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PHTHALIMIDOSULPHENYL CHLORIDE. PART 2[1]. SYNTHESIS OF UNUSUAL THIIRANE DERIVATIVES.

Giuseppe Capozzi*, Luciano Gori and Stefano Menichetti

Centro C N R "Chimica dei Composti Eterociclici", Dipartimento di Chimica Organica, Universita' di Firenze, Via G Capponi 9, 50121 Firenze, Italy

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Key Words

Phthalimidosulphenyl chloride addition to alkynes, vinylthio phthalimides reaction with hydrides, stereoselective synthesis of vinylthio thiuranes and di-vinyl disulphides

Abstract Vinylthio phthalimides 1, synthesized by addition of phtalimidosulphenyl chloride to some alkynes, react with 2 equivalents of lithiumtriethylboron hydride to give vinylthio substituted thiuranes 3 with high degree of diasteroselectivity The reaction of 1 with 1 equivalent of the same hydride affords divinyl disulphides 6 which resulted to be intermediates in the formation of thiuranes 3 since the reaction of 6 with 1 equivalent of lithiumtriethylboron hydride give the episulphides 3 in the same diastereoisomeric mixture Mechanisms for these reactions are proposed.

In the development of our studies on the reactivity of sulphenyl halides[2] we started an investigation on the chemistry of phthalimidosulphenyl chloride[1] This particular sulphenyl chloride, due to the presence of the sulphur-nitrogen bond offers the chance to link together the synthetic potential of sulphenyl chlorides and sulphenamides [2]

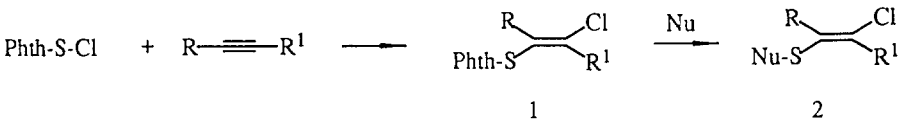
Sulphenamides can be considered mild sulphur electrophiles which can be usefully employed for the introduction of thio-substituted residues into organic molecules Thus *N*-thiophthalimido derivatives have been reacted with various nucleophiles including thiols[3], alcohols[4], amines[5], hydrides[6] and carbanions[1,7] to give symmetrical or unsymmetrical disulphides, sulphenic esters, *N*-substituted sulphenamides, thiuranes and sulphides respectively

Usually *N*-thiophthalimido derivatives are synthesized by reaction of the potassium or sodium salts of phthalimide with the appropriate sulphenyl halides[8] However it is also possible to prepare this class of compounds by reaction of phthalimidosulphenyl chloride with a nucleophile [6]

In a preliminary paper we reported the synthesis of phthalimidovinyl sulphenamides **1** by reaction of phthalimidosulphenyl chloride and alkynes and we outlined their reactivity towards nucleophiles such as carbanions and functionalized sodium amides[1] (Scheme 1) In all cases we obtained the substitution of the phthalimido residue with formation of compound of type **2**

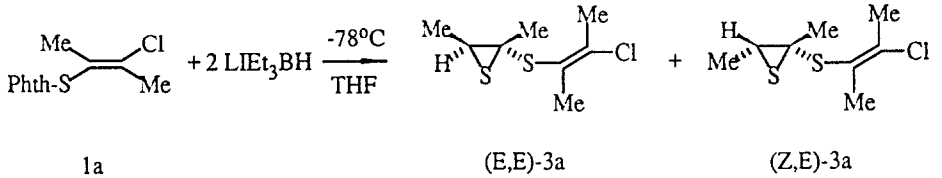
In this paper we report the reactivity of some phthalimidovinyl sulphenamides towards

aluminum and boron hydrides which leads to the formation of unexpected thiirane derivatives



Scheme 1

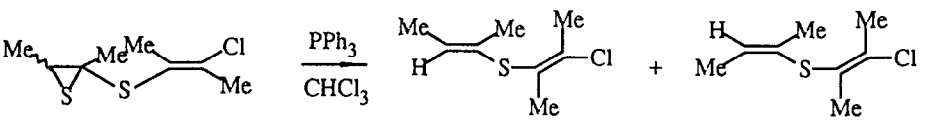
The reaction of **1a** (R = R^1 = Me) with 2 equivalents of lithium triethylboron hydride (Super-Hydride^R) in dry THF at -78^o under nitrogen, gave, in satisfactory yields (66%), the diastereomeric thiiranes **3a** as a 93 7 mixture of the *E,E* and *Z,E* isomers (equation 1) The same mixture of products was obtained when **1a** was reacted with other hydrides such as $NaBH_4$ or $LiAlH_4$



