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ACCESS TO DIETHYLENIC DITHIOESTERS BY THIO-CLAISEN REARRANGEMENT

FURTHER EXAMPLES OF REVERSIBILITY OF THE CLAISEN REARRANGEMENT

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Abstract - The stereochemistry of the deprotonation of β-unsaturated dithioesters with LDA has been examined : a stereochemically pure dienethiolate is formed from methyl buten-3-dithioate. Protonation of lithium dienethiolates mostly affords conjugated unsaturated dithioesters. S-alkylation of dienethiolates with allylic bromides furnishes quantitatively S-allyl ketene dithioacetals. The thermal rearrangement of these dithioacetals leads to diethylenic dithioesters under mild conditions (from 20°C to 100°C). The thio-Claisen transposition is thus confirmed as a facile sigmatropic shift. It is also demonstrated that the reverse reaction (retro thio-Claisen) proceeds simultaneously. The equilibrium mixture of ketene dithioacetal and dithioester is usually in the range of 70 : 30 to 95 : 5. Thiophilic addition to these diunsaturated dithioesters followed by treatment with alkyl halides affords diunsaturated dithioacetals. These masked ketones may be viewed as arising from alpha regioselective allylation of β-unsaturated ketones.

The regio-and stereoselective formation of C-C bonds by Claisen rearrangement has received a great deal of applications to organic synthesis [1-4].

In contrast much less is known about the thio-Claisen transposition in the non aromatic series. [4-6] It has recently been established [7-10] that the thermal reaction of precursors such as allyl vinylsulphides and propargyl ketene dithioacetals is thermodynamically favoured ($\Delta H^{\ddagger} \sim$ 20-25 kcal/mol) over the analogous reaction in the oxygen series. Some uses in synthesis have been reported. [11-18]

Y = R, SR

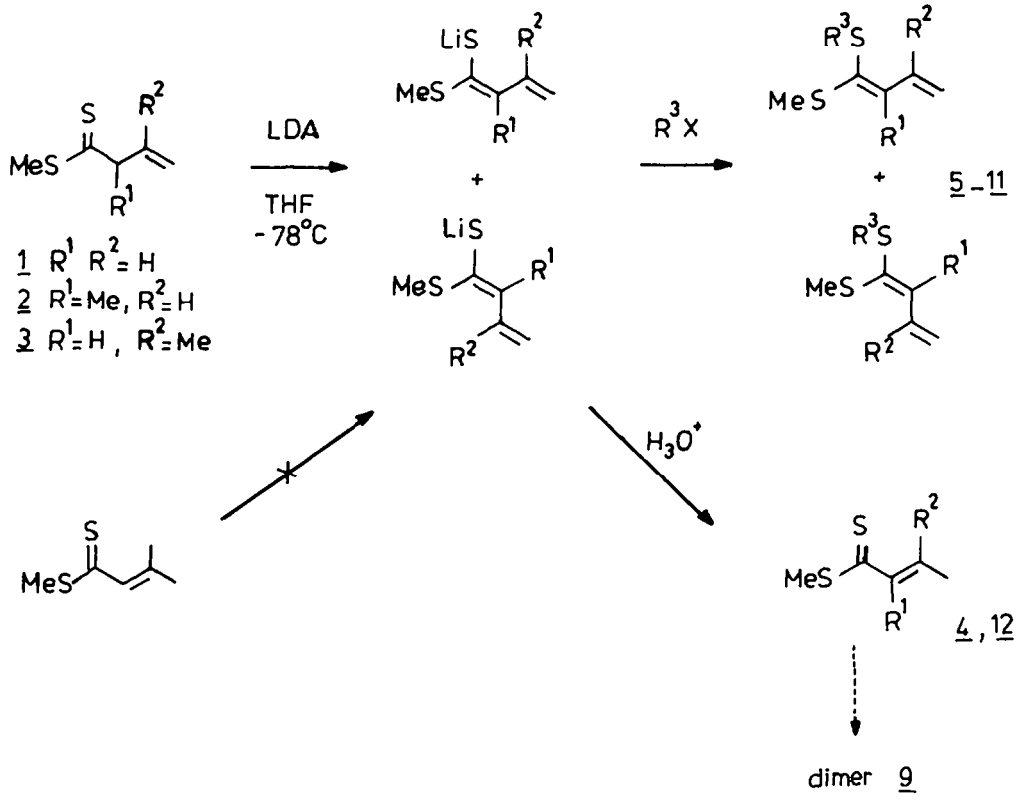
The goal of our work is an investigation of the synthesis of diunsaturated dithioesters by deprotonation of monounsaturated dithioesters, S-alkylation by allyl halides followed by [3.3] sigmatropic shift. We have achieved an allylation on the α position of thiocarbonyl compounds bearing a β unsaturation. We have also transformed the resulting dithioesters by one of the specific reactions [19] of this class of compounds : the thiophilic addition.

DEPROTONATION OF UNSATURATED DITHIOESTERS

STEREOCHEMISTRY AND ELECTROPHILIC ATTACK OF DIENETHIOLATES

β-Unsaturated dithioesters 1-3 are easily available from the reaction of allyl Grignard reagents with either phenyl isothiocyanate, methyl iodide and hydrogen sulphide [20] or with carbon disulphide and methyl iodide. [21] Basic isomerization of 3 affords [21] α-unsaturated dithioester 4.

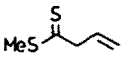
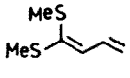
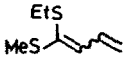
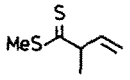
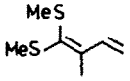
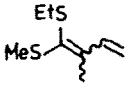
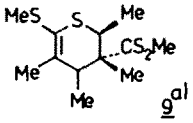
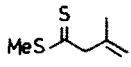
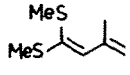
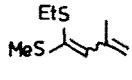
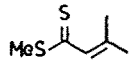
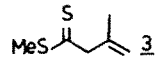
We have first looked at the stereochemistry of the deprotonation [21-23] of dithioesters 1-4 under kinetic conditions (LDA, THF, -78°C). Whereas aliphatic dithioesters are deprotonated instantaneously [24] at -78°C, the reaction of base with β-unsaturated substrates must be prolonged up to 30 min for 1 and 1 hr for 2 and 3. Reaction with methyl iodide at -78°C alkylates lithium dienethiolates on sulphur, quantitatively yielding ketene dithioacetals 5, 7, 10 (scheme 1, table 1). However deprotonation of the conjugated dithioester 4, which is even slower, does not selectively afford the dienethiolate, probably because of the strong reactivity of the dithioester as a Michael acceptor.

