209 (M^+, 20), 167 (2), 153 (3), 137 (3), 133 (5), 109 (6), 82 (25), 67 (base); CIMS (2-methylpropane), m/e 210 ($M^+ + H$, 17); HRMS, m/e 209.0943 ($C_{13}H_{11}N_3$ requires 209.0953).

2-Methyl-3-pentylprodigiosene (Desmethoxyprodigiosin, 2e). 2-Methyl-3-pentylpyrrole (4.4 mg, 0.029 mmol) was added to a solution of the aldehyde **21b** (4.7 mg, 0.029 mmol) in methanol (0.5 mL) at 25 °C, and the solution was warmed at 100 °C for 5 min. While still warm, concentrated hydrobromic acid (three drops) was added to the solution, and the reaction mixture was allowed to stand for 30 min (25 °C). The reaction mixture was concentrated in vacuo. Chromatography (neutral alumina, activity grade III, 2 cm × 10 cm, ether eluant) afforded **2e** as the free base. 2-Methyl-3-pentylprodigiosene (**2e**) in $CHCl_3$ was immediately converted to the HBr salt ($CHCl_3$ soluble) by treatment with 48% aqueous HBr to afford **2e**·HBr (4.8 mg, 10.8 mg theoretical, 44%) as a purple solid: ^1H NMR ($CDCl_3$, 200 MHz, ppm) 7.6 (m, 1 H), 7.15 (m, 1 H), 6.96 (m, 1 H), 6.88 (s, 1 H), 6.8 (m, 1 H), 6.58 (m, 1 H), 6.27 (m, 1 H), 2.62 (s, 3 H), 2.40 (t, 2 H, J = 7 Hz), 1.64 (m, 2 H), 1.35 (m, 4 H), 0.92 (t, 3, H, J = 7 Hz) [accompanied by the free base (or E isomer) [2.76 (t, 2H, J = 7 Hz), 2.56 (s, 3 H), 1.58 (m, 2 H), 0.90 (t, 3 H, J = 7 Hz)]: IR (KBr) ν_{max} 3745, 3451, 2925, 1635, 1602, 1561, 1510, 1278, 1129, 1059, 962, 789, 717 cm^{-1}; UV (95% EtOH, HCl) λ_{max} 568 nm;[1b] EIMS, m/e (relative intensity), 293 (M^+, 60), 237 (18), 236 (base), 193 (5), 151 (8), 108 (4), 94 (54), 80 (8); CIMS (2-methylpropane), m/e 294 ($M^+ + H$, 44); HRMS, m/e 293.1900 ($C_{19}H_{23}N_3$ requires 293.1892).

Acknowledgment. The financial support of the National Institutes of Health (CA 42056, RCDA CA 01134), the Searle Scholars Program, and the Alfred P. Sloan Foundation is gratefully acknowledged. We thank Professor P. L. Fuchs for suggesting the use of polymer bound palladium(II) acetate for 2,2′-bipyrrole formation, Dan Severance for conducting the computational studies, and Professors H. H. Wasserman and A. J. Castro and Imperial Chemical Industries for providing generous comparative samples of authentic, natural prodigiosin hydrochloride and prodigiosin, respectively. We gratefully acknowledge the use of software [CHEMLAB-II (Version 9.0)] developed and distributed by Molecular Design, Ltd.

Registry No. 1, 82-89-3; 1·HCl, 112373-40-7; **2a**, 22187-69-5; **2a**·HBr, 22187-70-8; **2e**, 112373-41-8; **2e**·HBr, 22187-75-3; **7**, 2166-14-5; **8**, 92144-07-5; **9**, 92144-13-3; **10**, 112373-15-6; **11**, 112373-16-7; **12a**, 112373-17-8; **12b**, 1193-62-0; **13a**, 21972-99-6; **13b**, 107962-24-3; **13c**, 92776-70-0; **14a**, 112373-18-9; **14b**, 107962-26-5; **14c**, 107962-25-4; **15a**, 112373-19-0; **15b**, 112373-20-3; **16a**, 112373-21-4; **16b**, 112373-22-5; **16c**, 112373-23-6; **16d**, 112373-24-7; **16e**, 23900-45-0; **16f**, 112373-25-8; **16g**, 112373-27-0; **16h**, 112373-28-1; **16i**, 112373-29-2; **16j**, 112373-30-5; **17c**, 112373-33-8; **17e**, 112373-31-6; **17f**, 112373-34-9; **17h**, 112373-35-0; **18a**, 112373-32-7; **18b**, 112373-42-9; **18c**, 112373-43-0; **20a**, 112373-36-1; **20a** (hydrazide), 112373-37-2; **20a** ((*p*-toluenesulfonyl)hydrazide), 112373-38-3; **20b**, 106480-92-6; **20b** (hydrazide), 112373-44-1; **20b** ((*p*-toluenesulfonyl)hydrazide), 112373-39-4; **21a**, 10476-41-2; **21b**, 22187-87-7; $CH_2{=}C(OCH_3)_2$, 922-69-0; $CH_3(CH_2)_3CH(OH)C{\equiv}CH$, 7383-19-9; $CH_3(CH_2)_3C(O)C{\equiv}CH$, 26119-02-8; $HOCH_2CH_2C{\equiv}CH$, 927-74-2; *t*-$BuSi(Me)_2O(CH_2)_2C{\equiv}CH$, 78592-82-2; $HOCH_2(CH_2)_2C{\equiv}CH$, 5390-04-5; *t*-$BuSi(Me)_2OCH_2C{\equiv}CEt$, 112373-26-9; $HOCH_2C{\equiv}CEt$, 6261-22-9; $PhCH_2O(CH_2)_2C{\equiv}CH$, 22273-77-4; $HO(CH_2)_3CH{=}CH_2$, 821-09-0; 2-methyl-3-pentylpyrrole, 18320-91-7; pyrrole, 109-97-7; 5-(ethoxycarbonyl)-2-methyl-3-valeroylpyrrole, 92198-32-8.

Supplementary Material Available: Summary Table and summary figure of the INDO and AMPAC, AM1, treatment of prodigiosin and 2-methyl-3-pentylprodigiosene (2 pages). Ordering information is given on any current masthead page. Optimized MM2 (MacroModel, version 1.1) geometries and total energy for linear, nonlinear (*E*/*Z*)-**1**, -**2a**, and -**2e** (4 pages), and the final results (bond lengths, bond angles, cartesian coordinates, interatomic distances, eigenvectors, net atomic charges and dipole contributions, atomic orbital electron populations, state energies, and C.I.) of the AMPAC, AM1 (version 1.0) optimization/SCF calculation for prodigiosin (**1**) and 2-methyl-3-pentylprodigiosene (**2e**) are available from D.L.B. upon request.

Inverse Electron Demand Diels–Alder Reactions of 3,6-Bis(methylthio)-1,2,4,5-tetrazine: 1,2-Diazine Introduction and Direct Implementation of a Divergent 1,2,4,5-Tetrazine → 1,2-Diazine → Benzene (Indoline/Indole) Diels–Alder Strategy†

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Received September 15, 1987

A full investigation of the scope of the participation of 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**) in [4 + 2] cycloaddition reactions is detailed. The use of the resulting 3,6-bis(methylthio)-1,2-diazine cycloadducts as direct precursors to the parent 4,5-substituted-1,2-diazines as well as alkyne/allene 1,2-diazines suitable for use in subsequent intramolecular Diels–Alder reactions is described. The latter application constitutes the direct implementation of a divergent 1,2,4,5-tetrazine → 1,2-diazine → benzene (indoline/indole) Diels–Alder strategy.

In recent efforts we have detailed the use of a series of inverse electron demand Diels–Alder reactions of electron-deficient heterocyclic azadienes[2–11] in [4 + 2] cycloaddition reactions with electron-rich dienophiles comprising a general approach to the introduction of a range of heteroaromatic systems, Scheme I. The approach has been proven to be well-suited for the preparation of highly substituted and highly functionalized heteroaromatic systems difficult to assemble by alternative methodology

† This paper is dedicated to Professor E. C. Taylor on the occasion of his 65th birthday.

(1) National Institutes of Health research career development award recipient, 1983–88 (CA 01134). Alfred P. Sloan research fellow, 1985–89.
(2) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. Boger, D. L. *Chem. Rev.* **1986**, *86*, 781.
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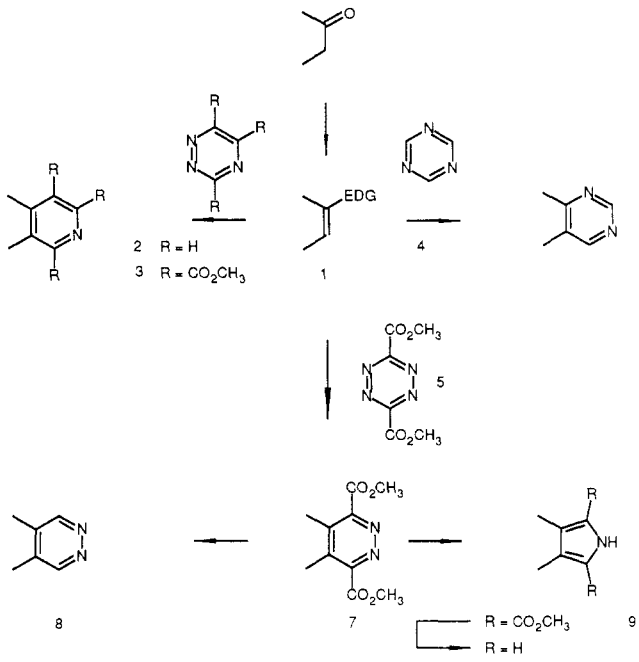
(4) Boger, D. L.; Panek, J. S. *J. Org. Chem.* **1982**, *47*, 3763. Boger, D. L.; Panek, J. S. *Tetrahedron Lett.* **1984**, *25*, 3175. Boger, D. L.; Duff, S. R.; Panek, J. S.; Yasuda, M. *J. Org. Chem.* **1985**, *50*, 5782.

