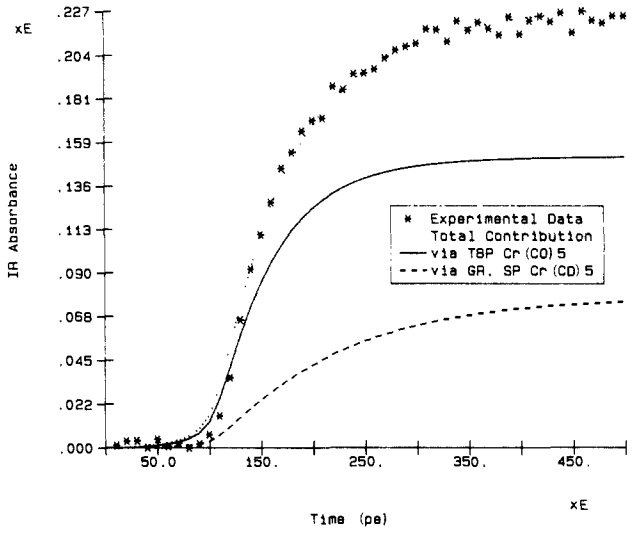

Figure 3. Increase in infrared absorbance at 1961 cm^{-1} by $Cr(CO)_5$·cyclohexane. The calculated individual contributions of ground state square pyramid (SP) and trigonal bipyramid (TBP) geometries are shown separately.

of $Cr(CO)_5$ (SP) which are equal to the gas-phase frequencies[6,7] also have been observed in our experiment with the same time transient.

Figure 2 shows that the rate of $Cr(CO)_6$ disappearance in cyclohexane solution is at the resolution limit of the apparatus. This absorption at 1986 cm^{-1} is similar to the gas-phase frequency, and the transient decay is significantly faster than the final product appearance rate.

Figure 3 shows the transient absorption at 1961 cm^{-1} which is the reported frequency of $Cr(CO)_5$·(CH) (CH = cyclohexane) with E symmetry.[15] The risetime is faster than the decay rate for "naked" $Cr(CO)_5$, which suggests that another channel exists for formation of $Cr(CO)_5$·(CH).

We propose that reaction mechanism 1 is compatible with both polarized light photolysis[16] and a theoretical model of dissociation.[17] In this model the excited state of $Cr(CO)_6$ correlates with an excited state of $Cr(CO)_5$ which decays to triplet trigonal bipyramid (TBP) and singlet square pyramid species (SP).

$$\begin{array}{ccccc} Cr(CO)_6{}^* & \xrightarrow{k_1} & Cr(CO)_5{}^* & \xrightarrow{k_2} & Cr(CO)_5\ (TBP) \\ & & \downarrow{\scriptstyle k_4} & & \downarrow{\scriptstyle k_3}\ L=CH \\ & & Cr(CO)_5\ (SP) & \xrightarrow[L=CH]{k_5} & Cr(CO)_5{\cdot}L \end{array} \qquad (1)$$

The curves in Figures 1-3 and another transient at 1920 cm^{-1} (not shown) were fit with a self-consistent set of rate constants by a response function deconvolution fitting procedure. We report the fitting results as first order or pseudo-first-order rate constants (s^{-1}) with standard deviation estimates of about 30%. The rate constants for k_1, k_2, k_3, k_4, and k_5 are $\geq 4.2 \times 10^{11}$, 2.5×10^{11}, 2.0×10^{10}, 1.3×10^{11}, and 8.6×10^{9}, respectively.

In addition, we tentatively have assigned a transient signal at a frequency of 1920 cm^{-1} for triplet state $Cr(CO)_5$ (TBP) that is compatible with the proposed kinetics. The 2.3 times faster reactivity of triplet state $Cr(CO)_5$ (TBP) than (SP) is interesting and suggests that the geometry or electronic configuration of unsaturated coordination is important in reactivity.

