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Acyclic Stereocontrol through the Thio-Claisen Rearrangement of Precursors bearing a Chiral Centre adjacent to Carbon 1

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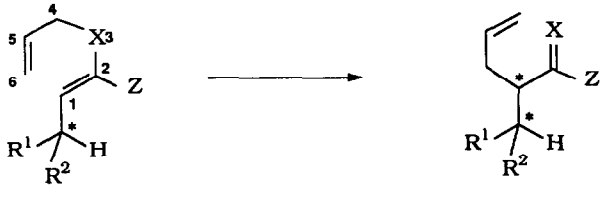
Abstract. The Claisen rearrangement of precursors bearing a stereogenic centre adjacent to carbon 1 of the pericyclic nucleus has been investigated in the sulfur series. Dithioesters having a methyl and various alkyl or alkenyls groups on the β-carbon were deprotonated by LDA. The resulting enethiolates were allylated on sulfur to give S-allyl ketenedithioacetals. The thio-Claisen transposition of the latter compounds was achieved either at room temperature or at 101°C to afford good yield of allylated dithioesters. Diastereomeric selectivities up to 95 : 5 have been observed. These results have been explained by a steric effect and correlated to allylic strain values.

The Claisen rearrangement is an efficient and highly used reaction for the creation of C-C bonds (1-4), especially in the field of natural product synthesis (3-10).

A very large number of stereochemical studies have appeared. Most of the examples known involve stereochemical elements present on the pericyclic nucleus. We wished to study the introduction of a chiral centre adjacent to carbon 1 of this nucleus (scheme 1), in order to provide a new means of control of the relative configuration of vicinal carbons in the challenging acyclic series (11).



Scheme 1

No general study of this question has been done so far (6, 12). Some reports (13-16) deal with the transposition of dianions bearing a hydroxyl and a methyl group on the stereogenic centre.

We undertook a study in the sulfur series because, from the initial work of Brandsma and his group (17-19) and other contributers (20-24), we know that:

• neutral precursors, such as S-allyl ketenedithioacetals, are easy to prepare from dithioesters through deprotonation and S-allylation.

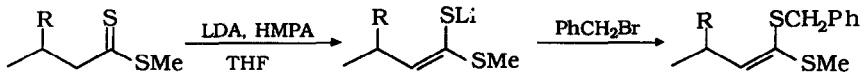
• the thio-Claisen transposition is thermally facile: it occurs at room temperature or by heating to 100°C at most. It is often a high yielding reaction.

A parallel investigation by Beslin and Perrio (25, 26) has shown that the introduction of R^1 = OH and R^2 = alkyl leads to a high diastereocontrol of the rearrangement in favour of *syn* products.

We wish to report our results dealing with alkyl, aryl and alkenyl groups as R^1 and R^2. Various selectivities have been observed and explained with steric effects. Extension to the field of synthesis of carbon chains bearing 3 contiguous stereogenic centres has also been achieved.

Results

Our study started with the effect of alkyl groups on the asymmetric centre. We introduced a methyl group and various alkyl substituents (scheme 2, table 1).



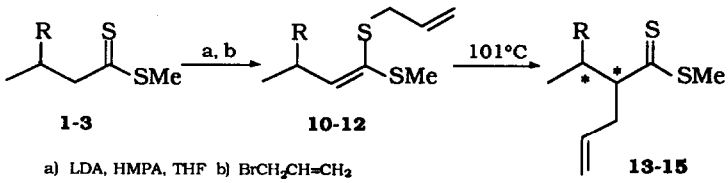
1-3 **4-6** **7-9**

Scheme 2

The starting materials are racemic dithioesters **1-3**, bearing a stereogenic centre in the beta position of the thiocarbonyl. Deprotonation by LDA (27) was not effective under standard conditions (THF, -78°C) and required the addition of HMPA and a temperature of -20°C. This may be related to steric hindrance on the adjacent carbon. Quantitative formation of enethiolates **4-6** was evidenced by quenching with benzyl bromide. Ketenedithioacetals **7-9** were quantitatively produced from the ensuing S-alkylation. ^{1}H NMR Analysis revealed that the Z isomers (20, 22) are preferentially formed with R = tBu (*Z*/*E* = 87 : 13) and are the only isomers observed with R = iPr, Ph.

These results provide further examples of *cis* deprotonation. It is a general property for thiocarbonyl compounds (11, 20, 22, 23, 28-31).

Preceding enethiolates **4-6** were treated with allyl bromide (scheme 3). After warming to room temperature and water quench, ketenedithioacetals **10-12** were isolated. ^{1}H NMR spectra show that these crude materials are compounds **10-12** accompanied by a minor amount of dithioesters **13-15**. A complete [3.3] sigmatropic shift was achieved after some days at room temperature or after some hours in refluxing methylcyclohexane (101°C).



Scheme 3

Excellent yields of dithioesters **13-15** were obtained (table 1). Ratios of diastereoisomers were determined by ^1H NMR. No appreciable variation of the selectivity *vs* the temperature has been observed in the range 20-101°C. The ratios were compared to the nature of the R group (scheme 3). With an isopropyl group one gets a modest selectivity, 77: 23. The phenyl group causes an increase. The t-butyl group affords a high selectivity (95 : 5).

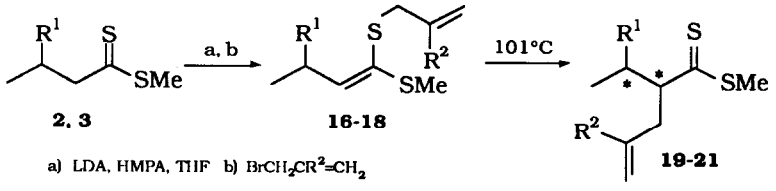
Table 1

Entry	R	Rearrangement Time Hours	Rearrangement Temperature °C	Product	Yield %	Ratio of Diastereoisomers
1	iPr	7	101	**13**	74	77 : 23
2	Ph	24	20	**14**	89	82 : 18
3	tBu	7	101	**15**	89	95 : 5

The assignment of the relative configuration of the major diastereoisomer has been attempted by various methods, unfortunately without any success so far.

The order of selectivity (iPr, Ph, tBu) follows the degree of steric hindrance of these substituents. We have here a steric effect which drives the transition state towards a preferred conformation.

Variation of the allylic moiety (scheme 4) was accomplished by introducing an R^2 substituent on carbon 5 of the pericyclic nucleus. Dithioesters **2** and **3** were deprotonated and the resulting enethiolates **5** and **6** were treated with allyl halides bearing a subsituent on carbon 2 of the allyl group. Dithioacetals **16-18** were heated at 101°C for some hours to provoke their rearrangement into dithioesters **19-21**.



