The reactivity of *N*,*N*-dialkyl-*N*-(3-phenylsulfinyltetrahydrofuran-2-ylidene)ammonium bromide*

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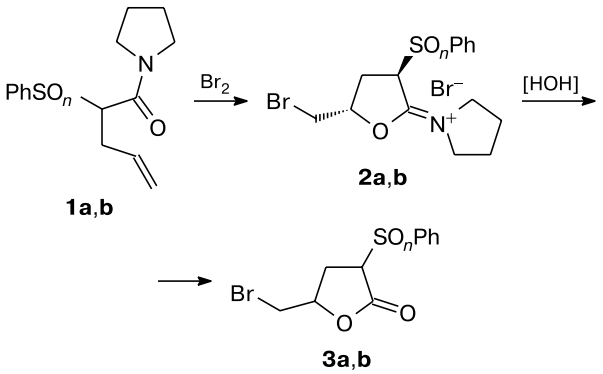
trans-Stereoselective electrophilic cyclization of (2*R**,S*S**)-*N*,*N*-diisopropyl-2-phenylsulfinylpent-4-enamide under the action of bromine afforded (3*R**,5*S**,S*S**)-*N*-(5-bromomethyl-3-phenylsulfinyltetrahydrofuran-2-ylidene)-*N*,*N*-diisopropylammonium bromide. Its transformations under the conditions of hydrolysis, dehydrobromination, and hydride reduction were studied.

Key words: (2*R**,S*S**)-*N*,*N*-diisopropyl-2-phenylsulfinylpent-4-enamide, bromocyclization, iminium compounds, (3*R**,5*S**,S*S**)-*N*-(5-bromomethyl-3-phenylsulfinyltetrahydrofuran-2-ylidene)-*N*,*N*-diisopropylammonium bromide, hydrolysis, hydride reduction.

Earlier,[1] we have reported on a novel approach to the synthesis of natural butanolides *via trans*-stereoselective electrophilic cyclization of *N*,*N*-dialkyl-2-phenylthio- and -2-phenylsulfonylpent-4-enamides (**1**) into iminium salts **2a,b** (Scheme 1). Hydrolysis of salts **2** gives substituted butano-4-lactones **3**, which are promising functionalized synthons of some natural metabolites.

Scheme 1



n = 0 (**a**), 2 (**b**)

Bromocyclization of a sulfinyl-containing substrate (n = 1) seemed to be a good challenge for the synthesis of sulfoxides of the type **3**, as well as in the optically active form (*cf.* Refs 2—4).

For this purpose, we initially used the earlier[1b] described phenylthio amide **4** as the starting material, which was smoothly oxidized into the corresponding sulfoxide **5** (Scheme 2). Allylation of the latter proved to be diastereoselective, leading to two diastereomers **6a** and **6b** in the ratio ~5 : 1. The major isomer **6a** was a labile oily product: even during its isolation by chromatography, it underwent partial elimination of the sulfenic acid residue to give diene amide **7**. Complete transformation of compound **6a** into diene **7** was attained by heating its solution in toluene. This fact can serve as indirect evidence for the stereochemistry of sulfinyl amide **6a**. Indeed, in terms of the current concepts, such a reaction is referred to as *syn*-elimination (*e.g.*, see Ref. 5). From consideration of two possible transition states **A** and **B**, it follows that this transformation will occur more easily in the former case since for the latter, the bulky (phenyl and dialkylamino) substituents should be arranged in the eclipsed conformation along the C(2)—S bond. Therefore, more labile sulfinyl amide **6a** should be assigned the relative 2*S**,S*R**-configuration of the substituents and its isomer **6b**, the 2*R**,S*R**-configuration.

The resulting pyrrolidine derivatives **6** reacted with bromine to give crystalline products **8**. Their ^{1}H NMR spectra contained signals characteristic of iminium salts **2**. However, the unexpectedly high labilities of these products precluded their reliable identification and made them unpromising for further transformations.

N,*N*-Diisopropyliminium salt **9** was more stable. It was obtained analogously from accessible phenylthioacetic acid **10** through the formation of its *N*,*N*-diisopropyl

