oxyphenoxy)-2-furoate, 80224-74-4; hydroquinone bis(2-carbethoxy-5-furyl ether), 113451-99-3; 5-cresoxy-2-furoic acid, 60698-27-3; 5-(phenylthio)-2-furoic acid, 61942-18-5; 5-(4-methoxyphenoxy)-2-furoic acid, 73420-66-3; 5-methoxy-2-furoic acid, 94084-62-5; 2,2-bis[4-[(2-carboxy-5-furyl)oxy]phenyl]propane, 113452-00-9; hydroquinone bis(2-carboxy-5-furyl ether), 113452-01-0; *N*-methyl-3-cresoxyphthalimide, 113452-02-1; methyl 2-iodobenzoate, 610-97-9; 2-cresoxybenzoic acid, 21905-69-1; 1,3-phenylene-*N*,*N*-bis(3-cresoxyphthalimide), 113452-03-2; *m*-phenylenediamine, 108-45-2; 4,4′-methylenedianiline-*N*,*N*′-bis(3-cresoxyphthalimide), 113452-04-3; 4,4′-methylenedianiline, 101-77-9; *N*-phenyl-3-methoxyphthalimide, 3039-43-8; 3-methoxyphthalic anhydride, 14963-96-3; 2,2-bis(4-hydroxyphenyl)propane bis(*N*-phenyl-3-phthalimidyl ether), 54395-38-9; *N*-phenyl-3-nitrophthalimide, 19065-85-1; hydroquinone bis(*N*-phenylphthalimid-3-yl ether), 54395-39-0; 5-methyl-2-furoic acid, 1917-15-3; 2-furoic acid, 88-14-2; 2-methoxyfuran, 25414-22-6; 2-(4-methoxyphenoxy)furan, 113474-66-1; 2-cresoxyfuran, 60698-28-4; 2-phenylthiofuran, 16003-14-8; maleic anhydride, 108-31-6; *N*-methylmaleimide, 930-88-1; *N*-phenylmaleimide, 941-69-5; methylacrylate, 96-33-3; acryloyl chloride, 814-68-6; dimethyl fumarate, 624-49-7; 3-cresoxyphthalic anhydride, 63181-77-1; *N*-phenyl-3-cresoxyphthalimide, 63181-79-3; methyl 2-cresoxybenzoate, 21905-72-6; dimethyl, 63181-72-6; 1,3-phenylene-*N*,*N*′-bis(phthalimide), 3006-93-7; 4,4′-methylenedianiline-*N*,*N*′-bis(phthalimide), 13676-54-5; *N*-phenyl-3-(phenylthio)phthalimide, 58045-34-4; *N*-phenyl-3-(4-methoxyphenoxy)phthalimide, 63197-27-3.

Dysidazirine, a Cytotoxic Azacyclopropene from the Marine Sponge *Dysidea fragilis*

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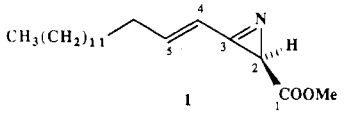
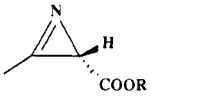
The cosmopolitan sponge *Dysidea fragilis* has been shown to produce several different sesquiterpenes and the nature of these natural products shows a marked geographic variation. For instance the sponge collected from Hawaii yielded the bicyclic sesquiterpenes upial[1] and the nakafurans 8 and 9.[2] Extraction of *D. fragilis* from Brittany, on the other hand, gave a series of sesquiterpenes based on the monocyclic sesquiterpene penlanfuran.[3] In surprising contrast to these reports we have found that *D. fragilis* (Montagu, 1818) collected in Fiji contains no sesquiterpenes but a new cytotoxic azacyclopropene carboxylic acid ester, dysidazirine (1). This represents the first example of this ring strained class of heterocycles from a marine source and, to our knowledge, only the second reported naturally occurring 2*H*-azirine.[4]

