Tetrahedron Vol 46, No 11, pp 3921–3928, 1990
Printed in Great Britain

0040–4020/90 $3 00+ 00

NEW ROUTES TO THIOKETENES AND PROPADIENETHIONE BY FLASH VACUUM THERMOLYSIS.

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(*Received in Belgium* 16 *March* 1990)

Abstract - *The retro-Diels-Alder reaction under flash vacuum thermolysis (FVT) conditions was applied to the synthesis of simple unstabilized thioketenes. Alternatively, these reactive thiocarbonyl compounds were obtained by FVT elimination of methyltrimethylsilyl sulfide from silylated ketene dithioacetals (and for thioketene itself from methyl trimethylsilyl dithioacetate). A synthesis of propadienethione associating these two thermolytic processes is also reported. The thermolysis products were identified by low temperature IR spectroscopy and immediate quenching with gaseous dimethylamine leading to the corresponding thioamides In the case of propadienethione, further reaction with the methanethiol formed in situ was observed.*

Flash vacuum thermolysis (FVT)[1] is an efficient gas phase method for the synthesis of reactive species, allowing spectroscopical and chemical investigation, either in the gas phase or after trapping at low temperature. In this paper, an application of this technique to the synthesis of thioketenes is presented. Most of these heteroallenes have a high tendancy to dimerize or polymerize, and their formation is often shown by low temperature spectroscopy, or by chemical trapping reactions[2]. FVT has been already used to prepare thioketenes, in particular from their dimers (desaurins)[3], cyclobutanedithiones[4], thiadiazoles[3,5,6], and dithioacetic acid[6] in the case of thioketene itself.

We describe herein two new routes to thioketenes : the retro-Diels-Alder reaction[7], and the elimination of methylthiotrimethylsilane from silylated ketene dithioacetals and methyl α-trimethylsilyldithioacetate. Our results concerning the synthesis of propadienethione are also reported[8].

Retro-Diels-Alder reactions (RDA)

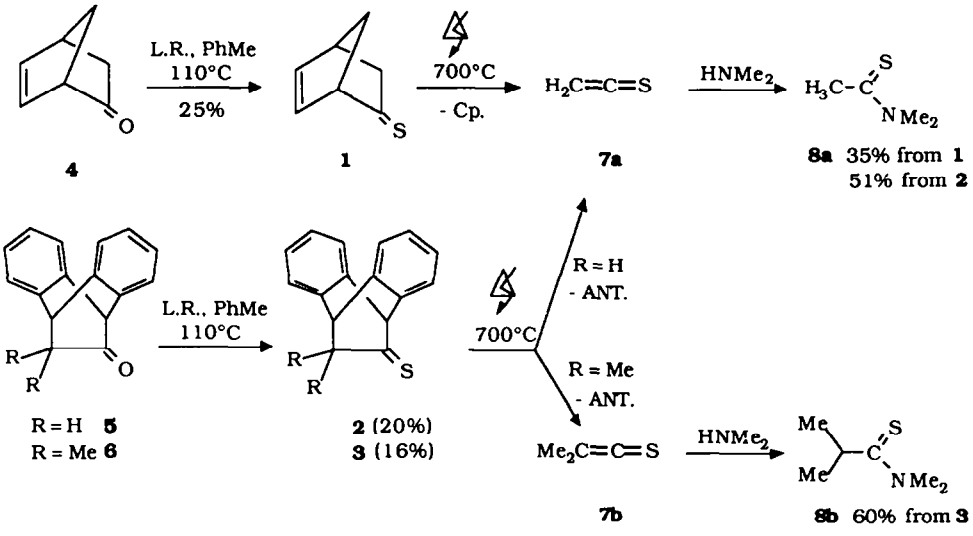
The RDA reaction under FVT conditions has already been used for the synthesis of some reactive thiocarbonyl compounds[9], but to the best of our knowledge it has not been applied to the preparation of thioketenes[2].

