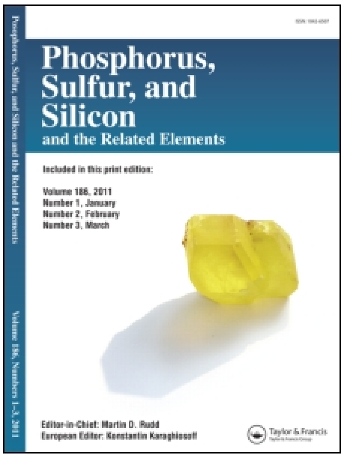

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SYNTHESIS OF POLYSULFIDES, SULFOXIDES AND SULFONES CONTAINING REACTIVE GROUPS

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SYNTHESIS OF POLYSULFIDES, SULFOXIDES AND SULFONES CONTAINING REACTIVE GROUPS

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Preparation of polysulfides, sulfoxides and sulfones (containing reactive groups: OH, Cl, COOR, CN SO_3Na) are presented; ^{13}C chemical shifts of these compounds have been recorded.

Key words: Sulfide; sulfoxide; sulfone; chlorosulfide; ^1H NMR; ^{13}C NMR.

INTRODUCTION

Many petroleum additives include heteroatoms, particularly sulfur and phosphorus. In this report we propose the synthesis of compounds including, apart from a simple chemical function, at least one sulfur atom.[1]

The synthesis we propose is very simple and can be used effectively also by industry. Our previous researches in the field of pertroleum additives[2] have shown that a sulfurated compound containing more than 2,5 sulfur atoms (average) per molecule becomes very corrosive. This characteristic is used to formulate lubricants for use with ferrous metals. Sulfurated compounds containing less sulfur are most often used to prepare lubricants for energy transmission (gear oils) and lubricants in contact with copper.

The synthesis reported in this paper mainly concerns the mono and disulfides and rarely trisulfides.

We have generally used the procedures described for the synthesis of similar compounds. Our main contribution in this field was the development of reliable synthetic methods which permit preparation of many sulfurated compounds.

The products mentioned in this report are generally not described in the literature. Some of them have been nevertheless subject of a description, claim or citation in a patent and have obtained thus a registry number.[3]

RESULTS

1) *Note.* Our previous work about lubricants[2] showed that t.butyl and methallyl radicals are some of the most efficient ones. That is the reason why we generally used these two radicals in our synthesis.

2) *Synthesis of polysulfurated alcohols.* Many ways to synthesize functionalized monosulfides are described.[4–10] The basic reaction is as follows (Table I):

TABLE I

Characteristics of monosulfurated alcohols: R—S—$(CH_2)_n$—OH

N°	R	n	Yield (%)	bp(°c) 1 mb	^{1}H NMR CH_2O CH_2=	^{1}H NMR CH_2S	^{1}H NMR CH_2	^{1}H NMR OH	^{1}H NMR CH_3
1	n.Butyl	2	77	69	3,70 t	2,60 m	1,50 m	3,10	0,95 m
2	t.Butyl	2	82	65	3,70 t	2,75 t		2,80	1,35 s
3	t.Butyl	3	77	78	3,70 t	2,60 t	1,85 m	1,80	1,35 s
4	t.Butyl	4	67	97	3,70 t	2,60 t	1,70 m	1,70	1,30 s
5	t.Butyl	5	88	95	3,60 t	2,50 m	1,55 m	1,60	1,30 s
6	t.Butyl	6	89	110	3,65 t	2,50 m	1,50 m	1,80	1,30 s
8	Methallyl	2	85	62	3,70 t 4,80 m	3,15 s 2,65 t		2,25	1,85 m
9	Methallyl	3	80	80	3,60 t 4,80 m	3,10 s 2,50 t	1,80 m	3,40	1,80 m
10	Methallyl	4	60	92	3,60 t 4,80 m	3,10 s 2,40 t	1,60 m	3,40	1,80 m
11	Methallyl	5	87	110	3,60 t 4,80 m	3,10 s 2,40 t	1,50 m	3,40	1,80 m
12	Methallyl	6	85	/	3,60 t 4,80 m	3,10 s 2,40 t	1,50 m	1,50	1,80 m
	$(t.BuS\text{-}CH_2)_2\text{-}CHOH$								
7			80	145	3,80 m	2,80 dd 2,60 dd J=15,7 Hz J=6,3 Hz		2,90	1,35 s

$$R\text{-}S\text{-}Na + Cl\text{-}(CH_2)_n\text{-}OH \longrightarrow R\text{-}S\text{-}(CH_2)_n\text{-}OH + NaCl$$

