(positive NOE's observed between H-2′$_{ax}$ and H-6′$_{ax}$, and H-3′$_{ax}$ and H-5′$_{ax}$) and that the indole rings are approximately perpendicular to the piperazine ring (positive NOE's observed between H-2′$_{ax}$ and H-2, and H-3′$_{eq}$ and H-2, positive NOE's observed between H-6′$_{ax}$ and H-4″, and H-5′$_{ax}$ and H-2″ as well as between H-6′$_{ax}$ and H-2″, and H-5′$_{ax}$ and H-4″).

The biogenesis of dragmacidin clearly involves the combination of two tryptamine units. Occurrence of hydroxyindole or hydroxytryptamine groups in marine natural products is limited to the presence of serotonin and N-methylated analogues[22] and the topsentins.[23] With the unusual location of hydroxyl in one of the indole rings, and the presence of the unoxidized piperazine ring, dragmacidin represents a new class of indole alkaloids in the marine environment.

Experimental Section

The sponge was collected June 6, 1984, by a Johnson-Sea-Link submersible at a depth of 148 m at Sweetings Cay, Bahamas, and stored frozen. A sample (94 g) of the fresh sponge was homogenized and extracted with methanol–toluene (3:1). The residue from evaporation was triturated with ethyl acetate to yield an oil (1.1 g), a portion of which (0.5 g) was chromatographed by vacuum liquid chromatography[24] (silica gel, *i*-PrOH–$CHCl_3$ (1:1)) to provide dragmacidin (**1a**, 90 mg) as a white powder.

Dragmacidin (1a): $[\alpha]^{20}_D$ −3 (*c* 13.2, acetone); IR (KBr) 3420, 3280, 1610 cm^{-1};) UV (MeOH) 220 nm (ϵ 52600), 275 (11700), 286 (sh, 10900), 293 (sh, 10100); ^{1}H NMR (360 MHz, acetone-d_6), see Table I; ^{13}C NMR (90 MHz, acetone-d_6), see Table I; HRFABMS, M$^+$ + H, obsd *m/z* 580.9173, $C_{21}H_{19}Br_3N_4O$, Δ 2.4 mmu.

Triacetyldragmacidin (1b). With use of standard reaction conditions and workup, dragmacidin (**1a**, 20 mg, 0.003 mmol) was treated with excess acetic anhydride and pyridine overnight and at room temperature. The residue was purified by chromatography on silica gel to obtain the triacetate **1b** (9.0 mg, 42%): ^{1}H NMR (acetone-d_6) δ 10.75 (br s, 1 H), 8.63 (d, 1 H, *J* = 1.8 Hz), 7.75 (d, 1 H, *J* = 8.6 Hz), 7.68 (s, 1 H), 7.65 (br s, 1 H), 7.45 (dd, 1 H, *J* = 1.8, 8.6 Hz), 7.23 (s, 1 H) 5.80 (m, 1 H), 4.17 (m, 1 H), 4.02 (m, 2 H), 3.31 (dd, 1 H, *J* = 5.4, 12.4 Hz), 2.92 (dd, 1 H, *J* = 6.1, 12.4 Hz), 2.67 (s, 3 H), 2.43 (s, 3 H), 2.29 (s, 3 H), 2.08 (s, 3 H); FABMS, *m/z* (relative intensity, bromine composition) 708 (M$^+$, 48, Br_3), 666 (34, Br_3), 588 (22, Br_3), 388 (11, Br_2), 357 (17, Br_2), 346 (13, Br_2), 333 (18, Br_2), 320 (45, Br), 304 (9, Br_2), 291 (100, Br_2), 278 (53, Br), 236 (38, Br), 221 (12, Br), 195 (20, Br); HREIMS, *m/z* 705.9406, $C_{27}H_{25}N_4O_4Br_3$, Δ −2.8 mmu.