Norbornenethione **1** and the ethano-anthracenic thiones **2** and **3** (scheme 1) are formal adducts of a diene [cyclopentadiene (Cp), anthracene (ANT)] and a thioketene. They were synthesized by thionation of the corresponding ketones **4**[10], **5**[11], **6**[12] with Lawesson's reagent (L.R.) [13] and isolated in moderate yields. In the case of the thione **1**, this was due to its poor stability and partial oligomerization in the reaction mixture, and for the thiones **2** and **3** to the low reactivity of the sterically hindered ketones **5** and **6** towards Lawesson's reagent in refluxing toluene. Furthermore, in these last cases, thionation at 110°C was accompanied by a partial retrodienic reaction, leading to the formation of anthracene.

We have studied the thermolysis of the precursors **1**, **2** and **3** by FVT - low temperature IR spectroscopy experiments. In all cases the cycloreversion was found to be complete at 700°C (10^{-5} Torr). A mixture of cyclopentadiene and the thioketene **7a** was obtained from compound **1**. The characteristic bands of

7a were clearly observed : 2985, 1750, 1325 and 718 cm^{-1} in good agreement with previously reported data.[14] Furthermore, when gaseous dimethylamine was injected at the oven exit throughout the entirety of the thermolysis, N,N-dimethylthioacetamide **8a** was isolated in 35 % yield, besides polymeric **7a**.

Scheme 1



Crystallization of anthracene at the oven exit allowed us to obtain pure thioketene **7a** from the ethanoanthracenic adduct **2**. In this case, trapping with dimethylamine gave the expected thioamide **8a** in 51 % yield.

In the same way FVT of the thione **3** gave dimethylthioketene **7b** (IR: 1820 (m), 1789 (vs), 1742 (s) cm^{-1} in agreement with ref. [4], other transient bands most probably due to **7b** were observed at 2980, 1370, 1172 and 1154 cm^{-1}). The corresponding isopropylthiocarboxamide **8b** was isolated in 60 % yield.

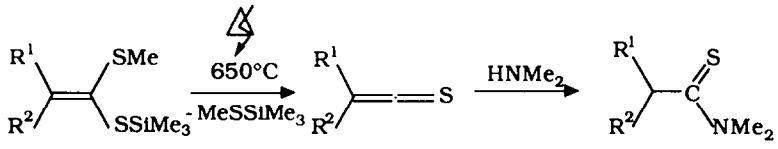
FVT of silylated ketene dithioacetals

Since the thermolysis of silylated ketene acetals [15] and monothioacetals [16] leads to ketenes by elimination of silylethers or silylsulfides, we anticipated that an analogous reaction from silylated ketene dithioacetals should lead to thioketenes. Monosilylated ketene dithioacetals **9a-h** (scheme 2) were prepared from the corresponding dithioesters by deprotonation and silylation [17], and then thermolyzed at *ca* 650°C (10^{-5} Torr). The thermolysis products were analysed by IR spectroscopy at -196°C. In each case, in addition to the known bands of $MeSSiMe_3$ [18], a very strong absorption was observed between 1738 (**7h**) and 1789 cm^{-1} (**7b**, see Table). These absorptions, which disappeared upon warming the sample carrier to *ca* -125°C, are characteristic of thioketenes.

The thioketenes **7a-h** were trapped by gaseous dimethylamine. However, the yields of isolated thioamides were moderate for thioketene **7a**, and the monoalkylthioketene **7c, d, h** because of their higher tendency to polymerize. When the dithioacetal **9a** was thermolyzed in the absence of dimethylamine an

insoluble polymer was obtained, and $MeSSiMe_3$ was the only product recovered in the soluble fraction (yield= 70 %).

Scheme 2

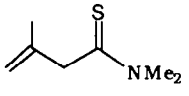


9 a-h **7 a-h** **8 a-h**

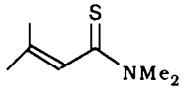
Table[a]

	R^1	R^2	$\upsilon_{C=C=S}$ of **7**	yield of **8**[b]
a	H	H	1750	20 %
b	Me	Me	1789	65 %
c	Et	H	1767 [19]	20 %
d	nPr	H	1770 [19]	30 %
e	Et	Me	1789	54 %
f	$-(CH_2)_3-$		1785 [20]	45 %
g	$-(CH_2)_4-$		1783 [21]	62 %
h	isopropenyl	H	1738 [c]	39 %

a References are given for those previously known thioketenes which have not been discussed in the text
b Determined by ^1H NMR.
c To our knowledge **7h** is the first mentioned α-ethylenic thioketene. In this case a mixture of two thioamides **8h** and **8'h** [31]was obtained. **8'h** resulted from the base-induced conjugation of **8h** in excess $HNMe_2$.



