Pergamon

Tetrahedron, Vol. 53, No. 51, pp. 17253-17264, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10178-8

Stereocontrolled Thio-Claisen Rearrangement of S-Allylic Ketene Aminothioacetals by an Hydroxysubstituted Adjacent Stereogenic Centre.

Pierre Beslin# * and Bruno Lelong

Laboratoire de Chimie Moléculaire et Thio-organique(UMR 6507),
ISMRA, Université de CAEN, 6, Boulevard du Maréchal Juin, 14050 Caen, France.

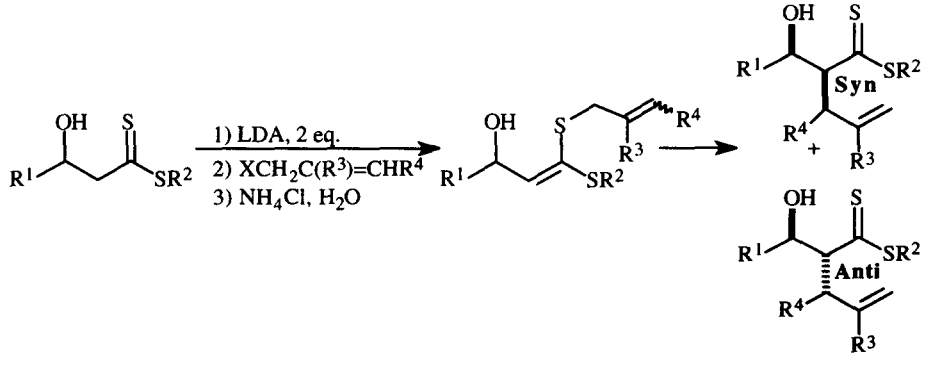
Abstract: *(Z)-S-allylic ketene aminothioacetals were prepared from N,N-Dimethyl β-hydroxythioamides 2-8 by deprotonation with LDA (2 eq.) at -78°C followed by S-alkylation with allylic bromide. Rearrangement of these compounds occured easily at room temperature affording major syn N,N-dimethyl β-hydroxy α-allylic thioamides 9-21 with a syn/anti ratio of 80/20 to 98/2. The syn configuration of the major diastereoisomer was confirmed by an univocal synthesis of syn thioamides 9 and 11. The structure assignments were confirmed by empirical ^{13}C NMR rules. The observed induction is well supported by a proposed transition state model.* © 1997 Elsevier Science Ltd.

Introduction

Claisen rearrangement [1] and its variant, Ireland-Claisen rearrangement [2] have been widely used for controlling the stereochemistry of new formed stereogenic centres. The high stereochemistry control of this reaction is a consequence of a high ordered transition state: a cyclic chair like transition state [3] with the ensued stereospecificity and 1,3 or 1,4-asymmetric inductions as it has been reported.[4]

External induction by a stereogenic centre appended to the hetero-1,5-hexadienic framework has been also exemplified and has allowed an efficient stereochemistry control over two and even three contiguous stereogenic centres.[5-7]

Recently, in our group, [8] we showed that thio-Claisen rearrangement performed with S-allylic ketene dithioacetals derived from β-hydroxydithioesters occured more easily than with oxygen analogues. A major α,β-syn diastereoisomer is always formed independently of the ketene double bond geometry (scheme 1). It is an unprecedented result.

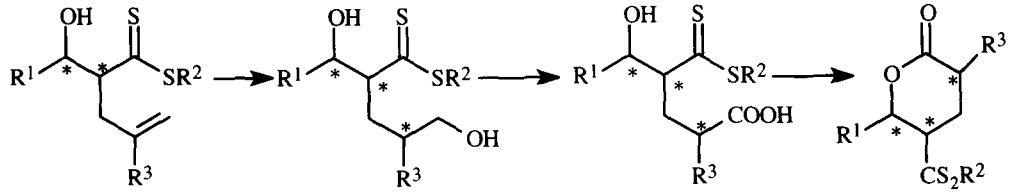


Scheme 1

e-mail: beslin@ismra.unicaen.fr ; fax number: 02-31-45-28-77

A similar result has been pointed out recently in sulfur chemistry by using a sulfinyl group instead of the hydroxysubstituted stereogenic centre.[9] Excellent diastereoisomeric excess in favour of syn diastereoisomer were then observed.

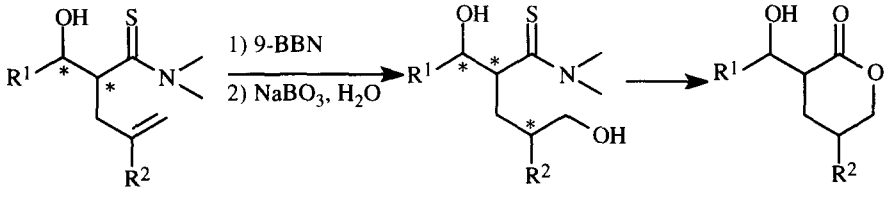
Following this result, we envisionned the conversion of the terminal double bond of the rearranged products into a terminal alcohol or acid in the aim to obtain a ring by lactonization with the secondary alcohol, opening thus the way to natural lactones such as invictolide [10] (scheme 2).



Scheme 2

Such a conversion may start with the hydroboration of the terminal double bond without alteration of the sulfur functionality and needs a high level of diastereoselectivity in the case of $R^3 \neq H$. The required diastereoselection may come from a chelating effect of the hydroborating reagent eventually by the hydroxyl group or the sulfur function or a steric effect as it has been reported by Evans. [11] It appeared after carefull examination in the literature that dithioester function may be reduced by BH_3,Me_2S only at high temperature.[12] As hydroboration reaction is usually done at low temperature, we then tested an hydroboration model reaction on a methyl 4-pentenedithioate and observed that even at low temperature the reaction was not chemoselective. A mixture of several products were formed (thiols and dithioesters and hemithiocetals).

We turned then, our attention, to the same reaction with the similar unsaturated backbone bearing a N,N-dimethylthioamide instead of a dithioester function. It is known that such thioamides are not reduced by an hydroborating agent as 9-BBN [13a,b] (Scheme 3).

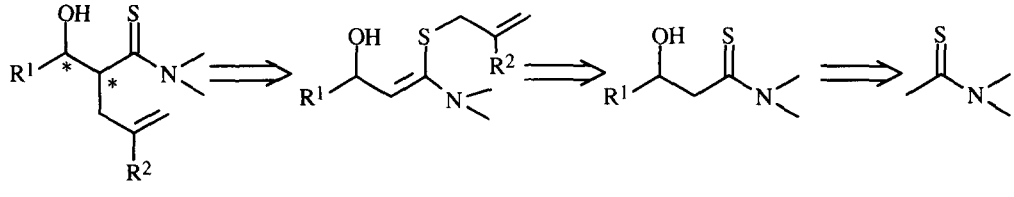


Scheme 3

RESULTS

In this paper we report the synthesis of the required β-hydroxy δ-unsaturated N,N-dimethylthioamides which will allow us in a next study to carry out successfully our initial goal.

According to the retrosynthetic scheme (scheme 4), the requisite unsaturated thioamides may be prepared by a thio-Claisen rearrangement of S-allylic ketene aminothioacetals, derived from β-hydroxythioamides, themselves availaible by an aldol reaction of N,N-dimethyl thioacetamide with appropriate aldehydes.



Scheme 4

Aldol reaction with thioamides have been already described by several groups who have studied the diastereoselectivity and the enantioselectivity of this reaction.[14]

The required β-hydroxy-N,N-dimethylthioamides **2-8** were easily prepared according to a known procedure [14] from N,N-dimethylthioamide **1** and various aldehydes. One of them bears a stereogenic centre α to the carbonyl function. In this particular case a 80/20 ratio of syn/anti diastereoisomer was formed and isolated as a partially separable mixture [15] (see table 1).

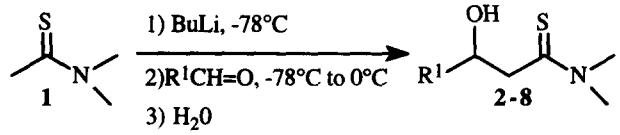


Table 1: Aldol synthesis

Entry	R^1	Yield*	Aldol
1	CH_3 **	83%	**2**
2	CH_3CH_2	70%	**3**
3	$(CH_3)_2CH$ **	81%	**4**
4	$(CH_3)_3C$ **	75%	**5**
5	C_6H_5 ***	85%	**6**
6	$C_6H_5CH_2$	70%	**7**
7	$C_6H_5CH(CH_3)$	90%	**8a-b** Syn / anti : 80 / 20

*yield: after purification by chromatography
**briefly described by Cinquini and coworkers.[16]
***briefly described by Goasdoué and coworkers.[14]

These β-hydroxy-N,N-dimethylthioamides were then better deprotonated with two equivalents of LDA at -40°C to form a chelated dianion of Z configuration. Alkylation of these dianions by allylic halides occured exclusively as expected[17] on the sulfur site to give the corresponding Z α-hydroxy S-allylic ketene dimethylamino thioacetals (the N,N-dimethyl ^1H NMR signal appears as a single singlet at 2.7 and only one).

Such S-allylic ketene aminothioacetals are prone to rearrange by a [3,3] sigmatropic shift into δ-unsaturated thioamides.[5a,13] Nevertheless asymmetric induction by an external asymmetric centre has never been reported with such S-allylic ketene dimethylamino thioacetals formed from thioamides.

Indeed, this rearrangement of the formed α-hydroxy S-allylic ketene aminothioacetal underwent at room temperature in 12 to 72 hours. In every case the major diastereoisomer is detected in a 80/20 to 98/2 ratio (see table 2). The diastereoisomeric ratio was determined by ^{13}C and ^1H NMR (integration measurement of N-dimethyl shifts for example).

