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Asymmetric Synthesis of β-Hydroxythioacetamides Mediated by Enantiomerically Pure Sulphinyl Derivatives.

Mauro Cinquini, Amedea Manfredi, Henriette Molinari and Angelo Restelli

Centro C.N.R. and Dipartimento di Chimica Organica e Industriale dell'Università
Via C. Golgi 19, 20133 Milano, Italy.

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Abstract. Enantiomerically pure p-tolyl sulphinyl-N,N-dimethylthioacetamide (1) was prepared starting from (-)-(S)-menthyl toluene-p-sulphinate. Aldol-type condensation of (1) and subsequent removal of the sulphinyl group open an entry to optically active β-hydroxy thioacetamides in 40-90% e.e.

The synthetic versatility of thioamides has been fully recognized in recent years.[1] The stereoselective generation of their enolates, as well as the application, inter alia, to highly diastereoselective aldol-type condensations have also been reported.[2] On these bases, we thought that an entry to chiral thioacetamides would have been valuable.

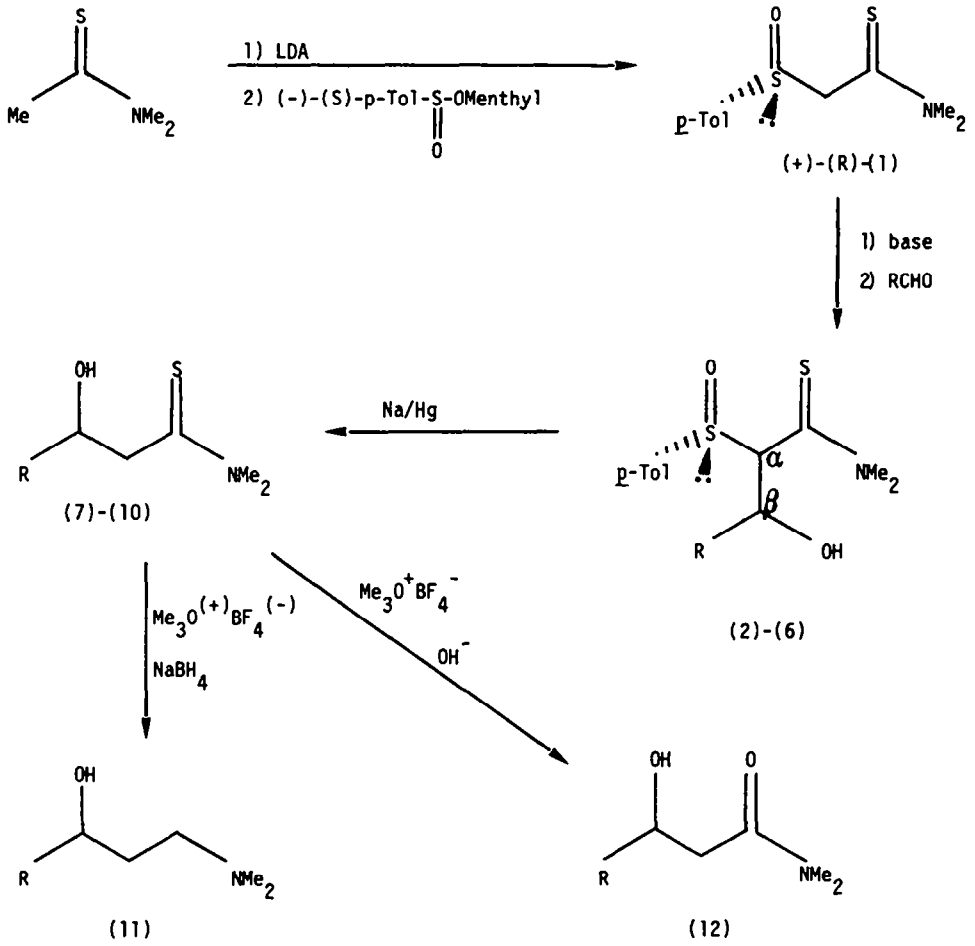
In line with a number of sulphoxide mediated asymmetric synthesis[3] recently reported by others[4-7] and our own group,[8-10] enantiomerically pure p-tolylsulphinyl-N,N-dimethyl thioacetamide (1) was prepared and tested in enantioselective aldol-type reactions.[11] As already pointed out for a related system,[8] in this new chiral synthon the sulphinyl moiety plays a double role, providing in the meantime the source of chirality and the substitution pattern required for efficient chiral enol acetate equivalents.[11] Compound (1) is readily synthesized by reaction of commercially available (-)-(S)— menthyl toluene-p-sulphinate with α-metallated N,N-dimethylthioacetamide in 60% yield. Multigram scale preparation is possible, (1) is a stable compound which can be stored for at least 6 months in the dark.