Tridebromodragmacidin (1c). An ethanolic solution (5 mL) of dragmacidin (**1a**, 13 mg, 0.002 mmol) and 10% Pd/C (ca. 1 mg) were shaken overnight at room temperature under 20 psi of hydrogen. The catalyst was removed by filtration and the filtrate evaporated. The residue was purified by chromatography on silica gel (chloroform/methanol 9:1) to obtain tridebromodragmacidin (**1c**) (7.0 mg, 90%): ^{1}H NMR (360 MHz, MeOH-d_4), see Table I; ^{13}C NMR (90 MHz, MeOH-d_4), see Table I; HRFABMS, M$^+$ + 1, obsd *m/z* 347.1870, Δ 0.2 mmu.

Acknowledgment. Mass spectral determinations were performed at the University of Illinois and by the Midwest Center for Mass Spectrometry, Lincoln, NE, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE 8211164). Harbor Branch Oceanographic Institution Contribution Number 639.

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Lanthanides in Organic Synthesis. Samarium Metal Promoted Selective Formation of Azoxy Compounds

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Application of lanthanides to organic synthesis has recently received more and more attention.[1] However, relatively few reports on the direct use of lanthanide metals in organic synthesis could be found.[2] We wish to report here the use of samarium metal (Sm) in selective synthesis of aromatic azoxy compounds from reduction of nitroarenes.

There are many methods for preparation of azoxy compounds by reduction of nitro compounds.[3] However, since side reactions (e.g., dehalogenation, polymerization, etc.) usually accompany the reductions, their use is limited. On the other hand, little information on the reduction of nitro compounds with lanthanides is currenty available.[1,4] Samarium diiodide (SmI_2) was reported to reduce nitrobenzenes to give the corresponding anilines.[4] However, the nitro group in nitrobenzaldehyde was not reduced by SmI_2.[4a,b]

In our studies on application of lanthanide elements to organic reactions,[2d,e,5] we found that Sm metal can reduce various nitroarenes (**1**) to give the corresponding azoxy compounds (**2**) selectively; a bromine, iodine, or carbonyl group in the substrates is retained. We now report the lanthanide metal mediated reduction of nitroarenes, which constitutes a new method for the synthesis of azoxy compounds.

Table I summarizes the results of the reaction of nitrobenzene with Sm and Yb metals under various reaction conditions. As shown in the table, reaction of nitrobenzene with Yb gives a mixture of azoxybenzene, *N*-phenylhydroxylamine, and aniline (run 1). However, in the case of Sm under the same conditions, azoxybenzene is formed selectively with 49% starting nitrobenzene recovered (run 2, Table I). Addition of both hexamethylphosphoric triamide (HMPA) and increased amounts of methanol greatly increased the reducing power of Sm (runs 3 and 5, Table I). A lower yield of the reduction product was obtained under refluxing conditions (run 4, Table I), the reason for which is not clear. The results of the lanthanide

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Table I. Reduction of Nitrobenzene with Lanthanide Metals[a]

run	Ln	Ln:$PhNO_2$, mmol	MeOH, mL	HMPA, mL	product yield, %[b,c] PhN=N-(→O)Ph	PhN=NPh	PhNHOH	$PhNH_2$	$PhNO_2$
1	Yb	1.5:0.5	0.5		33		46	5	
2	Sm	1.5:0.5	0.5		44				49
3	Sm	1.5:0.5	0.5	0.5	70	2			28
4	Sm	1.5:0.5[d]	0.5	0.5	13				86
5	Sm	1.5:0.5	2.0	0.5	78	19			

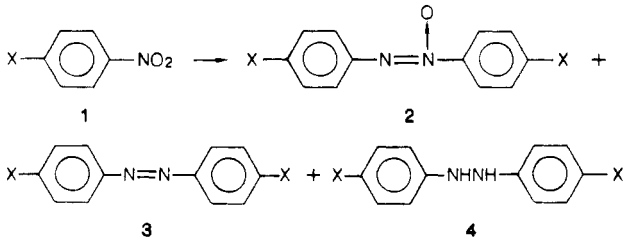
[a] All reactions were carried out at room temperature for 18 h in THF (4 mL) unless otherwise noted. [b] Isolated yield. [c] Retention time (min): PhN=N(→O)Ph; 9.68 at 200 °C; PhN=NPh, 4.11 at 200 °C; PhNHOH, 3.21 at 70 °C; $PhNH_2$, 4.11 at 70 °C; $PhNO_2$, 5.32 at 70 °C with an Apiezon L column (3 m). [d] 65 °C.

