476 *J. Org. Chem.* 1980, *45*, 476-479

Molecular Design by Cycloaddition Reactions. 34.[1] Cycloaddition Reactions of 1,4-[(*tert*-Butyloxycarbonyl)imino]-1,4-dihydronaphthalene

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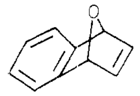
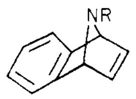
The cycloaddition reactions of 7-azabenzonorbornadiene (**2**) with cyclic polyolefins have been investigated. The reactions with tropone, tropolone, and fulvenes gave exo,endo-[4 + 2] adducts in good yields. Furan reacted with **2** to give a mixture of exo,endo and exo,exo adducts **7** and **8**. In the reaction with α-pyrone, initially formed isoindole (**9**) reacted with **2** to give adducts **10** and **11**. **9**, which was effectively generated by reaction of **2** with 3,6-di(2′-pyridyl)-*s*-tetrazine (**12**), was trapped by various dienophiles. The results are summarized in Table I. The steric effect of the 7-bridged substituent in the reaction with bicyclic dienophiles has been discussed.

The usefulness of 7-oxabenzonorbornadiene (**1**) as a dienophile and dipolarophile in the reaction with various dienes and dipolar compounds[2,3] has been shown. The high reactivity of **1** is due to both ring strain and orbital participation of the n electrons of the proximate oxygen atom.[4] Although 7-azabenzonorbornadiene (**2**) is considered to show similar structural features, no systematic studies of its cycloaddition reaction have been reported.



1

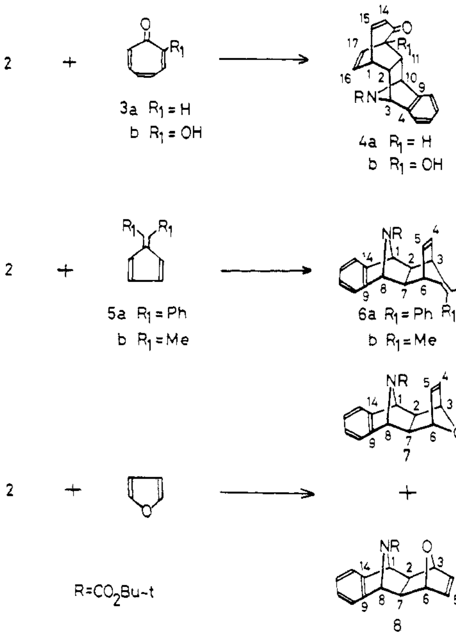


2

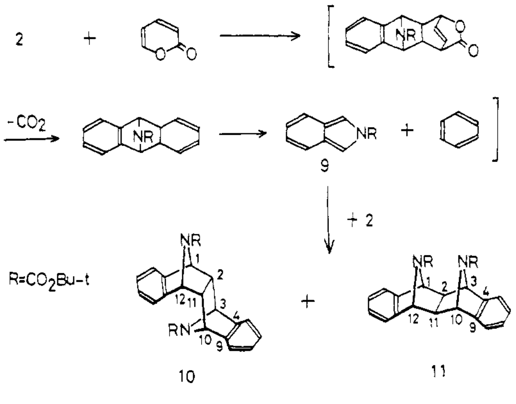
As a continuation of our studies on the chemistry of bridged benzoheterocycles,[2,3] we have investigated the cycloaddition reactions of 1,4-[(*tert*-butyloxycarbonyl)imino]-1,4-dihydronaphthalene (**2**, R = CO_2-*t*-Bu)[5] with cyclic dienes and trienes and the trapping reactions of isoindole (**9**), which is easily obtained from **2**.

Cycloaddition Reaction of 2 with Cyclic Polyenes. Reaction of **2** with tropone (**3a**) and tropolone (**3b**) in chlorobenzene at 120–130 °C gave adducts **4a** and **4b** in 100% and 60% yields, respectively (Scheme I). The nature of the products as 1:1 adducts was apparent from elemental analyses and mass spectra (**4a**, M^+ 349; **4b**, M^+ 365). The NMR spectra indicated the presence of the bicyclo[3.2.2]nona-3,6-dien-2-one system.[6] In the NMR spectrum of **4a**, the H-2 and H-11 signals appeared as a sharp doublet (J = 8.0 Hz) at δ 2.25 and 2.44, respectively. The absence of vicinal couplings between H-2 and H-1 (H-11 and H-12) and between H-2 and H-3 (H-11 and H-10) was confirmed by double-resonance experiments, indicating the exo,endo configuration.[7] Similarly, adduct **4b** was concluded to be the exo,endo-[4 + 2] cycloadduct.

