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DIMERIZATION OF α-ETHYLENIC DITHIOESTERS

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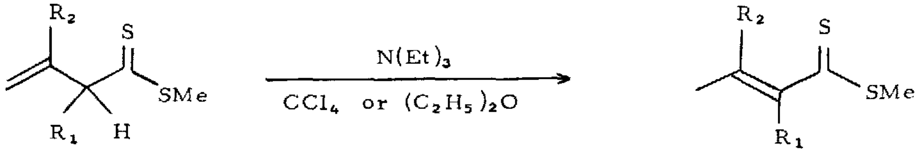
Summary : Methyl propenedithioate and three methyl 2-butenedithioates were prepared and all but one of these hetero-dienes gave dimers resulting from a [4 + 2] cycloaddition. Formation of a 1,5-dithiocin ring was also observed from the propenedithioate.

Only few examples of α-ethylenic dithioesters substituted on the double bond by an alkyl [1,2] alkylthio[3,4,5] or amino [6]-group appear in the literature. In our preceeding paper[1], we described the preparation of some β-unsaturated dithioesters starting from allylic Grignard reagents and phenylisothiocyanate and we mentionned that these compounds could be readily isomerized to α-ethylenic dithioesters more or less stable at room temperature.

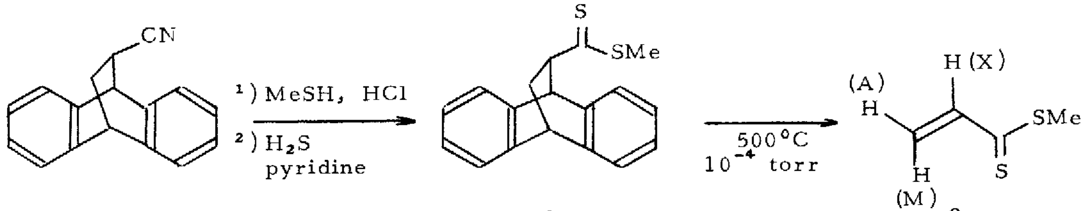
The three alkenedithiocarboxylates 4, 5 and 6 studied here were prepared by this process. Conjugation of the double bond from dithioesters 1, 2, 3 [1] could be achieved in ether or carbon tetrachloride containing 5 % of triethylamine.



		T °C	
1	$R_1 = R_2 = H$	-40°	4 (E)
2	$R_1 = CH_3$; $R_2 = H$	-40°	5 (E)
3	$R_1 = H$; $R_2 = CH_3$	+20°	6

The dithioesters 4 and 5 were found not to be stable at room temperature so the isomerization was performed at -40° C and the NMR spectra of these compounds were recorded at this temperature. ^1H NMR (CCl_4) δ : 4 : 2.60 (s, 3H), ABX_3 system : δ_A = 6.79 (1H), δ_B = 7.00 (1H), δ_X = 1.83 (3H), J_{AB} = 15, J_{AX} = -1,3, J_{BX} = 6,8 Hz ; 5 : 1.79 (dm, J= 7 Hz, 3H), 2.13 (m, 3H) ; 2.58 (s, 3H), 6.73 (qm, J= 7 Hz, 1H) ; 6 : 1.92 (s, br, 3H), 2.18 (s, br, 3H), 2.55 (s, 3H), 6.63 (m, 1H). ^{13}C NMR ($CDCl_3$) δ : 4 : 18.7, 19.4, 137.4, 137.9, 224.6 ; 5 : 15.3, 17.2, 20.2, 130.8, 144.5, 232.3 ; 6 : 19.3, 21.9, 28.53, 132.0, 148.9, 225.2.

Methyl propenedithioate 9 was obtained by flash thermolysis[7] of dithioester 8 prepared from the known nitrile 7[8] according to the usual procedure[9].

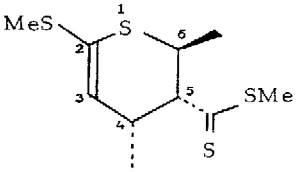


7 8 9

The unstable red dithioester 9 was trapped on a $CFCl_3$ or CD_2Cl_2 matrix at -196°C and its spectra were recorded at -90°C. ^{1}H NMR ($CFCl_3$) : 2.68 (s, 3H), ~AMX system δ_A = 5.56 (1H), δ_M = 6.48 (1H), δ_X = 6.95 (1H), $J_{AM} \sim 0$, J_{AX} = 10 Hz, J_{MX} = 17 Hz ; ^{13}C RMN (CD_2Cl_2) δ: 20.2, 123.6, 141.2, 226.2.

Except for dithioester 6[10] (disubstituted on C_3) these red dithioesters gave orange dimers at room temperature. Few examples of dimerizations of α-unsaturated thiocarbonyl compounds resulting from a [4 + 2] cycloaddition were previously reported in the literature. The dienophile moiety (C=C or C=S double bond) involved in these hetero-Diels-Alder reactions seems very much influenced by the nature of the substituents : dihydrothiopyran and dithiin rings were respectively obtained from aromatic[11,12,13] and aliphatic[14] α-ethylenic thioketones.

From dithioesters 4, 5 (solutions in CCl_4) and 9 (in $CFCl_3$) the dimers 10, 11, 12 were obtained[15], only one geometrical isomer in each case.



