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Tetrahedron: *Asymmetry* 14 (2003) 2827–2832

TETRAHEDRON: *ASYMMETRY*

New, recoverable and highly effective sulfinyl chiral auxiliary

Robert Kawęcki*

Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, PL-01-224 Warszawa, Poland

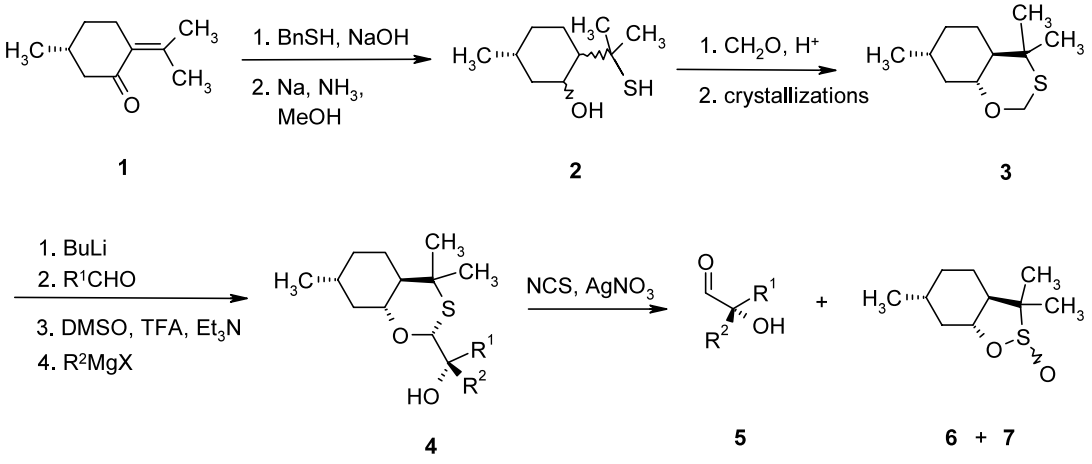
Received 9 July 2003; accepted 29 July 2003

Abstract—A facile synthesis of a bicyclic 8-menthylsulfinate is described. The reaction of this sultine with organometallic compounds leads to γ-hydroxysulfoxides, while the reaction with lithium amide affords 8-menthylsulfinamide. The chiral efficiency of the 8-menthylsulfinyl auxiliary was tested in the reaction of sulfinimines with Grignard reagents. A highly stereoselective addition of ethylmagnesium bromide to 8-menthylsulfinimine was observed (98% de).

1. Introduction

The good coordination properties of the sulfinyl oxygen atom and the large size differences of substituents on the sulfur atom have led to optically active sulfinyl groups being recognized as very efficient chiral auxiliaries.[1,2] Several alkyl- and arylsulfinyl auxiliaries are known, from which *p*-tolylsulfinyl group is used most frequently. However, the chiral efficiency when the *p*-toluenesulfinyl group is present is often insufficient. Recently Ellman et al. described the enantioselective synthesis of *t*-butanesulfinamide,[3] which appeared to be an excellent precursor for the preparation of enantiomerically enriched amines.[4] In some cases the *t*-butylsulfinyl group gave unsatisfactory results and more bulky substituents at the sulfur atom were needed.[5] The preparation of both enantiomers of efficient sulfinyl auxiliaries by an efficient route and in good yield is still a real challenge.

In 1981 Eliel and Lynch described the stereoselective synthesis of α-hydroxy aldehydes **5** (Scheme 1) using chiral 1,3-oxathiane **3** obtained from (+)-pulegone.[6] By-products of this synthesis were diastereoisomeric sultines, which were finally converted to the starting hydroxythiol **2**. Here it is proposed that diastereoisomerically pure sultine **6** may serve as a useful substrate for the synthesis of sulfinyl derivatives. Our earlier



Scheme 1.