1 - 6 (77-89%) and **9 - 12**(60-85%)

SCHEME I

This method applies also to secondary chloroalcohols (see compound **7**). However for preparing alcohol **8**, we recommend an inversion of the functions, due to the commercial availability of the starting products:

$$CH_2{=}C(Me)\text{-}CH_2\text{-}Cl + NaS(CH_2)_2\text{-}OH \longrightarrow CH_2{=}C(Me)\text{-}CH_2\text{-}S(CH_2)_2\text{-}OH + NaCl$$

8 (85%)

SCHEME II

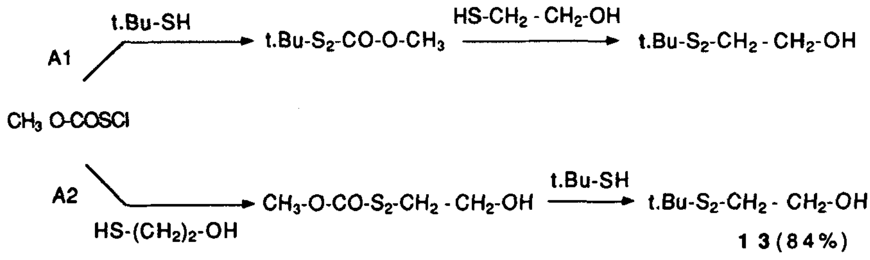
The symmetric disulfides are easily obtained by various methods (including the thiol oxidation[2] or the action of Na_2S_2 on a chloride) that we already used.[11]

Nevertheless, these methods do not apply to non-symmetric polysulfides and we have used method A and B to synthesize these compounds.

A Method

For disulfides the starting product of this synthesis is methoxycarbonylsulfenyl chloride ($CH_3—O—CO—SCl$) obtained via the published method.[12] Treatment of this compound with a thiol gave the desired derivative.[13]

Our aim was to obtain disulfide **13** with a t.butyl radical. To achieve this two possibilities exist:



SCHEME III

We tested these two theorical possibilities and observed that the A1 process does not lead to the required disulfide **13**, while this disulfide can be obtained with a 84% yield (Table II) with the A2 process.

This can be explained if we consider that in the 2nd step, the R'SH thiol's action against the RSX derivative is not prevented by bulky groups.

For the A1 possibility the R = t.Bu radical already fixed during the 1st step prevents the $HO(CH_2)_3SH$ thiol's approach.

A similar process is used for preparing ethylenic disulfide **14**:

$$CH_3\text{-}OCO\text{-}S_2\text{-}(CH_2)_2\text{-}OH \xrightarrow{CH_2=C(Me)\text{-}CH_2\text{-}SH} CH_2=C(Me)\text{-}CH_2\text{-}S_2\text{-}(CH_2)_2\text{-}OH$$

14 (95%)

SCHEME IV

For trisulfides, we used a similar method as described above using as the starting compound: methoxycarbonyl disulfanyl chloride.[14,15]

For that synthesis the use of an amine catalyst is necessary during the 2nd step. Among the compounds tested the *N*-methylmorpholine gave the best results (Table II):

$$CH_3\text{-}O\text{-}COS_2Cl \xrightarrow[\text{Yield>97\%}]{t.Bu\text{-}SH} t.Bu\text{-}S_3\text{-}CO\text{-}O\text{-}CH_3 \xrightarrow[\text{amine}]{HS\text{-}(CH_2)_2\text{-}OH} t.Bu\text{-}S_3\text{-}CH_2CH_2\text{-}OH$$