Table II. Reduction of Nitroarenes 1 with Lanthanide Metals[a]

run	Ln	X	Ln:1, mmol	product yield, %[b] 2	3	4
1	Sm	Me	1.5:0.5	79	5	
2	Yb	Me	2.5:0.5[c]	36[d]		
3	Sm	MeO	1.5:0.5	55		
4	Yb	MeO	2.0:0.5[c]	45[e]		
5	Sm	Cl	1.0:0.5	83		
6	Sm	Cl	1.5:0.5	59	10	30
7	Sm	Cl	2.0:0.5	11	14	71
8	Sm	Br	1.0:0.5	83		
9	Sm	I	1.0:0.5	81		
10	Sm	CN	1.0:0.5[f]	55	6	
11	Sm	MeCO	1.0:0.5[g]	70		
12	Sm	EtO_2CCH=CH	1.0:0.5	*h*		

[a] All reactions were carried out at room temperature for 18 h in THF (4 mL)/HMPA (0.5 mL)/MeOH (2 mL) unless otherwise noted. [b] Isolated yield. [c] MeOH (0.5 mL). No HMPA used. [d] *p*-Toluidine was also formed in 22% yield. [e] *p*-Anisidine was also formed in 36% yield. [f] Room temperature, 2.5 h. Prolonged reaction time gave complex products. [g] Room temperature, 4 h. [h] The corresponding ester-exchanged azoxy compound *p*-MeO_2CCH=CHC_6H_4N=N(→O)-C_6H_4CH=$CHCO_2Me$ was formed in 90% yield.

metal mediated reaction of various nitroarenes are summarized in eq 1 and Table II.



(1)

One can see from Table II that under proper conditions, a variety of nitroarenes (**1**) can be selectively reduced by Sm metal to their corresponding azoxy compounds (**2**). It also appears that Sm is more suitable than Yb for synthesis of azoxy compounds (runs 1 vs 2 and 3, Table I; runs 1 vs 2 and 3 vs 4, Table II). Interestingly, the bromine and iodine in the substrates remain unaffected during the reaction (runs 8 and 9, Table II), although iodobenzene itself reacts easily with Sm metal at room temperature.[5b,6] In the case of *p*-nitroacetophenone (run 11, Table II), the reaction occurred selectively at the nitro group rather than the carbonyl group which is in marked contrast to the reaction with SmI_2. In the latter case, the carbonyl group was preferentially reduced.[4a,b] In the reaction of ethyl 4-nitrocinnamate (run 12, Table II), the ester-exchanged azoxy derivative was obtained, and the C–C double bond

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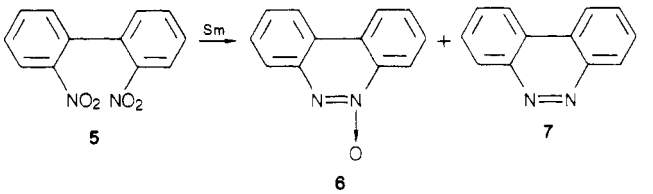
Scheme I



Sm: **5** **6** **7** **8**
2 : 0.5 18% 24% 40%
4 : 0.5 12% 65% 22%

in the substrate was not affected, although C–C multiple bonds conjugated with aromatic rings can be easily reduced by Yb metal.[2d] In the case of *p*-chloronitrobenzene, 2 equiv of Sm gave the azoxy compounds **2** selectively (run 5, Table II), whereas 4 equiv of Sm resulted in the formation of the corresponding hydrazine compound **4** as a main product (run 7, Table II). This result shows that it is possible to obtain different reduction products only by changing the ratio of Sm metal to nitro compounds.

It was also found that reaction of 2,2′-dinitrobiphenyl (**5**) with 8 equiv of Sm metal gave benzo[*c*]cinnoline *N*-oxide (**6**) and benzo[*c*]cinnoline (**7**) in 12% and 65% yields, respectively (Scheme I).