* Fax: 48-22-6326681; e-mail: rkaw@icho.edu.pl

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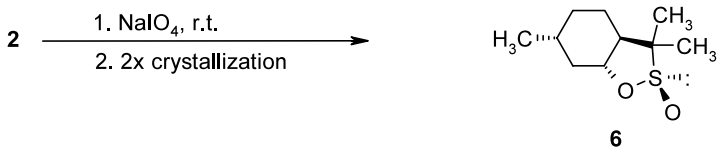
doi:10.1016/S0957-4166(03)00624-4



Scheme 2.

work showed that similar bicyclic sufinates derived from camphor, may serve as useful tools for stereoselective synthesis.[7]

2. Results and discussion

8-Menthylsulfinate **6** was directly obtained from 8-mercaptomenthol **2**, which may be synthesized in two steps on a large scale from (+)-pulegone according to Eliel's procedure.[8] Oxidation of hydroxythiol **2** with sodium metaperiodate in acetonitrile–water (Scheme 2) by method of Fellous et al.[9] gave a mixture of diastereoisomeric sultines (ratio ca. 1:2.3:2.8:6.3). Attempts to increase the diastereoisomeric ratio by epimerization at the sulfur atom (HCl, Et_2O) failed. Fortunately the main product of this reaction may be easily isolated by crystallization from cyclohexane. The total yield of the sultine **6** was 32% (de >98%). The large number of diastereoisomeric sultines arises from the low stereoselectivity of mercaptomenthol synthesis. Conjugate addition of benzyl mercaptan to pulegone gives a nonseparable mixture of isomers with 74% de (*trans*). Reduction of the carbonyl group in such mixture resulted in 5.9:2.1:1 product ratio.

Single-crystal X-ray diffraction studies on the sultine **6** established the (*S*)-configuration at the sulfur atom (Fig. 1).[10] Spectroscopic data corresponded well with one of diastereoisomers of the sultines obtained previously by Eliel.[11]

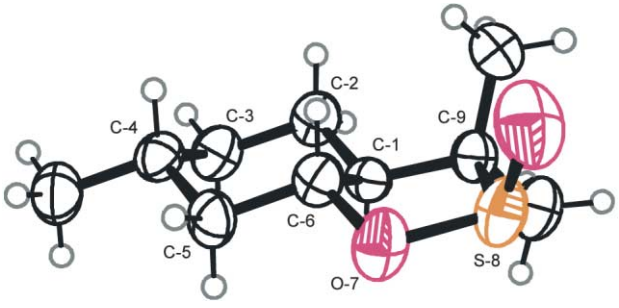
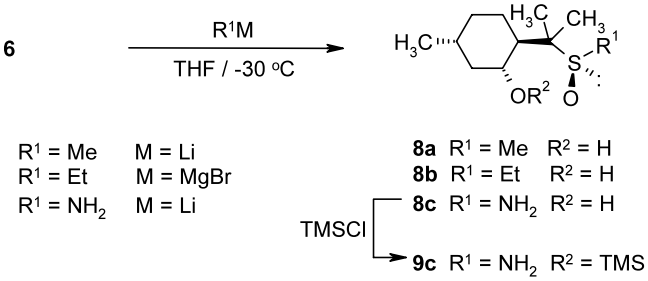


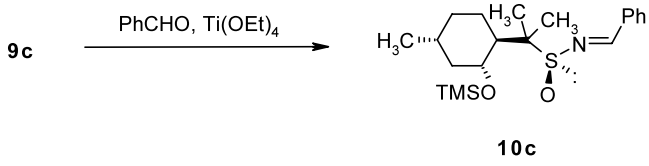
Figure 1. Graphical representation of X-ray crystal structure of sultine **6**.

Sultine **6** reacts with nucleophiles such as Grignard reagents or organolithium compounds to give γ-hydroxysulfoxides **8a–b** with formation of only a single product diastereoisomer being observed (Scheme 3). Analogously, the reaction with lithium amide gives optically active sulfinamide **8c**. The reaction of sulfinates with nucleophilic reagents proceeds usually with inversion of configuration at the sulfur atom.[12] The same stereochemical pathway has been observed previously for other bicyclic sulfinate.[13] On this basis we assigned the configuration at the sulfur atom in derivatives **8a–c**. Sulfinamide **8c** may serve as the starting material for the synthesis of optically active sulfinimines. Recent work by Davis and Ellman has demonstrated the utility of such compounds in the stereoselective synthesis of amino derivatives.[14,4] Actually, trimethylsilyloxy derivative **9c** has been found to be a better precursor for the synthesis of sulfinimines than **8c** because of greater stability and good solubility in nonpolar solvents.



