1-Methoxy-3-methyl-5-phenyl-1-hexene (14): 820 mg (80%); a mixture of four diastereomers (*E*:*Z* = ca. 7:3); ^{1}H NMR (270 MHz) δ 6.24 (0.3 H, d, *J* = 13.0 Hz), 6.12 (0.4 H, d, *J* = 12.5 Hz), 5.85 (0.15 H, d, *J* = 6.3 Hz), 5.82 (0.15 H, d, *J* = 6.9 Hz), 4.58–4.48 (0.7 H, m), 4.18–4.10 (0.3 H, m), 3.50 (0.45 H, s), 3.47 (0.45 H, s), 3.55 (1.2 H, s), 3.52 (0.9 H, s); IR ($CHCl_3$) 1655, 1110 cm^{-1}; MS *m*/*z* (rel intensity) 204 (M^+, 70), 157 (39), 105 (37), 85 (100); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1516.

Preparation of 17. To a cold (0 °C) stirred suspension of (methoxymethyl)triphenylphosphonium chloride (1.60 g, 4.68 mmol) in dry Et_2O (32 mL) was slowly added PhLi (4.68 mmol, 2.6 mL of a 1.8 M solution in cyclohexane/Et_2O). The mixture was stirred at rt for 30 min. A solution of hirsutinal (**16**) (1067 mg, 3.60 mmol) in dry Et_2O (5.5 mL) was then added drop by drop. After 5 min, an ethereal solution of (methoxymethyl)triphenylphosphorane (4.68 mmol), prepared in the manner described above, was added. The mixture was stirred at rt for 15 min; then it was poured into cold water. The whole was extracted with EtOAc. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography on silica gel (MeOH/$CHCl_3$, 1:9) to give 940 mg (80%) of **17**: a relatively unstable amorphous powder (*E*:*Z* = ca. 1:1); UV (MeOH) λ_{max} 225, 281 nm; ^{1}H NMR (500 MHz) δ 7.73 (1 H, br s, NH), 6.30 (0.5 H, d, *J* = 12.5 Hz), 6.00 (0.5 H, dt, *J* = 7.1, 1.3 Hz), 4.72 (0.5 H, ddd, *J* = 12.5, 7.6, 7.6 Hz), 4.36 (0.5 H, ddd, *J* = 7.1, 7.1, 7.1 Hz), 3.97 (1 H, m, H-3), 3.59 and 3.56 (3 H, s), 0.86 and 0.85 (3 H, t, *J* = 7.3 Hz); IR ($CHCl_3$) 3470, 1660 cm^{-1}; MS *m*/*z* (rel intensity) 324 (M^+, 32), 309 (45), 251 (100), 169 (13). HRMS calcd for $C_{21}H_{28}ON_2$ 324.2202, found 324.2191.

Preparation of the α,β-Unsaturated Aldehydes 3, 6, 9, 12, and 15. The preparation of (*E*)-6-phenyl-2-hexenal (**3**) is typical. To a stirred suspension of $Pd(OAc)_2$ (30 mg, 0.134 mmol) in CH_3CN (0.6 mL) at rt were added 5% aqueous $NaHCO_3$ (0.05 mL) and $Cu(OAc)_2 \cdot H_2O$ (54 mg, 0.268 mmol). The mixture was cooled to 0 °C; then a solution of the methyl enol ether **2** (51 mg, 0.268 mmol) in CH_3CN (0.35 mL) was added. The mixture was vigorously stirred at 0 °C for 1 h and then at rt for 1 h. The mixture was then poured into saturated aqueous NH_4Cl and the whole was extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography on silica gel (EtOAc/hexane, 1:7) to give 43 mg (92%) of **3**: ^{1}H NMR (270 MHz) δ 9.50 (1 H, d, *J* = 8.1 Hz), 6.84 (1 H, dt, *J* = 15.4, 6.8 Hz), 6.12 (1 H, ddt, *J* = 15.4, 8.1, 1.2 Hz); UV (EtOH) λ_{max} 218 nm; IR ($CHCl_3$) 1690 cm^{-1}; MS *m*/*z* (rel intensity) 174 (M^+, 5), 130 (52), 91 (100); HRMS calcd for $C_{12}H_{14}O$ 174.1043, found 174.1040.