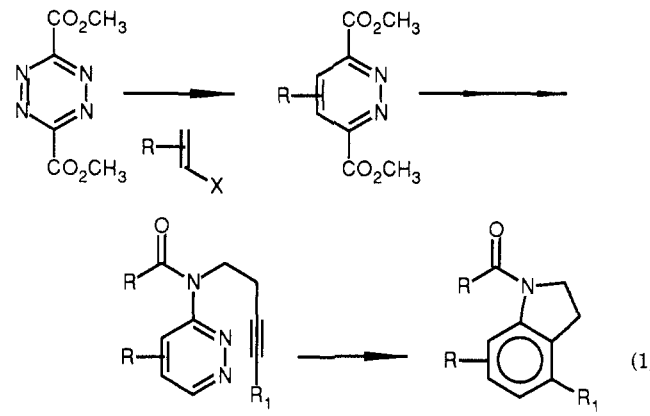
0022-3263/88/1953-1415$01.50/0

Scheme I

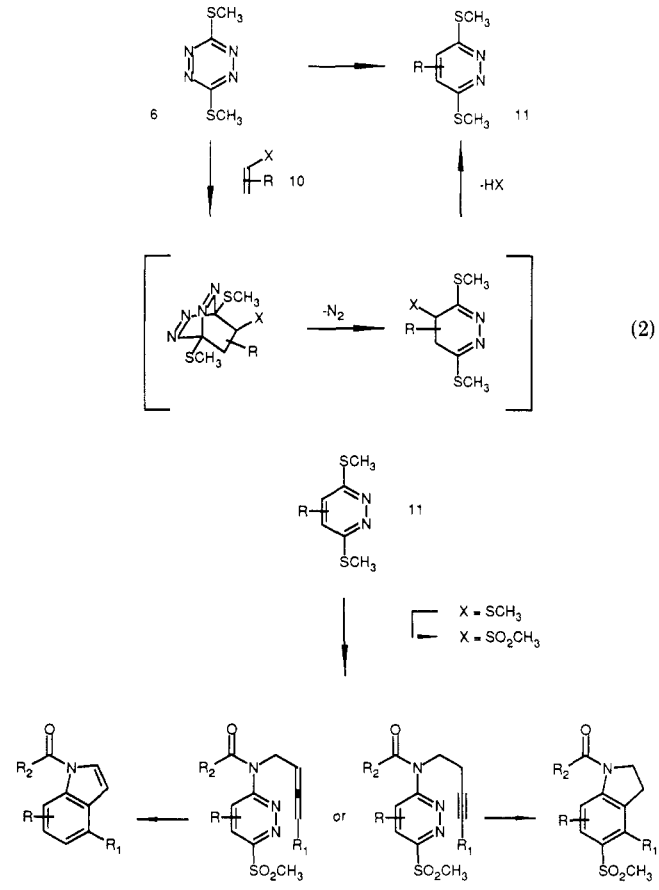


and has found application in the total syntheses of a range of naturally occurring materials.[5,8-11] The ability for unactivated 1,2-diazines to participate in selected intramolecular Diels–Alder reactions[12] and the demonstrated ability to employ the initial 1,2-diazine [4 + 2] cycloadducts derived from dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (**5**) as suitable, though indirect, precursors to the alkyne 1,2-diazines comprises a general 1,2,4,5-tetrazine → 1,2-diazine → indoline (benzene) Diels–Alder strategy, eq 1.[9]

In a continued exploration of the inverse electron demand Diels–Alder reactions of heterocyclic azadienes and in efforts to extend the 1,2,4,5-tetrazine → 1,2-diazine → benzene (indoline) Diels–Alder strategy to the total synthesis of the left-hand segment of CC-1065, the preparation and use of alternative 3,6-disubstituted 1,2,4,5-tetrazines has been under investigation. Herein, we detail our efforts on the investigation of the inverse electron demand Diels–Alder reactions of 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**) with electron-rich, neutral, conjugated, and electron-deficient dienophiles, which defines its potential for participation in [4 + 2] cycloaddition reactions, eq 2. The



(1)



(2)

use of the resulting 3,6-bis(methylthio)-1,2-diazine cycloadducts as immediate precursors to the parent 4,5-disubstituted 1,2-diazines and as *direct* precursors to alkyne/allene 1,2-diazines suitable for use in subsequent, divergent intramolecular Diels–Alder reactions for the controlled preparation of indolines/indoles is detailed.

[4 + 2] Cycloaddition Reactions of 3,6-Bis(methylthio)-1,2,4,5-tetrazine. Electron-rich alkynes (ynamines) and alkenes (enamines, ketene acetals, alkyl- and trimethylsilyl enol ethers, enol acetates, enamides) participate in well-defined inverse electron demand Diels–Alder reactions with 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**) providing the 1,2-diazine Diels–Alder products, Table I. A predictable order of reactivity was observed: ynamines (entry 1; 25 °C) > enamines (entries 2, 3, 6, 7; 25–60 °C) > ketene acetals (entry 8; 45–100 °C) > enamides (entry 9; 80–100 °C) > trimethylsilyl or alkyl enol ethers (entries 4, 5, 10; 100–140 °C) > enol acetates (entry 11; 130–140

(5) Lavendamycin methyl ester: Boger, D. L.; Duff, S. R.; Panek, J. S.; Yasuda, M. *J. Org. Chem.* **1985**, *50*, 5790.

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(8) Streptonigrin: Boger, D. L.; Panek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5745. Boger, D. L.; Panek, J. S. *J. Org. Chem.* **1983**, *48*, 621.

(9) PDE-II methyl ester: Boger, D. L.; Coleman, R. S. *J. Org. Chem.* **1986**, *51*, 3250. PDE-I, PDE-II, and PDE-I dimer methyl ester: Boger, D. L.; Coleman, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 2717.

(10) Prodigiosin: Boger, D. L.; Patel, M. *Tetrahedron Lett.* **1987**, *28*, 2499. Boger, D. L.; Patel, M. *J. Org. Chem.*, preceding paper in this issue.

(11) Octamethylporphyrin: Boger, D. L.; Coleman, R. S.; Panek, J. S.; Yohannes, D. *J. Org. Chem.* **1984**, *49*, 4405.

(12) Alkyne 1,2-diazines: Boger, D. L.; Coleman, R. S. *J. Org. Chem.* **1984**, *49*, 2240. Boger, D. L.; Coleman, R. S.; Invergo, B. J. *J. Org. Chem.* **1987**, *52*, 1521. Alkene 1,2-diazines: Jojima, T.; Takeshiba, H.; Konotsune, T. *Chem. Pharm. Bull.* **1972**, *20*, 2191; **1976**, *24*, 1581, 1588; **1980**, *28*, 198. Alkyne 1,2,4-triazines and alkyne 1,2,4,5-tetrazines: Taylor, E. C.; Macor, J. E. *J. Org. Chem.* **1987**, *52*, 4280. Taylor, E. C.; Pont, J. L. *J. Org. Chem.* **1987**, *52*, 4287.

(13) (a) Strube, R. E. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 967. (b) Sandström, J. *Acta Chem. Scand.* **1961**, *15*, 1575.

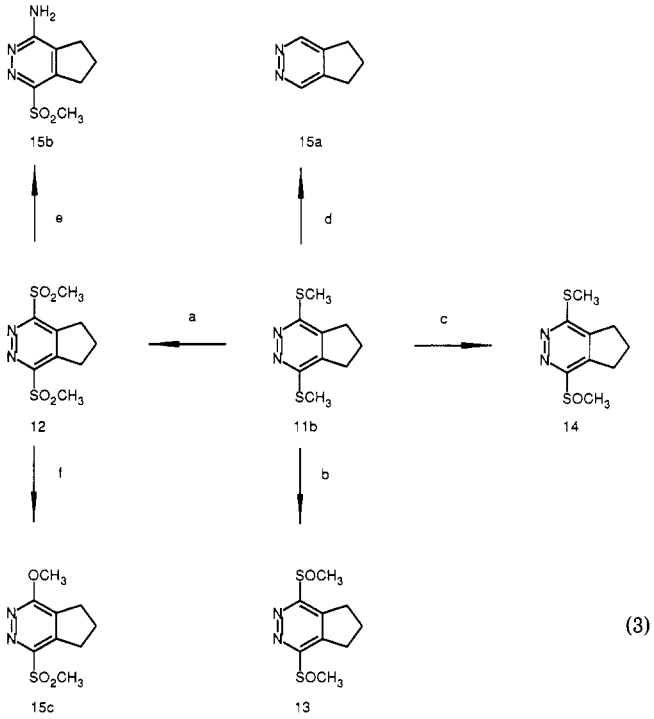
°C); which correlates well with the expected, nucleophilic character of the alkene/alkyne dienophile. The [4 + 2] cycloaddition reaction of ynamines and enamines with 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**) proceeds at room temperature and is accompanied by the immediate evolution of nitrogen (ynamines > enamines). In the case of enamines, the slow step of the reaction process is the final aromatization step involving the loss of the secondary amine from the intermediate dihydro-1,2-diazine and accounts for the reaction times and temperatures detailed in Table I.[14] Consequently, the conditions detailed in Table I for the [4 + 2] cycloaddition reactions of enamines with **6** are not representative of the initial, rapid inverse electron demand Diels–Alder reaction. In the instances when the [4 + 2] cycloaddition reaction of a thermally sensitive electron-rich dienophile with **6** was slow under conventional thermal reaction conditions, the use of pressure-promoted Diels–Alder conditions (13 kbar, 25 °C)[16] was found suitable for providing the 1,2-diazine Diels–Alder cycloadducts under conditions ensuring the stability of the dienophile, cf. Table I, entry 5.

Like the observed [4 + 2] cycloaddition reactions of dimethyl 1,2,4,5-tetrazine (**5**),[7] no evidence could be secured that would suggest that the reaction of nucleophilic olefins with 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**) proceeds by a stepwise, addition–cyclization reaction. Simple addition products derived from the interception of intermediates generated by initial nucleophilic addition of the electron-rich alkynes and olefins with **6** followed by the subsequent elimination of methyl mercaptide were not observed.[17]

Selected, conjugated and neutral alkynes (Table I, entries 12 and 13, 140–170 °C) and one example of a representative strained olefin (Table I, entry 15) were examined and found to participate in satisfactory, albeit sluggish, Diels–Alder reactions with **6**. Ethoxyacetylene, diphenylacetylene (Table I, entry 18), and electron-deficient dienophiles including methyl propiolate (Table I, entry 14), methyl phenylpropiolate (Table I, entry 17), and *p*-naphthoquinone showed modest signs of reaction or failed to react with **6** under thermal or pressure-promoted (6–13 kbar)[16] Diels–Alder conditions.[18]

Dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (**5**) does participate in [4 + 2] cycloaddition reactions with electron-rich, neutral, *and* electron-deficient dienophiles at reaction rates greater than that observed with **6**. With electron-rich olefins, both **5** and **6** provide 1,2-diazine Diels–Alder products in satisfactory yield, and, contrary to initial expectations, **5** has proven to be more reactive than **6** toward electron-deficient dienophiles despite an apparent less complementary diene/dienophile match. Consistent with this observed trend, 3,6-diamino-1,2,4,5-tetrazine[18] and its *N,N'*-diacyl derivatives failed to participate in [4 + 2] cycloaddition reactions with electron-rich, neutral, *or* electron-deficient dienophiles, Figure 1.