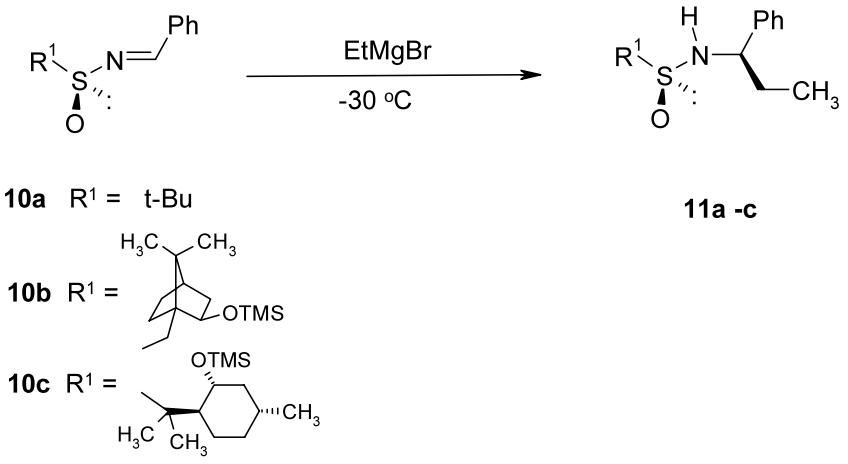
Scheme 3.

The chiral efficacy of the 8-menthylsulfinyl group was checked in the reaction of sulfinimines with Grignard reagents. Appropriate sulfinimines can be easily obtained by condensation of sulfinamide **9c** with aldehydes, preferably in the presence of $Ti(OEt)_4$.[15] In this way phenyl derivative **10c** was obtained in 92% yield (Scheme 4). The reaction with ethylmagnesium bromide afforded sulfinamide **11c**.



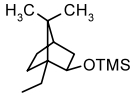
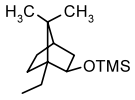
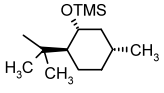
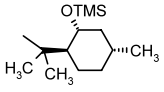
Scheme 4.

For comparison of diastereoselectivities this reaction was performed using *t*-butyl, 10-isobornyl, and 8-menthylsulfinimines **10a–c** in THF and CH_2Cl_2 (Scheme 5 and Table 1). The latter solvent gives much better results, as has been reported previously by Ellman et al.[16] The best stereoselectivity was obtained using 8-menthylsulfinimine whereby diastereoisomeric excess for the reaction performed in CH_2Cl_2 at −30°C was 98%.



Scheme 5.

Table 1. Addition of ethylmagnesium bromide to sulfinimines

Entry	R^1	Substrate	Product	Solvent	Temp. °C	Yield, %	D.e., %
1[a]	*t*-Bu	(R_S)-**10a**	**11a**	THF	-48	91[a]	0[a]
2	*t*-Bu	(S_S)-**10a**	(1'*R*)-**11a**	CH_2Cl_2	-30	82	64[b,c]
3		(S_S)-**10b**	(1'*R*)-**11b**	THF	-30	74	7[b]
4		(S_S)-**10b**	(1'*R*)-**11b**	CH_2Cl_2	-30	85	59[b]
5		(S_S)-**10c**	(1'*R*)-**11c**	THF	-30	93	74[b]
6		(S_S)-**10**c	(1'*R*)-**11c**	CH_2Cl_2	-30	80	98[b,d]

[a] Data from ref. 16

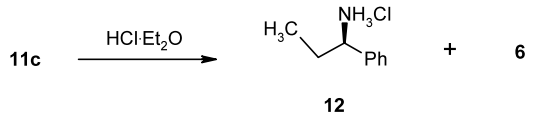
[b] De was determined by HPLC in crude reaction mixture. See Experimental part for details.

[c] At –48 °C de reported by Ellman *et al* in ref. 16 using (R_S)-**10a** was 84 %.

[d] The ee of the amine after cleavage with $Et_2O{\cdot}HCl$ was 98 %.