(*E*)-4-Phenyl-2-butenal (6): 45 mg (83%); ^{1}H NMR (270 MHz) δ 9.53 (1 H, d, *J* = 7.7 Hz), 6.97 (1 H, dt, *J* = 15.8, 6.4 Hz), 6.11 (1 H, ddt, *J* = 15.8, 7.7, 1.7 Hz), 3.65 (2 H, dd, *J* = 6.4, 1.7 Hz); UV (EtOH) λ_{max} 217 nm; IR ($CHCl_3$) 1690 cm^{-1}; MS *m*/*z* (rel intensity) 146 (M^+, 84), 117 (100), 115 (61), 91 (51). HRMS calcd for $C_{10}H_{10}O$ 146.0730, found 146.0730.

(*E*)-5,5-Dicarbethoxy-2-heptenal (9): 40 mg (94%); ^{1}H NMR (270 MHz) δ 9.50 (1 H, d, *J* = 7.7 Hz), 6.74 (1 H, dt, *J* = 15.8, 7.3 Hz), 6.14 (1 H, ddt, *J* = 15.8, 7.7, 1.3 Hz), 4.20 (4 H, q, *J* = 7.3 Hz), 2.88 (2 H, dd, *J* = 7.3, 1.3 Hz), 1.96 (2 H, q, *J* = 7.3 Hz), 1.26 (6 H, t, *J* = 7.3 Hz), 0.88 (3 H, t, *J* = 7.3 Hz); UV (EtOH) λ_{max} 216 nm; IR ($CHCl_3$) 1730, 1690 cm^{-1}; MS *m*/*z* (rel intensity) 256 (M^+, 7), 188 (66), 109 (100); HRMS calcd for $C_{13}H_{20}O_5$ 256.1309, found 256.1303.

(2*E*,12*Z*)-Heptadecadienal (12): 45 mg (90%); ^{1}H NMR (270 MHz) δ 9.51 (1 H, d, *J* = 8.1 Hz), 6.85 (1 H, dt, *J* = 15.4, 6.8 Hz), 6.11 (1 H, ddt, *J* = 15.4, 8.1, 1.3 Hz), 5.35 (2 H, m); UV (EtOH) λ_{max} 221 nm; IR ($CHCl_3$) 1690 cm^{-1}; MS *m*/*z* (rel intensity) 250 (M^+, 100), 232 (23), 193 (10), 166 (17), 134 (27), 109 (39), 95 (54), 81 (68); HRMS calcd for $C_{17}H_{30}O$ 250.2297, found 250.2290.

3-Methyl-5-phenyl-2-hexenal (15): *E*:*Z* = ca. 1:1, 42 mg (86%); ^{1}H NMR (270 MHz) δ 9.92 (0.5 H, d, *J* = 8.1 Hz), 9.73 (0.5 H, d, *J* = 8.1 Hz), 5.84 (0.5 H, dd, *J* = 8.1, 1.0 Hz), 5.80 (0.5 H, dd, *J* = 8.1, 1.0 Hz), 2.10 (1.5 H, d, *J* = 1.0 Hz), 1.90 (1.5 H, d, *J* = 1.0 Hz), 1.34 (1.5 H, d, *J* = 6.8 Hz), 1.27 (1.5 H, d, *J* = 6.8 Hz); UV (EtOH) λ_{max} 204, 237 nm; IR ($CHCl_3$) 1690, 1640 cm^{-1}; MS *m*/*z* (rel intensity) 188 (M^+, 7), 173 (9), 162 (8), 105 (100); HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1207.