Scheme I



Scheme II



Reaction of **2** with diphenyl- (**5a**) and dimethylfulvenes (**5b**) in chlorobenzene at 120–130 °C afforded [4 + 2] cycloadducts **6a** (56%) and **6b** (60%), respectively. The exo,endo configuration[7] was determined on the basis of NMR spectra (**6a**, $J_{1,2} = J_{7,8} = 0$ and $J_{2,3} = J_{6,7} = 2.2$ Hz; **6b**, $J_{1,2} = J_{7,8} = 0$ and $J_{2,3} = J_{6,7} = 3.0$ Hz). The hindered N inversion or N–C bond rotation[8] of **6a** at room temperature was suggested by observation of two singlets for nitrogen bridgehead protons at δ 4.96 (1 H) and 4.83 (1 H) which at 60 °C became a sharp singlet at δ 4.87 (2 H).

The similar reaction of **2** with excess furan in chlorobenzene at 120–130 °C for 90 h afforded a mixture of two 1:1 adducts, **7** (15%) and **8** (23%). The nature of the adducts was confirmed by their NMR spectra which showed **7** to be the exo,endo adduct ($J_{1,2} = J_{7,8} = 0$, $J_{6,7}$

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[1] Part 33 of this series: A. Kondo, T. Yamane, T. Ashida, T. Sasaki and K. Kanematsu, *J. Org. Chem.*, **43**, 1180 (1978).

[2] T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Uchide, *J. Chem. Soc., Perkin Trans. 1*, 2750 (1972).

[3] T. Sasaki, K. Kanematsu, K. Hayakawa, and A. Kondo, *J. Org. Chem.*, **38**, 4100 (1973).

[4] R. N. Warrener, *J. Am. Chem. Soc.*, **93**, 2346 (1971).

[5] L. A. Carpino and D. E. Barr, *J. Org. Chem.*, 31, 764 (1966).

[6] T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc., Perkin Trans. 1*, 1951 (1972).

[7] The former prefix always refers to the configuration with respect to the 7-azabenzonorbornadiene system.

[8] W. J. Delonghry and I. O. Sutherland, *Chem. Commun.*, 1104 (1971).

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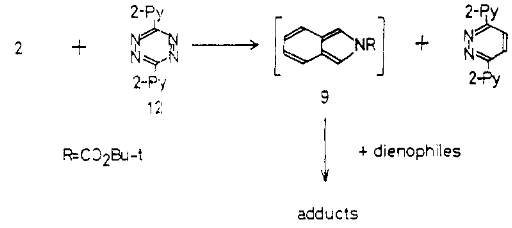
Scheme III



= $J_{2,3}$ = 3.0 Hz) and **8** to be the exo,exo isomer ($J_{1,2} = J_{7,8} = J_{6,7} = J_{2,3} = 0$).

