1,3-Dipolar Cycloadditions to Bicyclic Olefins. I. 1,3-Dipolar Cycloadditions to Norbornadienes[1)]

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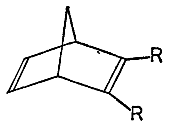
The 1,3-dipolar cycloadditions of phenylglyoxylonitrile oxide, benzonitrile-*N*-phenylimine, or *N*-phenyl-*C*-*p*-nitrophenylnitrone to norbornadiene, 2,3-dicyanonorbornadiene, and 2,3-bis(methoxycarbonyl)norbornadiene give the *endo*-adducts, together with the *exo*-adducts. These findings show that the 1,3-dipolar cycloadditions to norbornadienes do not follow the "*exo* rule." It is suggested that the present 1,3-dipolar cycloadditions are kinetically controlled reactions. The *endo*-side of norbornadienes is found to be homoconjugated by their NMR spectra. The homoconjugation must be responsible for the observed phenomenon.

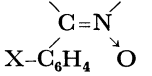
The "*exo* rule" has been deduced by Alder and Stein on the basis of the facts that phenyl azide (**7**) undergoes 1,3-dipolar cycloadditions to various bicyclic olefins with a moiety of a bicyclo[2.2.1]heptane skeleton to afford *only exo*-adducts.[2)] In fact, the 1,3-dipolar cycloadditions to norbornenes which have thus far been examined follow the "*exo* rule" without exception.[3)] Most norbornadienes also undergo cycloadditions by the "*exo* rule."[4)] However, in the cycloadditions of **7** to norbornadiene (**1**) and of benzonitrile oxide to **1**, small amounts of the *endo*-adducts were found to be formed in addition to large amounts of the *exo*-adducts.[5,6)] This fact stimulated us to elucidate whether or not the "*exo* rule" is applicable to 1,3-dipolar cycloadditions to norbornadienes; the formation of the *endo*-adduct is general. We carried out the 1,3-dipolar cycloadditions of phenylglyoxylonitrile oxide (**4**), benzonitrile-*N*-phenylimine (**5**), *C*,*N*-diphenylnitrone (**6a**), or *N*-phenyl-*C*-*p*-nitrophenylnitrone (**6b**) to **1**, 2,3-dicyanonorbornadiene (**2**), and 2,3-bis(methoxycarbonyl)norbornadiene (**3**). In these reactions, we found that the *endo*-adducts are formed in addition to the *exo*-adducts. On the basis of these results, we will discuss here the reason for the formation of the *endo*-adducts.



1 R=H
2 R=CN
3 R=CO_2CH_3

$C_6H_5\text{-CO-}\overset{+}{C}\text{=N-}\overset{-}{O}$ **4**

$C_6H_5\text{-}\overset{+}{C}\text{=N-}\overset{-}{N}\text{-}C_6H_5$ **5**



6a X=H
b X=*p*-NO_2

$C_6H_5\text{-}\overset{-}{N}\text{=N-}\overset{+}{N}$ **7**

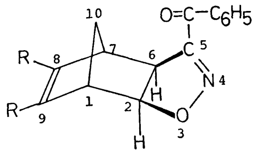
Results and Discussion

1,3-Dipolar Cycloadditions. The 1,3-dipolar cycloaddition of **4** to **1** was carried out as follows. To a stirred solution of α-chloro-α-hydroxyiminoacetophenone (**8**) with an excess of **1** in THF cooled in an ice bath, a solution of triethylamine in THF was added, drop by drop, over a period of one hour. The subsequent work-up of the reaction mixture gave a mixture of 5-benzoyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6exo}]deca-4,8-diene (**9a**), 5-benzoyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6endo}]deca-4,8-diene (**10a**), and bisadducts. Judging from the TLC, the bisadducts were composed of at least three isomers. Among the isomers, only 5,11-dibenzoyl-3,9-dioxa-4,10-diazatetracyclo[5.5.1.0^{2,6exo}0.^{8,12exo}]trideca-4,10-diene (**11**) has been isolated and characterized.