The 8-menthylsulfinyl moiety may be easily removed in an acidic environment releasing amine hydrochloride **12** and sultine **6** (Scheme 6). Usually the separation of the nonpolar sultine from the polar products is straightforward. Recovered sultine **6** does not change its enantiomeric or diastereoisomeric purity as can be seen from ^{1}H NMR spectra and may be used again. The enantiomeric excess of (+)-(1*R*)-1-phenylpropylamine obtained from 8-menthylsulfinamide **11c** (entry 6) was 98%.

N-Benzylidenesulfinamides **10a–c** possessing the (*S*) configuration at the sulfur atom give with ethylmagnesium bromide amines with an (*R*) configuration. Such a



Scheme 6.

stereochemical outcome of the Grignard addition is consistent with the model proposed by Ellman,[16] where a magnesium ion is coordinated to the sulfinyl oxygen atom forming a six-membered ring. It seems that the stereogenic centers in the menthyl group play a secondary role in this stereodifferentiation.

3. Conclusion

This preliminary study shows that 8-menthylsulfinate may be considered as an efficient sulfinyl chiral auxiliary. Despite the overall yield of the sultine **6** from (+)-pulegone being moderate, the synthesis is straightforward. If derivatives of 8-menthylsulfinamides are used, sulfinate **6** may be recovered in good yield without loss of stereochemical integrity. The main drawback of the presented chiral auxiliary is that only one enantiomer of pulegone is available at an affordable price, thus limiting the use of the sultine **6**. The presence of a hydroxyl group in sulfinamide **8c** may enable this molecule to be attached to solid support.

4. Experimental

4.1. General

NMR spectra were recorded at 200 and 500 MHz (^{1}H). All spectra were referenced to residual solvent peak (chloroform 7.26 and 77.0 ppm for ^{1}H and ^{13}C, respectively). CH_2Cl_2 was distilled from CaH_2. THF was distilled from sodium in the presence of sodium benzophenone ketyl. Melting points were not corrected. TLC plates were developed in $KMnO_4$ or phosphomolibdic acid solution. (*R*)-(+)-Pulegone was purchased from Aldrich. 8-Mercaptomenthol was prepared according to published procedure.[8] Sufinimines **10a**[15a] and **10b**[7] were prepared analogously as to **10c**. All experiments, except the synthesis of **6**, were conducted under an atmosphere of argon. The diastereoisomeric ratio of sulfinamides **11a–c** was established from the crude reaction mixture by HPLC (Lichrospher® Si 60 5 μ, 25×0.4 cm, 0.7 mL/min, λ 254 nm, hexane–*i*-PrOH 96.5:3.5). Enantiomeric excesses of the amines were determined by ^{1}H NMR using (*R*)-*t*-butylphenylphosphinothioic acid[17] as the chiral solvating agent. Crystals of **6** for X-Ray measurement were obtained from *n*-hexane. Crystallographic data for the structure **6** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 212983. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.1.1. (1*R*,4*R*,6*R*,S_S)-4,9,9-Trimethyl-7-oxa-8-thiabicyclo[4.3.0]nonane-8-oxide, 6. A solution of sodium periodate (33.0 g, 154 mmol) in 290 mL of water was slowly added to the solution of 8-mercaptomenthol (14.5 g, 77 mmol) in acetonitrile (145 mL) at rt (cooling with cold water bath). The resulting brown suspension was stirred for 3 h at rt. The mixture was transferred to the separation funnel and extracted four times with diethyl ether (60 mL). Combined organic extracts were washed with 10% solution of sodium thiosulfate until the solution became colorless. The organic layer was dried with $MgSO_4$, filtered and evaporated. Solid residue was crystallized twice from cyclohexane to give 4.0 g of colorless crystals (98% d.e.). Second batch of product (1.04 g) was obtained from collected filtrates by triple crystallization from cyclohexane. The total yield was 32%. D.e. was determined by ^{1}H NMR or HPLC (RP18, acetonitrile–water 50:50, 1 mL/min). Colorless crystals, mp 110–116°C (lit.[11] mp 119–121°C, from C_6H_6); $[\alpha]_D$ +173.6 (*c* 1.05, $CHCl_3$) (lit.[11] $[\alpha]_D$ +185.3 (*c* 5.375, C_6H_6)); ^{1}H NMR ($CDCl_3$) δ 0.77–1.06 (m, 1H), 1.00 (d, J=6.3 Hz, 3H), 1.08–1.85 (m, 6H), 1.10 (s, 3H), 1.41 (s, 3H), 2.18 (m, 1H), 4.44 (ddd, J=10.6, 10.6, 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.3, 21.6, 23.2, 23.6, 30.9, 33.6, 39.3, 54.9, 69.6, 86.5.