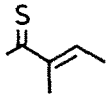


Scheme 1

To differenciate the isomeric cis and trans dienethiolates, we have carried out their alkylation with a radical other than methyl by using ethyl iodide as we already know that S-alkylation of enethiolates proceeds stereospecifically. [15,25] The NMR spectra of the obtained dithioacetals 8 and 11, recorded directly after extraction, exhibits two methylthio signals that can be assigned to cis and trans isomers in the ratios 60 : 40 and 67 : 33 (or vice versa). In the case of dithioester 1 an original observation has been made : a single ketene dithioacetal 6 has been formed. Though we have not determined the configuration of the principal or unique ketene dithioacetals 6,8,11, our group [15, 25] has formerly shown that the kinetic deprotonation of dithiopropanoates preferentially gives the cis (SLi and Me) lithium thioenolate. The high selectivity for the deprotonation of dithioester 1 can be linked to a possible, but weak, coordination between Li and the carbon-carbon double bond, or preferably to a higher stability of the ground state conformation of the dithioester. Other exemples of highly selective cis deprotonation have been reported with thioamides [16,26] and with a dialkyl thioketone. [27] To our knowledge, the stereochemistry of the analogous deprotonation of β-unsaturated carboxylic esters [28] is not known. Lithium dienolates of mainly cis configuration have been prepared from the α isomers. [29-31]

Table 1. Deprotonation of β-unsaturated dithioesters and electrophilic attack by RI or H_3O^+.

Dithioester	Deprotonation time at -78°C (min.)	Electrophile	Reaction conditions temp. (°C)	Reaction conditions time (min.)	Product	Isomeric ratio
 1	30	MeI	-78	15	 5	
"	"	EtI	0	75	 6	100 : 0
 2	60	MeI	-78	15	 7	
"	"	EtI	0	75	 8	60 : 40
"	"	NH_4Cl / H_2O	-78	inst.	 9[a]	
 3	60	MeI	-78	15	 10	
"	"	EtI	0	75	 11	67 : 33[b]
"	"	NH_4Cl / H_2O	-78	inst.	 4 +  3	80 : 20
"	"	"	0	75	"	100 : 0

a) [4 + 2] cycloaddition dimer [34] of dithioester 12 = 

b) After equilibration = 47 : 53.

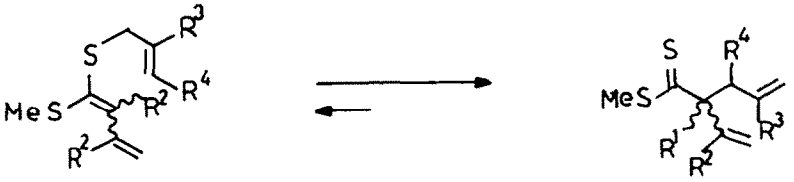
We have tested the configurationnal stability of the unsymmetrical ketene dithioacetals as a requirement for the stereocontrol of the sequence. CCl_4 solution of dithioacetals were kept at room temperature for weeks : NMR spectra of compounds 6 and 8 were unchanged. In contrast ketene dithioacetal 11 undergoes a slow evolution : after 3 weeks the isomer ratio is 47 : 53. Therefore we have to consider that the thio-Claisen rearrangement, wich will take place slowly at room temperature, will likely be preceded by the thermodynamic equilibration of cis and trans ketene dithioacetals.

Prior to treating dienethiolates by allylic halides we have looked at their protonation that will conduct to α-or (and) β-unsaturated dithioesters. For the the oxygen series, this reaction has been recently studied : one usually gets the non conjugate isomer.[28,32,33] We observed (table 1) that protonation by aqueous ammonium chloride of dienethiolate arising from dithioester 2 leads to the heterocycle 9, a [4 + 2] cycloadduct of the conjugate dithioester 12 to itself. [34] The reaction from dithioester 3 leads to the conjugate dithioester 4 mainly at -78°C, and selectively at 0°C.

THIO-CLAISEN REARRANGEMENT

Lithium dienethiolate, which were prepared as above by deprotonation of β-unsaturated dithioesters 1 - 3 at -78°C, were treated from -78°C to 0°C by four allylic bromides (allyl, methallyl, crotyl and prenyl). The resulting ketene dithioacetals 13 - 23 are somewhat labile compounds that could however be used as crude materials for the following step.

The thermolysis of dithioacetals 13 - 23 was carried out either neat at room temperature or in refluxing cyclohexane (80°C) or methyl cyclohexane (101°C) solution. Except in the case of compounds 19 and 23 (from prenyl bromide), we observed the formation of previously unknown diethylenic dithioesters 24 - 32 (scheme 2, table 2). This thio-Claisen rearrangement of neutral species occurs under relatively mild conditions. Brandsma et al and us have already measured [7,9,10] a significant decrease of the activation enthalpy of the [3.3] sigmatropic shift of unsaturated sulphides, as compared with the oxygen series.



A
13-18 , 20-22

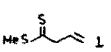
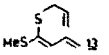
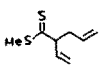
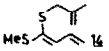
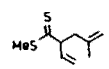
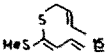
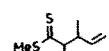
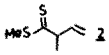
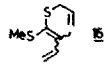
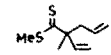
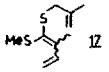
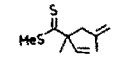
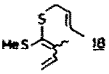
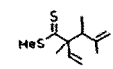
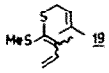
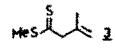
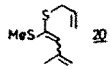
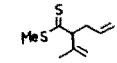
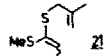
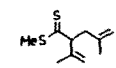
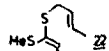
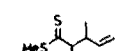
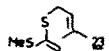
B
24-32

Scheme 2

Dithioesters 26, 29 and 32, bearing two chiral centres, were isolated as mixtures of diastereoisomers, even when the starting material was stereochemically homogeneous (table 2, entry 3). The Claisen and thio-Claisen rearrangement being stereospecific,[1-3, 35] we have to assume that dithioacetals 15, 18 and 22 (table 2, entries 3,6,10) underwent cis trans equilibration during heating and prior to the pericyclic reaction.

For two cases (table 2, entries 4, 8), NMR spectra of the reaction product indicated that it is devoid from starting dithioacetal : after liquid chromatography, dithioesters 27, 30 could be isolated with excellent yields. For entries 1-3, 5-6, and 9-10 we obtained a mixture of dithioester and dithioacetal even when heating was prolonged. This raised the question of an equilibrium between ketene dithioacetal A and dithioester B (scheme 2). In order to gain evidence for further exemples of retro-Claisen rearrangement [9-10], we needed to isolate pure dithioester B, submit it to the same reaction conditions and monitor the formation of dithioacetal A. We could accomplish the separation of dithioester B by medium pressure liquid chromatography in five instances 24 - 26 and 31 - 32.