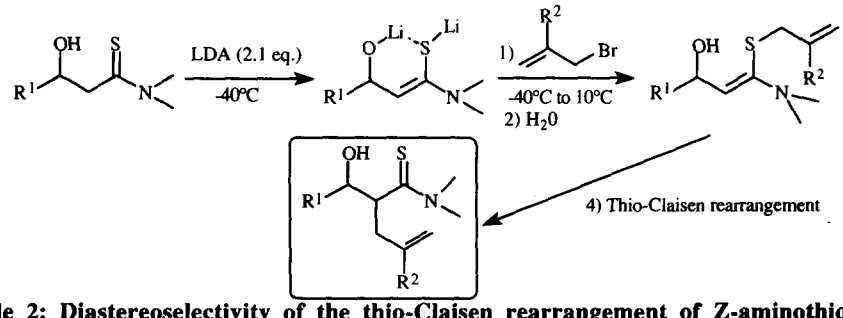


Table 2: Diastereoselectivity of the thio-Claisen rearrangement of Z-aminothiocetals

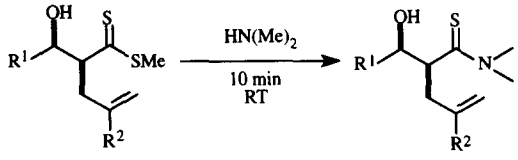
Entry	R^1	R^2	Yield*	Syn / Anti** Ratio	Thioamide
1	CH_3	H	55%	80 / 20	**9**
2	CH_3CH_2	H	70%	85 / 15	**10**
3	$(CH_3)_2CH$	H	61%	93 / 7	**11**
4	$(CH_3)_3C$	H	30%	>98 / 2	**12**
5	C_6H_5	H	40%	80 / 20	**13**
6	$C_6H_5CH_2$	H	75%	90 / 10	**14**
7	$C_6H_5CH(CH_3)$ syn **8a**	H	31%	>95 / 5	**15**
7'	$C_6H_5CH(CH_3)$ anti **8b**	H	31%	>95 / 5	**15**
8	CH_3	CH_3	52%	80 / 20	**16**
9	CH_3CH_2	CH_3	60%	85 / 15	**17**
10	$(CH_3)_2CH$	CH_3	56%	85 / 15	**18**
11	$(CH_3)_3C$	CH_3	56%	>98 / 2	**19**
13	$C_6H_5CH_2$	CH_3	55%	95 / 5	**20**
14	$C_6H_5CH(CH_3)$ syn**8a**	CH_3	45%	>95 / 5	**21**

(*yield: after purification ; **Syn/Anti Ratio was determined by ^1H and ^{13}C NMR)

As shown in the table, the diastereoisomeric excess increases with the steric hindrance (see entries 1-4 and 8-11). When R^1= benzyl, an improvement of the diastereoselectivity (entries 6, 7, 13 and 14) is evidenced, a possible π-stacking [18] effect may account for this increase.

Configuration determination of the major diastereoisomer which may exist as a syn or anti diastereoisomer was clearly assigned by chemical correlation.

A known syn β-hydroxy-δ-unsaturated dithioester (R^1 = CH_3 or iPr) prepared according to our precedent works [8a] was converted into the corresponding syn N,N-dimethylthioamide by a non epimerizating aminolysis reaction with N,N-dimethylamine (scheme 5). ^1H and ^{13}C NMR spectra of these thioamides were identical to those of the major thioamides **9** and **11** formed by thio-Claisen rearrangement.



Scheme 5

This assignment of syn configuration to the major rearranged thioamides **9** and **11** was extented to the thioamides **10** and **12-21**. It was confirmed by carefull examination of ^{13}C NMR spectra of each diastereoisomer. Some empirical rules concerning the ^{13}C NMR chemical shift values may be setted up (see table 3). These rules are slightly different from those reported for esters and dithioesters analogues. [8a,19]. Moreover the Anti minor configuration has been confirmed: the thioamide **10b Anti** has been cyclized into a trans-β-lactone whose coupling constant J $H_{C2}H_{C3}$ is 4 Hz (a trans coupling constant). This result will be described in a next publication.

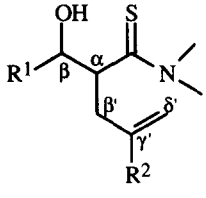
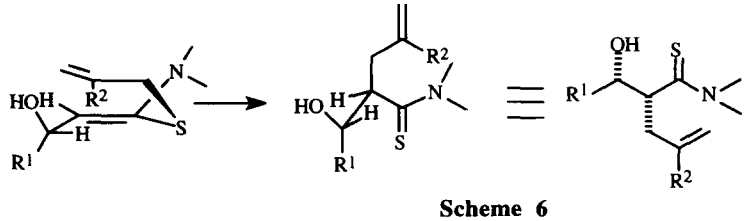


Table 3: Chemical shift rules

N°	Chemical Shift
1	δ(Cβ' syn) < δ(Cβ' anti)
2	δ(Cγ' syn) > δ(Cγ' anti)
3	δ(Cδ' syn) < δ(Cδ' anti)
4	δ(Cβ syn) < δ(Cβ anti)
5	δ(Cα syn) < δ(Cα anti)

Formation of a major syn diastereoisomer may be interpretated, with the model we proposed in our previous studies of the same rearrangement of S-allylic ketene dithioacetals issued from β-hydroxydithioesters. In the pseudo cyclic transition state, the external stereogenic centre adopts a conformation similar to that of the Houk model [20] and confirmed by Kahn and Hehre [21]: H lies in inside position, R^1 in outside position and the OH perpendicular to the ketene plan. The formation of C-C bond occurs on the more electronic rich face of the ketene (considered as the nucleophile) that is syn to the hydroxy group (see model below).



Scheme 6

From this model based on electronic effect, the formation of syn diastereoisomer is favoured. As the size of R^1 group increases, the steric effect may amplify this trend (see entries 1-4 and 8-11 of the table). If R^1= $PhCH_2$ or PhCH-Me, the formation of the syn diastereoisomer is favoured because of a possible π-stacking interaction.The phenyl ring lies underneath the ketene plan and then prevents a bottom side C-C bond formation (see entries 6, 7, 13 and 14).

CONCLUSION :

Various S-allylic ketene aminothioacetals prepared as single Z-diastereoisomers from thioamides(**2** - **$8_{a,b}$**) rearranged easily at room temperature, involving a sigmatropic-[3,3]-pathway, into a major syn β-hydroxy δ-unsaturated thioamides (**9-21**). The *external stereocontrol* is governed by stereoelectronic effects with, in some instance, an additional steric effect and consequently an enhanced diastereoselectivity.

Some works are in progress to perform the same rearrangement starting from enantiopure β-hydroxythioamides easily available.[16] Transformation of the terminal double bond bearing a prostereogenic

centre into a terminal alcohol is now under way. In addition we have already obtained, as in scheme 3, a separable 80/20 mixture of the diastereoisomeric corresponding diols from thioamides **10a and 10b**. The structure determination of the major diasteroisomer is under progress. Corresponding δ-lactone has been then formed by action of methyl iodide and hydrolysis. These last results will be reported in a next publication.

EXPERIMENTAL SECTION

General

All reactions were run under a positive nitrogen pressure. THF was distilled over sodium benzophenone ketyl. The chromatography columns were prepared with a suspension of silica gel 60 Merck in the eluting solvent: a mixture of petroleum ether and ethyl acetate in the ratio indicated. ^1H NMR 250 MHz and ^{13}C NMR 62.5 MHz spectra were run on a BRUCKER AC 250. The products were dissolved in $CDCl_3$ + TMS. Reported data are quoted in order: chemical shift in ppm, multiplicity (s, singulet ; d, doublet ; t, triplet ; q, quartet ; m, multiplet), coupling constant, number of H, assignment. IR absorbtion spectra were run on a PERKIN ELMER PC FT-IR instrument. Mass spectra were obtained at 70 eV with a NERMAG R10 RH spectrometer and the data tabulated as m/e and relative intensities. Elemental analyses were performed by "Service Central d'Analyse of CNRS" at Vernaison. The results are described as percentage.

General Procedure for Aldol Reaction between N,N-dimethylthioacetamide and Aldehydes.

To a solution of N,N-dimethylthioacetamide (10 mmol) in THF (50 ml), under nitrogen was added dropwise at -78°C a solution of n-butyllithium in THF (6,6 ml of a 1,6 M solution). After stiring for 1 h., the corresponding aldehyde (10,5 mmol) was added at -78°C. Then the temperature was risen up at 10°C in 1.5 h. The mixture was then quenched with water and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, filtrated and concentrated *in vacuo*.The products were purified by chromatography on silicagel.

N,N-dimethyl-3-hydroxybutanethioamide 2

From the reaction between N,N-dimethylthioacetamide and ethanal. Purification by chromatography (petroleum ether / ethyl acetate: 40 / 60) gives a yellow powder in 83 % yield. m.p.= 41°C.

δ_H 1.28 (d, 6.4 Hz, 3 H, C**H3**), 2.52-2.75 (m, 2 H, C**H2**C=S), 3.32 (s, 3H, NC**H3**), 3.51 (s, 3H, NC**H3**), 4.3-4.4 (m, 1H, C**H**OH), 4.42 (s, 1H, O**H**); δ_C 22.3 (**C**H3), 41.7 and 44.4 (N**C**H3), 49.6 (**C**H2C=S), 65.6 (**C**HOH), 201.5 (C=S); IR (KBr) (cm^{-1}): 3350 (ν O-H), 2966, 2928, 2892 (ν C-H), 1140 (ν C-O), 1398 (δ O-H); M/e % : **147** (100), M^+; 132 (17), $(M^+ - CH_3)^+$; 114 (71), $CH{=}CHC{=}SN(CH_3)_2^+$; 103 (48), $CH_3CH(OH)C{=}S^+$; 88 (65), $C{=}SN(CH_3)_2^+$; 70 (95), $CH{=}CHC{=}S$; 57 (46), $CH_3C{=}OCH_2^+$; 45 (65), $CH_3CH(OH)^+$; 44 (71), $N(CH_3)_2^+$; 43 (33), $CH_3C{=}O^+$; 41 (25), $CH_3CH{=}CH^+$.

Anal.: Calcd. for $C_6H_{13}NOS$: C, 48.95; H, 8.90; N, 9.51; S, 21.77. Found: C, 48.92; H, 9.16; N, 9.21; S, 21.93.

N,N-dimethyl-3-hydroxypentanethioamide 3

From the reaction between N,N-dimethylthioacetamide and propanal. Purification by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a yellow oil in 70 % yield.

δ_H 1.01 (t, 7.6 Hz, 3H, C**H3**), 1.44-1.72 (m, 2H, CH3-C**H2**), 2.54-2.78 (m, 2H, C**H2**C=S), 3.32 (s, 3H, NC**H3**), 3.51 (s, 3H, NC**H3**), 4.06-4.16 (m, 1H, C**H**OH), 4.25 (d, 2.74 Hz, 1H, O**H**); δ_C 10.2 (**C**H3), 29.4 (CH_3**C**H_2), 41.7 and 44.4 (N**C**H3), 48.0 (**C**H2C=S), 70.9 (**C**HOH), 201.7 (C=S); IR (NaCl) (cm^{-1}): 3404 ($_\nu$O-H), 2962, 2932, 2878 (ν C-H), 1110 (νC-O), 1394 (δ O-H); M/e %: **161** (100), M^+; 103 (8), $CH_3C{=}SN(CH_3)_2^+$; 72 (10), $CH_3CH_2CH(OH)CH_2^+$; 70 (29), $CH{=}CHC{=}S^+$; 55 (16), $CH{=}CHCH_2CH_3^+$; 44 (30), $N(CH_3)_2^+$.