Preparation of the α,β-Unsaturated Aldehyde 18. To a cold (−16 °C) stirred mixture of $Pd(OAc)_2$ (25.7 mg, 0.114 mmol), 10-camphorsulfonic acid monohydrate (27 mg, 0.108 mmol), and dry CH_3CN (1 mL) was added a solution of **17** (34.6 mg, 0.107 mmol) in dry CH_3CN (1 mL). After 80 min, the mixture was diluted with brine and was made alkaline by adding 10% aqueous NH_3. The whole was then extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography on silica gel (MeOH/$CHCl_3$, 1:6) to give 26.4 mg (80%) of **18**: an amorphous powder; ^{1}H NMR (270 MHz) δ 9.56 (1 H, d, *J* = 8.1 Hz), 7.93 (1 H, br s, NH), 6.81 (1 H, dd, *J* = 15.8, 8.1 Hz), 6.14 (1 H, dd, *J* = 15.8, 7.7 Hz), 4.27 (1 H, br s), 0.86 (3 H, t, *J* = 7.5 Hz); UV (EtOH) λ_{max} 224, 282 nm; IR ($CHCl_3$) 3460, 1685, 1630 cm^{-1}; MS *m*/*z* (rel intensity) 308 (M^+, 60), 307 (62), 279 (42), 184 (100); HRMS calcd for $C_{20}H_{24}O$ 308.1889, found 308.1885.

Supplementary Material Available: NMR spectra of new compounds (15 pages). Ordering information is given on any current masthead page.

A New Imidazole Alkaloid from the Marine Sponge *Leucetta microrhaphis*

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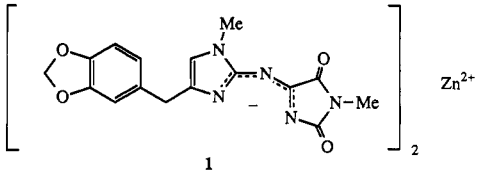
Imidazole alkaloids have recently been reported as antimicrobial constituents of the calcareous sponges *Leucetta chagosensis*[1,2] and *Clathrina clathrus*.[3] Among the more interesting of the imidazole alkaloids is clathridine, which was isolated from *C. clathrus* as a very stable zinc complex (**1**). As part of a continuing program to discover new bioactive metabolites from marine organisms, we examined a bright yellow sponge *Leucetta microhaphis* that was collected in Pohnpei in 1989. Nonpolar material from the methanolic extract of the frozen sponge tissue was chromatographed on silica gel followed by reversed-phase HPLC to obtain the known clathridine zinc complex (**1**, 0.01% dry wt), which was identified by comparison of physical and spectral data with literature values.[3] The more polar material was chromatographed on Sephadex LH-20 followed by reversed-phase HPLC to obtain a novel alkaloid, (9*E*)-clathridine 9-*N*-(2-sulfoethyl)imine (**2**, 0.018% dry wt).

(9*E*)-Clathridine 9-*N*-(2-sulfoethyl)imine (**2**) was isolated as yellow needles, mp 275–277 °C dec. The molecular formula, $C_{18}H_{20}N_6O_6S$, was determined by high-resolution mass measurement. The IR spectrum contained bands at 3410 (NH or OH), 1770 (carbonyl), and 1600 cm^{-1} (aromatic). In the ^{1}H NMR spectrum (1:5 $CDCl_3$/DMSO-d_6), the downfield signals at δ 7.01 (br s, 1 H), 6.91 (br d, 1 H, *J* = 7.9 Hz), and 6.84 (d, 1 H, *J* = 7.9 Hz) indicated the presence of a 1,2,4-trisubstituted benzene ring. The ^{13}C NMR signals due to the trisubstituted aromatic ring were assigned as shown in Table I by interpretation of the COLOC (*J* = 8 Hz) experiment. The chemical shifts of

(1) Carmely, S.; Kashman, Y. *Tetrahedron Lett.* **1987**, *28*, 3003.
(2) Carmely, S.; Ilan, M.; Kashman, Y. *Tetrahedron* **1989**, *45*, 2193.
(3) Ciminiello, P.; Fattorusso, E.; Magno, S.; Mangoni, A. *Tetrahedron* **1989**, *45*, 3873.
(4) Ciminiello, P.; Fattorusso, E.; Mangoni, A.; Di Blasio, B.; Pavone, V. *Tetrahedron* **1990**, *46*, 4387.