1,2-Diazine Introduction and Direct Implementation of a 1,2,4,5-Tetrazine → 1,2-Diazine → Benzene (Indoline/Indole) Diels–Alder Strategy. Reductive desulfurization of the 1,2-diazine Diels–Alder cycloadducts employing Raney nickel provides an approach to the preparation of the parent 4,5-substituted 1,2-diazines in a process that proved highly dependent on the reaction conditions employed, eq 3.[20,21] Reductive desulfurization



(3)

(a) 4 equiv of *m*-CPBA, CH_2Cl_2, −66 °C, 9 h, 90–100%, 66% (recrystallized) or 4 equiv of $KHSO_5$, CH_3OH, 0 °C to 25 °C, 4 h, 95%; (b) 2 equiv of *m*-CPBA, CH_2Cl_2, −66 °C, 9 h, 72%; (c) 1.2 equiv of $NaIO_4$, MeOH, 25 °C, 6 days, 64%; (d) 34 equiv of Raney nickel, EtOH, 25 °C, 2 h, 62%; (e) NH_3, DMF, 25 °C, 23 h, 99%; (f) 1.1 equiv of $NaOCH_3$, MeOH, 25 °C, 4 h, 97%

(14) The initial 3,6-bis(methylthio)-1,4-dihydro-1,2-diazine [4 + 2] cycloadduct derived from the room-temperature reaction of **6** with the morpholino enamine of cyclopentanone was isolated and characterized: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 3.62 (4 H, t, *J* = 6 Hz, CH_2OCH_2), 2.56 (4 H, rough t, *J* = 6 Hz, CH_2NCH_2), 2.50 (3 H, s, SCH_3), 2.48 (3 H, s, SCH_3), 2.40–1.60 (7 H, m, $CHCH_2CH_2CH_2$).

(15) (a) Druey, J.; Meier, Kd.; Eichenberger, K. *Helv. Chim. Acta* **1954**, *37*, 121. (b) Horning, R. H.; Armstutz, E. D. *J. Org. Chem.* **1955**, *20*, 707.

(16) (a) Isaacs, N. S. *Liquid High Pressure Chemistry*; Wiley-Interscience: New York, 1981. Sera, A.; Uchida, T.; Matsumoto, K. *Synthesis* **1985**, 1, 999. Matsumoto, K.; Uchida, T.; Acheson, R. M. *Heterocycl.* **1981**, *16*, 1367. Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. For the use of pressure-promoted Diels–Alder conditions in the use of 1,2,4-triazines, see ref 8 and Maddox, M. L.; Martin, J. C.; Muchowski, J. M. *Tetrahedron Lett.* **1980**, *21*, 7. Martin, J. C.; Muchowski, J. M. *J. Org. Chem.* **1984**, *49*, 1040. (b) The pressure-promoted (13–14 kbar, 25 °C) reactions were carried out in a Psika PA3-381 14 kbar pressure generator manufactured by Psika Pressure Systems, Ltd., Derbyshire, England, in Teflon tubes sealed with brass screw clamps employing Monoplex DDA (C. P. Hall Company) as the pressure transmission fluid. We do not recommend the use of this pressure generator.

(17) The reaction of the sodium or lithium enolate of acetophenone with **6** led to the generation of the simple addition product 6-(2-oxo-2-phenethyl)-3-(methylthio)-1,2,4,5-tetrazine: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 8.02 (2 H, m, Ar), 7.55 (3 H, m, Ar), 4.95 (2 H, s, $-CH_2-$), 2.75 (3 H, s, SCH_3); IR (KBr) ν_{max} 2920, 1680 (C=O), 1590, 1572, 1450, 1400, 1345, 1290, 1210, 1175, 1065, 990, 890, 750, 685, 640 cm^{-1}; EIMS, *m/e* (relative intensity) 246 (M^+, 3), 191 (4), 145 (7), 105 (base), 91 (1), 86 (6), 77 (39), 73 (33), 69 (3), 57 (7), 51 (15), 43 (7); HRMS, *m/e* for $C_{11}H_{10}N_4OS$ 246.0575, found 246.0582. The thermal and pressure-promoted [4 + 2] cycloaddition reactions of **6** with the morpholino enamine or trimethylsilyl enol ether of acetophenone do not lead to the generation of this product.

(18) Aryl amidines (benzamidine, 170 °C, 24 h, no reaction), imidates (80–170 °C), and thioimidates (80–140 °C) failed to react as nucleophilic heterodienophiles with **6**. Efforts to promote the reaction of methyl propiolate [Et_2AlCl, $ZnCl_2$, BF_3·OEt_2, $Cu(BF_4)_2$; CH_2Cl_2, −20 to 25 °C, no reaction] or 1-octyne, cyclopentene, and ethyl vinyl ether [$(4\text{-}BrC_6H_4)_3SbCl_5$, −78 to 25 °C, CH_2Cl_2, no reaction; cf. Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 5158] with **6** were unsuccessful.

(19) The 3,6-disubstitution of 1,2,4,5-tetrazine nucleus with electron-donating substituents was anticipated to decrease the observed reactivity toward electron-rich dienophiles and increase the reactivity toward electron-deficient dienophiles. For the preparation of 3,6-diamino-1,2,4,5-tetrazine (i) and *N,N'*-diacetyl-3,6-diamino-1,2,4,5-tetrazine (ii): Lin, C.-H.; Lieber, E.; Horwitz, J. P. *J. Am. Chem. Soc.* **1954**, *76*, 427. *N,N'*-Bis(methoxycarbonyl)-3,6-diamino-1,2,4,5-tetrazine (iii) was prepared by treatment of i with methyl chloroformate (pyridine, 25 °C, 72 h). Treatment of i–iii with 1,1-dimethoxyethylene and 4,4-dimethoxybut-3-en-2-one (dioxane, 100–125 °C, mesitylene, 125–135 °C) failed to provide products derived from [4 + 2] cycloaddition.

Table I. Diels–Alder Reactions of 3,6-Bis(methylthio)-1,2,4,5-tetrazine (6): Preparation of 3,6-Bis(methylthio)-1,2-diazines

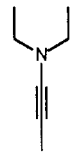
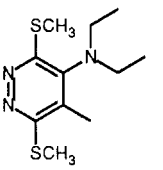
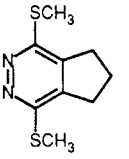
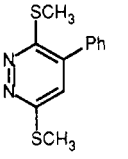
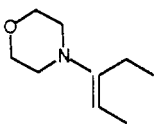
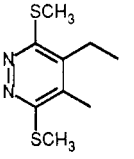
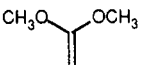
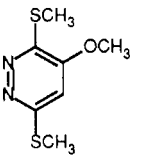
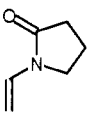
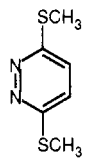
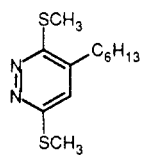
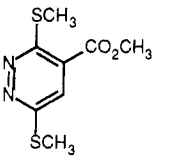
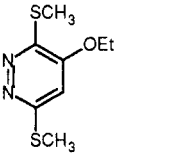
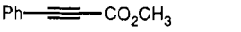
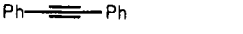
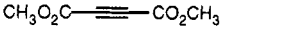
entry	dienophile 10	equiv 10	conditions: solvent, temp, °C (time, h)	1,2-diazine (11)[a]	% yield[b]
1		(2)[c]	dioxane, 25 (1)	 **11a**	96
2	 X = morpholine	(1.5)[d]	$CHCl_3$, 0 to 25 (2.5), 60 (10) CH_2Cl_2, 25 (20) dioxane, 25 (6)	 **11b**	97 55 48
3	X = pyrrolidine	(1.5)[d]	$CHCl_3$, 0 to 25 (2.5), 60 (10) dioxane, 25 (5)	**11b**	81 72
4	X = $OSiMe_3$	(1.5)[e]	mesitylene, 150 (11)	**11b**	61
5	 X = $OSiMe_3$	(3)[e] (2.5) (2.5)	CH_2Cl_2, 13 kbar, 25 (48) xylene, 140 (26) dioxane, 100 (24–30)	 **11c**	88 78 *f*
6	X = morpholine	(2.5)[d] (2.0)	$CHCl_3$, 25 (24), 65 (42) dioxane, 101 (51)	**11c**	65 23
7		(2.5)[g]	$CHCl_3$, 65 (13) $CHCl_3$, 25 (2–7)	 **11d**	67 57–66
8		(4)[h]	dioxane, 80 (13) toluene, 25–100 (13) CH_2Cl_2, 25–45 (13)	 **11e**	85 56 *f*
9		(2)[e]	dioxane, 100 (22) dioxane, 80 (16)	 **11f**	79 52
10		(4)[e]	xylene, 130 (19) dioxane, 100 (>48)	**11f**	87 *f*
11		(4)[e]	xylene, 140 (48) xylene, 100–130 (>48)	**11f**	86 *f*
12		(1.5)[e]	mesitylene, 166 (12)	**11c**	61
13		(2.5)[e] (2)	mesitylene, 140 (72) mesitylene, 160 (27)	 **11g**	66 41

Table I (Continued)

entry	dienophile **10**	equiv **10**	conditions: solvent, temp, °C (time, h)	conditions: 1,2-diazine (**11**)[a]	% yield[b]
14		(2)[e]	mesitylene, 160 (28)	 **11h**	13–19
15		(0.5)[e]	CH_2Cl_2, 43 (42)[i]	**11b**	19
16		(2)[e]	dioxane, 100 (14–72) toluene, 110 (3)	 **11i**	trace trace
17		(1.5–2)	mesitylene, 180 (7)		trace
18		(1.5–2)	mesitylene, 180 (4)		trace
19		(2) (4)	mesitylene, 25–180 (>48) neat, 13 kbar, 25 (24)		no reaction no reaction

[a] All products exhibited the expected or previously reported ^1H NMR, IR, and MS characteristics consisted with the assigned structure. All new compounds gave satisfactory C, H, N elemental analysis or HRMS exact mass information. [b] All yields are based on pure material isolated by chromatography (SiO_2). [c] Available from Fluka. [d] The morpholino and pyrrolidino enamines were prepared in benzene with the aid of the azeotropic removal of water: cf. Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovic, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207. [e] Available from Aldrich Chemical Company. [f] Trace of [4 + 2] cycloadduct detected. [g] The morpholino enamine was prepared in benzene with the aid of 4-Å molecular sieves: cf. Taguchi, K.; Westheimer, F. H. *J. Org. Chem.* **1971**, *36*, 1570. [h] Available from Wiley Organics. [i] In situ oxidation of the primary Diels–Alder product, dihydro-3,6-bis(methylthio)-4,5-cyclopenteno-1,2-diazine, accompanied by reduction of **6** provides the observed product **11b**.