Scheme 4

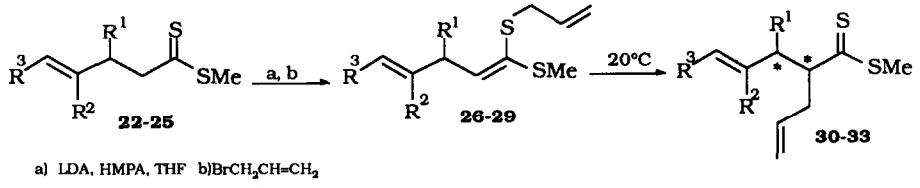
The ratio of diastereomers **19** (R^1 = Ph, R^2 = Me) is 78 : 22 and thus similar to compound **14** (R^1 = Ph, R^2 = H ; Table 1, entry 2). For dithioesters **20-21** (R^1 = tBu, R^2 = Br, Ph) a single isomer (> 90 : 10), analogous to compound **15** (Table 1, entry 3) was detected. The selectivities are therefore little affected by the introduction of a substituent on carbon 5 of the pericyclic nucleus.

Table 2

Entry	R^1	R^2	Rearrangement Time Hours	Rearrangement Temperature °C	Product	Yield %	Ratio of Diastereoisomers
1	Ph	Me	2	101	**19**	96	78 : 22
2	tBu	Br	6	101	**20**	60	≥ 90 : 10
3	tBu	Ph	8	101	**21**	45	≥ 90 : 10

After this first set of experiments involving steric effects, we wished to introduce substituents which were smaller than a methyl group. Inspection of A-strain values led us to compounds **22-25**, bearing an alkenyl group on the stereogenic centre.

The reaction sequence was carried out as previously: ketenedithioacetals **26-29** undergo a smooth rearrangement at ambient temperature to lead to diunsaturated dithioesters **30-33**.



a) LDA, HMPA, THF b)$BrCH_2CH{=}CH_2$

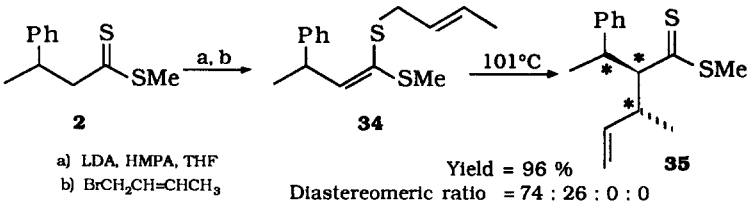
Scheme 5

With a phenyl (R^1) and a vinyl group (R^2 = R^3 = H) on the chiral centre, a mediocre selectivity has been observed (62 : 38). Replacing the R^1 group by a methyl improves the selectivity up to 81: 19. Introduction of a methyl substituent as R^2, instead of H, leads to the same diastereocontrol (82 : 18), whereas placing it as R^3 decreases the selectivity (72 : 28).

Table 3

Entry	R^1	R^2	R^3	Rearrangement Time Days	Rearrangement Temperature °C	Product	Yield %	Ratio of Diastereoisomers
1	Ph	H	H	2	20	**30**	100	62 : 38
2	Me	H	H	2	20	**31**	85	81 : 19
3	Me	Me	H	4	20	**32**	42	82 : 18
4	Me	H	Me	2	20	**33**	45	72 : 28

With a third class of precursors our goal has been to create three asymmetric centres during the rearrangement step. A substituent was added on carbon 6 (scheme 6). Dithioester **2** was metallated as previously and the resulting enethiolate was reacted with *E*-crotyl bromide. Heating the resulting ketenedithioacetal **34** at 101°C afforded dithioester **35** bearing 3 stereogenic centres, in excellent yield. The isomers could be analyzed by 200 MHz ^{1}H NMR. We have observed the presence of only two out of the 4 possible isomers, in a ratio of 74 : 26 : 0 : 0.



Scheme 6

Though we have not succeeded in the assignment of the relative configuration of these isomers,the above results provide useful information.

Discussion

We have confirmed that the thio-Claisen rearrangement proceeds under easy conditions: either at room temperature or, at most, at 101°C. In many cases excellent yields of dithioesters have been obtained. The sulfur version of this transposition is indeed an efficient method for allylation α to a thiocarbonyl group. It provides a synthesis of γ-unsaturated and γ,γ'-diunsaturated dithioesters.

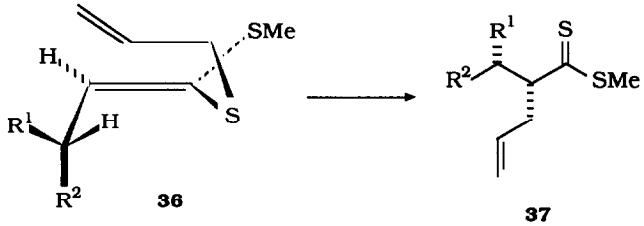
The introduction of a stereogenic centre adjacent to the ketenedithioacetal moiety causes various degrees of diastereocontrol. The initial experiments showed a steric effect (scheme 3). We tried to correlate the observed ratios to the allylic strain of the R substituents (32, 33).

Table 4

R	-ΔG° kcal / mol	Ratio of Diastereoisomers
Me	1.5-2.1	---
iPr	1.8-2.5	77:23
Ph	2.0-3.1	82:18
tBu	5.6	95:5

The A-Strain values for the substituents present on the chiral centre increase in the following order: Me, iPr, Ph, tBu (34, 35). For our first set of experiments we maintained a methyl group and we varied the R substituent. We have thus to compare the isomer ratio to the A-Strain of R relative to the A-Strain value of the methyl group (1.5-2.1). Such a correlation fits reasonably (Table 4). The large A-value of the t-butyl group allowed us to achieve a high degree of stereocontrol.

We propose a tentative model for the transition state **36** of this rearrangement (scheme 7). We consider a pseudo-cyclic chair form for the pericyclic system (4, 22, 36). In connection with studies by Houk and co-workers (37-39), we place the smallest group, hydrogen, in a staggered position to the carbon carbon double bond of the ketenedithioacetal. The medium sized R^1 group is located on the outside allylic staggered position. The largest group (R^2) will then occupy the least hindered position, *i.e.* the one perpendicular to the carbon-carbon double bond. The attack of the S-allyl chain will be anti-periplanar to this bulky R^2 group. Thus we predict that the major isomer formed **37** has the allyl chain and the smaller R^1 group in ***syn*** positions of the zig-zag chain.