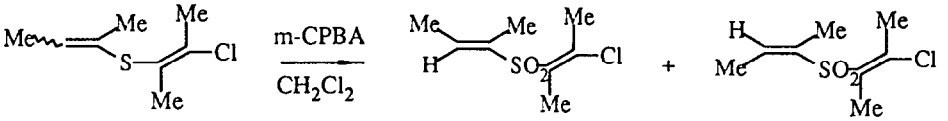
Equation 1

The structure of the thiiranes **3a** was deduced from nmr and GC-MS data The ^1H nmr spectrum of the major isomer (*E,E*)-**3a** showed two narrow quartets at 2 38 and 2 22 δ (J = 1 56 Hz) for the vinylic methyls, a singlet and a doublet at 1 76 and 1 58 δ for the two methyl groups of the thiirane ring, and a quartet at 3 23 δ (J = 6 11 Hz) for the hydrogen atom The *Z,E* isomer **3a** was present as minor component in the reaction mixture and showed a singlet at 1 80 δ and a doublet at 1 73 δ (J = 5 94 Hz) for the resonances of the thiirane methyl protons and a quartet at 3 07 δ for the methynic proton The resonances of the vinylic methyls of this isomer could be not detected, however it is reasonable to assume an accidental isocronism with the corresponding methyl groups of the major isomer The ^{13}C nmr spectrum of (*E,E*)-**3a** was also consistent with the proposed structure (see experimental)

The structure and the isomeric distribution of the thiiranes **3a** is also supported by the reaction sequence shown in equations 2 and 3 The desulphurization of the thiiranes by triphenylphosphine, a reaction which occurs with retention of configuration[9] gave the sulphides (*E,E*)-**4a** and (*Z,E*)-**4a** in 93 7 ratio The same isomeric distribution was found in the sulphones **5a** obtained by oxidation of **4a** with *m*-chloroperbenzoic acid. It is known this reaction proceeds without affecting the stereochemistry of the double bond[10], so that the stereochemistry of **5a** reflects that of **4a** and **3a**



Equation 2

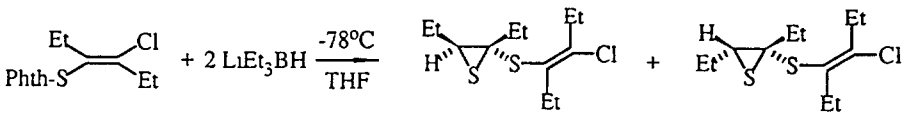


4a (E,E)-5a (Z,E)-5a

Equation 3

A close inspection of the chemical shifts of the vinylic protons of **4a** and **5a** clearly indicates that the major isomer has a *E,E* stereochemistry In fact it is well accepted that a sulphonyl group *cis* to a vinylic proton exerts quite a strong downfield shift on this proton[11] In our case the vinylic proton of the major isomer of **5a** was found at 6 74 δ while the minor isomer has the corresponding resonance a 6 20 δ Similarly the chemical shifts of the vinylic protons of **4a** (5 66 δ for the major isomer and 5 75 δ for the minor one) were also indicative of an *E,E* stereochemistry for the major isomer, since a vinylic proton *cis* to a sulphide sulphur is expected upfield with respect to the chemical shift of the corresponding proton *trans* to the same group [11]

An even higher diastereoselectivity (96 4) was observed in the synthesis of the thiiranes **3b** from the phthalimidovinylsulphenamide **1b** (R = R' = Et) and two equivalents of Super-Hydride (equation 4)

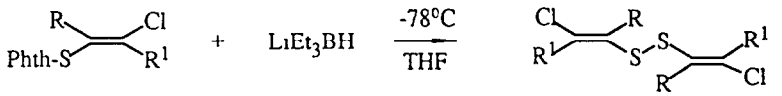


1b (E,E)-3b (Z,E)-3b

Equation 4

The formation of the thiiranes (*E,E*)-3 and (*Z,E*)-3 in the reaction of the sulphenamides **1** and hydride ions is not easily rationalizable

In order to have information on this reaction we reacted **1a** and **1b** with only one equivalent of $LiEt_3BH$ In this case we obtained good yields of the disulphides **6a** (95% yield) and **6b** (84% yield) respectively (equation 5)



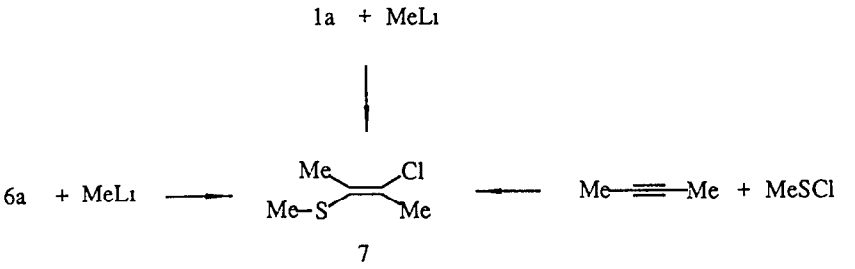
1a,b 6a,b

1a, 6a R = R^1 = Me

1b, 6b R = R^1 = Et

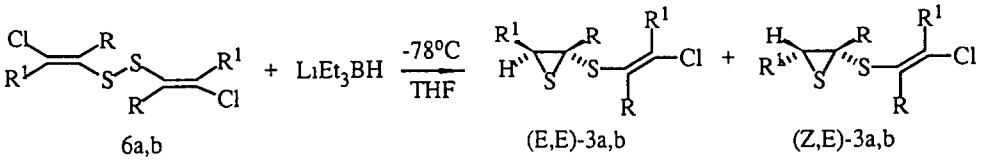
Equation 5

The *E,E* stereochemistry of the disulphides **6** was proved by the reaction of **6a** with methyl lithium which gave the methyl vinylsulphide **7** identical to the product formed in the addition of methanesulphenyl chloride to 2-butyne [12] Compound **7** was also obtained in the reaction of **1a** with methyllithium (Scheme 2)