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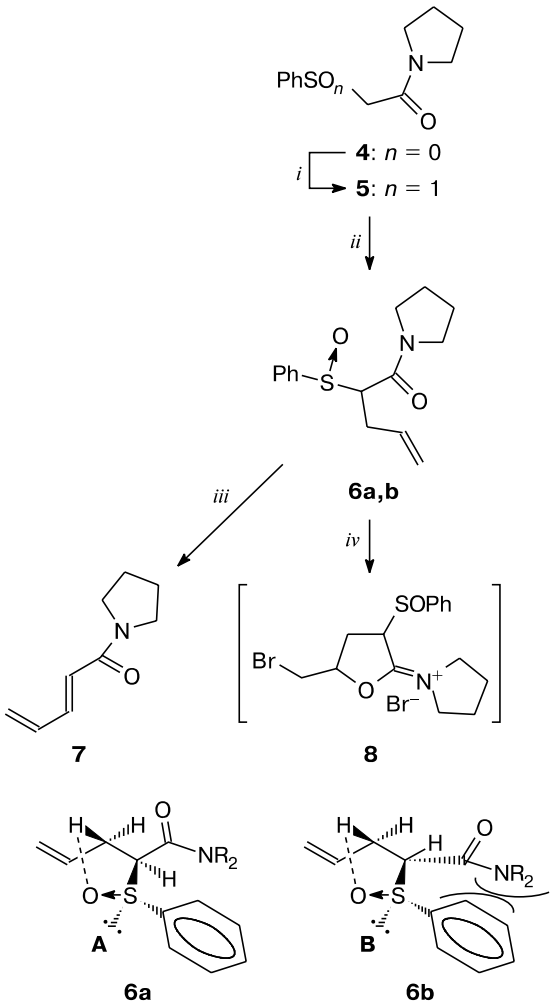
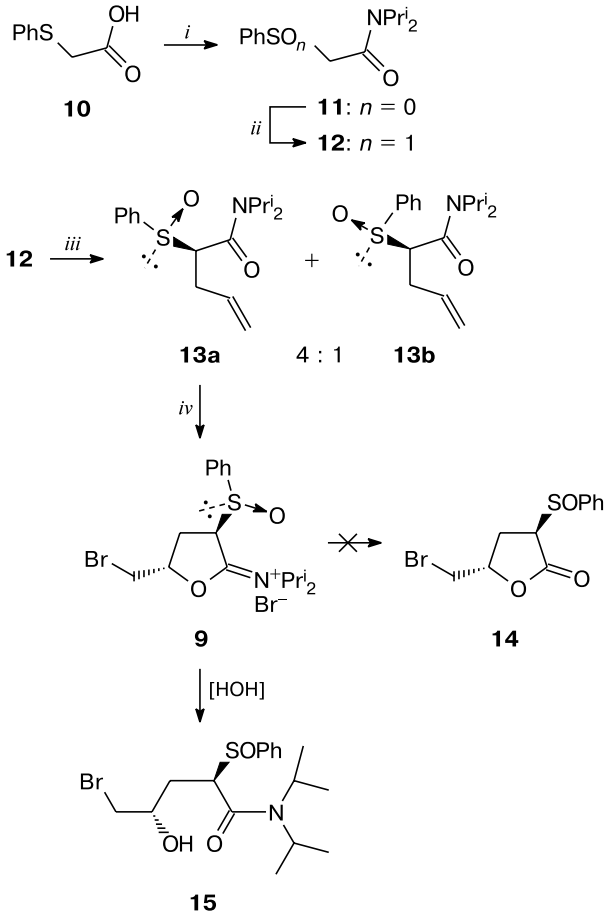
Scheme 2



Reagents and conditions: *i*. H_2O_2, AcOH, 20 °C; *ii*. NaH, CH_2Cl_2, then AllBr, 10 °C; *iii*. PhMe, Δ; *iv*. Br_2, $CHCl_3$, −10 °C.

Scheme 3



Reagents and conditions: *i*. 1) $SOCl_2$, 35—40 °C, 2) $HNPr^i_2$, CH_2Cl_2, −5→20 °C; *ii*. H_2O_2, AcOH, 20 °C; *iii*. 1) NaH, CH_2Cl_2—THF, 2) AllBr, 10 °C; *iv*. Br_2, $CHCl_3$, −10 °C.

amide **11** and oxidation into a known[6] sulfinyl derivative **12** (Scheme 3). A reaction of metalated (with NaH) sulfinyl amide **12** with allyl bromide proceeded diastereoselective (like the allylation of sulfoxide **5**) to give a mixture of the major (2*R**,S*S**)-stereoisomer **13a** and the labile oily (2*R**,S*R**)-isomer **13b** in the ratio ~4 : 1 (data from quantitative separation of the isomers by crystallization and column chromatography). As in the formation of iminium salts **2a,b** (see Ref. 1), *trans*-stereoselective bromocyclization of sulfinyl amide **13a** gave salt **9** in 74% yield.

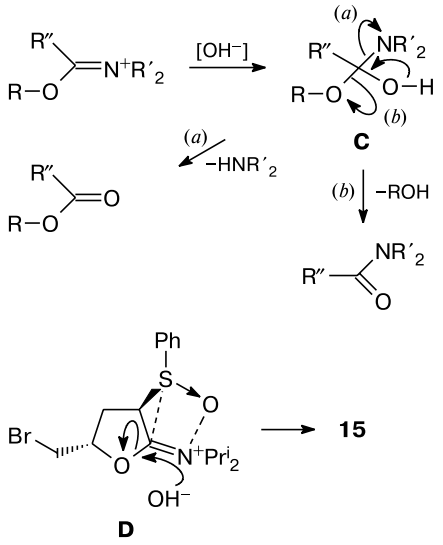
The structures of novel compounds **9** and **13** were confirmed by elemental analysis, physicochemical methods, and a comparison of their spectroscopic characteristics with literature data for related compounds. For instance, the relative *trans*-configuration of the substituents in the tetrahydrofuran ring of salt **9** is evident from the low coupling constant (1.7 Hz) of the HC(3) proton with one of the $H_2C(4)$ protons, which is also characteristic[1] of *trans*-stereoisomers **2a,b**. The relative configurations of the asymmetric centers in diastereomers **13** were assigned from the spectroscopic characteristics of related compounds.[7] For instance, the compact arrangement of signals for the methyl groups of the amide fragment in the ^{1}H NMR spectrum of the minor oily isomer **13b** at δ 1.2—1.5 corresponds to that for its earlier[7] described optically active (2*R*,S*R*)-analog. In the spectrum of the major crystalline stereoisomer **13a**, which can be assigned the (2*R**,S*S**)-configuration, respectively, the signal for one of the methyl groups appears at δ ~0.5 because of shielding of its protons by the SO group. From the same considerations, the relative configuration of the substituents in iminium salt **9** can also be assigned.