Scheme 7

The above model bears a *Z* geometry for the double bond in agreement with the preceding observation of a *cis* deprotonation. Inspection of molecular models and parallel experiments lead us to propose that the *E* isomer would give rise to the same diastereomer **37** and therefore the stereochemistry is roughly independant from the geometry of the ketene dithioacetal double bond.

We have noted experimentally that by use of groups such as S-methallyl (table 2), the selectivities are maintained. The above model is plausible for this series as well.

When a crotyl chain is used instead of an allyl one, the diastereomeric ratio of **35** is 74 : 26 : 0 : 0. We assume that the relative configuration of the carbon α to C=S and the carbon α to the phenyl group is the same as with an allyl chain (82 : 18) or a methallyl chain (78 : 22). The relative configuration of the carbon α to C=S and the stereogenic carbon of the allylic chain depends on the stereochemistry of the double bonds of precursors **34**, due to the specificity of the rearrangement *via* a pseudo-cyclic chair transition state (4, 20, 22, 36). Our starting material **34** has a *Z* configuration for the ketenedithioacetal moiety and an *E* crotyl chain. Thus we assign a ***syn*** arrangement for these two carbons (20), as drawn on scheme 6. It is remarkable that the third stereogenic centre was introduced without cost to the selectivity.

The second type of modifications that we have made deals with the introduction of unsaturated groups on the chiral centre of the ketenedithioacetals. The vinyl group has an A-Strain value of 1.3, smaller than that of a methyl group (1.5-2.1). The corresponding product **31** was obtained in an isomer ratio of 81: 19 (scheme 5). We tried to improve it by replacing the methyl groups with a phenyl groups (A = 2.0-3.1). However the selectivity dropped to 62: 38.

Our proposal can be compared to that reported during the investigation of the Claisen rearrangement of precursors bearing a hydroxyl group and various alkyl substituents on the stereogenic centre. Beslin and Perrio (25, 26) proposed a model in which they placed the hydroxyl group in the outside allylic position (R^1 = OH) for electronic reasons. Their results can also be correlated to allylic strains: A strain for OH is smaller than for an alkyl group. However, isomeric ratios are little affected by the nature of R^2 group (Me, Et, iPr, tBu).

So, with some exceptions, we propose that A-Strain effects can be used as rough guides for the prediction of the stereochemical control of such systems.

Conclusion

We have investigated the effect of a chiral centre adjacent to carbon 1 of the pericyclic nucleus of a Claisen rearrangement. A high degree of stereocontrol has been achieved when the stereogenic carbon bears a methyl and a t-butyl group. Steric hindrance leads to a privileged conformation. A *syn* structure was tentatively assigned to the major isomer. Various substituents have been introduced on the allyl chain. Compounds bearing 3 contiguous stereogenic carbons have been synthesized with good diastereoselectivity.

The sulfur version of this sigmatropic shift is an efficient method for the synthesis of unsaturated dithioesters. Thiocarbonyl compounds can now be recognized as tools for organic synthesis (24).

The effect of a stereogenic centre on carbon 6 of the pericyclic nucleus is reported in the accompanying paper (47).

EXPERIMENTAL SECTION

General

All reactions were run under a positive nitrogen pressure. THF was distilled over sodium benzophenone ketyl. Preparative liquid chromatographs were performed on a Jobin-Yvon Chromatospac Prep 10 chromatograph or by flash chromatography. The column was prepared with a suspension of silica gel in the eluting solvent: a mixture of cyclohexane and ethyl acetate in the ratio indicated below.
^{1}H NMR 60 MHz spectra were run on a Varian EM 360 spectrometer and ^{1}H NMR 200 Hz on a JEOL JNM-FX 200 XX. The products were dissolved in the mentioned solvent. ^{1}HNMR 400 MHz were executed on a Bruker spectrometer (We wish to thank Professor Davoust, University of Rouen). Only assigned data are reported. They are in order: chemical shift in ppm, multiplicity (s, singulet ; d, doublet ; t, triplet ; q, quartet, hept, heptuplet ; m, multiplet), coupling constant in hertz, assignment. ^{13}C NMR spectra were determined at 20,15 MHz with a Bruker WP 80 spectrometer operating with broad band ^{1}H decoupling. The solvent used is indicated below. IR absorption spectra were run on Perkin-Elmer 257 and 684. The compound was dissolved in CCl_4 or $CDCl_3$. U.V. spectra were executed on Beckmann Acta M6. The products were dissolved in cyclohexane. Mass spectra were obtained at 70 eV with Varian Mat CH5 or with Nermag spectrometers and the data tabulated as m/e and relative intensities in percent. Elemental analyses were performed by Service Central d'Analyse of CNRS at Vernaison. The results are described as percentages.

Starting Materials

Methyl 3,4-dimethylpentanedithioate 1. The reaction of 1-propenylmagnesium bromide (50 mmol) with phenyl isothiocyanate (7.0 g, 51.8 mmol), followed by treatment with iodomethane (14.2 g, 100 mmol) gave (40) methyl N-phenyl-2-butenimidothioate (7.18 g, 37.6 mmol). Yield: 75 %. The 1,4-addition of isopropylmagnesium bromide (52.9 mmol) to methyl N-phenyl-2-butenimidothioate (5.11 g, 26.8 mmol) furnished (40) methyl N-phenyl-3,4-dimethylpentanimidothioate (4.38 g, 18.7 mmol). Yield: 70 %. Treatment of the imidithioate (4.29 g, 18.3 mmol) with hydrogen sulfide conducted to the dithioester **1.** By chromatography with cyclohexane, dithioester **1** was isolated (1.06 g, 7.4 mmol). Yield: 42 %.

Methyl 3-phenylbutanedithioate 2. The dithioester **2** was prepared from 3-phenylbutanoic acid with Davy's reagent (41, 42). ^{1}H NMR 60 MHz (CCl_4): 1.28 (d, J = 7 Hz, 3H, MeCH), 2.52 (s, 3H, SMe), 7.22 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): 19.9, 20.9, 41.5, 60.0, 126.4, 127.0, 128.4, 237.2. UV (cyclohexane): λ = 304 nm (π-->π^*), log ε = 4.06, λ = 456 nm (n-->π^*), log ε = 1.38. Anal. calcd. for $C_{11}H_{14}S_2$: C,62.81 ; H, 6.71 ; S, 30.48. Found: C, 62.92 ; H, 6.43 ; S, 30.34.