Scheme 2

Further reaction of the disulphide **6a** (or **6b**) with one equivalent of $LiEt_3BH$ gave a mixture of the thiiranes **3a** (or **3b**) identical to that obtained directly from **1a** (or **1b**) and two equivalents of Super-Hydride (equation 6)

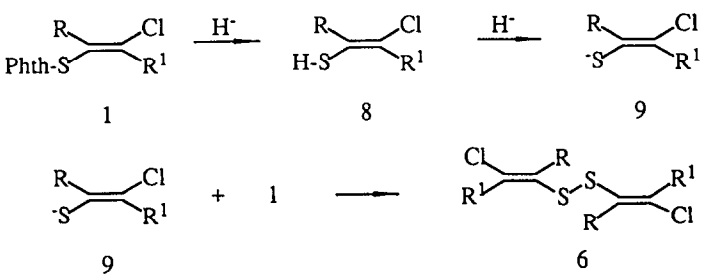


3a, 6a $R = R^1 = Me$

3b, 6b $R = R^1 = Et$

Equation 6

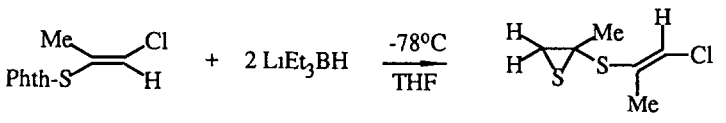
This result shows that the disulphides **6** are probable intermediates in the synthesis of the thiiranes **3** Moreover we have observed that minute amounts of the corresponding disulphides **6** were always present when sulphenamides **1** were reacted with two equivalents of $LiEt_3BH$ A rational for the formation of disulphides **6** from **1** is outlined in Scheme 3



Scheme 3

Attack of the hydride ion at sulphur is expected since it is a known reaction[6] in similar systems Furthermore thiolate ion attack at the sulphenamide sulphur is a general reaction for this class of compounds[3] The only point that deserves some comment is the observed retention of configuration of the thiolate ion **9** This implies that attack of **9** to **1** is faster than any *E-Z* isomerization of **9** which might occur *via* a thione intermediate

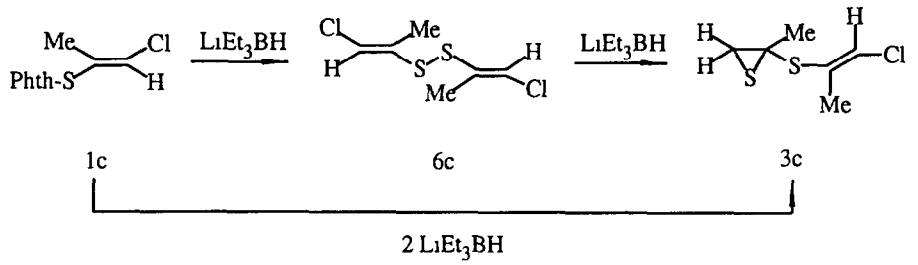
Sulphur-sulphur bond breaking and new carbon-sulphur bonds formation are the most relevant molecular rearrangements in the transformation of **6** into the thiiranes **3** (equation 6) With the aim of obtaining some insight on the mechanism of this rearrangement, we studied the reaction of the phthalimido derivative **1c** (R = Me, R' = H) with Super-Hydride Using two equivalents of the hydride we obtained exclusively the thiirane **3c** (equation 7)



1c 3c

Equation 7

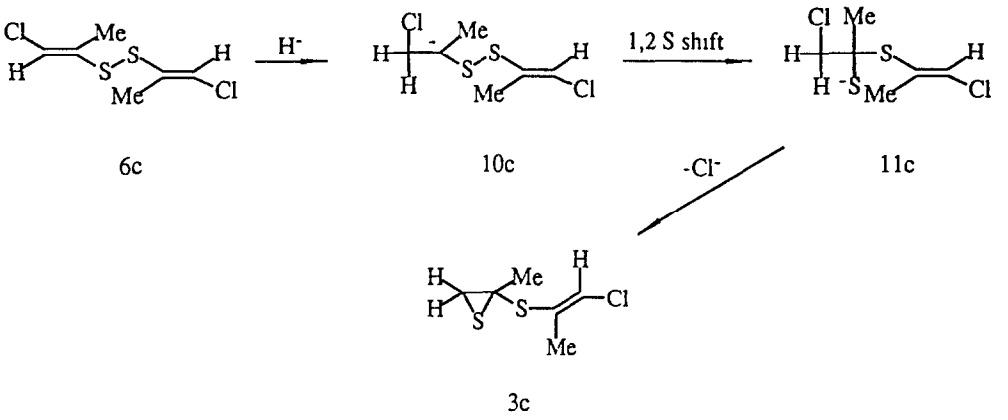
The behaviour of **1c** was found to be similar to that of **1a** and **1b** it reacted with one equivalent of $LiEt_3BH$ to give the corresponding disulphide **6c** which gave the thiirane **3c** upon reaction with a second equivalent of the hydride (Scheme 4)