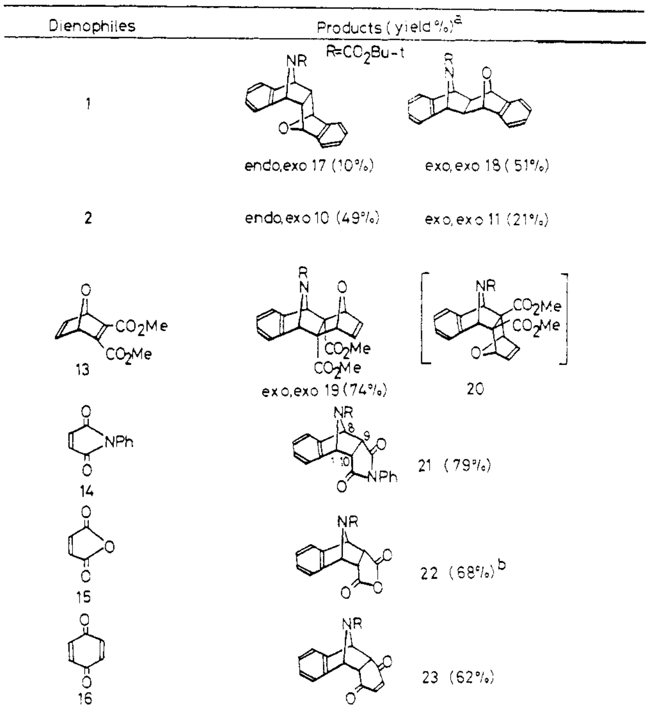
When a mixture of **2** and α-pyrone (1:1) was heated in toluene under reflux for 70 h, two products, **10** (49%) and **11** (8%), were obtained (Scheme II). Elemental analyses and mass spectra (M^+ 460) showed both products to be a 1:1 adduct of **2** to isoindole (**9**), which was formed in situ by succesive loss of carbon dioxide and benzene from the initial [4 + 2] cycloadduct. The stereochemistry of these adducts was determined by their NMR spectra. The difference in chemical shifts of the two *tert*-butyl groups of these adducts was diagnostic. While compound **11** showed only one singlet at δ 1.35 (18 H), compound **10** exhibited two *tert*-butyl signals at δ 1.10 (s, 9 H) and 1.35 (s, 9 H). The high-field shift of one *tert*-butyl signal of **10** was apparently due to the anisotropic effect of a proximate benzene ring. Furthermore, the coupling pattern of H-1 (H-12) and H-2 (H-11) of **10** (AA'BB' multiplet)[9] was indicative of the endo,exo configuration. The absence of the coupling with vicinal bridgehead protons in **11** ($J_{2,1} = J_{11,12} = J_{2,3} = J_{11,10} = 0$) is only compatible with the exo,exo configuration. Similar results were also observed in the reaction of **1** and α-pyrone.[10]

Attempted reactions of compound **2** with cycloheptatriene and cyclooctatetraene were unsuccessful even under more drastic conditions, although these polyolefins are well-known to react with electron-deficient dienophiles.[11]

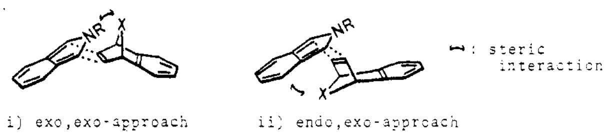
Cycloaddition Reaction of Isoindole (9). In connection with the above-mentioned study on the reactivity of **2**, we have also investigated the cycloaddition reaction of isoindole (**9**), which is easily generated from **2** by Warrener's method.[12] Thus, the reaction of **2** with 3,6-di(2'-pyridyl)-*s*-tetrazine (**12**) in chloroform or benzene at 0–25 °C afforded **9**, which was trapped by various dienophiles (Scheme III). Although electron-deficient dienophiles such as **14**–**16** could be added at the beginning of the reaction, the electron-rich dienophiles such as **1** and **13** were added after completion of the initial reaction in order to avoid their concomitant reaction with **12**. The results are summarized in Table I.

The structural assignment was made on the basis of elemental analyses and spectroscopic data (see Experimental Section). The NMR spectrum of the exo adducts (**11** and **18**) showed at room temperature two signals for nitrogen-bridgehead protons which became a one band signal at higher temperature, while that of the endo adducts (**10**, **17**, **21**–**23**) revealed one signal for two nitrogen-bridgehead protons even at room temperature. Reaction with **2** gave adducts **10** and **11**, which were identical with those obtained from the reaction of **2** with α-pyrone. In the case of **13**, isoindole (**9**) reacted selectively with the electron-deficient double bond to give adduct **19**, whose configuration was assigned on the basis of NMR analysis. Although the endo,exo structure[7] **20** could not be ruled out, an observation of two nonequivalent nitrogen-bridgehead proton signals suggested the product to be the exo,exo isomer (**19**).

Table I. Trapping Reaction of the Isoindole (9) with Dienophiles



[a] Yields are for isolated pure products. [b] Determined by NMR.



	exo,exo		endo,exo
2 X=NR	1	:	2.3
1 X=O	5.1	:	1
24 X=$<^{Me}_{Me}$	no adduct		

Figure 1.

Fulvenes, acenaphthylene, and 11-isopropylidenetricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (**24**) were found to be inert in the reaction with isoindole (**9**) and were recovered unchanged, whereas the reaction with norbornadiene, norbornene, and tropone resulted in the formation of an intractable complex mixture.

