles and served excellent trapping agents for unactivated olefinic compounds [14]. Phencyclone and 2,5-disubstituted-3,4-diphenylcyclopentadienones undergo stereospecific DA reaction with **2a** to give the *endo-exo* [4+2] π cycloadducts. It has been pointed out that cyclopentadienones approach to **2a** from the sterically less hindered *exo* site because the π-HOMO of the ethylenic group extends to the *exo* direction arisen from interaction with the strained σ-bonds connecting to the bridged oxygen [15a,b].

Scheme 4

R=COOMe
Ph, Me

2a
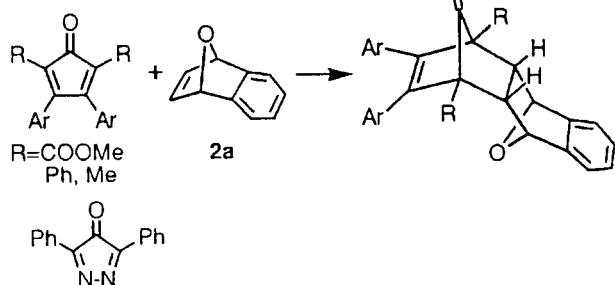
The frontier MO's of **1** calculated by MNDO-PM3 are closely similar to those of cyclopentadienone (Figure 2), implying that **1** can act as a dienone.
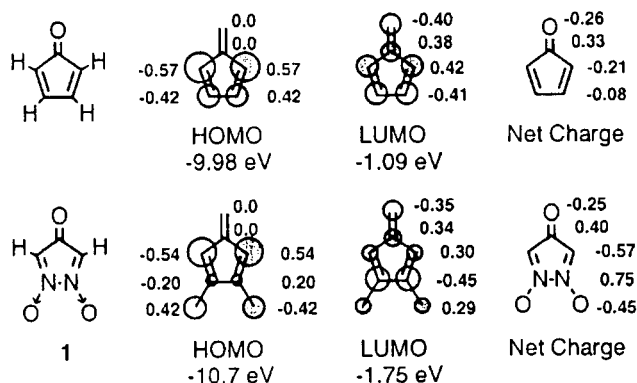
Figure 2. Frontier Orbitals of **1b**.

If the dioxides **1** might undergo DA reactions to olefines, the products obtained **3** are considered to be derived from thermally allowed six-electron [1s,4s]-sigmatropic rearrangement [16a,b] of the primary [4+2] π cycloadducts (B) and their stereochemistries are *exo-exo* type (Scheme 5).

We are convinced that the cycloaddition with **2a** can provide a clue to solve this question. As can be seen in

Scheme 5
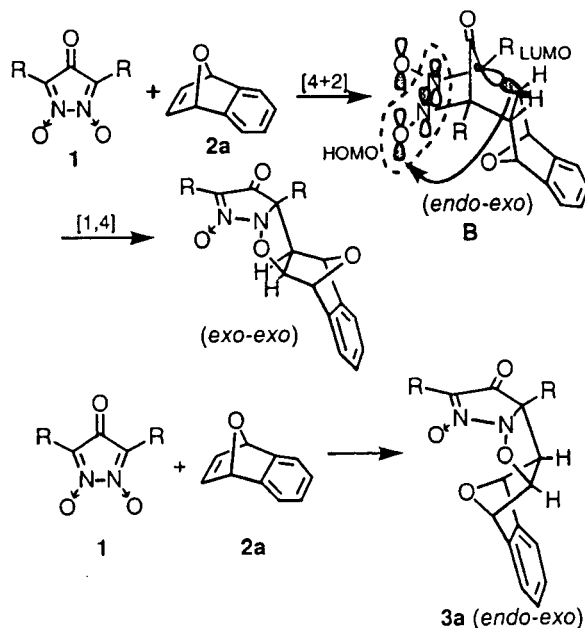
the ORTEP drawing (Figure 1), the cycloadduct (**3aa**) is *endo* with respect to the **1a** and *exo* with respect to **2a** (*endo-exo* type), clearly inconsistent with the *exo-exo* adduct derived from the consecutive pericyclic reaction pathway. This allows us to conclude that the 1,3-dipolar cycloadducts were derived from the direct 1,3-dipolar cycloaddition.

To know the general reaction behavior of bicyclo[2.2.1]heptadiene derivatives, the reaction with **2b** was studied. The reaction behavior with **2b** is quite different from that of **2a**. The dipolarophile **2b** mainly gave the *exo-exo* cycloadducts.

In order to account for the difference in the cycloaddition behavior between **2a** and **2b**, transition-state structures of the model reactions were calculated by MNDO-PM3 method using the SADDLE routine. The optimized transition structures are depicted in Figures 3 and 4.

ΔH_f 89.59 kcal/mol
endo-exo TS (TS1)

ΔH_f 91.22 kcal/mol
exo-exo TS (TS2)
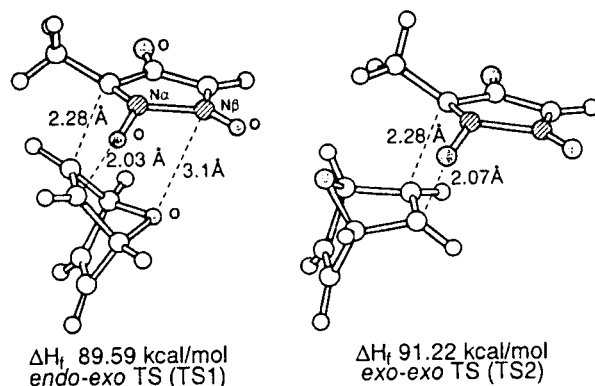
Figure 3. PM3-Calculated Transition Structures from the Model Reaction of **1c** with **2a**.

