given reaction type as predicted by the principle of least motion.[20] Thus, β is large for reactions requiring relatively little molecular reorganization in changing from ground to transition state, such as proton transfers from cyano carbon acids and single-electron transfers, and decreases in size for reactions requiring more molecular reorganization, such as E2 reactions.

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Registry No. 9-(*m*-ClC_6H_4)-fluorenyl, 73872-45-4; 9-PhS-fluorenyl, 71805-72-6; 2-$PhSO_2$-9-Ph-fluorenyl, 73872-40-9; (*p*-$CH_3OC_6H_4$)NSO_2CH_3, 84498-90-8; $C_6H_5NSO_2CH_3$, 61057-11-2; $C_6H_5NSO_2Ph$, 28627-70-5; (*m*-BrC_6H_4)NSO_2Ph, 84498-91-9; *p*-$CH_3OC_6H_4S^-$, 26971-83-5; $C_6H_5S^-$, 13133-62-5; *p*-$BrC_6H_4S^-$, 26972-20-3; 3,5-$Cl_2C_6H_3O^-$, 65800-69-3; 3,4,5-$Cl_3C_6H_2O^-$, 60154-34-9; 2,4,5-$Cl_3C_6H_2O^-$, 45773-92-0; 2,3,4,5-$Cl_4C_6HO^-$, 84498-92-0; 3-butenenitrile, 109-75-1.

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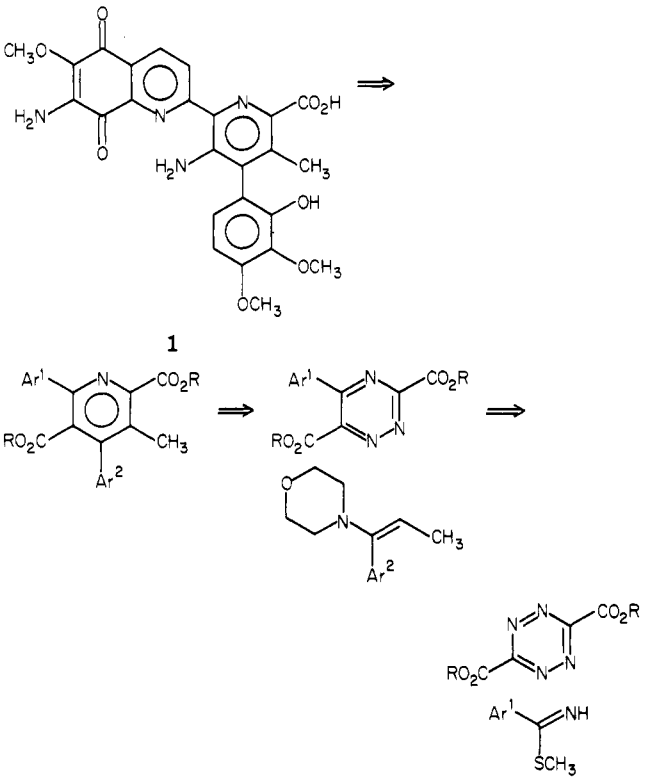
Formal Total Synthesis of Streptonigrin[1]

Summary: An efficient, formal total synthesis of streptonigrin (1) is detailed and is based on the implementation of two consecutive inverse electron demand Diels–Alder reactions: 1,2,4,5-tetrazine + *S*-methyl thioimidate (streptonigrin ABC ring construction) and 1,2,4-triazine + morpholino enamine (streptonigrin CD ring construction).

