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DIASTEREOSELECTIVE SYNTHESIS OF HIGHLY FUNCTIONALIZED HOMOALLYLIC AMINE DERIVATIVES VIA DIELS–ALDER ADDUCTS OF N-SULFINYL DIENOPHILES

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Abstract—Novel methodology for the diastereoselective synthesis of some branched functionalized homoallylic amine derivatives is described. The protocol starts with a 3,6-dihydrothiazine-1-oxide, which is readily obtained in a totally stereospecific manner by the hetero-Diels–Alder cycloaddition of an N-sulfinyl dienophile and a 1,3-diene. Various Grignard reagents have been added to these adducts to afford sulfoxide derivatives which have been manipulated stereoselectively via [2,3]- or [3,3]-sigmatropic rearrangements into branched homoallylic amines potentially useful for further synthetic transformations.

Recent publications from these laboratories have demonstrated that the [4 + 2]-cycloadducts of mono and bis N-sulfinyl dienophiles with 1,3-dienes are useful synthons for preparation of a number of different types of unsaturated nitrogen-containing acyclic molecules.[1] Efficient stereoselective methods for synthesis of unsaturated vicinal amino alcohols[1b,d] and unsaturated vicinal diamines[1e] were developed starting from these Diels–Alder adducts. In addition, it was found that both inter- and intramolecular[1d,f,g] versions of the cycloaddition provide adducts suitable for these transformations.

In these methods, product stereochemistry ultimately derives from the double bond geometry of the starting 1,3-diene. Thus, cycloaddition of a substituted diene such as **2** (Scheme 1) with an N-sulfinyl dienophile **1** produces a 3,6-dihydrothiazine-1-oxide **3** with predictable 1,4-"Alder" relative stereochemistry as shown. Ring opening of these adducts with a carbon nucleophile affords an allylic sulfoxide or sulfilimine intermediate **4** capable of undergoing [2,3]-sigmatropic rearrangement[1b,g] via an envelope-like transition state[2] to eventually yield a *single* substituted homoallylic amine stereoisomer **5**. Conversion of **4** to **5** involves a 1,4- to 1,2-chirality interchange controlled by transition state geometry and by the fact that substituent A on the sulfur-bearing carbon prefers a pseudo-equatorial position, determining to which diastereotopic face of the double bond in **4** group X is delivered.

In the examples cited above, the group transferred is either N or O. We now describe extensions of this methodology which allow stereoselective transfer of functionalized one- and two-carbon units to the double bond of a system such as **4**.

Initial experiments were conducted with adduct **6**, which is readily available as a 15:1 mixture of sulfur epimers from *E,E*-2,4-hexadiene and N-sulfinylbenzyl carbamate.[1d] Treatment of **6** with trimethylsilylmethylmagnesium chloride[3] at −40° afforded sulfoxide **7** which without purification was deoxygenated with diphosphorus tetraiodide[4] to afford sulfide **8** (77% from **6**). This compound was S-methylated with trimethyloxonium tetrafluoroborate to produce sulfonium salt **9**, which was treated with potassium t-butoxide (MeCN, −15°) yielding crystalline silyl sulfide **11** as a *single* stereoisomer (85% from **8**). The structure and stereochemistry of **11** were established unambiguously by X-ray crystallography.† An ORTEP plot of **11** is shown in the Fig. 1.

The formation of this product can be rationalized based upon the mechanistic model described in Scheme 1. Thus, deprotonation of sulfonium salt **9** gives ylid **10**, which subsequently undergoes [2,3]-sigmatropic rearrangement to silyl sulfide **11** via an envelope-like transition state.[2,5] If the methyl group on C-2 assumes a quasi-equatorial position in this transition state, the