Anal.: Calcd. for $C_7H_{15}NOS$: C, 52.14; H, 9.38; N, 8.69; S, 19.88. Found: C, 52.32; H, 9.51; N, 8.67; S, 19.99.

N,N-dimethyl-3-hydroxy-4-methyl-pentanethioamide 4

From the reaction between N,N-dimethylthioacetamide and 2-methylpropanal. Purication by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a yellow oil in 81 % yield.

δ_H 0.98 (d, 6.71 Hz, 3H, C**H3**CH), 1.00 (d, 6.71 Hz, 3H, C**H3**CH), 1.79 (oct, 6.71 Hz, 1H, $(CH_3)_2$**CH**), 2.58-2.81 (m, 2H, C**H2**C=S), 3.33 (s, 3H, NC**H3**), 3.51 (s, 3H, NC**H3**), 3.91-3.99 (m, 1H, C**H**OH), 4.09 (d, 2,75 Hz, 1H, O**H**); δ_C 18.0 and 18.7 (**C**H3), 33.4 ($(CH_3)_2$**C**H), 41.8 and 44.6 (N**C**H3), 45.6 (**C**H2C=S), 74.3 (**C**HOH), 202.2 (C=S); IR (NaCl) (cm^{-1}): 3408 (ν O-H), 2958, 2934, 2874 (νC-H), 1116 (νC-O), 1394 (δO-H); M/e %: **175** (100), M^+; 161 (6), $(CH_3)_2CH\text{-}CH(OH)CH_2C{=}SNCH_3^+$; 157 (16), $(CH_3)_2CHCH{=}CH_2C{=}SNCH_3^+$; 70 (29), $CH{=}CHC{=}S^+$; 44 (4), $N(CH_3)_2^+$; 43 (5), $(CH_3)_2CH^+$.

Anal.: calcd. for $C_8H_{17}NOS$: C, 54.82; H, 9.78; N, 7.99; S, 18.29. Found: C, 54.62; H, 9.90; N, 7.56; S, 17.63.

N,N-dimethyl-3-hydroxy-4,4-dimethyl-pentanethioamide 5

From the reaction between N,N-dimethylthioacetamide and 2, 2-dimethylpropanal. Purification by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a pale yellow oil in 75 % yield.

δ_H 0.97 (s, 9H, CH_3), 2.58-2.68 and 2.84-2.9 (m, 2H, CH_2C=S), 3.33 (s, 3H, NCH3), 3.52 (s, 3H, NCH3), 3.77-3.83 (m, 1H, CHOH), 3.94 (d, 2.74 Hz, 1H, OH); δ_C 26 [($\underline{C}H_3)_3C$], 34.7 [$(CH_3)_3\underline{C}$)], 41.9 and 44.7 (N$\underline{C}H_3$), 43.8 ($\underline{C}H_2$C=S), 77.2 ($\underline{C}$HOH), 202.5 (C=S); IR (NaCl) (cm^{-1}): 3406 (ν O-H), 2956, 2906, 2870 (ν C-H), 1118 (ν C-O), 1396 (δ O-H); M/e %: **189** (34), M^+; 132 (22), CH(OH)CH_2-C=SN$(CH_3)_2^+$; 88 (71), C=SN$(CH_3)_2^+$; 71 (49), CH_2=CHC=S^+; 70 (92), CH=CHC=S^+; 58 (56), $CH_2C=S^+$; 57 (99), $(CH_3)_3C^+$; 44 (84), N$(CH_3)_2^+$; **41** (100), $CH_3C=CH_2^+$.

Anal.: calcd. for $C_9H_{19}NOS$: C, 57.10; H, 10.12; N, 7.40; S, 16.93. Found: C, 56.99; H, 10.18; N, 7.18; S, 16.87.

N,N-dimethyl-3-hydroxy-3-phenylpropanethioamide 6

From the reaction between N,N-dimethylthioacetamide and benzaldehyde. Purification by recristallisation (ethyl ether / petroleum ether) gives white cristals in 85% yield. m.p. = 60°C.

δ_H 2.92 (d, 6.1 Hz, 2H, CH_2C=S), 3.22 (s, 3H, NCH3), 3.52 (s, 3H, NCH3), 4.78 (d, 3,1 Hz, 1H,OH), 5.3 (dt, 6.1 Hz and 3.1 HZ, 1H, CHOH), 7.26-7.44 (m, 5H, H aromat.); δ_C 41.8 and 44.5 (N$\underline{C}H_3$), 50.7 ($\underline{C}H_2$C=S), 72.0 ($\underline{C}$HOH), 126.0, 127.7 and 128.6 (o., m., p. aromat. $\underline{C}$), 143.1 (quatern. aromat. $\underline{C}$), 200.7 (C=S); IR (NaCl) (cm^{-1}): 3286 (ν O-H), 3026(ν C-H aromat.), 2932, 2868 (ν C-H), 1528 (ν C=C aromat.), 1116 (ν C-O), 1396 (δ O-H); M/e %: **209** (10), M^+; 105 (50), $C_6H_5C=O^+$; 88 (59), C=SN$(CH_3)_2^+$; 77 (88), $C_6H_5^+$; 70 (83), CH=CHC=S^+; **44** (100), N$(CH_3)_2^+$.

Anal.: calcd. for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69; S, 15.32. Found : C, 63.36; H, 7.27; N, 6.86; S, 15.48.

N,N-dimethyl-3-hydroxy-4-phenylbutanethioamide 7

From the reaction between N,N-dimethylthioacetamide and phenylethanal. Purification by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a pale yellow oil in 70 % yield.

δ_H 2.54-3.06 (m, 4H, Ph-CH_2 and CH_2C=S), 3.17 (s, 3H, NCH3), 3.46 (s, 3H, NCH3), 4.38 (d, 3,3 Hz, 1H, OH), 4.4-4.47 (m, 1H, CHOH), 7.19-7.33 (m, 5H, H aromat.); δ_C 41.7 and 44.4 (N$\underline{C}H_3$), 42.8 (Ph-$\underline{C}H_2$), 47.3 ($\underline{C}H_2$C=S), 70.9 ($\underline{C}$HOH), 126.6, 128.6 and 129.5 (o., m., p. aromat. $\underline{C}$), 138.3 (quatern. aromat. $\underline{C}$), 201.3 (C=S); IR (NaCl) (cm^{-1}): 3386 (ν O-H), 3060, 3026, 3000(ν C-H aromat.), 2932, (ν C-H), 1602, 1522 (ν C=C aromat.), 1120 (ν C-O), 1394 (δ O-H); M/e %: **223** (8), M^+; 205 (17), $C_6H_5CH_2CH=CH_2C=SN(CH_3)_2^+$; **187** (100); 157 (52,8); 103 (8,6), $C_6H_5CH=CH^+$; 91 (5), $C_6H_5CH_2^+$; 88 (5), C=SN$(CH_3)_2^+$; 45 (8).

Anal.: calcd. for $C_{12}H_{17}NOS$: C, 64.54; H, 7.67; N, 6.27; S, 14.36. Found: C, 63.25 ; H, 7.42; N, 6.81; S, 14.31.

N,N-dimethyl-3-hydroxy-4-phenylpentanethioamide 8

From the reaction between N,N-dimethylthioacetamide and 2-Phenyl-2-methylethanal. Separation by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a colorless oil in 90 % yield. Syn / Anti ratio 80 / 20.

syn isomer 8a: δ_H 1.42 (d, 6,9 Hz, 3H, CH3), 2.41-2.61 (m, 2H, CH_2C=S), 2.78-2.89 (m, 1H, $CHCH_3$), 3.00 (s, 3H, NCH3), 3.43 (s, 3H, NCH3), 4.14-4.2 (m, 1H, CHOH), 4.53 (d, 3,1 Hz, 1H, OH), 7.2-7.33 (m, 5H, H aromat.); δ_C 18.5 ($\underline{C}H_3$), 41.5 and 44.4 (N$\underline{C}H_3$), 46 ($\underline{C}HCH_3$), 46.5 ($\underline{C}H_2$C=S), 74.3 ($\underline{C}$HOH), 126.6, 127.9 and 128.7 (o.,m.,p. aromat. $\underline{C}$), 144.5 (quatern. aromat. $\underline{C}$), 201.6 (C=S).

anti isomer 8b: δ_H 1.38 (d, 7.2 Hz, 3H, CH3), 2.41-2.7 (m, 2H, CH_2C=S), 2.78-2.89 (m, 1H, $CHCH_3$), 3.11 (s, 3H, NCH3), 3.45 (s, 3H, NCH3), 3,99 (d, 2,2 Hz, 1H, OH), 4.28-4.36 (m, 1H, CHOH), 7.2-7.33 (m, 5H, H aromat.); δ_C 16.6 ($\underline{C}H_3$), 41.7 and 44.6 (N$\underline{C}H_3$), 45 ($\underline{C}HCH_3$), 45.6 ($\underline{C}H_2$C=S), 74.1 ($\underline{C}$HOH), 126.7, 128.4 and 128.5 (o., m., p. aromat. $\underline{C}$), 143.3 (quatern. aromat. $\underline{C}$), 201.6 (C=S).

IR (NaCl)(cm^{-1}): 3338 (ν O-H), 3082, 3056, 3026 (ν C-H aromat.), 2964, 2930, 2094 (ν C-H), 1600, 1494 (ν C=C aromat.), 1126 (ν C-O), 1394 (δ O-H); M/e %: **237** (11), M^+; **219** (100), $C_6H_5CH(CH_3)$-$CH=CH_2C=SN(CH_3)_2^+$; 214 (67); 186 (47); 88 (4), C=SN$(CH_3)_2^+$; 41 (5).

Anal.: calcd. for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.9; S, 13.51. Found: C, 65.87; H, 8.19; N, 5.9; S, 13.68.

General procedure for the Thio-Claisen rearrangement

To a solution of LDA (2,1 eq.) in 20 ml of dry THF under nitrogen was added dropwise at -50°C the corresponding β-hydroxythioamide (1 mmol). After stirring the solution between -40°C and -60°C for one hour, the corresponding allyl bromide (1,05 eq.) was added at -50°C. And the temperature was risen up slowly at 10°C. The mixture was then quenched with water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$ and left at room temperature for 12 to 24 h. After filtration and concentration in vacuo the products were purified by chromatography on silicagel.