Isolation and Structure of Dysidazirine (1). The methanol extract of *D. fragilis* was shown to be cytotoxic against L1210 cells and inhibited the growth of *Pseudomonas aeruginosa*, *Candida albicans*, and *Saccaromyces cerevisiae*. The dichloromethane-soluble portion of this extract was subjected to silica gel chromatography to give dysidazirine (1, $[\alpha]_D$ −165°) *as the major lipophilic component* of the sponge (4.2% of dry weight). Further elution gave a mixture of steroidal 5,7-dienes and their corresponding *endo*-peroxides.[5]

The electron impact mass spectrum of dysidazirine (1) displayed a molecular ion at *m*/*z* 307 and accurate mass measurement of the fragment ion due to the loss of COOMe (*m*/*z* 248.2376) provided the formula $C_{19}H_{33}NO_2$. Analysis of the spectroscopic data of 1 suggested a C-18 fatty acid derivative. Inspection of the ^1H NMR spectrum ($CDCl_3$) revealed a signal at δ 3.72 (s, 3 H) assigned to the methyl protons in a carbomethoxyl group. This was supported by the mass spectral loss of COOMe from the molecular ion (above), together with the ^{13}C NMR spectrum which showed signals at 172.0 ppm (quaternary) and 52.0 ppm (CH_3) and an infrared band at 1736 cm^{-1}. Two strongly coupled proton signals at δ 6.56 (d, 1 H, J = 15.5 Hz) and 6.70 (dt, 1 H, J = 15.5, 6.4 Hz) were assigned to a trans-disubstituted olefin. The signal at 6.70 ppm was further coupled to an allylic methylene signal at 2.37 (m, 2 H) which in turn was connected to a linear C-12 alkyl chain (1.52, m, 2 H; 1.26, br s, 20 H; 0.88, t, 3 H). An unpaired sp^2 signal (156.4 s) in the ^{13}C NMR spectrum was assigned to an imino double bond. The presence of a UV band (λ_{max} 222 nm, ε 16 600) showed that the olefin was conjugated to the imino group but not to the carbomethoxyl group as deduced by the differences in the chemical shifts for the olefinic protons of 1 and those of *trans*-methyl 2-octadecenoate.[6] The remaining ^{13}C NMR signals were an sp^3 methine at 28.1 ppm and those assigned to the alkyl side chain.

Four double-bond equivalents were indicated by the molecular formula; therefore, 1 requires one ring incorporating the imino nitrogen and the sole sp^3 methine carbon (28.1 ppm). This was shown to be a substituted





2*H*-azirine for the following reasons. A gated-coupled ^{13}C NMR spectrum revealed an exceptionally large $^1J_{CH}$ (189.5 Hz) for the C-2 methine carbon (28.1 ppm), typical of 2*H*-azirines.[7] The C-2 signal was shown to be correlated to the H-2 signal at 2.57 (s, 1 H) by a 2D ^1H–^{13}C correlation experiment. This agrees well with the H-2 signal (δ 2.44 ppm) of azirinomycin methyl ester (2).[4] The infrared band at 1770 cm^{-1} is assigned to the imino double bond and the exceptionally high frequency of this C=N stretch also supports a 2,3-disubstituted azirine.[8] The above substructures were assembled to give the structure 1. This was confirmed by long-range 2D ^1H–^{13}C correlations;[9] H-2

†Alfred Sloan Foundation Fellow, 1985–1989; NIH Career Development Awardee, 1987–1992.