Table 2 : Thio-Claisen rearrangement.

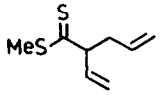
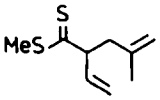
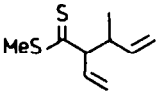
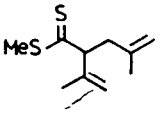
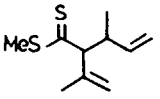
Entry	Starting material	Ketene dithioacetal [a]	Rearrangement conditions [b] temp. (°C)	time	Products dithioester	dithioacetal	Ratio [c] dithio/dithio-ester / acetal	Yield of isolated product(s) (%)
1	 1	 13	80	1hr	 24	+ 13	96:4	24 = 66
2	"	 14	"	1hr30mn	 25	+ 14 [d]	89 11	25 = 38 25+14 = 65
3	"	 15	"	1hr30min	 26 (diast 26 74)	+ 15 [d]	72 28	26 = 56
4	 2	 16	"	2hr15mn	 27		100:0	27 = 93
5	"	 17	"	6hr30mn	 28	+ 17 [d]	72 28	28+17=99
6	"	 18	101	24hr	 29 (diast. 62 38)	+ 18	23:77	
7	"	 19	"	7hr	19		0:100	
8	 3	 20	20	3days	 30		100 0	30 = 75
9	"	 21	"	4days	 31	+ 21	85:15	31 = 80
10	"	 22	"	13days	 32 (diast 58:42)	+ 22	81:19	32 = 60
11	"	 23	101	3hr20min	23		0:100	

a) Obtained by deprotonation of dithioesters at -78°C and reaction with allyl bromides from -78°C to 0°C. b) Reactions are carried out with a neat sample (20°C), or in refluxing cyclohexane (80°C) or methylcyclohexane (101°C) solutions. c) Determined by NMR of the crude product. d) Recovered as a mixture of geometrical isomers ; 14 = 50 : 50 ; 15 = 61 : 39 ; 17 = 49 : 51 ; 18 = 48 : 52 ; 19 = 52 : 48 ; 21 = 50 : 50 ; 22 = 51 : 49 ; 23 = 50 : 50.

These compounds were then kept at -18°, at room temperature, or heated up at 80°C (table 3). Examination of the NMR spectra of reaction mixtures reveals production of dithioacetals 13 - 15 and 21 - 22. It is truly demonstrative for entries 3, 9 and 10 where the concentration of dithioacetal is even easier to detect. This adds a second type of exemples of reversible thio-Claisen rearrangement : we have previously reported that γ-unsaturated thioketones are in equilibrium with allyl vinyl sulphides [9-10] . It is here the first reversible case observed with dithioesters. We suspect that careful analysis of other thio-Claisen products [4-6] could reveal equilibrium mixtures.

Our results confirm that the Claisen rearrangement; like other [3.3] sigmatropic shifts, proceeds under thermodynamic control ; this fact is often forgotten in the oxygen series [36] due to the large stability difference between reactant and product which drives the equilibrium towards the right. In contrast the sulphur compounds (e.g. A and B) exhibit close formation enthalpies.

Table 3. Reversibility of the thio-Claisen rearrangement

Entry of table 2	Starting material		Reaction conditions temp. (°C)	time	Products	Dithioester / Dithioacetal ratio
1		24	20[a]	14 days	24 + 13	95 : 5
			80[b]	2 hr 20 min	"	95 : 5
2		25	20[a]	14 days	25 + 14	94 : 6
			80[b]	2 hr 15 min	"	89 : 11
3		26	20[a]	14 days	26 + 15	80 : 20[c]
			80[b]	2 hr 40 min	"	72 : 28[d]
9		31	20[a]	4 days	31 + 21	73 : 27
			-18	14 months	"	78 : 22
10		32	20[a]	4 days	32 + 22	87 : 13[e]
			-18	18 months	"	85 : 15[f]

a) CCl_4 solution. b) Cyclohexane solution. c) Ratio of dithioester 26 diastereoisomers = 51 : 49. d) Preceding ratio= 32 : 68. e) Ratio of dithioester 32 diastereoisomers = 59 : 41. f) Preceding ratio = 58 : 42.

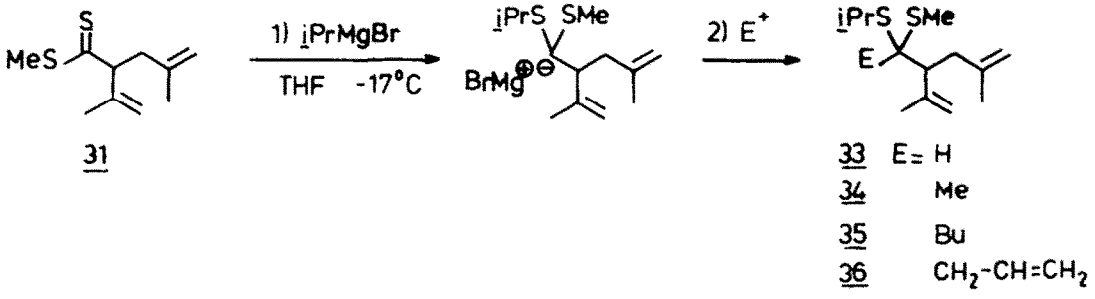
The position of the equilibrium between A and B varies according to the substitution of the carbon chain. The higher the steric bulk around the newly formed C-C bond, the more shifted towards the left (B→A) is the equilibrium. For S-prenyl dithioacetals 19 and 23 no rearrangement was observed under a variety of conditions (entries 7, 11). A plausible explanation is a total shifting towards the left (B ⟶ A).

From the synthetic point of view, diethylenic dithioester with moderate substitution can be prepared in good yield. This lead us to look at the chemical modification of these dithioesters.

THIOPHILIC ADDITION TO DIETHYLENIC DITHIOESTERS.

Our group has shown that dithioesters are equivalent to the acyl anion synthon by means of thiophilic addition of Grignard reagents [19,37] . This original method for preparation of dithioacetal anions followed by electrophilic attack has received a number of application for the creation of C-C bonds [19].

