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An improved and efficient procedure for the preparation of chiral sulfinates from sulfonyl chloride using triphenylphosphine

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Abstract

An improved procedure of the Sharpless method for the preparation of chiral sulfinates by triphenylphosphine is described. A mixture of sulfonyl chlorides and diacetone-D-glucose or *l*-menthol in the presence of triethylamine was treated with triphenylphosphine in CH_2Cl_2 at 0°C to give the sulfinates in good yields.

1. Introduction

Chiral sulfoxides are important stereocontrolling elements in asymmetric synthesis.[1] Andersen's method, the reaction of a chiral sulfinate with an organometallic reagent, is still the most practical method for the preparation of enantiomerically pure sulfoxides,[2] although catalytic or stoichiometric asymmetric oxidation of sulfides to chiral sulfoxides has been a subject of recent interest.[3] Various procedures for the preparation of chiral sulfinates, starting from sulfinic acids,[4] sulfinyl chlorides,[5] disulfides,[6] sodium sulfinates,[7] sulfonyl chlorides,[8] or chlorosulfinate,[9] have been reported. Among these procedures, the Sharpless method[8] is one of the most efficient and convenient methods for the preparation of menthyl arylsulfinates, which involves the reduction of readily available sulfonyl chlorides to sulfinyl chlorides with trimethylphosphite and subsequent in situ esterification with chiral alcohols in the presence of triethylamine. However, the reaction often requires long completion times, especially for the arenesulfonyl chlorides bearing electron-donating or bulky substituents on the phenyl ring which show low reactivity in the formation of the arenesulfinyl chlorides, giving the products in rather low yield. Furthermore, side products such as phosphorothiolates and disulfides are inevitably formed, probably due to the reaction being performed at high temperatures. We describe herein an improved procedure for the Sharpless method in the preparation of chiral sulfinates from sulfonyl chlorides using triphenylphosphine as a reducing agent.

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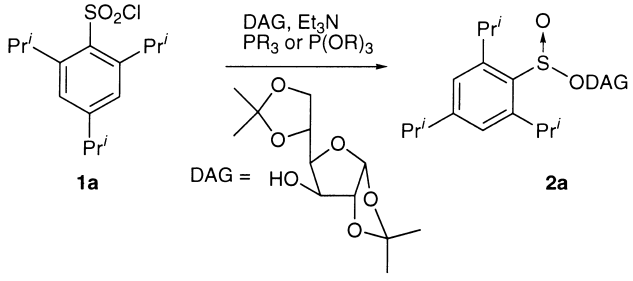
2. Results and discussion

In the course of our studies on the stereoselective radical β-addition to 2-(2,4,6-triisopropylbenzenesulfinyl)-2-cycloalkenones, we found that enantiomerically pure diacetone-D-glucosyl 2,4,6-triisopropylbenzenesulfinate **2a** could be successfully isolated by column chromatography.[10] Actually, we obtained a diastereomeric mixture of **2a** according to a modification of the reported method[11] through transformation of sodium 2,4,6-triisopropylbenzenesulfinate, obtained from sulfonyl chloride by reduction with zinc[12] and thionyl chloride to the corresponding sulfinyl chloride,[7a] followed by esterification with diacetone-D-glucose (DAG).[13] The yield of **2a**, however, was at best 50% by this procedure. We examined the preparation of DAG sulfinate **2a** from the corresponding sulfonyl chloride under different conditions (Eq. 1).



(1)