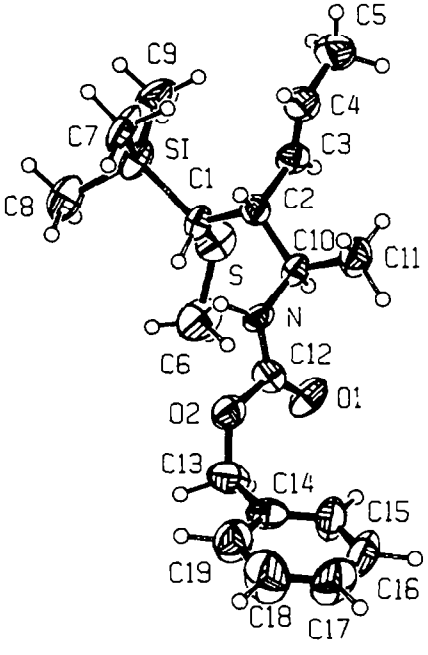
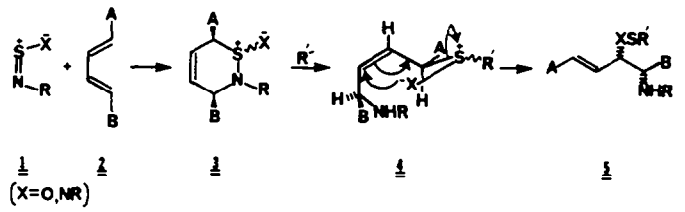


Fig. 1. ORTEP plot of silyl sulfide **11**.

† X-Ray data have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

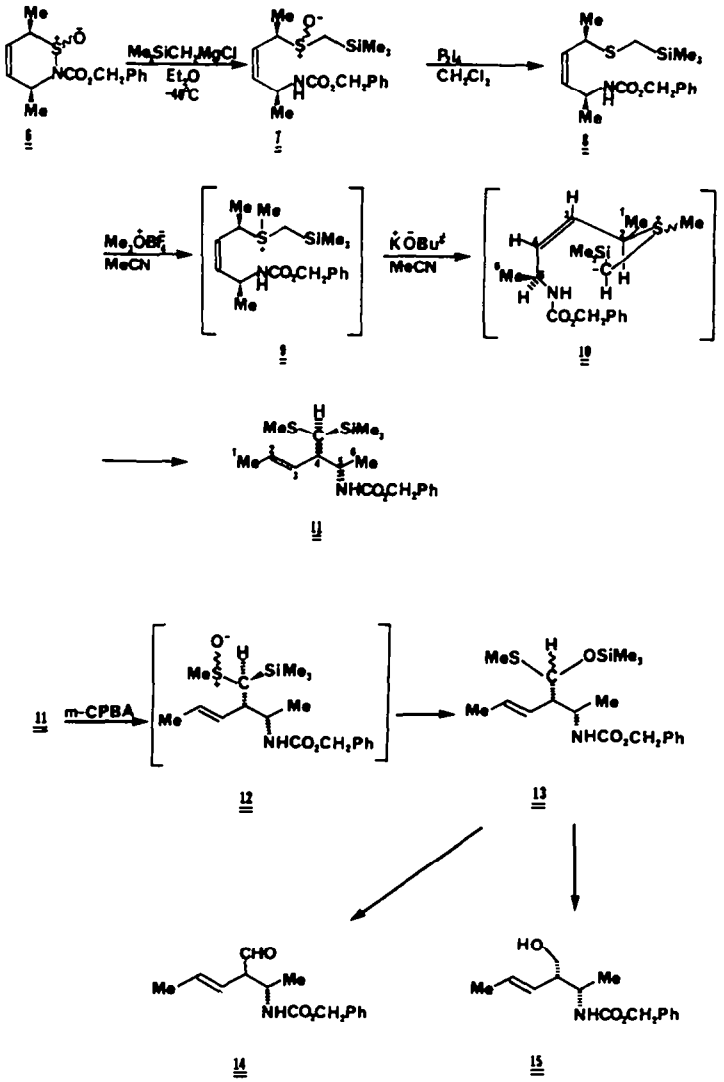


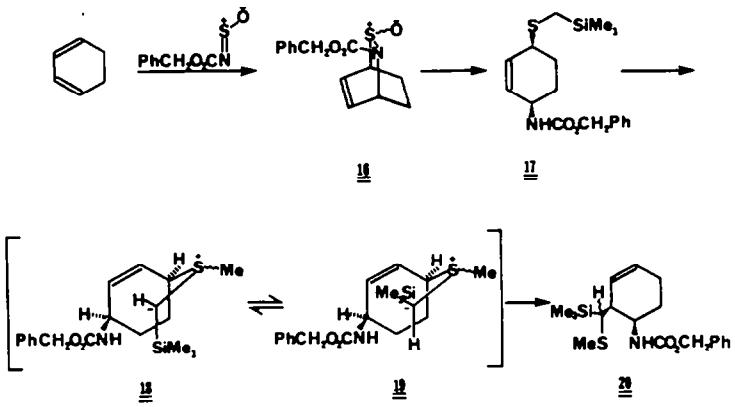
Scheme 1.