We looked at this reaction in the unreported case of diethylenic dithioesters. Treatment of dithioester 31 with isopropylmagnesium bromide [24,38] in THF at -17°C and then with water or alkyl halides furnished dithioacetals 33 - 36 (scheme 3). These products are masked forms of unsaturated ketones (34, 35) or aldehyde (33).



31

33 E = H
34 Me
35 Bu
36 CH_2-CH=CH_2

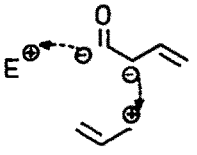
Scheme 3

CONCLUSION

Thio-Claisen rearrangement of S-allyldithioacetals, prepared from β-unsaturated dithioesters, proceeds at relatively low temperatures. Good yields of diethylenic dithioesters could be obtained in a number of cases. This complements the Ireland version [39] of the Claisen-rearrangement that has been used in the oxygen series with allyl α-unsaturated esters and the Yoshida method [17] starting from α-unsaturated thioamides.

When the substrates bear vicinal substituents on the newly formed C-C bond, we have observed that the retro thio-Claisen rearrangement occurs and thus evidenced for the second time the reversibility of this [3.3] sigmatropic shift.

The products could be elaborated by thiophilic addition of a Grignard reagent and alkylation. The overall sequence allows regiospecific α allylation of a β-ethylenic ketone by use of a dithioester as the following β-ethylenic acyl dianion :



EXPERIMENTAL SECTION

GENERAL

All reactions were run under a positive nitrogen pressure. THF was distilled over sodium benzophenone ketyl.

Preparative liquid chromatographies were performed on a Jobin-Yvon Chromatospac Prep 10 chromatograph connected to a differential difractometer and a fraction collector. The column was prepared by compressing at 8-9 bars a suspension of 100 to 200 g of Merck 60 H (5-40 microns) silica gel in the eluting solvent : mixture of cyclohexane and ethyl acetate in the ratio indicated below. Elution is carried out at a 5-6 bars pressure (flow rate : 10 cm^3/min.).

^1H NMR spectra were run on a Varian EM 360 spectrometer (CCl_4 solutions). Significant data are quoted in order : chemical shift in ppm, multiplicity (s, singlet ; d, doublet ; t, triplet ; q, quartet ; m, multiplet ; b, broad), coupling constant in hertz, assignement. ^{13}C NMR spectra were determined at 15.8 MHz with a Bruker WP 60 spectrometer ($CDCl_3$ solutions) operating with broad band ^1H decoupling. Mass spectra were obtained at 70 eV with a Varian Mat CH5 spectrometer and data are tabulated as m/e and relative intensities. Elemental analyses of thermally stable compounds were performed by Service Central d'Analyse of CNRS at Vernaison.

STARTING MATERIALS

Methyl buten-3-dithioate 1 was prepared by the reaction of allylmagnesium bromide with phenyl isothiocyanate followed by treatment with methyl iodide and hydrogen sulphide.[20] Dithioesters 2 and 3 were obtained from the reaction of corresponding allylic magnesium bromides with carbon disulphide and methyl iodide.[21]

GENERAL PROCEDURE FOR DEPROTONATION OF DITHIOESTERS 1-3 AND TREATMENT BY ALKYL IODIDES OR WATER.

The dithioester (amount : see below) is added dropwise to a solution of LDA (1.1 equivalent) in THF cooled at -78°C. The mixture is stirred at -78°C for 30 min (1) or 1h (2 and 3). The electrophile (1.2 equiv. of methyl iodide, ethyl iodide, or an excess of aqueous ammonium chloride) is added at the temperature indicated below and the reaction mixture is stirred over a period of time reported below. After alkylation, the mixture is quenched by an ammonium chloride solution at the same temperature and extracted by partition between ethyl ether and brine. The organic layer is dried on magnesium sulphate. Evaporation of the solvent furnishes thermally labile ketene dithioacetals 5-8 and compounds 3, 4, 9-11. Yields of crude products are quantitative (purity > 90%).

1,1-Bis (methylthio)-1,3-butadiene 5. From the reaction of dithioester 1 (51 mg, 0.385 mmol) with LDA and MeI at -78°C for 15 min. ^1H NMR : 2.22 (s, 2 SMe), 4.9-5.3 (m, $=CH_2$), 6.1-7.2 (m, 2 =CH).

1-Ethylthio-1-methylthio-1,3-butadiene Z or E 6. From the reaction of dithioester 1 (51 mg, 0.385 mmol) with LDA, EtI at -78° and then at 0°C for 75 min. Ratio of Z/E isomers 100 : 0 (or vice versa) from ^1H NMR(SMe signals) . ^1H NMR : 1.23 (t, J= 7 Hz, Me of SEt), 2.27 (s, SMe), 2.67 (q, J= 7 Hz, SCH_2), 4.9-7.4 (m, $=CH_2$ and 2 =CH).

1,1-Bis-(methylthio)-2-methyl-1,3-butadiene [21] 7. From the reaction of dithioester 2 (56 mg, 0.385 mmol) with LDA, MeI at -78° for 15 min. ^1H NMR : 2.07 (s, Me-C=), 2.20 and 2.28 (2 s, 2SMe), 5.0-5.4 (m, $=CH_2$), 7.0-7.6 (m, =CH).

1-Ethylthio-2-methyl-1-methylthio-1,3-butadiene Z and E 8. From the reaction of dithioester 2 (56 mg, 0.385 mmol) with LDA, EtI at -78°C and then at 0°C for 75 min. Ratio of Z/E isomers 60 : 40 (or vice versa) from ^1H NMR (SMe signals) . ^1H NMR : 1.19 (t, J= 7 Hz, Me of SEt), 2.09 (s, Me-C=), 2.23 and 2.28 (2 s, SMe of minor and major isomers), 2.65 (m, SCH_2), 5.0-5.5 (m,= CH_2), 7.1-7.7 (m, =CH).

2,3,4,5-Tetramethyl-6-methylthio-3-(methylthiothiocarbonyl)-2,3-dihydro-4H-thiopyran [34] 9. From the reaction of dithioester 2 (56 mg, 0.385 mmol) with LDA and NH_4Cl/H_2O at -78°C. ^1H NMR : identical to the reported [34] spectrum.

1,1-Bis (methylthio)-3-methyl-1,3-butadiene [21,40] 10. From the reaction of dithioester 3 (56 mg, 0.385 mmol) with LDA, MeI at -78°C for 15 min. ^1H NMR : identical to the reported [40] spectrum.