According to the reported procedure[8] [a mixture of sulfonyl chloride **1a** (1.5 equiv.), DAG (1 equiv.), triethylamine (1.5 equiv.), and trimethylphosphite (2 equiv.), CH_2Cl_2, reflux, 24 h] sulfinate **2a** was obtained in 11% yield together with significant formation of both phosphorothiolate and disulfide (entry 1, Table 1). In order to suppress the formation of disulfide, a CH_2Cl_2 solution of trimethylphosphite was added dropwise to a solution of sulfonyl chloride **1a**, DAG, and 10 equiv. of triethylamine in CH_2Cl_2 over a period of 1 h at 0°C, but the phosphorothiolate was still formed as the major product (20% yield) (entry 2). The reaction using triphenylphosphite afforded a complex mixture (entry 3), and tributylphosphine gave only disulfide in 18% yield due to its high reducing ability (entry 4). Finally, we found that the yield was dramatically improved when triphenylphosphine was used as a reducing agent. Thus, a CH_2Cl_2 solution of triphenylphosphine (1.0 equiv.) was added dropwise to a solution of sulfonyl chloride **1a**, DAG (1.0 equiv.), and triethylamine (10 equiv.) in CH_2Cl_2 over a period of 1 h at 0°C to give sulfinate **2a** in 90% yield without the formation of side products (entry 5). It is important to add triphenylphosphine slowly to suppress overreduction of the sulfinyl chloride, so that the sulfinate is formed immediately after the sulfinyl chloride is generated. In fact, the reaction was completed at the end of the addition of 1 equiv. of triphenylphosphine (1 h). The reaction at room temperature gave the product in high yield (entry 6), but at −45°C gave rise to only the disulfide in 24% yield (entry 7). Among the solvents examined, CH_2Cl_2 seems to be the best solvent for this reaction. Sulfinate **2a** was obtained with low diastereoselectivity under the reactions employed (see below).

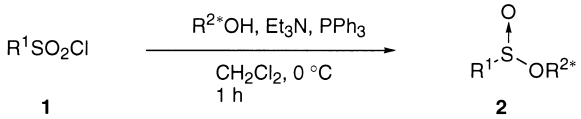
The DAG arenesulfinates, bearing bulky and electron-donating substituents on the phenyl ring such as **2a**, were conveniently obtainable from the corresponding sulfonyl chloride in high yield without isolation of the intermediately formed unstable arenesulfinyl chloride. Table 2 shows the results for the preparation of various sulfinates by the present procedure. Reactions of various arenesulfonyl chlorides also proceeded smoothly, and completed at the end of the addition of 1 equiv. of triphenylphosphine (1 h). Menthyl benzenesulfinate **2b** was obtained by the reaction with benzenesulfonyl chloride in 98% yield (entry 1). The reaction of *p*-toluenesulfonyl chloride with *l*-menthol gave menthyl sulfinate **2c** in 95% yield with a diastereomer ratio of 62:38 (entry 2). Diastereomeric ratios were determined by ^1H NMR

Table 1
Preparation of sulfinate **2a** from sulfonyl chloride **1a** under various conditions[a]

Entry	Phosphorus reagent	Solvent	Temp (°C)	Time (h)	Yield (%)	Ratio[b] (S_S) : (R_S)
1[c]	$P(OMe)_3$	CH_2Cl_2	reflux	24	11	50 : 50
2	$P(OMe)_3$	CH_2Cl_2	0 → rt	24	—	—
3	$P(OPh)_3$	CH_2Cl_2	0 → rt	24	—	—
4	PBu_3	CH_2Cl_2	0 → rt	24	— [d]	—
5	PPh_3	CH_2Cl_2	0	1	90	53 : 47
6	PPh_3	CH_2Cl_2	rt	1	81	50 : 50
7	PPh_3	CH_2Cl_2	-45	2	— [d]	—
8	PPh_3	PhMe	0	1	80	53 : 47
9	PPh_3	THF	0	1	72	46 : 54
10	PPh_3	Et_2O	0	1	56	46 : 54

[a] The reaction was carried out using **1a** (1 equiv), DAG (1 equiv), phosphorus reagent (1 equiv), and triethylamine (10 equiv) in 0.2 mol/L solution unless otherwise noted. [b] Determined by the ^1H nmr spectrum.
[c] **1a** (1.5 equiv), DAG (1 equiv), phosphorus reagent (2 equiv), and triethylamine (1.5 equiv) were used.
[d] No formation of **2a** was observed, but the disulfide was isolated (18 %; entry 4: 24% entry 7).

spectra. The reaction with *p*-toluenesulfonyl chloride with DAG gave DAG sulfinate **2d** in 99% yield with a diastereomer ratio of 71:29 (entry 3).