Acknowledgment. We acknowledge the financial support of the Medical Free Electron Laser Program of the Strategic Defense Initiative Organizations through the Midwest Biolaser Institute.

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Stereoselective Synthesis of (±)-Indolizidines 167B, 205A, and 207A. Enantioselective Synthesis of (-)-Indolizidine 209B

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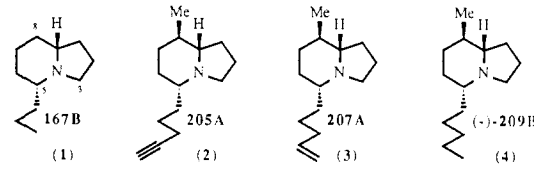
A large number of alkaloids have been isolated in minute quantity from the skin extracts of neotropical poison-dart frogs (family Dendrobatidae).[1] The scarcity of natural material, coupled with the intriguing biological activity of those compounds which have been studied,[1] makes these alkaloids ideal targets for total synthesis.[2] The 5,8-disubstituted indolizidines, for which no syntheses have been reported, have a structural similarity to the cardiotonic pumiliotoxins.[3] In this communication we now report the synthesis of indolizidines 167B (**1**), 205A (**2**), and 207A (**3**) by a general route involving the intramolecular dipolar cycloaddition of the (*Z*)-*N*-alkenylnitrone **8** to give the isoxazolidine **9** as the only isolated product (Scheme I).[4] The unique aspect of this approach is the rapid construction of the indolizidine skeleton from relatively simple molecules with a high degree of stereocontrol at C-5, C-8, and C-8a. Thus the homochiral hydroxylamine precursor **7d** can be used to prepare the enantiomerically pure indolizidine (-)-209B (**4**). A notable use of the intramolecular nitrone approach to all-cis 2,3,6-trisubstituted piperidines had previously been reported by LeBel and Balasu-



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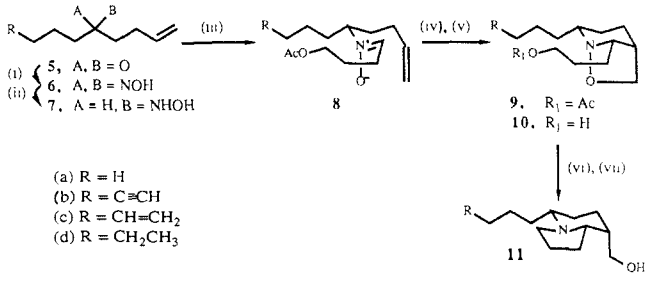
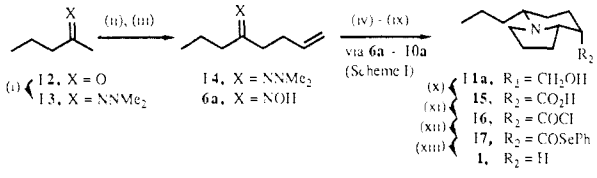
Scheme I[a]



[a] Reagents: (i) NH_2OH·HCl, NaOAc, H_2O, EtOH, room temperature; (ii) $NaCNBH_3$, MeOH, pH 3–4 (HCl/MeOH, methyl orange), −10 °C; (iii) 4-acetoxybutanal, CH_2Cl_2, 0 °C; (iv) $PhCH_3$, Δ, 16 h; (v) K_2CO_3 (catalyst), MeOH, room temperature; (vi) MsCl, Et_3N, CH_2Cl_2, −10 °C; (vii) Zn, HOAc, H_2O, 60 °C, 2 h.