Methyl 3,4,4-trimethylpentanedithioate 3. The 1,4-addition of tertiobutyllithium (11.2 mmol) onto methyl N-phenyl-2-butenimidothioate (10 mmol) furnished methyl N-phenyl-3.4.4-trimethyl-pentanimidothioate (1.7 g, 6.8 mmol). Yield: 68 %. The treatment of this product (1.7 g, 4.3 mmol) with hydrogen sulfide conducted (40) to product **3** (818 mg, 4.3 mmol). Yield: 100 %.

3-Bromo-2-phenylpropene. A mixture of freshly distilled 2-phenylpropene (α-methylstyrene) (14.3 ml, 110 mmol), N-bromosuccinimide (12.24 g, 68.70 mmol) and carbon tetrachloride (12 ml) was heating (43) under reflux for two hours, after which the mixture was distilled. A mixture of 3-bromo-2-phenylpropene (68 %) and 1-bromo-2-phenylpropene (32 %) was obtained. Yield calculated from NBS was 45 %. $Eb_{0.05}$ = 71-74°C.

Methyl 3-phenyl-4-pentenedithioate 22. To a solution of LDA (15 mmol) in THF (50 ml) cooled to -30°C, methyl ethanedithioate (1.59 g, 15 mmol) was added dropwise. The mixture was stirred for 10 mn, then cinnamyl bromide (2.96 g, 15 mmol) diluted in THF (15 ml) was added. After 30 mn at -30°C and 5 mn at RT, we quenched with aqueous ammonium chloride. We extracted by partition between ethyl ether and brine, then dried over magnesium sulphate and evaporated the solvents. The product rearranged completely after a day of standing at room temperature to give compound **22** (3.33 g, 15 mmol). Yield: 100 %. ^1H NMR 60 MHz (CCl_4): 2.50 (s, 3H, Me), 3.31 (d, J = 7.5 Hz, 2H, CH_2C=S), 4.75 - 5.16 (m, 2H, CH_2=), 5.63 - 6.25(m, 1H, CH=), 7.17 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): 19.8, 50.5, 56.9, 115.2, 126.6, 127.8, 128.3, 139.9, 235.8. MS: 77 (7), 91 (36), 115 (65), 117 (100), 207 (3), 222 (19).

Methyl 3-methyl-4-pentenedithioate 23. Dithioester **23** (2.28 g, 14.3mmol) was prepared in the same way as **22** from crotyl bromide (2.04 g, 15 mmol). Yield: 95 %. ^1H NMR: 60 MHz (CCl_4): 1.05 (d, J = 6.5 Hz, 3H, MeCH), 2.63 (s, 3H, SMe), 2.96 (s, 2H, CH_2C=S), 4.78 - 5.20 (m, 2H, CH_2=), 5.42 - 6.05 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$): 19.1, 19.9, 39.3, 58.4, 113.6, 142.2, 237.4.

Methyl 3,4-dimethyl-4-pentenedithioate 24. The reduction (44) of tiglic acid (3 g, 30 mmol) by lithium aluminium hydride (1.14 g, 30 mmol) gave 2-methyl-2-buten-1-ol (1.34 g, 15.6 mmol). Yield: 52 %. The bromination (45) of the alcohol (1.03 g, 12 mmol) by phosphorus tribromide (3.25 g, 12 mmol) furnished 1-bromo-2-methylbut-2-ene (1.04 g, 7 mmol). Yield: 58 %. Dithioester **24** was prepared in the same way as **22** from the bromide (447 mg,4.5 mmol) with methyl ethanedithioate (318 mg, 3 mmol). After one day at room temperature the rearrangement was complete. Chromatography with a mixture of cyclohexane-ethyl acetate (95/5) gave **24** (485 mg, 2.78 mmol). Yield: 93 %.^1H NMR: 60 MHz (CCl_4): 1.05 (d, J = 7 Hz, 3H, MeCH), 1.74 (d, J = 2 Hz, 3H, MeC=), 2.62 (s, 3H, SMe), 3.00 (s, 2H, CH_2C=S), 4.70 (d, J = 2 Hz, 2H, CH_2=). ^{13}C NMR ($CDCl_3$): 18.7, 19.8, 19.9, 42.7, 57.4, 110.3, 148.2, 237.7.MS: 41 (100), 53 (13), 59 (20), 69 (46), 83 (15), 91 (23), 93 (19), 111 (10), 159 (16), 174 (12).

Methyl (*E*)-3-methyl-4-hexenedithioate 25. The 1,2-addition (46) of methylmagnesium iodide (150 mmol) to crotonaldehyde (10.5 g, 150 mmol) gave 3-penten-2-ol (8.58 g, 99.8 mmol). Yield: 67 %. The bromination (45) of the alcohol (2.58 g, 30 mmol) by potassium tribromide (8.13 g, 30 mmol) conducted to 4-bromo-2-pentene (3.45 g, 23.2 mmol). Yield: 77 %. The preparation of product **25** from the bromide (447 mg, 3 mmol) with HMPA (734 mg, 4.5 mmol) and methyl ethanedithioate (318 mg, 3 mmol) was like that of **22**. The rearrangement was complete after 3 hours. Chromatography with a mixture of cyclohexane-ethyl acetate: 95/5 gave **25** (470 mg, 4.70 mmol). Yield: 90 %. ^1H NMR: 60 MHz (CCl_4): 0.97 (d, J = 7 Hz, 3H, MeCH), 1.58 (d, J = 4.5 Hz, 3H, MeC=), 2.53 (s, 3H, SMe), 2.85 (s, 2H, CH_2C=S), 5.15 - 5.40 (m, 2H, CH=CH). ^{13}C NMR ($CDCl_3$): 17.8, 19.7, 19.8, 38.6, 59.0, 124.1, 135.0, 237.7. MS: 41 (67), 69 (100), 91 (28), 107 (16), 121 (70), 141 (13), 159 (26), 174 (22). Anal. calcd. for $C_8H_{14}S_2$: C, 55.17 ; H, 8.05 ; S, 36.78. Found: C, 52.56 ; H, 8.02 ; S, 36.64.