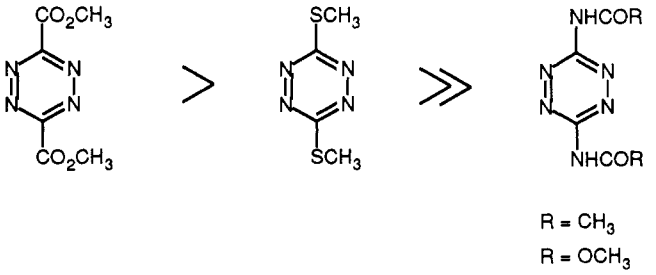
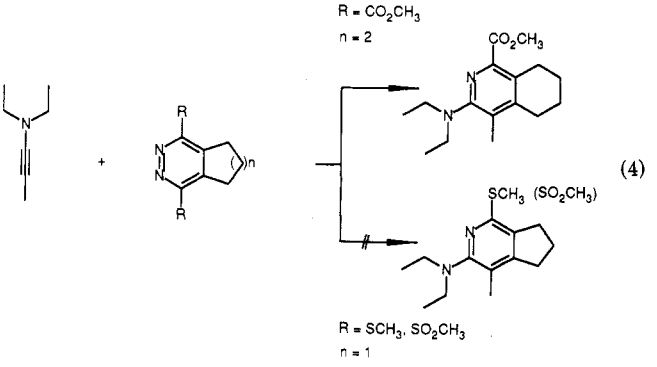


Figure 1.

of **11b** provided the parent 1,2-diazine **15** and was most satisfactorily conducted in absolute ethanol[20] employing W-2 Raney nickel.[20a] Related procedures customarily employed for reductive desulfurization, e.g. dry dioxane/W-2 Raney nickel (20–40%), proved less successful.

Selective sulfur oxidation of the 3,6-bis(methylthio)-1,2-diazine cycloadducts, e.g. **11b**, under a range of conditions employing 1, 2, and 4 equiv of oxidizing agent provided the monosulfoxide **14**, bis(sulfoxide) **13**, and bis(sulfone) **12** respectively, eq 3.[22] In contrast to the 3,6-bis(methoxycarbonyl)-1,2-diazine cycloadducts derived from **5**, which have proven sufficiently reactive to participate in selected [4 + 2] cycloaddition reactions with electron-rich dienophiles,[23] the bis(sulfone) **12** as well as **11b** failed to provide products derived from [4 + 2] cycloaddition upon treatment with selected electron-rich or nucleophilic dienophiles,[24] eq 4.



(4)

Selective, single nucleophilic displacement of the bis(sulfone) **12** proceeded under mild conditions (25 °C, THF) to provide functionalized 1,2-diazine monosulfones, eq 3 and 5. This selective single displacement reaction of the 1,2-diazine 3,6-bis(sulfone) **12** permits the direct introduction of alkyne/allene side chains suitable for use in subsequent intramolecular alkyne/allene 1,2-diazine Diels–Alder reactions,[12] eq 5. Consistent with prior observations,[12] thermolysis (235–240 °C, triisopropylbenzene, 22 h) of **16b** provided the indoline **19** (76%) while thermolysis of **17** failed to provide the corresponding Diels–Alder product.[25] In sharp contrast, the allene 1,2-diazine

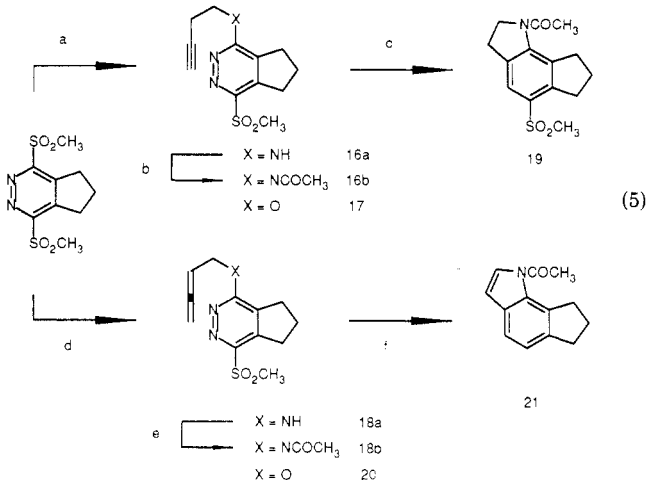
(20) Raney nickel, active catalyst commercially available from Aldrich Chemical Co., was employed. It was found that the catalyst must be carefully washed [4 days, 4×] prior to use.

(21) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287.

(22) (a) Gassmann, P. G.; Van Bergen, T. J.; Gilbert, D. P.; Cue, B. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 5495. (b) Grundmann, C.; Ulrich, H.; Kreutzberger, A. *Chem. Ber.* **1953**, *86*, 181.

(23) Boger, D. L.; Parikh, K., unpublished observations.

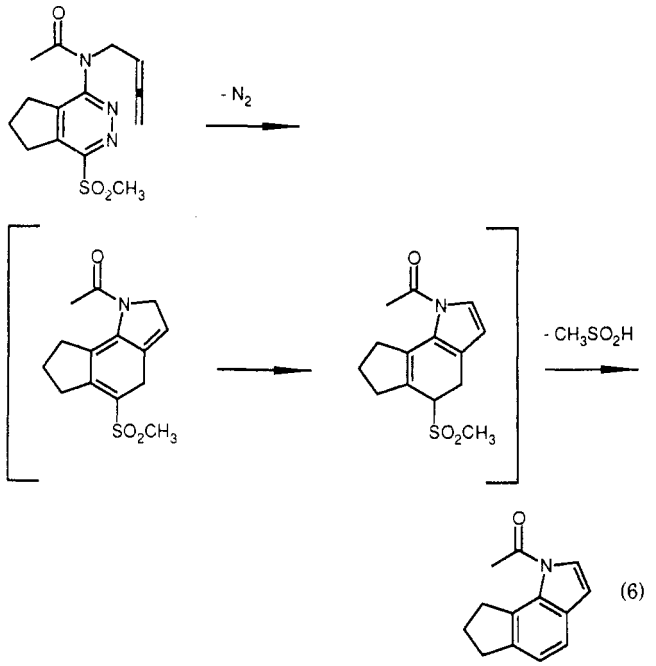
(24) Attempts to promote the [4 + 2] cycloaddition reaction of **11b** [1.0–2.0 equiv of $Et_2NC{\equiv}CCH_3$, 25 °C, 0%; 1.0–1.5 equiv of $(MeO)_2C{=}CH_2$, no reaction, 25–100 °C] or **12** [1.0–2.0 equiv of $Et_2NC{\equiv}CCH_3$, 25 °C, 0%; 1.0–5.0 equiv of $(MeO)_2C{=}CH_2$, no reaction, 25–100 °C] with electron-rich dienophiles failed to provide the expected products.



(5)

(a) For **16a** (X = NH), 5.0 equiv of $HC{\equiv}CCH_2CH_2NH_2{\cdot}CF_3CO_2H$, 7.0 equiv of K_2CO_3, DMF, 25 °C, 67 h, 70%; for **17** (X = O), 1.1 equiv of $NaOCH_2CH_2C{\equiv}CH$, THF, 25 °C, 20 min, 95%; (b) 0.5 equiv of anhydrous NaOAc, Ac_2O, 110 °C, 15 h, 72%; (c) **16b**, TIPB, 235–240 °C, 22 h, 76%; (d) for **18a** (X = NH), 5.0 equiv of $H_2C{=}C{=}CHCH_2NH_2{\cdot}CF_3CO_2H$, 7.0 equiv of K_2CO_3, DMF, 65–70 °C, 9.5 h, 68%; for **20**, (X = O), 1.8 equiv of $NaOCH_2CH{=}C{=}CH_2$, THF, 25 °C, 20 min, 98%; (e) 0.3 equiv of anhydrous NaOAc, Ac_2O, 110 °C, 21 h, 44% **18b** and 25% **21**; (f) **18b**, TIPB, 195 °C (21 h), 220 °C (5 h), 57% or **18b**, diglyme, 160 °C (27.5 h), 87%

18b was found to participate in the intramolecular Diels–Alder reaction under substantially milder thermal conditions (100–230 °C, 57–87%) than that of the corresponding alkyne 1,2-diazine **16b**. This may be attributed to the increased reactivity of the dienophile (allene alkene > alkyne) and the entropically favored (allene > alkyne) potential for achieving the productive conformation necessary for participation in the intramolecular Diels–Alder reaction.[26] In addition, the product of the thermal, intramolecular [4 + 2] cycloaddition of allene 1,2-diazine **18b** (diglyme, 160 °C, 27.5 h; TIPB, 195–220 °C, 26 h; dioxane, 100 °C, slow) proved to be the indole **21** presumably derived from thermal isomerization of the initial [4 + 2] allene 1,2-diazine cycloadduct to the corresponding 4,5-dihydroindole, eq 6, followed by subsequent loss of methanesulfinic acid[27] with aromatization. Consequently, this clean, divergent behavior of the intramolecular alkyne/allene 1,2-diazine Diels–Alder reaction permits the selected, controlled preparation of indoline or indole, e.g. **19**/**21**, in the implementation of the 1,2,4,5-tetrazine → 1,2-diazine → indoline/indole Diels–Alder strategy.