Discussion

It should be noted that the reaction of **9** with planar monocyclic dienophiles (**14**–**16**) gives only endo adducts (**21**–**23**), whereas the similar reaction of the unsubstituted isoindole affords a mixture of endo and exo adducts.[12,13] Obviously, the bulky group (COO-*t*-Bu) on the nitrogen atom of **9** played an important role in favoring the endo approach of dienophile in the transition state. In contrast, the reaction of **9** with bicyclic dienophiles such as **1** and

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(9) P. L. Watson and R. N. Warrener, *Aust. J. Chem.*, **20**, 1725 (1973).

(10) (a) L. F. Fieser and M. J. Haddadin, *J. Am. Chem. Soc.*, **86**, 2081 (1964); (b) *Can. J. Chem.*, **43**, 1599 (1965).

(11) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(12) G. M. Priestlay and R. N. Warrener, *Tetrahedron Lett.*, 4298 (1972).

(13) R. Bonnet and R. F. C. Brown, *J. Chem. Soc., Chem. Commun.*, 393 (1972).

2 afforded a mixture of endo and exo adducts. In these cases, the degree of bulkiness of the 7-bridge (X in Figure 1) was also important. As seen in the product ratio, the importance of the endo,exo approach (ii) increased with increasing bulkiness of X because of the severe steric hindrance between the X and *N*-COO-*t*-Bu groups in the exo,exo approach (i). In the case of **24**, the bridge X (>C=CMe$_2$) seemed to be too bulky to allow the approach in either way, and no products were obtained.

Experimental Section

Melting points were measured with a Yanagimoto apparatus. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. UV spectra were determined with a Hitachi spectrophotometer (Model 200-10). NMR spectra were taken at room temperature (δ) and 60 °C (δ^*) with a JEOL C-60-HL spectrometer and with a JEOL FX 60 FT NMR spectrometer, with tetramethylsilane as an internal standard. IR spectra were taken with a JASCO IRA-1 spectrometer. Mass spectra were obtained with a Hitachi RMS-4 mass spectrometer at 70 eV.

Reactions of 7-Azabenzonorbornadiene (2) with Cyclic Polyenes. (a) With Tropone (3a). A solution of tropone (**3a**) (110 mg, 1.04 mmol) and **2**[5] (243 mg, 1.0 mmol) in chlorobenzene (3 mL) was heated at 120–130 °C in a sealed tube for 100 h. Chromatography on silica gel with benzene–chloroform followed by recrystallization from chloroform–*n*-hexane gave adduct **4a** (332 mg, 95%) as colorless crystals: mp 208–210 °C; IR (KBr) 1684, 1658 cm^{-1}; NMR (CDCl$_3$) δ 1.38 (9 H, s), 2.25 (1 H, d, J = 8.0 Hz, H-11), 2.44 (1 H, d, J = 8.0 Hz, H-2), 3.51 (1 H, t, J = 7.4 Hz, H-1), 3.75 (1 H, br d, J = 7.4 Hz, H-12), 4.92 (2 H, br s, H-3 and H-10), 5.64 (1 H, dd, J = 11.0 and 1.5 Hz, H-14), 6.07 (1 H, t, J = 7.4 Hz, H-17), 6.44 (1 H, t, J = 7.4 Hz, H-16), 6.9–7.4 (5 H, m, ArH and H-15); UV (EtOH) λ_{max} 238 nm (ϵ 7016), 264 (2456), 271 (1544), 327 (56); mass spectrum, *m/e* 349 (M$^+$, 1%), 217 (42), 161 (88), 117 (100).

Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.53; H, 6.62; N, 3.98.

(b) With Tropolone (3b). A solution of tropolone (**3b**) (130 mg, 1.07 mmol) and **2** (243 mg, 1.0 mmol) in chlorobenzene (3 mL) was heated at 120–130 °C in a sealed tube for 110 h. Chromatography on silica gel with dichloromethane–*n*-hexane followed by recrystallization from dichloromethane–*n*-hexane gave adduct **4b** (220 mg, 60%) as colorless crystals: mp 191–193 °C; IR (KBr) 3480, 1682, 1654 cm^{-1}; NMR (CDCl$_3$) δ 1.40 (9 H, s), 2.11 (1 H, d, J = 7.5 Hz, H-2), 2.44 (1 H, d, J = 7.5 Hz, H-11), 3.65 (1 H, t, J = 7.6 Hz, H-1), 4.83 (1 H, br s, exchangeable, OH), 5.01 (1 H, s, H-3), 5.56 (1 H, s, H-10), 5.88 (1 H, d, J = 11.2 Hz, H-14), 5.94 (1 H, d, J = 7.6 Hz, H-17), 6.37 (1 H, t, J = 7.6 Hz, H-16), 7.0–7.5 (5 H, m, Ar H and H-15); UV (EtOH) λ_{max} 241 nm (ϵ 6793), 272 (1430), 327 (86); mass spectrum *m/e* 365 (M$^+$), 217, 161, 117.

