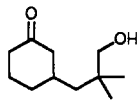
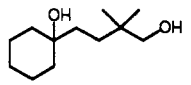
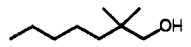
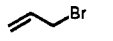
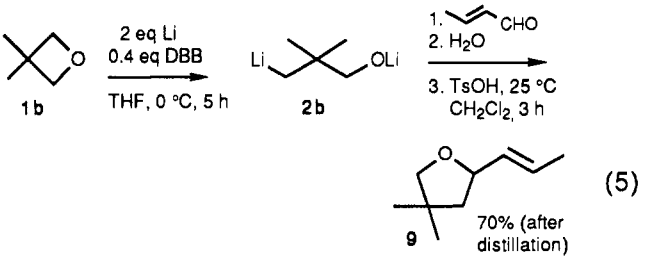
Table II. Reaction of 2b′ with Some Electrophiles

electrophile	product	yield, %
		78
		67
		60
		75

of Li) of DBB.[15] Equation 5 illustrates a one-pot synthesis of the vinyltetrahydrofuran **9** on a 6-g scale using this concept. However, when the unsubstituted **1a** was used instead, **2a** formed much less efficiently and a significant amount of 1-propanol was detected by GLC. It seems likely that in the latter case destruction of the dianion **2a** proceeded via abstraction of an α-proton from the sterically unhindered oxetane **1a**, a precedented type of deprotonation.[16]

This method of production of γ-lithioalkoxides nicely complements the other two methods that have been reported, reductive lithiation of a γ-chloroalkoxide[7a,12,17,18] and tin–lithium exchange of a γ-(tributylstannyl)alkoxide.[19] In the former method, the availability of substrates is severely limited and the yields are often poor, and only one example of the latter method has been reported. The major attraction of the present method is the ready availability of oxetanes and the ability to prepare them from epoxides;[5a] because the latter can frequently be obtained in optically active form,[20] optically active oxetanes and γ-lithioalkoxides should also become available.[21]



(5)

Acknowledgment. We thank the National Science Foundation for financial support and Professor Dennis Curran for a suggestion which stimulated this work.

Supplementary Material Available: Sample procedures for reductive lithiation of oxetanes and reactions of the dianions with electrophiles as well as spectral data for the products (19 pages). Ordering information is given on any current masthead page.

(15) For the use of LDMAN in the reductive lithiation of thioketals by the catalytic method, see: Cohen, T.; Matz, J. R. *Synth. Commun.* **1980**, 311.
(16) Schakel, M.; Vrielink, J. J.; Klumpp, G. W. *Tetrahedron Lett.* **1987**, *28*, 5747.
(17) Barluenga, J.; Flórez, J.; Yus, M. *Synthesis* **1983**, 378; **1985**, 846.
(18) The corresponding magnesium chloride derivatives have been prepared by an analogous procedure but reducing by magnesium rather than an aromatic radical anion.[14]
(19) Zidani, A.; Vaultier, M. *Tetrahedron Lett.* **1986**, *27*, 857.
(20) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765, and citations therein. Rao, A. S.; Palnikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323.
(21) Seebach has prepared optically active γ-lithioalkoxides from chloro alcohols.[12]

Stereoselective Addition Reactions of Chiral α-Sulfinyl Ketimine Anions with Ene Esters. Facile Asymmetric Syntheses of Indolo[2,3-*a*]quinolizidine and Yohimbanoid Alkaloids†

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Received September 5, 1989

Summary: A convenient route for the construction of chiral indolizidines and yohimbanoid alkaloids from the 1,4-addition/ring-closure reactions of chiral α-sulfinyl ketimine anions with ene esters is presented.