1 **2**

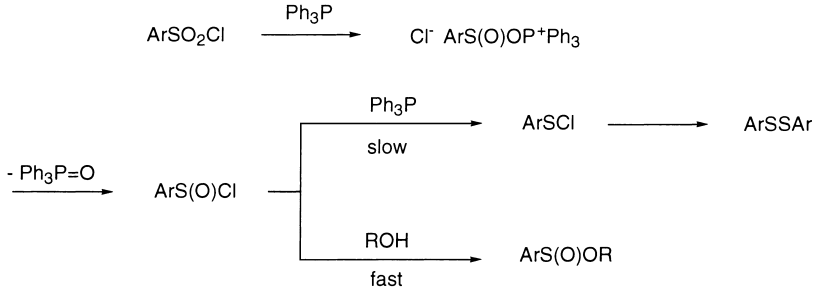
The diastereoselectivity of **2d** changed depending upon the amine of choice, although the change was not as drastic as that given by Alcudia;[6a,13] in the reaction of the sulfinyl chloride and DAG the S_S/R_S ratio turned out to be 88:12 with *i*-Pr_2NEt, and 35:65 with pyridine (entries 4 and 5). 4-Chlorobenzenesulfonyl chloride gave the menthyl sulfinate **2e** in 96% yield (entry 6). Arenesulfonyl chlorides bearing an electron-donating group such as 4-methoxybenzenesulfonyl chloride, 3,5-di-*tert*-butyl-4-methoxybenzenesulfonyl chloride, 2,4,6-trimethylbenzenesulfonyl chloride and 2,4,6-triisopropylbenzenesulfonyl chloride, gave the corresponding sulfinates **2f–j** in excellent yields (entries 7–11). 1-Naphthalenesulfinate **2k** was obtained in 95% yield (entry 12). Alkanesulfinates such as DAG methanesulfinate **2l** and DAG isopropanesulfinate **2m** were obtained in moderate yields (entries 13 and 14) and the corresponding menthyl sulfonates were not formed. The present procedure can generally be applied to the transformation of sulfonyl chlorides to sulfinates. The reaction of tosyl chloride with ethanol afforded sulfinate **2n** in 55% yield together with the disulfide, and *tert*-butyl *p*-toluenesulfinate **2o** was obtained in 83% yield without formation of either sulfonate or disulfide (entries 15 and 16). The diastereomerically pure sulfinates **2a–m** could be separated by column chromatography and/or by recrystallization. However, the pure diastereomer of sulfinates **2h** and **2i** could neither be separated by column chromatography nor by recrystallization as previously reported.[8,14] In comparison with the reaction using trimethylphosphite, triphenylphosphite and tributylphosphine, the present method using triphenylphosphine has characteristic advantages: triphenylphosphine enables selective reduction of sulfonyl chlorides to sulfinyl chlorides which leads to the predominant formation of sulfinates (Scheme 1). Hence, the procedure minimizes not only further reduction of sulfinyl chlorides to sulfenyl chlorides

Table 2
Preparation of DAG or menthyl arenesulfinates **2**

Entry	R^1	R^2*OH	Sulfinate	Yield (%)	Ratio (S_S) : (R_S)
1	C_6H_5	*l*-menthol	**2b**	98	65 : 35
2	*p*-$CH_3C_6H_4$	*l*-menthol	**2c**	95	62 : 38
3	*p*-$CH_3C_6H_4$	DAG	**2d**	99	71 : 29
4[a]	*p*-$CH_3C_6H_4$	DAG	**2d**	90	88 : 12
5[b]	*p*-$CH_3C_6H_4$	DAG	**2d**	78	35 : 65
6	4-ClC_6H_4	*l*-menthol	**2e**	96	60 : 40
7	4-$CH_3OC_6H_4$	*l*-menthol	**2f**	91	50 : 50
8	3,5-*t*Bu-4-CH_3O-C_6H_2	*l*-menthol	**2g**	99	62 : 38
9	2,4,6-$(CH_3)_3C_6H_2$	*l*-menthol	**2h**	93	66 : 34
10	2,4,6-$(CH_3)_3C_6H_2$	DAG	**2i**	98	59 : 41
11	2,4,6-(*i*Pr)$_3C_6H_2$	*l*-menthol	**2j**	99	70 : 30
12	1-$C_{10}H_7$	*l*-menthol	**2k**	95	61 : 39
13[c]	CH_3	DAG	**2l**	64	78 : 22
14	$(CH_3)_2CH$	DAG	**2m**	58	81 : 19
15	*p*-$CH_3C_6H_4$	EtOH	**2n**	55	—
16	*p*-$CH_3C_6H_4$	*t*BuOH	**2o**	83	—