(1) Schulte, G.; Scheuer, P. J.; McConnell, O. J. *J. Org. Chem.* **1980**, *45*, 552.
(2) Schulte, G.; Scheuer, P. J.; McConnell, O. J. *Helv. Chim. Acta* **1980**, *63*, 2159.
(3) Guella, G.; Guerriero, A.; Traldi, P.; Petra, F. *Tetrahedron Lett.* **1983**, *24*, 3897.
(4) Azirinomycin (10), an azacyclopropene antibiotic isolated from a strain of the soil bacterium *Streptomyces aureus*, bears a structural similarity to 1; Miller, T. W.; Tristam, E. W.; Wolf, F. J. *J. Antibiot.* **1971**, *24*, 48.
(5) Cf. Gunatilaka, A. A. L.; Gopichand, Y.; Schmitz, F. J.; Djerassi, C. *J. Org. Chem.* **1981**, *46*, 3860.
(6) Prepared from stearic acid by the following route; bromination (Br_2/PBr_3, 48 h) followed by dehydrobromination (potassium *tert*-butoxide/*tert*-butyl alcohol, reflux, 24 h) gave 2-octadecenoic acid which was esterified (MeOH/H_2SO_4, reflux, 16 h) to yield methyl *trans*-2-octadecenoate: δ 5.82 (dt, 1 H, J = 15.7, 1.5 Hz), 6.98 (dt, 1 H, J = 15.7, 6.8 Hz).
(7) Nair, V. *J. Magn. Reson.* **1974**, *6*, 483. Isomura, K.; Taniguchi, H. *Org. Magn. Reson.* **1977**, *9*, 559.
(8) Hassner, A. "Small Ring Heterocycles, Part 1: Aziridines, Azirines, Thiiranes, Thiirenes", from *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Taylor, E., Eds.; Interscience: New York, 1983; Vol. 42, p 220.
(9) A COLOC experiment, optimized for J_{CH} = 6 Hz, was performed on 1: Kessler, H.; Griesinger, C.; Zarlock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.

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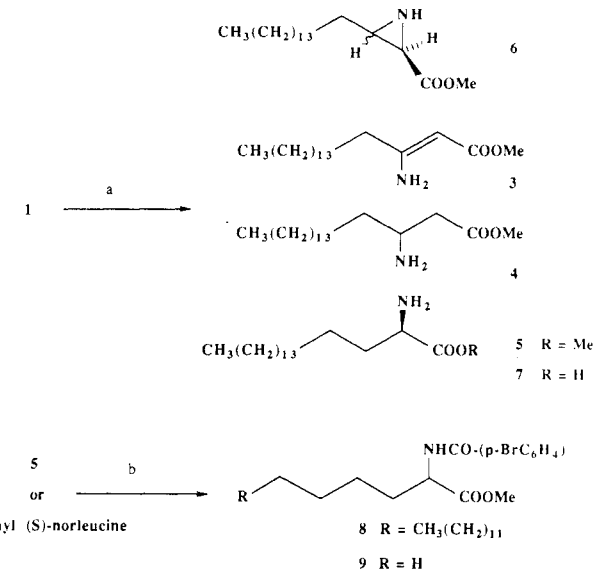
Chart I[a]



[a] (a) H_2, PtO_2, CH_2Cl_2, 5.5 h; (b) *p*-bromobenzoyl chloride, py, DMAP, CH_2Cl_2.

is correlated to C-1, C-2, and C-3, H-4 is correlated to C-2 and C-3, and H-5 is correlated to C-2 and C-4.

Absolute Configuration of Dysidazirine. Dysidazirine is strongly levorotatory ($[\alpha]_D$ −165°) and one of the few reported optically active 2*H*-azirines. For the purpose of determining the absolute configuration at C-2 in **1**, however, there were no suitable models for comparison. In lieu of this, it was more appropriate to convert **1** to a simple derivative which preserved the C-2 configuration and allowed correlation with a compound of known configuration.

Hydrogenation of **1** (Chart I) gave a mixture of products. The major product was the β-enamino ester **3** (*m/z* 311.2824, M^+), as evidenced by the UV spectrum (λ_{max} 275 nm, ε 17 300) and a one proton signal (4.55 s, 1 H) in the ^1H NMR spectrum, consistent with an olefinic proton of an enamine. Two isomeric amino esters, **4** and **5**, were obtained in low yield. The α-amino ester **5** (*m/z* 313, M^+), formed by hydrogenolysis of the β C–N bond of the putative aziridine intermediate **6**, is identical by ^1H NMR, IR, and MS with racemic methyl 2-aminooctadecanoate, prepared by ammonolysis of 2-bromostearic acid followed by esterification.[10] Hydrolysis of **5** (HCl, THF/H_2O, 12 h) gave the sparingly soluble α-amino acid **7** (mp 224–226 °C).