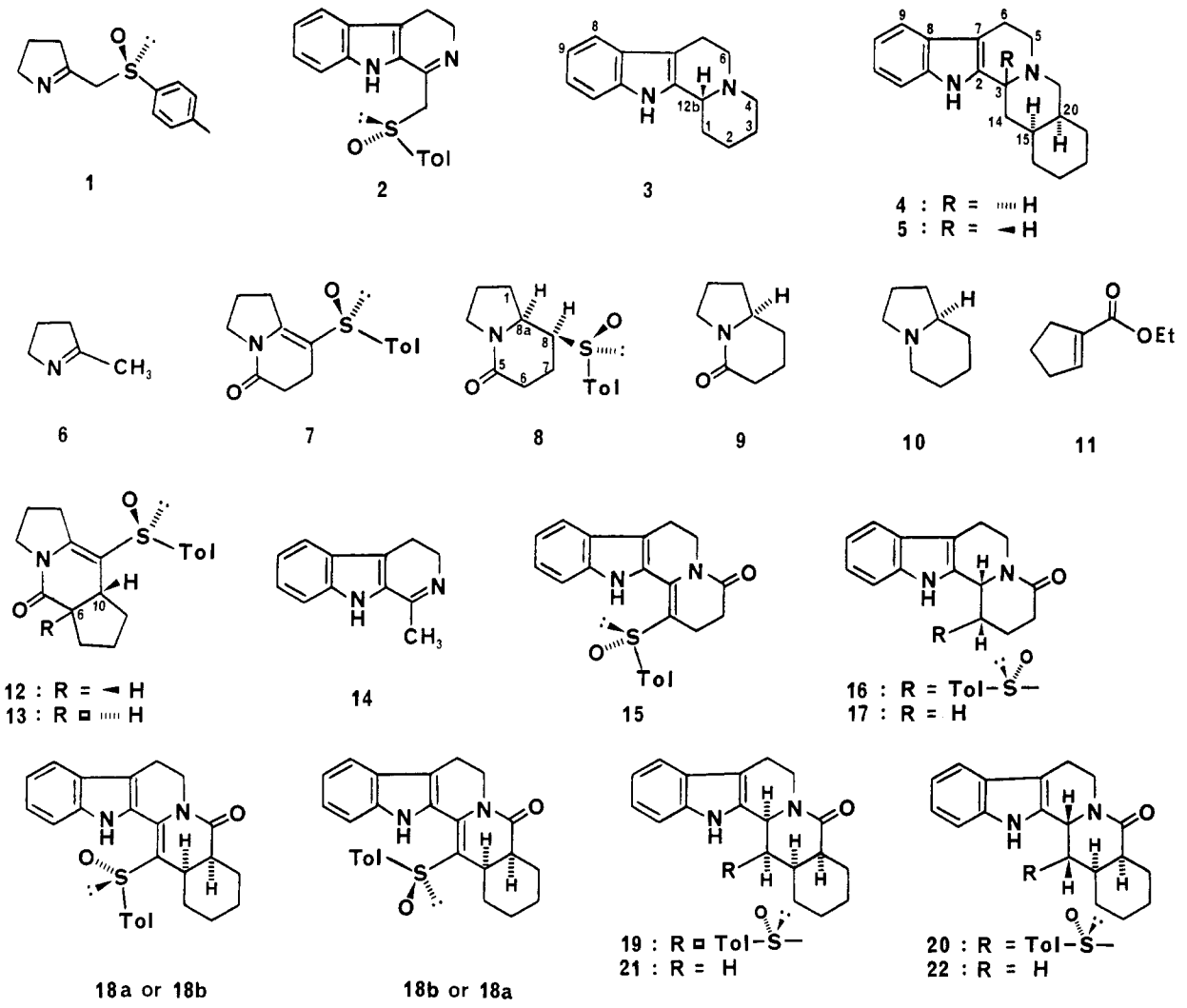
Sir: In the course of studies involving the enantioselective synthesis of functionalized indolizidines, such as (+)-castanospermine[2] via chiral sulfoxides,[3] the addition reactions of chiral α-sulfinyl ketimines with ene esters were investigated. Although the analogues silyl aldimines,[4a] tin aldimines,[4b] β-aminoalkenephosphonates,[4c] α-sulfinyl oxazolines,[5a,b] α-sulfinyl hydrazones,[5c–e] β-aminoalkenenitriles, and β-aminoalkene esters[6] have been reported, α-sulfinyl ketimines like **1** and **2** have not. Herein, we describe the preparation and stereoselective in situ addition/ring-closure reactions of α-sulfinyl ketimines and the utilization of **2** in the asymmetric syntheses of (−)-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine [(−)-**3**],[7] (−)-*allo*-