[a]The reaction was carried out using 10 equiv of *i*-Pr_2NEt in toluene. [b]The reaction was carried out using 1.5 equiv of the sulfonyl chloride, triphenylphosphine, and 10 equiv of pyridine in THF. [c]The reaction was carried out using 2 equiv of the sulfonyl chloride, triphenylphosphine, and triethylamine in CH_2Cl_2.

but also formation of undesired side products, inevitably formed in the reaction with phosphites or tributylphosphine.



Scheme 1.

3. Conclusion

Triphenylphosphine reduces sulfonyl chlorides to sulfinyl chlorides under mild reaction conditions to give a variety of *l*-menthyl and diacetone D-glucosyl arene- and alkanesulfinates in good yields. Thus, this reaction provides a convenient method for the preparation of various enantiomerically pure sulfoxides. Alkyl *p*-toluenesulfinates can also be prepared from *p*-toluenesulfonyl chloride.

4. Experimental

4.1. General procedures

Diethyl ether (ether) and THF were distilled before use from a deep blue solution resulting from addition of benzophenone and sodium. CH_2Cl_2 was distilled from calcium hydride. All reactions were monitored by thin layer chromatography on 0.25 mm Merck silica gel (60F-254) precoated glass plates, with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol with heating. Column chromatography was carried out on columns packed with Fuji Silysia silica gel BW-200. Melting points were measured on a Yanaco micro-melting point apparatus and are uncorrected. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded on a Varian Gemini-200 instrument, and chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane in $CDCl_3$. Infrared spectra were recorded on a Jasco FTIR-200 spectrometer; absorptions are given in reciprocal centimeters. Mass spectra (eV) were recorded on a Hitachi M-2000 spectrometer. Microanalyses were performed with a Perkin–Elmer 240 instrument. Optical rotations were measured on a Jasco DIP-4 polarimeter (100 mm, 1 cm^3 cell) operating at λ=589 nm corresponding to the sodium D line. HPLC analyses were performed on a Jasco Trirotor IV using 4.6×150 mm Cosmosil packed column (flow rate, 500 μL/min).

4.2. General procedure for the preparation of sulfinates **2**

To a solution of sulfonyl chloride **1** (3.8 mmol), an alcohol (3.8 mmol), and triethylamine (38 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of triphenylphosphine (3.8 mmol) in CH_2Cl_2 (10 mL) over a period of 1 h. The reaction mixture was concentrated under reduced pressure and then diluted with a mixed solvent of hexane and ethyl acetate (85:15). The resulted precipitates were filtered and washed successively with a mixed solvent of hexane and ethyl acetate (85:15). The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatography to afford sulfinate **2** as a mixture of diastereomers. Separation of the diastereomerically pure sulfinate was performed by column chromatography or by recrystallization.