N,N-dimethyl-2-(1-hydroxyethyl)-4-pentenethioamide 9

From the reaction between aldol **2** and allyl bromide. Separation by chromatography (petroleum ether / ethyl acetate: 40 / 60) gives a yellow oil in 55% yield. Syn / Anti ratio 80 / 20.

syn isomer 9a: δ_H 1.21 (d, 6,4 Hz, 3H, C**H3**), 2.49-2.77 (m, 2H, C**H2**CH=CH_2), 3.02-3.09 (m, 1H, C**H**C=S), 3.32 (s, 3H, NC**H3**), 3.48 (s, 3H, NC**H3**), 3.93-4.03 (m, 1H, C**H**OH), 4.35 (s, 1H, O**H**), 4.94-5.13 (m, 2H, CH=C**H2**), 5.61-5.78 (m, 1H, C**H**=CH_2); δ_C 21.4 (CH3), 34.1 (**C**H_2CH=CH_2), 42.3 and 44.6 (NCH_3), 53.4 (**C**HC=S), 69.1 (**C**HOH), 117.3 (CH=**C**H_2), 136.0 (**C**H=CH_2), 207.1 (C=S).

anti isomer 9b: δ_H 1.17 (d, 6.11 Hz, 3H, C**H3**), 2.35-2.64 (m, 2H, C**H2**CH=CH_2), 3-3.08 (m, 1H, C**H**C=S), 3.29 (s, 3H, NC**H3**), 3.46 (s, 3H, NC**H3**), 3.89-4.04 (m, 1H, C**H**OH), 3.92 (s, 1H, O**H**), 4.9-5.09 (m, 2H, CH=C**H2**), 5.58-5.74 (m, 1H, C**H**=CH_2); δ_C 21.2 (CH3), 38.1 (**C**H_2CH=CH_2), 42.3 and 44.7 (N**C**H_3), 54.6 (**C**HC=S), 70.0 (**C**HOH), 117.5 (CH=**C**H_2), 135.2 (**C**H=CH_2), 205.3 (C=S).

IR (NaCl) (cm^{-1}): 3384 (ν O-H), 3076 (ν C-H ethylen.), 2972, 2930 (ν C-H), 1640 (ν C=C), 1124 (ν C-O), 1394 (δ O-H); M/e %: **187** (2), M^+; 173 (11); 142 (17), CH_2=CHCHC=SN$(CH_3)_2^+$; 97 (50), CH_2=CHC=C=S^+; 88 (94), C=SN$(CH_3)_2^+$; **45** (100), CH_3CHOH^+; 44 (70), N$(CH_3)_2^+$; 43 (87), CH_3C=O.

Anal.: calcd. for $C_9H_{17}NOS$: C, 57.71; H, 9.15; N, 7.48; S, 17.12. Found: C, 56.49; H, 9.06; N, 7.29; S, 17.36.

N,N-dimethyl-2-(1-hydroxypropyl)-4-pentenethioamide 10

From the reaction between aldol **3** and allyl bromide. Separation by recristallisation (ethyl ether / petroleum ether) gives a white solid in 70% yield. Syn / Anti ratio 85 / 15.

syn isomer 10a: δ_H 0.99 (t, 7.4 Hz, 3H, C**H3**), 1.41-1.68 (m, 2H, CH_3C**H2**), 2.47-2.57 and 2.7-2.8 (m, 2H, C**H2**CH=CH_2), 2.95-3.19 (m, 1H, C**H**C=S), 3.34 (s, 3H, NC**H3**), 3.51 (s, 3H, NC**H3**), 3.66-3.71 (m, 1H, C**H**OH), 4.42 (s, 1H, O**H**), 4.98 (dd, 10.1 Hz and 1.5 Hz, 1H, CH=C**H**cisH), 5.1 (dd, 17.1 Hz and 1.5 Hz, 1H, CH=C**H**transH), 5.63-5.79 (m, 1H, C**H**=CH_2); δ_C 10.8 (CH_3), 28 (CH_3**C**H_2), 34.2 (**C**H_2CH=CH_2), 42.2 and 44.7 (N**C**H_3), 51.8 (**C**HC=S), 74.7 (**C**HOH), 117.2 (CH=**C**H_2), 136.1 (**C**H=CH_2), 205.3 (C=S).

anti isomer 10b: δ_H 1.00 (t, 7.3 Hz, 3H, C**H3**), 1.40-1.68 (m, 2H, CH_3C**H2**), 2.49-2.82 (m, 2H, C**H2**CH=CH_2), 3.12-3.21 (m, 1H, C**H**C=S), 3.35 (s, 3H, NC**H3**), 3.51 (s, 3H, NC**H3**), 3.66-3.76 (m, 1H, C**H**OH), 4.0 (d, 14.3 Hz, 1H, O**H**), 4.95-5.16 (m, 2H, CH=C**H2**), 5.63-5.81 (m, 1H, C**H**=CH_2); δ_C 10.7 (CH_3), 28.2 (CH_3**C**H_2), 38.2 (**C**H_2CH=CH_2), 42.1 and 44.5 (N**C**H_3), 52.7 (**C**HC=S), 75.0 (**C**HOH), 117.5 (CH=**C**H_2), 135.3 (**C**H=CH_2), 206.1 (C=S) .

IR (NaCl) (cm^{-1}): 3384 (ν O-H), 3076 (ν C-H ethylen.), 2962, 2934, 2876 (ν C-H), 1640 (ν C=C), 1124 (ν C-O), 1394 (δ O-H); M/e %: **201** (3), M^+; 186 (95), $(M^+ - CH_3)^+$; 142 (32), CH_2=CHCHC=SN$(CH_3)_2^+$; 97 (32), CH_2=CHC=C=S^+; 88 (65), C=SN$(CH_3)_2^+$; **44** (100), N$(CH_3)_2^+$.

Anal.: calcd for $C_{10}H_{19}NOS$: C, 59.66; H, 9.51; N, 6.96; S, 15.92. Found: C, 59.67; H, 9.49; N, 7.18; S, 15.82.

N,N-dimethyl-2-(1-hydroxy-2-methylpropyl)-4-pentenethioamide 11

From the reaction between aldol **4** and allyl bromide. Separation by chromatography (petroleum ether / ethyl acetate: 80 / 20) gives a yellow oil in 61% yield. Syn / Anti ratio 93 / 7.

syn isomer 11a: δ_H 0.94 (d, 6.7 Hz, 3H, C**H3**CH), 1.02 (d, 6.7 Hz, 3H, C**H3**CH), 1.83 (oct, 6.7 Hz, 1H, $(CH_3)_2$C**H**), 2.42-2.52 and 2.7-2.86 (m, 2H, C**H2**CH=CH_2), 3.31-3.41 (m, 2H, C**H**C=S and C**H**OH), 3.35 (s, 3H, NC**H3**), 3.52 (s, 3H, NC**H3**), 4.47 (d, 1.5 Hz, 1H, O**H**), 4.98 (dd, 10.1 Hz and 1.6 Hz, 1H, CH=C**H**cisH), 5.1 (dd, 17.1 Hz and 1.6 Hz, 1H, CH=C**H**transH), 5.6-5.8 (m, 1H, C**H**=CH_2); δ_C 19.3 and 19.5 (**C**H_3CH), 31.1 (CH_3**C**H), 34.2 (**C**H_2CH=CH_2), 42.1 and 44.8 (N**C**H_3), 49.2 (**C**HC=S), 78.4 (**C**HOH), 117.1 (CH=**C**H_2), 136.2 (**C**H=CH_2), 207.3 (C=S).

anti isomer 11b: δ_H 0.91 (d, 6.7 Hz, 3H, C**H3**CH), 0.99 (d, 6.7 Hz, 3H, C**H3**CH), 1.91 (oct, 6.7 Hz, 1H, $(CH_3)_2$C**H**), 2.46-2.68 (m, 2H, C**H2**CH=CH_2), 3.2-3.4 and 3.46-3.55 (m, 2H, C**H**C=S and C**H**OH), 3.37 (s, 3H, NC**H3**), 3.51 (s, 3H, NC**H3**), 4.05 (d, 8.2 Hz, 1H, O**H**), 4.98 (dd, 10.4 Hz and 1.5

Hz, 1H, CH=CH**cis**H), 5.13 (dd, 16.8 Hz and 1.5 Hz, 1H, CH=CH**trans**H), 5.66-5.82 (m, 1H, C**H**=CH_2); δ_C 17.9 and 20.1 ($\underline{C}H_3CH$), 31.1 ($CH_3\underline{C}H$), 38.1 ($\underline{C}H_2CH=CH_2$), 42.2 and 44.5 ($N\underline{C}H_3$), 50.1 ($\underline{C}HC=S$), 79.0 ($\underline{C}HOH$), 117.5 ($CH=\underline{C}H_2$), 135.3 ($\underline{C}H=CH_2$), 206 (C=S).

IR (NaCl) (cm^{-1}) : 3418 (ν O-H), 3076 (ν C-H ethylen.), 2960, 2872 (ν C-H), 1640 (ν C=C), 1148 (ν C-O), 1394 (δ O-H); M/e %: **215** (2), M^+; 200 (34), $(M^+ - CH_3)^+$; 172 (10), $CH_2=CHCH_2CH[CH(OH)]$-$C=SN(CH_3)_2^+$; **143** (100), $CH_2=CHCH_2CH_2$-$C=SN(CH_3)_2^+$; 142 (77), $CH_2=CHCH_2CHC=SN$-$(CH_3)_2^+$; 128 (71), $CH_3CH=C$-$C=SN(CH_3)_2^+$; 88 (93), $C=SN(CH_3)_2^+$; 70 (83), $CH=CHC=S^+$; 44 (35), $N(CH_3)_2^+$; 43,$CH_3CHCH_3^+$; 41 (23), $CH_2=CCH_3^+$.

Anal.: calcd. for $C_{11}H_{21}NOS$: C, 61.35; H, 9.83; N, 6.50; S, 14.89. Found: C, 59.67; H, 9.87; N, 6.46; S, 14.68.