† This paper is dedicated to Cal Y. Meyers on the occasion of his 60th birthday.
‡ Fellow of the Alfred P. Sloan Foundation, 1989–1991.

(1) Department of Chemistry, University of Kansas, Lawrence, KS 66045.
(2) Isolation and structure: (a) Hohenschutz, L.; Bell, E. A.; Jewess, P. J.; Lewothy, D. P.; Pryce, R. J.; Arnold, E.; Clardy, J. *Phytochemistry* **1981**, *20*, 811. Synthesis: (b) Bernotas, R. C.; Ganem, B. *Tetrahedron Lett.* **1984**, *25*, 165. (c) Hamana, H.; Ikota, N.; Ganem, B. *J. org. Chem.* **1987**, *52*, 5492.
(3) Hua, D. H.; Venkataraman, S.; Chan-Yu-King, R.; Paukstelis, J. V. *J. Am. Chem. Soc.* **1988**, *110*, 4741 and references 5 cited therein.
(4) (a) Corey, E. J.; Enders, D.; Bock, M. G. *Tetrahedron Lett.* **1976**, *1*, 7 and references cited therein. (b) Brocas, J.-M.; De Jeso, B.; Pommier, J.-C. *J. Organomet. Chem.* **1976**, *120*, 217. (c) Nagata, W.; Hayase, Y. *J. Chem. Soc. C* **1969**, 460.
(5) (a) Annunziata, R.; Cinquini, M.; Gilardi, A.; Cozzi, F. *Synthesis* **1983**, 1016. (b) Bernardi, A.; Colombo, L.; Gennari, C.; Prati, L. *Tetrahedron* **1984**, *40*, 3769. (c) Annunziata, R.; Cozzi, F.; Cinquini, M.; Colombo, L.; Gennari, C.; Poli, G.; Scolastico, C. *J. Chem. Soc., Perkin Trans. I* **1985**, 251. (d) Annunziata, R.; Cinquini, M.; Cozzi, F.; Gilardi, A.; Cardani, S.; Poli, G.; Scolastico, C. *J. Chem. Soc., Perkin Trans. I* **1985**, 255. (e) Annunziata, R.; Cardani, S.; Gennari, C.; Poli, G. *Synthesis* **1984**, 702.

0022-3263/89/1954-5659$01.50/0

Chart I



yohimban [(−)-4],[8] and (+)-3-*epi*-*allo*-yohimban [(+)-5][8] (Chart I).

We initially prepared (*R*)-sulfinyl ketimine 1 from the reaction of the α-anion[9] of (*R*)-*p*-tolyl methyl sulfoxide with 4-bromobutanenitrile in THF at 0 °C for 1 h. Only an 18% yield (of theoretical) of (+)-1 [$[\alpha]^{20}_{D}$ +146° (*c* 0.645 in CH_2Cl_2)] was realized and 54% of the starting sulfoxide was recovered (by column chromatography).[10] A better preparative method was sought. Treatment of 3 equiv of α-lithiated 3,4-dihydro-5-methyl-2*H*-pyrrole (**6**)[11] with *l*-(−)-(*S*)-menthyl *p*-toluenesulfinate[12] in THF at −50 °C for 1 h provided 92% yield (isolated) of (+)-1 having an identical optical rotation as that obtained from the first method.

