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_2Bu-*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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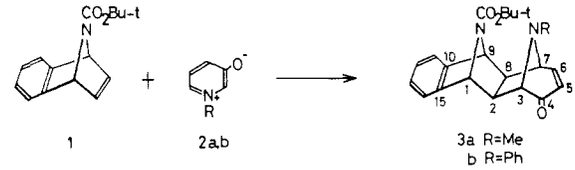
1,3-Dipolar cycloaddition of 7-azabenzonorbornadiene (**1**) with various dipolar compounds like 1-substituted pyridinium-3-olates (**2a,b**), *N*-phenylsydnone (**4**), nitrile oxides (**11a–e**), diazoalkanes (**13a,b**), azide (**15**), and nitrone (**18a,b**) afforded corresponding exo adducts in 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



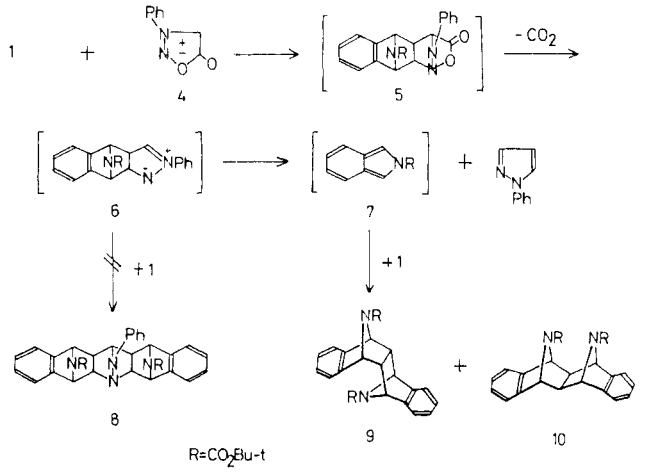
1 2a,b 3a R=Me b R=Ph

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

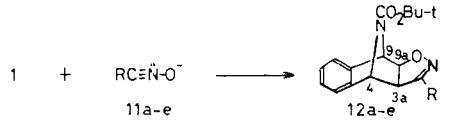
(2) (a) A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc. C*, 874 (1971); (b) N. Dennis, A. R. Katritzky, T. Matsuo, and S. K. Patron, *J. Chem. Soc., Perkin Trans. 1*, 746 (1974).

0022-3263/80/1945-0479$01.00/0

Scheme II



Scheme III



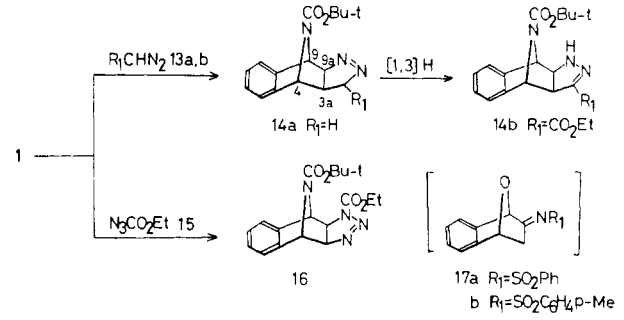
	R	yield, %
a	C_6H_5CO	45
b	C_6H_5	100
c	p-ClC_6H_4	100
d	p-$CO_2MeC_6H_4$	72
e	p-$NO_2C_6H_4$	40

spectrum at 60 °C showed sharp signals at δ 3.68 (1 H, s; H-3), 3.90 (1 H, d, J = 4.6 Hz; H-7), and 5.24 (2 H, s; H-1 and H-9). The absence of vicinal couplings between H-1 and H-2 and between H-8 and H-9 indicated the methine protons (H-2 and H-8) to be endo to the azabenzonorbornadiene system. Furthermore, the absence of vicinal couplings between H-2 and H-3 and between H-7 and H-8, confirmed by double resonance experiments, suggested H-2 and H-8 to be also endo to the bicyclo[3.2.1]octanone system. Thus, the adduct was assigned as the exo,exo cycloadduct **3a**. The product **3b** was similarly confirmed to be the exo,exo adduct.