As shown by ^{1}H nmr spectroscopy with the aid of the chiral shift reagent tris [3-(heptafluoropropylhydroxymethylene)-d-camphorate] Europium III Eu(hfc)$_3$, this reaction is stereospecific, and (1) is produced in ≥ 98% enantiomeric excess (e.e.). In agreement with the huge amount of data collected for analogous Andersen-type syntheses[3-10], the (+)-(R) absolute configuration at sulphur was assigned to (1).

As mentioned above, having a chiral thioacetamide synthon available, we studied its aldol condensation. Indeed, enolate generation from (+)-(R)-(1)

followed by aldehyde addition gave adducts (2)-(6) as diastereoisomeric mixtures. Subsequent removal of the sulphinyl group afforded β-hydroxy thioacetamides (7)-(10) in good to excellent e.e., once again established by ^{1}H nmr spectroscopy in the presence of Eu(hfc)$_3$ (Scheme 1).

Scheme 1.



(2), (7) R = Me
(3), (8) R = Bu^i
(4), (9), (11) R = Pr^i
(5), (10), (12) R = Bu^t
(6) R = Ph

It must be noted that alkylation of hydroxy thioamide and subsequent borohydride reduction allow an entry to the synthesis of γ-amino alcohols, as shown by the conversion of (9) into (11) (see experimental). Thus the sulphynil thioamide (1) behaves as a chiral synthon of a γ-amino carbanion.

As expected on the basis of previous work[4-10] on related systems the

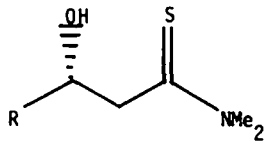
nature of the base used to generate the enolate of (+)-(R)-(1) turned out to be crucial. The best results were obtained with a bulky magnesium base such as Bu^tMgBr (0.75 mol per mol of substrate) and by working at -90°C in the condensation step, higher temperatures and substrate-base molar ratios leading to a decrease of chiral discrimination.

When BuLi was used as base, hydroxythioamides (7) and (9) were obtained in comparable enantiomeric purities, but in very low chemical yields. As mentioned above aldol condensation* of sulphinyl-thioamide (1) gave, after reductive removal of the sulphinyl groups (Na/Hg, Na_2HPO_4) the products (7)-(10) with moderate to high stereoselection.

The effect of the aldehyde R residue on the extent of the enantiomeric discrimination is quite difficult to account for. Indeed the best result (see Table 1) was obtained with isobutyraldehyde (e.e. 90%), the more bulky pivalaldehyde leading to a decrease in stereoselection (e.e. 55%). On the other hand acetaldehyde and isovaleric aldehyde not only gave a moderate enantiomeric excess, but the hydroxythioamides (7) and (8) had opposite chirality with respect to those of (9) and (10), as indicated by C.D. spectra, which showed opposite Cotton effects (see experimental).

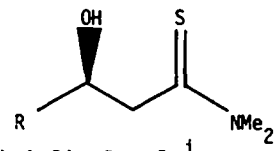
A more regular trend was previously[8] observed in the aldol-type condensation of N,N-dimethyl sulphinyl amides, the extent of chiral discrimination increasing with decreasing steric hindrance of the aldehyde R residue.