15 Yield=80%

SCHEME V

TABLE II

Characteristics of (poly)sulfurated alcohols: R—S_x—$(CH_2)_n$—OH

N°	R	n	x	Yield (%)	^{1}H NMR CH_2O CH_2=	^{1}H NMR CH_2S	^{1}H NMR CH_2	^{1}H NMR OH	^{1}H NMR CH_3
13	t.Butyl	2	2	84	3,90 t	2,90 t		2,70	1,35 s
14	Methallyl	2	2	95	3,90 t 4,90 m	3,30 s 2,80 t		2,10	1,80 m
15	t.Butyl	2	3	80	3,80 m	3,00 t		2,10	1,35 s
16	t.Butyl	3	2	63	3,90 m	2,90 t		2,40	1,35 s
17	t.Butyl	4	2	69	3,75 t	2,80 t	1,90 m	2,10	1,35 s
18	t.Butyl	5	2	74	3,65 t	2,75 t	1,70 m	1,50	1,30 s
19	t.Butyl	6	2	80	3,60 t	2,70 t	1,50 m	1,60	1,30 s
21	Methallyl	3	2	62	3,70 t 4,90 t	3,30 s 2,80 t	1,90 m	2,60	1,80 m
22	Methallyl	4	2	40	3,70 t 4,90 t	3,30 s 2,70 m	1,80 m	1,90	1,80 m
23	Methallyl	5	2	68	3,70 m 4,90 m	3,30 s 2,70 m	1,60 m	3,40	1,80 m
24	Methallyl	6	2	71	3,60 m 4,90 m	3,30 s 2,70 m	1,50 m	1,50	1,80 m
$(t.Bu\text{-}S_2\text{-}CH_2)_2\text{-}CHOH$									
20				61	4,15 m	2,95 dd 2,85 dd		2,40	1,35 s

For the synthesis of trisulfides A1 as well as A2 methods can be used. Effectively, even with a t.butyl radical, the thiol can attack. These A methods always give very pure compounds. We must nevertheless notice that the starting compounds used must be synthesized in several steps.

B Method

In opposition with the previous one, the B procedure does not need sophisticated preparations for the starting compounds. Nevertheless, it always gives mixed products (with t.butyl radical). This is no inconvenience in industry but is an obstacle for the fundamental researcher who wishes to get a pure compound.

The separation of the products obtained is feasible in the laboratory by silicate gel-chromatography. The general idea of the method is to introduce solid sulfur in a thiolate, the introduced sulfur quantity determining the "x" value. We most often used a $x = 2$ value. $x = 3$ can be tried, too, but the yields obtained for the desired compound are rarely >50%. For $x = 4$, a precipitation of sulfur in the reaction is observed.

The non-isolated dithiolate is then treated with a chloroalcohol to give the desired disulfide and as an impurity t.Bu-S-S-t.Bu. The yields given in Table II correspond to the compounds isolated after chromatography and elimination of the main impurities:

$$\text{t.Bu-SNa} \xrightarrow[\text{EtOH}]{\text{(S)}} \text{t.Bu-S}_2\text{-Na} \xrightarrow{\text{Cl-(CH}_2)_n\text{-OH}} \text{t.Bu-S}_2\text{-(CH}_2)_n\text{-OH} + \text{t.Bu-S}_2\text{-t.Bu} + \text{NaCl}$$

16 - 19 (63-80%)

SCHEME VI

Note: Industrially, the presence of t.Bu-S_2-t.Bu is not disturbing because this product is known for its good extreme-pressure and anti-wear properties. Compound **20** is similarly prepared (61%).

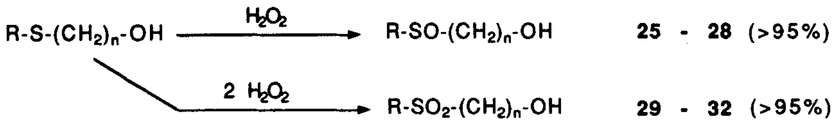
The methods used to prepare aliphatic disulfide alcohols do not apply to ethylenic compounds because in this case the reactions lead to mixtures and to low yields (<40%). To prepare the desired compounds, we used a method similar to that of Alonso *et al.*[16] and Brois *et al.*[13] (Table II):

$$\text{CH}_2\text{=C(Me)-CH}_2\text{-SNa} + \text{HO-(CH}_2)_n\text{-S}_2\text{O}_3\text{Na} \longrightarrow \text{CH}_2\text{=C(Me)-CH}_2\text{-S}_2\text{-(CH}_2)_n\text{-OH} + \text{Na}_2\text{SO}_3$$

21 -24 (40-71%)

SCHEME VII

3) *Preparation of sulfoxides and sulfones.* The isolated sulfide alcohols allow preparation of the related sulfoxides and sulfones by oxidation with H_2O_2. The procedure used furthermore allows isolating a sulfoxide not contaminated by the sulfone and vice versa (Table III).