4.3. Diacetone-D-glucosyl 2,4,6-triisopropylbenzenesulfinate **2a**

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2a** in 90% yield as a mixture of diastereomers. The R_S-isomer was separated in 29% yield by recrystallization from hexane–Et_2O. R_S-**2a**: mp 140–141°C (hexane–Et_2O); $[\alpha]_D^{24}$ +10.0 (*c* 1.42, acetone); (lit.[10a]; mp 142–143°C; $[\alpha]_D^{18}$ +11.0 (*c* 1.04, acetone)); ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3H), 1.24 (d, J=6.9 Hz, 6H), 1.28 (d, J=6.8 Hz, 12H), 1.34 (s, 3H), 1.39 (s, 3H), 1.52 (s, 3H), 2.89 (heptet, J=7.1 Hz, 1H), 3.90–4.07 (m, 5H), 4.19 (dd, J=2.8, 8.0 Hz, 1H), 4.84 (d, J=2.7 Hz, 1H), 4.88 (d, J=3.6 Hz, 1H), 5.89 (d, J=3.8 Hz, 1H), 7.08 (s, 2H); IR (neat) 2970, 2875, 1600, 1470, 1380, 1270, 1220, 1170, 1130, 1075, 1025, 950, 880, 850, 825, 700 cm^{-1}. The mother liquor was concentrated to give the diastereomeric mixure, in which the S_S-isomer was enriched. The S_S-isomer was separated in 20% yield by column chromatography (hexane:ethyl acetate=85:15). S_S-**2a**: oil; $[\alpha]_D^{24}$ −34.8 (*c* 0.356 acetone); (lit.[10a]; $[\alpha]_D^{18}$ −36.2 (*c* 0.636 acetone)); ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.25 (d, J=6.9 Hz, 6H), 1.29 (d, J=5.4 Hz, 6H), 1.30 (d, J=5.7 Hz, 6H), 1.36 (s, 3H), 1.44 (s, 3H), 1.52 (s, 3H), 2.89 (heptet, J=6.9 Hz, 1H), 3.93–4.13 (m, 4H), 4.22 (dd, J=2.7, 8.0 Hz, 1H), 4.34 (ddd, J=7.9, 5.4, 5.5 Hz, 1H), 4.61 (d, J=3.6 Hz, 1H), 4.85 (d, J=2.7 Hz, 1H), 5.81 (d, J=3.6 Hz, 1H), 7.10 (s, 2H); IR (neat)

2970, 2930, 2880, 1600, 1570, 1470, 1430, 1380, 1260, 1220, 1160, 1140, 1080, 1025, 950, 880, 850, 830 cm^{-1}.

4.4. l-*Menthyl benzenesulfinate* ***2b***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2b** in 98% yield as a mixture of diastereomers. A diastereomeric mixture; ^1H NMR ($CDCl_3$) δ 0.70–2.34 (m, 18H), 4.14 (dt, J=4.5 Hz, 1H, S_S), 4.22 (dt, J=4.6 Hz, 1H, R_S), 7.30–7.34 (m, 1H), 7.51–7.55 (m, 2H), 7.70–7.75 (m, 2H); IR (neat) 2955, 2930, 2870, 1445, 1370, 1140, 960, 910, 850, 780, 750, 700 cm^{-1}. Diastereomers could not be separated (lit.[15]; mp 49–51°C (methanol); $[\alpha]_D^{25}$ −205.5 (*c* 2.0 acetone)).

4.5. l-*Menthyl* p-*toluenesulfinate* ***2c***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2c** in 95% yield as a mixture of diastereomers. The pure S_S-isomer was obtained in 17% yield by recrystallization from acetone. A drop of conc. HCl was added to the mother liquor to convert the R_S-isomer to the S_S-isomer. The second recrystallization from acetone gave the S_S-isomer in another 17% yield. S_S-**2c**: mp 106–108°C (acetone); $[\alpha]_D^{26}$ −196 (*c* 0.75, acetone); (lit.[7]; mp 103–105°C; $[\alpha]_D^{25}$ −200 (*c* 1.23, acetone)); ^1H NMR ($CDCl_3$) δ 0.70–1.72 (m, 16H), 2.05–2.33 (m, 2H), 2.42 (s, 3H), 4.12 (dt, J=4.6, 11 Hz, 1H), 7.32 (d, J=7.9 Hz, 2H), 7.60 (d, J=8.2 Hz, 2H); IR (KBr) 2950, 2920, 2860, 2850, 1600, 1500, 1500, 1460, 1390, 1370, 1350, 1140, 1110, 1080, 960, 920, 850, 820, 780, 770 cm^{-1}.