8h



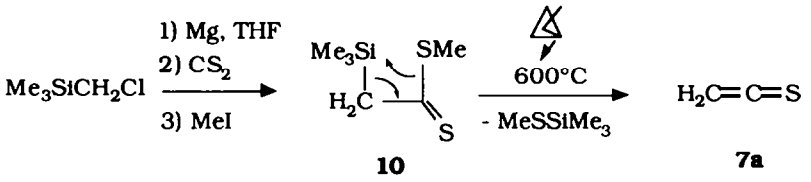
8'h

FVT of methyltrimethylsilyldithioacetate

Methyltrimethylsilyldithioacetate **10** (scheme 3) was prepared from Me_3SiCH_2Cl, CS_2 and MeI [22]. It was expected to give thioketene **7a**, as does its isomer **9a**, by thermal elimination of $MeSSiMe_3$. Indeed, an analogous reaction leading to ketene from methyltrimethylsilylacetate has been reported [23].

FVT of dithioacetate **10** was effected at 600°C. No starting dithioester was detected in the IR spectrum of the reaction products, which only showed the bands of $MeSSiMe_3$ [18] and thioketene **7a** . The yield of $MeSSiMe_3$, recovered together with an insoluble polymer,was 60%. However the thioamide **8a** was obtained in only 25% yield after trapping with $HNMe_2$.

Scheme 3



10 **7a**

The four-centres elimination mechanism without initial isomerisation to the silylated ketene acetal, which has previously been proposed for the thermolysis of methyltrimethylsilylacetate [23], can also be assumed for the thermal decomposition of the corresponding dithioester **10**. In fact, this latter reaction **10** → **7a**, complete at 600°C, appeared to be more favorable than the corresponding cleavage of **9a**, requiring 650°C under the same experimental conditions.

Propadienethione

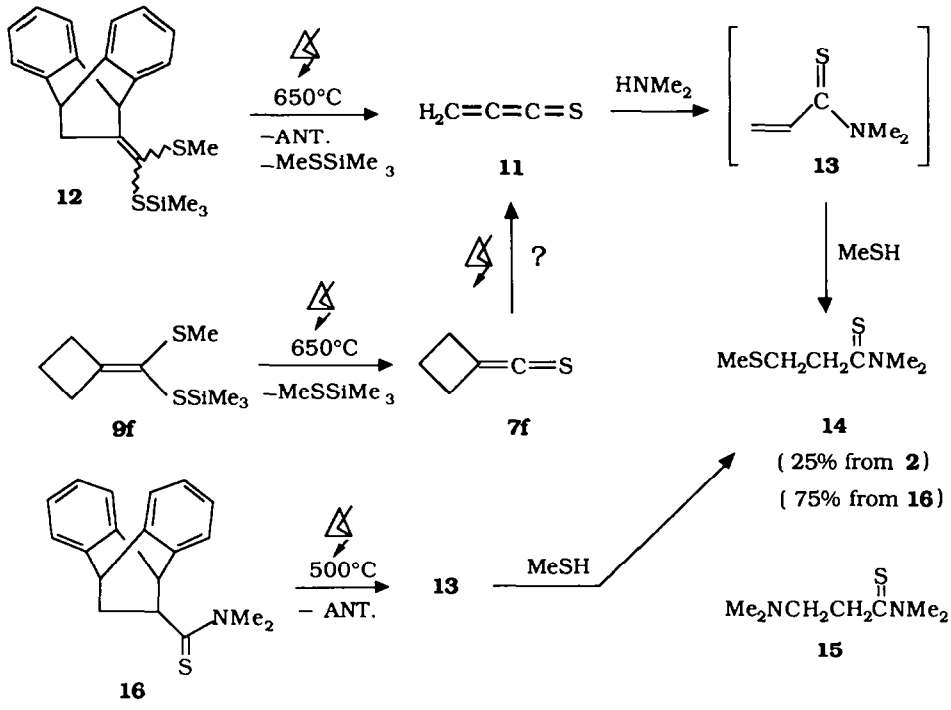
If, at the beginning of our work, the synthesis of the unstable heterocumulenes propadienone [24] and propadieneselone [25] had already been reported, nothing was known about propadienethione **11**. Only two stable homologues of this methylenethioketene had been described [26].