Anal. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.31; H, 6.41; N, 3.81.

(c) With 6,6-Diphenylfulvene (5a). A solution of 6,6-diphenylfulvene (**5a**) (230 mg, 1.0 mmol) and **2** (243 mg, 1.0 mmol) in chlorobenzene (3 mL) was heated in a sealed tube at 130 °C for 24 h. Chromatography on silica gel with dichloromethane–*n*-hexane followed by recrystallization from dichloromethane–*n*-hexane gave adduct **6a** (260 mg, 60%) as colorless crystals: mp 202–203 °C; IR (KBr) 1687 cm^{-1}; NMR (CDCl$_3$) δ 1.38 (9 H, s), 2.41 (2 H, dd, J = 2.2 and 1.5 Hz, H-2 and H-7), 3.52 (2 H, m, H-3 and H-6), 4.83 (1 H, s, H-1 or H-8), 4.96 (1 H, s, H-1 or H-8), 6.25 (2 H, dd, J = 3.4 and 1.5 Hz, H-4 and H-5), 6.9–7.3 (14 H, m, ArH); δ^* (CDCl$_3$) 1.37 (9 H, s), 2.39 (2 H, dd, H-2 and H-7), 3.50 (2 H, m, H-3 and H-6), 4.87 (2 H, s, H-1 and H-8), 6.23 (2 H, dd, H-4 and H-5), 6.9–7.3 (14 H, m, ArH).

Anal. Calcd for $C_{33}H_{31}NO_2$: C, 83.69; H, 6.60; N, 2.96. Found: C, 83.83; H, 6.82; N, 2.94.

(d) With 6,6-Dimethylfulvene (5b). A solution of 6,6-dimethylfulvene (**5b**) (220 mg, 2.08 mmol) and **2** (486 mg, 2.0 mmol) in chlorobenzene (3 mL) was heated in a sealed tube at 130 °C for 19 h. Workup as above gave adduct **6b** (420 mg, 56%) as colorless crystals: mp 190–192 °C; IR (KBr) 1675 cm^{-1}; NMR (CDCl$_3$) δ 1.38 (9 H, s), 1.47 (6 H, s), 2.12 (2 H, dd, J = 3.0 and 1.5 Hz, H-2 and H-7), 3.39 (2 H, m, H-3 and H-6), 4.77 (1 H, s, H-1 or H-8), 4.89 (1 H, s, H-1 or H-8), 6.14 (2 H, dd, J = 2.8 and 1.5 Hz, H-4 and H-5), 6.9–7.3 (4 H, m, ArH).

Anal. Calcd for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.95; H, 7.83; N, 3.88.

(e) With Furan. A solution of furan (1 mL) and **2** (120 mg, 0.49 mmol) was heated in a sealed tube at 130 °C for 90 h. After evaporation of solvent, the resulting residue was subjected to silica gel chromatography (dichloromethane–*n*-hexane). The first fraction gave adduct **8** (36 mg, 23%) as colorless crystals: mp 187–188 °C (dichloromethane–*n*-hexane); IR (KBr) 1682, 1393, 1171 cm^{-1}; NMR (CDCl$_3$) δ 1.48 (9 H, s), 1.90 (2 H, s, H-2 and H-7), 4.9–5.2 (4 H, m like t, H-1, H-3, H-6, and H-8), 6.40 (2 H, s, H-4 and H-5), 7.14 (4 H, m, Ar H); δ^* (CDCl$_3$) 1.50 (9 H, s), 1.89 (2 H, s, H-2 and H-7), 4.96 (2 H, s, H-1 and H-8 or H-3 and H-6), 5.10 (2 H, s, H-1 and H-8 or H-3 and H-6), 6.39 (2 H, s, H-4 and H-5), 7.13 (4 H, m, Ar H).

Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.10; H, 6.93; N, 4.56.