Iminium salt **9** was further subjected to hydrolysis under the same conditions as for related derivatives **2a,b**.[1b] However, in contrast to the transformations of the latter,

the hydrolysis did not give the corresponding lactone **14**, yielding only hydroxy amide **15**.

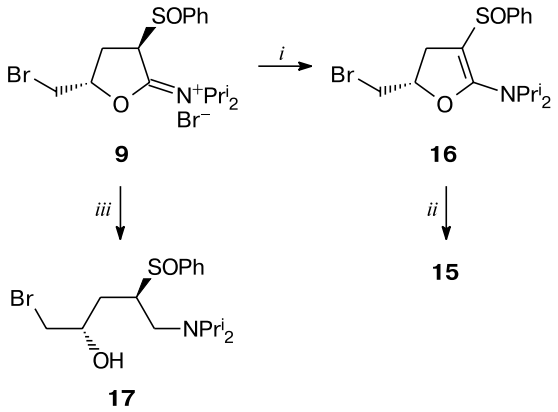
In terms of current concepts, the hydrolysis of imidates along pathway (*a*) (cleavage of the C—N bond, Scheme 4) or pathway (*b*) (cleavage of the C—O bond) is determined by the structure of the starting salt and the stereoelectronic features of the transition state (**C**).[7,8] Considering the plausible transition state (**D**) in the hydrolysis of iminium salt **9**, one can assume its possible stabilization by an electrostatic interaction of the highly polarized S—O bond of the sulfinyl residue with the amide dipole N^+=C—O (*cf.* Ref. 7). Such a stabilization is impossible in phenylthio- (**2a**) and phenylsulfonyl-containing salts (**2b**), which is probably responsible for the difference in their hydrolyses.

Scheme 4



The unfavorable (from the viewpoint of our approach to the synthesis of natural butanolides) pathway of the direct hydrolytic decomposition of iminium salt **9** prompted us to search for an alternative method of its transformation into lactone **14**. For instance, treatment of salt **9** with sodium hydride in THF afforded labile enamine **16** in good yield. Hydrolysis of the latter unexpectedly gave hydroxy amide **15**. It turned out that this transformation can be effected as a "one pot" synthesis in DMF (enamine **16** is detected by TLC) followed by addition of water to the reaction mixture (Scheme 5). Hydride reduction of salt **9** with $NaBH_4$ also failed: accompanying hydrogenolysis of the C—O bond gave amino alcohol **17** instead of the expected hemiaminal. Note that transformations of C-alkoxy-substituted iminium salts under the action of the above reagents probably have not been studied hitherto.

Scheme 5



Reagents and conditions: *i*. NaH, THF, 20 °C or NaH, DMF, 20 °C; *ii*. H_2O; *iii*. $NaBH_4$, MeOH, 0→20 °C.

In conclusion, it should be noted that the presented results, although not leading to the goal of our investigations, are of certain interest. Taking into account the accessibility of homochiral sulfinyl amides of the type **13** (see Ref. 2), one can accomplish a sufficiently simple stereoselective construction of polyfunctional molecules (**9**, **15**, and **17**) containing two new asymmetric centers.

Experimental

IR spectra (ν/cm^{-1}) were recorded on a Specord M-82 instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ with reference to signals for the solvent (δ 7.27 and 77.0, respectively). Mass spectra (EI, 70 eV) were recorded on a Kratos MS-30 instrument. R_f values were measured on Silufol plates with fixed SiO_2 layers. Melting points were measured on a Kofler hot stage. Column chromatography was carried out on Silica gel 60 (0.04—0.06 mm, Fluka).

Solvents, including light petroleum with b.p. 40—70 °C, were purified and dried according to standard procedures. Bromine was distilled over P_2O_5. The reagents ($SOCl_2$, $HNPr^i_2$, pyrrolidine, NaH, $NaBH_4$, and allyl bromide) were purchased from Aldrich.

Phenylthioacetamide **4** (see Ref. 1b) and phenylthioacetic acid **10** (see Ref. 9) were prepared according to known procedures.

(±)-*N*-[(Phenylsulfinyl)acetyl]pyrrolidine (5). Hydrogen peroxide (30%, 3.4 mL, 44 mmol) was added at 0 °C for 5 min to a stirred solution of sulfide **4** (4.8 g, 21.7 mmol) in AcOH (20 mL). The reaction mixture was kept at 20 °C for 3 h and then diluted with water (30 mL). The product was extracted with CH_2Cl_2. The extract was washed with water, a saturated solution of $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was crystallized from EtOAc. The yield of sulfoxide **5** was 4.44 g (87%), colorless crystals, m.p. 125—127 °C. ^1H NMR, δ: 1.83 (m, 4 H, 2 CH_2); 3.10 (m, 1 H, HCN); 3.46 (m, 3 H, HCN); 3.66, 4.00 (both d, 1 H each, H_2CS, J = 13.1 Hz); 7.49—7.58 (m, 3 H, H arom.); 7.70-7.78 (m, 2 H, H arom.) (*cf.* Ref. 10).

***N*-(2-Phenylsulfinylpent-4-enoyl)pyrrolidines (6).** Sodium hydride (0.24 g of a ~55% dispersion in mineral oil, ~5.5 mmol) was added in portions at 10 °C (Ar) for 15 min to a stirred solution of compound **5** (1.19 g, 5.0 mmol) in CH_2Cl_2 (15 mL). After 10 min, allyl bromide (0.72 g, 6 mmol) was added. The reaction mixture was stirred at this temperature for 2 h and decomposed with water (30 mL). The product was extracted with Bu^tOMe. The organic layer was separated, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on SiO_2 with CH_2Cl_2—Bu^tOMe (3 : 1) as an eluent. The yield of sulfinylalkene **6a** was 1.03 g (~75%), a colorless oil, R_f 0.38 (CH_2Cl_2—Bu^tOMe, 3 : 1). Compound **6a** was contaminated with diene **7** (~5%, ^1H NMR data). The yield of sulfinylalkene **6b** was 0.2 g (14%), R_f 0.30 (CH_2Cl_2—Bu^tOMe, 3 : 1), colorless crystals, m.p. 100—102 °C (Bu^tOMe).