Treatment of sulfoxide (+)-1 with 1 equiv of *n*-BuLi in THF (−78 °C, 30 min; −30 °C, 15 min) followed by 1.2 equiv of methyl acrylate (−30 °C, 15 min; 25 °C, 2 h) afforded 60% yield (isolated) of indolizidinone **7**.[13] Apparently **7** is formed from the 1,4-addition of the sulfinyl ketimine allylic anion of **1** with methyl acrylate, the attack occurring from the α-carbon of the sulfoxide to give the

(6) (a) Ishibashi, H.; Sato, K.; Maruyama, K.; Ikeda, M.; Tamura, Y. *Chem. Pharm. Bull.* **1985**, *33*, 4593. (b) Yamada, Y.; Matsui, M. *Agric. Biol. Chem.* **1970**, *34*, 724. (c) Yamada, Y.; Hatano, K.; Matsui, M. *Agric. Biol. Chem.* **1970**, *34*, 1536. (d) Nagasaka, T.; Inoue, H.; Hamaguchi, F. *Heterocycles* **1983**, *20*, 1099.

(7) Isolation: (a) Johns, S. R.; Lamberton, J. A.; Occolowitz, J. L. *Aust. J. Chem.* **1966**, *19*, 1951. Synthesis of the racemic form: (b) Meyers, A. I.; Loewe, M. F. *Tetrahedron Lett.* **1984**, 2641. (c) Fujii, T.; Ohba, M.; Sasaki, N. *Heterocycles* **1984**, *22*, 1805 and references cited therein. ^{13}C NMR spectra: (d) Gribble, G. W.; Nelson, R. B.; Johnson, J. L.; Levy, G. C. *J. Org. Chem.* **1975**, *40*, 3720. Biological activities: (e) Horiuchi, H.; Yano, S.; Watanabe, K.; Yamanaka, E.; Aimi, N.; Sakai, S. *Res. Commun. Chem. Rathol. Pharmacol.* **1988**, *59*, 407. (f) Huff, J. R.; Baldwin, J. J.; DeSolms, S. J.; Guare, J. P., Jr.; Hunt, C. A.; Randall, W. C.; Sanders, W. S.; Smith, S. J.; Vacca, J. P.; Zrada, M. M. *J. Med. Chem.* **1988**, *31*, 641. (g) Safrazbekyan, R. R.; Sukasyan, R. S.; Arzanunts, E. M. *Biol. Zh. Arm.* **1975**, *28*, 53.

(8) Synthesis, racemates: (a) Naito, T.; Miyata, O.; Tada, Y.; Nishiguchi, Y.; Kiguchi, T.; Ninomiya, I. *Chem. Pharm. Bull.* **1986**, *34*, 4144. (b) Kametani, T.; Suzuki, T.; Unno, K. *Tetrahedron* **1981**, *37*, 3819 and references cited therein. Optically active form: (c) Bartlett, L.; Dastoor, N. J.; Hrbek, J., Jr.; Klyne, W.; Schmid, H.; Snatzke, G. *Helv. Chim. Acta* **1971**, *54*, 1238. ^{13}C NMR spectra: (d) Morales-Rios, M. S.; Espineira, J.; Joseph-Nathan, P. *Magn. Reson. Chem.* **1987**, *25*, 377. (e) Wenkert, E.; Chang, C. J.; Chawla, H. P. S.; Cochran, D. W.; Hagaman, E. W.; King, J. C.; Orito, K. *J. Am. Chem. Soc.* **1975**, *98*, 3645. Biological activities: (f) Creveling, C. R.; Daly, J. W.; Parfitt, R. T.; Witkop, B. *J. Med. Chem.* **1968**, *11*, 596.

(9) (*R*)-*p*-Tolyl methyl sulfoxide was treated with (diisopropylamino)magnesium bromide in THF at −30 °C for 15 min and 0 °C for 30 min.