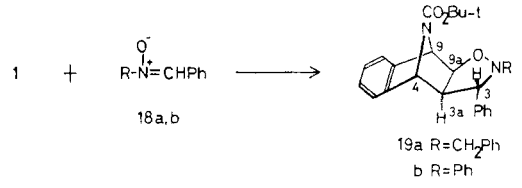
The reaction of compound **1** with N-phenylsydnone **4**[4] under similar conditions gave a mixture of two products, **9** and **10**, in 50% and 13% yields, respectively (Scheme II). These products were identical with authentic samples which were obtained from the reaction of **1** with α-pyrone.[1] The formation of **9** and **10** can be explained by a series of reactions as depicted in Scheme II. The successive loss of carbon dioxide and 1-phenylpyrazole from the initial cycloadduct **5** affords isoindole **7** which in turn reacts with **1** to give **9** and **10**. No formation of **8** suggests the rapid decomposition of **6** to the isoindole **7**.

Reactions of 1 with Nitrile Oxides.[5] The reactions of compound **1** with nitrile oxides **11a–e** prepared in situ from the corresponding hydroximic acid chlorides in ether at ambient temperature gave adducts **12a–e** in 40–100% yields. The results are summarized in Scheme III. Elemental analyses and mass spectra showed products **12a–e** to be 1:1 cycloadducts. In NMR spectra (Table I), the absence of vicinal couplings ($J_{3a,4}$ and $J_{9,9a}$) indicated the exo configuration of these adducts.

Scheme IV



Scheme V



Reactions of 1 with Diazoalkanes and Azides. The reactions of compound **1** with diazomethane (**13a**), ethyl diazoacetate (**13b**), and ethyl azidoformate (**15**) in ether or benzene at room temperature gave 1:1 adducts **14a**, **14b**, and **16** in 90%, 42%, and 63% yields, respectively (Scheme IV). The structural assignment of these adducts was made on the basis of their NMR spectra (Table I). Product **14b** was considered to be formed by a 1,3-H shift of the initial 1,3-dipolar cycloadduct. Such an isomerization of Δ^1-pyrazoline to Δ^2-pyrazoline is known.[6]

The similar reaction of benzenesulfonyl azide and tosyl azide with compound **1** gave rise to a complex mixture, from which no products could be characterized. In contrast, 7-oxabenzonorbornadiene is known to react with these reagents to give imines **17a** and **17b** in good yields.[7]

Reactions of 1 with Nitrones. The reaction of compound **1** with C-phenyl-N-benzylnitrone (**18a**) and C,N-diphenylnitrone (**18b**) under reflux in toluene for 8–9 h gave 1:1 adducts **19a** and **19b** in 65% and 75% yields, respectively (Scheme V). The NMR spectrum of adduct **19a** exhibited signals at δ 7.0–7.5 (14 H, m; ArH), 5.14 (2 H, s; H-4 and H-9), 4.35 (1 H, d, J = 6.5 Hz; H-9a), 3.74 (3 H, m; benzyl H_2 and H-3), 2.71 (1 H, t, J = 6.8 and 6.5 Hz; H-3a), and 1.48 (9 H, s; t-Bu). The absence of couplings between nitrogen-bridgehead protons and methine protons ($J_{3a,4} = J_{9a,9} = 0$) indicated the exo configuration. The stereochemistry at C-3 was determined by the coupling constant ($J_{3,3a}$ = 6.8 Hz), which suggested the trans geometry of H-3 and H-3a.[8] The exclusive formation of this stereoisomer was apparently due to the steric hindrance of the bulky substituted nitrogen bridge of **1**. The NMR spectrum of adduct **19b** indicated that it was the exo adduct bearing an endo phenyl group at C-3.

The above results show that 7-azabenzonorbornadiene (**1**) is an effective dipolarophile. It is noteworthy that the electron-rich olefin **1** reacts even with the electron-rich dipolar compounds, as exemplified by the adduct forma-