Sir: Streptonigrin (1) was first isolated from the broth of *Streptomyces flocculus* by Rao and Cullen,[2a] and through the chemical degradative and spectral studies of Woodward, Biemann, and Rao,[2b] the correct structure was proposed in 1963 and later confirmed in an X-ray crystal study.[2c] Since that time streptonigrin has been the subject of extensive biological and chemical studies.[3] It has been found to be active against Gram-positive and Gram-negative bacteria as well as a number of tumors including herpes simplex I/III and mouse mammary tumors. Although the toxicity associated with the administration of streptonigrin has decreased the potential clinical use of this agent, reports of its use in combination therapy with vincristine, prednisone, and bleomycin have been described.[3] Moreover, recent studies on the chemical mechanism by which streptonigrin exerts its biological effects, efforts to define the essential structural requirements for activity, and investigations on the biosynthesis of streptonigrin have renewed interest in this and related antitumor antibiotics.[4]

Scheme I



1

The complex structural features of streptonigrin (1), a substituted quinone quinoline possessing a pentasubstituted pyridine, the chemical and biological interest in streptonigrin, and the potential application of structurally related analogues have provided the incentive for much synthetic work[5] which has resulted in two reported total syntheses.[5a,b]

The synthetic utility of the inverse electron demand Diels–Alder reactions of heterocyclic azadienes has gone largely unrecognized due to the ambiguities concerning the mode of cycloaddition, the lack of useful, electron-rich dienophiles, and the lack of demonstrated or dependable synthetic procedures and applications. Herein, we disclose a short, convergent formal total synthesis of streptonigrin (1) based on the implementation of two consecutive inverse electron demand Diels–Alder reactions: the first for construction of the ABC ring system (1,2,4,5-tetrazine + *S*-

(1) Presented in part at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982.

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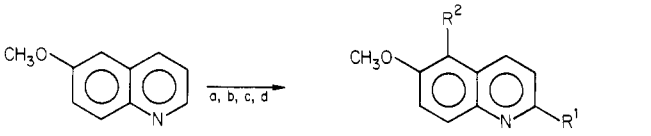
methyl thioimidate)[6a] and the latter for CD ring construction (1,2,4-triazine + morpholino enamine),[6b] Scheme I. This approach represents a simple, two-step assemblage of the entire carbon framework of streptonigrin (1), illustrates the synthetic potential of such processes, and indicates that this approach may be additionally suited for the preparation of streptonigrin analogues and related antitumor antibiotics.[4]

The substrate for the first Diels–Alder reaction was prepared as shown in Scheme II. Treatment of 6-methoxyquinoline (2)[7] with *p*-toluenesulfonyl chloride (1.6 equiv), potassium cyanide (3.0 equiv) in CH_2Cl_2–H_2O[8] for a prolonged reaction period (120 h, 25 °C) afforded 2-cyano-6-methoxyquinoline (**3**, 81%)[9] directly without isolation of the Reissert intermediate. Nitration cleanly yielded **4**[9] (1.5 equiv of 70% HNO_3 in H_2SO_4, 82%) and conversion of the nitrile to the *S*-methyl thioimidate **6**[9] (H_2S, dioxane, 78%; 2.0–4.0 equiv of CH_3I, CH_3CN, 80 °C; $NaHCO_3$, H_2O–$CHCl_3$, 56%)[10] completed the preparation of the required dienophile.

Scheme II[a]



2

3, R^1 = CN; R^2 = H
4, R^1 = CN; R^2 = NO_2
5, R^1 = C(=S)NH_2; R^2 = NO_2
6, R^1 = C(=NH)SCH_3; R^2 = NO_2

[a] (a) 1.6 equiv of *p*-TsCl, 3.0 equiv of KCN, CH_2Cl_2–H_2O, 120 h, 25 °C, 81%; (b) 1.5 equiv of 70% HNO_3, H_2SO_4, 25 °C, 82%; (c) H_2S, cat. Et_2NH, dioxane, 0–25 °C, 24 h, 75–80%; (d) 2–4 equiv of CH_3CN, 2 h, 80 °C; saturated aqueous $NaHCO_3$ –$CHCl_3$, 15 min, 25 °C, 56%.