Compound **6a**. IR (thin film), ν/cm^{-1}: 644, 664, 692, 748, 812, 860, 916, 964, 1012, 1044, 1064, 1104, 1168, 1192, 1228, 1252, 1288, 1308, 1340, 1404, 1436, 1476, 1596, 1616, 1636, 1656, 1712, 2240, 2876, 2972, 3056. MS, *m/z* (I_{rel} (%)): 250 (1), 234 (15), 186 (20), 179 (3), 170 (4), 152 (3), 151 $[M - PhSOH]^+$ (33), 150 (38), 149 (10), 148 (6), 126 (27), 125 (54), 124 (8), 122 (9), 113 (8), 112 (16), 110 (85), 109 (71), 101 (29), 98 (33), 97 (15), 95 (14), 87 (6), 84 (24), 83 (20), 82 (45), 81 (100), 78 (61), 77 (56), 71 (18), 70 (84), 69 (34), 66 (42), 65 (20), 63 (17), 58 (17), 57 (87), 56 (29), 55 (83). ^1H NMR, δ: 1.30—1.76 (m, 4 H, 2 CH_2); 2.35 (m, 1 H, HC(3)); 2.92—3.35 (m, 5 H, HC(3), 4 HCN); 3.59 (dd, 1 H, HCS, J = 5.4 Hz, J = 9.6 Hz); 5.07 (br.d, 1 H, HC=, J = 10.0 Hz); 5.20 (ddd, 1 H, HC=, J = 1.3 Hz, J = 2.8 Hz, J = 17.1 Hz); 5.73 (dddd, 1 H, —HC=, J = 7.1 Hz, J = 7.1 Hz, J = 10.0 Hz, J = 17.1 Hz); 7.44—7.53 (m, 3 H, H arom.); 7.67—7.74 (m, 2 H, H arom.).

Compound **6b**. Found (%): C, 65.02; H, 6.97; N, 4.73; S, 11.56. $C_{15}H_{19}NO_2S$. Calculated (%): C, 64.95; H, 6.90; N, 5.05; S, 11.56. IR (KBr), ν/cm^{-1}: 644, 692, 756, 808, 848, 900, 920, 940, 1008, 1020, 1052, 1072, 1080, 1108, 1124, 1176, 1232, 1256, 1292, 1304, 1332, 1340, 1436, 1460, 1480, 1580, 1632, 1644, 1876, 2012, 2100, 2328, 2872, 2912, 2948, 2968, 3008, 3048, 3252. MS, *m/z* (I_{rel} (%)): 153 (4), 152 (32), 151 $[M - PhSOH]^+$ (37), 127 (10), 126 (43), 125 (23), 124 (15), 122 (25), 110 (12), 109 (67), 108 (23), 98 (56), 97 (25), 84 (3), 83 (13), 82 (54), 81 (90), 79 (18), 78 (91), 77 (71), 74 (10), 71 (18). 70 (92), 69 (38), 66 (14), 65 (35), 63 (19), 57 (14), 56 (61), 55 (100). ^1H NMR, δ: 1.92 (m, 4 H, 2 CH_2); 2.18, 2.51 (both m, 1 H each, $H_2C(3)$); 3.39—3.60 (m, 3 H, 3 HCN); 3.75 (m, 1 H, HCN); 3.84 (dd, 1 H, HCS, J = 3.8 Hz, J = 10.8 Hz); 4.95—5.08 (m, 2 H, H_2C=); 5.61 (dddd, 1 H, —HC=, J = 6.9 Hz, J = 6.9 Hz, J = 10.1 Hz, J = 17.0 Hz); 7.50—7.58 (m, 3 H, H arom.); 7.64—7.72 (m, 2 H, H arom.).

***N*-(Penta-2*E*,4-dienoyl)pyrrolidine (7).** A solution of amide **6a** (1.33 g, 4.79 mmol) in toluene (20 mL) was heated (Ar) at 80 °C for 7 h and then concentrated *in vacuo*. The residue was chromatographed on SiO_2 with light petroleum—Bu^tOMe (3 : 1) as an eluent. The yield of diene **7** was 0.51 g (73%), colorless crystals, m.p. 170 °C (decomp., light petroleum). Found (%): C, 71.87; H, 8.90; N, 9.03. $C_9H_{13}NO$. Calculated (%): C, 71.49; H, 8.67; N, 9.26. IR (KBr), ν/cm^{-1}: 664, 704, 716, 816, 860, 924, 948, 976, 1008, 1048, 1116, 1168, 1192, 1224, 1244, 1288, 1304, 1344, 1408, 1440, 1508, 1540, 1608, 1652, 1712, 2880, 2956, 2984. MS, *m/z* (I_{rel} (%)): 152 $[M + 1]^+$ (4), 151 $[M]^+$ (11), 124 (3), 108 (4), 98 (27), 83 (4), 82 (27), 81 (90), 72 (4), 71 (13). 70 (100), 66 (4), 57 (9), 56 (19), 55 (43). ^1H NMR, δ: 1.92 (m, 4 H, 2 CH_2); 3.54 (m, 4 H, 2 CH_2N); 5.42 (br.d, 1 H, HC(5), J = 10.0 Hz); 5.57 (br.d, 1 H, HC(5), J = 16.9 Hz); 6.22 (br.d, 1 H, HC(2), J = 14.9 Hz); 6.48 (ddd, 1 H, HC(4), J = 10.0 Hz, J = 10.8 Hz, J = 16.9 Hz); 7.28 (br.dd, 1 H, HC(3), J = 10.8 Hz, J = 14.9 Hz).