The second fraction gave adduct **7** (24 mg, 15%) as colorless crystals: mp 165–167 °C (dichloromethane–*n*-hexane); IR (KBr) 1670, 1440, 1173 cm^{-1}; NMR (CDCl$_3$) δ 1.38 (9 H, s), 2.46 (2 H, dd, J = 3.0 and 1.7 Hz, H-2 and H-7), 4.73 (1 H, s, H-1 or H-8), 4.85 (2 H, m, H-3 and H-6), 4.91 (1 H, s, H-1 or H-8), 6.36 (2 H, s, H-4 and H-5), 7.13 (4 H, m, Ar H).

Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 72.97; H, 6.95; N, 4.67.

(f) With α-Pyrone. A solution of α-pyrone (84 mg, 1.0 mmol) and **2** (243 mg, 1.0 mmol) in toluene (3 mL) was refluxed for 70 h. Chromatography of the reaction mixture on silica gel (dichloromethane–*n*-hexane) gave **11** (20 mg, 8%) and **10** (113 mg, 49%) in the order of elution. Adduct **11**: mp 219–220 °C (chloroform–*n*-hexane); IR (KBr) 1672, 1360, 1167 cm^{-1}; NMR (CDCl$_3$) δ 1.35 (18 H, s), 1.87 (2 H, s, H-2 and H-11), 5.17 and 5.23 (4 H, each s, H-1, H-3, H-10, and H-12), 6.9–7.2 (8 H, m, Ar H); δ^* (CDCl$_3$) 1.34 (18 H, s), 1.85 (2 H, s, H-2 and H-11), 5.20 (4 H, s, H-1, H-3, H-10, and H-12), 6.9–7.2 (8 H, m, ArH); mass spectrum *m/e* 460 (M$^+$ 10%).

Anal. Calcd for $C_{28}H_{32}N_2O_4$: C, 73.02; H, 7.00; N, 6.08. Found: C, 73.27; H, 6.96; N, 5.79.

Adduct **10**: mp 208–210 °C (chloroform–*n*-hexane); IR (KBr) 1700, 1680, 1367, 1171 cm^{-1}; NMR (CDCl$_3$) δ 1.11 (9 H, s), 1.35 (9 H, s), 2.63 (2 H, m, H-2 and H-11), 4.49 (1 H, s, H-3 or H-10), 4.59 (1 H, s, H-3 or H-10), 5.09 (2 H, m, H-1 and H-12), 6.9–7.2 (8 H, m, Ar H); δ^* (CDCl$_3$) 1.10 (9 H, s), 1.34 (9 H, s), 2.63 (2 H, m, H-2 and H-11), 4.52 (2 H, s, H-3 and H-10), 5.07 (2 H, m, H-1 and H-12), 6.9–7.2 (8 H, m, Ar H); mass spectrum *m/e* 460 (M$^+$ 10%), 348 (61), 243 (20), 217 (43), 161 (100).

Anal. Calcd for $C_{28}H_{32}N_2O_4$: C, 73.02; H, 7.00; N, 6.08. Found: C, 73.23; H, 6.94; N, 5.84.

Trapping of the Isoindole (9) with Dienophiles. (a) With 7-Oxabenzonorbornadiene (1). A mixture of 7-azabenzonorbornadiene (**2**) (243 mg, 1.0 mmol) and 3,6-di(2-pyridyl)-*s*-tetrazine (**12**) (236 mg, 1.0 mmol) in chloroform (2 mL) was stirred at 0 °C until the red color of the tetrazine had disappeared (4 h), and then the dienophile **1** (150 mg, 1.04 mmol) was added. After stirring for 1 day at room temperature, evaporation to dryness at reduced pressure followed by chromatography on silica gel (dichloromethane–*n*-hexane as eluant) gave adducts **17** (39 mg, 10%) and **18** (197 mg, 51%) in the order of elution. Adduct **17**: mp 184–186 °C; IR (KBr) 1687, 1370, 1167 cm^{-1}; NMR (CDCl$_3$) δ 1.37 (9 H, s), 2.76 (2 H, m, H-2 and H-11), 4.67 (2 H, s, H-3 and H-10), 5.10 (2 H, m, H-1 and H-12), 7.0–7.4 (8 H, m, Ar H).

Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.51; H, 6.50; N, 3.71.