The absolute configuration was established in the case of compound (10), and hence in the case of compounds (7)-(9), by chemical correlation with hydroxyamide (-)-(S)-(12). Alkylation of (-)-(10) with $Me_3O^+BF_4^-$ and subsequent treatment with sodium hydroxide in phase-transfer conditions (see experimental) afforded (-)-(12). Thus (-)-(10), (-)-(9), (+)-(7) and (+)-(8) have the (S) absolute configuration.



(S)-(7) R = Me

(S)-(8) R = Bu^i



(S)-(9) R = Pr^i

(S)-(10) R = Bu^t

To gain a further insight in the stereochemical path of the condensation of aldehydes with (1) we attempted the isolation of the sulphinyl adducts (3), (4), and (6).+

Reaction of (+)-(R)-(1) with Pr^i—CHO afforded only two diastereoisomeric products (4a), (4b)§ in 95:5 ratio, which could be separated by flash

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* Unfortunately the reaction is limited to aldehydes, ketones such as acetophenone being unreactive.

+ Compound (2) is unstable and must be directly desulphurized.

§ With a,b we indicate diastereoisomeric products.

chromatography. This indicates that, at least in this case, complete stereoselection is achieved at the carbon α to the sulphinyl group, a behaviour not unprecedented.[7,8,10]

In the case of Bu^t-CHO reaction with sulphinylthioamide (1) resulted in the formation of two diastereoisomers (3a,b) in 66:33 ratio (by ^1H nmr); however flash chromatography lead to the preferential decomposition of the minor product (3b) which was isolated only in trace amounts.

A tentative assignment of anti or syn[11] relative stereochemistry at C_α and C_β rests on the values of the coupling constants $^{3J}H\text{-}C_\alpha\text{-}C_\beta\text{-}H$; for the anti isomers (4a) and (3b) J = 7.15 Hz and J = 6.7 Hz, respectively, for the syn isomers (4b) and (3a), J = 4.0 Hz and 4.1 Hz, respectively. (Similar values, namely J = 7.6 Hz and J = 3.7 Hz were observed[8] for the adduct of a sulphinyl amide with Pr^i-CHO). When PhCHO was condensed with (+)-(R)-(1) a major diastereoisomer (anti) was obtained in 9:1 ratio, with a $^{3J}H\text{-}C_\alpha\text{-}C_\beta\text{-}H$ = 8.5 Hz. Thus PhCHO behaves like Pr^i-CHO, the anti adduct being predominant in both cases. Unfortunately all attempts of reductive desulphurization of (6) resulted in extensive retro aldol-reaction.

Table 1. Enantioselective synthesis of β-hydroxythioacetamides (7)-(10) from enolates of (+)-(R)-(1) and RCHO.

R	Base	Yield[a] (%)	$[\alpha]_D^{25}$ [b]	e.e.[c] (%)	n_D^{20}
Me	Bu^t-MgBr[d,e]	75	+ 87.5	64	1.547
Me	BuLi[f,e]	15	+ 80	59	1.547
Bu^i	Bu^t-MgBr[d,e]	52	+ 41.5	40	-
Pr^i	Bu^t-MgBr[d,e]	75	-105.0	90	1.520
Pr^i	Bu^t-MgBr[g]	67	-100.0	81	1.520
Pr^i	BuLi[f,e]	15	-103.0	88	1.520
Bu^t	Bu^t-MgBr[d,e]	40	- 63.0	55	1.528

[a] Overall yields of (7)-(10) from (+)-(R)-(1).

[b] c 1, $CHCl_3$.

[c] As determined by ^1H NMR spectroscopy with the aid of $Eu(hfc)_3$.

[d] 0.75 Mol. equiv. of base.

[e] Condensation time 60 min, condensation temperature -90°C.

[f] 1.1 Mol. equiv. of base.

[g] 0.5 Mol. equiv. of base; condensation time 60 min, condensation temperature -78°C.