Scheme 4

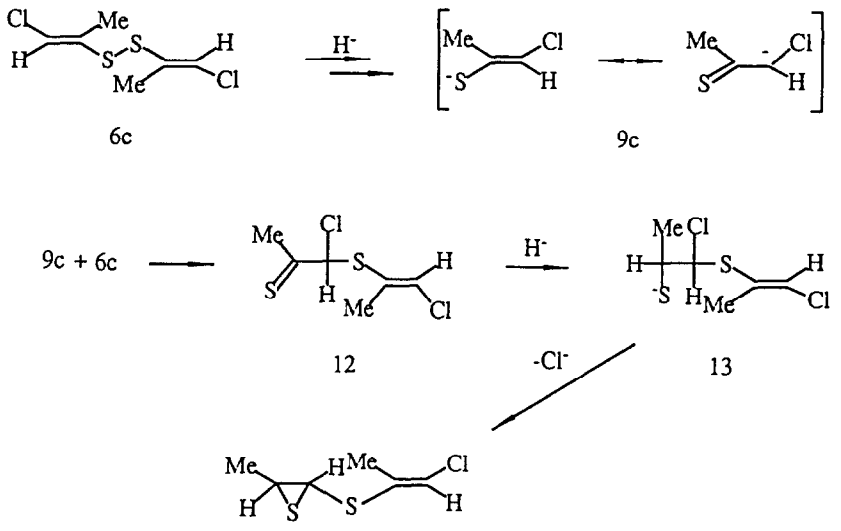
The formation of **3c**, as well as that of **3a** and **3b**, can be rationalized by assuming that the attack of the hydride ion at the halogen substituted vinylic carbon of **6c** generates the sulphur stabilized carbanion **10c** (Scheme 5) 1,2-Sulphur shift gives the thiolate ion **11c** and intramolecular nucleophilic substitution of chloride ion yields the thiirane **3c.**

Albeit other mechanisms may be operative, some can be ruled out by taking into account the structure of **3c** In particular we can rule out initial attack of the hydride ion at the disulphide linkage of **6c** which generates **9c** (Scheme 6). In fact a different thiirane derivative **14** is expected if the new carbon-sulphur bond is formed by attack of **9c** on **6c**



6c 10c 11c 3c

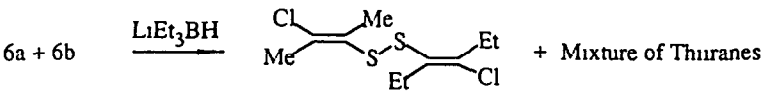
Scheme 5



6c 9c 12 13 14

scheme 6

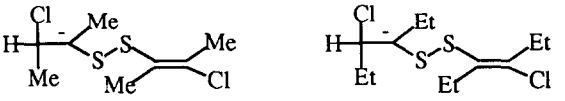
Indeed in our reaction conditions hydride ion attack at the disulphide sulphur of **6** is a reaction that takes place We observed scrambling of the vinylthio residues when a mixture of **6a** and **6b** was reacted with less than one equivalent of Super-Hydride (equation 8) However our results indicate that this reaction cannot be responsible for the formation of the thiiranes **3**



Equation 8

The last point to discuss is the remarkable diastereoselectivity observed in the formation of **3a**

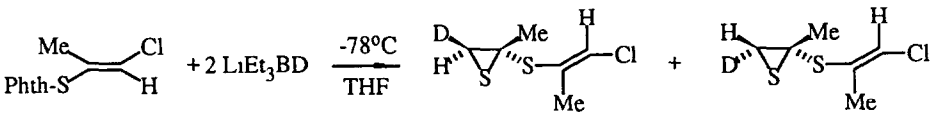
and **3b** According to the proposed mechanism (Scheme 5) this behaviour can be explained assuming different stabilities for the conformers of the carbanions **10a** and **10b** (Figure 1), obtained by hydride attack on chloro substituted carbon of the disulphides **6a** and **6b**, and/or activation energies for the 1,2-sulphur shift leading to the (*E,E*)-**3a** and (*E,E*)-**3b** lower that leading to the corresponding *Z,E* isomers



10a 10b

Figure 1

This hypothesis is supported by the reaction of the disulphide **6c** with lithium triethylboron deuteride ($LiEt_3BD$) which gave a 1 1 mixture of the two diastereomeric deuterated thiiranes **15** (equation 9)