ΔH_f 89.59 kcal/mol
endo-exo TS (TS1)
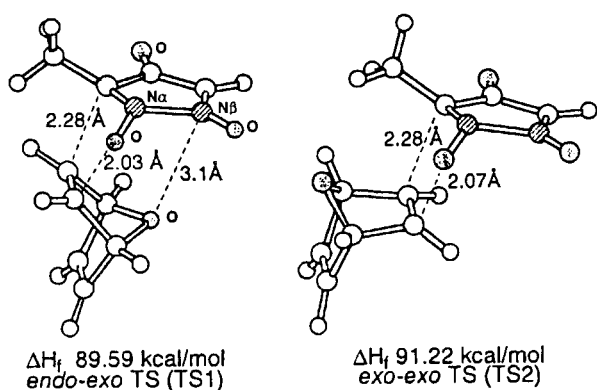
ΔH_f 91.22 kcal/mol
exo-exo TS (TS2)

Figure 4. PM3-Calculated Transition Structures from the Model Reaction of **1c** with **2b**.

In the cycloaddition with **2a**, the *endo* transition state (TS1) is more stable than the *exo* one (TS2). Careful inspection of the calculated geometry of TS1 indicates that the transition state is stabilized by coulombic interaction between the epoxy oxygen atom and the positively charged nitrogen atoms of the nitrone moieties, in which the distances among the oxygen and two nitrogen atoms (N_α and N_β) are 3.151 and 3.100Å, respectively and the net charges of N_α and N_β are calculated to be 0.41 and 0.85, respectively. On the other hand, the cycloaddition to **2b** is predicted to proceed through the *exo-exo* transition state. The *endo* TS (TS3) is calculated to be less stable than the *exo* TS (TS4), in which the steric repulsion between the bridged methylene proton and the remaining π-system is operative. The distance between the nitrogen atom (N_α) and the bridged hydrogen atom is 2.529Å [17].

It is noted that the remaining nitrone moiety involved in the cycloadducts did not show any cycloaddition reactivity toward **2a** and **2b**.

EXPERIMENTAL

All melting points are uncorrected. Nuclear magnetic resonance spectra were taken with Hitachi R-600 (60 MHz ¹H-nmr) and JEOL GX-400 (400 MHz ¹H-nmr and 100 MHz ¹³C-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. The ir spectra were recorded on 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 75eV. MO calculations were performed on a FACOM M-780 computer in the Computer Center of Kumamoto University and a Fujitsu S-4/2 workstation.

Materials.

2,5-Bis(methoxycarbonyl)-3,4-diazacyclopentadienone dioxide (**1a**), 2,5-diphenyl-3,4-diazacyclopentadienone dioxide

(**1b**), 2-methyl-5-phenyl-3,4-diazacyclopentadienone dioxide (**1c**) and 2,5-diphenyl-3,4-diazacyclopentadienone dioxide (**1d**) were prepared according to the established method [1a]. Dipolarophiles **2a** and **2b** were commercially available materials.

Cycloaddition of 2,5-Disubstituted-3,4-diazacyclopentadienone dioxide (**1a-d**) with Epoxynaphthalene (**2a**) and Norbornadiene (**2b**).

General Procedure of Cycloaddition.

A solution of **1a** and an excess amount of dipolarophile in chloroform or benzene was heated at 40-80° until a tlc spot of **1** could not be recognized. After cooling, the solvent was evaporated off under reduced pressure. The residue was purified by recrystallization or by chromatography on silica gel.

The results are summarized in Tables 1, 2, 3 and 4.

X-ray Crystallographic study.

A single crystal of **1aa** was prepared by slow evaporation of an ethanol-acetone solution. The density was measured by flotation in an aqueous potassium iodide solution, $Dm = 1.467$ g/cm³, $Dc = 1.492$ g/cm³. The cell constants were obtained from least-squares refinement of the 2θ angle of 20 reflections. The crystals are monoclinic, space group $P2_1/n$ (No. 14) which was judged from the systematic absence of reflections and there are four molecules ($z = 4$) in the unit cell of dimensions $a = 12.747(5)$, $b = 10.596(11)$, $c = 12.401(5)$Å , $\beta =91.47(3)°$, $V=1674(1)$Å³.

Intensity data were collected on RIGAKU AFC-6 automated diffractometer with a graphite monochromated Mo-K_α radiation (40 kV-20 mA) 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 every measurement of 100 reflections, and no decay was observed. A total 3253 independent reflections were measured, and after Lorentz and polarization corrections were applied, 2293 were treated as observed ($Fo>3\sigma F$, $2\theta <55°$) . No correction was applied for absorption.

The structure was solved by the direct method using the program MULTAN78 [4] . An overall temperature factor of 2.01 was obtained from a Wilson plot. An E map calculated with 493 signed E's (E>1.2) , which gave a combined figure of merit of 1.509, revealed the all position of the nonhydrogen atoms. The structure was refined by the block-diagonal least-squares method using the program BDLS [5] . The all hydrogens were placed in calculated positions. Keeping their vibrational amplitudes for the hydrogen fixed (B(H)=B(C) + 1.0) , and refining, we obtained a final R factor of 0.049. The weighting schemes used were $w = 1.0$ for $Fo<20.0$, $w = 400/Fo^2$ for $Fo>20.0$ for the observed reflections.

All calculations were performed on the FACOM M-780 computer in the Kumamoto University Information Processing Center with the Universal Crystallographic Computation Program (UNICS III) [5,6].

Acknowledgment.

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