***N*,*N*-Diisopropyl-2-phenylthioacetamide (11).** Acid **10** (3.13 g, 18.6 mmol) was added in portions at 35—40 °C (Ar) for 5 min to a stirred mixture of $SOCl_2$ (12.5 mL) and DMF (~0.1 mL). The reaction mixture was kept at this temperature for 1 h and then the excess of $SOCl_2$ was removed *in vacuo* (30 Torr, 40 °C, bath). The oily residue was dissolved in CH_2Cl_2 (16 mL) and a solution of diisopropylamine (4.1 g, 40.5 mmol) in CH_2Cl_2 (12 mL) was added with stirring (Ar) at −5 to 0 °C for 20 min. The reaction mixture was warmed to 20 °C, stirred for 2 h, and treated with water. The organic layer was separated, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was distilled to give amide **11** (3.32 g, 71%) as a viscous liquid, b.p. 140—143 °C (0.1 Torr). ^1H NMR, δ: 1.23, 1.38 (both d, 3 H each, 2 CH_3, J = 6.7 Hz); 3.43, 4.01 (both sept, 1 H each, 2 CH, J = 6.7 Hz); 3.75 (s, 2 H, H_2CS); 7.19—7,36 (m, 3 H, H arom.); 7.42—7.49 (m, 2 H, H arom.) (*cf.* Ref. 11).

(±)-*N*,*N*-Diisopropyl-2-phenylsulfinylacetamide (12). Hydrogen peroxide (30%, 3 mL, 38.4 mmol) was added at 0 °C for 5 min to a stirred solution of sulfide **11** (4.82 g, 19.2 mmol) in AcOH (19 mL). The reaction mixture was kept at 20 °C for 5 h and then diluted with water (30 mL). The product was extracted with CH_2Cl_2. The extract was washed with water, a saturated solution of $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was crystallized from $MeOBu^t$. The yield of sulfoxide **12** was 4.17 g (81%), colorless crystals, m.p. 138—140 °C. ^1H NMR, δ: 1.04, 1,17, 1.28, 1.35 (all d, 3 H each, 4 CH_3, J = 6.8 Hz); 3.49, 3.83 (both sept, 1 H each, 2 CH, J = 6.8 Hz); 3.72, 4.05 (both d, 1 H each, H_2CS, J = 13.8 Hz); 7.46—7.57 (m, 3 H, H arom.); 7.69—7.81 (m, 2 H, H arom.) (*cf.* Ref. 6).

(2*R,S*S**)-*N*,*N*-Diisopropyl-2-phenylsulfinylpent-4-enamide (13a) and (2*R**,S*R**)-*N*,*N*-diisopropyl-2-phenylsulfinylpent-4-enamide (13b).** Sodium hydride (0.86 g of a ~55% dispersion in mineral oil, ~19.7 mmol) was added in portions at 10 °C (Ar) for 20 min to a stirred solution of amide **12** (4.82 g, 18.0 mmol) in a mixture of THF (27 mL) and CH_2Cl_2 (27 mL). After 30 min, allyl bromide (2.61 g, 21.6 mmol) was added. The reaction mixture was stirred at this temperature for 1 h and then decomposed with water (30 mL). The product was extracted with Bu^tOMe. The organic layer was separated, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crystallization of the residue from light petroleum gave amide **13a** (3.19 g), m.p. 107—108 °C. The mother liquor was concentrated *in vacuo* and the residue was chromatographed on SiO_2. Gradient elution (light petroleum → light petroleum—Bu^tOMe, 1 : 1) gave an additional crop of amide **13a** (0.88 g), m.p. 106—108 °C, R_f 0.28 (Bu^tOMe), and amide **13b** (0.64 g), a colorless oil, R_f 0.35 (Bu^tOMe).

Amide **13a** (74% yield). Found (%): C, 66.48; H, 8.41; N, 4.49; S, 10.09. $C_{17}H_{25}NO_2S$. Calculated (%): C, 66.41; H, 8.20; N, 4.56; S, 10.43. IR ($CHCl_3$), ν/cm^{-1}: 664, 692, 724, 812, 844, 924, 1000, 1036, 1044, 1084, 1136, 1156, 1208, 1240, 1280, 1340, 1372, 1444, 1476, 1636, 2350, 2936, 2972, 3004, 3064, 3084. MS, *m/z* (I_{rel} (%)): 261 (3), 260 (4), 233 (5), 182