N,N-dimethyl-2-(1-hydroxy-2,2-dimethylpropyl)-4-pentenethioamide 12

From the reaction between aldol **5** and allyl bromide. Purification by chromatography (petroleum ether / ethyl acetate: 80 / 20) gives a yellow oil in 30% yield. Syn / Anti ratio > 98 / 2.

syn isomer 12a: δ_H 1.00 (s, 3H, (CH_3)$_3$C), 2.53-2.62 and 2.77-2.9 (m, 2H, $CH_2CH=CH_2$), 3.34 (s, 3H, NCH_3), 3.4-3.47 (m, 2H, CHC=S and CHOH), 3.51 (s, 3H, NCH_3), 4.31 (d, 1.8 Hz, 1H, OH), 4.96 (dd, 10.1 Hz and 1.3 Hz, 1H, CH=CH**cis**H), 5.08 (dd, 16.8 Hz and 1.3 Hz.1H, CH=CH**trans**H), 5.58-5.75 (m, 1H, C**H**=CH_2); δ_C 27.2 (($\underline{C}H_3$)$_3$C), 35.8 ((CH_3)$_3\underline{C}$), 36.1 ($\underline{C}H_2CH=CH_2$), 42.3 and 44.8 ($N\underline{C}H_3$), 48.3 ($\underline{C}HC=S$), 80.4 (CHOH), 117 ($CH=\underline{C}H_2$), 136.2 ($\underline{C}H=CH_2$), 209.6 (C=S).

anti isomer 12b: not detected

IR (NaCl) (cm^{-1}): 3380 (ν O-H), 3074 (ν C-H ethylen.), 2954, 2868 (ν C-H), 1638 (ν C=C), 1098 (ν C-O), 1396 (δ O-H); M/e %: **229** (7), M^+; 214 (36), $(M^+ - CH_3)^+$; 142 (54), $CH_2=CHCH_2CHC=SN(CH_3)_2^+$; 88 (84), $C=SN(CH_3)_2^+$; **70** (100), $CH=CHC=S^+$; 44 (41), $N(CH_3)_2^+$; 43 (79), $CH=CHOH^+$; 41 (45), $CH_2=CHCH_2^+$. Anal.: calcd. for $C_{12}H_{23}NOS$: C, 62.84; H, 10.11; N, 6.11; S, 13.98. Found: C, 62.38; H, 10.09; N, 5.85; S, 13.80.

N,N-dimethyl-2-(1-hydroxy-1-phenylmethyl)-4-pentenethioamide 13

From the reaction between aldol **6** and allyl bromide. Separation by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a yellow oil in 40% yield. Syn / Anti ratio 80 / 20.

syn isomer 13a: δ_H 2.38-2.48 and 2.77-2.89 (m, 2H, $CH_2CH=CH_2$), 3.23 (s, 3H, NCH_3), 3.3-3.39 (m, 1H, CHC=S), 3.45 (s, 3H, NCH_3), 4.73 (d, 0.9 Hz, 1H, OH), 4.87-5.02 (m, 3H, CHOH and CH=CH**cis**H and CH=CH**trans**H), 5.46-5.62 (m, 1H, C**H**=CH_2), 7.22-7.41 (m, 5H, **H** aromat.); δ_C 33.7 ($\underline{C}H_2CH=CH_2$), 42.2 and 44.7 ($N\underline{C}H_3$), 54.9 ($\underline{C}HC=S$), 75.0 (CHOH), 117.4 ($CH=\underline{C}H_2$), 126.3, 127.6 and 128.4 (o., m., p. aromat. **C**), 135.6 ($\underline{C}H=CH_2$), 142.2 (quatern. aromat. **C**), 206 (C=S).

anti isomer 13b: δ_H 2.41-2.51 and 2.68-2.89 (m, 2H, $CH_2CH=CH_2$), 2.96 and 3.37 (s, 6H, NCH_3), 3.42-3.49 (m, 1H, CHC=S), 4.75 (d, 7.3Hz, 1H, CHOH), 4.95-5.12 (m, 3H, OH and CH=CH**cis**H and CH=CH**trans**H), 5.6-5.77 (m, 1H, C**H**=CH_2), 7.25-7.35 (m, 5H, **H** aromat.); δ_C 38.3 ($\underline{C}H_2CH=CH_2$), 41.9 and 44, 6 ($N\underline{C}H_3$), 54.6 ($\underline{C}HC=S$), 76.4 (CHOH), 117.6 ($CH=\underline{C}H_2$), 126.4, 127.8 and 128.4 (o., m., p. aromat. **C**), 135.1 ($\underline{C}H=CH_2$), 142.9 (quatern.aromat. **C**), 203.6 (C=S).

IR (NaCl) (cm^{-1}): 3286 (ν O-H), 3062, 3028 (ν C=C-H ethylen. and aromat.), 2974 and 2934 (ν C-H), 1640 (ν C=C), 1602 and 1520 (ν C=C aromat.), 1096 (ν C-O), 1396 (δ O-H); M/e %: **249** (10), M^+; 234 (7), $(M^+ - CH_3)^+$; 207 (12), $C_6H_5C=OCH_2$-$C=SN(CH_3)_2^+$; 142 (33), $CH_2=CHCH_2CHC=SN(CH_3)_2^+$; 88 (16), $C=SN(CH_3)_2^+$; 84 (84), $CH_2=CHCH_2CHCHOH^+$; **77** (100), $C_6H_5^+$.

Anal.: calcd. for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68; N, 5.62; S, 12.86. Found: C, 68.66; H, 8.00; N, 5.65; S, 13.08.

N,N-dimethyl-2-(1-hydroxy-2-phenylethyl)-4-pentenethioamide 14

From the reaction between aldol **7** and allyl bromide. Separation by chromatography (petroleum ether / ethyl acetate: 70 / 30) gives a yellow oil in 60% yield. Syn / Anti ratio 90 / 10.

syn isomer 14a: δ_H 2.48-3.16 (m, 5H, $CH_2CH=CH_2$, CHC=S and Ph-CH_2), 2.89 (s, 3H, NCH_3), 3.43 (s, 3H, NCH_3), 3.94-3.97 (m, 1H, CHOH), 4.38 (d, 0.6 Hz, 1H, OH), 4.98 (dd, 9.9 Hz and 1.5 Hz, 1H, CH=CH**cis**H), 5.12 (dd, 17 Hz and 1.5 Hz, 1H, CH=CH**trans**H), 5.6-5.8 (m, 1H, C**H**=CH_2), 7.14-7.34 (m, 5H, **H** aromat.); δ_C 34.0 ($\underline{C}H_2CH=CH_2$), 40.8 (Ph-$\underline{C}H_2$), 41.7 and 44, 6 ($N\underline{C}H_3$), 49.6 ($\underline{C}HC=S$), 74.8 ($\underline{C}HOH$), 117.3 ($CH=\underline{C}H_2$), 126.7, 128.7 and 129.5 (o., m., p. aromat. **C**), 135.8 ($\underline{C}H=CH_2$), 138.3 (quatern. aromat. **C**), 206.8 (C=S).

anti isomer 14b: δ_H 2.48-3.16 (m, 5H, **CH2**CH=CH2, **CH**C=S and Ph-**CH2**), 2.93 (s, 3H, N**CH3**), 3.49 (s, 3H, N**CH3**), 4.0-4.1(m, 1H, **CH**OH), 4.83 (d, 9Hz, 1H, CHO**H**), 4.96-5.15 (m, 2H, CH=CH**cis**H and CH=CH**trans**H), 5.6-5.8 (m, 1H, C**H**=CH2), 7.14-7.34 (m, 5H, **H** aromat.); δ_C 37.9 (**C**H2CH=CH2), 42.1 (Ph-**C**H2), 41.7 and 44, 3 (N**C**H3), 50.4 (**C**HC=S), 74.3 (**C**HOH), 117.8 (CH=**C**H2), 126.5, 128.6 and 129.2 (o., m., p. aromat. **C**), 135.0 (**C**H=CH2), 138.6 (quatern. aromat. **C**), 205.0 (C=S).

IR (NaCl) (cm^{-1}): 3370 (ν O-H), 3074, 3026 (ν C=C-H ethylen.and aromat.), 2934 (ν C-H), 1640 (ν C=C), 1600 and 1518 (ν C=C aromat.), 1100 (ν C-O), 1416 (δ O-H); M/e %: **263** (17), M^+; **248** (100), $(M^+ - CH_3)^+$; 222 (15), $C_6H_5CH_2$-CH(OH)CHC=SN$(CH_3)_2^+$; 204 (29), $C_6H_5CH_2CH$=CHC=SN$(CH_3)_2^+$; 173 (44), $C_6H_5CH_2C$=OCHCH2CH=CH_2^+;91 (16), $C_6H_5CH_2^+$; 88 (16), C=SN$(CH_3)_2^+$.

Anal. : calcd. for $C_{15}H_{21}NOS$: C, 68.40; H, 8.04; N, 5.32; S, 12.17. Found: C, 66.47; H, 8.34; N, 5.22; S, 12.35.

N,N-dimethyl-2-(1-hydroxy-2-phenylpropyl)-4-pentenethioamide 15

From the reaction between aldol syn **8a** and allyl bromide. Purification by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a yellow oil in 30% yield. Syn / Anti ratio >95 / 5.

syn syn isomer 15a: δ_H 1.41 (d, 7 Hz, 3H, Ph-CHC**H3**), 2.47-3.25 (m, 4H, **CH2**CH=CH2, **CH**C=S and Ph-**CH**CH3), 2.62 (s, 3H, N**CH3**), 3.39 (s, 3H, N**CH3**), 3.67 (m, 1H, **CH**OH), 4.88-5.1 (m, 3H, **OH** and CH=C**H2**), 5.46-5.68 (m, 1H, C**H**=CH2), 7.2-7.36 (m, 5H, **H** aromat.); δ_C 18.9 (CH3), 33.5 (**C**H2CH=CH2), 41.4 and 44.6 (N**C**H3), 43.8 (Ph-**C**H), 48.4 (**C**HC=S), 77.8 (CHOH), 117.1 (CH=**C**H2), 126.9, 127.9 and 128.9 (o., m., p. aromat. **C**), 135.8 (**C**H=CH2), 144.6 (quatern. aromat. **C**), 207.4 (C=S).

syn anti isomer 15b: not detected

From the reaction between aldol anti **8b** and allyl bromide. Purification by chromatography (petroleum ether / ethyl acetate: 60 / 40) gives a yellow oil in 30% yield. Syn / Anti ratio >95 / 5.

anti syn isomer 15c: δ_H 1.33 (d, 7.3 Hz, 3H, Ph-CHC**H3**), 2.4-3.2 (m, 4H, **CH2**CH=CH2, **CH**C=S and Ph-**CH**CH3), 2.9 (s, 3H, N**CH3**), 3.47 (s, 3H, N**CH3**), 4.01-4.05 (m, 1H, **CH**OH), 4.88-5.1 (m, 3H, **OH** and CH=C**H2**), 5.55-5.78 (m, 1H, C**H**=CH2), 7.2-7.36 (m, 5H, **H** aromat.); δ_C 19.2 (CH3), 36.4 (**C**H2CH=CH2), 41.7 and 44.5 (N**C**H3), 42.5 (Ph-**C**H), 50.7 (**C**HC=S), 78.7 (CHOH), 117.3 (CH=**C**H2), 126.5, 128.4 and 128.5 (o., m., p. aromat. **C**), 135.7 (**C**H=CH2), 144.1 (aromat. quatern. **C**), 206.0 (C=S).

anti anti isomer 15d: not detected

IR (NaCl) (cm^{-1}): 3336 (ν O-H), 3080, 3026 (ν C=C-H ethylen.and aromat.), 2970, 2932, 2872 (ν C-H), 1638 (ν C=C), 1602 and 1494 (ν C=C aromat.), 1120 (ν C-O), 1436 (δ O-H); M/e %: 277 (17), M+; 269 (100), $(M+ - CH_3)^+$; 236 (19), C_6H_5CH-$(CH_3)CH(OH)CHC$=SN$(CH_3)_2^+$; 214 (50), 200 (21), $CH(CH_3)CH(OH)$-CH(C=SN-$(CH_3)_2)CH_2CH$=CH_2^+; 186 (27); 143 (38), CH_2=$CHCH_2CH_2$-C=SN$(CH_3)_2^+$; 88 (18), C=SN$(CH_3)_2^+$; 77 (3), $C_6H_5^+$.