Scheme II[a]



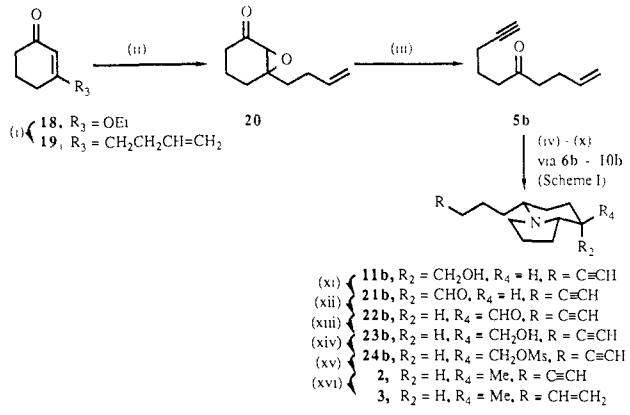
[a] Reagents: (i) H_2NNMe_2, EtOH, Δ (86%); (ii) *n*-BuLi, THF, −78 °C, 1 h; allyl bromide, THF, −78 °C → 0 °C, 2 h (91%); (iii) NH_2·OH·HCl, NaOAc, EtOH, H_2O, room temperature (97%); (iv) $NaCNBH_3$, MeOH, pH 3–4 (HCl/MeOH, methyl orange), −10 °C; (v) 4-acetoxybutanal, CH_2Cl_2, 0 °C; (vi) $PhCH_3$, Δ, 16 h (40%, three steps); (vii) K_2CO_3 (catalyst), MeOH, room temperature (84%); (viii) MsCl, Et_3N, CH_2Cl_2, −10 °C; (ix) Zn, HOAc, H_2O, 60 °C, 2 h (95%, two steps); (x) Jones reagent, Me_2CO, room temperature (67%); (xi) $(COCl)_2$, DMF (catalyst), CH_2Cl_2, room temperature; (xii) PhSeH, py, THF, PhH, room temperature (78%, two steps); (xiii) *n*-Bu_3SnH, AIBN (catalyst), PhH, Δ (62%).

bramanian in the synthesis of (±)-pumiliotoxin C.[5]

Attention was first directed toward the synthesis of the 5-substituted 167B (**1**) (Scheme II), whose structure had only been tentatively assigned.[6] Regioselective alkylation[7] of 2-pentanone **12** with allyl bromide via the *N,N*-dimethylhydrazone **13** and direct displacement of *N,N*-dimethylhydrazine with hydroxylamine gave the oxime **6a**. Sodium cyanoborohydride reduction gave the unstable[8] (±)-*N*-alkenylhydroxylamine **7a**, which was condensed with 4-acetoxybutanal to give exclusively the (*Z*)-nitrone **8a**. Cyclization in refluxing toluene gave the isoxazolidine **9a**. Alkaline hydrolysis of the acetate, mesylation accompanied by spontaneous cyclization, and reductive N–O bond cleavage (Zn/HOAc) gave the 5,8-disubstituted indolizidine **11a**. Removal of the C-8 substituent was achieved by oxidation[9] to the carboxylic acid and subsequent decarboxylation[10] via the seleno ester **17** to give (±)-167B (**1**).[11a]

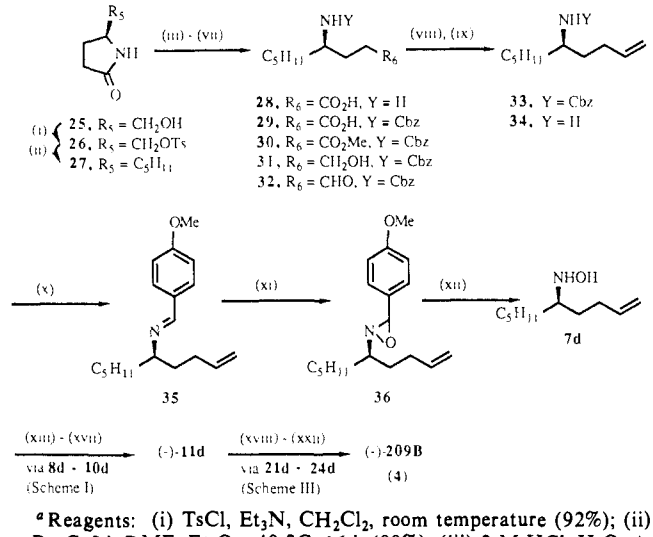
The C-8 substituent in **11** is also ideally suited for manipulation in the synthesis of the 5,8-disubstituted alkaloids 205A (**2**) and 207A (**3**) (Scheme III). The acetylenic side chain was obtained by Eschenmoser fragmentation[12] of the α,β-epoxy ketone **20**, via its tosylhydrazone, to give the acetylenic ketone **5b**. Conversion to the oxime **6b** and $NaCNBH_3$ reduction gave the unstable