relative stereochemistry at C-4 and C-5 in **11** will be as indicated, and an *E* double bond will be produced. Interestingly, a single stereoisomer was also generated at the silicon-bearing center. This selectivity is the result of the trimethylsilyl group of the ylid having a quasi-equatorial position in the transition state for rearrangement indicated in structure **10**. Such a conformation is favorable since it would preclude non-bonded interactions of the silyl group with the substituents on C-5. Therefore, the rearrangement of **9** to **11** is totally stereoselective, and generates three chiral centers and a double bond all of predictable configuration.

A few further transformations were performed on rearrangement product **11**. Oxidation of **11** with *m*-chloroperbenzoic acid gave sulfoxide **12** which upon standing at room temperature spontaneously underwent a silyl Pummerer rearrangement[5] affording silyl ether **13**. Cleavage of **13** under acidic conditions or using Bu_4NF provided aldehyde **14**, but always as a mixture of epimers. Since this β,γ-unsaturated aldehyde was so prone to epimerization, a procedure was used whereby the aldehyde was reduced *in situ* with sodium cyanoborohydride to afford hydroxymethyl **15** as a pure stereoisomer.

A similar series of experiments was performed with the dihydrothiazine oxide produced from the Diels–Alder cycloaddition of a cyclic diene. Thus, N-

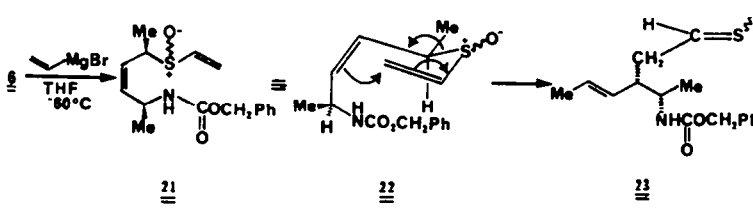




Scheme 2.

sulfinylbenzyl carbamate added to cyclohexadiene to produce **16** as a separable 1.2:1 mixture of sulfur epimers (Scheme 2).[6] Treatment of the mixture of adducts **16** with trimethylsilylmethylmagnesium chloride as above gave a sulfoxide which was immediately reduced with P_2I_4 to afford silyl sulfide **17** (74% from **16**). Alkylation of **17** with trimethyloxonium tetrafluoroborate, followed by potassium t-butoxide promoted [2,3]-sigmatropic rearrangement led to **20**, which in this case was produced as a 1.5:1 mixture of epimers at the silicon-bearing carbon (50% from **17**). The lack of selectivity in formation of this center probably reflects a relatively small difference in energy between rigid sulfonium ylid conformations **18** and **19** (Scheme 2), as compared to the acyclic freely rotating system **10**. It is also possible that the chirality at sulfur, established in the alkylation step, plays a role in determining product stereochemistry in these rearrangements.[2]

We have found that a two-carbon unit can also be transferred from sulfur stereoselectively. Reaction of Diels–Alder adduct **6** with vinylmagnesium bromide at −60°, followed by workup at room temperature directly afforded sulfine **23** as a single isomer assigned the stereochemistry shown on mechanistic grounds.[7] This transformation presumably occurs via opening of dihydrothiazine oxide **6** to vinyl sulfoxide **21** which undergoes a [3,3]-sigmatropic rearrangement. If this



process involves a chair-like transition state like **22** having the methyl group on the sulfur-bearing carbon quasi-equatorial, sulfine **23** will have the stereochemistry shown. Interestingly, the sulfine function is configurationally pure, but we have not been able to establish its stereochemistry. Although sulfines are well known,[7] they have not previously been prepared by this type of thio-Claisen rearrangement. The fact that the rearrangement occurs under such mild thermal conditions may indicate that this is a type of alkoxyl accelerated pericyclic reaction,[8] and further studies of this chemistry are warranted.[11]

We are currently pursuing extensions of the methodology outlined here, and hope to apply this chemistry to the synthesis of some nitrogen-containing natural products.