$[M - PhSO]^+$ (51), 181 $[M - PhSOH]^+$ (24), 166 (4), 163 (4), 138 (4), 137 (7), 100 (83), 99 (20), 87 (26), 86 (91), 85 (22), 82 (32), 81 (89), 80 (22), 70 (5), 59 (11), 58 (23), 54 (100). ^{1}H NMR, δ: 0.45, 1.01 (both d, 3 H each, 2 CH_3, J = 6.7 Hz); 1.14, 1.29 (both d, 3 H each, 2 CH_3, J = 6.8 Hz); 3.04 (m, 2 H, CH_2); 3.16 (sept, 1 H, CH, J = 6.8 Hz); 3.61 (sept, 1 H, CH, J = 6.7 Hz); 3.76 (dd, 1 H, HCS, J = 6.1 Hz, J = 8.5 Hz); 5.14 (ddd, 1 H, HC=, J = 0.8 Hz, J = 1.6 Hz, J = 9.9 Hz); 5.26 (ddd, 1 H, HC=, J = 1.3 Hz, J = 2.9 Hz, J = 17.1 Hz); 5.78 (dddd, 1 H, —HC=, J = 7.3 Hz, J = 7.4 Hz, J = 9.9 Hz, J = 17.1 Hz); 7.44—7.54 (m, 3 H, H arom.); 7.72—7.82 (m, 2 H, H arom.). ^{13}C NMR, δ: 20.05, 20.12, 20.45 and 20.70 (4 CH_3); 33.97 (CH_2); 46.43, 49.48 (2 CHN); 71.69 (CHS), 119.10 (C(5)); 132.88 (C(4)); 125.66, 128.91, 131.43, 142.79 (C arom.); 166.03 (C(1)).

Amide **13b** (12% yield). IR (KBr), ν/cm^{-1}: 640, 692, 744, 848, 920, 1000, 1040, 1050, 1124, 1164, 1204, 1220, 1280, 1344, 1372, 1392, 1444, 1456, 1476, 1616, 2936, 2972, 3004, 3076. MS, m/z (I_{rel} (%)): 308 $[M + 1]^+$ (4), 307 $[M]^+$ (11), 260 (1), 259 (4), 216 (7), 184 (1), 183 (12), 182 $[M - PhSO]^+$ (67), 149 (11), 140 (17), 128 (25), 126 (47), 100 (82), 86 (100), 55 (54). ^{1}H NMR, δ: 1.22, 1.33 (both d, 3 H each, 2 CH_3, J = 6.6 Hz); 1.38, 1.46 (both d, 3 H each, 2 CH_3, J = 6.8 Hz); 2.22 (ddddd, 1 H, $H^AC(3)$, J = 1.1 Hz, J = 1.1 Hz, J = 3.8 Hz, J = 7.1 Hz, J = 13.3 Hz); 2.39 (ddddd, 1 H, $H^BC(3)$, J = 1.1 Hz, J = 1.1 Hz, J = 6.9 Hz, J = 10.6 Hz, J = 13.3 Hz); 3.52 (sept, 1 H, CH, J = 6.6 Hz); 3.95 (dd, 1 H, HCS, J = 3.8 Hz, J = 10.6 Hz); 4.28 (sept, 1 H, CH, J = 6.8 Hz); 4.94—5.08 (m, 2 H, H_2C=); 5.58 (dddd, 1 H, —HC=, J = 6.9 Hz, J = 7.1 Hz, J = 9.9 Hz, J = 16.9 Hz); 7.48—7.69 (m, 5 H, H arom.).

(3*R,5*S**,S*S**)-*N*-(5-Bromomethyl-3-phenylsulfinyltetrahydrofuran-2-ylidene)-*N*,*N*-diisopropylammonium bromide (9).** A solution of Br_2 (0.96 g, 6.0 mmol) in $CHCl_3$ (8 mL) was added at −10 °C (Ar) for 20 min to a stirred solution of amide **13a** (1.57 g, 5.0 mmol) in $CHCl_3$ (16 mL). After 10 min, Bu^{t}OMe (36 mL) was added and the reaction mixture was kept at 0 °C for 1 h. The amorphous product that formed was filtered off, washed with Bu^{t}OMe, dried *in vacuo* (2 Torr), and crystallized from MeOH—Bu^{t}OMe. The yield of salt **9** was 1.74 g (74%), colorless crystals, m.p. 131—136 °C. Found (%): C, 43.93; H, 5.44; Br, 34.36; N, 2.99; S, 6.89. $C_{17}H_{25}Br_2NO_2S$. Calculated (%): C, 43.70; H, 5.39; Br, 34.20; N, 3.00; S, 6.86. IR (KBr), ν/cm^{-1}: 516, 560, 656, 676, 688, 732, 756, 784, 896, 972, 1040, 1056, 1080, 1116, 1168, 1252, 1268, 1376, 1392, 1420, 1444, 1664, 2364, 2936, 2968, 2992. MS, m/z (I_{rel} (%)): 467 $[M]^+$ (1), 404 (5), 373 (1), 370 (5), 354 (2), 344 (5), 342 (7), 326 (3), 310 (4), 303 (6), 301 (36), 300 (36), 288 (17), 265 (3), 264 (24), 262 (27), 222 (15), 220 (28), 219 (16), 218 (41), 206 (22), 204 (38), 191 (4), 190 (6), 185 (8), 182 (10), 178 (13), 164 (6), 161 (17), 141 (22), 133 (28), 128 (44), 112 (8), 110 (56), 109 (39), 97 (46), 95 (39), 93 (34), 86 (25), 85 (100), 83 (65), 81 (62), 80 (71), 79 (42), 78 (43), 77 (35), 76 (61), 70 (50), 69 (46), 66 (37), 65 (42), 59 (36), 57 (33), 55 (62). ^{1}H NMR, δ: 1.58, 1.66 (both d, 3 H each, 2CH_3, J = 6.9 Hz); 1.64, 1.80 (both d, 3 H each, 2CH_3, J = 6.7 Hz); 2.50 (ddd, 1 H, $H^AC(4)$, J = 1.7 Hz, J = 7.3 Hz, J = 14.5 Hz); 2.90 (ddd, 1 H, $H^BC(4)$, J = 9.3 Hz, J = 9.4 Hz, J = 14.5 Hz); 3.69 (dd, 1 H, H^ACBr, J = 4.4 Hz, J = 11.5 Hz); 3.90 (dd, 1 H, H^BCBr, J = 7.7 Hz, J = 11.5 Hz); 4.08 (sept, 1 H, CH, J = 6.9 Hz); 5.11 (sept, 1 H, CH, J = 6.7 Hz); 5.31 (dddd, 1 H, HC(5), J = 4.4 Hz, J = 7.3 Hz, J = 7.7 Hz, J = 9.3 Hz); 6.52 (dd, 1 H, HCS, J = 1.7 Hz, J = 9.4 Hz); 7.60—7.70 (m, 3 H, H arom.); 7.86—7.93 (m, 2 H, H arom.).