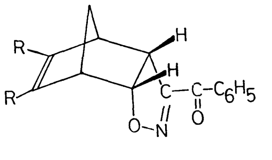
The cycloadditions of **4** to **2** and **4** to **3** were carried out by a method like that described above. In these reactions, the reagent, **4**, attacked the more electron-rich unsubstituted double bond of **2** and **3** to give 5-benzoyl-8,9-dicyano-3-oxa-4-azatricyclo[5.2.1.0^{2,6exo}]deca-4,8-diene (**9b**) and 5-benzoyl-8,9-bis(methoxycarbonyl)-3-oxa-4-azatricyclo[5.2.1.0^{2,6exo}]deca-4,8-diene (**9c**) as the *exo*-adducts and 5-benzoyl-8,9-dicyano-3-oxa-4-azatricyclo[5.2.1.0^{2,6endo}]deca-4,8-diene (**10b**) and 5-benzoyl-8,9-bis(methoxycarbonyl)-3-oxa-4-azatricyclo[5.2.1.0^{2,6endo}]deca-4,8-diene (**10c**) as the *endo*-adducts. The bisadducts and the monoadducts produced by the attack of **4** on the more electron-poor double bond were not detected at all. These findings show that **4** acts as an electron-accepting 1,3-dipole toward **2** and **3**.

The nitrilimine, **5**, which was prepared from *N*-phenylbenzenecarbohydrazonoyl chloride (**12**) and triethylamine in benzene, reacted with an excess of **1** in benzene to afford a mixture of 3,5-diphenyl-3,4-diazatricyclo[5.2.1.0^{2,6exo}]deca-4,8-diene (**13**), 3,5-diphenyl-3,4-diazatricyclo[5.2.1.0^{2,6endo}]deca-4,8-diene (**14**),[7)] and bisadducts.

The reaction of the nitrone **6a** with an excess of **1** in toluene gave two *exo*-monoadducts(4,5^{endo}-diphenyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6exo}]dec-8-ene (**15a**) and 4,5^{exo}-diphenyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6exo}]dec-8-ene (**16a**)[8)]) and bisadducts. When a solution of the nitrone **6b** in benzene containing an excess of **1** was refluxed, however, an *endo*-adduct (4-phenyl-5^{exo}-*p*-nitrophenyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6endo}]dec-8-ene (**17b**)) was obtained, together with two *exo*-monoadducts (4-phenyl-5^{endo}-*p*-nitrophenyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6exo}]dec-8-ene (**15b**) and 4-phenyl-5^{exo}-



9a R=H
b R=CN
c R=CO_2CH_3



10a R=H
b R=CN
c R=CO_2CH_3

Table 1. Yield and product composition

Olefin	1,3-Dipole	Product: Monoadduct Yield[a] (%)	Composition (%) exo	Composition (%) endo	exo/endo	Bisadduct Yield[a] (%)
1	**4**	76	**9a** (81)	**10a** (19)	4.3[b]	17
2	**4**	90	**9b** (68)	**10b** (32)	2.1	0
3	**4**	95	**9c** (75)	**10c** (25)	3.0[b]	0
1	**5**	95	**13** (87)	**14** (13)	6.7	4
1	**5**	79[c]	**13**[c]	—c)		6
1	**6a**	73	**15a** (56) and **16a** (44)	**17a** (0)		7
1	**6a**	54[d]	**15a**[d]	—d)		2.8
1	**6b**	76	**15b** (67) and **16b** (29)	**17b** (4)	24	7
1	**7**	67[e]	**18**[e] (92)	**19**[e] (8)	11[e]	f)

a) The yields are based on the starting 1,3-dipoles. b) The ratio is different from that shown in a previous communication.[g] c) Ref. 4d. d) Ref. 4c. e) Ref. 5. f) A small amount of bisadducts was obtained in the reaction reported in Ref. 5. g) Ref. 1.

p-nitrophenyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6exo}]dec-8-ene (**16b**)) and bisadducts.