Anal.: calcd for $C_{16}H_{23}NOS$: C, 69.27; H, 8.36; N, 5.05; S, 11.56. Found: C, 69.0; H, 8.45; N, 5.0; S, 11.43.

N,N-dimetyl-2-(1-hydroxyethyl)-4-methyl-4-pentenethioamide 16

From the reaction between aldol **2** and methallyl bromide. Purification by chromatography (petroleum ether / ethyl acetate: 40 / 60) gives a yellow oil in 63% yield. Syn / Anti ratio 80 / 20.

syn isomer 16a: δ_H 1.24 (d, 6.4 Hz, 3H, **CH3**CHOH), 1.75 (s, 3H, CH_2C(**CH3**)=CH_2), 2.47-2.78 (m, 2H, **CH2**C(CH_3)=CH_2), 3.13-3.2 (m, 1H, **CH**C=S), 3.33 (s, 3H, N**CH3**), 3.5 (s, 3H, N**CH3**), 3.94-4.02 (m, 1H, **CH**OH), 4.34 (s, 1H, OH), 4.72-4.74 (m, 2H, $CH_2C(CH_3)$=C**H2**); δ_C 21.3 (**C**H3CHOH), 23.4 (**C**H3C=CH), 37.7 (**C**H2C=CH2), 42.1 and 44.7 (N**C**H3), 52.2 (**C**HC=S), 69.4 (**C**HOH), 112.5 (CH=**C**H2), 143.6 (**C**H=CH2), 207.7 (C=S).

anti isomer 16b: δ_H 1.25 (d, 6.2Hz, 3H, **CH3**CHOH), 1.73 (s, 3H, CH_2C(**CH3**)=CH_2), 2.4-2.78 (m, 2H, **CH2**C(CH_3)=CH_2), 3.13-3.22 (m, 1H, **CH**C=S), 3.36 (s, 3H, N**CH3**), 3.51 (s, 3H, N**CH3**), 4.0-4.11 (m, 1H, **CH**OH), 4.34 (s, 1H, OH), 4.74-4.76 (m, 2H, $CH_2C(CH_3)$=C**H2**); δ_C 21.4 (**C**H3CHOH), 23.4 (**C**H3C=CH), 37.7 (**C**H2C=CH2), 42.2 and 44.7 (N**C**H3), 53.1 (**C**HC=S), 70.1 (**C**HOH), 112.9 (CH=**C**H2), 142.7 (**C**H=CH2), 205.4 (C=S).

IR (NaCl) (cm^{-1}): 3404 (ν O-H), 3074 (ν C=C-H ethylen.), 2968, 2932 (ν C-H), 1648 (ν C=C), 1126 (ν-C-O), 1374 (δ O-H); M/e %: **201** (31), M^+; **186** (100), $(M^+ - CH_3)^+$; 156 (10), CH_2=$CH(CH_3)CH_2$-CHC=SN$(CH_3)_2^+$; 88 (10), C=SN$(CH_3)_2^+$; 45 (7), N$(CH_3)_2^+$.

Anal.: calcd. for $C_{10}H_{19}NOS$: C, 59.66; H, 9.51; N, 6.96; S, 15.92. Found: C, 59.72; H, 9.41; N, 6.83; S, 15.88.

N,N-dimethyl-2-(1-hydroxypropyl)-4-methyl-4-pentenethioamide 17

From the reaction between aldol **3** and methallyl bromide. Separation by chromatography (petroleum ether / ethyl acetate: 80 / 20) gives a yellow oil in 60% yield. Syn / Anti ratio 85 / 15.

syn isomer 17a: δ_H 1.00 (t, 7.3 Hz, 3H, C**H**$_3$CH$_2$), 1.39-1.74 (m, 2H, CH$_3$C**H**$_2$), 1.74 (s, 3H, C**H**$_3$C=CH), 2.43-2.49 and 2.73-2.83 (m, 2H, C**H**$_2$C=CH$_2$), 3.23-3.29 (m, 1H, C**H**C=S), 3.33 (s, 3H, NC**H**$_3$), 3.5 (s, 3H, NC**H**$_3$), 3.61-3.68 (m, 1H, C**H**OH), 4.4 (s, 1H, OH), 4.71-4.73 (m, 2H, C=C**H2**); δ_C 10.7 (**C**H$_3$CH$_2$), 23.4 (**C**H$_3$C=CH), 27.9 (CH$_3$**C**H$_2$), 37.7 (**C**H$_2$C=CH$_2$), 42.0 and 44 8 (N**C**H$_3$), 50.4 (**C**HC=S), 74.9 (**C**HOH), 112.4 (CH=**C**H$_2$), 143.6 (**C**H=CH$_2$), 207.9 (C=S).

anti isomer 17b: δ_H 1.00 (t, 7.3 Hz, 3H, C**H**$_3$CH$_2$), 1.39-1.74 (m, 2H, CH$_3$C**H**$_2$), 1.75 (s, 3H, C**H**$_3$C=CH), 2.45-2.65 (m, 2H, C**H**$_2$C=CH$_2$), 3.23-3.29 (m, 1H, C**H**C=S), 3.35 (s, 3H, NC**H**$_3$), 3.5 (s, 3H, NC**H**$_3$), 3.61-3.68 (m, 1H, C**H**OH), 4.2 (s, 1H, OH), 4.78 (s, 2H, C=C**H2**); δ_C 10.7 (**C**H$_3$CH$_2$), 23.3 (**C**H$_3$C=CH), 28.4 (CH$_3$**C**H$_2$), 37.7 (**C**H$_2$C=CH$_2$), 41.7 and 44 6 (N**C**H$_3$), 51.2 (**C**HC=S), 75.4 (**C**HOH), 113.0 (CH=**C**H$_2$), 143.6 (**C**H=CH$_2$), 206.2 (C=S).

IR (NaCl) (cm^{-1}): 3398 (ν O-H), 3074 (ν C=C-H ethylen.), 2964, 2934, 2876 (ν C-H), 1646 (ν C=C), 1108 (ν C-O), 1374 (δ O-H); M/e %: **215** (11), M^+; **200** (100), $(M^+ - CH_3)^+$; 186 (9), CH(OH)CH(C=SN(CH$_3$)$_2$)CH$_2$CH(CH$_3$)=CH$_2^+$; 156 (8), CH$_2$=CH-(CH$_3$)CH$_2$CHC=SN(CH$_3$)$_2^+$; 88 (9), C=SN(CH$_3$)$_2^+$; 41 (6), CH=CHCH$_3^+$.

Anal.: calcd. for $C_{11}H_{21}NOS$: C, 61.35; H, 9.83; N, 6.50; S, 14.89. Found: C, 61.08; H, 9.96; N, 6.49; S, 14.75.

N,N-dimethyl-2-(1-hydroxy-2-methylpropyl)-4-methyl-4-pentenethioamide 18

From the reaction between aldol **4** and methallyl bromide. Separation by chromatography (petroleum ether / ethyl acetate: 80 / 20) gives a yellow oil in 75 % yield. Syn / Anti ratio 85 / 15.

syn isomer 18a: δ_H 0.95 (d, 6.4 Hz, 3H, (C**H**$_3$)$_2$CH), 1.04 (d, 6.4 Hz, 3H, (C**H**$_3$)$_2$CH), 1.73 (s, 3H.C**H**$_3$C=CH), 1.73-1.92 (m, 1H, (CH$_3$)$_2$C**H**), 2.23-2.42 and 2.8-3.05 (m, 2H, C**H**$_2$C=CH$_2$), 3.26-3.31 (m, 1H, C**H**OH), 3.34 (s, 3H, NC**H**$_3$), 3.51 (s, 3H, NC**H**$_3$), 3.45-3.52 (m, 1H, C**H**C=S), 4.53 (s, 1H, OH), 4.69 and 4.72 (s, 2H, C=C**H2**); δ_C 19.4 and 19.5 ((**C**H$_3$)$_2$CH), 23.6 (**C**H$_3$C=CH), 31.2 ((CH$_3$)$_2$**C**H), 37.5 (**C**H$_2$C=CH$_2$), 41.8 and 44.9 (N**C**H$_3$), 47.9 (**C**HC=S), 78.5 (**C**HOH), 112.2 (CH=**C**H$_2$), 143.7 (**C**H=CH$_2$), 208.0 (C=S).

anti isomer 18b: δ_H 0.92 (d, 6.7 Hz, 3H, (C**H**$_3$)$_2$CH), 1.0 (d, 6.4 Hz, 3H, (C**H**$_3$)$_2$CH), 1.75 (s, 3H.C**H**$_3$C=CH), 1.85-2.0 (m, 1H, (CH$_3$)$_2$C**H**), 2.45-2.62 (m, 2H, C**H**$_2$C=CH$_2$), 3.36-3.52 (m, 2H, C**H**C=S and C**H**OH), 3.37 (s, 3H, NC**H**$_3$), 3.49 (s, 3H, NC**H**$_3$), 4.17 (s, 1H, OH), 4.8 (s, 2H, C=C**H2**); δ_C 18.1 and 20.2 ((**C**H$_3$)$_2$CH), 23.3 (**C**H$_3$C=CH), 31.2 ((CH$_3$)$_2$**C**H), 41.5 (**C**H$_2$C=CH$_2$), 42.0 and 44.6 (N**C**H$_3$), 48.5 (**C**HC=S), 79.0 (**C**HOH), 113.2 (CH=**C**H$_2$), 142.4 (**C**H=CH$_2$), 206.6.0 (C=S).