(2*R,4*S**,S*S**)-*N*,*N*-Diisopropyl-5-bromo-4-hydroxy-2-phenylsulfinylpentanamide (15).** ***A.*** A solution of salt **9** (0.47 g, 1 mmol) and $NaOAc \cdot 3H_2O$ (0.2 g, 1.47 mmol) in aqueous EtOH (6 mL) was stirred at 50 °C for 30 min and then concentrated *in vacuo*. Water (5 mL) was added to the residue and the product was extracted with Bu^{t}OMe. The extract was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crystallization of the residue from light petroleum—Bu^{t}OMe gave hydroxy amide **15** (0.28 g, 84%), m.p. 125—127 °C. Found (%): C, 50.62; H, 6.75; Br, 19.34; N, 3.48; S, 7.76. $C_{17}H_{26}BrNO_3S$. Calculated (%): C, 50.50; H, 6.48; Br, 19.76; N, 3.46; S, 7.93. IR ($CHCl_3$), ν/cm^{-1}: 496, 604, 664, 692, 820, 848, 872, 924, 1036, 1084, 1124, 1136, 1164, 1240, 1280, 1315, 1344, 1360, 1376, 1425, 1448, 1476, 1620, 2460, 2876, 2936, 2972, 3008, 3064, 3572, 3664. MS, m/z (I_{rel} (%)): 405 (12) and 403 (12) $[M]^+$, 357 (3), 281 (12), 280 (63), 278 (59), 265 (4), 264 (14), 262 (20), 252 (17), 238 (8), 236 (15), 222 (4), 220 (8), 218 (12), 208 (7), 199 (9), 198 (43), 185 (5), 184 (31), 180 (54), 179 (37), 177 (43), 161 (6), 158 (10), 157 (12), 156 (45), 154 (23), 140 (10), 135 (16), 128 (20), 126 (50), 123 (34), 121 (40), 115 (24), 110 (46), 109 (43), 101 (19), 100 (54), 99 (36), 97 (49), 95 (32), 87 (30), 86 (100), 83 (38), 82 (25), 81 (63), 80 (68), 79 (49), 78 (30), 77 (55), 72 (21), 70 (37), 69 (36), 66 (28), 65 (39), 58 (18), 57 (25), 55 (54). ^{1}H NMR, δ: 0.53 (d, 3 H, CH_3, J = 6.7 Hz); 1.08 (d, 3 H, CH_3, J = 6.6 Hz); 1.15, 1.31 (both d, 3 H each, 2CH_3, J = 6.8 Hz); 2.50 (m, 2 H, CH_2); 3.24 (sept, 1 H, CH, J = 6.8 Hz); 3.50 (br.d, 1 H, HCBr, J = 5.1 Hz); 3.54 (br.d, 1 H, HCBr, J = 5.1 Hz); 3.83 (m, 2 H, CH, HC(4)); 4.08 (dd, 1 H, HCS, J = 5.2 Hz, J = 7.8 Hz); 7.46—7.56 (m, 3 H, H arom.); 7.72—7.83 (m, 2 H, H arom.). ^{13}C NMR, δ: 20.13, 20.25, 20.36 and 20.78 (4 CH_3); 35.37 (CH_2); 39.18 (CH_2Br); 46.54, 49.74 (2 CHN); 68.42, 69.18 (CHS, CHO), 125.72, 125.94, 129.01, 142.25 (C arom.); 166.39 (C(1)).

B. Sodium hydride (52 mg of a ~55% dispersion in mineral oil, ~1.2 mmol) was added in portions at 20 °C for 5 min to a stirred suspension of salt **9** (0.47 g, 1 mmol) in DMF (5 mL). The mixture grew completely homogeneous. After 20 min, water (5 mL) was added and the mixture was kept for 20 min. The product was extracted with Bu^{t}OMe. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on SiO_2 with light petroleum—Bu^{t}OMe (1 : 1) as an eluent. The yield of hydroxy amide **15** was 0.27 g (67%). The product obtained was virtually identical (m.p., ^{1}H NMR) with that described above.