Scheme III[a]



[a] Reagents: (i) CH_2=$CHCH_2CH_2MgBr$, THF, 0 °C; H_3O^+, 0 °C (96%); (ii) H_2O_2, NaOH (catalyst), MeOH, room temperature (98%); (iii) H_2NNHTs, CH_2Cl_2, HOAc, −15 °C, 15 h; room temperature 6 h (69%); (iv) NH_2OH·HCl, NaOAc, EtOH, H_2O, room temperature (92%); (v) $NaCNBH_3$, MeOH, pH 3–4 (HCl/MeOH, methyl orange), −10 °C; (vi) 4-acetoxybutanal, CH_2Cl_2, 0 °C; (vii) $PhCH_3$, Δ, 16 h (63%, three steps); (viii) K_2CO_3 (catalyst), MeOH, room temperature (95%); (ix) MsCl, Et_3N, CH_2Cl_2, −10 °C; (x) Zn, HOAc, H_2O, 60 °C, 2 h (99%, two steps); (xi) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C → room temperature; (xii) K_2CO_3 (catalyst), MeOH, room temperature; (xiii) $NaBH_4$, EtOH, 0 °C (57%, three steps); (xiv) MsCl, Et_3N, CH_2Cl_2, 0 °C, 1 h; (xv) $LiEt_3BH$, THF, 0 °C (90%, two steps); (xvi) Lindlar, H_2, EtOAc, room temperature (100%).

Scheme IV[a]



[a] Reagents: (i) TsCl, Et_3N, CH_2Cl_2, room temperature (92%); (ii) *n*-Bu_2CuLi, DME, Et_2O, −40 °C, 16 h (88%); (iii) 2 M HCl, H_2O, Δ, 6 h (100%); (iv) CbzCl, NaOH, H_2O, THF, room temperature, 5 h (89%); (v) HCl, MeOH, room temperature (100%); (vi) DIBAL, THF, $PhCH_3$, −78 °C, 1 h (99%); (vii) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C → room temperature (86%); (viii) Ph_3P=CH_2, DMSO, room temperature (91%); (ix) 4,4′-di-*tert*-butylbiphenyl, Li, THF, −78 °C, 30 min (95%); (x) *p*-MeO-C_6H_4-CHO, CH_2Cl_2, room temperature (100%); (xi) mCPBA, CH_2Cl_2, −78 °C → room temperature (88%); (xii) NH_2OH·TsOH, MeOH, room temperature; NaOH, H_2O; (xiii) 4-acetoxybutanal, CH_2Cl_2, 0 °C (25–45%, two steps); (xiv) $PhCH_3$, Δ, 16 h (89%); (xv) K_2CO_3 (catalyst), MeOH, room temperature (86%); (xvi) MsCl, Et_3N, CH_2Cl_2, −10 °C, 1 h; (xvii) Zn, HOAc, H_2O, 60 °C, 2 h (86%, two steps); (xviii) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C → room temperature; (xix) basic Al_2O_3 chromatography, EtOAc, hexane; (xx) $NaBH_4$, EtOH, 0 °C (65%, three steps); (xxi) MsCl, Et_3N, CH_2Cl_2, 0 °C, 1 h; (xxii) $LiEt_3BH$, THF, 0 °C (87%, two steps).