(10) An acid–base reaction takes place between the anion and 4-bromobutanenitrile. The α-lithiomethyl *p*-tolyl sulfoxide gave only recovered starting materials under the same conditions.

(11) (a) Bielawski, J.; Brandange, S.; Lindblom, L. *J. Heterocycl. Chem.* **1978**, *15*, 97. The anion was derived from the cyclic imine and 1 equiv of lithium diisopropylamide (LDA) in THF at 0 °C for 15 min. (b) Houk, K. N.; Strozier, R. W.; Rondan, N. G.; Fraser, R. R.; Chuaqui-Offermanns, N. *J. Am. Chem. Soc.* **1980**, *102*, 1426.

(12) Philipps, H. *J. Chem. Soc.* **1925**, *127*, 2552.

(13) All enantiomers are depicted with the indicated absolute stereochemistry. All new compounds displayed satisfactory ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), UV, IR, and low-resolution mass spectra (both EI and CI) and satisfactory elemental analyses.

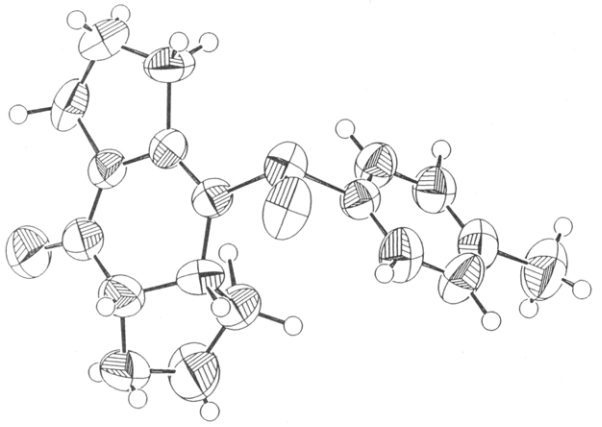
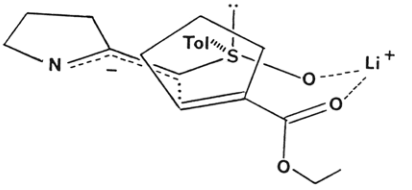


Figure 1. ORTEP drawing of X-ray crystallographically determined structure of **12**. Carbon, nitrogen, oxygen, and sulfur atoms are drawn as 50% ellipsoids. Hydrogen atoms are drawn as 0.1-Å diameter spheres.

enolate anion; the latter then undergoes proton abstraction from α-CH of the sulfoxide moiety, followed by ring closure. Importantly, the reduction of **7** with 3 equiv of $NaCNBH_3$ in AcOH with a catalytic amount of CF_3COOH at 25 °C for 2 h and 50 °C for 4 h proceeds completely stereoselectively to give 73% yield of **8** [$[\alpha]^{20}_D$ +181° (*c* 0.48 in CH_2Cl_2)] as a single enantiomer.[14a] The stereochemistry of C-8a of **8** was proven by degradation of **8** to (*R*)-(−)-indolizidine (**10**).[14b] Treatment of **8** with W-2 Raney nickel[15] in refluxing ethanol for 1.5 h gave 98% yield of amide **9**; $[\alpha]^{20}_D$ −2.5° (*c* 0.7 in CH_2Cl_2). Reduction of **9** with 2 equiv of lithium aluminum hydride in ether at 25 °C for 2 h provided 85% yield of (*R*)-**10**; $[\alpha]^{20}_D$ −11.3° (*c* 1.76, EtOH)[16] [lit.[14] $[\alpha]^{23}_D$ −10.2 ± 0.6° (*c* 1.76, EtOH) for *R* configuration]. The stereochemistry at C-8 of **8** was assumed on the basis of the coupling constant ($J_{8,8a}$ = 5.2 Hz)[17] obtained from ^{1}H NMR irradiation experiments. Although asymmetric addition to chiral α-sulfinyl-α,β-unsaturated carbonyl compounds is known,[18] chiral β-sulfinyl enamides like **7** have not been reported previously.[19]