EXPERIMENTAL

Preparation of sulfide **8**. A soln of 0.85 M trimethylsilylmethylmagnesium chloride[3] in ether (1.2 ml, 1.01 mmol) was added to a soln of **6**[14] (0.26 g, 0.927 mmol) in anhyd THF (6 ml) at −40°. The mixture was stirred for 30 min, diluted with 15 ml of sat NH_4Cl aq and was extracted with ether (3 × 10 ml). The extract was washed with brine (2 × 10 ml), dried and concentrated *in vacuo* to yield crude sulfoxide **7** (0.320 g) as a colorless oil: IR(film) 3275, 3050, 2975, 1710, 1530, 1450, 1380, 1250, 1030, 1000, 850, 780, 740, 700 cm^{-1}.

Because of its instability,[14] sulfoxide **7** was immediately deoxygenated. To a suspension of diphosphorus tetraiodide (0.360 g, 0.623 mmol) in dry CH_2Cl_2 (6 ml) was added **7** (0.210 g, 0.584 mmol) in CH_2Cl_2 (10 ml).[4] The mixture was stirred vigorously for 10 min, diluted with water and was extracted with ether (3 × 25 ml). The organic extract was washed with sat $NaHSO_3$ aq, $NaHCO_3$ aq, brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (1:4 EtOAc–hexane) to yield **8** (0.164 g, 77% from **6**) as a white solid. An analytical sample recrystallized from CH_2Cl_2–hexane had m.p. 77–79°: IR (KBr) 3350, 3050, 2975, 2925, 1700, 1520, 1450, 1250, 1100, 1050, 850, 780, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.08 (s, 9H), 1.22 (d, J = 6.6 Hz, 3H), 1.27 (d, J = 6.8 Hz, 3H), 1.76 (s, 2H), 3.69 (m, 1H), 4.50 (m, 1H), 4.82 (NH), 5.09 (s, 2H), 5.01–5.40 (m, 2H), 7.35 (m, 5H); CI MS ($m+1/z$) 354, 353, 352, 351, 339, 338, 337, 336, 233, 232, 231. Exact mass calc for $C_{18}H_{29}NO_2SSi$ 351.1688. Found 351.1704.

Preparation of rearranged silyl sulfide **11**. To a soln of trimethyloxonium tetrafluoroborate (0.220 g, 1.47 mmol) in anhyd acetonitrile (3 ml) at −15° was added **8** in 3 ml of anhyd acetonitrile. The mixture was stirred for 30 min at −15° and t-

BuOK (0.185 g, 1.64 mmol) was added. The mixture was stirred for 1 h at −15°, was poured into water and was extracted with ether (3 × 20 ml). The organic phase was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatography (1:4 EtOAc–hexane) yielded sulfide **11** (0.354 g, 85%). An analytical sample recrystallized from CH_2Cl_2–hexane had m.p. 101–102°: IR(film) 3325, 3100, 3075, 3040, 2975, 2925, 2900, 1700, 1530, 1450, 1410, 1380, 1330, 1280, 1250, 1240, 1100, 1080, 1050, 980, 860, 840, 780, 750, 700, 610 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.38 (m, 5H), 5.42 (m, 2H), 5.10 (s, 2H), 4.73 (d, J = 8.8 Hz, NH), 4.02 (m, 1H), 1.88–2.20 (m, 2H), 2.09 (s, 3H), 1.66 (d, 3H, J = 4.7 Hz), 1.12 (d, 3H, J = 6.5 Hz), 0.05 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 1.84, 17.81, 19.45, 37.27, 50.69, 66.52, 127.96, 128.07, 128.28, 128.40, 128.46, 130.54, 136.71, 155.74; CI MS ($m+1/z$) 368, 367, 366, 365, 364, 352, 351, 350. (Found: C, 62.98; H, 8.67. Calc for $C_{19}H_{31}NO_2SSi$: C, 62.42; H, 8.55%.)

Crystal structure determination of silyl sulfide **11**. M = 365.61. Monoclinic, $P2_1/c$, a = 9.409(2), b = 25.766(6), c = 9.162(4) Å, β = 92.59(3)°, V = 2218.9 Å^3, Z = 4, D_c = 1.09 g cm^{-3}, $F(000)$ = 792. MoK_α radiation, λ = 0.71073, μ = 2.02 cm^{-1}.