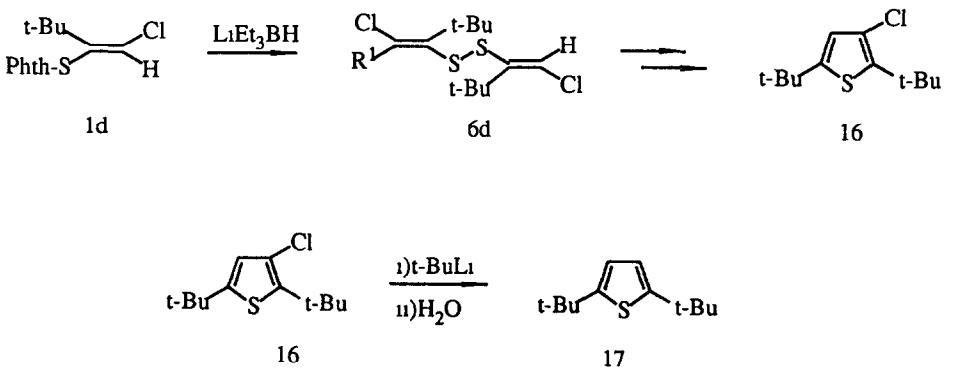


1c (E,E)-15 (Z,E)-15

Equation 9

Thus it seems that steric hindrance exerts a strong effect in the stereochemistry of the reaction whether on the conformer population of **10** or their rearrangement rate

To verify this hypothesis we reacted the phthalimidovinylsulphide **1d** (R = *t*-Bu, R' = H) with two equivalents of $LiEt_3BH$, unfortunately we did obtain any thiirane On the other hand the reaction of **1d** with one equivalent of Super-Hydride gave the corresponding disulphide **6d** as an unstable compound which in solution or on silica gel decomposed to 3-chloro-2,5-di-*t*-butylthiophene **16** (Scheme 7)



1d 6d 16 16 17

Scheme 7

The structure of **16** is based on gc-ms analysis and on ^{1}H and ^{13}C nmr data Moreover reductive dehalogenation of **16** with *t*-butyllithium afforded the 2,5-di-*t*-butylthiophene **17** (Scheme 7) which was identified by comparison with literature data [13]

The unusual behaviour of the *t*-butyl substituted disulphide **6d** and the possible intervention of a thione intermediate[14] in the formation of the 3-chloro-2,5-di-*t*-butylthiophene **13** are currently under study in this laboratory

In conclusion we have shown that the reaction of phthalimidovinyl sulphenamides with hydride represents a valuable method for the synthesis of both the divinyldisulphides **6** and the thiiranes **3**, an unusual class of substituted thiiranes

By choice of reaction conditions it is possible to modulate the reaction and generate vinylthiolate ions which stereospecifically give the divinyldisulphides The disulphides themselves can be utilized for the regiospecific and highly diastereoselective synthesis of vinylthio substituted thiiranes

Experimental

All the reactions were run under an atmosphere of dry nitrogen 2-Butyne, 3-hexyne, propyne, 3,3-dimethyl-1-butyne, Super-Hydride^{R}, Super-Deuteride^{R}, Methyllithium and *t*-Butyllithium were purchased from Aldrich and used without further purification Phthalimidosulphenyl chloride was synthesized using a literature procedure[6]. Silica gel (E.Merck 70-230 Mesh) was used for column chromatography All ^{1}H nmr spectra were performed in $CDCl_3$ and were recorded at 200 MHz on a Varian Gemini 200 or at 600 MHZ on a Bruker AMX 600 (for compound **3b**), residual $CHCl_3$ was used as reference at 7 26 ppm. ^{13}C Nmr were recorded at 50 MHz and chemical shifts were referenced to the central peak of the solvent ($CDCl_3$) at 77 00 ppm GC-MS spectra were performed with a Auto-Hrgc-Ms QMD 1000 Carlo Erba Melting points were measured on a Buchi 510 Melting Point and are uncorrected Microanalysis were obtained with an Elementary Analyzer 245 C Perkin-Elmer

General procedure for the synthesis of *N*(vinylthio)phthalimides 1

To a solution of 3 3 eq of alkyne in 5 mL of anhydrous CH_2Cl_2 in an inert atmosphere (N_2), a solution of phthalimidosulphenyl chloride in 8 mL of anhydrous CH_2Cl_2 was added at 0 ^{o}C *via* a syringe The reaction mixture was kept at 0 ^{o}C for 15 min then allowed to warmed up to room temperature After an additional 15 min the colorless solution was diluted with 50 mL of CH_2Cl_2, washed twice with saturated $NaHCO_3$ and twice with water

The organic layer was dried (Na_2SO_4) and evaporated to give a crude material which was chromatographed on silica gel (eluent petroleum ether diethyl ether= 3 1) and recrystallized using *n*-hexane

1a Yield 94% mp 121-122 ^{o}C. ^{1}H nmr ($CDCl_3$) δ 8 00-7 90 (m, 2 H arom), 7 80-7.70 (m, 2 H, arom), 2 62 (q, J = 1 55 Hz, 3H), 2 05 (q, 3 H) ^{13}C nmr ($CDCl_3$) δ 167 72,(s); 136 42(s), 134 65(d),