The anion derived from (+)-**1** (vide supra) also underwent reaction with ethyl 1-cyclopentenecarboxylate (**11**)[20]

Scheme I



(−78 °C, 15 min; 25 °C, 4) to provide tricyclic sulfoxide **12**,[21] which was isolated by column chromatography in 70% yield, along with 2% of its diastereomer **13**. None of the other possible stereoisomers was detected. A single-crystal X-ray structure determination of **12** (Figure 1) firmly established the stereochemistry at S, C-6, and C-10. The crystals are monoclinic, space group $P2_1$. The absolute configuration of the molecule was confirmed by the technique using S atom's anomalous dispersion.[22] The presumed stereochemistry of the minor product (**13**) is based on the coupling constant, $J_{6,10}$ = 14 Hz (axial–axial coupling). The "trans-fused eight-membered" cyclic transition state (Scheme I) in the 1,4-addition reaction of **11** is suggested from the X-ray molecular structure.

This 1,4-addition reaction was utilized in the asymmetric syntheses of quinolizine (−)-**3**, *allo*-yohimban [(−)-**4**], and 3-*epi*-*allo*-yohimban [(+)-**5**] to demonstrate the generality of this result. The same procedure used in the preparation of **1** was employed to prepare sulfoxide (+)-**2** [$[\alpha]^{20}_D$ +411° (*c* 0.66, CH_2Cl_2)] from harmalane (**14**).[23] Treatment of 1 equiv of **14** with 2 equiv of LDA in THF at 0 °C for 15 min, followed by the addition of 1 equiv of *l*-(−)-(*S*)-menthyl *p*-toluenesulfinate at −50 °C for 1 h, gave 83% yield of (+)-**2**. Addition of the N,α-dianion of (+)-**2** (2 equiv of LDA in THF at −78 °C for 1 h) with 1 equiv of methyl acrylate at 25 °C for 4 h provided 90% yield of **15**. Reduction of **15** with 2 equiv of $NaCNBH_3$ in AcOH at 50 °C for 3 h stereoselectively gave an 85% yield of **16**. The stereochemistry at C-12b was predicted from the conversion of **7** to **8** as noted, while the syn disposition at C-1 and -12b is supported by ^{1}H NMR 2D NOESY and 2D COSY experiments. Desulfurization of **16** with Raney nickel in EtOH–THF at 65 °C for 12 h followed by reduction with $LiAlH_4$ in ether gave a 75% yield of (−)-**3**; $[\alpha]^{20}_D$ −14° (*c* 1, MeOH) [lit.[7] $[\alpha]_D$ −12.5° (*c* 1, MeOH)].

The addition reaction of the N,α-dianion of **2** with methyl 1-cyclohexenecarboxylate at 25 °C for 1 h, then 60 °C for 14 h,[24] gave 78% of **18a** [$[\alpha]^{22}_D$ −52.4° (*c* 1.95, CH_2Cl_2)] and 10% of **18b** [$[\alpha]^{22}_D$ −229° (*c* 0.91, CH_2Cl_2)], which we believe are rotamers (restricted rotation around the C_{14}–S bond).[25] When the reaction was conducted at

(14) (a) Lithium *n*-butylcopper hydride was also used to reduce **7**, a mixture of byproducts was produced, and **8** and its diastereomers were not detected. (b) Ringdahl, B.; Pinder, A. R.; Pereira, W. E.; Oppenheimer, N. J. Jr.; Craig, J. C. *J. Chem. Soc., Perkin Trans. I* **1984**, 1.

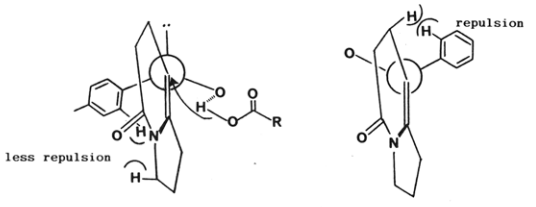
(15) Mozingo, R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 181.