4.6. *Diacetone*-D-*glucosyl* p-*toluenesulfinate* ***2d***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=80:20) to afford sulfinate **2d** in 90% yield as a mixture of diastereomers. Recrystallization from hexane–Et_2O gave almost pure S_S-isomer in 40% yield which was further recrystallized to give the diastereomerically pure S_S-isomer in 30% yield. S_S-**2d**: mp 99–100°C (hexane–Et_2O); $[\alpha]_D^{25}$ −122 (*c* 0.478, acetone) (lit.[6a]; mp 95–96°C (hexane); $[\alpha]_D^{25}$ −125 (*c* 0.42 acetone)); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.30 (s, 6H), 1.45 (s, 3H), 2.45 (s, 3H), 3.88–4.18 (m, 4H), 4.50 (d, J=2.8 Hz, 1H), 4.83 (d, J=3.6 Hz, 1H), 5.92 (d, J=3.6 Hz, 1H), 7.35 (d, J=7.8 Hz, 2H), 7.66 (d, J=8.2 Hz, 2H); IR (KBr) 2990, 2950, 2920, 2895, 1600, 1460, 1375, 1225, 1170, 1140, 1090, 1055, 1020, 860, 825, 720 cm^{-1}.

4.7. l-*Menthyl* p-*chlorobenzenesulfinate* ***2e***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2e** in 96% yield as a mixture of diastereomers. The pure S_S-isomer was obtained in 40% yield by recrystallization from acetone. S_S-**2e**: mp 87–88°C (acetone); $[\alpha]_D^{26}$ −177 (*c* 0.858 acetone); (lit.[8]; mp 83.5–86.5°C; $[\alpha]_D^{25}$ −180 (*c* 0.65 acetone)); ^1H NMR ($CDCl_3$) δ 0.71–1.74 (m, 16H), 2.03–2.32 (m, 2H), 4.14 (dt, J=4.5, 11 Hz, 1H), 7.50 (d, J=8.7 Hz, 2H), 7.65 (d, J=8.7 Hz, 2H); IR (KBr) 3080, 3050, 2950, 2925, 2870, 1575, 1480, 1460, 1390, 1140, 1090, 1010, 960, 920, 850, 830, 780, 770, 750 cm^{-1}.

4.8. l-*Menthyl* p-*methoxybenzenesulfinate* ***2f***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2f** in 91% yield as a mixture of diastereomers. The S_S-isomer was separated in 8% yield by recrystallization from acetone. A drop of conc. HCl was added to the mother liquor to convert the R_S-isomer to the S_S-isomer. The second recrystallization from acetone gave the S_S-isomer in 16% yield. Combined crops were further recrystallized from acetone to give the diastereomerically pure S_S-isomer in 11% yield. S_S-**2f**: mp 116–118°C (acetone); $[\alpha]_D^{25}$ −189 (*c* 0.582 acetone); (lit.[8]; mp 111–115°C; $[\alpha]_D^{25}$ −191.2 (*c* 1.21, acetone)); ^{1}H NMR ($CDCl_3$) δ 0.70–1.74 (m, 16H), 2.05–2.33 (m, 2H), 3.86 (s, 3H), 4.11 (dt, 4.4, 11 Hz, 1H), 7.01 (d, J=8.8 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H); IR (KBr) 2950, 2925, 2890, 2870, 1600, 1500, 1450, 1310, 1255, 1130, 1090, 1030, 960, 920, 850, 830, 760 cm^{-1}.

4.9. l-*Menthyl 3,5-di*-tert-*butyl-4-methoxybenzenesulfinate* ***2g***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2g** in 99% yield as a mixture of diastereomers. The R_S-isomer was separated in 36% yield by recrystallization from acetone. A drop of conc. HCl was added to the mother liquor to convert the S_S-isomer to the R_S-isomer. The second recrystallization from acetone gave the R_S-isomer in 28% yield. Combined crops were further recrystallized from acetone to give the diastereomerically pure R_S-isomer in 38% yield. R_S-**2g**: mp 134–135°C (acetone); $[\alpha]_D^{25}$ +49.4 (*c* 0.802, acetone) (lit.[10a]; mp 138–139°C (acetone); $[\alpha]_D^{20}$ +50.4 (*c* 0.40, acetone)); ^{1}H NMR ($CDCl_3$) δ 0.74–1.75 (m, 16H), 1.44 (s, 18H), 2.07–2.24 (m, 2H), 3.71 (s, 3H), 4.21 (dt, J=4.6, 11 Hz, 1H), 7.59 (s, 2H); IR (KBr) 2950, 2925, 2880, 2860, 1455, 1400, 1225, 1130, 1010, 960, 920, 850, 770, 760 cm^{-1}.