Adduct **18**: mp 265–267 °C; IR (KBr) 1695, 1402, 1175 cm^{-1}; NMR (CDCl$_3$) δ 1.49 (9 H, s), 1.94 (2 H, s, H-2 and H-11), 5.18–5.41 (4 H, three-line pattern, H-1, H-3, H-10 and H-12), 7.0–7.3 (8 H, m, Ar H); δ^* (CDCl$_3$) 1.48 (9 H, s) 1.94 (2 H, s, H-2 and H-11), 5.28 (2 H, br s, H-1 and H-12 or H-3 and H-10), 5.37 (2 H, br s, H-1 and H-12 or H-3 and H-10), 7.0–7.3 (8 H, m, Ar H).

Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.27; H, 6.63; N, 3.81.

(b) With 7-Azabenzonorbornadiene (2). A solution of **2** (486 mg, 2.0 mmol) and tetrazine **12** (236 mg, 1.0 mmol) in benzene (3 mL) was refluxed for 4 h. Evaporation and chromatography on silica gel (dichloromethane–*n*-hexane) gave adducts **10** (225

J. Org. Chem. 1980, *45*, 479-482 479

mg, 49%) and 11 (97 mg, 21%) in the order of elution.

(c) With Dimethyl 7-Oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (13). A mixture of 2 (243 mg, 1.0 mmol) and tetrazine 12 (236 mg, 1.0 mmol) in chloroform (2 mL) was stirred at 0 °C until the red color of the tetrazine had disappeared (4 h), and then the dienophile 13 (250 mg, 1.19 mmol) was added. After the mixture had refluxed for 7 h, evaporation of solvent and chromatography on silica gel (dichloromethane–*n*-hexane) gave the adduct 19 (315 mg, 74%): mp 182–184 °C; IR (KBr) 1733, 1688, 1250 cm^{-1}; NMR (CDCl$_3$) δ 1.45 (9 H, s), 3.46 (6 H, s), 5.1–5.5 (4 H, m, H-1, H-3, H-6 and H-8), 6.53 (2 H, s, H-4 and H-5), 7.12 (4 H, m, Ar H).

Anal. Calcd for $C_{23}H_{25}NO_7$: C, 64.62; H, 5.90; N, 3.28. Found: C, 64.64; H, 5.92; N, 3.21.

(d) With *N*-Phenylmaleimide (14). A mixture of 2 (243 mg, 1.0 mmol), tetrazine 12 (236 mg, 1.0 mmol), and dienophile 14 (173 mg, 1.0 mmol) in chloroform (3 mL) was stirred at room temperature for 1 day. Chromatography on silica gel (dichloromethane–*n*-hexane) followed by recrystallization from chloroform–*n*-hexane gave adduct 21 (310 mg, 79%) as colorless prisms: mp 172–174 °C; IR (KBr) 1780, 1707 cm^{-1}; NMR (CDCl$_3$) δ 1.43 (9 H, s), 3.90 (2 H, m, H-9 and H-10), 5.55 (2 H, m, H-1 and H-8), 6.38 (2 H, m, Ar H), 7.1–7.5 (7 H, m, Ar H).

Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.18. Found: C, 70.68; H, 5.75; N, 6.96.

(e) With Maleic Anhydride (15). A mixture of 2 (243 mg, 1 mmol), tetrazine 12 (236 mg, 1.0 mmol), and dienophile 15 (173 mg, 1.0 mmol) in chloroform was stirred at room temperature for 1 day. Because of its instability, adduct 22 was not isolated by chromatography. The yield was 68%, and the structure of the adduct was determined by the NMR spectrum of the crude reaction mixture: NMR (CDCl$_3$) δ 1.40 (9 H, s), 4.02 (2 H, m, H-9 and H-10), 5.48 (2 H, m, H-1 and H-8), 7.2–7.5 (4 H, m, Ar H).

(f) With *p*-Benzoquinone (16). A mixture of 2 (243 mg, 1.0 mmol), tetrazine 12 (236 mg, 1.0 mmol), and dienophile 16 (108 mg, 1.0 mmol) in chloroform (3 mL) was refluxed for 2 h. Evaporation of the solvent and chromatography on silica gel (dichloromethane-*n*-hexane) gave adduct 23 (202 mg, 62%): mp 145 °C (dichloromethane–*n*-hexane); IR (KBr) 1682, 1655 cm^{-1}; NMR (CDCl$_3$) δ 1.43 (9 H, s), 3.54 (2 H, m H-9 and H-10), 5.47 (2 H, m, H-1 and H-8), 5.99 (2 H, s, olefin H), 7.0–7.3 (4 H, m, Ar H).

Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 69.88; H, 5.65; N, 4.17.

Registry No. **1**, 573-57-9; **2**, 5176-28-3; **3a**, 539-80-0; **3b**, 533-75-5; **4a**, 72331-12-5; **4b**, 72331-13-6; **5a**, 2175-90-8; **5b**, 2175-91-9; **6a**, 72331-14-7; **6b**, 72331-15-8; **7**, 72331-16-9; **8**, 72376-88-6; **9** (R = CO$_2$Bu-*t*), 72331-17-0; **10**, 72331-18-1; **11**, 72376-89-7; **12**, 1671-87-0; **13**, 1829-60-3; **14**, 941-69-5; **15**, 108-31-6; **16**, 106-51-4; **17**, 72331-19-2; **18**, 72376-90-0; **19**, 72331-20-5; **21**, 72331-21-6; **22**, 72331-22-7; **23**, 72331-23-8; furan, 110-00-9; α-pyrone, 504-31-4.

Molecular Design by Cycloaddition Reactions. 35.[1] 1,3-Dipolar Cycloaddition Reactions of 1,4-[(*tert*-Butyloxycarbonyl)imino]-1,4-dihydronaphthalene

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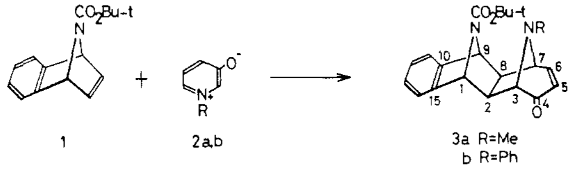
1,3-Dipolar cycloaddition of 7-azabenzonorbornadiene (1) with various dipolar compounds like 1-substituted pyridinium-3-olates (**2a**,**b**), *N*-phenylsydnone (4), nitrile oxides (**11a–e**), diazoalkanes (**13a**,**b**), azide (**15**), and nitrone (**18a**,**b**) afforded corresponding exo adducts in good yields.

1,4-[(*tert*-Butyloxycarbonyl)imino]-1,4-dihydronaphthalene (1) has been shown to have a reactivity which is similar to that of its oxa analogue in the cycloaddition reaction with cyclic polyolefins.[1] As a reasonable extension, we have investigated the 1,3-dipolar cycloaddition reaction of 1 with various dipolar compounds. Compound 1 was found to be an effective dipolarophile.

Results and Discussion

Reaction of 1 with Betaines. The reaction of 7-azabenzonorbornadiene (1) with 1-methyl- and 1-phenylpyridinium-3-olates (**2a** and **2b**)[2] under reflux in toluene for 8–10 h gave 1:1 adducts **3a** and **3b** in 70% and 40% yields, respectively (Scheme I). The structural proof was based on elemental analyses and spectroscopic data. The IR spectrum of **3a** showed a characteristic α,β-unsaturated carbonyl band at 1670 cm^{-1} and a urethane carbonyl band at 1682 cm^{-1}. The mass spectrum exhibited a parent ion peak at *m*/*e* 352 and characteristic fragment peaks at *m*/*e* 217 (6%, $C_{13}H_{15}NO_2$, isoindole) and 135 (100%, C_8H_9NO, cycloreversion). The NMR spectrum at room temperature exhibited signals of aromatic protons at δ 6.9–7.3 (4 H, m), vinyl protons at δ 6.93 (1 H, m; H-6) and 5.82 (1 H, dd, *J* = 10.0 and 1.5 Hz; H-5), nitrogen-bridgehead protons at δ 5.26 (2 H, m; H-1 and H-9) and 3.6–4.0 (2 H, m; H-3 and H-7), methine protons at δ 2.28 (1 H, d, *J* = 7.0 Hz; H-8) and 2.06 (1 H, d, *J* = 7.0 Hz; H-2), *N*-methyl protons at δ 2.41 (3 H, s), and *tert*-butyl protons at δ 1.45 (9 H, s). While the nitrogen-bridgehead protons appeared as ambiguous multiplets probably because of the restricted N inversion or the hindered N–C bond rotation,[3] the NMR

Scheme I



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[1] Part 34 of this series: T. Sasaki, T. Manabe, and S. Nishida, *J. Org. Chem.*, preceding paper in this issue.

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