0022-3263/92/1957-2176$03.00/0



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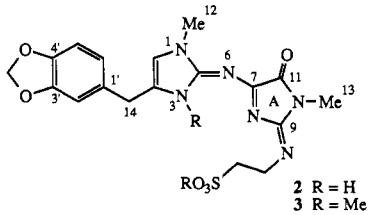
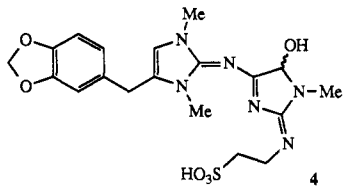


2 R = H
3 R = Me



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the ^{13}C NMR signals, together with a ^{13}C NMR signal at δ 100.7 (t) and a ^{1}H NMR signal at 5.97 (s, 2 H), implied that there was a methylenedioxy ring at C-3′ and C-4′ on the aromatic ring. In the COLOC spectrum, another methylene signal at δ 4.03 (s, 2 H) was correlated to both C-1′ and C-6′ signals and to a sp^2 quaternary carbon signal at δ 130.9 (s), indicating that the methylene group was flanked by both the aromatic ring and an olefinic bond. Furthermore, the olefinic proton signal at δ 7.14 (s) was correlated to carbon signals at 130.9 (s) and 144.0 (s), the latter signal being correlated to an *N*-methyl signal at 3.67 (s, 3 H). Nuclear Overhauser enhancement (NOEDS) experiments provided further information: irradiation of the *N*-methyl signal at δ 3.67 caused a 7% enhancement of the olefinic signal at 7.14. Methylation of **2** with excess ethereal diazomethane gave **3**, which contained two additional *N*-methyl groups, one of which was shown by an NOE experiment to be close to the C-14 methylene group. From these data, we deduced that compound **2** was closely related to clathridine.

Comparison of the ^{1}H and ^{13}C NMR data of (9*E*)-clathridine 9-*N*-(2-sulfoethyl)imine (**2**) with those of clathridine revealed that the major difference was an additional two-carbon unit attached to ring A. The ^{1}H NMR spectrum of **2** contained signals at δ 2.94 (t, 2 H, J = 6.5 Hz) and 3.95 (t, 2 H, J = 6.5 Hz) that were assigned to a taurine moiety. Consideration of the molecular formula and the COLOC correlations from the remaining *N*-methyl signal at δ 3.13 (s, 3 H) to two downfield carbon signals at 164.0 (s) and 165.0 (s) results in two possibilities for the ring-A portion of **2**. Either of the carbonyl groups at C-9 or C-11 could be condensed with taurine to obtain two possible structures that could not be differentiated from the spectral data. The location of the taurine chain was determined as follows. Reduction of the methylation product **3** with sodium borohydride in methanol gave an alcohol **4** in which the remaining carbonyl has been reduced and the sulfate ester has been hydrolyzed. The ^{1}H NMR spectrum contained a new signal at δ 5.25 (s, 1 H) that showed a 4% NOE enhancement when the ring-A *N*-methyl signal was irradiated. Since it was shown that only the "amide" carbonyl, rather than the "urea" carbonyl, is reduced to a hydroxyl group under these conditions,[1] the taurine group must be at C-9.

Table I. ^{1}H and ^{13}C NMR Spectral Data of (9*E*)-Clathridine 9-*N*-(2-Sulfoethyl)imine (2) in 1:5 $CDCl_3$/DMSO-d_6 Solution