Synthesis of Ketenedithioacetals and Thio-Claisen Rearrangement

General Procedure

To a solution of LDA (2.8 mmol) in THF (14 ml) cooled to -20°C, the dithioester was added dropwise (2.8 mmol), then hexamethylphosphoramide (2.45 ml, 14 mmol; CAUTION : toxic) and the alkyl halide (2.8 mmol). The mixture was stirred for 5 mn at -20°C, then 15 mn at RT. We quenched with aqueous ammonium chloride, and extracted by partition between pentane and brine. The organic layers were dried over magnesium sulphate. The solvents were evaporated. The crude material is the S-allyl ketenedithioacetal, often accompanied by a minor amount of rearranged dithioester. The rearrangement is effected completely either by letting the product stand at room temperature or by heating it in methylcyclohexane at reflux (101°C) for a period indicated below. The obtained dithioesters were isolated by liquid chromatography. They are orange. The ketenedithioacetals and the dithioesters are very fragile, thus we could generally not obtain correct elemental analyses.

(*Z*)-1-Benzylthio-1-methylthio-3,4-dimethyl-1-pentene 7. Reaction of methyl 3,4-dimethylpentanedithioate **1** (493 mg, 2.8 mmol) with benzyl bromide (479 mg, 2.8 mmol) gave compound **7** (0.48 g, 1.82 mmol). Yield: 65 %. Ratio of *Z*/*E* isomers ≥ 93 : 7 from ^{1}H NMR 60 MHz (MeCH signals). ^{1}H NMR 60 MHz (CCl_4): 0.75 (d, J = 5.2 Hz, 6H, MeCH), 2.20 (s, 3H, SMe), 3.70 and 3.88 (AB, J = 12.8 Hz, 2H, SCH_2), 5.70 (d, J = 9.8 Hz, 1H, HC=), 7.10-7.30 (m, 5H, Ph). MS: 43 (11), 65 (13), 77 (5), 85 (52), 91 (100), 223 (53), 266 (12).

(*Z*)-1-Benzylthio-1-methylthio-3-phenyl-1-butene 8. Reaction of methyl 3-phenylbutanedithioate **2** (588 mg, 2.8 mmol) with benzyl bromide (0.33 ml, 2.8mmol), followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, afforded ketenedithioacetal **8** (682 mg, 2.27 mmol). Yield: 94 %. Ratio of *Z*/*E* isomers ≥ 93 : 7 from ^{1}H NMR 200 MHz (MeCH signals). ^{1}H NMR 200 MHz (CCl_4 + 5 % C_6D_6): 0.99 (d, J = 7.0 Hz, 3H, MeCH), 2.17 (s, 3H, SMe), 3.84 (s, 2H, SCH_2), 5.91 (d, J = 9.4 Hz, 1H, =CH). ^{13}C NMR ($CDCl_3$): 16.8, 21.0, 37.6, 40.4, 126.0, 127.0, 128.4, 129.0, 130.0, 138.6, 142.4, 145.1. MS: 43 (100), 58 (27), 91 (16), 105 (7), 161 (5), 209 (4), 264 (1), 300 (4).

(*Z*)- and (*E*)-1-Benzylthio-3,4,4-trimethyl-1-methylthio-1-pentenes 9. Reaction of methyl 3,4,4 trimethylpentanedithioate **3** (53.2 mg, 0.28 mmol) with benzyl bromide (0.033 ml, 0.28 mmol) furnished product **9** (53 mg, 0.190 mmol). Yield: 68 %. Ratio of Z/E isomers 87 : 13 from ^{1}H NMR 200 MHz (=CH signals). ^{1}H NMR 200 MHz (CCl_4 + 5 % C_6D_6): 0.56 (d, J = 7.0 Hz, 3H, MeCH), 0.73 (s, 9H, tBu), 2.23 (s,3H, SMe), 3.75 and 3.98 (AB, J = 13.4 Hz, 2H, SCH_2), 5.79 (d, J = 10.0 Hz, 1H, =CH of *E*), 5.89 (d, J = 10.2 Hz, 1H, =CH of *Z*).

(*Z*)-3.4-Dimethyl-1-methylthio-1-(2-propenylthio)-1-pentene 10. Proceded from the reaction of methyl 3.4-dimethylpentanedithioate **1** (239 mg, 1.35 mmol) with allyl bromide (115 microl, 1.35 mmol). An ^{1}H NMR 60 MHz spectrum of the crude product was run three hours after hydrolysis. We observed a mixture of ketenedithioacetal **10** and dithioester **13** (92 : 8).^{1}H NMR 60 MHz (CCl_4): 0.75 -1.05 (M, iPr masking the signal of MeCH), 2.20 (s, 3H, SMe), 3.30 (d, J = 7.0 Hz, 2H, SCH_2), 4.80-5.25 (m, 2H, H_2C=), 5.40-5.65 (m, 1H, HC=), 5.82 (d, J = 10.0 Hz, 1H, HC=CSMe).

Methyl 2-(1.2-dimethylpropyl)-4-pentenedithioate 13. Thermolysis of **10** under reflux in methylcyclohexane for 7 hours, followed by chromatography with cyclohexane, gave dithioester **13** (208 mg, 0.96 mmol). Ratio of A/B diastereoisomers 77 : 23 from ^{1}H NMR 200 MHz (MeCH signals). Yield: 74 %. ^{1}H NMR 60 MHz (CCl_4): 0.81 (d, J = 6.60 Hz, 6H, Me_2CH of A), 0.90 (d, J = 6.60 Hz, 6H, Me_2CH of B), 0.95 (d, J = 6.84 Hz, 3H, MeCH of A), 1.04 (d, J = 6.84 Hz, 3H, MeCH of B), 2.62 (s, 3H, SMe), 4.65-5.10 (m, 2H, H_2C=), 5.20-5.75 (m, 1H, HC=). ^{13}C NMR: 10.9, 15.5 (A), 15.9 (B), 21.8 (A), 22 (B), 29.0, 38.4 (B), 38.9 (A), 44.7, 64.4, 116.2, 135.8 (A), 136.0 (B), 244.1. MS: 43 (33), 69 (31), 99 (29), 131 (51), 146 (100), 173 (53), 201 (16), 216 (9).

(*Z*)-1-Methylthio-1-(2-propenylthio)-3-phenyl-1-butene 11. Proceded from the reaction of methyl 3-phenylbutanedithioate **2** (588 mg, 2.8 mmol) with allyl bromide (0.25 ml, 2.8 mmol). An ^{1}H NMR 60 MHz spectrum of the crude product was run one hour after hydrolysis. We observed a mixture of ketenedithioacetal **11** and dithioester **14** (90 : 10). ^{1}H NMR 60 MHz (CCl_4): 1.32 (d, J = 7.0 Hz, 3H, MeCH), 2.03 (s, 3H, SMe), 3.35 (d, J = 7.0 Hz, 2H, SCH_2), 4.83 - 5.27 (m, 2H, CH_2=), 5.38 - 6.31 (m, 1H, CH=), 6.10 (d, J = 10.0 Hz, 1H, CH of ketenedithioacetal), 7.19 (s, 5H, Ph).