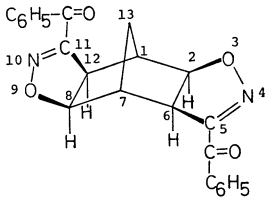
The yields of the adducts and the product compositions are summarized in Table 1, together with the data of Findlay *et al.*[5] and Huisgen *et al.*[4c,d] As has been described above, the formation of the *endo*-adducts was observed in all reactions except for that of **6a** with **1**. This fact led us to conclude that the "*exo* rule" is not applicable to 1,3-dipolar cycloadditions to norbornadienes.

Analyses of NMR Spectra of Adducts. The *exo*- and *endo* assignments of each mono-adduct were based on the NMR data (Tables 2 and 3). The coupling contant between the bridgehead proton and the adjacent *endo*-proton of an *exo*-isomer was in the range from 0 to 1 Hz, while the coupling constant between the bridgehead proton and the adjacent *exo*-proton of an *endo*-isomer was in the range from 4 to 5 Hz. These coupling constants were consistent with the values cited in the literature.[9]

Table 3. Coupling constants in adducts[a,b]

Adducts	*exo* or *endo*	Coupling constants $J_{1,2}$	$J_{2,6}$	$J_{5,6}$	$J_{6,7}$
9a	*exo*	~0	9.0	—	~0
9b	*exo*	0—1	9.5	—	0—1
9c	*exo*	0—1	8.5	—	0—1
10a	*endo*	4.0	9.5	—	4.0
10b	*endo*	4.0	10.0	—	4.0
10c	*endo*	4.0	10.0	—	4.0
13	*exo*	~0	9.0	—	~0
14	*endo*	4.0	11.0	—	4.0
15a	*exo*	~1	7.0	9.0	~1
15b	*exo*	~1	7.0	9.5	~1
16a	*exo*	~1	7.0	7.0	~1
16b	*exo*	~1	7.0	7.0	~1
17b	*endo*	4.5	8.0	6.5	4.5

a) The spectra were recorded at 60 MHz. b) J values in Hz.



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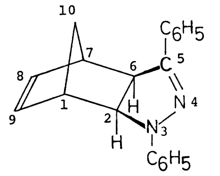

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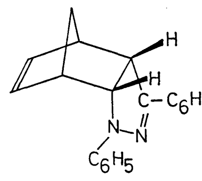
The *exo*-adduct **9c** exhibited the chemical shifts of methyl groups of two methoxycarbonyl groups at δ 3.78 and 3.81 ppm, while the *endo*-adduct **10c** at δ 3.33 and 3.78 ppm. The value of δ 3.33 ppm was assinged as being due to the methoxycarbonyl group attached to the C_8 position of **10c**. The molecular model of **10c**

Table 2. Chemical shifts of adducts[a,b]

Adducts	Protons H_1 and H_7	H_2	H_5	H_6	H_8 and H_9
9a	3.31	4.99	—	3.78	6.07 and 6.35
9b	3.78 and 3.92	5.20	—	4.06	—
9c	3.73	5.19	—	4.05	—
10a	3.40	5.37	—	4.09	6.05
10b	3.96	5.77	—	4.55	—
10c	3.71 and 3.82	5.57	—	4.40	—
13	3.25 and 3.46	4.39	—	3.77	6.15 and 6.34
14	3.46 and 3.60	4.79	—	4.12	5.89
15a	2.26 and 3.06	4.57	4.67	2.90	6.05 and 6.14
15b	2.20 and *ca.* 3	4.66	4.83	3.04	6.07 and 6.17
16a	2.85 and 3.00	4.52	3.80	2.63	6.03 and 6.19
16b	2.89 and 3.00	4.53	3.95	2.58	6.06 and 6.22
17b	2.8—3.3	5.12	3.88	3.16	6.23 and 6.33

a) The spectra were recorded at 60 MHz. b) Expressed in δ ppm units, with TMS as the internal standard, in $CDCl_3$ solution.