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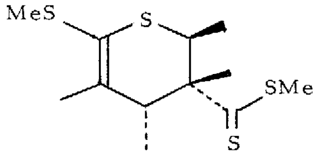

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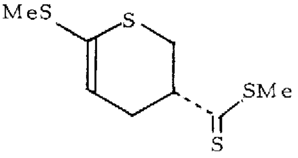
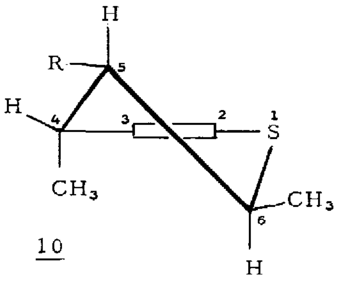


12

^{1}H NMR (CCl_4) : 10 : 1.00 (d, J= 7 Hz, C_4-CH_3), 1.22 (d, J= 6.2 Hz, C_6-CH_3), 2.25 (s, C_2-SCH_3), 2.57 (s, CSSCH_3), ~2.6 (m partially masked, H_4), 3.39 (dd, H_5, JH_5H_6= 10 Hz, JH_5H_4= 4 Hz), 3.75 (dq, H_6, JH_6H_5= 10 Hz, JH_6-CH_3= 6.2 Hz, a doublet was observed for this proton when the methyl group at 1.22 was irradiated), 5.87 (d, H_3, JH_3H_4= 6.4 Hz ; 11 : 0.90 (d, J= 6.8 Hz, C_4-CH_3) 1.16 (d, J= 6,5 Hz, C_6-CH_3), 1.48 (s, C_5-CH_3), 2.05 (s, C_3-CH_3), 2.27 (s, C_2-SCH_3), 2.32 (q partially masked, H_4, J= 6,8 Hz), 2.60 (s, CSSCH_3), 4.44 (q, H_6, J= 6,5 Hz) ; 12 : 2.30 (s, C_2-SCH_3), 2.63 (s, CSSCH_3), 2.12 to 3.88 (m, 5H), 5.99 (dd, H_3, J_1 ~ 6 Hz, J_2 ~ 3 Hz).

The ^{13}C NMR spectra of these dimers confirm the occurrence of the dithioester function (δ C=S is respectively observed at 237.2, 244.3 and 240.9 ppm for 10, 11 and 12) and the regioselectivity of the addition is readily deduced from the multiplicity and chemical shifts of signals in ^{1}H NMR spectra.

In particular, for dimer 10, the expected doublet of doublet for the proton H_5 adjacent to the dithioester group is observed at 3.39. More over, the values of the coupling constants between H_5H_6, H_5H_4 and H_3H_4 in dimer 10 are consistent with a stereochemistry which results from a cycloaddition of the monomer 4 (E) involving an endo transition state [16].



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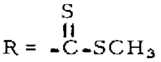


$R = -\overset{\overset{S}{\|}}{C}-SCH_3$

$J_{H_5H_6} = 10$ Hz

$J_{H_5H_4} = 4$ Hz

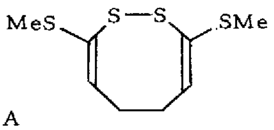
$J_{H_3H_4} = 6.4$ Hz

$J_{H_6-CH_3} = 6.2$ Hz

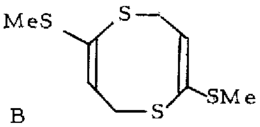
The high value (10 Hz) for $J_{H_5H_6}$ indicates a trans axial configuration between these two protons and an almost rigid conformation similar to the one suggested by Quiniou and al. for the dimer of a 4-methoxythiochalcone [11].

Although the NMR spectrum of 11 does not enable us to determine its stereochemistry, an endo transition state (promoted by secondary orbital interactions [16]) can be assumed for its formation. An attempt to purify 11 by distillation (13 Torr, 160°C) gave a red distillate containing a mixture of monomer 5 E (85 %) and dimer 11 (15 %). A complete cycloreversion was obtained by flash thermolysis (10^{-2} Torr, 250°C).

At room temperature, an exclusive formation of dimers 10 and 11 was observed but the dimerization of the methyl propenedithioate 9 was not so selective and in particular some polymerization occurred. If the pure dimer 12 was isolated after chromatography on silicagel (eluant : pentane), the NMR spectrum of the crude dimerization product showed, beside the signals of 12, those of a by-product 13. More over, when the initial solution of the monomer 9 was maintained at -50°C and the evolution was followed by NMR, we could observe almost exclusively the formation of 13 : ^1H NMR (CD_2Cl_2) δ : 2.30 (s, 6H) ; 3.75 (~ d, J= 7.6 Hz, 4H), 5.87 (t, J= 7.6 Hz, 2H) ; ^{13}C NMR (CD_2Cl_2) δ : 17.24 ($S\underline{C}H_3$), 34.48 ($\underline{C}H_2$), 128.59 (=$\underline{C}$-SCH_3), 134.66 ($\underline{C}H$=) ; mass spectrum : $M^{+\cdot} = 236$. At room temperature 13 slowly isomerizes to the [4 + 2] dimer 12 and polymerization is observed simultaneously.



A



B

Two dimeric structures A and B can be proposed for 13, both in agreement with the observed NMR coupling constant (7.6 Hz) between adjacent methylene and methine protons [17]. However, the 4,8-bis methylthio-2H, 6H-1,5 dithiocin B is the structure which is the most consistent with the observed chemical shift (3.75 ppm) of the methylene protons deshielded by both a sulfur atom and a double bond in α and α'. Besides, the same type of dimer was previously obtained by thermal dimerization of the benzothiete [18].

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[15] Dimerization of 4 and 5 could be followed by NMR and for 20 %-solution of the monomer in CCl_4, half-dimerization time was ~ 38 min (4 ⟶ 10) and ~ 75 min (5 ⟶ 11) ; 11 cristallized in methanol (F : 38°C), microanalysis : Calc.% : C 49.27, H 6.89, S 43.84 ; found C 49.08, H 6.75, S 43.68, Mass spectra m/e (%) : 292 (12), 205 (11), 146 (21), 131 (100), 120 (12), 99 (75), 65 (31), 59 (17), 55 (15), 45 (13).

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