131 82(s); 126 74(s), 123.93(d), 24 60(q), 20 04(q) MS, m/z, (relative intensity) 267,(M^+, 23), 232,(M - Cl, 28); 148, ($PhthH^+$, 60) 120, (M - Phth, 100) Anal Calcd for $C_{12}H_{10}ClNO_2S$ C, 53 83, H, 3 76, N, 5 23 Found, C, 54 15; H, 3 73; N, 5 08

1b Yield 86% mp 96-98 °C ^1H nmr ($CDCl_3$) δ 8 00-7 90 (m, 2 H arom), 7 80-7 70 (m, 2 H, arom), 3 09 (q, J = 7 44 Hz, 2 H), 2 33 (q, J = 7 39, 2 H), 1 37 (t, J = 7 39 Hz, 3 H), 1 22 (t, J = 7 44 Hz, 3 H) ^{13}C nmr ($CDCl_3$) δ 168 14(s), 143 44(s), 134 84(d), 132 53(s), 132 10(s), 124 01(d), 30 97(t), 26 60(t), 12 92(q), 11 85(q) MS, m/z, (relative intensity) 295,(M^+, 17), 260, M - Cl, 45) 148,($PhthH^+$, 100) Anal Calcd for $C_{14}H_{14}ClNO_2S$ C, 56 85, H, 4 77, N, 4 73 Found, C, 56 55, H, 4 66, N, 4 98

1c Yield 87% mp 106-108 °C ^1H nmr ($CDCl_3$) δ 8 00-7 90 (m, 2 H arom), 7 80-7 70 (m, 2 H, arom); 6 66 (q, J = 1 38 Hz, 1 H), 2 01 (d, 3 H) ^{13}C nmr ($CDCl_3$) δ 167 80(s), 134 99(d), 134 03(s), 131 88(s), 124 22(d), 122 27(d), 17 02(q) MS, m/z,(relative intensity) 253, (M^+, 24), 218, (M - Cl, 22), 148, ($PhthH^+$, 100) Anal Calcd for $C_{11}H_8ClNO_2S$ C, 52 08, H, 3 18, N, 5 52 Found, C, 52 00, H, 3 01, N, 5 62

1d Yield 92% mp 79-80 °C ^1H nmr ($CDCl_3$) δ 8 00-7 86 (m, 2 H arom), 7 85-7 72 (m, 2 H, arom), 6 43 (s, 1 H), 1 39 (s, 9 H) ^{13}C nmr ($CDCl_3$) δ 167 71(s), 145 33(s), 134 97(d), 131 99(s), 124 20(d), 119 50(d), 37 40(s), 28 59(q) MS, m/z, (relative intensity) 295, (M^+, 62), 260, (M - Cl, 66), 148, ($PhthH^+$, 50), 41,(100) Anal Calcd for $C_{14}H_{14}ClNO_2S$ C, 56 85, H, 4 77, N, 4 73 Found, C, 56 88, H, 5 00, N, 4 81

General procedure for the synthesis of thiiranes 3

To a solution of 2 eq of the adducts **1** in 5 mL of anhydrous THF in a inert atmosphere (N_2) at -78 °C 4 mL of Super-Hydride^R (Aldrich 1 M in THF) were added via a syringe After 10 min at -78 °C, 10 mL of saturated NH_4Cl were added, the reaction mixture warmed at room temperature and washed twice with 20 mL of diethyl ether The organic layers were recollected, dried (Na_2SO_4), and evaporated To the crude material so obtained 50 mL of *n*-pentane were added and the solid phthalimide precipitated was filtered off Evaporation of the solvent gave the crude thiiranes which were chromatographated on silica gel using *n*-hexane as eluent Attempt to further purify the thiiranes **3** by vacuum distillation gave extensive decomposition, mainly due to desulphurization

3a Yield 66% oil Spectroscopic data refer to the (*E,E*) major isomer ^1H nmr ($CDCl_3$) δ 3 23 (q, J = 6 11 Hz 1 H), 2 38 (q, J = 1 56 Hz, 3 H), 2 22 (q, J = 1 56 3 H), 1 76 (s, 3 H), 1 58 (d, J = 6 11 Hz, 3 H) ^{13}C nmr ($CDCl_3$) δ 134 83(s), 125 06(s), 52 82(s), 45 16(d), 24 43(q), 23 52(q), 21 61(q), 16 77(q) MS, m/z, (relative intensity) 208, (M^+, 7), 173, (M - Cl, 100) Anal Calcd for $C_8H_{13}ClS_2$ C, 46 02, H, 6 28 Found, C, 45 82, H, 6 47

3b Yield 48% oil Spectroscopic data refer to the (*E,E*) major isomer ^1H nmr (600 MHz, $CDCl_3$) δ 3 18 (A part of an $AMNX_3$ system, J_{AM} and J_{AN} = 5 40 and 9 00 Hz, 1 H), 2 84-2 69 (CD part of an CDY_3 systems + E part of an EFZ_3 system, 3 H), 2 34 (F part of an EFZ_3 system, J_{EF} = 21 60 Hz, J_{FZ} = 7 20 Hz, 1 H), 2 02 (M part of an $AMNX_3$ system, J_{MN} = 20 70 Hz, J_{AM} = 5 4 Hz, J_{MX} = 7 20 Hz, 1 H), 1 91 (G part of an GKW_3 system, J_{GK} = 21 60 Hz, J_{GW} = 7 20 Hz, 1 H), 1 70 (K part of an GKW_3 system, J_{KG} = 21 60 Hz, J_{KW} = 7 20 Hz, 1 H), 1 55 (N part of an $AMNX_3$ system, J_{NM} = 20 70 Hz, J_{NA} = 5 4 Hz, J_{NX} = 7 20 Hz, 1 H), 1 18 (Y part of an CDY_3 system, J_{YC}