As described above, the present reaction has some notable characteristics compared with other methods for the synthesis of azoxy compounds.[3] For example, in the reduction of bromo- and iodonitrobenzenes by Mg[3c] and Tl[3g] metals in MeOH or Al reagents,[3f] since the halogens were usually eliminated, or complex products were formed, no haloazoxy derivatives or only low yields of them could be obtained. In the reduction of alkyl-substituted nitrobenzenes by sodium alcoholates, polymers were usually formed, and little azoxy compounds could be obtained.[3b,h] In contrast, in our cases none of these side reactions was observed (runs 1, 8, 9, and 11, Table II). Therefore, the present method, because of its simplicity and high selectivity, constitutes a useful alternative to the commonly accepted procedures for the synthesis of azoxy compounds.

Experimental Section

General Methods. Infrared spectra were recorded on a Hitachi 270-30 IR spectrometer. ^1H NMR were recorded on a Hitachi R-600 spectrometer and are reported in ppm from internal tetramethylsilane on the δ scale with splitting pattern and relative integrated area. The letter designates the multiplicity of the signal: s, singlet; d, doublet; t, triplet, m, multiplet. Mass spectra were obtained on a JEOL GC-MS JMS-GH-100 apparatus. Analytical GLC was carried out on a Shimadzu GC-3BF gas chromatograph equipped with a flame ionization detector using a 1.5 m × 3 mm stainless steel column packed with Apiezon L on Chromosorb W. Melting points were taken on a Yanaco micro melting point apparatus and are uncorrected. Samarium (20 mesh) and ytterbium (40 mesh) metals were obtained from Rare Metallic Co. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2 prior to use. The starting nitro compounds were commercial grades and purified by distillation or recrystallization

before use. All reactions were carried out under N_2.

Reactions of Nitro Compounds. In a 50-mL centrifuge tube were placed a magnetic stirring bar and a proper amount of Sm powder under air, and the tube was sealed with a serum cap. Pure nitrogen was then passed through, and the Sm was dried by heating under the stream of nitrogen. Two drops of allyl iodide was added by a micro syringe and the metal was heated slightly by a heat gun to activate the Sm metal.[7] Addition of 2 mL of THF gave a dark blue slurry, which after introduction of 0.5 mL of HMPA became purple. To this slurry was dropped the proper amount of nitro compounds with THF (2 mL) and MeOH (2 mL) by a syringe, and the mixture was then stirred at room temperature for the proper time (see the tables, Scheme I, and the related discussion in the text). The products were treated with 2 N HCl and then extracted with ether or CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the products were isolated by medium-pressure liquid chromatography (silica gel) and identified by NMR, IR, mass spectra, melting point, and retention time comparison with those of authentic samples (Table I). Some physical properties of the products are recorded below.

Azobenzene: mp 68–69 °C (lit.[8] mp 68 °C); mass spectrum, *m/e* 182 (M^+).

Azoxybenzene: mp 35–36 °C (lit.[9] mp 36 °C); mass spectrum, *m/e* 198 (M^+).

4,4'-Dimethylazoxybenzene: mp 68–69 °C (lit.[10] mp 68 °C); ^1H NMR (CCl_4) δ 2.40, 2.43 (a pair of s, 6 H), 7.09–7.40 (m, 4 H), 7.98–8.24 (m, 4 H); mass spectrum, *m/e* 226 (M^+).

4,4'-Dimethoxyazoxybenzene: mp 119–120, 135–137 °C (lit.[10] mp 118, 136 °C); ^1H NMR (CCl_4) δ 3.86 (s, 6 H), 6.94 (d of d, J = 8.0, 1.2 Hz, 4 H), 8.24 (d of d, J = 8, 1.2 Hz, 4 H); mass spectrum, *m/e* 258 (M^+).

4,4'-Dichloroazoxybenzene: mp 156–157 °C (lit.[10] mp 155–156 °C); mass spectrum, *m/e* 267 (M^+).

4,4'-Dichloroazobenzene: mp 188–189 °C (lit.[11] mp 186–187 °C); mass spectrum, *m/e* 251 (M^+).

1,2-Bis(4-chlorophenyl)hydrazine: mp 128–129 °C (lit.[12] mp 122 °C); ^1H NMR (CCl_4) δ 5.48 (br s, 2 H), 6.67 (d, J = 8.0 Hz, 4 H), 7.12 (d, J = 8.0 Hz, 4 H); mass spectrum, *m/e* 253 (M^+).