(16) It can be assumed that (*R*)-**4** prepared here is 100% optically pure, since the precursor **5** is 100% enantiomerically pure.

(17) The bulky sulfinyl group should be in the equatorial position, consequently the C_8-H is in the axial position. The observed *J* value of 5.2 Hz suggests an axial–equatorial coupling, and hence, C_{8a}-H must be in the equatorial position. This is in line with the NMR results reported by Speckamp: Wijnberg, B. P.; Speckamp, W. N.; Oostreen, A. R. C. *Tetrahedron* **1982**, *38*, 209.

(18) (a) Posner, G. H.; Mallamo, J. P.; Hulce, M.; Frye, L. L. *J. Am. Chem. Soc.* **1982**, *104*, 4731. (b) Davis, R.; Kern, J. R.; Kurz, L. J.; Pfister, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 7873 and references cited therein.

(19) In the reduction of **7** to **8**, presumably the acid stereoselectively protonates the double bond at C-8 as depicted below. The resulting α-amido carbocation is then attacked by the hydride from the opposite side of the bulky sulfinyl group.



(20) Büchi, G.; Hoshtrasser, U.; Pawlak, W. *J. Org. Chem.* **1973**, *38*, 4348.

(21) Two new chiral centers, C-6 and 10, are created from this enantioselective addition reaction. This tricyclic skeleton is related to *Penicillium cyclopium* alkaloids, cyclopiamines: Bond, R. F.; Boeyens, J. C. A.; Holzapfel, C. W.; Steyn, P. S. *J. Chem. Soc., Perkin Trans. I* **1979**, 1751.

(22) Final $R(+)$ = 0.0602, $R_w(+)$ = 0.0868, $R(-)$ = 0.0639, and $R_w(-)$ = 0.0921.

(23) (a) Spath, E.; Lederer, E. *Ber.* **1930**, *63B*, 2102. (b) Ninomiya, I.; Tada, Y.; Kiguchi, T.; Yamamoto, O.; Naito, T. *Heterocycles* **1978**, *9*, 1527. (c) Fodor, G.; Nagubandi, S. *Tetrahedron* **1980**, *36*, 1279.

(24) At 25 °C for 4 h, only a 5% yield of **18a** was formed and there was an 80% recovery of **2**. Sulfoxides **18a** and **18b** are separable by silica gel column chromatography; 1% THF in CH_2Cl_2 as eluent. Isomers **19** and **20** are also separable by column chromatography.

(25) Heating of **18a** (100 °C) and **18b** (120 °C) independently in DMSO-d_6 gave the same unidentified dehydrosulfinylation product, although **18a** and **18b** were not interconverted at either temperature. Optical rotations, ^{1}H and ^{13}C NMR spectra, IR and UV spectra, and TLC R_f values of **19** and **20** obtained from **18a** are identical, respectively, with those obtained from **18b**. Spectral data of 3-*allo*-yohimban-21-one (**21**) are identical with those reported.[8a]

70 °C for 20 h, equimolar amounts of **18a** and **18b** were obtained (70% yield). The stereochemistry at C-15 and -20 was shown by transforming **18a** and **18b** separately into (−)-**4** and (+)-**5** via the three-step sequence described above ($NaCNBH_3$, Raney Ni, and $LiAlH_4$), in 57% and 55% overall yields, respectively. (−)-**4**: $[\alpha]^{20}_D$ −81° (*c* 0.35, EtOH) [lit.[8c] $[\alpha]^{21}_D$ −79.2° (*c* 0.35, EtOH)]. (+)-**5**: $[\alpha]^{20}_D$ +190° (*c* 0.4, pyridine) [lit.[8c] $[\alpha]^{23}_D$ +190.4° (*c* 0.4, pyridine)]. Reduction of **18a** with 1.2 equiv of $NaCNBH_3$ in AcOH at 50 °C gave an 82% yield of **19** [$[\alpha]^{22}_D$ +241° (*c* 0.85, CH_2Cl_2)] and **20** [$[\alpha]^{22}_D$ +129° (*c* 0.15, CH_2Cl_2)] in a 2:1 ratio, while rotamer **18b** provided an 80% yield of **19** and **20** in a 1:2.[25] The stereochemistry shown for C-14 of **19** and **20** is presumed on the basis of the coupling constant $J_{3,14}$ = 1 Hz for **19** and 7 Hz for **20** (equatorial–axial coupling).