Although neither enantiomer of **7** has been previously characterized, the antipodes of several homologous straight long chain α-amino alkanoic acids and their specific rotations (all are approximately of magnitude 23–30°) are known.[11] Measurement of the optical rotation of **7** in several solvents (6 M HCl, 1:2 dioxane/3 M HCl, glacial acetic acid) failed to give a reliable specific rotation due to the very low solubility of **7** and the relatively weak rotatory power of these α-amino acids. The absolute configuration of **1** was, therefore, determined by measurement of the circular dichroic spectrum of **8**, the corresponding 2-*N*-(*p*-bromobenzamide) of **5**, and comparison with that of the *p*-bromobenzamide of methyl (*S*)-norleucine (**9**). Compound **9** exhibited a distinct positive Cotton effect at 241 nm (Δε +1.88, Figure 1), associated with the *p*-bromobenzamido group, and a negative Cotton effect at 222 nm (Δε −1.59). The circular dichroic spectrum of **8** was essentially the reverse of that of **9** and, therefore, **8**, **7**, **5**, and dysidazirine (**1**) all have the 2*R* configuration.

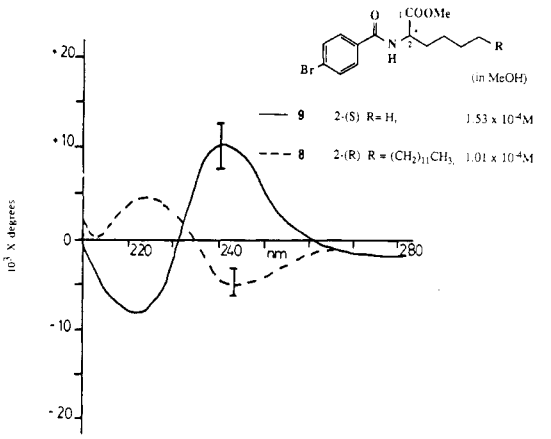


Figure 1. Circular dichroic spectra of *p*-bromobenzamides **8** and **9** in methanol.

A possible biosynthesis of **1** is not clear. The C-2 configuration of **1** is opposite to that of azirinomycin (**10**) but is the same as that of D-sphingosine. Sphingosine, a C-18 lipophilic amino alcohol, is a well-known component of glycolipids in animal cell membranes;[12] however, it is not clear whether the similarity with this sponge metabolite, **1**, is merely coincidental or suggests a modified but parallel biogenesis. Dysidazirine is cytotoxic to L1210 cells at 0.27 μg/mL and inhibited the growth of Gram negative bacteria (*P. aeruginosa*) and yeast (*C. albicans*, *S. cerevisiae*) at a minimum concentration of 4 μg per disk in a standard paper disk assay.

Experimental Section

FT infrared spectra were recorded on a Beckmann 2100 Fourier transform infrared spectrometer. ^1H NMR spectra (200 Mz) and ^{13}C NMR spectra (50.3 Mz) were recorded in $CDCl_3$ on an IBM AF 200 spectrometer and are referenced to residual chloroform (δ 7.26) for proton and the center line of the $CDCl_3$ signal (77.00 ppm) for carbon. Circular dichroism was measured on a Jasco J40A spectropolarograph.