Table I. Cycloaddition Reaction of 1,2,4-Triazine 8 with Morpholino Enamine 9

conditions: equiv of **9**, solvent, temp (time)	% yield[a] (**10**/**11**)
4.0, CH_3CN, 80 °C (12–24 h)	15–26 (4:1)[b]
2.0, CH_3CN, 120 °C (16 h)[c]	30 (1:1)
2.0–6.0, $CHCl_3$, 45–80 °C (12–48 h)	*d*
2.0, $CHCl_3$, 120 °C (16 h)[c]	30 (1:1)
4.0, $CHCl_3$, 120 °C (42 h)	68 (1:1)

[a] Yield of purified material isolated by column chromatography (SiO_2). [b] 35–45% 1,2,4-triazine **8** recovered. [c] Reaction run in a sealed reaction vessel. [d] Trace of **10** detected chromatographically.

Construction of the streptonigrin ABC ring system was accomplished by employing the inverse electron demand Diels-Alder reaction of dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (**7**)[11] with *S*-methyl thioimidate **6**[6a] (80 °C, dioxane, 22–24 h) and gave the quinoline substituted 1,2,4-triazine **8**[9] (72%). In contrast to the results of related studies, aryl *S*-methyl thioimidates, e.g., **6**, behave as dependable heterodienophiles with **7** and no trace of competing reactions or cycloadditions could be detected.[6a] Treatment of **8** with the morpholino enamine of 2-(benzyloxy)-3,4-dimethoxypropiophenone **9**[12] afforded **10** and finished the construction of the pentasubstituted pyridine and completed the assemblage of the tetracyclic carbon skeleton of streptonigrin (Scheme III). The conversion of **10** to **12**, a key intermediate in the synthesis of streptonigrin (**1**) described by Kende and co-workers,[5a] completed the formal synthesis.

Table I summarizes representative details of our investigation of the pyridyl biaryl CD ring construction of streptonigrin. In agreement with the results of our preliminary study probing the mode of cycloaddition of 3,5,6-tricarboethoxy-1,2,4-triazine with aryl pyrrolidine enamines,[6b] the morpholino enamine **9**[12] cycloadds exclusively across C-3/C-6 of 1,2,4-triazine **8** and the nucleophilic carbon of the electron-rich dienophile prefers attack at C-3. However, the decreased reactivity of **8** towards cycloaddition and the relative instability of the morpholino enamine **9**[12] dictate a select set of reaction conditions for cycloaddition (Table I). Although the factors governing the regioselectivity are not completely understood, the

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(9) All new compounds gave satisfactory C, H, N analysis (±0.40%) or high-resolution mass spectral information and exhibited the expected ^1H NMR, ^{13}C NMR, IR, and mass spectral characteristics consistent with the assigned structure.

3: mp 175–176 °C; ^1H NMR ($CDCl_3$) δ 8.70 (2 H, t, *J* = 12 Hz, aromatic), 7.68 (1 H, s, aromatic), 7.67–7.07 (2 H, m, aromatic), 3.96 (3 H, s, Ar OCH_3); ^{13}C NMR ($CDCl_3$) δ 160.0 (C-6), 144.6 (C-8a), 135.6 (C-4), 131.5 (C-8), 130.8 (C-4a/C-2), 130.3 (C-2/C-4a), 124.6 (C-5), 123.8 (C-3), 117.9 (-CN), 104.7 (C-7), 55.8 (Ar OCH_3). Anal. Calcd for $C_{11}H_8N_2O$: C, 71.72; H, 4.38; N, 15.21. Found: C, 71.45; H, 4.21; N, 15.00.

4: mp 140–142 °C dec; ^1H NMR ($CDCl_3$) δ 8.26 (2 H, 5, *J* = 12 Hz, aromatic), 7.75 (1 H, d, *J* = 12 Hz, aromatic), 7.67 (1 H, d, *J* = 12 Hz, aromatic), 4.14 (3 H, s, Ar OCH_3); ^{13}C NMR (Me_2SO-d_6) δ 151.2 (C-6), 141.2 (C-8a), 134.4 (C-4), 133.2 (C-5), 131.9 (C-2), 130.8 (C-8), 126.3 (C-3), 121.2 (C-4a), 119.7 (C-7), 114.1 (CN), 57.8 (Ar OCH_3). Anal. Calcd for $C_{11}H_7N_3O_3$: C, 57.64; H, 3.08; N, 18.34. Found: C, 57.28; H, 3.00; N, 18.45.