Table 2. Diastereoselective synthesis of adducts (3), (4) and (6) from magnesium enolate of (+)-(R)-(1) and RCHO.[a]

R	Yield (%)	d.r.[b]	$[\alpha]_D^{25}$[c,d]	m.p.[c]
Bu^i	85	66:33[e]	-94.5	130-132
Pr^i	77	95:5	-97.1	138-140
Ph	55	90:10	-71.5	-[f]

[a] 0.75 Mol. equiv. of Bu^{t}MgBr; condensation temperature -90°C; condensation time 60 min.

[b] Diastereoisomeric ratio (d.r.) was established by ^{1}H NMR spectroscopy.

[c] Of the major diastereoisomer.

[d] c 1 in $CHCl_3$.

[e] By ^{1}H NMR.

[f] Waxy solid n_D^{25} 1.595.

EXPERIMENTAL.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP-80 and on a Varian XL-200 instruments, using tetramethylsilane as internal standard and $CDCl_3$ as solvent. Optical rotations were measured on a Perkin Elmer 241 spectrometer. Elemental analyses were performed with a Perkin Elmer 240 instrument. Circular dichroism spectra were obtained with a Jobin-Yvonne Mark III dichrograph. Silica gel was used for analytical and column chromatography. Organic extracts were dried over sodium sulphate and filtered before removal of the solvent under reduced pressure. Anhydrous solvents were distilled under nitrogen atmosphere before use, THF and diethylether from lithium alluminium hydride, methanol from magnesium turnings. All reactions employing anhydrous solvents were run under argon. Aldehydes were commercial products and were distilled before use; (-)-(S) menthyl-p-toluene sulphinate, commercially available from Fluka, had $[\alpha]_D^{25}$ = -202.5 (c = 1, acetone)[3]. N,N-dimethylthioacetamide was prepared following a reported procedure[12] and crystallized from ethyl acetate: petroleum ether 2:1. It had m.p. 73-74°C (lit.[13] m.p. 74°C).

Synthesis of (+)-(R) sulphinylthioacetamide (1).

To a stirred solution of diisopropylamine (2.9 ml, 20 mmol) in THF (50 ml) at 0°C, a 1.35 N solution of n-BuLi in hexane (15 ml) was added. The mixture was stirred at 0°C for 15 min, then cooled at -78°C and N,N-dimethylthioacetamide (20 mmol) in THF (20 ml) was added dropwise. The reaction was warmed up at -40°C, cooled again at -78°C and a solution of

(-)-(S)-menthyl toluene-p-sulphinate (2.94 g, 10 mmol) in THF (20 ml) was added and stirring was continued at -78°C for 15 min. The reaction was quenched with saturated ammonium chloride solution (30 ml) and the organic phase separated. The aqueous phase was extracted twice with dichloromethane (100 ml), and the combined organic phases dried and evaporated in vacuo. The resulting oil was washed with pentane and then with diisopropylether to make it solid. It was crystallized from a mixture ethyl acetate: petroleum ether 2:1, m.p. 96-98°C; yield 60%, $[\alpha]_D^{25}$ = +176.1 (c = 1, $CHCl_3$). Found: C% 54.72; H% 6.28; N% 5.76. $C_{11}H_{15}NOS_2$ requires: C% 54.74; H% 6.26; N% 5.80. ^{1}H NMR: 7.64-7.33 (AA'BB' system, 4H aromatic protons); 4.60-4.06 (AB system, 2H, CH_2-SO); 3.46-3.25 (2s, 6H, $N(CH_3)_2$); 2.43 (s, 3H, $\underline{CH_3}$-Ar).

Synthesis of (7)-(10).