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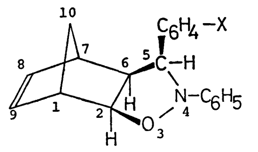
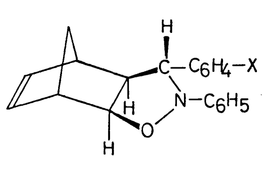
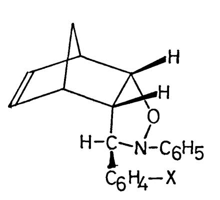


15a X=H
b X=p-NO$_2$

reveals that one of the two methoxycarbonyl groups lies in the shielding cone of the benzene ring of the benzoyl group attached on the C_5 position. The vinyl protons of **14** which are placed above the carbon-nitrogen double bond appeared in a field higher by 0.26—0.45 ppm than that of the corresponding vinyl protons of **13**. This upfield shift is probably due to the diamagnetic anisotoropy effect of the carbon-nitrogen double bond.[10] The chemical shifts of H_2 and H_5 of the *exo*-adduct **15a** were determined by means of the following observation. The former proton appeared as a doublet of triplets with a small coupling constant (J=*ca.* 1 Hz), while the latter proton appeared as a simple doublet. The small coupling was attributed to a "W-letter" coupling between $H_{10\text{-}anti}$ and $H_{2\text{-}endo}$ and to the coupling between H_1 and $H_{2\text{-}endo}$. The chemical shifts of H_2 and H_5 of the adducts **15b**, **16a**, and **16b** were also determined in the same way. The configurations of each isoxazoline moiety of **15a** and **16a**, both of which were *exo*-adducts, as shown in Table 3, were determined on the basis of the magnitude of the coupling constant between H_5 and H_6: the larger value (J=9.0 Hz) was assigned to the *cis*-coupling constant between H_5 and H_6 of **15a**, and the smaller value (J=7.0 Hz) to the *trans*-coupling constant between H_5 and H_6 of **16a**. Such an assignment has also been carried out for the two *exo*-adducts formed by the cycloaddition of the nitrone **6a** to norbornene.[4c)] In the Δ^2-isoxazoline system, J_{cis} has been observed to be always larger than J_{trans}.[11)] The assignments of the configurations of **15b** and **16b** were carried out in the same manner. The value (J=6.5 Hz) of the coupling constant between H_5 and H_6 of the endo-adduct **17b** corresponds reasonably to the *trans*-coupling constant.

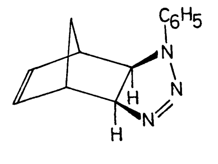


16a X=H
b X=p-NO$_2$



17a X=H
b X=p-NO$_2$

The presence of the symmetry along a C_2 axis of the bisadduct **11** was confirmed by a double-resonance technique: when the bridging methylene protons were irradiated with an additional radio frequency at their resonance position, the broad singlet was sharpened, but not divided into two singlets.



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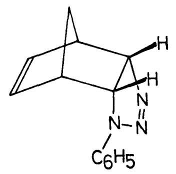
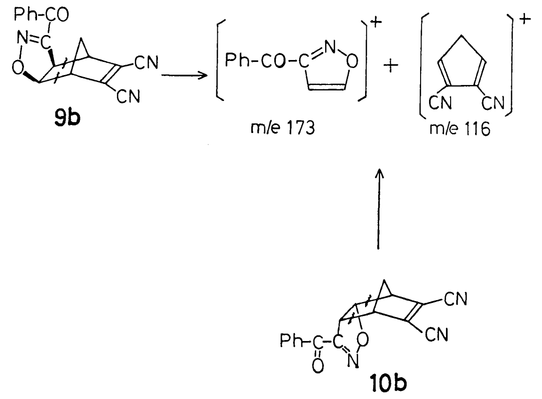