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hydroxylamine **7b**, which was immediately condensed with 4-acetoxybutanal to give the (*Z*)-nitrone **8b**.[13] Thermal cyclization (80%), ester hydrolysis, mesylation, and N–O bond cleavage gave the indolizidine **11b** in excellent yield. Conversion to 205A (**2**) required epimerization at C-8 and deoxygenation. This was achieved by oxidation[14] to the aldehyde **21b**, base-catalyzed epimerization[5,15] to the equatorial aldehyde **22b**, and reduction to the epimeric alcohol **23b**. Mesylation and displacement[16] with Super-Hydride gave (±)-205A (**2**).[11b,17] Lindlar reduction of 205A (**2**) afforded (±)-207A (**3**).[11b]

An asymmetric synthesis of the 5,8-disubstituted indolizidine alkaloids can, in principle, be achieved by using an enantiomerically pure *N*-alkenylhydroxylamine precursor **7**. This approach would depend on the hitherto unexplored formation of such α-chiral *N*-alkenylnitrones[18] and their use in intramolecular cycloadditions without loss of stereochemical integrity. Spurred on by the prospect of oxidizing chiral amines to chiral hydroxylamines,[19] we prepared the enantiomerically pure amine **34** in 53% overall yield from (*S*)-5-(hydroxymethyl)-2-pyrrolidone (**25**)[20] by a chain-extension sequence (Scheme IV).[21] Noteworthy was the novel use of the Ireland debenzylation procedure[22] for the removal of the benzyloxycarbamate protecting group [**33** → **34**] (95%). Formation of the imine **35**, selective oxidation to the oxaziridine **36**, and cleavage with hydroxylamine gave the chiral *N*-alkenylhydroxylamine **7d**. Application of the previously described intramolecular nitrone methodology and subsequent elaboration (Scheme IV) gave enantiomerically pure (−)-209B (**4**) in ten steps (15% overall yield from **34**).[23]

In summary, the *N*-alkenylnitrones **8** have been shown to serve as extremely efficient precursors for the stereocontrolled construction of enantiomerically pure 5,8-disubstituted indolizidine alkaloids by a general strategy which should make these compounds readily available for biological evaluation.[17]

Acknowledgment. We thank the S.E.R.C. (U.K.) for supporting this work, I.C.I. Pharmaceuticals (A.L.S.) and the Rohm and Haas Company (S.F.W.) for the award of CASE studentships, and Drs. J. W. Daly and T. Spande (NIH) for a preprint of ref 1c. A.L.S. is the recipient of a Sidney Sussex College research studentship.

Supplementary Material Available: Spectra (NMR, IR, MS) of new compounds described in this paper (5 pages). Ordering information is given on any current masthead page.

(13) A typical procedure for the conversion **6b** → **8b** and subsequent cyclization to **9b** is illustrated as follows. A solution of oxime **6b** (1.59 g, 9.64 mmol) in methanol (40 mL) was cooled to −10 °C under argon and treated with methyl orange indicator (5 drops) and sodium cyanoborohydride (0.91 g, 14.46 mmol). Hydrochloric acid (6 M solution in water/methanol) was added dropwise with stirring to maintain a red coloration until reduction was complete (ca. 30 min). The solution was made strongly alkaline with 20% aqueous sodium hydroxide solution, poured into saturated aqueous sodium chloride solution containing ice (50 mL), and extracted with dichloromethane (4 × 50 mL). The organic extracts were added directly to a solution of 4-acetoxybutanal (2.1 g, 16.1 mmol) in dry dichloromethane (20 mL) containing anhydrous $MgSO_4$ at 0 °C with stirring. After 1 h, the solution was filtered and evaporated in vacuo to give the crude nitrone **8b**, which was dissolved in dry toluene (250 mL) and refluxed under argon under Dean–Stark conditions for 15 h. Evaporation in vacuo and purification by flash chromatography on silica (hexane/ether 5:1 → 3:1) gave isoxazolidine **9b** (1.70 g, 63%) as a pale yellow liquid.