5: mp 236–246 °C dec; ^1H NMR (Me_2SO-d_6) δ 10.20 (2 H, br s, NH_2), 8.43 (1 H, d, *J* = 9 Hz, aromatic), 8.31 (2 H, t, *J* = 11 Hz, aromatic) 8.03 (1 H, d, *J* = 9 Hz, aromatic), 4.12 (3 H, s, Ar OCH_3); ^{13}C NMR (Me_2SO-d_6) δ 194.0 (Ar C=S), 150.4 (C-6), 150.1 (C-2), 139.2 (C-8a), 134.5 (C-4), 133.6 (C-5), 129.5 (C-8), 123.7 (C-3), 120.9 (C-4a), 118.6 (C-7), 57.7 (Ar OCH_3). Anal. Calcd for $C_{10}H_9N_3O_3S$: C, 50.19; H, 3.44; N, 15.97. Found: C, 50.00; H, 3.42; N, 16.10.

6: mp 190–192 °C; ^1H NMR ($CDCl_3$) δ 8.28 (1 H, d, *J* = 12 Hz, aromatic), 8.25 (1 H, d, *J* = 12 Hz, aromatic), 8.18 (1 H, s, NH), 8.07 (1 H, d, *J* = 12 Hz, aromatic), 7.60 (1 H, d, *J* = 12 Hz, aromatic), 4.09 (3 H, s, Ar OCH_3), 2.45 (3 H, s, SCH_3); ^{13}C NMR (Me_2SO-d_6) δ 169.4 (C=NH), 153.3 (C-6), 149.8 (C-2), 140.2 (C-8a), 134.2 (C-4), 133.5 (C-5), 130.0 (C-8), 121.1 (C-4a), 120.9 (C-3), 118.2 (C-7), 57.5 (Ar OCH_3), 11.4 (SCH_3). Anal. Calcd for $C_{12}H_{11}N_3SO_2$: C, 51.98; H, 3.98; N, 15.16. Found: C, 51.58; H, 4.04; N, 14.89.

8: mp 230–235 °C; ^1H NMR ($CDCl_3$) δ 8.77 (1 H, d, *J* = 11 Hz, aromatic), 8.28 (1 H, d, *J* = 11 Hz, aromatic), 8.21 (1 H, d, *J* = 12 Hz, aromatic), 7.67 (1 H, d, *J* = 12 Hz, aromatic), 4.17 (3 H, s, CO_2CH_3), 4.13 (3 H, s, CO_2CH_3), 4.10 (3 H, s, Ar OCH_3); ^{13}C NMR (Me_2SO-d_6) 164.9 (C=O), 161.8 (C=O), 155.7 (C-2′), 151.6 (C-5′), 151.0 (C-6), 150.9 (C-6′/C-2), 149.0 (C-2/C-6′), 140.3 (C-8a), 134.4 (C-4), 133.5 (C-5), 131.1 (C-8), 122.2 (C-4a), 121.5 (C-3), 119.3 (C-7), 57.7 (Ar OCH_3), 53.5 (CO_2-CH_3), 53.3 (CO_2CH_3); high-resolution MS *m/e* for $C_{17}H_{13}N_5O_7$ requires 399.0814, found 399.0787.

Spectra of compound **10** were identical in all respects with spectra of authentic **10** provided by Professor A. S. Kende. **10**: ^1H NMR ($CDCl_3$) δ 8.64 (1 H, d, *J* = 11 Hz, aromatic), 8.35–8.02 (2 H, m, aromatic), 7.48 (1 H, d, *J* = 11 Hz, aromatic), 7.20–6.95 (5 H, m, Ph), 6.86 (1 H, d, *J* = 11 Hz, aromatic), 6.72 (1 H, d, *J* = 8 Hz, aromatic), 5.06 (1 H, d, *J* = 13 Hz, CH_2), 4.81 (1 H, d, *J* = 13 Hz, CH_2), 4.06 (3 H, s, CO_2CH_3/Ar OCH_3), 4.02 (3 H, s, CO_2CH_3/Ar OCH_3), 3.93 (3 H, s, Ar OCH_3), 3.90 (3 H, s, Ar OCH_3), 3.62 (3 H, s, CO_2CH_3), 2.26 (3 H, s, Ar CH_3); high-resolution MS *m/e* for $C_{35}H_{31}O_{10}N_3$ requires 653.2007, found 653.2019.