= J_{YD} = 7 2 Hz, 3 H), 1 16 (Z part of an EFZ_3 system, J_{ZE} = J_{ZF} = 7 2 Hz, 3 H); 1 10 (W part of an GKW_3 system, J_{WG} = J_{WK} = 7 2 Hz, 3 H), 1 11 (X part of an $AMNX_3$ system, J_{XM} = J_{XN} = 7 20 Hz, 3 H) ^{13}C nmr ($CDCl_3$) δ 140 20(s), 131 08(s), 59 84(s), 55 12(d), 30 37(t); 28 25(t); 27 08(t), 25 03(t); 13 38(q), 12 77(q), 12.35(q), 11 67(q) MS, m/z, (relative intensity)· 264, (M^+, 4), 229, (M - Cl, 65), 73, (100)

3c Yield 57% oil ^1H nmr ($CDCl_3$) δ 6 40 (q, J = 1 48 Hz 1 H); 2 77 (d, J = 1 40 Hz, 1 H), 2 69 (d, J = 1 40, 1 H), 2 16 (d, J = 1.48 Hz, 3 H), 1 86 (s, 3 H) ^{13}C nmr ($CDCl_3$) δ 132 29(s); 120 04(d), 47 18(s); 35 08(t), 29.12(q), 19 02(q) MS, m/z, (relative intensity). 180, (M^+, 3), 145, (M - Cl, 100)

Desulphurization of 3a to the divinylsulphide 4

To a solution of 50 mg (0 24 mmol) of **3a** in 2 mL of dry $CHCl_3$ 63 mg of triphenylphosphine (0 24 mmol) were added at room temperature The reaction mixture was kept for 90 h at this temperature, after this time GC and GC-MS analysis of the crude material showed the presence of the two isomeric vinyl sulphides in a 93 7 ratio Purification *via* preparative TLC using *n*-hexane as eluent gave 35 mg (83% yield) of **4a** as an oil still constituted by a 93 7 mixture of the *E,E* and *Z,E* isomers

Spectroscopic data refer to the (*E,E*) major isomer ^1H nmr ($CDCl_3$) δ 5 67 (A part of an AM_3X_3 system J_{AM} = 1 40 Hz, J_{AX} = 5 94 Hz, 1 H); 2 35 (q, J = 1 56 Hz, 3 H), 2 05 (q, J = 1 56, 3 H), 1 82 (M part of an AM_3X_3 system, J_{AM} = 1 40 Hz, J_{MX} = 1 08 Hz, 3 H), 1.70 (X part of an AM_3X_3 system, 3 H) ^{13}C nmr ($CDCl_3$) δ 128 64(s), 128 14(s), 126 32(s), 124 79(d), 24 21(q), 21 83(q), 17 65(q), 14 58(q) MS, m/z, (relative intensity) 176, (M^+, 41), 141, (M - Cl, 100)

Oxidation of 4a to the sulphone 5

A solution of 13 mg (0 074 mmol) of **4a** in 2 mL of CH_2Cl_2 was oxidized using 51 mg (0 16 mmol) of *m*-chloroperbenzoic acid After 20 h at room temperature the reaction mixture was diluted with 10 mL of *n*-pentane, washed several times with a 10% NaOH solution and dried with $CaCl_2$, evaporation of the solvent gave 13 mg (87% yield) of **5a** as an oil constituted by a 93 7 mixture of the *E,E* and *Z,E* isomers

Spectroscopic data refer to the (*E,E*) major isomer ^1H nmr ($CDCl_3$) δ 6 74 (A part of an AM_3X_3 system J_{AM} = 1 30 Hz, J_{AX} = 6 94 Hz, 1 H), 2 58 (q, J = 1 59 Hz, 3 H), 2 05 (q, J = 1 59, 3 H), 1 87 (M part of an AM_3X_3 system, J_{AM} = 1 30 Hz, J_{MX} = 1 10 Hz, 3 H), 1 83 (X part of an AM_3X_3 system, 3 H) ^{13}C nmr ($CDCl_3$) δ 145 99(s), 136 67(s), 136 39(s), 131 85(d), 24 29(q), 17 89(q), 14 00(q), 10 92(q)

General procedure for the synthesis of disulphides 6

This reaction was carried out using the same procedure used for the synthesis of the thiiranes **3**, but using 1 mole equivalent of Super-Hydride^R was used The disulphides were purified by column chromatography (eluent petroleum ether) and distilled using a kugel-rohr apparatus