(3) W. J. Delonghry and I. O. Sutherland, *Chem. Commun.*, 1104 (1971).
(4) J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935).
(5) P. S. Anderson, M. E. Christy, E. L. Engelhardt, G. F. Lundell, and G. S. Ponticello, *J. Heterocycl. Chem.*, **14**, 213 (1977).
(6) E. Büchner and A. Papendieck, *Justus Liebigs Ann. Chem.*, **273**, 232 (1893).
(7) T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Uchide, *J. Chem. Soc., Perkin Trans. 1*, 2750 (1972).
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Table I. NMR Spectra of Cycloadducts (δ, $CDCl_3$, Hz)

compd	H-3a	H-9a	H-4	H-9	*t*-Bu	ArH and other protons
12a	3.96 (d, J = 7.5)	4.98 (d)	5.50 (s)		1.30 (s)	7.0–7.7 (7 H, m), 8.10–8.35 (2 H, m)
12b	3.94 (d, J = 7.6)	5.03 (d)	5.43 (s)	5.50 (s)	1.27 (s)	7.0–7.8 (9 H, m)
12c	3.90 (d, J = 7.8)	5.03 (d)	5.38 (s)	5.49 (s)	1.29 (s)	7.0–7.8 (8 H, m)
12d	3.93 (d, J = 7.5)	5.04 (d)	5.37 (s)	5.59 (s)	1.28 (s)	7.0–7.5 (4 H, m), 7.77 (2 H, d, J = 8.2), 8.08 (2 H, d), 3.94 (s; Me)
12e	3.96 (d, J = 7.8)	5.12 (d)	5.40 (s)	5.52 (s)	1.31 (s)	7.0–7.3 (4 H, m), 7.92 (2 H, d, J = 8.0), 8.34 (2 H, d)
14a	2.21 (m)	5.00 (br d, J = 7.4)	4.87 (s)	5.55 (s)	1.29 (s)	7.0–7.5 (4 H, m), 4.45 (2 H, dd, J = 6.6 and 2.2; H-3)
14b	3.60 (d, J = 9.0)	4.27 (d)	5.48 (s)		1.41 (s)	7.0–7.5 (4 H, m), 7.63[a] (1 H, br s; NH)
16	4.04 (d, J = 8.0)	4.97 (d)	5.47 (s)	5.60 (s)	1.35 (s)	7.0–7.6 (4 H, m), 4.45 (2 H, q, J = 7.0; CH_2CH_3), 1.44 (3 H, t, J = 7.0; CH_2CH_3)

[a] Exchangeable by D_2O.

tion in the reaction with betaine **2a**, which is reported to react only with olefins containing a strongly electron-withdrawing group.[9]

Experimental Section[10]

Reactions of 7-Azabenzonorbornadiene (1) with Betaines 2a, 2b, and 4. (a) With 1-Methylpyridinium-3-olate (2a). A solution of **1** (243 mg, 1 mmol) and 1-methylpyridinium-3-olate (**2a**) (120 mg, 1.1 mmol) in toluene (3 mL) was refluxed for 8 h. After evaporation to dryness, chromatography on silica gel (benzene–chloroform) followed by recrystallization from benzene gave adduct **3a** (245 mg, 70%) as yellow prisms: mp 228–230 °C; IR (KBr) 1682, 1670 cm^{-1}; NMR ($CDCl_3$) δ 1.45 (9 H, s), 2.06 (1 H, d, J = 7.5 Hz; H-2), 2.28 (1 H, d, J = 7.5 Hz; H-8), 2.41 (3 H, s; NMe), 3.6–4.0 (2 H, m; H-3 and H-7), 5.26 (2 H, m; H-1 and H-9), 5.82 (1 H, dd, J = 10.0 and 1.5 Hz; H-5), 6.93 (1 H, m; H-6), 6.9–7.3 (4 H, m; ArH); δ* ($CDCl_3$) 1.45 (9 H, s), 2.09 (1 H, d, J = 7.5 Hz; H-2), 2.30 (1 H, d, J = 7.5 Hz; H-8), 2.43 (3 H, s; NMe), 3.68 (1 H, s; H-3), 3.90 (1 H, d, J = 4.6 Hz; H-7), 5.24 (2 H, s; H-1 and H-9), 5.86 (1 H, dd, J = 10.0 and 1.5 Hz; H-5), 6.91 (1 H, dd, J = 10.0 and 4.6 Hz; H-6), 6.95–7.3 (4 H, m; ArH); mass spectrum, m/e 352 (M^+, 9%), 217 (6), 161 (53), 135 (100), 117 (46), 107 (65), 91 (8).

Anal. Calcd for $C_{21}H_{24}N_2O_3$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.27; H, 6.86; N, 7.84.