Extraction of *Dysidea fragilis* (Montagu, 1818). The frozen sponge (40 g wet weight, 4.7 g dry weight) was soaked in MeOH for 2 h. The MeOH extract was filtered off and fresh MeOH added. The combined extracts were evaporated and the oily aqueous residue partitioned against CH_2Cl_2. The CH_2Cl_2-soluble fraction was concentrated in vacuo to give a red oil (359 mg) which was subjected to flash chromatography[13] using a gradient of diethyl ether in hexanes. A minor UV-active fraction was eluted followed by dysidazirine (**1**, 196 mg, 4.2% of dry weight), a mixture of steroidal 5,7-dienes and their corresponding epidioxides (23 mg, 0.5%),[5] and more polar lipids.

Dysidazirine (1), low melting solid: $[\alpha]_D$ −165° (*c* 0.5, MeOH); UV (MeOH) 222 nm (ε 16 600); FTIR (neat) 1770, 1736 cm^{-1}; ^1H NMR δ 0.88 (t, 3 H, *J* = 6.5 Hz), 1.26 (br s, 20 H), 1.52 (m, 2 H), 2.37 (dt, 2 H, *J* = 6.4 Hz), 2.57 (s, 1 H), 3.72 (s, 3 H), 6.56 (d, 1 H, *J* = 15.5 Hz), 6.7 (dt, 1 H, *J* = 15.5, 6.4 Hz); ^{13}C NMR 14.0 q, 22.6 t, 27.7 t, 28.1 d (C-2, $^1J_{CH}$ = 189.5 Hz), 29.0 t, 29.2 t, 29.4 t × 2, 29.5 t × 4, 31.8 t, 33.1 t, 52.0 q, 112.8 d, 155.6 d, 156.4 s,

(10) Hell, C. *Ber.* **1891**, *24*, 2395. The crude 2-aminooctadecanoic acid so prepared was esterified by heating a solution of the acid in dry MeOH saturated with dry HCl and recrystallization of the resulting racemic hydrochloride salt of **5** from ethyl acetate, mp 110–112 °C (lit. mp 112 °C, Fischer, E. *Justus Liebigs Ann. Chem.* **1908**, *363*, 339). The free base was obtained by partitioning of the hydrochloride between CH_2Cl_2 and aqueous 10% potassium carbonate solution.

(11) Birnbaum, S. M.; Fu, S.-C. J.; Greenstein, J. P. *J. Biol. Chem.* **1953**, *203*, 333.

(12) Kanfer, J. N.; Hakamori, S-I. *Sphingolipid Biochemistry*, Plenum Press: New York, 1983.

(13) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

172.0 s; EIMS, m/z (relative intensity) 307 (M^+, 18), 278 (14), 264 (18), 248 (31), 152 (67), 139 (28), 138 (30), 83 (46), 81 (38), 80 (40), 69 (40), 68 (36), 67 (46), 57 (42), 55 (100).

Hydrogenolysis of Dysidazirine (1): Methyl (*R*)-2-Aminooctadecanoate (5) and β-Enamino Ester 3. A solution of 1 (32.7 mg) in CH_2Cl_2 (2.0 mL) was added to a stirred slurry of prehydrogenated platinum oxide (21 mg) in CH_2Cl_2 (2.0 mL) under 1 atm of hydrogen. The mixture was stirred for 5.5 h and then eluted through a short column of silica (0.6 × 4 cm) with 1:1 ethyl acetate/hexanes to provide three fractions.

(i) A UV-active, nonpolar fraction (15.8 mg). Purification of this by HPLC (Partisil M9/50, 1:3 ethyl acetate/hexanes) gave pure β-enamino ester **3** (3.5 mg).

β-Enamino ester 3: low melting solid, FTIR (neat) 3440, 3330, 1741, 1672, 1651, 1620, 1578 cm^{-1}; UV (MeOH) 275 nm (ε 17 300); ^1H NMR δ 0.89 (t, 3 H, J = 6.4 Hz), 1.26 (br s, 28 H), 1.50 (m, 2 H), 2.13 (t, 2 H, J = 7.6 Hz), 3.66 (s, 3 H), 4.55 (s, 1 H); EIMS, m/z (relative intensity) 311 (M^+, 69), 280 (66), 129 (79), 128 (100), 116 (97), 115 (100), 83 (92), 74 (54), 69 (53), 57 (100), 55 (97); HRMS, m/z 311.2813, $C_{19}H_{37}NO_2$ requires 311.2824.