Methyl 2-(1-phenylethyl)-4-pentenedithioate 14. After letting **11** stand at RT for 24 hours, followed by chromatography with cyclohexane, product **14** was isolated (617 mg, 2.48 mmol). Ratio of A/B diastereoisomers 82 : 18 from ^{1}H NMR 200 MHz (MeCH signals). Yield: 89 %. ^{1}H NMR 200 MHz (CCl_4 + 5 % C_6D_6): 1.16 (d, J = 6.6 Hz, 3H, MeCH of A), 1.34 (d, J = 6.8 Hz, 3H, MeCH of B), 2.30 (s, 3H, SMe of B), 2.60 (s, 3H, SMe of A), 4.62 - 4.98 (m, 2H, CH_2=), 5.30 - 5.65 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$): 19.3, 20.6, 38.3 (B), 40.3 (A), 46.0 (B), 46.6 (A), 67.2 (B), 67.5 (A), 116.2 (A), 116.6 (B), 126.6, 127.7, 127.9, 128.0, 128.6, 135.6, 145.0, 242.4. MS: 43 (100), 97 (48), 105 (96), 145 (62), 161 (14), 203 (15), 235 (5), 250 (21).

(*Z*)-3,4,4-Trimethyl-1-methylthio-1-(prop-2-enylthio)-1-pentene 12. Proceded from the reaction of methyl 3,4,4-trimethylpentanedithioate **3** (266 mg, 1.4 mmol) with allyl bromide (0.125 ml, 1.4 mmol). ^{1}H NMR 60 MHz: 0.87 (s, 9H, tBu), 2.03 (s, 3H, SMe), 3.33 (d, J = 7.0 Hz, 2H, SCH_2), 5.93 (d, J = 10.0 Hz, 1H, =CH of ketenedithioacetal).

Methyl 2-(1,2,2-trimethylpropyl)-4-pentenedithioate 15. Thermolysis of **12** under reflux in methylcyclohexane for 7 hours, followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, furnished compound **15** (287 mg, 1.25 mmol). Ratio of A/B diastereoisomers 95 : 5 from ^{1}H NMR 400 MHz (SMe signals). Yield: 89 %. ^{1}H NMR 400 MHz: 0.95 (s, 9H, tBu), 1.00 (d, J = 8 Hz, 3H, MeCH), 2.54 (s, 3H, SMe of B), 2.57 (s, 3H, SMe of A), 4.89 (ddt, J_1 = 11.3 Hz, J_2 = 1.1 Hz andJ_3 =

1.1 Hz, 1H, H of H_2C= *trans* to the chain), 4.95 (ddt, J_1 = 19.4 Hz, J_2 = 2.2 Hz andJ_3 = 1.1 Hz, 1H, H of H_2C= *cis* to the chain), 5.62 (ddt, J_1 = 19.4 Hz, J_2 = 11.3 Hz andJ_3 = 8.0 Hz, 1H, H of =CH-). ^{13}C NMR ($CDCl_3$): 10.4, 19.2, 27.5, 28.2, 35.3, 36.0, 48.8, 59.8, 115.8, 136.5, 245.2. MS: 85 (81), 91 (35), 131 (31), 145 (42), 146 (20), 173 (100), 215 (12), 230 (17).

(*Z*)-1-(2-Methylprop-2-enylthio)-1-methylthio-3-phenyl-1-butene 16. Proceded from the reaction of methyl 3-phenylbutanedithioate **2** (588 mg, 2.8 mmol) with 3-chloro-2-methylpropene (0.28 ml, 2.8 mmol). An ^1H NMR 60 MHz spectrum of the crude product was run four hours after hydrolysis. We observed a mixture of ketenedithioacetal **16** and dithioester **19** (94 : 6). ^1H NMR 60 MHz (CCl_4): 1.30 (d, J = 7 Hz, 3H, MeCH), 1.77 (s, 3H, MeC=), 2.19 (s, 3H, SMe), 3.31 (s, 2H, SCH_2), 5.99 (d, J = 10 Hz, 1H, =CH of ketenedithioacetal), 7.08 (s, Ph).

Methyl 4-methyl-2-(1-phenylethyl)-4-pentenedithioate 19. Thermolysis of **16** under reflux in methylcyclohexane for 2 hours, followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, conducted to dithioester **19** (702 mg, 2.66 mmol). Ratio of A/B diastereoisomers 78 : 22 from ^1H NMR at 200 MHz (MeC = signals). Yield: 96 %. ^1H NMR 200 MHz (CCl_4 + 5 % C_6D_6): 1.17 (d, J = 6.8 Hz, 3H, MeCH of A), 1.36 (d, J = 6.8 Hz, 3H, MeCH of B), 1.55 (s, 3H, MeC = of A), 1.71 (s, 3H, MeC = of B), 2.30 (s, 3H, SMe of B), 2.60 (s, 3H, SMe of A). ^{13}C NMR ($CDCl_3$): 19.4, 20.7, 21.8 (A), 22.3 (B), 42.2 (B), 44.5 (A), 46.3 (B), 46.9 (A), 65.6 (B), 65.7 (A), 112.6 (A), 112.9 (B), 126.1, 126.6, 127.7, 127.9, 128.6, 142.6, 145.2, 242.6. MS: 91 (46), 105 (100), 111 (39), 159 (26), 161 (22), 217 (5), 250 (3), 264 (8).

(*Z*)-1-(2-Bromoprop-2-enylthio)-3,4,4-trimethyl-1-methylthio-1-pentene 17. Proceded from the reaction of methyl 3,4,4-trimethylpentanedithioate **3** (124.45 mg, 0.65 mmol) with 2.3-dibromopropene (130 mg, 0.65 mmol). ^1H NMR 60 MHz (CCl_4): 0.88 (s, tBu hiding the MeCH signal), 2.25 (s, 3H, SMe), 3.68 (d, J = 4 Hz, 2H, SCH_2), 5.43 and5.75 (2m, 2H, H_2C=), 6.10 (d, J = 10 Hz, 1H, HC=).