(b) With 1-Phenylpyridinium-3-olate (2b). Similar treatment of **1** (243 mg, 1 mmol) and 1-phenylpyridinium-3-olate (**2b**) (180 mg, 1.1 mmol) gave adduct **3b** (170 mg, 40%) as yellow prisms: mp 205–207 °C (benzene); IR (KBr) 1680, 1670 cm^{-1}; NMR ($CDCl_3$) δ 1.03 (9 H, s), 2.28 (1 H, d, J = 7.0 Hz; H-2), 2.46 (1 H, d, J = 7.0 Hz; H-8), 4.5–5.0 (2 H, m; H-3 and H-7), 5.2–5.5 (2 H, m; H-1 and H-9), 5.75 (1 H, dd, J = 9.8 and 1.6 Hz; H-5), 6.6–7.5 (10 H, m; H-6 and ArH); mass spectrum, m/e 414 (M^+, 20%), 217 (4), 197 (46), 161 (63), 117 (80), 91 (100).

Anal. Calcd for $C_{26}H_{26}N_2O_3$: C, 75.34; H, 6.32; N, 6.76. Found: C, 75.23; H, 6.50; N, 6.69.

(c) With *N*-Phenylsydnone 4. A solution of **1** (490 mg, 2.02 mmol) and *N*-phenylsydnone **4** (324 mg, 2 mmol) was refluxed for 23 h. Chromatography on silica gel (dichloromethane–*n*-hexane) gave adducts **9** (230 mg, 50%) and **10** (60 mg, 13%) in the order of elution.

Reactions of 7-Azabenzonorbornadiene (1) with Nitrile Oxides 11a–e. General Procedure. Nitrile oxides prepared in situ from the corresponding hydroximic acid chlorides (1 mmol) and triethylamine (1 mmol) in dry ether (4 mL) were treated with **1** (1 mmol) in dry ether (4 mL) at room temperature. The mixture was filtered to remove triethylamine hydrochloride and concentrated in vacuo to give 1:1 adducts (**12a–e**).

(a) Adduct 12a (176 mg, 45%): mp 134–136 °C (dichloromethane–*n*-hexane); IR (KBr) 1680, 1633 cm^{-1}.

Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.14. Found: C, 70.85; H, 5.98; N, 7.24.

(b) Adduct 12b (362 mg, 100%): mp 173–174 °C; IR (KBr) 1670 cm^{-1}; mass spectrum, m/e 217 (M^+ – 145, 100%), 161 (81), 145 (97), 117 (94).

Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 72.89; H, 6.22; N, 7.67.

(c) Adduct 12c (396 mg, 100%): mp 165–166 °C; IR (KBr) 1678 cm^{-1}.

Anal. Calcd for $C_{22}H_{21}N_2O_3Cl$: C, 66.58; H, 5.33; N, 7.06. Found: C, 66.52; H, 5.33; N, 7.12.

(d) Adduct 12d (302 mg, 72%): mp 150–152 °C; IR (KBr) 1717, 1682 cm^{-1}; mass spectrum, m/e 217 (M^+ – 203, 29%), 203 (77), 172 (69), 161 (64), 117 (89), 57 (100).

Anal. Calcd for $C_{24}H_{24}N_2O_5$: C, 68.56; H, 5.75; N, 6.66. Found: C, 68.65; H, 5.98; N, 6.36.

(e) Adduct 12e (163 mg, 40%): mp 167–168 °C; IR (KBr) 1672 cm^{-1}.

Anal. Calcd for $C_{22}H_{21}N_3O_5$: C, 64.86; H, 5.20; N, 10.31. Found: C, 64.89; H, 5.40; N, 10.08.

Reactions of 7-Azabenzonorbornadiene (1) with Diazoalkanes and Azide. (a) With Diazomethane (13a). A solution of **1** (100 mg, 0.41 mmol) and excess diazomethane in ether (10 mL) was stirred for 2 days at room temperature. Evaporation to dryness and recrystallization from dichloromethane–*n*-hexane gave adduct **14a** (127 mg, 90%) as colorless crystals: mp 118–120 °C; IR (KBr) 1687, 1552 cm^{-1}.

Anal. Calcd for $C_{16}H_{19}N_3O_2$: C, 67.34; H, 6.71; N, 14.73. Found: C, 67.09; H, 6.58; N, 14.81.