(6)

Experimental Section

Proton nuclear magnetic spectra (^1H NMR) were recorded on a Varian XL-200, General Electric QE-300, or Varian FT-80 spectrometer, and chemical shifts are reported in parts per million (ppm) relative to internal tetramethylsilane (δ 0.00). Infrared spectra (IR) were recorded on a Perkin-Elmer 1420 spectrometer as KBr pellets (solids) and thin films (liquids). Melting points (mp) were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Electron impact mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were recorded on a Finnegan 4000 spectrometer. High resolution mass spectra (HRMS) were recorded on a Kratos MS-50 spectrometer. Chromatography (flash chromatography[28]) was performed on 230–400-mesh silica gel. Tetrahydrofuran (THF) and ether (Et_2O) were distilled from sodium benzophenone ketyl. Methylene chloride (CH_2Cl_2) and chloroform ($CHCl_3$) were distilled from phosphorus pentoxide. Mesitylene, dioxane, toluene, xylene, and triisopropylbenzene (Aldrich) were distilled from calcium hydride. All extraction and chromatographic solvents, ethyl ether (Et_2O), ethyl acetate (EtOAc), and hexane, were distilled prior to use. All other solvents and reagents were used as received from commercial sources.

Diels–Alder Reactions of 3,6-Bis(methylthio)-1,2,4,5-tetrazine (6): General Procedure for the Preparation of 3,6-Bis(methylthio)-4,5-disubstituted-1,2-diazines. 4-(Diethylamino)-3,6-bis(methylthio)-5-methyl-1,2-diazine (11a). A solution of 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**, 100 mg, 0.57 mmol) in dioxane (0.6 mL) under nitrogen was treated with *N,N*-diethylamino-1-propyne (0.16 mL, 1.15 mmol, 2.0 equiv) at 25 °C and the resulting solution was stirred for 1 h. Removal of the solvent in vacuo and chromatography (SiO_2, 2% EtOAc–hexane eluant) afforded pure **11a** (142 mg, 147 mg theoretical yield, 96%) as a viscous, yellow oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 3.15 (4 H, q, J = 6 Hz, CH_2CH_3), 2.69 (3 H, s, SCH_3), 2.58 (3 H, s, SCH_3), 2.18 (3 H, s, CH_3), 1.04 (6 H, t, J = 6 Hz, CH_2CH_3); IR (film) ν_{max} 2970, 2920, 1540, 1490, 1430, 1400, 1375, 1320, 1280, 1250, 1220, 1190, 1160, 1075, 1010, 960, 935, 800, 610 cm^{-1}; EIMS, m/e (relative intensity) 257 (M^+, 30), 242 (100), 228 (36), 212 (4), 194 (7), 180 (7), 166 (9), 148 (6), 134 (4), 120 (5), 99 (4), 93 (10), 83 (16), 72 (19), 56 (6), 45 (10); HRMS, m/e for $C_{11}H_{19}N_3S_2$ 257.1020, found 257.1026.

3,6-Bis(methylthio)-4,5-cyclopenteno-1,2-diazine (11b). A solution of 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**, 2.01 g, 11.5 mmol) in benzene (8 mL) at 0 °C was treated with *N*-(1-cyclopentenyl)morpholine (4 mL, 25.0 mmol, 2.2 equiv) and the resulting solution was allowed to warm to room temperature and further stirred for 1 h. *p*-Toluenesulfonic acid (214 mg, 0.1 equiv) was added to the reaction mixture at room temperature and the resulting reaction mixture was warmed at 80 °C (17 h). After removal of the solvent in vacuo, the crude reaction mixture was passed through a plug of silica gel (30 g) to yield 2.9 g of crude **11b**. Recrystallization (absolute ethanol) afforded 1.96 g (2.44 g theoretical yield, 80%) of 3,6-bis(methylthio)-4,5-cyclopenteno-1,2-diazine (**11b**). Removal of ethanol from the filtrate and chromatography of the residue afforded an additional 182 mg of **11b** (combined yield of **11b**: 88%): mp 105–106 °C (white needles, ethanol); ^1H NMR ($CDCl_3$, 200 MHz) δ 2.83 (4 H, t, J

(25) The failure of **17** to participate in a productive intramolecular Diels–Alder reaction may be attributed in part to the instability of **17** and the dihydrobenzofuran Diels–Alder product to the conditions of thermolysis, cf. ref 9 and 12.

(26) For recent studies of the intramolecular allene (dienophile) Diels–Alder reaction, see: Yamaguchi, Y.; Yamada, H.; Hayakawa, K.; Kanematsu, K. *J. Org. Chem.* **1987**, *52*, 2040.

(27) A selected thermal elimination of an unactivated aryl sulfone has been reported to occur at 200 °C, see: Colter, A. K. *J. Org. Chem.* **1971**, *36*, 1898. For the thermal elimination of an activated aryl sulfone, see: Delombaert, S.; Ghosez, L. *Tetrahedron Lett.* **1984**, *25*, 3475.

(28) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

= 7 Hz, $CH_2CH_2CH_2$), 2.72 (6 H, s, SCH_3), 2.16 (2 H, p, J = 7 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 3000, 2960, 2920, 2840, 1570, 1430, 1285, 1210, 1180, 1040, 995, 960, 910, 635 cm^{-1}; EIMS, m/e (relative intensity) 212 (M^+, base), 197 (2), 179 (39), 169 (6), 154 (42), 145 (7), 132 (6), 119 (17), 110 (2), 97 (3), 92 (6), 82 (5), 77 (13), 65 (8), 58 (1), 45 (14), 39 (10); HRMS, m/e for $C_9H_{12}N_2S_2$ 212.0442, found 212.0436.

Anal. Calcd for $C_9H_{12}N_2S_2$: C, 50.91; H, 5.69; N, 13.21; S, 30.20. Found: C, 50.95; H, 5.38; N, 13.09; S, 30.38.

3,6-Bis(methylthio)-4-phenyl-1,2-diazine (11c): mp 68–69 °C (white needles, hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.45 (5 H, s, Ar), 7.05 (1 H, s, C5-H), 2.75 (3 H, s, SCH_3), 2.65 (3 H, s, SCH_3); IR (KBr) ν_{max} 3040, 2920, 1570, 1490, 1430, 1410, 1345, 1305, 1280, 1142, 960, 892, 850, 760, 740, 715, 690 cm^{-1}; EIMS, m/e (relative intensity) 248 (M^+, base), 233 (4), 215 (16), 201 (4), 190 (2), 168 (2), 158 (12), 148 (5), 128 (11), 114 (4), 95 (4), 89 (10), 77 (5), 69 (2), 57 (2), 51 (5), 45 (16), 39 (2); HRMS, m/e for $C_{12}H_{12}N_2S_2$ 248.0442, found 248.0440.

3,6-Bis(methylthio)-4-ethyl-5-methyl-1,2-diazine (11d): ^1H NMR ($CDCl_3$, 200 MHz) δ 2.70 (2 H, q, J = 6Hz, CH_2CH_3), 2.69 (6 H, s, SCH_3), 2.25 (3 H, s, CH_3), 1.18 (3 H, t, J = 6 Hz, CH_2CH_3); IR (film) ν_{max} 2960, 2920, 2875, 1550, 1460, 1425, 1370, 1315, 1290, 1240, 1190, 1090, 1070, 1050, 1010, 960, 910, 845, 780 cm^{-1}; EIMS, m/e (relative intensity) 214 (M^+, base), 199 (88), 181 (34), 165 (7), 153 (8), 135 (6), 121 (32), 105 (4), 91 (11), 85 (25), 77 (10), 65 (17), 59 (7), 45 (73), 39 (41); HRMS, m/e for $C_9H_{14}N_2S_2$ 214.0598, found 214.0606.

3,6-Bis(methylthio)-4-methoxy-1,2-diazine (11e): mp 103–105 °C (white needles, hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 6.50 (1 H, s, C5-H), 3.90 (3 H, s, OCH_3), 2.70 (3 H, s, SCH_3), 2.65 (3 H, s, SCH_3); IR (KBr) ν_{max} 3000, 2950, 2920, 1570, 1500, 1450, 1410, 1365, 1330, 1310, 1285, 1130, 1005, 965, 910, 840 cm^{-1}; EIMS, m/e (relative intensity) 202 (M^+, base), 187 (2), 269 (20), 155 (4), 140 (9), 131 (12), 116 (4), 109 (29), 97 (1), 85 (15), 69 (13), 53 (2), 45 (21), 40 (5); HRMS, m/e for $C_7H_{10}N_2OS_2$ 202.0234, found 202.0278.

Anal. Calcd for $C_7H_{10}N_2OS_2$: C, 41.62; H, 4.99; N, 13.87; S, 31.74. Found: C, 41.56; H, 5.03; N, 13.87; S, 31.69.

3,6-Bis(methylthio)-1,2-diazine (11f): mp 125–126.5 °C (white needles, hexane) (lit.[15a] mp 126–127 °C); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.11 (2 H, s, C4- and C5-H), 2.70 (6 H, s, SCH_3); IR (KBr) ν_{max} 3060, 2920, 1570, 1430, 1390, 1300, 1150, 1000, 960, 830, 770 cm^{-1}; EIMS, m/e (relative intensity) 172 (M^+, base), 139 (50), 125 (14), 114 (23), 99 (3), 92 (1), 85 (34), 79 (19), 72 (38), 65 (1), 52 (8), 45 (44), 39 (6); HRMS, m/e for $C_6H_8N_2S_2$ 172.1029, found 172.0127.

3,6-Bis(methylthio)-4-(*n*-hexyl)-1,2-diazine (11g): ^1H NMR ($CDCl_3$, 200 MHz) δ 6.86 (1 H, s, C5-H), 2.69 (6 H, s, SCH_3), 2.50 (2 H, t, J = 4 Hz, CH_2Ar), 1.63 (2 H, m, $ArCH_2CH_2(CH_2)_3CH_3$), 1.31 (6 H, m, $Ar(CH_2)_2(CH_2)_3CH_3$), 0.90 (3 H, rough t, CH_3); IR (film) ν_{max} 2960, 2920, 2860, 1575, 1490, 1460, 1445, 1360, 1310, 1140, 1122, 960, 725 cm^{-1}; EIMS, m/e (relative intensity) 256 (M^+, 47), 241 (26), 209 (76), 199 (base), 186 (27), 165 (4), 153 (9), 140 (4), 125 (4), 105 (2), 91 (4), 79 (5), 69 (7), 55 (5), 41 (35); HRMS, m/e for $C_{12}H_{20}N_2S_2$ 256.1068, found 256.1070.