With a view to obtaining the new thiocumulene **11**, we prepared the ethanoanthracenic dithioacetal **12** (scheme 4). From this compound, it was expected that the thermal elimination of $MeSSiMe_3$ could be associated with a retrodienic reaction to yield the expected product **11**. In fact, FVT of **12** at 650°C led quantitatively to anthracene which crystallized at the oven exit, indicating that a retro-Diels-Alder reaction had occurred. Moreover, the absorptions of $MeSSiMe_3$ were observed in the low temperature (-196°C) IR spectrum of the volatile thermolysis products, together with two main transient bands at 2105 (s) and 2170 (m) cm^{-1} disappearing at -150°C. These bands, found in the same region as those of the previously mentioned homologues of **11** (2035 and 2000 cm^{-1}) [26], were very close to the two characteristic bands of propadienone (antisym. C=C=C stretch, 2127, 2171 cm^{-1}) [24].

The trapping of propadienethione with dimethylamine did not lead as expected to N,N-dimethyl thioacrylamide **13**[27]. The only identified product was the β-methylthiopropanethioamide **14** (yield= 25 %) resulting from the 1,4-addition of methanethiol on the thioacrylamide **13**. Methanethiol is most probably generated in a reaction between $MeSSiMe_3$ and the excess $HNMe_2$. Thiols are known to be very good nucleophiles, especially in basic media (an excess of $HNMe_2$ in the present case), where they react as thiolates. This is probably why the product obtained is the β-methylthio-thioamide **14** and not the N,N-dimethyl-3-dimethylaminopropane thioamide**15**. The structure of **14** was confirmed by reacting the thioacrylamide **13**, obtained by the thermolysis of the ethanoanthracenic compound **16** [27], with methanethiol.

Recently, the thermolysis at 800°C of cyclopenteno-1,2,3-thiadiazole was used to obtain propadienethione **11**, characterized by microwave spectroscopy [28]. Trimethylenethioketene **7f** was described as an intermediate in this reaction. Since we had already synthesized compound **7f** by the elimination of $MeSSiMe_3$ from the corresponding ketene dithioacetal **9f** at 650°C, a direct synthesis of propadienethione **11** was attempted by FVT of **9f** at temperatures higher than 650°C.

Scheme 4



In the low temperature IR spectrum of the thermolysis products of **9f** at 800°C, two very weak bands were indeed observed at 2105 and 2170 cm^{-1}. At 900°C no increase of these bands was detected, and instead of the signal of thioketene **7f** (1785 cm^{-1}) a new band at 1742 cm^{-1} was observed. We were not able to characterize by chemical trapping the product formed at this high temperature. However, the disappearance of the 1742 cm^{-1} signal at -150°C and its similarity with that of the α-ethylenic thioketene **7h** (1738 cm^{-1}) could suggest a radical mediated ring opening of trimethylenethioketene **7f** leading to an unstable conjugated thioketene.

Experimental part

The following apparatus were used : ^1H NMR, Varian A 60 D and EM 360 (60 MHz). ^{13}C NMR, Bruker WP 80 SY (20,15 MHz). δ are given in ppm relative to internal $SiMe_4$ and J in Hz. IR, Perkin Elmer 1420. MS, Nermag R 10 10H.

FVT :

IR experiments. *ca.* 0.02 g of precursor was vaporized through a quartz oven (l= 12 cm, i.d. : 1,6 cm ; 10^{-5} Torr) fitted on an "Air Liquide" optical cryostat (NaCl sample carrier and windows). The IR spectrum were recorded *in situ* (frozen film at -196°C).

Trapping experiments. 0.1 g of precursor were thermolysed (same FVT conditions as for IR spectrum), and, during the whole thermolysis, an excess of gaseous $HNMe_2$ was slowly injected at the oven exit. The

products were condensed in a liquid nitrogen trap, then warmed to room temperature. After evaporation of the volatile products, the residue was taken up with $CDCl_3$ and filtered. ^1H NMR analysis of the soluble part showed that it was mostly constituted (at least 90 %) of the expected thioamide, and the yields were determined using a benzene or dioxane standard.