19

Thermal Stability of the exo-*Adducts (**9b** and **9c**) and the* endo-*Adducts (**10b** and **10c**).* When the *exo*-adduct, **9c**, and the *endo*-adducts, **10b** and **10c**, were each heated under reflux in THF for 2 h, they were recovered unchanged. The *exo*-adduct **9b**, when heated under the same conditions, gave a dirty mixture including **9b**, but not **10b**. The mass spectra of **9b** and **10b** showed the same fragmentation pattern (m/e 173, m/e 116, and no molecular ion peak; sample injection at 200 °C). This finding implies that the adducts **9b** and **10b** are liable to undergo the retro-Diels-Alder reaction by thermal decomposition to 2,3-dicyanocyclopentadiene and 3-benzoylisoxazole, rather than to the starting moieties, **2** and **4**. In addition, isoxazoles can not act as dipolarophiles.[3i)]



Scheme 1.

From above findings, we suggest that the present 1,3-dipolar cycloadditions are kinetically controlled reactions.

An Explanation for the Formation of the endo-*Adducts.* 1,3-Dipoles cannot undergo cycloadditions from the *endo*-side of norbornene. This is probably because of the steric hindrance of the *endo*-5,6-hydrogens. On the other hand, in the case of norbornadiene, it is possible that, 1,3-dipoles attack the carbon-carbon double bond from the *endo*-side because of the absence of such steric hindrance. This is insufficient, however, to explain the formation of the *endo*-adducts. If the *endo*-side of norbornadiene suffers from no steric hindrance, the *endo*-adduct should be produced in a higher yield than the *exo*-adduct, or at least in an amount equal to that of the *exo*-adduct. As the results shown in Table 1 do not accord with this prediction, an alternative factor must be responsible for the observed phenomena.

We show in Fig. 1 that there is a good linear relationship between the δ values of the vinyl protons of five norbornadienes (**1**, **2**, **3**, **20**, and **21**) and the values of

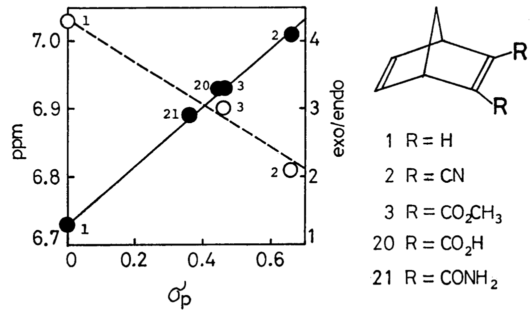


Fig. 1. Chemical shifts (TMS as an internal standard, in DMSO-d_6 solutions) of vinyl protons of 2,3-disubstituted norbornadienes *vs.* Hammett's σ_ps (—●—), and the exo/endo product ratios *vs.* Hammett's σ_ps (---○---)

Hammett's δ_ps[12] of the substituents. The phenomenon that the δ values of the vinyl protons are shifted to lower fields by the electron-withdrawing groups is likely to be attributable to homoconjugation on the *endo*-side of norbornadienes. The presence of homoconjugation between the two non-neighbouring carbon-carbon double bonds has also been found by investigating the photoelectron spectroscopy of norbornadiene.[13]

Inagaki *et al.* have proposed that the π-electron distribution of norbornene extends to the *exo*-side more than to the *endo*-side because of the interaction between the π-orbital and the methano-bridge orbital or the back-side of the anti C–H bond orbital at the C_7 position.[14] Such an interaction may also be present in norbornadiene. On the *endo*-side of norbornadiene, however, homoconjugation is present, as has been described above. This homoconjugation may result in extending the π-electron distribution toward the *endo*-side. Consequently, the difference in the π-electron distribution between the *exo*- and *endo*-sides of norbornadiene may be smaller than that of norbornene.

Thus, we may assume that the homocinjugation on the *endo*-side of norbornadiene brings about the formation of the *endo*-adducts in the cycloadditions of the electron-accepting 1,3-dipoles to norbornadienes.

Experimental

Materials. The precursors of 1,3-dipoles(**8**[15] and **12**[4d]), 1,3-dipoles(**6a**[16] and **6b**[16]), a norbornadiene **3**,[17] and norbornadiene-2,3-dicarboxylic acid(**20**)[17] were prepared by the method described in the literature. The **1** was purchased and distilled before use.