1-Ethylthio-3-methyl-1-methylthio-1,3-butadiene Z and E 11. From the reaction of dithioester 3 (56 mg, 0.385 mmol) with LDA, EtI at -78° and then 0°C for 75 min. Ratio of Z/E isomers 67 : 33 (or vice versa) from ^1H NMR(SMe signals). ^1H NMR : 1.23 (t, J= 7 Hz, Me of SEt), 1.78 (bs, Me-C=), 2.23 and 2.25 (2s, SMe of major and minor isomers), 2.8 (m, SCH_2), 4.97 (bs, $=CH_2$), 6.3-6.9 (m, =CH).

Mixture of methyl 3-methylbuten-2-dithioate [20] 4 and *methyl 3-methylbuten-3-dithioate* [20,21] 3. From the reaction of dithioester 3 (56 mg, 0.385 mmol) with LDA and NH_4Cl/H_2O at -78°C. Isomeric ratio 4/3 80 : 20 from ^1H NMR spectrum.[20]

Methyl 3-methylbuten-2-dithioate 4. From the reaction of dithioester 3 (56 mg ; 0.385 mmol) with LDA, and NH_4Cl/H_2O at 0°C. ^1H NMR spectrum identical to reported data.[10]

GENERAL PROCEDURE FOR THE SYNTHESIS OF KETENE DITHIOACETALS 13-23

The dithioester (0.385 - 16 mmol) is added dropwise to a solution of LDA (1.1 equivalent) in THF (10-70 ml) cooled at -78°C. The mixture is stirred at -78°C for 30 mn (1) or 1 hr (2 and 3). The allyl bromide (1.2 equiv.) is added at -78°C. The reaction mixture is stirred at -78°C for 10 min and then at 0°C for 1 hr - 1 hr 30 min. It is quenched by aqueous ammonium chloride and extracted by partition between ethyl ether and brine. The organic layer is dried over magnesium sulphate. Evaporation of the solvent affords ketene dithioacetals 13-23 which where used without purification. Yields of crude products are quantitative. In most cases, the thio-Claisen rearrangement products are already detectable in the NMR spectra of the ketene dithioacetals.

1-Methylthio-1-(2-propen-1-yl) thio-1,3-butadiene Z or E 13. From the reaction of dithioester 1 (400 mg, 3.02 mmol) with LDA and allylbromide. Isomeric ratio Z/E 100 : 0 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 2.26 (s, SMe), 3.35 (d, J= 7 Hz, SCH_2), 4.8-5.3 (m, 2 $=CH_2$), 5.4-6.1 (m, 1 =CH), 6.3-7.0 (m, 2 =CH).

1-Methylthio-1-(2-methyl-2-propen-1-yl)-thio-1,3-butadiene Z or E 14. From the reaction of dithioester 1 (400 mg, 3.02 mmol) with LDA and methallylbromide. Isomeric ratio Z/E 100 : 0 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 1.77 (d, J= 1 Hz, Me-C=), 2.25 (s, SMe), 3.33 (s, SCH_2), 4.6-5.4 (m, 2 $=CH_2$), 6.2-7.2 (m, 2 =CH).

1-Methylthio-1- (2-buten-1-yl)-thio-1,3-butadiene Z or E 15. From the reaction of dithioester 1 (400 mg, 3.02 mmol) with LDA and crotylbromide. Ratio of Z/E isomers 100 : 0 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 1.62(dd, J= 5 Hz, 1Hz, Me-C=),2.24 (s, SMe), 3.26 (dd, J= 6 Hz, 1.5 Hz, SCH_2), 4.9-6.2 (m, 2 $=CH_2$ and =CH), 7.1-7.6 (m, H-C(=)-C=).

2-Methyl-1-methylthio-1-(2-propen-1-yl) thio-1,3-butadiene Z and E 16. From the reaction of dithioester 2 (1.463 g, 10 mmol) with LDA and allylbromide. Isomeric ratio Z/E 44 : 56 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 2.1 (s, Me-C=), 2.23 and 2.27 (2s, SMe of major and minor isomers), 3.33 and 3.44 (2bd, J= 6 Hz, SCH_2, of minor and major isomers, 4.9-6.2 (m, 2 $=CH_2$ and =CH), 7.1-7.6 (m, HC(=)-C=).

2-Methyl-1-methylthio-1-(2-methyl-2 propen-1-yl)-thio-1,3-butadiene Z and E 17. From the reaction of dithioester 2 (1.463 g, 10 mmol) with LDA and methallylbromide. Isomeric ratio Z/E 42 : 58 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 1.78 (d, J= 1 Hz, Me-C=), 2.10 (s, Me-C(=)-C=), 2.20 and 2.27 (2 s, SMe of major and minor isomers), 3.26 and 3.37 (2 bs, SCH_2 of major and minor isomers), 4.53-5.40 (m, 2 $=CH_2$), 7.0-7.5 (m, =CH).

2-Methyl-1-methylthio-1-(2-buten-1-yl) thio-1,3-butadiene Z and E 18. From the reaction of dithioester 2 (1.463 g, 10 mmol) with LDA and crotylbromide. Ratio of Z/E isomers 63 : 37 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 1.64 (dd, J= 5 Hz,1 Hz, Me-C=), 2.09 (s, Me-C(=)-C=), 2.23 and 2.30 (2s, SMe of minor and major isomers), 3.25 and 3.34 (2 bd, J= 6 Hz, SCH_2 of minor and major isomers), 5.0-5.8 (m, $=CH_2$ and 2 =CH), 7.0-7.6 (m, H-C(=)-C=).

2-Methyl-1-methylthio-1- (3-methyl-2-buten-1-yl) thio-1,3-butadiene Z and E 19. From the reaction of dithioester 2 (53 mg, 0.385 mmol) with LDA and prenylbromide. Isomeric ratio Z/E 62 : 38 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 1.66 (bs, $Me_2C=$), 2.04 and 2.06 (2 s, Me-C(=)-C= of minor and major isomers), 2.24 and 2.32 (2s, SMe of minor and major isomers), 3.25 and 3.38 (2 bd, J= 6.5 Hz, SCH_2 of major and minor isomers), 4.9-5.4 (m, $=CH_2$ and =CH), 7.0-7.5 (m, H-C(=)-C=).

3-Methyl-1-methylthio-1-(2-propen-1-yl) thio-1,3-butadiene Z and E 20. From the reaction of dithioester 3 (1.463 g, 10 mmol) with LDA and allylbromide. Ratio of Z/E isomers 32 : 68 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 1.97 (bs, Me-C=), 2.26 and 2.28 (2 s, SMe of major and minor isomers), 3.40 (bd, J= 7 Hz, SCH_2), 4.7-5.2 (m, 2 $=CH_2$), 5.4-6.1 (m, =CH), 6.35 (bs, H-C(=)-C=).