Data were collected to a maximum θ of 20° on an Enraf-Nonius CAD4 diffractometer by the $\omega/2\theta$ scan method using monochromatized MoK_α radiation. A total of 2059 reflections were collected of which 1197 had $I > 3\sigma(I)$ and were used in structure solution and refinement. Data were corrected for Lorentz and polarization factors and then for empirical absorption.

The structure was determined by direct methods using MULTAN'82. The first E map calculated with 271 E's > 1.57 revealed all 24 non-H atoms. Refinement by full-matrix least-squares calculations† with anisotropic thermal parameters for the non-H atoms lowered R is 0.093. A difference map calculated at this stage revealed maxima at positions expected for H atoms which were included in the subsequent refinement in geometrically idealized positions (C—H and N—H 1.08 Å) with an overall isotropic thermal parameter. The weights used in the refinement were derived from the counting statistics. Scattering factors used in the refinement were taken from those of Stewart *et al.*[9] and for the non-H atoms from those of Cromer and Mann.[10] Refinement converged with R = 0.077 and $R_w = [\Sigma w\Delta^2/\Sigma wF_0^2]^{1/2} = 0.087$. A difference map calculated at the conclusion of the refinement was essentially featureless.

Synthesis of alcohol **15**. To a soln of **11** (37 mg, 0.10 mmol) in 1 ml of dry CH_2Cl_2 was added *m*-chloroperoxybenzoic acid (85%, 21 mg, 0.10 mmol) at −40° under N_2. The soln was stirred for 10 min at −40° and was poured into 10 ml of 10% $NaHCO_3$ aq at 0°. The mixture was diluted with 50 ml of cold ether, and the ether layer was washed twice with 10 ml of cold 10% $NaHCO_3$ aq, cold brine, dried with $MgSO_4$, and concentrated *in vacuo* to give 35 mg of crude sulfoxide **12**.

Rearrangement to silyl ether **13** was effected by either allowing **12** to stand overnight at 25° as a soln in 5 ml of dry THF under N_2 or by refluxing a soln of **12** in 5 ml of THF for 5 min and subsequently allowing the soln to stand for 4 h at 25°. The soln was treated with 2 ml of water, sodium cyanoborohydride (63 mg, 1.0 mmol), and 6 drops of 5% HCl aq, stirred for 20 h at 25°, and extracted with 3 × 10 ml of ether. The combined organic layers was washed with brine, dried with $MgSO_4$, and concentrated *in vacuo* to give 31 mg of crude **15**. Flash chromatography of this material on silica (1:1 hexane–ether) gave 12 mg (46% from **11**) of alcohol **15** as a colorless oil: IR(film) 3420, 3330, 1700, 1510, 1338, 1252, 1055, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.36 (m, 5H), 5.60 (dq, 1H, J = 15.3, 6.0 Hz), 5.41 (ddq, 1H, J = 8.8, 15.3, 1.1 Hz), 5.11 (s, 2H), 4.81 (br d, 1H, J = 8.5 Hz, NH), 3.82 (ddq, 1H, J = 8.5, 8.5, 6.8 Hz), 3.68 (br ddd, 1H, J = 4, 4.9, 11.3 Hz), 3.56 (br ddd, 1H, J = 3.8, 8.5, 11.3 Hz), 2.57 (br dd, 1H, J = 4, 8.5 Hz, OH), 2.05 (dddd, 1H, J = 3.8, 4.9, 8.5, 8.8 Hz), 1.71 (dd, 3H, J = 1.1, 6.0 Hz), 1.13 (d, 3H, J = 6.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 156.5, 136.3, 129.4, 129.0, 128.5, 128.2, 128.1, 66.9, 63.6, 51.9, 47.0, 18.8, 18.2; CI MS ($m+1/z$) 265, 264 (M + 1), 263 (M), 220.