6a Yield 95% bp 65 ^oC 5 10^{-3} mmHg ^1H nmr ($CDCl_3$) δ 2 34 (q, J = 1 53 Hz, 6H), 2 20 (q, 6 H) ^{13}C nmr ($CDCl_3$) δ 134 14(s), 127 42(s), 23 97(q), 20 66(q) MS, m/z, (relative intensity) 242, (M^+, 34), 121, (65), 45,(100) Anal Calcd for $C_8H_{12}Cl_2S_2$ C, 39 51, H, 4 97 Found C, 39 86, H, 5 25

6b Yield 84% bp 70 °C 1 10^{-3} mmHg ^{1}H nmr ($CDCl_3$) δ 2 69 (q, J = 7 38 Hz, 4 H), 2 61 (q, J = 7 41 Hz, 4 H), 1 09 (t, J = 7 38 Hz, 6 H), 1 08 (t, J = 7 41 Hz, 6 H) ^{13}C nmr ($CDCl_3$) δ 141 00(s); 132 83(s), 30 39(t), 26 70(t), 12 80(q), 11 77(q) MS, m/z, (relative intensity) 298, (M^+, 10), 149, (50), 59 (100) Anal Calcd for $C_{12}H_{20}Cl_2S_2$ C, 48 15, H, 6 74 Found C, 48 37, H, 7 10

6c Yield 87% bp 50 °C 1 10^{-2} mmHg ^{1}H nmr ($CDCl_3$) δ 6 39 (q, J = 1 42 Hz, 1 H), 2 10 (d, 3 H) ^{13}C nmr ($CDCl_3$) δ 133 93(s), 118 99(d), 17 37(q) MS, m/z, (relative intensity) 214 (M^+, 3), 107, (34), 45, (100) Anal Calcd for $C_6H_8Cl_2S_2$ C, 33 49, H, 3 75 Found C, 33 34, H, 3 83

6d This compound decomposes in solution or on silica gel Nmr spectroscopic data of the crude material obtained after usual work-up showed the presence of only one compound ^{1}H nmr ($CDCl_3$) δ 6 42 (s, 2 H), 1 36 (s, 18 H) ^{13}C nmr ($CDCl_3$) δ 143 74(s), 123 19(d), 37 64(s), 29 47(q)

Transformation of 1d in 2,5-di-*t*-butyl-3-chloro thiophene 16

A solution of 252 mg (1 17 mmol) of crude **6d** in 10 mL of chloroform was kept seven days at room temperature After this time the ^{1}H nmr spectrum showed the complete decomposition of the disulphide **6d** into the thiophene **16** Preparative TLC on silica gel using *n*-hexane as eluent gave 214 mg (85 % yield) of **16** as an oily material ^{1}H nmr ($CDCl_3$) δ 6 57 (s, 1 H), 1 44 (s, 9 H), 1 32 (s, 9 H) ^{13}C nmr ($CDCl_3$) δ 151 26(s), 142 71(s), 124 29(s), 118 14(d), 34 33(s), 34 15(s), 31 83(q), 29 82(q). MS, m/z, (relative intensity) 230, (M^+, 68), 215, (100) Anal Calcd for $C_{12}H_{19}ClS$ C, 62 45, H, 8 30 Found C, 61 84 H, 8 39

2,5-Di-*t*-buthyl thiophene 17

To a solution of 14 mg (0 06 mmol) of **16** in 2 mL of anhydrous THF in a inert atmosphere (N_2) kept at -78 °, 0 038 mL of *t*-Butyllithium (1 7 M in hexane) were added After 1 5 h at -78 ° 0 1 mL of water were added and the reaction mixture warmed at room temperature, diluted with 20 mL of ether and washed with saturated NH_4Cl solution The organic layer was dried (Na_2SO_4) and evaporation of the solvent gave a crude material which was purified by preparative TLC, eluent *n*-hexane, to give 4 mg (33 5% yield) of **17** ^{1}H nmr ($CDCl_3$) δ 6 60 (s, 2 H), 1 36 (s, 18 H), (CCl_4, TMS) δ 6 46 (s, 2 H), 1 34 (s, 18 H) Litt[13] ^{1}H nmr (CCL_4, TMS) δ 6 45 (s, 2 H), 1 33 (s, 9 H)

(*E*)-1,2-Dimethyl-2-chloro-vinyl methyl sulphide 7

To a solution of 500 mg (2 06 mmol) of **6a** in 20 mL of anhydrous THF in a inert atmosphere (N_2) at -78° 1 06 mL of methyllithium (2 M in diethyl ether) were added The reaction mixture was kept 30 min at -78°, warmed to room temperature, quenched with 100 mL of a saturated NH_4Cl solution and then washed twice with 50 mL of diethyl ether The organic layers were recollected, dried (Na_2SO_4), and evaporated to give a crude material which was purified by preparative TLC, eluent *n*-hexane, and distillation on a kugel-rohr apparatus to give 100 mg (71% yield) of **7** B p 70 °C 27 mmHg ^{1}H nmr ($CDCl_3$) δ 2 45 (q, J = 1 53 Hz, 3 H), 2 23 (s, 3 H); 2 01 (q, 3 H) Litt[12] b p 50 °C 10 mmHg

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