(5*S,S*S**)-5-Bromomethyl-2-(*N*,*N*-diisopropylamino)-3-phenylsulfinyl-4,5-dihydrofuran (16).** Sodium hydride (52 mg of a ~55% dispersion in mineral oil, ~1.2 mmol) was added in portions at 20 °C (Ar) for 5 min to a stirred suspension of salt **9** (0.47 g, 1.0 mmol) in THF (8 mL). The reaction mixture was stirred at this temperature for 3 h and then concentrated *in vacuo*. The product was extracted with Bu^{t}OMe. The extract was concentrated *in vacuo* and the residue was crystallized from $CHCl_3$—light petroleum. The yield of enamine **16** was 0.29 g (76%), colorless crystals, m.p. 68—70 °C (on storage at 20 °C for 2 days, the crystals turned into a light brown oil). IR (KBr), ν/cm^{-1}: 416, 468, 512, 536, 588, 656, 664, 688, 752, 812, 844, 872, 896, 912, 996, 1008, 1040, 1088, 1108, 1128, 1164, 1204, 1228, 1252, 1304, 1336, 1368, 1384, 1428, 1456, 1476, 1592, 2472, 2856, 2968, 3064. MS, m/z (I_{rel} (%)): 387 and 385 $[M]^+$ (1), 371 (10), 370 (32), 368 (33), 340 (3), 339 (30), 338, (23), 337

(26), 328 (15), 326 (14), 310 (37), 308 (37), 297 (6), 296 (30), 294 (35), 268 (13), 266 (24), 261 (23), 260 (25), 251 (7), 250 (32), 248 (27), 226 (13), 220 (69), 218 (63), 209 (7), 208 (14), 206 (57), 205 (15), 204 (60), 190 (10), 187 (15), 180 (13), 178 (14), 176 (13), 164 (15), 163 (25), 162 (18), 161 (27), 149 (9), 144 (24), 138 (15), 135 (40), 133 (13), 130 (14), 129 (26), 128 (50), 126 (30), 125 (34), 118 (18), 114 (19), 110 (57), 109 (49), 100 (47), 98 (19), 97 (42), 96 (43), 95 (48), 94 (15), 91 (14), 85 (77), 84 (56), 83 (89), 82 (25), 81 (22), 80 (53), 77 (53), 76 (63), 71 (25), 70 (37), 69 (7), 68 (18), 65 (25), 60 (15), 59 (37), 57 (43), 55 (77), 54 (70), 53 (86), 45 (50), 43 (100). ^{1}H NMR, δ: 1.34, 1.35 (both d, 6 H each, 4 CH_3, J = 6.8 Hz); 1.96 (dd, 1 H, HC(4), J = 6.8 Hz, J = 12.8 Hz); 3.06 (dd, 1 H, HC(4), J = 9.4 Hz, J = 12.8 Hz); 3.32 (d, 2 H, H_2CBr, J = 5.8 Hz); 3.99 (sept, 2 H, CH, J = 6.8 Hz); 4.69 (dddd, 1 H, HC(5), J = 5.8 Hz, J = 5.8 Hz, J = 6.8 Hz, J = 9.4 Hz); 7.38—7.63 (m, 5 H, H arom.).

(2*S,4*R**,S*S**)-1-Bromo-5-(*N*,*N*-diisopropylamino)-4-phenylsulfinylpentan-2-ol (17).** Sodium borohydride (80 mg, ~2.0 mmol) was added in portions at 0 °C (Ar) for 10 min to a stirred solution of salt **9** (0.94 g, 2.0 mmol) in MeOH (15 mL). The reaction mixture was warmed to 20 °C, stirred at this temperature for 15 min, and concentrated *in vacuo*. The product was extracted with Bu^{t}OMe. The extract was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crystallization of the residue from MeCN gave amino alcohol **17** (0.54 g, 70%), colorless crystals, m.p. 102—103 °C. Found (%): C, 52.44; H, 7.67; Br, 20.02; N, 3.53; S 8.03. $C_{17}H_{28}BrNO_2S$. Calculated (%): C, 52.30; H, 7.23; Br, 20.47; N, 3.59; S, 8.21. IR (KBr), ν/cm^{-1}: 668, 688, 724, 740, 848, 892, 926, 952, 1004, 1048, 1064, 1080, 1120, 1156, 1176, 1208, 1228, 1284, 1295, 1315, 1328, 1364, 1384, 1396, 1428, 1440, 1460, 1476, 1560, 1584, 1764, 2356, 2824, 2872, 2920, 2964, 3068, 3268. MS, m/z (I_{rel} (%)): 265 (5), 263 (5) $[M - PhSO]^+$, 250 (8), 248 (8), 183 (6), 170 (6), 168 (28), 154 (3), 153 (3), 149 (6), 142 (5), 141 (15), 140 (100), 127 (11), 126 (25), 115 (9), 114 (74), 110 (65), 109 (27), 101 (8), 98 (43), 86 (23), 84 (45), 83 (41), 82 (35), 80 (20), 78 (36), 77(24), 72 (37), 70 (53), 69 (30), 66 (30), 65 (22), 57 (21), 56 (63), 55 (49). ^{1}H NMR, δ: 1.02 (d, 6 H, 2CH_3, J = 6.4 Hz); 1.05 (d, 6 H, 2 CH_3, J = 6.2 Hz); 1.90 (m, 2 H, HC(3)); 2.62 (m, 1 H, HCS); 2.87—3.15 (m, 5 H, 2 HC, HC(5), H_2CBr); 3.21 (dd, 1 H, HC(5), J = 5.9 Hz, J = 10.2 Hz); 3.86 (dddd, 1 H, HC(2), J = 4.7 Hz, J = 6.3 Hz, J = 6.4 Hz, J = 6.4 Hz); 5.40 (br.s, 1 H, OH); 7.46—7.65 (m, 5 H, H arom.). ^{13}C NMR, δ: 19.59, 20.99 (4 CH_3); 30.58 (CH_2); 37.47 (CH_2N); 45.34 (CH_2Br); 48.39 (2 CHN); 59.40 (CHS), 67.95 (CHO); 124.77, 129.10, 131.02, 141.84 (C arom.).

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