SCHEME VIII

TABLE III

Characteristics of sulfoxides and sulfones R—SO_y—$(CH_2)_n$—OH

N°	R	n	y	Yield (%)	^{1}H NMR CH_2O CH_2=	^{1}H NMR CH_2S	^{1}H NMR CH_2	^{1}H NMR OH	^{1}H NMR CH_3
25	t.Butyl	2	1	>95	4,20 m	2,75 m		3,50	1,30 s
26	t.Butyl	3	1	>95	3,80 m	2,70 m	2,10 m	4,50	1,30 s
27	t.Butyl	5	1	>95	3,60 m	2,50 m	1,60 m	4,60	1,30 s
28	Methallyl	2	1	>95	4,10 m	3,30 s		3,50	1,90 m
					5,10 m	3,00 m			
29	t.Butyl	2	2	>95	4,20 m	3,20 m		2,20	1,40 s
30	t.Butyl	3	2	>95	3,70 m	3,10 m	2,10 m	2,70	1,40 s
31	t.Butyl	5	2	>95	3,60 m	3,00 m	1,60 m	2,80	1,40 s
32	Methallyl	2	2	>95	4,10 m	3,50 s		3,80	2,00 m
					5,20 m	3,20 m			

4) *Preparation of sulfurated esters.* The sulfurated alcohols treated with propanoic and lauric acids, give the para toluensulfonic acid as catalyst the related esters with good yields (Table IV):

$$\text{R-S-(CH}_2)_n\text{-OH} + \text{CH}_3\text{-(CH}_2)_m\text{-COOH} \xrightarrow{\text{APTS}} \text{R-S-(CH}_2)_n\text{-O-CO-(CH}_2)_m\text{-CH}_3$$

33 - 42 (81-96%)

SCHEME IX

Note: The esters **39** and **40** were obtained from a sulfurated secondary alcohol.

5) *Uses of sulfurated chlorides.* We were not directly interested in the sulfide alcohols because they are scarcely involved in lubricant formulas. Nevertheless these compounds could lead us to new functionalized sulfur derivatives. The **43** to **49** chlorides are obtained by classical reaction of thionyl chloride upon the previously mentioned alcohols. The yields are always good (Table V).

The sulfurated chlorides lead to functionalized compounds.[1] We shall only mention in this report the nitriles and sulfonates (Table VI) obtained through the

TABLE IV

Characteristics of esters R—S—$(CH_2)_n$—OCO—$(CH_2)_m$—Me

N°	R	n	m	Yield, (%)	^{1}H NMR CH_2O $CH_2=$	^{1}H NMR CH_2S	^{1}H NMR CH_2	^{1}H NMR CH_2	^{1}H NMR CH_3
33	t.Butyl	2	1	85	4,20 t	2,75 t	2,35 q		1,35 s 1,05 t
34	t.Butyl	2	10	83	4,20 t	2,75 t	2,30 m 1,60 m	1,30 m	1,35 s 1,05 t
35	t.Butyl	3	1	93	4,20 m	2,60 m	2,35 q 1,90 m		1,30 s 1,15 t
36	t.Butyl	3	10	90	4,15 m	2,60 m	2,30 m 1,90 m	1,60m 1,30 m	1,30 s 0,90 t
37	t.Butyl	6	1	90	4,00 m	2,50 m	2,20 q 1,60 m		1,30 s 1,10 t
38	t.Butyl	6	10	96	4,00 m	2,50 m	2,30 m 1,60 m	1,30 m	1,30 s 0,90 t
41	Methallyl	2	1	83	4,20 t 4,90 m	3,15 s 2,65 t	2,35 q		1,80 m 1,15 t
42	Methallyl	2	10	81	4,20 t 4,90 m	3,10 s 2,65 t	2,60 m 1,60 m	1,30 m	1,80 m 0,90 t
$(t.Bu\text{-}S\text{-}CH_2)_2\text{-}CH\text{-}OCO\text{-}(CH_2)_m\text{-}Me$									
39			1	82	5,00 m	2,80 dd 2,90 dd	2,40 q		1,30 s 1,10 t
40			10	78	5,00 m	2,80 dd 2,90 dd	2,30 q 1,60 m	1,30 m	1,30 s 0,90 t