4.1.2. (1*R*,2*R*,5*R*,R_S)-2-[1-(Methylsulfinyl)-1-methylethyl]-5-methylcyclohexanol, 8a. To the solution of sultine **6** (277 mg, 1.37 mmol) in THF (8 mL) was added methyllithium (2.74 mL, 1 M solution in cumene and THF) at −30°C. The reaction mixture was stirred for 3 h at −30°C and quenched with satd NH_4Cl solution. The mixture was extracted with CH_2Cl_2 and collected organic extracts were dried with $MgSO_4$. Evaporation of the solvents gave colorless solid which was crystallized from mixture of hexane and chloroform. Yield 187 mg (63%). Mp 139–142°C; $[\alpha]_D$ +40.7 (*c* 1.42, CH_2Cl_2); IR (KBr) 3316, 3221 (OH), 998, 989 (S=O); ^{1}H NMR ($CDCl_3$) δ 0.72–1.54 (m, 5H), 0.88 (d, J=6.4 Hz, 3H), 1.18 (s, 3H), 1.30 (s, 3H), 1.59–1.75 (m, 1H), 1.77–2.0 (m, 2H), 2.42 (s, 3H), 3.42 (br, 1H), 3.57 (ddd, J=4.4, 10.4, 10.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.8, 17.0, 21.8, 26.6, 31.1, 31.8, 34.2, 45.2, 50.6, 60.6, 70.4. Anal calcd for $C_{11}H_{22}O_2S$ C, 60.51; H, 10.16; S, 14.68. Found C, 60.36; H, 10.24; S, 14.74.

4.1.3. (1*R*,2*R*,5*R*,R_S)-2-[1-(Ethylsulfinyl)-1-methylethyl]-5-methylcyclohexanol, 8b. Prepared analogously as above. Yield 97%. Mp 162–165°C; $[\alpha]_D$ +99.5 (*c* 1.76, CH_2Cl_2); IR (KBr) 3204 (OH), 968 (S=O); ^{1}H NMR ($CDCl_3$) δ 0.69–1.41 (m, 4H), 0.87 (d, J=6.5 Hz, 3H), 1.17 (s, 3H), 1.28 (s, 3H), 1.31 (t, J=7.4 Hz, 3H), 1.43–1.72 (m, 2H), 1.75–2.0 (m, 2H), 2.23–2.43 (m, 1H), 2.73–2.93 (m, 1H), 3.57 (ddd, J=4.4, 10.4, 10.4 Hz, 1H), 3.78 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 8.5, 17.4, 17.6, 21.8, 26.5, 31.1, 34.2, 38.9, 45.2, 50.4, 60.8, 70.3. Anal calcd for $C_{12}H_{24}O_2S$ C, 62.02; H, 10.41; S, 13.80. Found C, 61.84; H, 10.47; S, 13.65.

4.1.4. (1*R*,2*R*,4*R*,S_S)-2-(2-Hydroxy-4-methylcyclohexyl)propane-2-sulfinamide, 8c. To the gray suspension of lithium amide, prepared by addition of lithium pieces (554 mg, 79 mmol) to liquid ammonia (ca. 120 mL) in