IR (NaCl) (cm^{-1}): 3356 (ν O-H), 3074 (ν C=C-H ethylen.), 2960, 2932, 2872 (ν C-H), 1646 (ν C=C), 1112 (ν C-O), 1394 (δ O-H); M/e %: **229** (6), M^+; **214** (100), $(M^+ - CH_3)^+$; 186 (43), CH(OH)CH(C=SN(CH$_3$)$_2$)CH$_2$CH(CH$_3$)=CH$_2^+$; 156 (15), CH$_2$=CH(CH$_3$CH$_2$CHC=SN(CH$_3$)$_2^+$; 88 (6), C=SN(CH$_3$)$_2^+$; 41 (11), CH=CH-CH$_3^+$.

Anal.: calcd for $C_{12}H_{23}NOS$: C, 62.84; H, 10.11; N, 6.11; S, 13.98. Found: C, 62.58; H, 10.14; N, 6.12; S, 13.90.

N,N-dimethyl-2-(1-hydroxy-2,2-dimethylpropyl)-4-methyl-4-pentenethioamide 19

From the reaction between aldol **5** and methallyl bromide. Purification by chromatography (petroleum ether / ethyl acetate: 80 / 20) gives a yellow oil in 55% yield. Syn / Anti ratio > 98 / 2.

syn isomer 19a: δ_H 1.02 (s, (C**H**$_3$)$_3$C), 1.74 (s, 3H.C**H**$_3$C=CH), 2.49-2.59 and 2.8-2.91 (m, 2H, C**H**$_2$C=CH$_2$), 3.36-3.39, (m, 1H, C**H**OH), 3.32 (s, 3H, NC**H**$_3$), 3.49 (s, 3H, NC**H**$_3$), 3.5-3.56 (m, 1H, C**H**C=S), 4.25-4.33 (m, 1H, OH), 4.66-4.72 (m, 2H, C=C**H2**); δ_C 23.5 (**C**H$_3$C=CH), 27.2 ((**C**H$_3$)$_3$C), 35.9 ((CH$_3$)$_3$**C**), 39.4 (**C**H$_2$C=CH$_2$), 42.1 and 44.8 (N**C**H$_3$), 47.1 (**C**HC=S), 80.7 (**C**HOH), 112.4 (CH=**C**H$_2$), 143.7 (**C**H=CH$_2$), 210.3 (C=S).

anti isomer 19b : not detected

IR (NaCl) (cm^{-1}): 3382 (ν O-H), 3074 (ν C=C-H ethylen.), 2968, 2954 (ν C-H), 1646 (ν C=C), 1118 (ν C-O), 1394 (δ O-H).

M/e %: 243 (7), M^+; 228 (100), $(M^+ - CH_3)^+$; 186 (31), $CH(OH)CH(C{=}SN(CH_3)_2)$-$CH_2CH(CH_3){=}CH_2^+$; 156 (60), $CH_2{=}CH(CH_3)CH_2CHC{=}SN(CH_3)_2^+$; 114 (52), $CH_2{=}CC{=}SN(CH_3)_2^+$; **88** (100), $C{=}SN(CH_3)_2^+$; 70 (93), $CH{=}CHC{=}S^+$; 43 (79), $CH{=}CHOH^+$; 41 (36), $CH_2{=}CCH_3^+$.
Anal.: calcd. for $C_{13}H_{25}NOS$: C, 64.15; H, 10.35; N, 5.75; S, 13.17. Found: C, 63.95; H, 10.3; N, 5.8; S, 13.05.

N,N-dimethyl-2-(1-hydroxy-2-phenylethyl)-4-methyl-4-pentenethioamide 20

From the reaction between aldol **7** and methallyl bromide. Separation by chromatography (petroleum ether / ethyl acetate: 80 / 20) gives a yellow solid in 55% yield. Syn / Anti ratio: 95 / 5.

syn isomer 20a: δ_H 1.71 (s, 3H.C**H**$_3$C=CH), 2.7-3.25 (m, 5H, C**H**$_2$C=C**H**$_2$, Ph-C**H**$_2$ and C**H**C=S), 2.81 (s, 3H, NC**H**$_3$), 3.41 (s, 3H, NC**H**$_3$), 3.9-3.98 (m, 1H, C**H**OH), 4.47 (d, 1.22 Hz 1H, OH), 4.68-4.71 (m, 2H, C=C**H**$_2$), 7.2-7.37 (m, 5H, H aromat); δ_C 23.5 (**C**H$_3$C=CH), 37.2 (**C**H$_2$CH=CH$_2$), 40.6 (Ph-**C**H$_2$), 41.4 and 44.7 (N**C**H$_3$), 48.0 (**C**HC=S), 75.0 (**C**HOH), 112.5 (CH=**C**H$_2$), 126.7, 128.7 and 129.6 (o., m., p. aromat. **C**), 138,2 (quatern. aromat. **C**),143.3 (**C**H=CH$_2$), 207.4 (C=S).

anti isomer 20b: δ_H 1.66 (s, 3H.C**H**$_3$C=CH), 2,4-3,5 (m, 5H, C**H**$_2$C=C**H**$_2$, Ph-C**H**$_2$ and C**H**C=S), 2.90 (s, 3H, NC**H**$_3$), 3.46 (s, 3H, NC**H**$_3$), 4.01-4.2 (m, 1H, C**H**OH), 4.78 (s, 1H, OH), 4.93-4.97 (m, 2H, C=C**H**$_2$), 7.2-7.37 (m, 5H, H aromat.); δ_C 23.0 (**C**H$_3$C=CH), 37.2 (**C**H$_2$CH=CH$_2$), 41.2 (Ph-**C**H$_2$), 41.8 and 44.3 (N**C**H$_3$), 48.5 (**C**HC=S), 73.9 (**C**HOH), 113.4 (CH=**C**H$_2$), 126.4, 128.6 and 129.2 (o., m., p. aromat. **C**), 138,8 (quatern. aromat.**C**),142.1 (**C**H=CH$_2$), 205.6 (C=S).
IR (NaCl) (cm^{-1}): 3368 (ν O-H), 3068, 3024 (ν C=C-H ethylen. and aromat.), 2964, 2928 (ν C-H), 1644 (ν C=C ethylen.), 1602, 1494 (ν C=C aromat.), 1114 (ν C-O), 1394 (δ O-H); M/e % : **277** (3), M^+; 262 (19), $(M^+ - CH_3)^+$; 186 $(M^+ - C_6H_5CH_2)^+$; 157 (73), $CH_2{=}CH(CH_3)CH_2CH_2C{=}SN(CH_3)_2^+$; 156 (60), $CH_2{=}CH(CH_3)$-$CH_2CHC{=}SN(CH_3)_2^+$; 91 (77), $C_6H_5CH_2^+$; 88 (98), $C{=}SN(CH_3)_2^+$; 77 (25), $C_6H_5^+$; **70** (100), $CH{=}CHC{=}S^+$.
Anal.: calcd. for $C_{17}H_{25}NOS$: C, 69.27; H, 8.36; N, 4.05; S, 11.56. Found: C, 68.61; H, 8.12; N, 4.87; S, 13.00.

N,N-dimethyl-2-(1-hydroxy-2-phenylpropyl)-4-methyl-4-pentenethioamide 21

From the reaction between aldol syn **8a** and methallyl bromide. Purification by chromatography (petroleum ether / ethyl acetate: 80 / 20) gives a yellow oil in 45% yield. Syn-Syn / Syn-Anti ratio > 95/5.

syn syn isomer 21a: δ_H 1.41 (d, 6.7 Hz, 3H, PhCH(C**H**$_3$)), 1.58 (s, 3H.C**H**$_3$C=CH), 2.36-2.45 (m, 1H, Ph-C**H**CH$_3$)), 2.58 (s, 3H, NC**H**$_3$), 2.78-2.97 (m, 2H, C**H**$_2$C=CH$_2$), 3.02-3.10 (m, 1H, C**H**C=S), 3.37 (s, 3H, NC**H**$_3$), 3.64-3.70 (m, 1H, C**H**OH), 4.57-4.62 (m, 2H, C=C**H**$_2$), 4.93 (d, 0.7 Hz 1H, OH), 7.18-7.38 (m, 5H, H aromat.); δ_C 19.1 (PhCH(**C**H$_3$), 23.4 (**C**H$_3$C=CH), 37.0 (**C**H$_2$CH=CH$_2$), 44.0 (Ph-**C**H(CH$_3$)), 41.2 and 44.6 (N**C**H$_3$), 47.3 (**C**HC=S), 78.0 (**C**HOH), 112.4 (CH=**C**H$_2$), 126.9, 128.0 and 128.9 (o., m., p. aromat. **C**), 144.6 (quatern. aromat. **C**),143.2 (**C**H=CH$_2$), 208.0 (C=S).

syn anti isomer 21b: not detected.

From the reaction between aldol **8b** and methallyl bromide. Purification by chromatography (petroleum ether / ethyl acetate : 80 / 20) gives a yellow oil in 45% yield. Syn / Anti ratio > 95/5.

Anti-syn isomer 21c: δ_C 19.1 (PhCH(**C**H$_3$), 23.4 (**C**H$_3$C=CH), 39.6 (**C**H$_2$CH=CH$_2$), 42.8 (Ph-**C**H(CH$_3$)), 41.5 and 44.2 (N**C**H$_3$), 49.3 (**C**HC=S), 78.5 (**C**HOH), 112.7 (CH=**C**H$_2$), 126.5, 127.5 and 128.5 (o., m., p. aromat. **C**), 144.4 (quatern. aromat. **C**),143.4 (**C**H=CH$_2$), 206.7 (C=S).