(b) With Ethyl Diazoacetate (13b). A solution of **1** (243 mg, 1 mmol) and ethyl diazoacetate (**13b**) (120 mg, 1.05 mmol) in benzene (2 mL) was stirred for 1 day at room temperature. Similar workup gave adduct **14b** (150 mg, 42%): mp 112–114 °C (dichloromethane–*n*-hexane); IR (KBr) 1708, 1665, 1552 cm^{-1}.

Anal. Calcd for $C_{19}H_{23}N_3O_4$: C, 63.85; H, 6.48; N, 11.76. Found: C, 64.12; H, 6.38; N, 11.59.

(c) With Ethyl Azidoformate (15). A solution of **1** (243 mg, 1.0 mmol) and ethyl azidoformate (**15**) (120 mg, 1.04 mmol) in benzene (2 mL) was stirred for 2 days at room temperature. Workup as before gave adduct **16** (207 mg, 63%) as colorless crystals: mp 109–111 °C (chloroform–*n*-hexane); IR (KBr) 1748, 1696, 1520 cm^{-1}.

Anal. Calcd for $C_{18}H_{22}N_2O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.25; H, 5.89; N, 15.75.

Reactions of 7-Azabenzonorbornadiene (1) with Nitrones 18a,b. (a) With *C*-Phenyl-*N*-benzylnitrone (18a). A solution of **1** (243 mg, 1 mmol) and *C*-phenyl-*N*-benzylnitrone (**18a**) (230 mg, 1.09 mmol) in toluene (3 mL) was refluxed for 8 h. After evaporation to dryness, chromatography on silica gel (dichloromethane–*n*-hexane) followed by recrystallization from chloroform–*n*-hexane gave adduct **19a** (290 mg, 65%) as colorless crystals: mp 153–154 °C; IR (KBr) 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.48 (9 H, s), 2.71 (1 H, t, J = 6.8 and 6.5 Hz; H-3a), 3.74 (3 H, m; CH_2-Ph and H-3), 4.35 (1 H, d, J = 6.5 Hz; H-9a), 5.14 (2 H, s; H-4 and H-9), 7.0–7.5 (14 H, m; ArH); mass spectrum, m/e 454

(9) N. Dennis, A. R. Katritzky, and Y. Takeuchi, *Angew. Chem., Int. Ed. Engl.*, **15**, 1 (1976).
(10) See Experimental Section of ref 1.

(M^+, 100%), 217 (14), 161 (60), 117 (75).

Anal. Calcd for $C_{29}H_{30}N_2O_3$: C, 76.63; H, 6.65; N, 6.16. Found: C, 76.87; H, 6.58; N, 5.99.

(b) With *C,N*-Diphenylnitrone (18b). A solution of 1 (243 mg, 1.0 mmol) and *C,N*-diphenylnitrone (**18b**) (200 mg, 1.02 mmol) in toluene (2 mL) was refluxed for 9 h. Similar workup gave the adduct **19b** (320 mg, 72%): mp 160–162 °C (dichloromethane–*n*-hexane); IR (KBr) 1682 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (9 H, s), 2.87 (1 H, t, J = 6.6 Hz; H-3a), 4.27 (1 H, br s; H-3), 4.59 (1 H, d, J = 6.6 Hz; H-9a), 5.25 (2 H, s; H-1 and H-7), 7.0–7.5 (14 H, m; ArH).

Anal. Calcd for $C_{28}H_{28}N_2O_3$: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.38; H, 6.70; N, 6.16.

Cyclizations and Rearrangements of Propynylsulfamides: X-ray Crystal Structure of 2,3-Dihydro-2-acetyl-3,3-dimethyl-4-[(1*E*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-Dioxide