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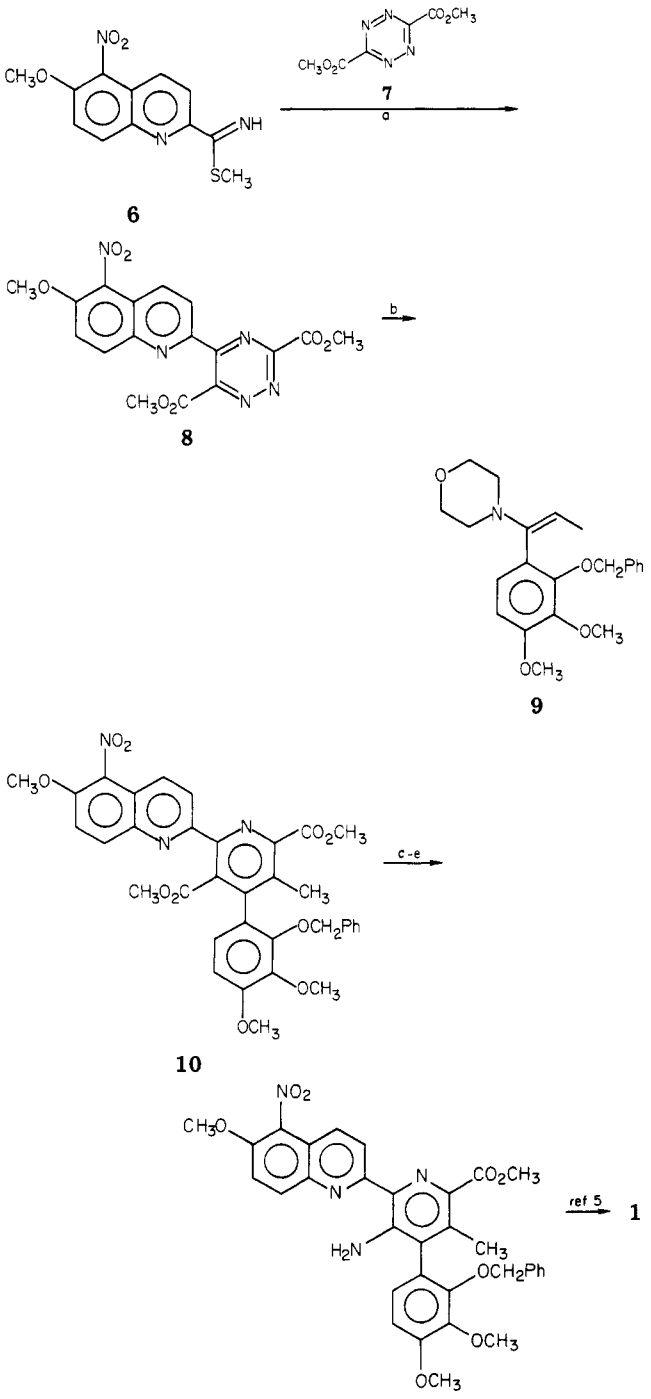
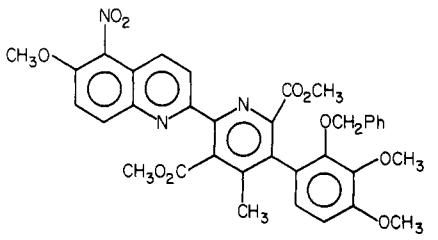
(12) 2-(Benzyloxy)-3,4-dimethoxypropiophenone was prepared as described: Liao, T. K.; Wittek, P. J.; Cheng. C. C. *J. Heterocycl. Chem.* **1976**, *13*, 1283. Morpholino enamine **9** was prepared with the aid of $TiCl_4$; see White, W. A.; Weingarten, H. *J. Org. Chem.* **1967**, *32*, 213. The instability of the pyrrolidine enamine of 2-(benzyloxy)-3,4-dimethoxypropiophenone precluded its use in a successful cycloaddition with 1,2,4-triazine **8**.