Preparation of dihydrothiazine oxides **16**. A soln of N-sulfinylbenzylcarbamate (3.8 g, 20 mmol) in 20 ml of dry toluene was treated with 1,3-cyclohexadiene (1.6 g, 20 mmol) at 25° under N_2. The soln was stirred for 10 h at 25° and toluene was removed *in vacuo*. Flash chromatography of the residue on silica gel (1:2 hexane–ether) afforded 1.69 g (30%) of **16a** as a white solid and 1.41 g (25%) of **16b** as a colorless oil.

Compound **16a**: IR(film) 1715, 1382, 1295, 1230, 1118, 1098, 730, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.36 (m, 5H), 6.80 (ddd, 1H, J = 8.0, 6.1, 1.0 Hz), 6.29 (ddd, 1H, J = 8.0, 7.2, 1.3 Hz), 5.27 (d, 1H, J = 12.4 Hz), 5.21 (d, 1H, J = 12.4 Hz), 5.04 (m, 1H), 3.96 (m, 1H), 2.86 (m, 1H), 2.39–2.17 (m, 1H), 1.64–1.38 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 154.4, 139.2, 134.8, 127.9, 127.6, 127.3, 127.2, 67.7, 55.3, 47.5, 24.1, 10.5; CI MS ($m+1/z$) 279 (M + 2), 278 (M + 1), 277 (M), 140.

Compound **16b**: IR(film) 1710, 1380, 1295, 1230, 1120, 1098, 725, 698, 645 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.36 (m, 5H), 6.66 (ddd, 1H, J = 8, 7, 1.3 Hz), 6.33 (br dd, 1H, J = 8, 7 Hz), 5.30 (d, 1H, J = 12.5 Hz), 5.24 (d, 1H, J = 12.5 Hz), 5.17 (m, 1H), 4.25 (m, 1H), 1.9–1.5 (m, 2H), 1.23 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 154.1, 135.7, 134.8, 127.9, 127.6, 127.3, 127.2, 67.9, 54.9, 48.0, 23.3, 14.4; CI MS ($m+1/z$) 279 (M + 2), 278 (M + 1), 277 (M). Exact mass calc for $C_{14}H_{15}NO_3S$ 277.0772.

Synthesis of sulfide **17**. A soln of 1.0 M trimethylsilylmethylmagnesium chloride in ether (2.2 ml, 2.2 mmol)[3] was added to a soln of dihydrothiazine oxides **16** (555 mg, 2.0 mmol) in 10 ml of THF at −60°. The mixture was stirred for 30 min at −60° giving a white ppt. The mixture was diluted with 20 ml of sat NH_4Cl aq and diluted with 50 ml of ether and 1 ml of water. The aqueous phase was extracted twice with 20 ml of ether. The combined organic extract was dried with $MgSO_4$ and concentrated *in vacuo* to give 703 mg of crude sulfoxide as a viscous colorless oil: ^{1}H-NMR ($CDCl_3$, 60 MHz) δ 7.20 (s, 5H), 5.90 (m, 2H), 5.05 (br d, 1H, J = 8 Hz), 4.95 (s, 2H), 4.12 (m, 1H), 3.01 (m, 1H), 2.20 (d, 1H, J = 14 Hz), 1.85 (d, 1H, J = 14 Hz), 1.78 (m, 4H).

A soln of the crude sulfoxide (703 mg) in 50 ml of dry CH_2Cl_2 was added to a suspension of P_2I_4 (1.3 g, 2.2 mmol) in 20 ml of dry CH_2Cl_2 under N_2 at 25°. The mixture was stirred for 10 min at 25°, and diluted with 50 ml of water. The aqueous phase was extracted three times with 100 ml of ether. The combined organic layer was washed with sat $NaHSO_3$ aq, sat $NaHCO_3$ aq, brine, dried with $MgSO_4$, and concentrated *in vacuo* to give 682 mg of a colorless oil. Flash chromatography of this material on silica gel (3:1 hexane–ether) gave 519 mg (74% from **16**) of sulfide **17** as a colorless oil: IR(film) 3320, 3025, 1702, 1242, 842, 699 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.36 (m, 5H), 5.86 (ddd, 1H, J = 1.7, 3.4, 10.0 Hz), 5.70 (ddd, 1H, J = 1.5, 2.9, 10.0 Hz), 5.11 (s, 2H), 4.80 (br d, 1H, J = 8.4 Hz, NH), 4.26 (br m, 1H), 3.23 (br m, 1H), 1.99–1.75 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 155.5, 136.3, 130.4, 129.7, 128.2, 127.8, 127.7, 66.3, 46.3, 42.6, 26.3, 25.3, 17.0, −2.0; CI MS ($m+1/z$) 351, 350 (M + 1), 349 (M), 230, 199, 149. Exact mass calc for $C_{18}H_{27}NO_2SSi$ 349.1532. Found 349.1532.