TABLE V
Characteristics of chlorides $R—S—(CH_2)_n—Cl$

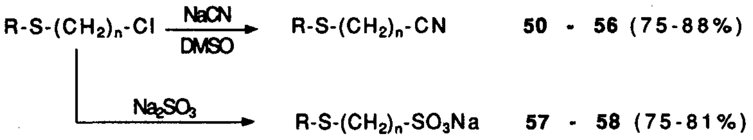
N°	R	n	Yield (%)	bp(°c) (1 mb)	^{1}H NMR CH_2Cl $CH_2=$	^{1}H NMR CH_2S	^{1}H NMR CH_2	^{1}H NMR CH_3
43	t.Butyl	2	81	57	3,60 t	2,80 t		1,30 s
44	t.Butyl	3	90	70	3,60 m	2,70 m	2,00 m	1,30 s
45	t.Butyl	5	90	90	3,50 m	2,50 m	1,60 m	1,30 s
47	Methallyl	2	86	54	3,60 t 4,90 m	3,15 s 2,80 t		1,80 m
48	Methallyl	3	89	61	3,60 m 4,90 m	3,10 s 2,60 m	2,00 m	1,80 m
49	Methallyl	5	91	90	3,50 m 4,90 m	3,10 s 2,30 m	1,60 m	1,80 m
$(t.Bu-S-CH_2)_2-CH-Cl$								
46			81	95	4,10 m	3,10 dd 2,90 dd		1,30 s

TABLE VI
Characteristics of nitriles and sulfonates

N°	R	n	Yield (%)	^{1}H NMR CH_2CN $CH_2=$	^{1}H NMR CH_2S	^{1}H NMR CH_2	^{1}H NMR CH_3
$R-S-(CH_2)_n-CN$							
50	t.Butyl	2	76	2,60 m	2,60 m		1,30 s
51	t.Butyl	3	86	2,60 m	2,60 m	1,90 m	1,30 s
52	t.Butyl	5	88	2,70 m	2,60 m	1,60 m	1,30 s
54	Methallyl	2	75	2,70 m 4,90 m	3,10 s 2,70 m		1,80 m
55	Methallyl	3	85	2,50 m 4,90 m	3,10 s 2,50 m	1,90 m	1,80 m
56	Methallyl	5	87	2,50 m 4,90 m	3,10 s 2,40 m	1,60 m	1,80 m
$(t.Bu-S-CH_2)_2-CHCN$							
53			79	4,00 m	3,00 dd 2,90 dd		1,30 s
$R-S-(CH_2)_n-SO_3Na$							
57	t.Bu	2	81		3,00 m		1,30 s
58	t.Bu	3	75		2,85 m	2,00 m	1,30 s

methods described below. For sulfonates the reactions are very slow and often need several days.

The purification of these products is achieved through a Dowex 50 type ion exchange column:



SCHEME X

The nitrile **53** (79%) was obtained from a sulfuratd secondary chloride.

CONCLUSION

The compounds mentioned in this report, although prepared via known methods, are generally not described and have extreme-pressure, anti-wear and anti-oxidation properties.

These properties are described in the cited patents.[1] They are also starting products for a second generation of petroleum additives: the phosphoro-sulfurated derivatives that we shall describe in a second publication.

Our first aim was the introduction of sulfur into simple molecules, while avoiding a too high sulfur percentage because of the corrosion.

The mechanical tests made with the synthesized products confirm two essential points:

—The importance of the used alkyl or alkenyl groups' structure: we verify again the very beneficial effects of t.butyl and methyallyl groups.

—The importance of a polysulfide implies an intermediate system between monosulfide and trisulfide. In fact, a mixture based upon disulfide with an average value of the "*x*" factor in -Sx- of about 1,4 to 2,4 depending on the applications.

In this report we have presented procedures by means of which pure compounds can be isolated. Our synthesis methods provide very good yields for mixtures of mono, di and trisulfides, whose sulfur average content corresponds to the values mentioned above.

EXPERIMENTAL

^{13}C NMR and ^{1}H NMR spectra were recorded on a BRUKER AM-400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. For the assignment of the various carbons we used a spin echo and/or a polarization transfer. All the compounds presented have not been analyzed in ^{13}C NMR. Those that were analysed are presented in Tables VII–IX. Chemical shifts are in ppm units (abbreviations: s (singulet), d (doublet), t (triplet) m (multiplet)). The presence and position of the OH function are checked by a D_2O treatment. The signal for that function is often a broad singulet. Liquid products are not always distilled. Effectively, a decomposition can appear during this procedure. For distillable products the boiling point is indicated.