	chemical shift		
no.	^{1}H	^{13}C	COLOC
2		144.0 (s)	H-5, Me-12
4		130.9 (s)	H-5, H-14
5	7.14 (s, 1 H)	116.9 (d)	
7		160.0 (s)	
9		165.0 (s)	Me-13
11		164.0 (s)	Me-13
12	3.67 (s, 3 H)	32.6 (q)	
13	3.13 (s, 3 H)	26.0 (q)	
14	4.03 (s, 2 H)	29.9 (t)	
16	3.95 (t, 2 H, J = 6.5 Hz)	49.8 (t)	
17	2.94 (t, 2 H, J = 6.5 Hz)	38.3 (t)	
1′		131.1 (s)	H-14, H-5′
2′	7.01 (br s, 1 H)	109.2 (d)	H-14, H-6′
3′		147.3 (s)	
4′		145.0 (s)	H-5′, H-6′
5′	6.84 (d, J = 7.9 Hz)	108.1 (d)	
6′	6.91 (br d, J = 7.9 Hz)	121.8 (d)	H-14, H-2′
7′	5.97 (s, 2 H)	100.7 (t)	

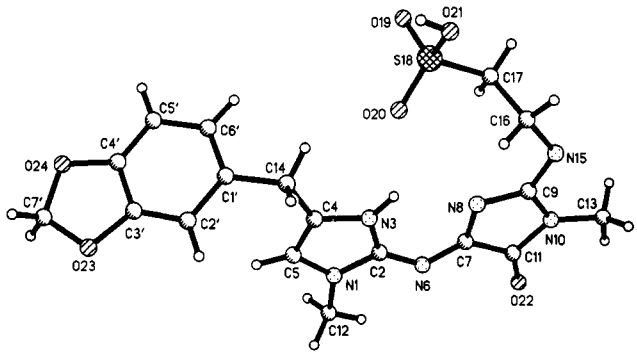

Figure 1. A computer-generated perspective drawing of the final X-ray model of (9*E*)-clathridine 9-*N*-(2-sulfoethyl)imine (**2**).

In order to confirm the structure and to establish the geometry about the C-9 imine bond, single-crystal X-ray crystallographic analysis was performed. A computer-generated perspective drawing of (9*E*)-clathridine 9-*N*-(2-sulfoethyl)imine (**2**) is given in Figure 1. There is a hydrogen bond between N3-H and N8 and the two heterocyclic rings are essentially coplanar. The taurine residue appears to sterically inhibit the formation of a 2:1 zinc complex similar to that formed by clathridine.

Experimental Section

Isolation and Purification of (9*E*)-Clathridine 9-*N*-(2-Sulfoethyl)imine (2). The bright yellow sponge *L. microrhaphis* was collected by SCUBA from Mutok Harbor, Pohnpei, in 1989 and was immediately frozen. The frozen sponge tissue (92 g, dry wt) was sliced and extracted exhaustively with methanol. The methanolic extract was evaporated to yield a brown aqueous suspension that was triturated successively with hexane and a 9:1 mixture of $CHCl_3$/BuOH. The hexane soluble material was chromatographed on silica gel using 7:3 $CHCl_3$/MeOH as eluant to yield a yellow oil. Further purification by reversed-phase HPLC on a Dynamax C_{18} column (3:2 MeOH/H_2O) resulted in the isolation of clathridine zinc complex (1, 9 mg, 0.01% dry wt) that was crystallized from methanol, mp 159–160 °C. The $CHCl_3$/BuOH-soluble material was chromatographed on Sephadex LH-20 eluted with methanol. The fractions from a yellow band were combined and evaporated to yield a brown powder that was further purified by reversed-phase HPLC on a Dynamax C_{18} column (45:55 MeOH/H_2O) to obtain (9*E*)-clathridine 9-*N*-(2-sulfoethyl)imine (2, 17 mg, 0.018% dry wt).

(9*E*)-Clathridine 9-*N*-(2-sulfoethyl)imine (2): yellow needles; mp 275–277 °C; IR ($CHCl_3$) 3400, 3000, 2470 (broad and weak), 1770, 1680, 1620, 1600, 1510, 1490, 1240 cm^{-1}; UV (MeOH) 382 mn (ϵ 13650), 278 (8610), 232 (9530); ^{1}H NMR ($CDCl_3$/