3-Methyl-1-methylthio-1-(2-methyl-2-propen-1-yl) thio-1,3-butadiene Z and E 21. From the reaction of dithioester 3 (2.340 g, 16 mmol) with LDA and methallylbromide. Isomeric ratio Z/E 41 : 59 (or vice versa) from ^1H NMR spectrum (SMe signals). ^1H NMR : 1.73 (bs, Me-C=), 1.95 (bs, Me-C(=)-C=), 2.24 and 2.27 (2s, SMe of major and minor isomers), 3.29 and 3.36 (2 bs, SCH_2 of major and minor isomers), 4.5-5.0 (m, 2 $=CH_2$), 6.36 and 6.41 (2 bs, =CH of major and minor isomers),

3-Methyl-1-methylthio-1-(2-buten-1-yl) thio-1,3-butadiene Z and E 22. From the reaction of dithioester 3 (1.463 g, 10 mmol) with LDA and crotylbromide. Ratio of Z/E isomers 52 : 48 (or vice versa) from ^{1}H NMR spectrum (SMe signals). ^{1}H NMR : 1.68 (bs, Me-C=), 1.99 (bs, Me-C(=)-C=), 2.25 and 2.29 (2s, SMe of minor and major isomers), 3.30 (bt, J= 6 Hz, SCH_2), 4.7-5.8 (m, $=CH_2$ and =CH), 6.4 (m, H-C(=)-C=).

3-Methyl-1-methylthio-1-(3-methyl-2-buten-1-yl)thio-1,3-butadiene Z and E 23. From the reaction of dithioester 3 (1.0 g, 6.837 mmol) with LDA and prenylbromide. Isomeric ratio Z/E 50 : 50 (or vice versa) from ^{1}H NMR spectrum (SMe signals). ^{1}H NMR : 1.69 (bs, Me_2C=), 1.99 (bs, Me-C(=)-C=), 2.26 and 2.31 (2s, SMe of isomers), 3.33 and 3.43 (2 bd, J= 6,5 Hz, SCH_2 of isomers), 5.0-5.4 (m, $=CH_2$ and =CH), 6.35 and 6.42 (2 bs, H-C(=)-C= of isomers). MS : 39 (23 %), 41 (59 %), 45 (15%), 69 (47 %), 97 (31 %), 98 (38 %), 99 (21 %), 131 (21 %), 145 (100 %), 214 (4 %). Column chromatography on silica gel with a 99 : 1 mixture of cyclohexane and ethyl acetate gives 23 with a yield of 62 %.

GENERAL PROCEDURE FOR THE THIO-CLAISEN REARRANGEMENT.

The thermolyses of preceding ketene dithioacetals were performed with a catalytic amount of 4-tert-butylcatechol in an inert atmosphere under one of the following conditions :

- neat substrate at 20°C
- reflux of the substrate in a solution of cyclohexane (80°C) or methyl cyclohexane.

The products were then submitted to medium pressure liquid chromatography. In most cases the diethylenic dithioesters were isolated pure and were kept at -18°C. Due to their thermal lability, satisfactory microanalyses could generally not be obtained.

Methyl-2-ethenyl-4-pentenedithioate 24. Thermolysis of 13 (3.02 mmol) at 80°C for 1hr furnishes a 96 : 4 mixture of 24 and 13. Chromatography (cyclohexane) of this mixture gives pure 24 (342 mg, 1.98 mmol). Yield : 66 %. ^{1}H NMR : 2.57 (s, SMe), 2.65 (m, CH_2), 3.75 (q, J= 7 Hz, CH-C=S), 4.8 -5.3 (m, 2 $=CH_2$), 5.3 -6.2 (m, 2 =CH). ^{13}C NMR : 19.2, 40.9, 64.7, 116.3, 117.1, 135.0, 139.5, 240.4 (C=S). MS : 39 (86 %), 41 (56 %), 45 (55 %), 58 (25 %), 71 (18 %), 84 (25 %), 91(50%), 115 (17 %), 131 (100 %), 172 (5 %).

Methyl 2-ethenyl-4-methyl-4-pentenedithioate 25. Thermolysis of 14 (3.02 mmol) at 80°C for 1 hr 30 min provides a 89 : 11 mixture of 25 and 14. Chromatography (cyclohexane) of this mixture affords pure 25 (211 mg, 1.14 mmol) with a yield of 38 % and a mixture of 25 and 14 with a yield of 65 %. ^{1}H NMR : 1.70 (bs, Me-C=), 2.50 (d, J= 7 Hz, CH_2), 2.57 (s, SMe), 3.93 (q, J= 7 Hz, CH-C=S), 4.6-5.3 (m, 2 $=CH_2$), 5.6-6.3 (m, =CH). ^{13}C NMR : 19.3, 22.3, 45.1, 63.1, 113.2, 116.1, 139.8, 142.2, 240.9 (C=S). MS : 39 (20 %), 41 (10 %), 45 (13 %), 55 (16 %), 84 (17 %), 91 (25 %), 115 (11 %), 131 (100 %), 135 (10 %), 186 (4 %).

Methyl 2-ethenyl-3-methyl-4-pentenedithioate 26. Thermolysis of 15 (3.02 mmol) at 80°C for 1 hr 30 min furnishes a 72 : 28 mixture of 26 and 15. Chromatography (cyclohexane) of this mixture gives pure 26 (318 mg, 1.706 mmol). Yield : 56 %. Ratio of diastereisomers 26 : 74 from ^{1}H NMR (d of Me signals). ^{1}H NMR : 0.95 and 1.02 (d, J= 7 Hz, Me of major and minor diast.), 2.52 and 2.58 (s, SMe of minor and major diast.), 2.9 m, [CH-(Me)], 3.46 (t, J= 9 Hz, CH-C=S), 4.7-5.2 (m, 2 $=CH_2$), 5.3-6.3 (m, 2 =CH). ^{13}C NMR : 17.9 ; 19.2 ; 30.8 ; 40.6 ; 43.6 ; 70.7 ; 71.3 ; 114.8 ; 116.6 ; 139.5 ; 140.7 ; 141.2 ; 240.8 (C=S). MS : 27 (100 %), 29 (69 %), 39 (82 %), 45 (48 %), 55 (62 %), 84 (27 %), 91 (30 %), 115 (12 %), 131 (56.%), 186 (3 %);

Methyl 2-ethenyl-2-methyl-4-pentenedithioate 27. Thermolysis of 16 (10 mmol) at 80°C for 2 hr 15 min affords 27. Chromatography of compound 27 on silica gel with a 99 : 1 mixture of cyclohexane and ethyl acetate gives pure 27 (1.747 g, 9.38 mmol). Yield : 93 % ^{1}H NMR : 1.45 (s, Me), 2.6 (s, SMe), 2.64 (d, J= 7 Hz, CH_2), 4.6-5.6 (m, 2 $=CH_2$), 5.8-6.4 (m, 2 =CH). ^{13}C NMR : 20.4, 25.4, 47.2, 60.1, 114.6, 118.1, 133.9, 143.3, 246.3 (C=S). SM : 28 (100 %), 39 (25 %), 41 (24 %), 67 (20 %), 91 (25 %), 95 (10 %), 97 (23 %), 98 (21 %), 99 (8 %), 130 (8 %), 145 % (80 %), 186 (3 %).