the presence of catalytic amount of $FeCl_3 \cdot 6H_2O$, was added at −65°C a solution of sultine **6** (2.05 g, 10.1 mmol) in THF (30 mL). The reaction mixture was stirred at −65°C for 30 min and carefully quenched with solid NH_4Cl (5.3 g). The ammonia was evaporated and THF was removed under vacuum. The residue was dissolved in 15 mL of H_2O and 25 mL of CH_2Cl_2. Organic layer was separated and aqueous solution was extracted three times with CH_2Cl_2. Combined organic extracts were dried and evaporated to give colorless solid (2.14 g, 96%) pure enough for next step. Analytical sample was prepared by recrystallization from hexane–CH_2Cl_2. Yield 82%. Mp 108–114°C; $[\alpha]_D = +5.0$ (*c* 1.41, CH_2Cl_2); IR (KBr) 3367, 3208 (NH), 1024 (S=O); ^{1}H NMR ($CDCl_3$) δ 0.75–1.15 (m, 2H), 0.89 (d, $J = 6.6$ Hz, 3H), 1.22 (s, 3H), 1.24 (s, 3H), 1.3–1.55 (m, 2H), 1.6–2.05 (4H), 3.1 (br, 1H), 3.48 (ddd, $J = 3.8$, 10.3 Hz, 1H), 4.3 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 17.4, 20.0, 21.8, 26.2, 31.3, 34.3, 45.6, 47.1, 62.5, 71.1. Anal calcd for $C_{10}H_{21}NO_2S$: C, 54.76; H, 9.65; N, 6.39; S, 14.62. Found: C, 54.89; H, 9.75; N, 6.59; S, 14.57.

4.1.5. (1*R*,2*R*,4*R*,S_S)-2-(2-Trimethylsilyloxy-4-methylcyclohexyl)propane-2-sulfinamide, 9c. To the solution of sulfinamide **8c** (2.14 g, 9.8 mmol) in pyridine (30 mL) and HMDS (16.1 mL, 78.1 mmol) was added TMSCl (4.95 mL, 39 mmol) at rt. The mixture was stirred for 16 h and saturated solution of $NaHCO_3$ was added (cooling with cold water bath). The mixture was diluted with water (20 mL) and extracted with CH_2Cl_2. Combined extracts were dried with $MgSO_4$ and the solvents were removed by evaporation under vacuum (50°C). The product was purified by chromatography on short column (silicagel, elution with ethyl acetate and hexane 4:3, then 2:1). Yield 1.88 g (66%). Colorless crystals, Mp 64–68°C; $[\alpha]_D$ −13.2 (*c* 1.78, CH_2Cl_2); IR (film) 3227 (NH), 1066, 1045 (S=O); ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.72–1.08 (m, 3H), 0.86 (d, $J = 6.6$ Hz, 3H), 1.12 (s, 3H), 1.19 (s, 3H), 1.26–1.49 (m, 1H), 1.56 (m, 4H), 3.49 (br, 2H), 3.60 (ddd, $J = 4.2$, 9.8, 10.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.8, 15.1, 16.6, 21.8, 26.1, 31.0, 34.1, 45.3, 48.7, 62.1, 72.7. HR LSIMS calcd for $C_{13}H_{29}O_2NNaSiS$ 314.1586 (M+Na). Found 314.1583.

4.1.6. (1*R*,2*R*,4*R*,S_S)-*N*-[(1*E*)-Benzylidene]-2-(2-trimethylsilyloxy-4-methylcyclohexyl)propane-2-sulfinamide, 10c. To the solution of sulfinamide **9c** (970 mg, 3.3 mmol) and benzaldehyde (387 mg, 3.65 mmol) in THF (12 mL) was added tetraethoxytitanium (1.51 g, 6.6 mmol) and the mixture was stirred at rt for 16 h. A saturated solution of KCl (4 mL) was added and the suspension was filtered through Celite. The precipitate was washed with ethyl acetate. The filtrate was dried ($MgSO_4$) and evaporated. Chromatography on silicagel (CH_2Cl_2 and hexane 1:1 then AcOEt and hexane 1:1) gave colorless oil (1.16 g, 92%). $[\alpha]_D$ +87.1 (*c* 1.15, CH_2Cl_2); IR (film) 1605, 1573 (C=N), 1069 (S=O); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 0.76–1.23 (m, 3H), 0.91 (d, $J = 6.4$ Hz, 3H), 1.01 (s, 3H), 1.25 (s, 3H), 1.31–1.54 (m, 1H), 1.58–1.74 (m, 1H), 1.82–2.12 (m, 3H), 3.76 (ddd, $J = 4.2$, 10.1, 10.6 Hz, 1H), 7.39–7.52 (m, 3H), 7.78–7.90 (m, 2H), 8.54 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 1.0, 16.5, 17.4, 21.9, 26.1, 31.2, 34.4, 45.4, 49.0, 64.9, 73.0, 128.7, 129.3, 132.0, 134.3, 162.3. HR LSIMS calcd for $C_{20}H_{34}O_2NSiS$ 380.2080 (M+H). Found 380.2087.