Selective Oxidations of 11b: Preparation of Bis(sulfone) 12, Bis(sulfoxide) 13, and Monosulfoxide 14. 3,6-Bis(methylsulfonyl)-4,5-cyclopenteno-1,2-diazine (12). A solution of 3,6-bis(methylthio)-4,5-cyclopenteno-1,2-diazine (**11b**, 106 mg, 0.50 mmol) in CH_2Cl_2 (1.7 mL) at −66 °C was treated with *m*-chloroperbenzoic acid (*m*-CPBA, 431 mg, 2.0 mmol, 4 equiv of 80%) and the reaction mixture was stirred for 9 h (−66 °C). The reaction mixture was warmed to room temperature, diluted with CH_2Cl_2 (10 mL), and washed with 5% aqueous $NaHCO_3$ (60 mL). The aqueous phase was subsequently extracted with CH_2Cl_2 (15 mL × 4). The combined organic layer was washed with saturated aqueous NaCl (25 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo to afford 142 mg of crude, essentially pure 3,6-bis(methylsulfonyl)-4,5-cyclopenteno-1,2-diazine (**12**). Recrystallization (ethyl acetate–hexane) afforded 91 mg (138 mg theoretical yield, 66%) of pure **12**: mp 210–212 °C (white needles, methanol); ^1H NMR ($CDCl_3$, 200 MHz) δ 3.51 (6 H, s, SO_2CH_3), 3.45 (4 H, t, J = 7 Hz, $CH_2CH_2CH_2$), 2.35 (2 H, p, J = 7 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 3040, 3000, 2960, 2920, 2280, 1510, 1450, 1405, 1389, 1310, 1280, 1190, 1125, 1970, 775, 650 cm^{-1}; EIMS, m/e (relative intensity) 276 (M^+, 3), 212 (8), 156 (40), 139 (base), 117 (7), 111 (32), 91 (3), 75 (16), 63 (6), 50 (9), 39 (3); HRMS, m/e for $C_9H_{12}N_2O_4S_2$ 276.0238, found 276.0232.

Anal. Calcd for $C_9H_{12}N_2O_4S_2$: C, 39.12; H, 4.38; N, 10.14; S, 23.21. Found: C, 38.83; H, 4.36; N, 10.19; S, 22.94.

3,6-Bis(methylsulfinyl)-4,5-cyclopenteno-1,2-diazine (13). A solution of **11b** (102 mg, 0.48 mmol) in CH_2Cl_2 (1.6 mL) at −66 °C was treated with *m*-chloroperbenzoic acid (*m*-CPBA, 209 mg, 2 equiv of 80%) and further stirred at −66 °C (9 h). The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with 5% aqueous $NaHCO_3$ (25 mL). The aqueous phase was extracted with CH_2Cl_2 (15 mL × 3), the combined organic layer was washed with saturated aqueous NaCl (15 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo to afford 85 mg (118 mg theoretical yield, 72%) of 3,6-bis(methylsulfinyl)-4,5-cyclopenteno-1,2-diazine (**13**): mp 162–165 °C (white needles, ethyl acetate); ^1H NMR ($CDCl_3$, 200 MHz) δ 3.43 (4 H, t, J = Hz, $CH_2CH_2CH_2$), 3.13 (6 H, s, $SOCH_3$), 2.28 (2 H, p, J = 7 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 3000, 2950, 2910, 1510, 1450, 1400, 1310, 1290, 1060, 960, 935, 680, 650 cm^{-1}; EIMS, m/e (relative intensity) 244 (M^+, 3), 277 (12), 196 (15), 181 (1), 149 (4), 119 (30), 63 (base); HRMS, m/e for $C_9H_{12}N_2O_2S_2$ 244.0340, found 244.0338.

4,5-Cyclopenteno-3-(methylsulfinyl)-6-(methylthio)-1,2-diazine (14). A solution of **11b** (89 mg, 0.42 mmol) in methanol (1 mL) was treated with sodium periodate (108 mg, 0.50 mmol, 1.2 equiv) at room temperature and the resulting reaction mixture was stirred for 6 days (25 °C). The reaction mixture was diluted with water (20 mL) and extracted with CH_2Cl_2 (20 mL × 4). The combined organic layer was dried (Na_2SO_4), and the solvent was removed in vacuo. Chromatography (SiO_2, 2–10% ethyl acetate–hexane, gradient elution) afforded 62 mg (96 mg theoretical yield, 64%) of 4,5-cyclopenteno-3-(methylsulfinyl)-6-(methylthio)-1,2-diazine (**14**): mp 76.5–78 °C (white plates, ethyl acetate–hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 3.35 (2 H, t, J = 7 Hz, C4-$CH_2CH_2CH_2$-C5), 3.05 (3 H, s, $SOCH_3$), 2.82 (2 H, t, J = 7 Hz, C4-$CH_2CH_2CH_2$-C5), 2.77 (3 H, s, SCH_3), 2.25 (2 H, p, J = 7 Hz, $CH_2CH_2CH_2$); EIMS, m/e (relative intensity) 228 (M^+, 25), 211 (51), 180 (64), 165 (3), 154 (5), 138 (9), 125 (10), 119 (base), 110 (14), 97 (6), 92 (20), 82 (16), 77 (7), 69 (10), 63 (33), 47 (91); HRMS, m/e for $C_9H_{12}N_2OS_2$ 228.0391, found 228.0383.

Reductive Desulfurization of 3,6-Bis(methylthio)-1,2-diazines: Preparation of 4,5-Cyclopenteno-1,2-diazine (15a). A slurry of Raney nickel (1.41 g wet, 34 equiv)[20] and 3,6-bis(methylthio)-4,5-cyclopenteno-1,2-diazine (**11b**, 41 mg, 0.19 mmol) in ethanol (3 mL) was stirred vigorously at room temperature (2 h). The Raney nickel was removed by filtration (ethyl acetate wash) through Celite. The removal of solvent in vacuo (31 mg of crude **15a**) and chromatography (SiO_2, 33–100% EtOAc–hexane gradient elution) afforded 15 mg (23 mg theoretical yield, 62%) of 4,5-cyclopenteno-1,2-diazine (**15a**): mp 83–85.5 °C (white needles, hexane–EtOAc; lit.[15b] mp 85–87 °C); ^1H NMR ($CDCl_3$, 80 MHz) δ 9.10 (2 H, s, Ar H), 2.98 (4 H, t, J = 6 Hz, $CH_2CH_2CH_2$), 2.14 (2 H, p, J = 6 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 3416, 3075, 3002, 2966, 2873, 2846, 1579, 1559, 1460, 1433, 1303, 1262, 1210, 1138, 1041, 995, 923, 902, 771; EIMS, m/e (relative intensity) 120 (M^+, 77), 91 (base), 77 (1), 65 (13), 51 (4), 39 (8); HRMS, m/e for $C_7H_8N_2$ 120.0687, found 120.0691.

6-Amino-3-(methylsulfonyl)-4,5-cyclopenteno-1,2-diazine (15b). A solution of 3,6-bis(methylsulfonyl)-4,5-cyclopenteno-1,2-diazine (**12**, 1.0 g, 3.62 mmol) in *N,N*-dimethylformamide (20 mL) saturated with ammonia was stirred at 25 °C (23 h). The product begins to precipitate as a white solid after 5 h. The precipitate was collected by filtration and washed with water (20 mL) and CH_2Cl_2 (20 mL). The collected solid was dried under vacuum to afford 6-amino-3-(methylsulfonyl)-4,5-cyclopenteno-1,2-diazine (**15b**, 770 mg, 772 mg theoretical yield, 99%) as a white powdery solid: mp 285 °C dec (white powdery solid, H_2O); ^1H NMR (DMSO, 300 MHz) δ 7.10 (s, 2 H, NH_2), 3.50 (s, 3 H, SO_2CH_3), 3.00 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.70 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.10 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 3409, 3304, 3128, 3019, 2985, 2928, 2742, 2670, 1647, 1581, 1508, 1465, 1431, 1418, 1400, 1324, 1301, 1251, 1214, 1196, 1180, 1133, 1100, 1031, 952, 912, 779 cm^{-1}; EIMS, m/e (relative intensity) 213 (M^+, 15), 149 (base), 134 (9), 120 (4), 109 (9), 104 (6), 94 (25), 77 (33), 65 (80), 51 (28); HRMS, m/e for $C_8H_{11}N_3O_2S$ 213.0572, found 213.0562.

4,5-Cyclopenteno-6-methoxy-3-(methylsulfonyl)-1,2-diazine (15c). A solution of sodium methoxide (0.099 mL of 4.37 M, 0.43 mmol, 1.1 equiv) was added slowly to a solution of **12** (108 mg, 0.393 mmol) in methanol (0.8 mL) under argon at room temperature, and the resulting reaction mixture was stirred for 4 h (25 °C). The reaction mixture was diluted with water (10 mL), extracted with methylene chloride (10 mL × 4), and dried (Na_2SO_4), and the solvent was removed under reduced pressure to afford pure 4,5-cyclopenteno-6-methoxy-3-(methylsulfonyl)-1,2-diazine (**15c**, 88 mg, 90 mg theoretical yield, 97%) as a white powdery solid: mp 118–120 °C (white needles, ethanol); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.20 (s, 3 H, OCH_3), 3.45 (s, 3 H, SO_2CH_3), 3.35 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.40 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.25 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 3047, 2961, 2938, 1574, 1462, 1426, 1396, 1359, 1325, 1300, 1195, 1179, 1144, 1110, 1079, 972, 950, 762 cm^{-1}; EIMS, m/e (relative intensity) 228 (M^+, base), 213 (9), 199 (6), 164 (43), 149 (43), 134 (7), 119 (76), 92 (22), 79 (15), 65 (37), 56 (4); HRMS, m/e for $C_9H_{12}N_2O_3S$ 228.0569, found 228.0562.