DMSO-d_6) see Table I; (5:1 $CDCl_3/CD_3OD$) δ 6.83 (br s, 1 H, H-2'), 6.81 (br s, 2 H, H-5' and H-6'), 6.54 (br s, H-5), 5.99 (s, 2 H, H_2-7'), 4.14 (t, 2 H, J = 6.5 Hz, H_2-16), 4.07 (br s, 2 H, H_2-14), 3.75 (s, 3 H, Me-12), 3.28 (s, 3 H, Me-13), 3.20 (t, 2 H, J = 6.5 Hz, H_2-17); ^{13}C NMR ($CDCl_3$/DMSO-d_6) see Table I; HRFABMS obsd m/z = 449.1236 (MH^+, $C_{18}H_{21}N_6O_6S$ requires 449.1243); CIMS m/z 341 [$MH^+ - (CH_2CH_2SO_3H)$], 232 (100).

Methylation of (9*E*)-Clathridine 9-*N*-(2-Sulfoethyl)imine (2). A stirred solution of **2** (3.0 mg) in methanol (1 mL) was treated with excess ethereal diazomethane solution for 2 h. The excess reagent was destroyed by adding 1% aqueous acetic acid, and then chloroform (2 mL) was added. The organic layer was washed with H_2O (3 × 2 mL) and dried over Na_2SO_4, and the solvent was removed to obtain a yellow oil (3.2 mg) that was purified by reversed-phase HPLC (C_{18} column, 7:3 MeOH/H_2O) to obtain the methyl ester **3** (2.0 mg): ^1H NMR ($CDCl_3$) δ 6.79 (d, 1 H, J = 7.6 Hz, H-5'), 6.66 (dd, 1 H, J = 7.6, 2 Hz, H-6'), 6.65 (br s, 1 H, H-2'), 6.36 (s, 1 H, H-5), 5.98 (s, 2 H, H-7'), 4.04 (t, 2 H, J = 7.2 Hz, H-16), 3.90 (s, 3 H, SO_3Me), 3.80 (br s, 2 H, H-14), 3.51 (s, 3 H, Me-12), 3.43 (t, 2 H, J = 7.2 Hz, H2-17), 3.38 (s, 3 H, NMe-3), 3.14 (s, 3 H, Me-13); ^{13}C NMR ($CDCl_3$) δ 165.3 (s), 163.4(s), 159.9 (s), 148.2 (s), 147.0 (s), 146.5 (s), 128.8 (s), 128.3 (s), 121.7 (d), 115.3 (d), 108.8 (d), 108.7 (d), 101.3 (t), 55.7 (q), 50.8 (t), 42.6 (t), 34.5 (q), 31.2 (q), 30.4 (t), 25.6 (q).

Reduction of Methyl Ester 3. Sodium borohydride (3.0 mg) was added to a solution of **3** (1.8 mg) in methanol (0.5 mL), and the solution was stirred for 30 min at room temperature, after which time the excess reagent was destroyed with dilute acetic acid. The solvent was evaporated, and the product was extracted with chloroform (3 × 2 mL) and purified by reversed-phase HPLC (C_{18} column, 1:1 MeOH/H_2O) to obtain **4** (0.9 mg): ^1H NMR (10:1 $CDCl_3/CD_3OD$) δ 6.79 (d, 1 H, J = 8 Hz, H-5'), 6.66 (br d, 1 H, J = 8 Hz, H-6'), 6.65 (br s, 1 H, H-2'), 6.47 (s, 1 H, H-5), 5.99 (s, 2 H, H-7'), 5.25 (s, 1 H, H-11), 4.00 (m, 2 H, H-16), 3.83 (br s, 2 H, H-14), 3.61 (m, 1 H, H-17), 3.30 (m, 1 H, H-17), 3.54 (s, 3 H, Me-12), 3.38 (s, 3 H, NMe-3), 3.06 (s, 3 H, Me-13); HRFABMS obsd m/z 465.1559 (MH^+), $C_{19}H_{25}N_6O_6S$ requires 465.1556.