The ^1H NMR spectra of thioamides **8a-d** [29, 30] were previously described. The new thioamides **8e-g** were identified by their ^1H NMR and mass spectra.

N,N,2-trimethylbutanethioamide **8e** : ^1H NMR ($CDCl_3$) : 0.88 (t, J= 7, 3H, CH_3), 1.21 (d, J= 6, 3H, CH_3), 1.72 (dq, J= 8 and 7, 2H, CH_2), 3.02 (tq, J= 7 and 6, 1H, CH), 3.32 and 3.50 (2s, 6H, NMe_2). MS : m/z (%) 145 ($M^{+\cdot}$, 100), 130 (13), 117 (26), 112 (34), 103 (43), 88 (63), 84 (33), 74 (17).

N,N-dimethylcyclobutanecarbothioamide **8f** : ^1H NMR ($CDCl_3$) : 1.5-2.9 (m, 6H, 3 CH_2), 3.1-3.7 (m, 1H, CH), 3.27 and 3.43 (2s, 6H, NMe_2). MS : m/z (%) 143 ($M^{+\cdot}$, 100), 128 (27), 114 (54), 110 (16), 100 (13), 88 (24), 82 (19), 71 (43), 65 (11).

N,N-dimethylcyclopentanecarbothioamide **8g** : ^1H NMR ($CDCl_3$) : 1.5-2.1 (m, 8H, 4 CH_2), 2.9-3.2 (m, 1H, CH), 3.30 and 3.48 (2s, 6H, NMe_2). MS : m/z (%) 157 ($M^{+\cdot}$, 54), 128 (13), 124 (54), 116 (100).

A mixture of the β-ethylenic thioamide **8h** [31] (yield : 22 %) and its conjugated isomer **8'h**[31](17%) was obtained from the thioketene **7h**. ^1H NMR signals of each compound were attributed from this mixture. MS were obtained by GLC/MS coupling experiments.

N,N,3-trimethylbut-3-enethioamide **8h** : ^1H NMR ($CDCl_3$) : 1.80 (broad s, 3H, CH_3), 3.28 and 3.54 (2s, 6H, NMe_2), 3.63 (broad s, 2H, CH_2), 4.73 (narrow m, 1H, HC=), 4.93 (narrrow m, 1H, HC=). MS : m/z (%) 143 (M^+, 100), 142 (78), 128 (89), 110 (14), 99 (29), 95 (29), 88 (91), 85 (17), 82 (15), 73 (21), 71 (20), 70 (57), 65 (22).

N,N,3-trimethylbut-2-enethioamide **8'h** : ^1H NMR ($CDCl_3$) : 1.70 (broad s, 3H, CH_3), 1.80 (broad s, 3H, CH_3), 3.30 and 3.50 (2s, 6H, NMe_2), 5.97 (narrow m, 1H, HC=). MS : m/z (%) 143 ($M^{+\cdot}$,100), 142 (60), 128 (51), 110 (13), 99 (45), 95 (42), 88 (23), 85 (14), 74 (13), 71 (12), 70 (26), 65 (22).

Thioketones

Norbornenethione **1**. Norbornenone (1.08 g, 10 mmol.) and Lawesson's reagent (2.02 g, 5 mmol.) were refluxed in toluene (20 mL) for 2 hours. Toluene was then evaporated. The resulting oil was passed through a short silica gel column (50 g) using a 80/20 mixture of petroleum ether and CH_2Cl_2 as eluent. Norbornenethione **1** (0.31 g, yield= 25 %) was isolated as a red oil.

^1H NMR (CCl_4) : 1.93 (m, 2H, CH_2), 2.32 (~ s, 2H, H_2C-C=S), 3.34 (~ s, 1H, CH), 3.71 (m, 1H, HC-C=S), 6.02 (m, 1H, HC=), 6.46 (dd, J= 6 and 2, 1H, HC=). ^{13}C NMR ($CDCl_3$) : 43.14, 51.57, 52.30, 69.02, 131.68, 148.08, 263.03 (C=S). IR (CCl_4) : 3070, 2985, 2940, 2875, 1414, 1329, 1303, 1240, 1208, 1186, 1142, 1080, 905, 702 cm^{-1}. MS : m/z (%) 124 (M^+, 18), 66 (100), 58 (21), 39 (38). Anal.: C_7H_8S : Calc. % S 25.82, found : 25.83.