(ii) Further elution (ethyl acetate) gave a ninhydrin-positive fraction (8 mg) which was purified by HPLC (Partisil M9/50, 5:95 2-propanol/ethyl acetate) to afford ester **5** (2.8 mg).

Methyl (*R*)-2-aminooctadecanoate (5): oil, FTIR (neat) 3394, 1723 cm^{-1}; ^1H NMR δ 0.89 (t, 3 H, J = 6.5 Hz), 1.26 (br s, 30 H), 3.45 (br t, 1 H, J = 6.1 Hz), 3.72 (s, 3 H); EIMS, m/z (relative intensity) 313 (M^+, 20), 257 (23), 255 (86), 255 (86), 254 (98), 102 (49), 88 (63), 57 (67), 55 (78), 56 (100), 55 (78). Amino ester **5** was identical (by ^1H NMR, IR, MS) with racemic methyl 2-aminooctadecanoate prepared by ammonolysis of 2-bromostearic acid.[10]

The hydrochloride salt of **5** was prepared by evaporation of a solution of **5** (0.5 mg) in MeOH (1 mL) containing concentrated hydrochloric acid (2 drops). Crystallization from ethyl acetate gave colorless needles, mp 114–115 °C (cf. lit.[10] for racemic compound, mp 112 °C).

(iii) Finally, elution with 10% 2-propanol/ethyl acetate gave a second, polar ninhydrin-positive fraction (3.1 mg), containing the β-amino ester **4**: ^1H NMR δ 2.28 (dd, 1 H, J = 15.7, 8.9 Hz), 2.48 (dd, 1 H, J = 15.7, 4.0 Hz), 3.18 (m, 1 H), 3.70 (s, 3 H). Irradiation of the H-3 signal (δ 3.18) collapsed the diastereotopic methylene proton signals (δ 2.28, 2.48) to an AB quartet.

Hydrolysis of Ester 5: (*R*)-2-Aminooctadecanoic Acid (7). Hydrochloric acid (6 M, 1.0 mL) and water (1.0 mL) were added to a solution of **5** in THF (2.0 mL), and the mixture was heated at reflux under nitrogen (12 h). After cooling, the volatiles were removed under reduced pressure and the residue was crystallized from glacial acetic acid to afford the sparingly soluble α-amino acid **7**: mp 224–226 °C (cf. lit.[10] mp 221–222 °C for racemic compound); FABMS, m/z 300 (MH^+).

***p*-Bromobenzamides of Amino Acid Methyl Esters.** A solution of ester **5** (2.8 mg, 9.0 μmol) in dry CH_2Cl_2 (0.5 mL) was treated with pyridine (0.10 mL), (dimethylamino)pyridine (DMAP), and a solution of *p*-bromobenzoyl chloride (5.9 mg, 27 μmol) in CH_2Cl_2 (0.6 mL). The mixture was allowed to warm to room temperature over 30 min and then treated with ice-cold saturated sodium bicarbonate solution (0.5 mL). After 15 min the mixture was partitioned against CH_2Cl_2 (2 × 3 mL) and the combined organic layers were washed with water (1 mL), dried over sodium sulfate, and evaporated to afford crude benzamide (6.3 mg). This was purified by HPLC (silica gel, 4:25 ethyl acetate/hexanes) to give pure methyl (*R*)-2-(*p*-bromobenzamido)octadecanoate (**8**, 2.5 mg).