Scheme III[a]



[a] (a) dioxane, 80 °C, 24 h, 2.0 equiv of 7, 72%; (b) see Table I. (c) 12.0 equiv of PhSeNa, THF-HMPA, 70 °C, 36 h; CH_3OH, HCl cat., 25 °C, 18-22 h; (d) 5.0 equiv of $(PhO)_2P(O)N_3$, benzene, reflux, 2.5 h; H_2O, reflux, 2.5 h; (e) excess CH_3I, K_2CO_3, THF, 65 °C, 22 h, 16% from 10.

results in Table I indicate a clear trend, illustrating that the vigorous reaction conditions required for complete reaction eliminate the observed regioselectivity and as such the choice of reaction conditions[13] can determine the relative amount of 11.



11

Thus, the successive implementation of two inverse electron demand Diels-Alder reactions of heterocyclic azadienes provided the basis for a simple, convergent formal total synthesis of streptonigrin (1). A continued study of the factors governing the mode and regioselectivity of the cycloaddition reactions of 1,2,4-triazines, efforts to improve this approach to streptonigrin (1), and extension of this methodology to the synthesis of related antitumor antibiotics will be reported in due course.

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Registry No. 1, 3930-19-6; 2, 5263-87-6; 3, 5467-79-8; 4, 83220-09-1; 5, 83220-10-4; 6, 83220-11-5; 7, 2166-14-5; 8, 83220-12-6; 9, 83220-13-7; 10, 83220-14-8; 11, 83220-15-9.

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N-Acyl-β-enamino Ketones: Versatile Heterocyclic Synthons[1]

Summary: *N*-Acyl-β-enamino ketones are readily prepared from the potassium enolates of methyl ketones and diethyl *N*-(substituted)dithiocarbonimidates in tetrahydrofuran at room temperature; use of the corresponding isothiourea allows introduction of an NEt_2 substituent into the 3-position of the enamino ketone. 1,3-Oxazinium and 1,3-thiazinium salts are readily formed from these *N*-acyl-β-enamino ketones on treatment with 70% $HClO_4$ in Ac_2O or CF_3SO_3H.

Sir: In recent papers[2] a versatile synthesis of functionalized 1,5-enediones and their application in pyridine syntheses were described. We now report an equally versatile route to their nitrogen-containing analogues, *N*-acyl-β-enamino ketones, and the application of these enamino ketones in the synthesis of functionalized six-membered heterocyclic systems such as 1,3-oxazinium and 1,3-thiazinium salts. *N*-Acyl-β-enamino ketones have been

(13) All attempts to catalyze the cycloaddition reaction of 8 with 9 by the addition of conventional Lewis acid catalysts ($AlCl_3$, BF_3·OEt_2, anhydrous $FeCl_3$, $Cu(BF_4)_2$, $Cu(AcAc)_2$, $Co(AcAc)_2$, and $Ni(AcAc)_2$) lead to decomposition of enamine 9.

(14) Chicago Community Trust Co./Searle Scholar recipient, 1981-1985.

(1) (a) Partial support of this work by NSF Grant CHE 79-01704 is gratefully acknowledged. (b) Abstracted in part from the Ph.D. thesis of G.R.T. (1980).

(2) Potts, K. T.; Cipullo, C.; Ralli, P.; Theodoridis, G. *J. Am. Chem. Soc.* **1981**, *103*, 3584, 3585; *J. Org. Chem.* **1982**, *47*, 3027.

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