Methyl 2-ethenyl-2,4-dimethyl-4-pentenedithioate 28. Thermolysis of 17 (10 mmol) at 80°C for 6 h 30 min provides a 72 : 28 mixture of 28 and 17. Chromatography of this mixture on silica gel with a 95 :5 mixture of cyclohexane and ethyl acetate affords this mixture with a yield of 99 %. ^{1}H NMR : 1.50 (s, Me), 1.64 (d, J= 1 Hz, Me-C=), 2.53 (s, SMe), 2.70 (s, CH_2), 4.6-5.4 (m, 2 $=CH_2$), 6.0-6.5 (m, =CH).

Methyl 2-ethenyl-2,3-dimethyl-4-pentenedithioate 29. Thermolysis of 18 (10 mmol) at 101°C for 24 hr, then chromatography (cyclohexane) on silica gel furnishes a 23 : 77 mixture of 29 and 18. Ratio of diastereoisomers 62 : 38 from ^{1}H NMR spectrum (s of SMe and s of Me-C-C=S signals). ^{1}H NMR : 0.92 and 0.96 (2 d, J= 7 Hz, Me-(CH) of major and minor diast.), 1.39 and 1.43 (2s, Me-C-C=S of major and minor diast.), 2.52 and 2.54 (2s, SMe of minor and major diast.), 3.1-3.7 (m, CH-C=), 4.7-5.3 (m, 2 $=CH_2$), 5.5-6.6 (m, 2 =CH).

Methyl 2-(propen-2-yl)-4-pentenedithioate 30. Thermolysis of 20 (15 mmol) at 20°C for 3 days gives 30. Column chromatography of the crude product on silica gel with a 99 : 1 mixture of cyclohexane and ethyl acetate affords pure 30 (2.093 g, 11.23 mmol). Yield : 75 %. ^{1}H NMR : 1.72 (d, J= 1.5 Hz, Me-C=), 2.56 (s, SMe), 2.70 (m, CH_2), 3.8 (t, J= 7 Hz, CH-C=S), 4.8-5.1 (3 m, 2 =CH_2), 5.3-6.0 (m, =CH). ^{13}C NMR : 19.7, 20.3, 38.5, 66.7, 114.0, 116.7, 135.6, 144.2, 221.7 (C=S). MS : 39 (38 %), 41 (39 %), 67 (21 %), 91 (29 %), 95 (36 %), 97 (29 %), 98 (21 %), 129 (20 %), 145 (100 %), 186 (5 %).

Methyl 4-methyl-2-(propen-2-yl)-4-pentenedithioate 31. Thermolysis of 21 (16 mmol) at 20° for 4 days provides a 85 :15 mixture of 31 and 21. Chromatography of this mixture on silica gel with a 99 : 1 mixture of cyclohexane and ethyl acetate gives pure 31 (2.800 g, 13.97 mmol). Yield : 80 %. ^{1}H NMR : 1.76 (bs, 2 Me C=), 2.64 (s, SMe), 2.65 (d, J= 7 Hz, CH_2-C=), 4.07 (t, J= 7 Hz, CH-C=S), 4.7, 4.88 and 5.03 (3m, 2 =CH_2). ^{13}C NMR : 19.7, 20.3, 22.3, 42.4, 64.8, 112.6, 113.9, 142.7, 144.5, 240.1 (C=S). MS : 39 (23 %), 55 (22 %), 67 (17 %), 91 (20 %), 95 (24 %), 97 (22 %), 98 (20 %), 111 (19 %), 129 (10 %), 145 (100 %), 200 (3 %). Anal. Calcd. for $C_{10}H_{16}S_2$: C, 59.94 ; H, 8.06 Found : C, 59.45 ; H, 8.22.

Methyl 3-methyl-2-(propen-2-yl)-4-pentenedithioate 32. Thermolysis of 22 (10 mmol) at 20°C for 13 days affords a 81 : 19 mixture of 32 and 22. Column chromatography (cyclohexane) of this mixture on silica gel furnishes pure 32 (1.200 g, 5.99 mmol). Yield : 60 %. Ratio of diastereoisomers 58 : 42 from ^{1}H NMR (d of Me signals). ^{1}H NMR : 0.92 and 0.97 (d, J= 7 Hz, Me-(CH) of minor and major diast.), 1.74 (m, Me-C=), 2.50 and 2.55 (s, SMe of minor and major diast.), 2.7-3.4 (m, CH-C=) 3.61 (d, J= 12 Hz, CH-C=S), 4.6-5.2 (m, 2 =CH), 5.3-6.0 (m, =CH). ^{13}C NMR : 18.1, 18.5, 19.6, 30.8, 40.6, 40.9, 73.7, 114.3, 114.9, 115.2, 115.5, 140.9, 141.5, 143.3, 144.0, 238.4 and 239.1 (C=S of minor and major diast.). MS : 28 (100 %), 55 (18 %), 67 (8 %), 91 (9 %), 97 (12 %), 98 (13 %), 99 (6 %), 129 (6 %), 145 (50 %), 200 (3 %). Anal. Calcd. for $C_{10}H_{16}S_2$: C, 59.94 ; H, 8.06 . Found : C, 59.60 ; H, 7.70.

PROCEDURE FOR MONITORING THE RETRO-THIO-CLAISEN REARRANGEMENT.

The thermal behaviour of dithioesters 24-26 and 31-32 (~ 50 mg) which were isolated in a pure state as above, was studied in two of the following conditions :

- neat compound at -18°C
- CCl_4 solution at 20°C
- reflux of a cyclohexane solution (80°C)

Reaction times are indicated in table 3. Analyses of dithioester/ketene dithioacetal ratios were effected by ^{1}H NMR (table 3).