6-[(3-Butynyl)amino]-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (16a). The trifluoroacetic acid salt of 1-amino-3-butyne[29] (576 mg, 3.15 mmol, 4.0 equiv) was added to a solution of **12** (217 mg, 0.79 mmol, 1.0 equiv) and potassium carbonate (544 mg, 3.94 mmol, 5.0 equiv) in *N,N*-dimethylformamide (5.0 mL) and the resulting reaction mixture was stirred at 25 °C (67 h). After the initial 48 h (25 °C), additional trifluoroacetic acid salt of 1-amino-3-butyne (1.0 equiv) and potassium carbonate (2.0 equiv) were added to the reaction mixture. The reaction mixture was poured into water (30 mL), extracted with methylene chloride (25 mL × 5), dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography (SiO_2, 30% ethyl acetate–hexane) afforded 6-[(3-butynyl)amino]-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (**16a**, 148 mg, 209 mg theoretical yield, 70%) as a white crystalline solid: mp 160–163 °C (white plates, EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.86 (q, 2 H, J = 6 Hz, CH_2CH_2NH), 3.41 (s, 3 H, SO_2CH_3), 3.34 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.78 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.64 (td, 2 H, J = 6, 3 Hz, $HC{\equiv}CCH_2CH_2NH$), 2.27 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.05 (t, 1 H, J = 3 Hz, $HC{\equiv}CCH_2$); IR (KBr) ν_{max} 3364, 3273, 3007, 2957, 2917, 1594, 1491, 1472, 1436, 1413, 1400, 1364, 1305, 1170, 1128, 1047, 955, 912, 777, 750, 682 cm^{-1}; EIMS, m/e (relative intensity) 265 (M^+, base), 226 (51), 213 (70), 186 (95), 170 (4), 149 (11), 133 (7), 119 (60), 105 (6), 92 (14), 79 (17), 65 (29), 53 (12); HRMS, m/e for $C_{12}H_{15}N_3O_2S$ 265.0885, found 265.0882.

***N*-Acetyl-6-[(3-butynyl)amino]-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (16b).** A solution of **16a** (140 mg, 0.53 mmol) and anhydrous sodium acetate (0.5 equiv, 36 mg, 0.26 mmol) in acetic anhydride (5 mL) under argon was stirred vigorously at 110 °C (15 h). The cooled reaction mixture was diluted with water (25 mL) and extracted with methylene chloride (20 mL × 5). Removal of methylene chloride and residual acetic anhydride under reduced pressure and chromatography (SiO_2, 25–40% EtOAc–hexane, gradient elution) afforded *N*-acetyl-6-[(3-butynyl)amino]-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (**16b**, 119 mg, 163 mg theoretical yield, 72%) as a pale yellow solid: mp 122–123 °C (white plates, ether); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.22 (rough t, 2 H, $CH_2NHCOCH_3$), 3.00 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.55 (td, 2 H, J = 6.3 Hz, $CH_2C{\equiv}CH$), 2.54 (s, 3 H, SO_2CH_3), 2.49 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.30 (br s, 3 H, $COCH_3$), 2.28 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 1.97 (t, 1 H, J = 3 Hz, $CH_2C{\equiv}CH$); IR (KBr) ν_{max} 3992, 3009, 2931, 1659, 1554, 1531, 1427, 1390, 1367, 1336, 1308, 1249, 1210, 1182, 1166, 1136, 1122, 1062, 1021, 999, 960, 766, 758, 683 cm^{-1}; EIMS, m/e (relative intensity) 307 (M^+, 3), 277 (18), 264 (14), 255 (16), 240 (26), 226 (base), 186 (52), 119 (20), 94 (10), 77 (24), 65 (24), 57 (19), 53 (33); HRMS, m/e for $C_{14}H_{17}N_3O_3S$ 307.0991, found 307.0993.

6-(3-Butynyloxy)-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (17). 3-Butyn-1-ol (1.1 equiv, 0.065 mL, 0.85 mmol) was added dropwise to a slurry of sodium hydride (34.1 mg of 60% dispersion in oil, 0.85 mmol) in tetrahydrofuran (2.6 mL) under argon at room temperature and the resulting slurry was stirred at 25 °C (15 min). 3,6-Bis(methylsulfonyl)-4,5-cyclopenteno-1,2-diazine (**12**, 214 mg, 0.775 mmol, 1.0 equiv) was added and the resulting reaction mixture was stirred at 25 °C (20 min). The reaction mixture was diluted with cold water (10 mL) and extracted with methylene chloride (10 mL × 4). Removal of the solvent under reduced pressure and chromatography (SiO_2, 50% EtOAc–hexane) afforded 6-(3-butynyloxy)-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (**17**, 196 mg, 206 mg theoretical yield 95%) as a colorless oil, which solidified (white solid) upon cooling: mp 95–96.5 °C (white, irregular crystals, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.74 (t, 2 H, J = 6 Hz, CH_2CH_2O), 3.45 (s, 3 H, SO_2CH_3), 3.37 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.97 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.79 (td, 2 H, J = 6,3 Hz, $HC{\equiv}CH_2CH_2O$), 2.26 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.02 (t, 1 H, J = 3 Hz, $HC{\equiv}CCH_2$); IR (KBr) ν_{max} 3263, 3032, 3012, 2991, 2966, 2922, 1701, 1653, 1576, 1540, 1507, 1436, 1421, 1358, 1306, 1242, 1211, 1193, 1160, 1121, 1074, 981, 963, 947, 912, 765, 754, 742, 706, 684 cm^{-1}; EIMS, m/e (relative intensity) 266 (M^+, 1), 258 (1), 214 (8), 199 (2), 187 (2), 159 (2), 149 (4), 135 (3), 95 (5), 83 (base), 66 (6); HRMS, m/e for $C_{12}H_{14}N_2O_3S$ 266.0725, found 266.0716.

Attempts to promote the intramolecular Diels–Alder reaction of **17** (190–240 °C, TIPB, 12–48 h) resulted in the slow disappearance of **17** without detection of a [4 + 2] cycloadduct.

***N*-Acetyl-6,7-cyclopenteno-4-(methylsulfonyl)-2,3-dihydroindole (19).** A solution of **16b** (26 mg, 0.083 mmol) in degassed triisopropylbenzene (TIPB, 4.5 mL) under argon was warmed at 235–240 °C (22 h). The reaction mixture was cooled to room temperature and chromatography (SiO_2, 0–80% EtOAc–hexane) afforded *N*-acetyl-6,7-cyclopenteno-4-(methylsulfonyl)-2,3-dihydroindole (**19**, 18 mg, 25 mg theoretical yield, 76%) as a white, crystalline solid: mp 153–155 °C (hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (s, 1 H, Ar H), 4.11 (t, 2 H, J = 8 Hz, CH_2CH_2N), 3.26 (t, 2 H, J = 8 Hz, CH_2CH_2N), 3.13 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 3.04 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 3.01 (s, 3 H, SO_2CH_3), 2.29 (s, 3 H, $COCH_3$), 2.08 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$; IR (KBr) ν_{max} 3014, 2997, 2962, 2917, 1669, 1585, 1490, 1451, 1436, 1391, 1365, 1335, 1326, 1313, 1283, 1268, 1232, 1200, 1167, 1136, 1058, 1039, 1014, 1001, 978, 961, 905, 887, 850, 823, 762, 724 cm^{-1}; EIMS, m/e (relative intensity) 279 (M^+, 30), 237 (base), 222 (3), 204 (2), 174 (66), 158 (65), 143 (3), 128 (19), 105 (8), 91 (4), 91 (10), 77 (10), 65 (3); HRMS, m/e for $C_{14}H_{17}NO_3S$ 279.0929, found 279.0918.

6-[(2,3-Butadienyl)amino]-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (18a). The trifluoroacetic acid salt of 1-amino-2,3-butadiene (5.0 equiv, 499 mg, 2.73 mmol)[30] was added to a solution of **12** (150 mg, 0.545 mmol, 1.0 equiv) and potassium carbonate (7.0 equiv, 527 mg, 3.82 mmol) in *N,N*-dimethylformamide (1.2 mL) at room temperature and the resulting reaction solution was warmed at 65–70 °C (9.5 h). The cooled reaction mixture was poured into water (20 mL) and extracted with methylene chloride (20 mL × 5). Removal of methylene chloride and residual *N,N*-dimethylformamide under reduced pressure and chromatography (SiO_2, 30% EtOAc–hexane) afforded 6-[(2,3-butadienyl)amino]-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (**18a**, 99 mg, 144 mg thoretical yield, 68%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.44 (apparent p, 1 H, J = 6 Hz, $H_2C{=}C{=}CH$), 4.88 (m, 2 H, $H_2C{=}C{=}CH$), 4.80 (br s, 1 H, NH), 4.28 (m, 2 H, $H_2C{=}C{=}CHCH_2$), 3.40 (s, 3 H, SO_2CH_3), 3.31 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.74 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.24 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$); IR (neat) ν_{max} 3373, 2926, 1957, 1670, 1589, 1497, 1414, 1353, 1306, 1167, 1123, 1036, 958, 912, 854, 767 cm^{-1}; EIMS, m/e (relative intensity) 265 (M^+, 41), 264 (55), 226 (5), 212 (2), 186 (base), 170 (3), 149 (3), 133 (4), 119 (43), 92 (17), 79 (25), 68 (76), 53 (51); HRMS, m/e for $C_{12}H_{15}N_3O_2S$ 265.0885, found 265.0881.

***N*-Acetyl-6-[(2,3-butadienyl)amino]-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (18b).** A solution of **18a** (98 mg, 0.37 mmol) and anhydrous sodium acetate (14 mg, 0.3 equiv) in acetic anhydride (5.0 mL) under argon was stirred vigorously at

(29) 1-Amino-3-butyne was prepared by alkylation of phthalimide with 3-butyn-1-ol (PPh_3, DEAD, THF; Mitsunobo, O. *Synthesis* **1981**, 1) and deprotection with methylamine (25 °C, benzene; Wolfe, S.; Hasan, S. K. *Can. J. Chem.* **1970**, *48*, 3572).