The procedure for (-)-(9) is typical: to a stirred solution of (+)-(R)-(1) (242 mg, 1 mmol) in THF (50 ml) kept at -90°C, a 0.51 N solution of Bu^tMgBr in diethylether (or 1.35 N solution of n-BuLi in hexane) was added (see Table 1 for base:substrate molar ratios). The enolate precipitated and gave a white suspension. After 30 min stirring at -90°C isobutyraldehyde (0.28 ml, 3 mmol) was added at once. After 2h condensation time the reaction was quenched by addition of saturated ammonium chloride solution (5 ml) and the organic phase separated. The aqueous layer was extracted twice with dichloromethane (2x5 ml), the combined organic phase dried and evaporated in vacuo. The crude residue was taken into dry methanol (15 ml) and anhydrous sodium dihydrogen phosphate (1.2 g) was added. To the resulting slurry, cooled at -20°C, 10% sodium amalgam (1.7 g) was added in one portion. The mixture was stirred at -20°C for 2 h, then filtered and added of saturated ammonium chloride solution (5 ml). The organic solvent was evaporated in vacuo and the resulting aqueous phase extracted twice with dichloromethane (20 ml). The organic phase was dried and concentrated to give a crude oil which was purified by flash-chromatography (diethylether or diethylether/hexane as eluant) to give (-)-(9). Compounds (7)-(10) are thick oils.

Compound (7): C% 48.92; H% 8.90; N% 9.49. $C_6H_{13}NOS$ requires: C% 48.94; H% 8.90; N% 9.51. ^{1}H NMR 4.42 (bs, 1H, OH); 4.14 (X part of an ABX system, 1H, CH-O); 3.52-3.32 (2s, 6H, $N(CH_3)_2$); 2.8-2.5 (AB part of an ABX system, 2H, $\underline{CH_2}$-CH); 1.29-1.28 (d, 3H, $\underline{CH_3}$-CH).

Compound (8): C% 57.07; H% 10.10; N% 7.43. $C_9H_{19}NOS$ requires: C% 57.09; H% 10.12; N% 7.39. ^{1}H NMR: 4.3-4.2 (X part of an ABX system, 1H, CH-O); 3.5-3.3 (2s, 6H, $N(CH_3)_2$); 2.7-2.5 (AB part of an ABX system, 2H, CH_2-C=S); 1.95-1.8 (M part of an ABMX system, 1H, $\underline{CH}(CH_3)_2$); 1.6, 1.5-1.25, 1.15 (AB part of an ABMX system, 2H, $\underline{CH_2}$-CH-$(CH_3)_2$; 0.97, 0.96-0.94, 0.93 (dd, 6H, $(\underline{CH_3})_2$-CH).

Compound (9): C% 54.83; H% 9.81; N% 7.95. $C_8H_{17}NOS$ requires: C% 54.82; H% 9.78; N% 7.99. ^{1}H NMR: 4.16 (bs, 1H, OH); 4-3.6 (X part of an ABX system, 1H, CH-O); 3.51-3.33 (2s, 6H, $N(CH_3)_2$); 2.75-2.64 (AB part of an ABX system, 2H, CH_2C=S); 1.83-1.67 (m, 1H, $\underline{CH}(CH_3)_2$); 0.97, 0.96-0.94, 0.93 (dd, 6H, $(\underline{CH_3})_2$-CH).

Compound (10): C% 57.06; H% 10.15; N% 7.39. $C_9H_{19}NOS$ requires: C% 57.09; H% 10.12; N% 7.39. ^{1}H NMR 3.83-3.75 (X part of an ABX system, 1H, CH-O); 3.51-3.33 (2s, 6H, $N(CH_3)_2$); 2.91-2.56 (AB part of an ABX system, 2H, $\underline{CH_2}$-CH); 2.82-2.80 (d, 1H, OH); 1.0 (s, 9H, $(CH_3)_3C$).

Synthesis of intermediates (3), (4) and (6) via magnesium enolates.

The products of condensation between the sulphoxide (+)-(R)-(1) and the aldehydes were obtained as described above. The crude oil was then purified by flash-chromatography (diethyl ether or diethylether/hexane as eluant). The major isomer was obtained pure in each case; physical properties are reported in Table 2. Compounds (3), (4) and (6) are thick oils that become solids when stored in the refrigerator at -20°C.