4,4'-Dibromoazoxybenzene: mp 173–175 °C (lit.[13] mp 175 °C); mass spectrum, *m/e* 356 (M^+).

4,4'-Diiodoazoxybenzene: mp 208–210 °C (lit.[14] mp 207–208 °C); mass spectrum, *m/e* 450 (M^+).

4,4'-Dicyanoazoxybenzene: mp 222–223 °C (lit.[15] mp 221 °C); IR (KBr) 2228 cm^{-1} (CN); mass spectrum, *m/e* 248 (M^+).

4,4'-Dicyanoazobenzene: mp 282 °C (sublime); IR (KBr) 2228 cm^{-1} (CN); mass spectrum, *m/e* 232 (M^+).

4,4'-Diacetylazoxybenzene: mp 191–193 °C; ^1H NMR ($CDCl_3$) δ 2.65, 2.68 (a pair of s, 6 H), 7.86–8.70 (m, 8 H); IR (KBr) 1690 cm^{-1} (CO); mass spectrum, *m/e* 282 (M^+).

Dimethyl 4,4'-azoxycinnamate: mp 221–223, 276–278 °C (lit.[16] mp 219–221, 254–257 °C); ^1H NMR ($CDCl_3$) δ 3.82 (s, 6 H), 6.49 (d of d, J = 16.2, 1.8 Hz, 2 H), 7.48–8.44 (m, 10 H); IR (KBr) 1728 cm^{-1} (CO); mass spectrum, *m/e* 366 (M^+).

Benzo[*c*]cinnoline *N*-oxide (6): mp 139–140 °C (lit.[17] mp 139 °C); mass spectrum, *m/e* 196 (M^+).

Benzo[*c*]cinnoline (2): mp 157–158 °C (lit.[3f] mp 156 °C); mass spectrum, *m/e* 180 (M^+).

Acknowledgment. This research was supported in part by Grant-in-Aids from the Ministry of Education, Science and Culture.

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Regiospecific Synthesis of Arenesulfonamide Derivatives of 3,5-Diamino-1,2,4-triazole[1]

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For several years we have been engaged in a search for new herbicides which act by inhibiting the enzyme acetolactate synthase.[3] We have needed substantial quantities of *N*-(5-amino-1*H*-1,2,4-triazol-3-yl)arenesulfonamides **1** as part of that program. A straightforward approach to **1** involving the reaction of arenesulfonyl chlorides with 3,5-diamino-1,2,4-triazole is not operable due to the multiple sites of reaction for the latter compound toward electrophiles.[4] Consequently, we chose to explore new approaches to **1**.

We have developed a new synthesis of **1** which addresses the problem of regiocontrol in the introduction of the arylsulfonyl functionality (Scheme I). The general strategy is derived from an approach to the regioselective synthesis of derivatives of 3,5-diamino-1,2,4-triazole in which the exocyclic nitrogen atoms bear alkyl groups.[6] We have observed that dimethyl *N*-cyanodithiocarbonimidate (**2**) reacts with arenesulfonamides **3** under basic conditions to give *N'*-cyano-*N*-(arylsulfonyl)-*S*-methylisothioureas **4** in good yield (Table I). The bases that have been employed for this conversion are NaOH or K_2CO_3. Intermediates **4** react with hydrazine to afford **1** (Table II). An excess of hydrazine greater than 2 equiv is required for the latter reaction to proceed at a convenient rate. The examples illustrate the variety of aryl substitutions that are tolerated in this synthesis.

An alternative approach to **4** is illustrated in the synthesis of **4d** in Scheme II. Compound **3d** is reacted with base and CS_2 followed by CH_3I to afford **5** in 61% yield. Reaction of **5** with cyanamide under basic conditions gave **4d** in 69% yield.

Future reports will detail the utilization of **1** in the synthesis of herbicidal arenesulfonamide derivatives of 2-amino-1,2,4-triazolo[1,5-*a*]pyrimidine.[7]

Experimental Section[8]

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Arenesulfonamides **3d**,[9] **3f**,[10] **3g**,[11] and **3h**[12] were

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