Synthesis of silyl sulfides **20**. A soln of **17** (350 mg, 1.0 mmol) in 5 ml of acetonitrile was treated with a soln of trimethyloxonium tetrafluoroborate (192 mg, 1.3 mmol) in 5 ml of acetonitrile at −5° under N_2. The soln was stirred for 30 min at −5°, t-BuOK (170 mg, 1.5 mmol) was added, and the mixture was stirred for 60 min at −5°. The mixture was diluted with water and was extracted with ether. The combined organic layer was washed with water and brine, dried with $MgSO_4$, and concentrated *in vacuo* to give 306 mg of a yellow oil. Flash chromatography of this material on silica gel (3:1 hexane–ether) gave 181 mg (50%) of an inseparable 1.5:1

† All computer programs used were part of the Enraf-Nonius Structure Determination Package (CSDP Plus, Version 1.0), Enraf-Nonius, Delft, Holland, 1982, and implemented on a PDP 11/34 computer.

mixture of **20a** and **b**: IR(film) 3350, 1715, 1503, 1252, 1222, 865, 840, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) **20a**: δ 7.35 (m, 5H), 5.9–5.7 (m, 2H, includes NH), 5.49 (br d, 1H, J = 10.2 Hz), 5.15 (d, 1H, J = 12.2 Hz), 5.08 (d, 1H, J = 12.2 Hz), 3.99 (m, 1H), 2.90–2.70 (m, 1H), 2.09 (m, 3), 2.04 (s, 3), 2.0–1.2 (m, 1H), 1.57 (d, 1H, J = 2.6 Hz), 0.13 (s, 9); **20b**: δ 7.35 (m, 5H), 5.9–5.7 (m, 2H, includes NH), 5.49 (brd, 1H, J = 10.2 Hz), 5.14 (d, 1H, J = 12.3 Hz), 5.07 (d, 1H, J = 12.3 Hz), 4.14 (m, 1H), 2.90–2.70 (m, 1H), 2.15 (s, 3H), 2.09 (m, 3H), 1.75 (d, 1H, J = 4 Hz).

Preparation of sulfine **23**. To a soln of **6** (140 mg, 0.50 mmol) in 4 ml of THF was added vinylmagnesium bromide (0.55 ml, 1.0 M in THF) at $-60°$. The resulting soln was stirred for 30 min at $-60°$, giving a white ppt. The mixture was diluted with 20 ml of sat NH_4Cl aq, 1 ml of water, and the mixture was diluted with 20 ml of ether. The aqueous phase was extracted twice with 10 ml of ether and the combined organic layer was dried with $MgSO_4$. The solvent was removed *in vacuo* to give 156 mg (100%) of white **23**: IR(film) 3340, 1695, 1540, 1262, 1105 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 8.14 (dd, 1H, J = 8, 8 Hz), 7.36 (m, 5H), 5.55 (dq, 1H, J = 15, 6.4 Hz), 5.23 (ddd, 1H, J = 1.5, 9.5, 15 Hz), 5.11 (d, 1H, J = 12.4 Hz), 5.09 (d, 1H, J = 12.4 Hz), 4.72 (br d, 1H, J = 9 Hz, NH), 3.76 (br dq, 1H, J = 9, 7 Hz), 2.98 (ddd, 1H, J = 5, 8, 15 Hz), 2.70 (ddd, 1H, J = 7.5, 8, 15 Hz), 2.32 (br ddd, 1H, J = 5, 8, 9.5 Hz), 1.71 (dd, 3H, J = 1.5, 6.4 Hz), 1.12 (d, 3H, J = 7 Hz); ^{13}C-NMR ($CDCl_3$) δ 176.1, 155.6 130.0, 128.4, 128.3, 128.2, 128.0, 127.9, 66.6, 49.4, 47.2, 28.4, 18.0, 17.9; CI MS ($m+1/z$) 307.

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