Preparation of 2. Into a solution of ammonium chloride (24 g) in aq ammonia (240 cm^3), **3** (47 g, 0.226 mol) was added, after which the mixture was stirred vigorously for 5 h at room temperature. The resulting white solid was separated by filtration, washed with ether, dried, and recrystallized from MeOH–EtOH to yield norbornadiene-2,3-dicarboxamide(**21**) mp 209—211 °C (dec) (lit,[18] 211—212 °C) in a quantitative yield. To a stirred suspension of **21**(5.0 g, 2.8 mmol) in DMF (28 g), cooled in an ice bath, a solution of thionyl chloride (10.0 g, 84 mmol) in DMF (10 g) was added, drop by drop, over a 30-min period. When the addition of the thionyl chloride solution was complete, the reaction mixture became a clear yellowish liquid. Then, the ice bath was removed and the solution was stirred for 2 days at room temperature. The resulting brown solution was poured into 150 g of ice-water, neutralized (aq Na_2CO_3), and extracted (ether 100 cm^3 × 3). The resulting solution was dried($MgSO_4$) and evaporated to dryness to give a yellowish solid (3.77 g). It was chromatographed on alumina. Elution with benzene afforded colorless pure **2** (3.38 g, 85%): mp 44—46 °C (lit,[18] 44—45 °C).

Reaction of 4 with 1. Into a stirred solution of **1** (2.00 g, 21.7 mmol) and **8** (1.84 g, 10.0 mmol) in dry THF (30 cm^3) cooled in an ice bath, a solution of triethylamine (TEA)(1.30 g, 13 mmol) in dry THF (20 cm^3) was added, drop by drop, over a 1-h period. After an additional 1 h of stirring at the same temperature, the resulting triethylammonium chloride was removed by filtration. It was chlomatographed on silica gel (200—300 mesh). Elution with benzene gave 1.81 g (76%) of a mixture of **9a** and **10a**. The NMR spectrum of the mixture showed that the exo/endo ratio was 81/19. Further elution with benzene afforded 0.316 g (17%) of a mixture of bisadducts ($C_{23}H_{18}O_4N_2$ by elemental analysis). The TLC of the mixture showed three spots (elution with benzene–ether (9:2)). It was recrystallized from EtOH–benzene to give 0.18 g of **11**: mp 181—182 °C; IR(KBr) 1650 (C=O) and 1565 cm^{-1}; NMR ($CDCl_3$) δ=1.55 (s, 2, CH_2), 3.15 (s, 2, H_1 and H_7), 3.83 (d, 2, J=8 Hz, H_6 and H_{12}), 4.76 (d, 2, J=8 Hz, H_2 and H_8), and 7.3—8.3 ppm (m, 10).

Found: C, 71.63; H, 4.82; N, 6.99%. Calcd for $C_{23}H_{18}O_4N_2$: C, 71.49; H, 4.70; N, 7.25%.

A mixture of **9a** and **10a** was column chromatographed on silica gel once again. Elution with benzene–hexane (6:1) gave **9a**. It was recrystallized from EtOH to afford colorless needles: mp 65—66 °C; IR(KBr) 1640 (C=O) and 1557 cm^{-1}.

Found: C, 75.20; H, 5.35; N, 5.77%. Calcd for $C_{15}H_{13}O_2N_1$: C, 75.30; H, 5.48; N, 5.85%.

Further elution with the same solvent gave **10a**. It was recrystallized from EtOH–H_2O to yield colorless needles: mp 53—54 °C; IR(KBr) 1655 (C=O) and 1560 cm^{-1}.

Found: C, 75.28; H, 5.35; N, 5.55%. Calcd for $C_{15}H_{13}O_2N_1$: C, 75.30; H, 5.48; N, 5.85%.