4.10. l-*Menthyl 2,4,6-trimethylbenzenesulfinate* ***2h***[8]

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=95:5) to afford sulfinate **2h** in 93% yield as a mixture of diastereomers. A diastereomeric mixture; ^{1}H NMR ($CDCl_3$) δ 0.77–2.33 (m, 18H), 2.28 (s, 3H), 2.59 (s, 6H), 4.06 (dt, J=4.7, 10 Hz, 1H, S_S-isomer), 4.08 (dt, 4.7, 10 Hz, 1H, R_S-isomer), 6.85 (s, 2H); IR (neat) 2960, 2930, 2870, 1600, 1455, 1140, 960, 850, 755, 645 cm^{-1}.

4.11. *Diacetone*-D-*glucosyl 2,4,6-trimethylbenzenesulfinate* ***2i***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=60:40) to afford sulfinate **2i** in 98% yield as a mixture of diastereomers. A diastereomeric mixture; ^{1}H NMR ($CDCl_3$) δ 1.20–1.58 (m, 12H), 2.29 (s, 3H, R_S-isomer), 2.30 (s, 3H, S_S-isomer), 2.59 (s, 6H, R_S-isomer), 2.60 (s, 6H, S_S-isomer), 3.89–4.32 (m, 4H), 4.69–4.73 (m, 1H), 4.82–4.85 (m, 1H), 5.87 (d, J=3.6 Hz, 1H, S_S-isomer), 5.91 (d, J=3.5 Hz, 1H, R_S-isomer), 6.85 (s, 2H, R_S-isomer), 6.87 (s, 2H, S_S-isomer); IR (KBr) 2990, 2940, 2900, 1600, 1455, 1380, 1260, 1220, 1170, 1140, 1080, 1025, 850, 830, 730, 625 cm^{-1}. Calcd for $C_{21}H_{30}O_7S$: C, 59.14; H, 7.09. Found: C, 59.00; H, 7.23.

4.12. l-*Menthyl 2,4,6-triisopropylbenzenesulfinate* ***2j***[8]

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=95:5) to afford sulfinate **2j** in 99% yield as a mixture of diastereomers. A diastereomeric mixture;

^{1}H NMR ($CDCl_3$) δ 0.74–2.37 (m, 18H), 1.25 (s, 12H, S_S-isomer), 1.26 (s, 12H, R_S-isomer), 1.28 (s, 6H, S_S-isomer), 1.30 (s, 6H, R_S-isomer), 2.89 (heptet, J=6.9 Hz, 1H), 3.98–4.17 (m, 3H), 7.08 (s, 2H); IR (neat) 2960, 2930, 2870, 1600, 1470, 1390, 1370, 1130, 960, 920, 880, 850, 780, 750, 650 cm^{-1}.

4.13. l-*Menthyl 1-naphthalenesulfinate* ***2k***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2k** in 95% yield as a mixture of diastereomers. The pure S_S-isomer was obtained in 21% yield by recrystallization from acetone. S_S-**2k**: mp 120–122°C (acetone); $[\alpha]_D^{26}$ −394 (*c* 0.335, acetone); (lit.[16]; mp 118–119; $[\alpha]_D^{25}$ −432.1 (*c* 1.84 acetone); ^{1}H NMR ($CDCl_3$) δ 0.44 (d, J=6.9 Hz, 3H), 0.74–1.68 (m, 13H), 1.87–2.03 (m, 1H), 2.38–2.49 (m, 1H), 4.15 (dt, J=4.4, 11 Hz, 1H, S_S), 7.55–7.67 (m, 3H), 7.91–8.05 (m, 2H), 8.19–8.22 (m, 1H), 8.32–8.37 (m, 1H); IR (KBr) 2960, 2930, 2870, 1610, 1560, 1380, 1345, 1150, 1130, 950, 920, 850, 810, 770, 670 cm^{-1}.