THIOPHILIC ADDITION [37, 38, 24] TO DITHIOESTER 31 AND ALKYLATION

Dithioester 31 (2-3 mmol) was added dropwise to a 0.25 M THF solution of iso-propylmagnesium bromide (5-6 equivalents) cooled at -17°C. The mixture is stirred over a period of 1 hr. The electrophile is added and, for alkyl halides, the reaction mixture is stirred at -17°C for the time indicated below. After quenching by aqueous ammonium chloride, it is extracted with ethyl ether and brine. The organic layer is dried over magnesium sulphate and concentrated in vacuo. The residue is chromatographed on silica gel.

2,5 Dimethyl-3-(isopropylthiomethylthio) methyl-1,5-hexadiene 33. Reaction of dithioester 31 (397 mg, 1.98 mmol) with iPrMgBr and H_3O^+ followed by chromatography (cyclohexane/ethyl acetate 99 : 1) gives 33 (272 mg, 1.12 mmol). Yield : 56 %. Ratio of diastereoisomers 61 : 39 from ^{1}H NMR (d of Me from iPr). ^{1}H NMR : 1.25 and 1.29 (d, J= 7 Hz, Me of iPr for minor and major diast.), 1.69 (bs, 2Me-C=), 2.03 and 2.06 (s, SMe of minor and major diast.), 2.17-2.88[(m, CH_2-C= and CH-C$(SR)_2$],3.11 (sept, J= 7 Hz, CH of iPr),3.69 (bd, J= 7,5 Hz, CH-$(SR)_2$), 4.6-5.0 (m, 2=CH_2). ^{13}C NMR : 11.2, 13.4, 18.3, 18.9, 21.9, 22.6, 23.3, 23.8, 34.7, 35.2, 39.5, 39.7, 48.9, 49.9, 54.6, 55.6, 112,1, 114.1, 114.6, 143.9, 144.1, 144.4. MS : 41 (52 %), 43 (47 %), 55 (42 %), 79 (26 %), 93 (93 %), 99 (100 %), 121 (85 %), 135 (86 %), 153 (20 %), 244 (15 %).

2,5 Dimethyl-3-(1-isopropylthio-1-methylthio) ethyl-1,5-hexadiene 34. Reaction of dithioester 31 (600 mg, 3 mmol) with iPrMgBr and methyl iodide for 1 hr 50 min and column chromatography with a 99 : 1 mixture of cyclohexane and ethyl acetate furnishes 34 (380 mg, 1.470 mmol). Yield : 49 %. Ratio of diastereoisomers 67 : 33 from ^{1}H NMR spectrum (d of Me from iPr). ^{1}H NMR : 1..25 and 1.29 (d, J= 7 Hz, Me of iPr for minor and major diast.), 1.46 and 1.50 (s, Me-C$(SR)_2$ of minor and major diast.), 1.65 and 1.75 (bs, 2Me-C=), 2.03 and 2.05 (s, SMe of major and minor diast.), 3.0 (sept, J= 7 Hz, CH of iPr), 4.5-4.9 (m, =CH_2). ^{13}C NMR : 13.1, 13.4, 13.5, 18.5, 21.1, 21.5, 22.0, 22.1, 22.4, 24.1, 24.7, 25.3, 25.6, 25.7, 26.0, 26.2, 34.7, 36.6, 37.3, 37.4, 54.0, 54.2, 63.3, 78.7, 112.0, 116.0, 116.3, 144.0. MS : 41 (65 %), 59 (51 %), 79 (32 %), 91 (35 %), 107 (41 %), 111 (26 %), 113 (100 %), 135 (75 %), 215 (25 %), 258 (3 %).

2,5 Dimethyl-3-[(1-isopropylthio-1-methylthio)-1-pentyl]-1,5-hexadiene 35. Reaction of dithioester 31 (600 mg, 3 mmol) with iPrMgBr, then butylbromide and hexamethylphosphoramide for 2 hr 45 min at -17°C affords 35. Column chromatography (cyclohexane/ethyl acetate 99 : 1) gives pure 35 (430 mg, 1.43 mmol). Yield : 48 %. Ratio of diastereoisomers 58 : 42 from ^{1}H NMR (d of Me from iPr). ^{1}H NMR : 0.92 (m, Me and CH_2 of butyl), 1.29 and 1.32 (d, J= 7 Hz, Me of iPr for major and minor diast.), 1.64 and 1.82 (bs, 2Me-C=), 2.05 and 2.10 (s, SMe of major and minor diast.), 3.04 (sept, J= 7 Hz, CH of iPr), 4.5-4.9 (m, 2 $=CH_2$). ^{13}C NMR : 13.8, 14.1, 14.2, 21.9, 22.0, 22.1, 22.5, 23.2, 25.7, 25.9, 27.4, 34.4, 34.6, 38.2, 38.5, 39.3, 54.2, 54.4, 67.2, 78.7, 111.9, 112.0, 116.5, 116.7. MS : 41 (97 %), 55 (75 %), 93 (49 %), 121 (52 %), 155 (100 %), 177 (91 %), 191 (60 %), 209 (35 %), 257 (32 %), 300 (5 %).

4-Isopropylthio-7-methyl-4-methylthio-5-(1-propen-2-yl)-1,7-octadiene 36. Reaction of dithioester 31 (400 mg, 2 mmol) with iPrMgBr and allylbromide for 2 hr at -17°C furnishes 36. Chromatography (cyclohexane) gives pure 31 (309 mg, 1.09 mmol). Yield : 54 %. Ratio of diastereoisomers 51 : 49 from ^{1}H NMR (s of SMe signals). ^{1}H NMR : 1.24 and 1.26 (d, J= 7 Hz, Me of iPr for major and minor diast.), 1.55 and 1.72 (bs, 2Me-C=), 1.95 and 1.98 (s, SMe of major and minor diast.), 2.23-2.65 (m, CH-C(SR)$_2$ and 2 CH_2-C=), 3.02 (hept, J= 7 Hz, CH of iPr), 4.3-5.1 (m, 3 $=CH_2$), 5.3-6.1(m, =CH). ^{13}C NMR : 22.0, 25.7, 34.5, 38.1, 43.0, 43.7, 54.1, 66.1, 109.5, 112.2, 116.9, 117.1, 117.6, 134.5, 134.7, 143.8, 143.9, 144.0. MS : 41 (100 %), 43 (51 %), 55 (52 %), 105 (51 %), 119 (39 %), 139 (68 %), 161 (43 %), 175 (34 %), 241 (37 %), 284 (3 %).

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