Reaction of 4 with 2. Into a stirred solution of **2** (710 mg, 5.00 mmol) and **8** (460 mg, 2.50 mmol) in dry THF (40 cm^3), cooled in an ice bath, a solution of TEA (330 mg, 3.26 mmol) in dry THF (10 cm^3) was added, drop by drop, over a 1-h period. After an additional 1 h's stirring, the resulting triethylammonium chloride was removed by filtration. After the removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene gave 351 mg of **2**. Further elution with benzene afforded **9b** (440 mg, 61%), which was subsequently recrystallized from EtOH to give colorless prisms: mp 140—141 °C; IR(KBr) 2220(C≡N), 1640(C=O), and 1570 cm^{-1}.

Found: C, 70.73; H, 3.67; N, 14.56%. Calcd for $C_{17}H_{11}O_2N_3$: C, 70.58; H, 3.83; N, 14.53%.

Elution with benzene–ethyl acetate (1:1) gave **10b** (208 mg, 29%). It was recrystallized from MeOH to afford colorless sticks: mp 127—127.5 °C; IR(KBr) 2225(C≡N) and 1660 cm^{-1} (C=O).

Found: C, 70.73; H, 3.64; N, 14.81%. Calcd for $C_{17}H_{11}O_2N_3$: C, 70.58; H, 3.83; N, 14.53%.

Reaction of 4 with 3. To a stirred solution of **3** (1.04 g, 5.00 mmol) and **8** (0.92 g, 5.00 mmol) in dry THF (15 cm^3), cooled in an ice bath, a solution of TEA (0.65 g, 6.50 mmol) in dry THF (10 cm^3) was added, drop by drop, over a 1-h period. After an additional 1 h's stirring at the same temperature, the resulting ammonium chloride was removed by filtration. After the evaporation of the solvent, a yellowish oily residue was solidified by the addition of a few drops of

95% EtOH. The solid was separated by filtration and dried under a vacuum to give 1.69 g (95%) of a mixture of **9c** and **10c**. The NMR spectrum of the mixture showed that the exo/endo ratio was 75/25. The mixture was chromatographed on silica gel. Elution with benzene–ether (20: 1) gave **9c**. It was recrystallized from 95% EtOH to give colorless sticks: mp 113—114 °C; IR(KBr) 1740 (ester C=O), 1715 (ester C=O), 1657 (C=O), 1635, and 1573 cm^{-1}.

Found: C, 64.14; H, 4.61; N, 3.76%. Calcd for $C_{19}H_{17}O_6N_1$: C, 64.22; H, 4.82; N, 3.94%.

Further elution with the same solvent afforded **10c**. It was recrystallized from 95% EtOH to give colorless sticks: mp 151—153 °C; IR(KBr) 1740(ester C=O), 1650(C=O), and 1620 cm^{-1}.

Found: C, 64.07; H, 4.65; N, 3.94%. Calcd for $C_{19}H_{17}O_6N_1$: C, 64.22; H, 4.82; N, 3.94%.

*Reaction of **5** with **1**.* A mixture of **1** (3.00 g, 32.6 mmol) and **12** (576 mg, 2.50 mmol) was dissolved in dry benzene 10 cm^3). Into the solution, TEA (1.3 cm^3) was added all at once, after which the solution was stirred for 24 h at room temperature. The resulting ammonium chloride was removed by filtration. The evaporation of the solvent left a yellow residue. It was chromatographed on alumina. Elution with benzene gave 680 mg (95%) of a mixture of **13** and **14**. The *exo*/*endo* ratio was 87/13 (from NMR). The developing solvent was changed to ethyl acetate to give 55 mg (4%) of a mixture of bisadduts (mp 281—305 °C (dec); $C_{33}H_{28}N_4$). A mixture of the monoadducts was chromatographed on alumina once again. Elution with hexane–benzene (3: 7) gave **13**. It was recrystallized from EtOH to give pale yellow needles: mp 134—135 °C (lit,$^{4d)}$ 133—135 °C). Further elution with the same solvent afforded **14**. It was recrystallized from EtOH to give pale yellow needles: mp 110—111 °C; IR(KBr) 1595, 1550, and 1500 cm^{-1}.