In summary, highly efficient constructions of functionalized chiral indolizidines have been explored. The stereoselective reduction of β-sulfinyl enamides offers a new arena for further investigation. The synthetic methodology used to prepare the indolizidines and yohimbanoid alkaloids is facile and should be applicable to the construction of (+)-castanospermine,[2] (+)-swansonine,[26] and other biologically active alkaloids.[27] Related asymmetric induction in the reactions of **1** with β-substituted-α,β-unsaturated esters, aldehydes, and other electrophiles will be reported shortly.

Acknowledgment. We gratefully acknowledge financial support from the National Institute of General Medical Sciences (Grant GM36336) and the National Science Foundation (Grant CHE-8800654). This project is in part funded by Wesley Foundation, Wichita, KS (Grant 8802041). The Wesley Foundation is an independent, nonprofit organization dedicated to improving the quality of life in Kansas through financial support for health related programs. We are indebted to Mr. Ken Walsh, Coal Research Center, Southern Illinois University at Carbondale, for obtaining mass spectra.

Supplementary Material Available: Optical rotations and ^1H and ^{13}C NMR spectral data for compounds **1–22**, fractional coordinates and equivalent isotropic thermal parameters (Table 1), anisotropic thermal parameters (Table 2), bond distances and bond angles (Tables 3 and 4), and torsion angles (Table 5) for sulfoxide **12** (14 pages); F_o and F_c lists (Table 6) (7 pages). Ordering information is given on any current masthead page.

(26) For a review: Grundon, M. F. *Nat. Prod. Rep.* **1985**, 235.

(27) These studies are being actively pursued.

Articles

Total Synthesis of Furanether B

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Received March 1, 1989

The first total syntheses of furanether B, a member of the lactarane class of sesquiterpenes, have been completed starting from 1-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**3**). After ketone reduction, Pauson–Khand cycloaddition (propyne–$Co_2(CO)_6$, benzene, heat) gives rise to a 75% yield of stereoisomeric tricyclic enones **5** and **6**. Reduction and methylation of enone **5**, removal of the ketone (Barton), and oxidation of the remaining alcohol function give **13**. The natural product is obtained upon regiospecific formylation, conversion to the *S*-butyl derivative, and generation of the furan via a modification of Garst's procedure using a thiomethylene ylide under phase-transfer conditions. A similar sequence beginning with **6** also provides access to **13**, but most of the steps proceed in somewhat lower yields.

Introduction

In a previous publication we reported an efficient synthetic entry into the highly functionalized 11-oxatricyclo[5.3.1.$0^{2,6}$]undecane ring system that would be potentially useful in the synthesis of natural products of the lactarane type, which are found in mushrooms of the genera Lactarius and Russula.[1] Synthetic work in this area has been very limited, with only a small number of total syntheses involving one subclass of compounds,[2] together with a few demonstrations of interconversion of naturally occurring compounds.[3,4] Herein we report the first total synthesis of furanether B (**1**), a fungal metabolite isolated by Vita-Finzi in 1980, utilizing our earlier methodology.[5]

Results and Discussion

Our general entry to the ring system involved octacarbonyldicobalt-catalyzed cycloaddition of 8-oxabicyclo-

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