Compound (3): C% 58.70; H% 7.70; N% 4.25. $C_{16}H_{25}NO_2S_2$ requires: C% 58.68; H% 7.69; N% 4.28. ^{1}H: NMR (for the major product) (3a) 7.3 (AA'BB' system, 4H, aromatic protons); 4.61-4.44 (m, 1H, CH-O); 4.11, 4.06 (d, 1H, CH-SO); 3.18-2.63 (2s, 6H, $(CH_3)_2N$); 2.41 (s, 3H, $\underline{CH_3}$-Ar); 1.6-1.5 (m, 1H, $CH(CH_3)_2$); 1.27-1.24 (m, 2H, $\underline{CH_2}$-$CH(CH_3)_2$); 0.96, 0.95-0.92, 0.91 (2d, 6H, $(\underline{CH_3})_2CH$); $J_{CHOH-CH2}$ = 4.0 Hz. NMR (for the minor product) (4b): 7.3 (AA'BB' system, 4H, aromatic protons); 4.97-4.72 (m, 1H, CH-O); 4.07, 3.97 (d, 1H, CH-SO); 3.13-2.62 (2s, 6H, $(CH_3)_2N$); 2.35 (s, 3H, $\underline{CH_3}$-Ar); 1.9 (m, 1H, $\underline{CH}$-$(CH_3)_2$); 1.27-1.24 (m, 2H, $\underline{CH_2}$-$CH(CH_3)_2$); 0.92, 0.88-0.83, 0.79 (2d, 6H,

$(C_H)_2CH$) $J_{CHOH-CH2}$ = 7.15 Hz. Attempts to separate the diastereoisomers by flash chromatography lead to extensive decomposition of (3b).
Compound (4): C% 57.45; H% 7.42; N% 4.47. $C_{15}H_{23}NO_2S_2$ requires: C% 57.47; H% 7.40; N% 4.47. ^{1}H NMR (for the major product) (4a): 7.3 (AA'BB' system, 4H, aromatic protons); 4.67, 4.63-4.59, 4.55 (dd, 1H, CH-O); 4.22-4.13 (d, 1H, CH-SO); 3.76 (bs 1H, OH); 3.18-2.62 (2s, 6H, $(CH_3)_2N$); 2.18-2.14 (m, 1H, $\underline{CH}(CH_3)_2$); 2.22 (s, 3H, $\underline{CH_3}$-Ar); 1.1, 1.02-0.9, 0.8 (2d, 6H, $(\underline{CH_3})_2CH$); $J_{CHOH-CH2}$ = 6.7 Hz. ^{1}H NMR (for the minor product) (4b): 7.4 (AA'BB' system, 4H, aromatic protons); 4.27, 4.22 (d, 1H, CH-SO); 4.16, 4.11-4.07, 4.02 (dd, 1H, CH-O); 3.18-2.25 (2s, 6H, $(CH_3)_2N$); 2.42 (s, 3H, CH_3-Ar); 1.6-1.5 (m, 1H, $CH(CH_3)_2$); 1.19, 1.02-0.91, 0.83 (2d, 6H, $(CH_3)_2CH$), $J_{CHOH-CH2}$ = 4.1 Hz.
Compound (6): C% 62.20; H% 6.08; N% 4.06. $C_{18}H_{21}NO_2S_2$ requires: C% 62.22; H% 6.09; N% 4.03. ^{1}H NMR (for the major product): 7.7-7.2 (m, 9H, aromatic protons); 6.00, 5.89 (d, 1H, CH-O); 4.4 (bs, 1H, OH); 4.3, 4.2 (d, 1H, CH-SO); 2.9-2.4 (2s, 6H, $(CH_3)_2N$); 2.24 (s, 3H, $\underline{CH_3}$-Ar); $J_{CHOH-CH2}$ = 8.15 Hz. In this case only the major diastereoisomer was obtained pure enough to allow the assignement for all the resonances.