The ethanoanthracenic thiones **2** and **3** were obtained in a similar way but the reaction time was 5 hours.

9,10-dihydro-9,10-ethanoanthracene-11-thione **2**. Yield= 20 %.Red crystals. mp= 167-169°C.^1H NMR ($CDCl_3$) : 2.79 (d, J= 2.5, 2H, CH_2), 4.59 (t, J= 2.5, 1H, CH), 5.55 (s, 1H, HC-C=S), 7.0-7.4 (m, 8H, aromatic). ^{13}C NMR ($CDCl_3$) : 46.64, 53.06, 73.79, 123.76, 124.71, 126.82, 127.48, 137.77, 142.17, 251.35 (C=S). IR (KBr) : 3065, 3020, 1478, 1467, 1455, 1403, 1338, 1257, 1122, 1100, 768, 742, 664, 648, 620, 590, 523 cm^{-1}. MS : m/z (%) 236 (M^+, 7), 202 (2), 178 (100), 58 (2), 44 (5). Anal.: $C_{16}H_{12}S$: calc. % S 13.57, found : 13.41.

12,12-dimethyl-9,10-dihydro-9,10-ethanoanthracene-11-thione **3**. Yield = 16 % Red crystals. mp= 125°C. ^{1}H NMR ($CDCl_3$) : 1.05 (s, 6H, 2 Me), 4.31 (s, 1H, CH), 5.68 (s, 1H, HC-C=S), 7.05-7.50 (m, 8H, aromatic). ^{13}C NMR ($CDCl_3$) : 31.75 (2 Me), 55.07, 58.90, 74.66, 124.30, 125.19, 126.79, 127.03, 136.59, 141.89, 261.78 (C=S). MS : m/z (%) 264 ($M^{\cdot+}$, 6), 178 ($ANT^{\cdot+}$, 100). Anal.: $C_{18}H_{16}S$.: calc.% C 81.77, H 6.10, S 12.14, found : C 81.44, H 6.22, S 12.29.

Dithioesters

Most of the dithioesters used were known compounds and were prepared by usual methods [32].

Methyl cyclobutanecarbodithioate

Cyclobutanecarboxylic acid (4 g, 0.02 mol) and 2,4-bis(methylthio)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Davy's reagent,[33] 7.95 g, 0.028 mol) were refluxed in dioxane (120 mL) for 15 mn. Heating was stopped and phosphorus pentasulfide (1.78 g, 0.004 mol) was added. After another 5 mn reflux, the solution was allowed to cool to room temperature, then poured in 600 mL of water and 200 mL of petroleum ether. The mixture was decanted and the organic layer dried with sodium sulfate. After filtration, evaporation of the solvent and chromatography on silica gel (eluent : petroleum ether), the head fraction (2.86 g of a yellow liquid) was distilled under reduced pressure (bp= 60°C/0.25 Torr). 2.14 g (yield= 37 %) of pure methyl cyclobutanecarbodithioate were obtained.

^{1}H NMR (CCl_4) : 1.6-2.7 (m, 6H, $3CH_2$), 2.58 (s, 3H, SMe), 3.78 (m~q, 1H, CH). ^{13}C NMR ($CDCl_3$) : 17.33, 19,22, 30.73, 53.94, 243.40 (C=S). Anal.: $C_6H_{10}S_2$: calc. % S 43.73, found : 43.84.

Silylated ketene dithioacetals.

They were prepared according to the method described in ref.[17] We found these compounds to be poorly stable, especially **9a**, and **9h**. They must be used soon after their preparation.