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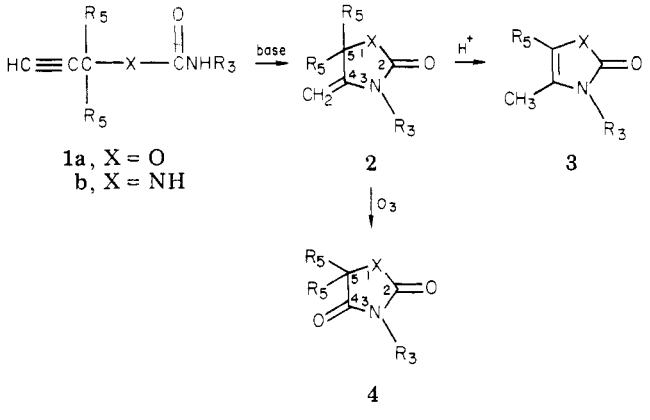
The base-catalyzed cyclization of 2-propynylsulfamides and the subsequent amino-Claisen rearrangement of one of these products are described. The X-ray structure of 2,3-dihydro-2-acetyl-3,3-dimethyl-4-[(1*E*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-dioxide has been determined.

Base-catalyzed cyclizations of 2-propynyl carbamates (**1a**) and 2-propynylureas (**1b**) produce five-membered rings (**2a,b**) with exocyclic double bonds. Acid-catalyzed



1a, X = O
b, X = NH

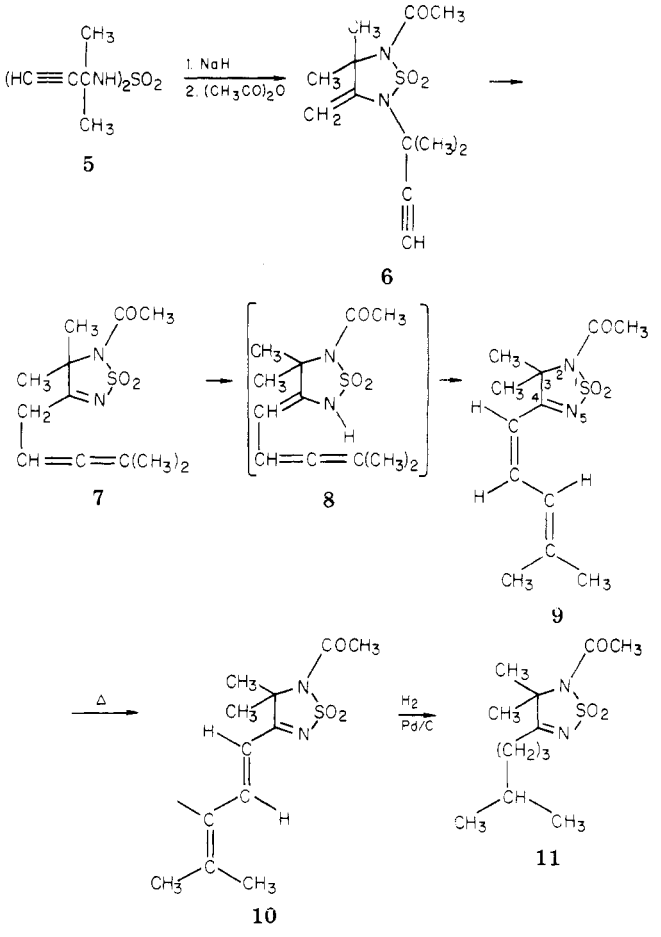
2 3

4

tautomerization to the endocyclic isomer **3** can occur if one or both groups at the 5-position are hydrogen.[2,3] Recently we reported the isolation of 5,5-disubstituted imidazolidinones (**2b**) and oxazolidines (**2a**)[4] where isomerization is blocked. Ozonolysis of these derivatives gave 2,4-imidazolidinediones (**4b**) and 2,4-oxazolidinediones (**4a**). These compounds are medicinally useful as anticonvulsants,[5,6] and this method appears to be the best way of introducing tertiary alkyl (hydrophobic) groups into the 3-position of the ring **4**.

This report deals with the similar cyclization of *N,N'*-bis(1,1-dimethyl-2-propynyl)sulfamide, the subsequent rearrangement of the cyclized product, **6**, and the X-ray structure determination of the final rearranged product, **10**.

Treatment of sulfamide **5** with sodium hydride and acetic anhydride, depending on the reaction conditions, led to the isolation of three products: 2-acetyl-3,3-dimethyl-4-methylene-5-(1,1-dimethyl-2-propynyl)-1,2,5-thiadiazolidine 1,1-dioxide (**6**), 2,3-dihydro-2-acetyl-3,3-



5 6 7 8 9 10 11

dimethyl-4-[(1*Z*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadia-

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