Single Crystal X-ray Diffraction Analysis of (9*E*)-Clathridine 9-*N*-(2-Sulfoethyl)imine (2). (9*E*)-Clathridine 9-*N*-(2-sulfoethyl)imine (**2**) crystallized as yellow blocks, and a single crystal with dimensions 0.4 × 0.4 × 0.4 mm was selected for further analysis. Preliminary photographs displayed orthorhombic symmetry with accurate lattice constants, determined by a least-squares fit of 25 diffractometer-measured 2θ values in the range $30° \leq 2\theta \leq 45°$, of a = 8.363 (2), b = 10.586 (2), and c = 22.800 (3) Å. Systematic absences indicated space group $P2_12_12_1$, and density considerations required one molecule of $C_{18}H_{20}N_6O_6S$ for the asymmetric unit. A total of 1621 reflections with $2\theta \leq 116°$ were measured using a variable speed θ:2θ scan. Periodically monitored check reflections showed no significant decomposition. After correction for Lorentz, polarization, and background effects, a total of 1552 (97%) reflections were judged observed ($|F_o| \geq 3\sigma|F_o|$). The structure was solved using the SHELXTL library of programs. Full-matrix least-squares refinements with anisotropic non-hydrogen atoms and fixed riding hydrogens have converged to a conventional crystallographic discrepancy index of R = 0.046 and R_w = 0.067 with $w = \sigma^2(F + 0.0005F^2)$. The final difference electron density map was essentially featureless with ±0.38 eÅ^3. Additional crystallographic details are available as supplementary material.

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Supplementary Material Available: Tables of crystal data, data collection, solution and refinement, fractional coordinates, bond distances, bond angles, and thermal factors for (9*E*)-clathridine 9-*N*-(sulfoethyl)imine (**2**) (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

ω-Heteroatom Effect on the Nickel-Catalyzed Reactions of Benzylic Thioethers with Grignard Reagents

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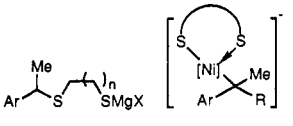
The nickel-catalyzed cross-coupling reactions of aryl, vinylic, and allylic organosulfur compounds with the Grignard reagent are well-documented.[1] It is noted that simple benzylic thioethers are relatively unreactive under these conditions.[2] To illustrate, the reaction of α-thiomethoxytoluene with PhMgBr in the presence of $NiCl_2L_2$ (L = Ph_3P or dppp) afforded diphenylmethane in only 9% yield and over 70% of the starting material was recovered. The impediment may arise from the difficulty in achieving an intermolecular oxidative addition process cleaving the carbon–sulfur bond. We recently reported that benzylic dithioacetals react with Grignard reagents in the presence of the nickel catalyst to give the corresponding styrenes[3,4] or geminal dialkylated products[3,5] in good yields. Occasionally, the reaction can proceed at room temperature. The involvement of intermediate **1** has been speculated (Scheme I).[4] Although **1** is a benzylic thioether, an appropriately located anionic sulfur moiety may effectively coordinate to the nickel catalyst to form a chelation complex which may undergo a smooth *intramolecular* oxidative addition across the benzylic carbon–sulfur bond. In order to test the validity of this conjecture, we have carried out a systematic study to investigate the effect of different ω-heteroatoms in the thioether chain on the reactivity of the benzylic carbon–sulfur bond in the nickel-catalyzed reactions.

Results and Discussion

As just mentioned, **1** is the key intermediate for the olefination reaction of the benzylic dithioacetal with the Grignard reagent and can readily proceed a formal elimination process to give an olefin.[4] We have therefore synthesized various benzylic thioethers **2** (see Experimental Section) for comparison.

At room temperature, **2** was treated with 4 equiv of MeMgI in the presence of 5 mol % of $NiCl_2(PPh_3)_2$ for 18 h. The results are compiled in Table I. Both the chain length connecting the benzylic sulfur atom to the ω-heteroatom and the nature of the heteroatom affect the reactivity of **2**.

Under the reaction conditions, **2a–e** rapidly react with the Grignard reagent to generate the corresponding thiolate anion **4**, which would associate with the nickel to give intermediate **1** (X = S). Further intramolecular oxidative addition across the benzylic carbon–sulfur bond gives **5**,



4 **5**

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