4.14. *Diacetone*-D-*glucosyl methanesulfinate* ***2l***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=60:40) to afford sulfinate **2l** in 64% yield as a mixture of diastereomers. Recrystallization from hexane–Et_2O gave the S_S-isomer in 52% yield. Further recrystallization gave a diastereomerically pure S_S-isomer in 31% yield. S_S-**2l**: mp 96–98°C (hexane–Et_2O); $[\alpha]_D^{26}$ −61.8 (*c* 2.64 acetone) (lit.[6a]; mp 92–94°C; $[\alpha]_D^{25}$ −60.0 (*c* 2.7 acetone)); ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.35 (s, 3H), 1.43 (s, 3H), 1.52 (s, 3H), 2.70 (s, 3H), 3.98–4.33 (m, 4H), 4.62 (d, J=3.7 Hz, 1H), 4.78 (d, J=2.1 Hz, 1H), 5.92 (d, J=3.8 Hz, 1H); IR (KBr) 2990, 2950, 1375, 1260, 1220, 1160, 1140, 1070, 1020, 825 cm^{-1}.

4.15. *Diacetone*-D-*glucosyl 2-propanesulfinate* ***2m***

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=80:20) to afford sulfinate **2m** in 58% yield as a mixture of diastereomers. Each diastereomer was separated by column chromatography (hexane:ethyl acetate=80:20). S_S-**2m**: 30%; R_f 0.28 (hexane:ethyl acetate=70:30); $[\alpha]_D^{26}$ −67.3 (*c* 0.358 acetone) (lit.[6a]; $[\alpha]_D^{25}$ −50.0 (*c* 0.3 acetone)); ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J=7.0, 6H), 1.32 (s, 3H), 1.35 (s, 3H), 1.43 (s, 3H), 2.80 (heptet, J=7.0 Hz, 1H), 3.96–4.37 (m, 4H), 4.60 (d, J=3.6 Hz, 1H), 4.72 (d, J=2.3 Hz, 1H), 5.91 (d, J=3.6 Hz, 1H); IR (KBr) 2990, 2940, 2900, 1740, 1460, 1380, 1260, 1220, 1160, 1140, 1080, 1020, 830 cm^{-1}. R_S-**2m**: 8%; R_f 0.38 (hexane:ethyl acetate=70:30); $[\alpha]_D^{26}$ +14.4 (*c* 0.194 acetone) (lit.[6a] $[\alpha]_D^{25}$ +11.0 (*c* 2.9 acetone)); ^{1}H NMR ($CDCl_3$) δ 1.27 (d, J=7.0, 6H), 1.31 (s, 3H), 1.32 (s, 3H), 1.42 (s, 3H), 1.50 (s, 3H), 2.82 (heptet, J=7.0 Hz, 1H), 3.94–4.19 (m, 4H), 4.71 (br, 1H), 4.81 (d, J=3.6 Hz, 1H), 5.91 (d, J=3.6 Hz, 1H); IR (KBr) 2990, 2940, 2900, 1460, 1380, 1260, 1220, 1170, 1140, 1080, 1020, 840, 740 cm^{-1}.

4.16. *Ethyl* p-*toluenesulfinate* ***2n***[4b]

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=80:20) to afford sulfinate **2n** in 55% yield. ^{1}H NMR ($CDCl_3$) δ 1.28 (t, J=7.1 Hz, 3H), 2.43 (s, 3H), 3.72 (dq, J=7.1, 10 Hz, 1H), 4.10 (dq, J=7.1, 10 Hz, 1H), 7.34 (d, J=6.6 Hz, 2H), 7.60 (d, J=6.6 Hz, 2H); IR (KBr) 2980, 2930, 2900, 1600, 1500, 1450, 1390, 1140, 1090, 1010, 890, 820, 720, 630 cm^{-1}.

4.17. tert-*Butyl* p-*toluenesulfinate* **2o**[17]

Purification of the crude product was performed by column chromatography (hexane:ethyl acetate=90:10) to afford sulfinate **2o** in 83% yield. ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 9H), 2.41 (s, 3H), 7.31 (d, J=8.0 Hz, 2H), 7.56 (d, J=8.0 Hz, 2H); IR (KBr) 2975, 2925, 1600, 1500, 1450, 1395, 1370, 1250, 1170, 1130, 1110, 1080, 860, 790, 720 cm^{-1}.

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