TABLE VII

^{13}C NMR of aliphatics compounds

Alcohols

N°	C-OH (C1)	C-S	C2	C3	C4	C5	t.Bu (C)	t.Bu (Me)
1	60,2	35,1			31,5	21,6		13,3
2	61,5	31,9					42,3	31,1
3	61,8	24,9	32,4				42,0	30,8
4	62,6	26,1	32,1	28,0			41,8	30,9
5	62,3	25,0	32,3	27,8	29,2		41,3	30,9
6	62,2	25,2	32,3	28,0	28,7	29,6	41,3	30,9
7	69,8	34,9					42,3	30,9
13	60,4	42,3					47,8	29,2
15	59,4	41,6					48,8	29,3
16	60,9	37,0	31,9				47,7	29,9
17	62,0	40,3	31,6	25,3			47,3	29,7
18	62,3	40,4	32,4	24,4	28,7		47,2	29,6
19	62,4	40,7	32,4	25,2	29,1	28,1	47,4	29,8
26	60,5	42,6	26,9				53,4	22,6
27	61,5	45,1	31,9	24,9	23,2		52,5	22,3
30	60,3	42,4	23,6				58,8	23,1
31	61,7	45,2	31,0	24,8	20,2		58,7	23,2

Chlorides

N°	C-Cl (C1)	C-S	C2	C3	C4	t.Bu (C)	t.Bu (Me)
43	43,2	30,7				42,5	30,8
44	43,4	24,9	32,3			41,6	30,5
45	44,5	26,1	32,0	27,7	28,8	41,4	30,7

Nitriles

N°	C-CN (C1)	C-S	C2	C3	C4	CN	t.Bu (C)	t.Bu (Me)
50	18,8	23,9				118,0	42,8	30,6
51	15,9	26,5	25,4			118,8	42,0	30,6
52	16,5	27,2	24,5	27,6	28,4	188,3	41,2	30,4

Preparation of monosulfurated alcohols. To a solution of 95% ethanol (100 ml) and NaOH (120 nmol), the thiol (120 mmol) is added dropwise at 50°C. The mixture is stirred at this temperature for 30 minutes and then cooled at 20°C. The chloride derivative (120 mmoles) is added; the mixture is refluxed for six hours and cooled. It is then filtered and neutralized with 2N HCl. The organic layer is extracted with methylene chloride, washed with water, dried over Na_2SO_4 and evaporated under reduced pressure.

Preparation of polysulfurated alcohols. A Method: Compounds **13** and **14**. The starting compound MeO—CO—S—Cl is prepared via the described[12] method. It is a liquid presenting a typical signal at

TABLE VIII

^{13}C NMR of unsaturated compounds

Alcohols

N°	CH_2=	C=	CH_2O	CH_2S	SCH_2	CH_2	CH_2	CH_2	CH_2	CH_3
	C1	C2	Cn	C3	C4	C	C6	C7	C8	
8	113,2	140,5	60,0	38,4	33,3					20,0
9	113,1	140,9	61,4	39,1	27,4	31,6				20,3
10	112,3	141,1	62,1	39,1	30,5	25,2	31,7			20,4
11	112,8	141,1	62,4	39,1	30,6	28,6	24,8	32,2		20,3
12	112,8	141,1	62,5	39,1	30,6	28,8	28,4	25,2		20,4
21	114,7	140,5	60,7	46,5	35,1	31,7				20,6
23	114,7	140,5	62,4	46,5	38,4	28,8	24,8	32,1		20,6
24	114,5	140,5	62,4	46,5	38,4	28,1	28,9	25,2		20,6
28	118,2	135,2	53,7	61,2	55,4					20,6
32	118,3	135,1	53,5	62,5	55,9					20,6

Chlorides

N°	CH_2=	C=	CH_2Cl	CH_2S	SCH_2	CH_2	CH_2	CH_2	CH_3
	C1	C2	Cn	C3	C4	C5	C6	C7	
47	113,6	140,6	42,4	39,3	32,6				20,1
48	113,3	140,8	43,3	39,1	27,6	31,7			20,3
49	112,8	141,0	44,4	39,1	30,4	28,1	25,8	31,8	20,3

Nitriles

N°	CH_2=	C=	CH_2CN	CH_2S	SCH_2	CH_2	CH_2	CH_2	CN	CH_3
			C1			C2	C3	C4		
55	113,4	140,3	15,7	38,8	29,0	24,4			118,6	20,1
56	112,9	140,2	16,7	39,1	30,2	24,7	27,4	27,9	119,1	20,2