4.1.7. General procedure for the addition of ethylmagnesium bromide to sulfinimines. To a cooled (−30°C) solution of sulfinimine (0.33 mmol) in CH_2Cl_2 or THF (2.5 mL) was added an ether solution of ethylmagnesium bromide (0.57 mL, 1 mmol). The mixture was stirred for 3.5 h at −30°C and then quenched with saturated aqueous solution of NH_4Cl (3 mL). The organic layer was separated and the water phase was extracted with CH_2Cl_2. Combined extracts were dried ($MgSO_4$) and evaporated.

4.1.7.1. (1*S*,1′*R*,2*R*,4*R*,S_S)-7,7-Dimethyl-*N*-(1′-phenylpropyl)-2-trimethylsilyloxybicyclo[2.2.1]heptane-1-methanesulfinamide, 11b. The product was purified by chromatography on silicagel (CH_2Cl_2 and MeOH 100:1). Colorless solid, yield 85%. Major diastereoisomer: IR (neat) 3430 (NH), 1088, 1047, 1021 (S=O); ^{1}H NMR ($CDCl_3$) δ −0.11 (s, 9H), 0.7–1.1 (m, 2H), 0.78 (s, 3H), 0.80 (t, $J = 7.3$ Hz, 3H), 0.96 (s, 3H), 1.16–1.38 (m, 1H), 1.50–1.89 (m, 6H), 2.47 and 3.18 (AB, $J = 12.6$ Hz, 2H), 3.81 (dd, $J = 7.2$, 3.4 Hz, 1H), 4.0 (d, $J = 2.4$ Hz, 1H), 4.23 (ddd, $J = 2.6$, 6.4, 8.5 Hz, 1H), 7.18–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.1, 10.5, 20.0, 20.4, 27.2, 30.0, 31.2, 41.7, 44.5, 48.6, 50.0, 56.0, 59.8, 76.7, 127.4, 127.7, 128.3, 141.1. HR LSIMS calcd for $C_{22}H_{38}NO_2SSi$ 408.23925 (M+H). Found 408.24085.

4.1.7.2. (1*R*,1′*R*,2*R*,4*R*,S_S)-*N*-(1′-phenylpropyl)-2-(2-trimethylsilyloxy-4-methylcyclohexyl)propane-2-sulfinamide, 11c. Major diastereoisomer: colorless oil, IR (neat) 3223 (NH), 1067, 1047 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 9H), 0.65–1.08 (m, 3H), 0.84 (t, $J = 7.6$ Hz, 3H), 0.86 (d, $J = 7.3$ Hz, 3H), 1.12 (s, 3H), 1.20 (s, 3H), 1.25–1.46 (m, 1H), 1.52–1.92 (m, 6H), 3.19 (bd, $J = 3.8$ Hz, 1H), 3.51 (ddd, $J = 10.4$, 10.4, 4.0 Hz, 1H), 4.22 (m, 1H), 7.2–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.7, 10.6, 16.4, 17.3, 21.9, 26.0, 31.1, 31.7, 34.4, 45.4, 48.3, 60.7, 62.3, 73.0, 127.1, 127.7, 128.2, 142.2. HR LSIMS calcd for $C_{22}H_{40}NO_2SSi$ 410.25490 (M+H). Found 410.25618.

4.1.8. Recovery of the sultine 6. To the solution of sulfinamide **11c** (0.25 mmol) in diethyl ether (2 mL) was added $HCl \cdot Et_2O$ (1.5 mL, ca. 1 M). After 30 min the precipitated hydrochloride **12** was filtered and washed with hexane. The filtrate was evaporated to give sultine **6** which may be purified by crystallization from cyclohexane. Free amine was obtained from hydrochloride **12** by standard workup.

Acknowledgements

This work was financially supported by Institute of Organic Chemistry Polish Academy of Sciences in Warsaw grants for statute activity. The author would like to thank Dr. Sc. Zofia Urbańczyk-Lipkowska for X-ray measurement and analysis.

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