(30) Casara, P. *Tetrahedron Lett.* **1984**, *25*, 1891. *N*-Boc Propargylamine was prepared as described: Metcalf, B.; Casara, P. *Tetrahedron Lett.* **1975**, 3337. Metcalf, B.; Biy, P.; Danzin, C.; Jung, M.; Casara, P.; Vevert, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 2551.

110 °C (21 h). The cooled reaction mixture was diluted with water (25 mL) and extracted with methylene chloride (20 mL × 5). Removal of methylene chloride and residual acetic anhydride under reduced pressure and chromatography (SiO_2, 0–40% EtOAc–hexane) afforded pure **18b** (50 mg, 113 mg theoretical yield, 44%) as a pale yellow oil and **21** (18 mg, 73 mg theoretical yield, 25%) as a white, crystalline solid. For **18b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.34 (apparent p, 1 H, J = 6 Hz, H_2C=C=$CH$$CH_2$), 4.82 (m, 2 H, H_2C=C=CH), 4.62 (m, 2 H, H_2C=C-CHCH_2), 3.50 (s, 3 H, SO_2CH_3), 3.42 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.89 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.27 (br s, 3 H, $COCH_3$), 2.21 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 2983, 2931, 2288, 1957, 1734, 1677, 1558, 1534, 1391, 1313, 1243, 1215, 1183, 1166, 1127, 1045, 1012, 963, 915, 860, 759, 703, 657 cm^{-1}; EIMS, m/e (relative intensity) 307 (M^+, 10), 264 (base), 240 (6), 226 (28), 212 (1), 186 (91), 170 (3), 158 (5), 133 (5), 119 (17), 92 (8), 79 (14), 68 (21), 53 (36).

1-Acetyl-6,7-cyclopentenoindole (21). A solution of **18b** (46 mg, 0.149 mmol) in degassed triisopropylbenzene (TIPB, 4.6 mL) under argon was warmed at 195 °C (21 h), 220 °C (5 h). The reaction mixture was cooled to room temperature and chromatography (SiO_2, 0–10% EtOAc–hexane) afforded 1-acetyl-6,7-cyclopentenoindole (**21**, 17 mg, 30 mg theoretical yield, 57%) as a pale red solid: mp 117.5–118.5 °C (white needles, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33 (d, 1 H, J = 8 Hz, Ar H), 7.30 (d, 1 H, J = 4 Hz, CH=CHNCOCH$_3$), 7.19 (d, 1 H, J = 8 Hz, Ar H), 6.61 (d, 1 H, J = 4 Hz, CH=CHNCOCH$_3$), 3.44 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 3.02 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.62 (s, 3 H, $COCH_3$), 2.07 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$); IR (KBr) ν_{max} 2924, 1715, 1586, 1546, 1466, 1446, 1411, 1385, 1366, 1317, 1302, 1212, 1048, 1036, 958, 921, 906, 875, 813, 720 cm^{-1}; EIMS, m/e (relative intensity) 199 (M^+, 36), 189 (2), 163 (2), 157 (base), 129 (14), 115 (2), 102 (3), 89 (2), 77 (6), 63 (4), 51 (7); HRMS, m/e for $C_{13}H_{13}NO$ 199.0997, found 199.0999.

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.22; H, 6.67; N, 7.10.

A solution of **18b** (11.1 mg, 0.036 mmol) in 2-methoxyethyl ether (diglyme, 3.0 mL) was stirred at 160 °C (27.5 h). The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. Chromatography (SiO_2, 10% EtOAc–hexane eluant) afforded 1-acetyl-6,7-cyclopentenoindole (**21**, 6.3 mg, 7.2 mg theoretical yield, 87%) as a white crystalline solid.[32]

6-(2,3-Butadienyloxy)-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (20). 2,3-Butadien-1-ol (0.16 mL, 2.0 mmol)[31] was added to a slurry of sodium hydride (83 mg of 60% oil dispersion, 2.0 mmol) at 25 °C in tetrahydrofuran (5 mL). After 10 min, **12** (303 mg, 1.1 mmol, 0.55 equiv) was added and the resulting reaction mixture was stirred at 25 °C (20 min). The reaction mixture was diluted with cold water (20 mL) and extracted with methylene chloride (15 mL × 5). Removal of the solvent under reduced pressure and chromatography (SiO_2, 0–40% EtOAc–hexane, gradient elution) afforded 6-(2,3-butadienyloxy)-4,5-cyclopenteno-3-(methylsulfonyl)-1,2-diazine (**20**, 211 mg, 215 mg theoretical yield, 98%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.54 (p, 2 H, J = 7 Hz, H_2C=C=CH), 5.15 (m, 2 H, H_2C=C=CH), 4.88 (m, 2 H, H_2C=C=CHCH_2O), 3.45 (s, 3 H, SO_2CH_3), 3.36 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.95 (t, 2 H, J = 7 Hz, $CH_2CH_2CH_2$), 2.25 (p, 2 H, J = 7 Hz, $CH_2CH_2CH_2$); IR (neat) ν_{max} 2958, 2932, 2420, 2259, 1957, 1735, 1573, 1455, 1419, 1350, 1312, 1237, 1191, 1154, 1121, 1069, 966, 944, 906, 854, 766, 649, 620 cm^{-1}; EIMS, m/e (relative intensity) 266 (M^+, 3), 227 (1), 213 (3), 187 (35), 150 (4), 119 (26), 105 (2), 91 (10), 77 (7), 69 (base), 53 (95); HRMS, m/e for $C_{12}H_{14}N_2O_3S$ 266.0725, found 266.0725.

Attempts to promote the intramolecular Diels–Alder reaction of **20** (190–240 °C, TIPB, 12–48 h; diglyme, 130–160 °C, 24 h) resulted in the slow disappearance of **20** without the appearance of a [4 + 2] cycloadduct.[33]

Acknowledgment. This work was assisted by the financial support of the National Institutes of Health (CA 41986, 42056) and the Alfred P. Sloan Foundation.

Registry No. **6**, 1672-34-0; **8**, 36239-33-5; **9**, 1672-33-9; **11a**, 112740-78-0; **11b**, 112740-79-1; **11c**, 112740-80-4; **11d**, 112740-81-5; **11e**, 112740-82-6; **11f**, 37813-54-0; **11g**, 112740-83-7; **11h**, 112740-84-8; **12**, 112740-85-9; **13**, 112740-86-0; **14**, 112740-87-1; **15a**, 6250-96-0; **15b**, 112740-88-2; **15c**, 112740-89-3; **16a**, 112740-90-6; **16b**, 112740-91-7; **17**, 112740-92-8; **18a**, 112740-93-9; **18b**, 112740-94-0; **19**, 112740-95-1; **20**, 112740-96-2; **21**, 112740-97-3; Me_2NC≡CMe, 19006-23-6; $(MeO)_2C$=CH_2, 922-69-0; EtOCH=CH_2, 109-92-2; PhC≡CH, 536-74-3; $Me(CH_2)_5C$≡CH, 629-05-0; HC≡CCO_2Me, 922-67-8; EtOC≡CH, 927-80-0; PhC≡CCO_2Me, 4891-38-7; PhC≡CPh, 501-65-5; $MeCO_2C$≡CCO_2Me, 762-42-5; HC≡$C(CH_2)_2NH_2{\cdot}HO_2CCF_3$, 112740-98-4; $HO(CH_2)_2C$≡CH, 927-74-2; H_2NCH_2CH=C=$CH_2{\cdot}HO_2CCF_3$, 112740-99-5; HOCH$_2$CH=C=CH_2, 18913-31-0; HO_2CCH_2Cl, 79-11-8; *N*-(1-cyclopentenyl)morpholine, 936-52-7; *N*-(1-cyclopentenyl)pyrrolidine, 7148-07-4; 1-(trimethylsiloxy)cyclopentene, 19980-43-9; 1-(trimethylsiloxy)-1-phenylethene, 13735-81-4; 4-(1-phenylethenyl)-morpholine, 7196-01-2; 4-(1-ethyl-1-propenyl)morpholine, 13654-48-3; 1-ethene-2-pyrrolidinone, 88-12-0; 1-acetoxyethene, 108-05-4; cyclopentene, 142-29-0; 3,6-bis(methylthio)-4-ethoxypyridazine, 112741-00-1; 2-(1-methylene-2-propenyl)-4-methylsulfonyl-2,5,6,7-tetrahydro-1*H*-cyclopenta[*d*]pyridazin-1-one, 112741-01-2; 6-(2-oxo-2-phenethyl)-3-(methylthio)-1,2,4,5-tetrazine, 112741-02-3; potassium trithiocarbonate, 584-10-1; trithiocarbadiglycolic acid, 6326-83-6; thiocarbohydrazide, 2231-57-4.

Supplementary Material Available: Full experimental details for the preparation of 3,6-bis(methylthio)-1,2,4,5-tetrazine (**6**) are provided (4 pages). Ordering information is given on any current masthead page.

(31) Bailey, W. J.; Fujiwara, E. *J. Am. Chem. Soc.* **1955**, *77*, 165. Karlson, S.; Froyen, P.; Skattebol, L. *Acta Chem. Scand., Ser. B.* **1976**, *B30*, 664.

(32) Thermolysis of **18b** (DMF, 130 °C, 55 h) provided **19** (66%).

(33) Thermolysis of **20** (diglyme, 130–160 °C, 24 h) provided the product (37%) derived from Claisen rearrangement of the allene allyl ether: mp 134 °C dec (white needles, hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.50 (1 H, dd, J = 18, 11 Hz, H_2C=CH), 5.63 (s, 1 H, C=CH_2), 5.41 (1 H, s, C=CH_2), 5.26 (1 H, d, J = 11 Hz, cis H_2C=CH), 4.94 (1 H, d, J = 18 Hz, trans H_2C=CH), 3.29 (2 H, t, J = 7 Hz), 3.25 (s, 3 H, SO_2CH_3), 2.95 (2 H, t, J = 7 Hz), 2.23 (2 H, p, J = 7 Hz); IR (KBr) ν_{max} 3447, 2924, 1675, 1576, 1560, 1507, 1472, 1312, 1137, 965 cm^{-1}; EIMS, m/e (relative intensity) 266 (M^+, 15), 187 (8), 149 (13), 119 (8), 91 (6), 83 (9), 69 (base), 57 (43); CIMS (isobutane), m/e 267 (M^+ + H, base); HRMS m/e for $C_{12}H_{14}N_2O_3S$ 266.0725, found 266.0726.