Anti-anti isomer 21d: not detected

IR (NaCl) (cm^{-1}): 3362 (ν O-H), 3072, 3028 (ν C=C-H ethylen. and aromat.), 2964, 2930 and 2872 (ν C-H), 1644 (ν C=C ethylen.), 1602, 1514 (ν C=C aromat.), 1098 (ν C-O), 1394 (δ O-H); M/e %: **291** (9), M^+; 276 (43), $(M^+ - CH_3)^+$; 236 (5), C_6H_5CH-$CH_3)CH(OH)CH_2C{=}SN(CH_3)_2^+$; 218 (25), $C_6H_5CH(CH_3)$-$CH{=}CHC{=}SN(CH_3)_2^+$, 186 (60), $(M^+ - C_6H_5CH(CH_3))^+$, 157 (60), $CH_2{=}CH(CH_3)CH_2CH_2$-$C{=}SN(CH_3)_2^+$, 156 (60), $CH_2{=}CH(CH_3)CH_2CHC{=}SN(CH_3)_2^+$; **105** (100), $C_6H_5CH(CH_3)^+$; 88 (22), $C{=}SN(CH_3)_2^+$; 77 (26), $C_6H_5^+$; 55 (11), $CH_2{=}CH(CH_3)CH_2^+$.
Anal.: calcd. for $C_{18}H_{27}NOS$: C, 70.77; H, 8.91; N, 4.59; S, 10.49. Found: C, 70.38; H, 8.64; N, 4.64; S, 10.85.

Synthesis of thioamides from dithioesters.

In a solution of dithioester (1 mmol) in THF, N,N-dimethylamine gaz in excess was bubbled for 10 minutes at room temperature. The mixture is then washed with brine and extracted with ether and dried over $MgSO_4$. After filtration and concentration *in vacuo*, the products were purified by chromatography on silicagel.

N,N-dimethyl-2-(1-hydroxyethyl)4-methyl-4-pentenethioamide 16

From the reaction between methyl-(1-hydroxyethyl)-4-methyl-4-pentenedithioate [8a], in ratio Syn / Anti 8/2 and dimethyl amine gaz. Purification by chromatography (petroleum ether/ethyl acetate) gives **16a** and **16b** in 80 % yield. Syn / Anti ratio 8/2.

N,N-dimethyl-2-(1-hydroxy-2-methylpropyl)-4-methyl-4-pentenethio-amide 18

From the reaction between Methyl-(1-hydroxy-2-methyllpropyl)-4-methyl-4-pentenedithioate [8a] (Syn / Anti 100 / 0) and dimethyl amine. Purification by chromatography (petroleum ether / ethyl acetate) gives **18a** in 90 % yield. (Syn / Anti 100 / 0).

REFERENCES

1. (a) Rhoads S.J. and Raulins N.R., *Org. React.*, **1975**, *22*, 1. (b) Ziegler F.E., *Acc. Chem. Res.*, **1977**, *10*, 227; *Chem. Rev.*, **1988**, *88*, 1423. (c) Bennett G.B., *Synthesis*, **1977**, 589. (d) Desimoni G., Tacconi G., Barco A. and Pollini G.P., *Natural Products Synthesis through Pericyclic Reactions*, Caserio M.C. (ed.), ACS Monograph 180, Washington, **1983**, 267. (e) Lutz R.P., *Chem. Rev.*, **1984**, *84*, 205. (f) Hill R.K., *Asymmetric Synthesis Vol. 3*, Morrison J.D. (ed.), Academic Press, Orlando, **1984**, 503. (g) Nogradi M., *Stereoselective Synthesis*, Ebel H.F. (ed.), VCH, Weinheim, **1987**, 281. (h) Blechert S., *Synthesis*, **1989**, 71. (i) Kallmerten J. and Wittman M.D., *Studies in Natural Products Chemistry Vol. 3: Stereoselective Synthesis (Part B)*, Atta-ur-Rahman (ed.), Elsevier, Amsterdam, **1989**, 233. (j) Martin S.F. and Guinn D.E., *Synthesis* , **1991**, 245. (k) Masse C. E. and Panek J. S., *Chem. Rev.*, **1995**, *95*, 1293. (l) Rousseau G., *Tetrahedron*, **1995**, *51*, 2777.
2. (a) Ireland R. E., Mueller R.H. and Willard A. K., *J. Am. Chem. Soc.* , **1976**, *98*, 2868. (b) Pereira S. and Srebnik M., *Aldrichimica acta*, **1993**, *26*, 17.
3. Doering W. von E. and Roth W. R., *Tetrahedron*, **1962**, *18*, 67.
4. (a) Fujisawa T., Tajima K. and Sato T., *Chem. Lett.*, **1984**, 1669. (b) Heathcock C.H., Finkelstein B.L., Jarvi E.T., Radel P.A. and Hadley C.R., *J. Org. Chem.*, **1988**, *53*, 1922. (c) Grattan T. J. and Whitehurst J. S., *J. Chem. Soc., Chem. Commun.*, **1988**, 43; *J. Chem. Soc. Perkin Trans. 1*, **1990**, 11. (d) Mikami K., Takahashi K. and Nakai T., *J. Am. Chem. Soc.*, **1990**, *112*, 4035. (e) Sabol J.S., *Tetrahedron Lett.*, **1990**, *31*, 27. (f) Paterson I. and Hulme A.N., *Tetrahedron Lett.*, **1990**, *31*, 7513. (g) Davidson A.H., Eggleton N. and Wallace I.H., *J. Chem. Soc., Chem. Commun.*, **1991**, 378. (h) Sparks M.A. and Panek J.S., *J. Org. Chem.*, **1991**, *56*, 3431.
5. (a) Welch J.T. and Eswarakrishnan S., *J. Am. Chem. Soc.*, **1987**, *109*, 6716. (b) Pratt D.V. and Hopkins P.B., *Tetrahedron Lett.*, **1987**, *28*, 3065. (c) Ziegler F.E., Kneisley A., Thottathil J.K. and Wester R.T., *J. Am. Chem. Soc.*, **1988**, *110*, 5434. (d) Wovkulich P.M., Tang P.C., Chadha N.K., Batcho A.D., Barrish J.C. and Uskokovic M.R., *J. Am. Chem. Soc.*, **1989**, *111*, 2596.
6. (a) Kametani T., Suzuki T., Nishimura M., Sato E. and Unno K., *Heterocycles*, **1982**, *19*, 205. (b) Suzuki T., Sato E., Kamada S., Tada H., Unno K. and Kametani T., *J. Chem. Soc. Perkin Trans. 1*, **1986**, 387. (c) Davidson A.H. and Wallace I.H., *J. Chem. Soc., Chem. Commun.*, **1986**, 1759. (d) Mulzer J., Graske K.-D. and Kirste B., *Liebigs Ann. Chem.*, **1988**, 891. (e) Tadano K.-I., Minami M. and Ogawa S., *J. Org. Chem.*, **1990**, *55*, 2108. (f) Kahn S. D. and Hehre W. J., *J. Org. Chem.*, **1988**, *53*, 301.
7. (a) Kurth M.J. and Yu C.-M., *Tetrahedron Lett.*, **1984**, *25*, 5003; *J. Org. Chem.*, **1985**, *50*, 1840. (b) Kurth M.J. and Beard R.L., *J. Org. Chem.*, **1988**, *53*, 4085. (c) Kurth M.J., Beard R.L., Olmstead M. and Macmillan J.G., *J. Am. Chem. Soc.*, **1989**, *111*, 3712. (d) Fujisawa T., Tajima K., Ito M. and Sato T., *Chem. Lett.*, **1984**, 1169.
8. (a) Beslin P. and Perrio S., *Tetrahedron*, **1991**, *47*, 6275. (b) Beslin P. and Perrio S., *Tetrahedron*, **1992**, *48*, 4135. (b) Metzner P., Thuillier A., "*Sulfur Reagents in Organic Synthesis*", Academic Press, London, **1994**.
9. (a) Fromont C.; Metzner P., *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *95-96*, 421-422. (b) Alayrac C, Fromont F. and Metzner P., *Angew. chem.Int. Engl.*, **1997**, *36*, 371-372.
10. Pilli R.A. and Murta M.M., *J. Org. Chem.*, **1993**, *58*, 338-342 and cited references.
11. Evans D. A., Bartroli J.and Godel T., *Tetrahedron Lett.*, **1982**, *23*, 4577.
12. a) Jabre I., Saquet and Thuillier A., *J. Chem. Research, (S)*, **1990**, 106. (b) Jabre I., Saquet and Thuillier A., *J. Chem. Research, (S)*, **1990**, 755.
13. (a)Tamaru Y. T., Haralda T, and Yoshida Z., *J. Am. Chem. Soc.*, **1980**, *102*, 2392. (b)Tamaru Y. T., Furukawa Y., Mizutani M., Kitao O. and Yoshida Z., *J. Org. Chem.*, **1983**, *48*, 3631.
14. (a) Goasdoué C., Goasdoué N. and Gaudemar M., J. Organomet. Chem., **1981**, *208*, 279. (b) Goasdoué C., Goasdoué N. and Gaudemar M., Tetrahedron Lett., **1983**, *24*, 4001. (c) Goasdoué C., Goasdoué N. and Gaudemar M., *J. Organomet. Chem.*, **1984**, *263*, 273. (d) Tamaru Y. T., Haralda T., Mizutani M., Takeshi H and Yoshida Z., *J. Am. Chem. Soc.* , **1980**, *102*, 7808. (e) Tamaru Y. T., Amino, Y.,Furukawa Y., Kagotani M. and Yoshida Z., *J. Am. Chem. Soc.* , **1982**, *104*, 4018. (f) 11 : Tamaru Y. T., Hioki T. and Yoshida Z., *Tetrahedron Lett.*, **1984**, *25*, 5793.(g) Tamaru Y. T., Okada M., Kitao O. and Yoshida Z., *Tetrahedron Lett.*, **1984**, *25*, 5797.
15. Meyers A. I. and Walkup R. D., *Tetrahedron*, **1985**, *41*, 5089.
16. Cinquini M, Manfredi A, Molinari H and Restelli A, *Tetrahedron*, **1985**, *41*, 4936.
17. (a) Beslin P. and Vallée Y., *Tetrahedron*, **1985**, *41*, 2691. (b) Beslin P., Metzner P. and Vallée Y., *Tetrahedron Lett.*, **1983**, *23*, 2436.
18. Graham B. J. and Brant J.C., *Synthesis*, **1995**, 475.
19. Heathcock C. H., Pirrung M.C. and Sohn J. E., *J.Org.Chem.*, **1979**, *44*, 4294.
20. (a) Houk K. N., Moses S. R., Wu Y. D., Rondan N. G., Jäger V., Schohe R. and Fronczek F. R., *J. Am. Chem. Soc.*, **1984**, *106*, 3880. (b) Houk K.N., Paddon-Row M.N., Rondan N.G., Wu Y.-D., Brown F.K., Spellmeyer D.C., Metz J.T., Li Y. and Loncharich R.J., *Science*, **1986**, *231*, 1108.
21. Kahn S. D. and Hehre W. J., *J. Org. chem.*, **1988**, *53*, 301.

(*Received in Belgium* 14 *July* 1997; *accepted* 9 *October* 1997)