Methyl 4-bromo-2-(1,2,2-trimethylpropyl)-4-pentenedithioate 20. Thermolysis of **17** under reflux in methylcyclohexane for 6 hours, followed by chromatography with cyclohexane, afforded product **20** (121.20 mg, 0.93 mmol). Yield: 60 %. Ratio of A/B diastereoisomers ≥ 90 : 10 from ^1H NMR at 200 MHz (SMe signals).^1H NMR 200MHz (CCl_4): 1.02 (s, tBu hiding the MeCH signal), 2.57 (s, 3H, SMe), 5.28 and 5.41 (2s, 2H, H_2C=). ^{13}C NMR: 10.2, 19.3, 28.1, 35.4, 43, 48.4, 56.7, 119.1, 132.1, 243.3. UV (hexane): λ max = 304 nm (π -> π*), log ε = 4.01, λ max = 453 nm (n -> π*), log ε = 1.26. Anal. calcd for $C_{12}H_{21}S_2Br$: C, 46.60 ; H, 6.79 ; S, 20.71. Found: C, 46.98 ; H 6.80 ; S, 20.84.

(*Z*)-3,4,4-Trimethyl-1-methylthio-1-(2-phenylprop-2-enylthio)-1-pentene 18. Proceded from the reaction of methyl 3,4,4-trimethylpentanedithioate **3** (120 mg, 0.63 mmol) with 3-bromo-2-phenylpropene (201.73 mg, 0.63 mmol). Ratio of **18/21** = 75 : 25 from ^1H NMR 60 MHz. ^1H NMR 60 MHz (CCl_4): 0.80 (s, 9H, tBu), 2.18 (s, 3H, SMe), 3.80 (e, 2H, SCH_2), 5.18 (m, 2H, H_2C=), 5.94 (d, J = 10 Hz, 1H, HC=CSMe), 7.30 (m, 5H, Ph).

Methyl 4-phenyl-2-(1,2,2-trimethylpropyl)-4-pentenedithioate 21. Thermolysis of **18** under reflux in methylcyclohexane for 8 hours, followed by chromatography with cyclohexane, gave dithioester **21** (87 mg, 0.285 mmol). Ratio of A/B diastereoisomers ≥ 90 : 10 from ^1H NMR 60 MHz. Yield: 45 %. ^1H NMR 60 MHz (CCl_4): 0.86 (s, 9H, tBu), 2.48 (s, 3H, SMe), 4.83 and4.94 (2m, 2H, H_2C=), 7.15 (s, 5H, Ph).

(*Z*)-1-Methylthio-3-phenyl-1-(prop-2-enylthio)-1,4-pentadiene 26. Proceded from the reaction of methyl 3-phenyl-4-pentenedithioate **22** (2.0 g, 9 mmol) with allyl bromide (0.780 ml, 9 mmol). An ^1H NMR 60 MHz spectrum of the crude product was run three hours after hydrolysis. We observed a mixture of ketenedithioacetal **26** and dithioester **30** (91 : 9). ^1H NMR 60 MHz (CCl_4): 2.20 (s, 3H, Me), 3.32 (d, J = 7 Hz, 2H, SCH_2), 4.57 - 6.17 (m, 3H, $CH=CH_2$), 5.96 (d, J = 9 Hz, 1H, =CH of ketenedithioacetal), 7.05 (s, 5H, Ph).

Methyl 3-phenyl-2-(prop-2-enyl)-4-pentenedithioate 30. After letting **26** stand at RT for 2 days, followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, dithioester **30** was obtained (2.36 g, 9 mmol). Ratio of A/B diastereoisomers 62 : 38 from ^{13}C NMR (assuming similar relaxation times). Yield: 100 %. ^1H NMR 60 MHz (CCl_4): (s, 3H, SMe of B), 2.58 (s, 3H, SMe of A), 4.53 - 6.37 (m, 3H, $CH=CH_2$), 7.22 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): 19.3 (A), 19.4 (B), 39.5 (A), 39.9 (B), 56.9 (A), 57.4 (B), 64.9 (B), 65.4 (A), 116.1 (A), 116.6, 116.9 (B), 126.5, 126.9, 128.3, 128.4, 128.7, 128.9, 135.3 (A), 135.5 (B), 138.9 (A), 139.7 (B), 240.8. MS: 91 (30), 97 (26), 115 (35), 117 (100), 118 (11), 131 (15), 145 (15), 221 (11), 247 (3), 262 (3).

(Z)-3-Methyl-1-methylthio-1-(prop-2-enylthio)-1,4-pentadiene 27. Proceded from the reaction of methyl 3-methyl-4-pentenedithioate **23** (480 mg, 3 mmol) with allyl bromide (0.26 ml, 3 mmol). An ^{1}H NMR 60 MHz spectrum of the crude product was run two hours after hydrolysis. We observed a mixture of ketenedithioacetal **27** and dithioester **31** (80 : 20). ^{1}H NMR 60 MHz (CCl_4): 1.07 (d, J = 7 Hz, 3H, MeCH), 2.05 (s, 3H, Me), 3.35 (d, J = 7 Hz, 2H, SCH_2), 4.71 - 6.27 (m, 3H, $CH=CH_2$), 5.77 (d, J = 9.5 Hz, 1H, =CH of ketenedithioacetal).

Methyl 3-methyl-2-(prop-2-enyl)-4-pentenedithioate 31. After letting **27** stand at RT for 2 days, followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, compound **31** was isolated (509 mg, 2.55 mmol). Ratio of A/B diastereoisomers 81 : 19 from ^{13}C NMR (assuming similar relaxation times). Yield: 85 %. ^{1}H NMR 60 MHz (CCl_4): 0.94 (d, J = 7 Hz, MeCH of A), 1.08 (d, J = 7 Hz, 3H, MeCH of B), 2.40 (s, 3H, SMe of B), 2.60 (s, 3H, SMe of A), 4.66 - 6.03 (m, 3H, $CH=CH_2$). ^{13}C NMR ($CDCl_3$): 17.6 (B), 18.8 (A), 19.1 (B), 19.2 (A), 38.1 (B), 39.8 (A), 43.5 (B), 44.7 (B), 65.7 (B), 65.9 (A), 114.3 (B), 115.4 (A), 116.3 (A), 116.5 (B), 135.6 (B), 141.0 (B), 141.9 (A), 241.1 (B), 242.0 (A). MS: 55 (76), 91 (39), 97 (100), 111 (34), 145 (18), 159 (18), 185 (14), 200 (2).