Found: C, 83.65; H, 6.39; N, 9.86%. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78%.

*Reaction of **6a** with **1**.* A mixture of **1** (1.84 g, 20.0 mmol) and **6a** (978 mg, 5.00 mmol) was dissolved in dry toluene (5 cm^3) and heated under reflux for 4 h. A large amount of the solvent was removed *in vacuo*. Then, the concnetrated solution was chromatographed on silica gel. Elution with toluene gave **15a** (595 mg, 41%). It was recrystallized from MeOH to afford colorless needles: mp 110—111 °C (lit,$^{4c)}$ 111° C). Further elution with toluene afforded **16a** (467 mg, 32%). It was recrystallized from MeOH to give colorless needles: mp 76—77 °C; IR(KBr) 1595, 1490, and 1450 cm^{-1}.

Found: C, 83.26; H, 6.56; N, 4.71%. Calcd for $C_{20}H_{19}O_1N_1$: C, 83.01; H, 6.62; N, 4.84%.

The final elution with toluene gave a mixture of bisadducts in a 7% yield (88 mg): mp 218—233 °C (dec)(elemental analysis; $C_{33}H_{30}O_2N_2$).

*Reaction of **6b** with **1**.* A solution of **1** (1.84 g, 20.0 mmol) and **6b** (1.21 g, 5.00 mmol) in dry benzene (20 cm^3) was heated under reflux for 18 h. The solution was concentrated and chromatographed on silica gel. Elution with benzene gave the following products: **15b** (859 mg, 51%): mp 121—122 °C (pale yellow sticks from MeOH); IR(KBr) 1600, 1520 (NO_2), 1495, and 1350 cm^{-1} (NO_2).

Found: C, 72.06; H, 5.47; N, 8.31%. Calcd for $C_{20}H_{18}O_3N_2$: C, 71.84; H, 5.43; N, 8.38%. **16b** (353 mg, 22%): mp 153—154 °C (pale yellow sticks from MeOH); IR(KBr) 1595, 1510 (NO_2), 1490, and 1350 cm^{-1} (NO_2).

Found: C, 71.86; H, 5.44; N, 8.63%. Calcd for $C_{20}H_{18}O_3N_2$: C, 71.84; H, 5.43; N, 8.38%. **17b** (43 mg, 3%): mp 138—140 °C (pale yellow needles from MeOH); IR(KBr) 1595, 1510(NO_2), 1490, and 1355 cm^{-1} (NO_2).

Found: C, 71.81; H, 5.49; N, 8.15%. Calcd for $C_{20}H_{18}O_3N_2$: C, 71.84; H, 5.43; N, 8.38%. A mixture of bisadducts (83 mg; 7%): mp 231—246 °C (dec)($C_{33}H_{28}O_6N_4$).

*Examination of the Thermal Stability of **9b**, **9c**, **10b**, and **10c**.* A solution of **10b** (53 mg) in THF (3 cm^3) was heated under reflux for 2 h. The solvent was then evaporated to give a white solid composed of only one component (TLC). The NMR spectrum of the solid was identical with that of **10b**. **9c** and **10c** were treated in the same way. They were also recovered unchanged. When a solution of **9b** (53 mg) in THF (3 cm^3) was heated under the same conditions, a dirty mixture was obtained. It contained **9b**, but not **10b** (TLC, NMR).

The mass spectra of **9b** and **10b** showed the same pattern. MS (80 eV) *m*/*e* 173, 116, 105, 89, 77, 51, and 28.

*NMR Measurements of Norbornadienes (**1**, **2**, **3**, **20**, and **21**).* The NMR spectra of norbornadienes (**1**, **2**, **3**, **20**, and **21**) were recorded at 60 MHz, using TMS as the internal standard, in DMSO-d_6 solutions (10% solutions); δ values of vinyl protons: 6.73 (**1**), 7.01 (**2**), 6.93 (**3**), 6.93 (**20**), and 6.89 ppm (**21**).

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