2-methyl-1-methylthio-1-trimethylsilylthioprop-1-ene ***9b*** : ^{1}H NMR (CCl_4) : 0.27 (s, 9H, $SiMe_3$), 2.00 (~ s, 6H, 2Me), 2.25 (s, 3H, SMe). ^{13}C NMR ($CDCl_3$) : 1.26 ($SiMe_3$), 17.31 (SMe), 23.20 (Me), 23.72 (Me), 120.14 (=C), 143.36 (=C). IR (film) : 2955, 2915, 1240, 835 cm^{-1}. MS : m/z (%) 206 ($M^{\cdot+}$, 6), 147 (100), 120 (28), 105 (93), 93 (62), 86 (77).

(mehylthiotrimethylsilylthiomethylene)cyclobutane **9f** : ^{1}H NMR (CCl_4): 0.30 (s, 9H, $SiMe_3$), 1.7-2.2 (m, 2H, CH_2), 2.23 (s, 3H, SMe), 2.75 (~ t, 4H, $2CH_2$). ^{13}C NMR ($CDCl_3$) : 1.35 ($SiMe_3$), 15.22 (CH_2), 16.50 (SMe), 32.22 and 32.92 ($\underline{C}H_2$-C=), 116.44 and 151.82 (C=C).

(Methylthiotrimethylsilylthiomethylene)cyclopentane **9g** : ^{1}H NMR ($CDCl_3$): 0.30 (s, 9H, $SiMe_3$), 1.0-1.7 (m, 8H, 4 CH_2), 1.99 (s, 3H, SMe). ^{13}C NMR ($CDCl_3$) : 1.30 ($SiMe_3$), 16.86 (SMe), 26.65, 27.10, 34.20, 35.77, 115.47 (=C), 155.83 (=C). IR (film) : 2960, 1250, 840 cm^{-1}. MS : m/z (%) 232 ($M^{\cdot+}$, 27), 219 (24), 147 (9), 112 (100), 79 (18), 75 (41), 73 (53).

3-methyl-1-methylthio-1-trimethylsilylthiobuta-1,3-diene **9h** : only one isomer observed by ^{1}H NMR (CCl_4) : 0.30 (s, 9H, $SiMe_3$), 1.27 (s, 3H, Me), 2.00 (s, 3H, SMe), 4.93 and 4.98 (2 narrow m, 2H, H_2C=), 6.10 (~ s, 1H, HC=). ^{13}C NMR ($CDCl_3$) : 1.50 ($SiMe_3$), 17.80 (SMe), 23.38 ($\underline{C}H_3$-C=), 117.16, 129.05, 132.08, 148.35 (ethylenic carbons).

Propadienethione

11-(methylthiotrimethylsilylthiomethylene)-9,10-dihydro-9,10-ethanoanthracene **12** was prepared by the usual method[17] from the corresponding dithioester [34]. It was obtained as a mixture of the two expected stereoisomers. We describe the major isomer (unattributed stereochemistry). ^{1}H NMR (CCl_4) : 0.10 (s, 9H, $SiMe_3$), 2.32 (s, 3H, SMe), 2.48 (d, J= 2.5, 2H, CH_2), 4.17 (t, J= 2.5, 1H, CH), 5.82(s, 1H, CH), 6.8-7.4

(m, 8H, aromatic). ^{13}C NMR ($CDCl_3$) : 1.05 ($SiMe_3$), 17.54 (SMe), 40.27 (CH_2), 45.52 (CH), 52.27 (CH), 123.33, 123.80, 125.99, 141.42 (=C), 144.06 (=C). IR (CCl_4) : 2980, 2960, 2880, 1470, 1260, 850 cm^{-1}. MS : m/z (%) 368 (M^+, 1), 291 (100), 219 (26), 203 (23), 178 (73), 147 (44), 73 (92).

Thermolysis of **12** with injection of $HNMe_2$ at the oven exit gave N,N-dimethyl-3-methylthiopropanethioamide **14** (slightly yellow oil, 25 % yield after chromatography on silica gel, eluent : CH_2Cl_2). ^1H NMR ($CDCl_3$) : 2.27 (s, 3H, SMe), 2.98 (s, 4H, CH_2CH_2), 3.34 and 3.50 (2s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$) : 15.98 (SMe), 33.48, 41.57, 42.42, 44.56, 202.11 (C=S). MS : m/z (%) 163 (M^+, 25), 148 (100), 116 (10), 88 (44), 84 (20), 74 (18), 73 (12), 71 (28), 70 (18), 61 (14), 45 (19), 44 (36).

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