Benzamide 8: mp 76–77 °C (ethyl acetate/hexanes); $[\alpha]_D$ +9° (*c* 0.2, MeOH); UV (MeOH) 241 nm (ε 19 500); CD (MeOH) 223 nm (Δε +1.4), 242 (−1.7); IR 3303, 2917, 2850, 1744, 1643, 1592 cm^{-1}; ^1H NMR δ 0.89 (t, 3 H, J = 6.7 Hz), 1.25 (br s, 28 H), 1.7–2.1 (m, 2 H), 3.80 (s, 3 H), 4.80 (ddd, 1 H, J = 7.7, 6.8, 5.5 Hz), 6.60 (br d, 1 H, J = 7.7 Hz), 7.60 (d, 2 H, J = 8.8 Hz), 7.68 (d, 2 H, J = 8.8 Hz); EIMS m/z (relative intensity) 497 (M^+, 34), 495 (38), 439 (73), 437 (74), 313 (96), 273 (83), 271 (87), 185 (100), 183 (100), 57 (44), 56 (36), 55 (45).

A suspension of (+)-(*S*)-norleucine (Aldrich, 100 mg) in dry MeOH (10 mL) was cooled to 0 °C and saturated with HCl. The resulting clear solution was heated under reflux (3 h), cooled, and evaporated. A portion (50 mg) of the resulting crude methyl ester hydrochloride was *p*-bromobenzoylated as for **5** except for the addition of triethylamine (3 equiv) to neutralize the HCl. Crystallization from ethyl acetate/hexanes gave pure methyl (*S*)-2-(*p*-bromobenzamido)hexanoate (**9**, 66 mg, 77%) as colorless needles.

Benzamide 9: mp 94–95 °C; UV (MeOH) 241 nm (ε 12 200); CD (MeOH) 222 nm (Δε −1.59), 240 (+1.88); FTIR 3350, 2956, 1744, 1655 cm^{-1}; ^1H NMR δ 0.91 (t, 3 H, J = 7.0 Hz), 1.35 (m, 4 H), 1.70–2.10 (m, 2 H), 3.80 (s, 3 H), 4.81 (ddd, 1 H, J = 7.6, 6.9, 5.5 Hz), 6.64 (br d, 1 H, J = 7.6 Hz), 7.61 (d, 2 H, J = 8.7 Hz), 7.67 (d, 2 H, J = 8.7 Hz); EIMS, m/z (relative intensity) 329 (M^+, 19), 327 (18), 273 (47), 271 (60), 270 (64), 268 (67), 185 (100), 183 (100), 157 (22), 155 (23).

Acknowledgment. We thank Avril Ayling for identification of the sponge, Dr. Udey Raj and the Institute of Marine Resources, University of the South Pacific, for use of facilities, and the Ministry of Home Affairs, Fiji. This work was supported by NIH Grants CA 36622 and CA 01179.

Registry No. 1, 113507-74-7; 3, 113507-75-8; 5, 113532-98-2; 7, 100680-17-9; 8, 113507-76-9; 9, 113507-77-0; *p*-BrC_6H_4COCl, 586-75-4; (±)-(*S*)-norleucine, 327-57-1.

On the Mechanism of Sodium Cyanoborohydride Reduction of Tosylhydrazones

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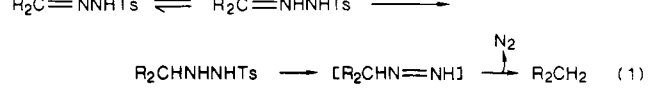
Reduction of tosylhydrazone derivatives of saturated ketones and aldehydes with sodium cyanoborohydride in acidic media is a synthetically useful method for the conversion of carbonyl compounds to the corresponding alkanes.[1] With α,β-unsaturated tosylhydrazones, this reduction produces alkenes[2] with double bond migration to the site originally occupied by the carbonyl group.[1c,3] The reaction course for the reduction of α,β-unsaturated tosylhydrazones has been shown[2,4] to proceed with initial protonation of the tosylhydrazone to form an imminium cation followed by hydride reduction of the C=N double bond.[1,2,5] Subsequent *p*-toluenesulfinate elimination and then loss of N_2 afford the corresponding reduced hydrocarbon (eq 1).[6] Similar results have also been found in



(1)

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