(Z)-3,4-Dimethyl-1-methylthio-1-(prop-2-enylthio)-1,4-pentadiene 28. Proceded from the reaction of methyl 3,4-dimethyl-4-pentenedithioate **24** (522 mg, 3 mmol) with allyl bromide (0.26 ml, 3 mmol). ^{1}H NMR 60 MHz (CCl_4): 1.10 (d, J = 7 Hz, 3H, MeCH), 1.70 (d, J = 1 Hz, 3H, MeC=), 2.25 (s, 3H, SMe), 3.38 (d, J = 7 Hz, 2H, SCH_2), 4.66 - 6.05 (m, 3H, $CH=CH_2$), 5.70 (d, J = 9.5 Hz, 1H, =CH of ketenedithioacetal).

Methyl 3,4-dimethyl-2-(prop-2-enyl)-4-pentenedithioate 32. After letting **28** stand at RT for 4 days, followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, product **32** was isolated (267 mg, 1.25 mmol). Ratio of A/B diastereoisomers 82 : 18 from ^{13}C NMR (assuming similar relaxation times). Yield: 42 %. ^{1}H NMR 60 MHz (CCl_4): 0.93 (d, J = 7 Hz, 3H, MeCH of A), 1.09 (d, J = 7 Hz, 3H, MeCH of B), 2.57 (s, 3H, SMe of B), 2.62 (s, 3H, SMe of A). 4.53 - 5.03 (m, 3H, $CH=CH_2$). ^{13}C NMR ($CDCl_3$): 16.9 (B), 17.9 (A), 18.4, 19.2 (A), 19.6 (B), 40.1, 47.2 (B), 48.1 (A), 63.8 (B), 64.4 (A), 112.1 (B), 112.7 (A), 116.2 (A), 117.4 (B), 135.7, 147.4, 242.6. MS: 41 (66), 69 (25), 91 (46), 97 (68), 145 (46), 157 (32), 167 (100), 173 (78), 181 (43), 199 (93), 214 (49).

(Z)-3-Methyl-1-methylthio-1-(prop-2-enylthio)-1,4-hexadiene 29. Proceded from the reaction of methyl 3-methyl-4-hexenedithioate **25** (418 mg, 2.4 mmol) with allyl bromide (0.21 ml, 2.4 mmol). An ^{1}H NMR 60 MHz spectrum of the crude product was run three hours after hydrolysis. We observed a mixture of ketenedithioacetal **29** and dithioester **33** (84 : 16). ^{1}H NMR 60 MHz (CCl_4): 1.02 (d, J = 7 Hz, 3H, MeCH), 1.46 (s, 3H, MeC=), 2.16 (s, 3H, SMe), 3.28 (d, J = 7 Hz, 2H, SCH_2), 4.75 - 5.85 (m, 3H, $CH=CH_2$), 5.65 (d, J = 9 Hz, 1H, $CH=CS_2$).

Methyl 3-methyl-2-(prop-2-enyl)-4-hexenedithioate 33. After letting **29** stand at RT for 2 days, followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, dithioester **33** was isolated (233 mg, 1.09 mmol). Ratio of A/B diastereoisomers 72 : 28 from ^{13}C NMR (assuming similar relaxation times). Yield: 46 %. ^{1}H NMR 60 MHz (CCl_4): 0.91 (d, J = 7 Hz, 3H, MeCH of A), 1.05 (d, J = 7 Hz, 3H, MeCH of B), 1.70 (d, J = 4 Hz, 3H, MeC=), 2.57 (s, 3H, SMe of B), 2.63 (s, 3H, SMe of A), 4.70 - 5.86 (m, 3H, $CH=CH_2$). ^{13}C NMR ($CDCl_3$): 17.8 (A), 18.0 (B), 19.1 (A), 20.0 (B), 38.0 (B), 39.9 (A), 42.4 (A), 43.7 (A), 66.1 (B), 66.4 (A), 96.2, 116.1 (A), 116.3 (B), 124.7 (B), 125.9 (A), 132.5 (B), 133.8 (B), 134.7 (A), 135.7 (A), 242.2. MS: 41 (57), 69 (100), 91 (24), 97 (40), 145 (19), 173 (16), 199 (20), 214 (3).

(Z)-1-(But-2-enylthio)-1-methylthio-3-phenyl-1-butene 34. Proceded from the reaction of methyl 3-phenylbutanedithioate **2** (588 mg, 2.8 mmol) with 4-bromobut-2-ene (0.29 ml, 2.8 mmol). ^{1}H NMR 60 MHz (CCl_4): 1.32 (d, J = 7.0 Hz, 3H, MeCHPh), 1.60 (d, J = 4.5 Hz, 3H, MeCH=), 2.19 (s, 3H, SMe), 3.28 (d, J = 6.6 Hz, 2H, SCH_2), 5.27 - 5.57 (m, 2H, CH=CH), 6.07 (d, J = 10.0 Hz, 1H, =CH of ketenedithioacetal), 7.15 (s, SPh)

Methyl 3-methyl-2-(1-phenylethyl)-4-pentenedithioate 35. Thermolysis of **34** under reflux in methylcyclohexane for 6 hours, followed by chromatography with a mixture of cyclohexane and ethyl acetate 95/5, conducted to compound **35** (724 mg, 2.75 mmol). Ratio of A/B diastereoisomers 74 : 26 from ^{1}H NMR 200 MHz (SMe signals). Yield: 98 %. ^{1}H NMR 200 MHz (CCl_4 + 5 % C_6D_6): 0.88 (d, J = 6.6 Hz, 3H, MeCHCH = of B), 0.96 (d, J = 6.6 Hz, 3H, MeCHCH = of A), 1.14 (d, J = 6.6 Hz, 3H, MeCPh of B), 1.22 (d, J = 6.4 Hz, 3H, MeCPh of A), 2.47 (s, 3H, SMe of A), 2.56 (s, 3H, SMe of B), 4.74 - 5.05 (m, 2H, CH_2=), 5.68 (m, 1H, CH = of A), 5.99 (m, 1H, CH = of B). ^{13}C NMR ($CDCl_3$): 16.1, 18.6 (A), 19.3 (B), 19.7 (A), 20.7 (B), 39.5 (B), 40.7 (A), 43.2 (A), 43.7 (B), 71.4 (A), 71.7 (B), 113.9 (A), 114.9 (B), 126.4, 127.1, 127.7, 128.4, 139.5, 142.3 (A), 142.7 (B), 145.1, 238.5 (B), 239.1 (A). MS: 91 (38), 105 (100), 159 (53), 161 (42), 209 (14), 217 (21), 249 (8), 264 (26).

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