Synthesis of γ-amino-alcohol (11).
To a stirred suspension of $Me_3O^+BF_4^-$ (3.70 mmol, 1.2 equiv.) in methylene chloride (3.7 ml) cooled at 0°C under argon, a solution of (-)-(9) (537.25 mg 3.07 mmol) in methylene chloride (3 ml) was added. The reaction mixture was stirred at 0°C for 5 min, the cooling bath was removed, and stirring was continued for 3 hours. The methylene chloride was removed in vacuo, the residue was dissolved in anhydrous methanol (5 ml) and the resulting solution was cooled at 0°C. Excess $NaBH_4$ (300 mg, 8 mmol) was added in portions over 5 minutes. The reaction mixture was stirred at 0°C for an additional 5 min, the cooling bath was removed and stirring was continued overnight. The organic solvent was then evaporated in vacuo, the residue dissolved in methylene chloride and then filtered to remove the inorganic salts. The solution was treated with 10% aqueous HCl (5 ml), the aqueous layer separated, basified with 10% aqueous NaOH to pH = 10, and extracted with diethylether. The organic solvent was removed under reduced pressure to give compound (11) (65% yield) as a thick oil.
It had n_D^{25} = 1.5420, $[\alpha]_D^{25}$ = +11.77 (c = 0.6 in $CHCl_3$). Found: C% 66.12; H% 13.21; N% 9.65. $C_8H_{19}NO$ requires: C% 66.15; H% 13.19; H% 9.64. ^{1}H NMR: 3.6-3.4 (X part of an ABMX system, 1H, CH-O); 2.7-2.55 (AB part of an ABMX system, 2H, $\underline{CH_2}$-CHOH); 2.45-2.3 (CD part of an ABCD system, 2H, $\underline{CH_2}$-N); 2.24 (s, 6H, $(CH_3)_2$-N); 1.6-1.3 (M part of an ABMX system, 1H, $\underline{CH}(CH_3)_2$); 0.97, 0.96-0.94, 0.93 (dd, 6H, $(\underline{CH_3})_2CH$).

Conversion of hydroxythioacetamide (10) into hydroxyacetamide (12).[15]
To a stirred solution of hydroxythioacetamide (10) (0.61 g, 0.323 mmol) in methylene chloride (5 ml), trimethyloxonium fluoroborate (0.57 g, 0.388 mmol) was added. The solution was allowed to stand at r.t. overnight, then treated with an excess at 50% aqueous NaOH and the stirring was continued for 5 days. The organic layer was separated, washed with water (1x10ml), dried and the solvent evaporated under vacuum. The crude oil was purified by flash-chromatography (diethylether:methanol 95:5 as eluant) to give (12) in 20% yield. $[\alpha]_D^{23}$ = -42 (c 1, $CHCl_3$), lit.[8] $[\alpha]_D^{23}$ = -70.9 (c 1, $CHCl_3$) for a 90% enantiomerically enriched compound. The product had physical and spectral data in agreement with those reported in literature.[8]

Enantiomeric excess determination.
The enantiomeric purities of compounds (1) and (7)-(10) were checked by ^{1}H NMR spectroscopy with the aid of the chiral shift reagent Eu(hfc)$_3$ in conditions pre-established with their racemic counterparts, which were prepared by condensation of the lithium enolate of N,N-dimethylthioacetamide with the appropriate aldehyde at -40°C. A 5:1 substrate: shift reagent molar ratio generally gave satisfactory peak-separation. A good agreement between the optical rotation values and the e.e. evaluated by ^{1}H NMR was observed for (7)-(10).

Circular dichroism measurements.
Circular dichroism measurements were carried on in $CHCl_3$, c=10^{-3} mol/l Compound (+)(7) and (+)(8) had two positive Cotton effect (C.e.) centered at λ_{max} 340 nm and λ_{max} 270 nm..

Compound (-) (9) had a positive C.e. centered at λ_{max} 365 nm, and two negative C.e. centered at λ_{max} 335 nm and λ_{max} 270 nm. Compound (-) (10) had a positive C.e. centered at λ_{max} 360 nm, and two negative C.e. centered at λ_{max} 330 nm and λ_{max} 270 nm.

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