(14) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482.

(15) The two epimeric aldehydes were readily distinguished in the ^1H NMR spectrum by the characteristic aldehyde signals (δ_{ax} CHO 10.0 (d, J = 2.0 Hz), δ_{eq} CHO 9.65 (d, J = 2.0 Hz)). Integration of the ^1H NMR spectrum of the equilibrium mixture indicated the ratio **22b**/**21b** = 16.7:1. The aldehydes were not easily separated, but the corresponding 8-hydroxymethyl compounds were readily separated by flash chromatography on silica eluting with $EtOAc/NH_3$ mixtures.

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(17) The pharmacology of 205A will be communicated in due course.

(18) A few α-chiral nitrones have been prepared and used in intramolecular cycloaddition reactions. These were, however, C-alkenylnitrones and hence did not require the formation of α-chiral *N*-alkenylhydroxylamines. See: Wovkulich, P. M.; Uskoković, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 3958–3959. Baggiolini, E. G.; Lee, H. L.; Pizzolato, G.; Uskoković, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6460–6462.

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(21) (a) Cuprate displacement of tosylate: Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7777–7782, 7783–7788. (b) The aldehyde **32** was found to be in the form of the corresponding hemi-aminal. (c) Wittig olefination: Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128–1129.

(22) Ireland, R. E.; Smith, M. G. *J. Am. Chem. Soc.* **1988**, *110*, 854–860.

(23) $[\alpha]^{22}_D$ = −94.3°, *c* 1.85, MeOH. The enantiomeric excess was judged to be >95% by chiral shift studies on **9d**. The optical rotation of the natural 209B is not available at present due to insufficient material having been isolated.

Intramolecular Reactions of 2-*O*-Organosilyl Glycosides: Highly Stereoselective Synthesis of *C*-Furanosides

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Our investigations on the Lewis acid-mediated reactions of substituted sugars have demonstrated that glycofuranosides bearing, at *O*-2, a carbon nucleophilic substituent such as a benzyl[2] or an allyl[3] group, undergo readily internal *C*-glycosidation, a reaction that leads to "cyclic" 1,2-*cis*-*C*-furanosides. These results suggested that an intramolecular process might provide a reliable approach to the stereoselective synthesis of *C*-furanosides. The stereochemical outcome of the reactions of glycofuranosyl derivatives with *C*-nucleophiles such as allyltrimethylsilane,[4] silyl enol ethers,[5] or activated aromatic systems[5e,6] is indeed largely unpredictable, and the availability of a stereocontrolled approach to *C*-furanosides, which constitute important precursors of *C*-nucleosides,[7] aryl *C*-glycosides,[8] and polyethers[9] antibiotics, is highly desirable.

We therefore looked for substituents that would make the general process represented in Scheme I feasible. In particular, on the basis of the well-documented chemistry of aryl- and vinylsilanes, which undergo ipso substitution in reactions with electrophiles,[10] a functionalized organosilyl substituent appeared to be an appropriate candidate. Initial investigations were not very encouraging as the 2-*O*-phenyldimethylsilyl derivative of xylofuranoside **1** led, on reaction with tin(IV) chloride, to the expected α-*C*-glycosylated benzene in 18% yield only as well as to a large amount of desilylated, anomerized xylofuranoside α-**1** (65%) and to the cyclic dimer of **1**, compound **2**[11] (8%). However, we considered that the low yield of the internal reaction was due

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(11) This compound (**2**) is the tetra-*O*-(4-chlorobenzyl) derivative of 1,2′-anhydro-2-*O*-(α-D-xylofuranosyl)-α-D-xylofuranose. Details on its structure are provided in the Supplementary Material.

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