TABLE IX

^{13}C NMR of esters

N°	C=O	C-OCO	C-S	C2	C3	C4	t.Bu	t.Bu	Et	Et
	C1						C	Me	CH_2	CH_3
33	173,7	63,6	26,8				41,9	30,7	29,3	8,7
35	173,7	62,7	24,3	27,1			41,4	30,5	28,7	8,7
37	173,3	63,6	27,1	27,6	25,1	27,9	41,2	30,5	29,0	8,7

N°	C=O	C-OCO	CH_2S	CH_2	CH_2	CH_2	CH_2	Me	t.Bu	t.Bu
	C1							C12	C	Me
34	173,4	63,8	26,8	22,6 (C3) 34,2 (C2)	29,5 (C6) 29,2 (C5) 29,0 (C4)	27,1 (C9) 29,2 (C8) 29,4 (C7)	24,8 (C11) 31,8 (C10)	14,0	42,2	30,9

3,9 ppm (^1H NMR). To a mixture of methoxycarbonylsulfenyl chloride (6,3 mmol) and methanol (40 ml) 2-mercaptoethanol (24 mmol) is added dropwise at 0°C. This mixture is stirred at this temperature during 1 hour. Methanol is then removed under reduced pressure and the liquid obtained is immediately used for the next part of the synthesis. During this first step, the MeO—CO—S_2—$(CH_2)_2OH$ compound is obtained with a 90% yield.

^1H NMR δ: 3,90 s(Me); 3,70 t(CH_2O); 2,85 t(CH_2S); 2,5 s(OH).

In a three necked flask is introduced 21 mmoles of the disulfide, 5 ml of methanol and one drop of triethylamine. The thiol (21 mmoles) is added and the solution is stirred during 1 hour at 25°C. Methanol is removed under reduced pressure and a yellow liquid is obtained (Table II).

A Method: trisulfide **15**. The starting compound MeO—CO—SS—Cl is prepared via the described[14,15] method. It is a liquid having a typical signal at 4,0 ppm (^1H NMR). To a mixture of methoxycarbonyldisulfenyl chloride (6,3 mmol) and CH_2Cl_2 (40 ml) t.butyl mercaptan (7 mmoles) dissolved in CH_2Cl_2 (6 ml) is added dropwise. This mixture is stirred at 20°C during 1 hour. The volatiles are then removed under reduced pressure and the liquid obtained is immediately used for the next part of the synthesis. During this first step, the MeO—CO—S_3—t.Bu compound is obtained with a quantitative yield.

^1H NMR ∂: 3,90 s(Me); 1,3 s(Me).

To 5 ml of deuterated chloroform are added MeO—CO—S_3—t.Bu (2 mmol), mercaptoethanol (2,2 mmol) and *N*-methylmorpholine (20 mg). The mixture is stirred at 20°C for 24 hours and during this time the reaction is studied by ^1H NMR. After addition of 0,2 N HCl, the solvent is evaporated and a yelow liquid (80%) is obtained (Table II).

B Method: Compounds **16–20**. To a solution of 95% ethanol (50 ml) and NaOH (135 mmol), 2,2-dimethyl propanethiol (120 mmol) is added dropwise. Sulfur (130 mmoles) is then added portionwise at 50°C. The temperature is maintained until complete dissolution. The mixture is cooled to 25°C and the chloride derivative (130 mmol) is added dropwise. The final mixture is refluxed for 6 hours. After elimination of the sodium chloride and treatment with 2N HCl, the organic phase is collected. The aqueous phase is then extracted with CH_2Cl_2 and the organic parts are washed with water and dried on Na_2SO_4. The solvent is evaporated in vacuo and a yellow liquid is obtained. It can be purified by chromatography (Table II).

Preparation of ethylenic disulfide **21–24**. The first step is related to the hydroxyalkylthiosulfate preparation. To a solution of chlorinated alcohol (50 mmol) in methanol (40 ml), water (around 10 ml) is added until the solution becomes turbid. The mixture is refluxed and sodium thiosulfate (63 mmol) dissolved in 25 ml water is added. The mixture is refluxed for 2 hours. The methanol is then evaporated under reduced pressure. The residue is diluted with water and washed with hexane: then, the aqueous phase is kept at 0°C. The second step is related to the sodium thiolate preparation. NaOH (60 mmol) is dissolved in water (5 ml) and methallylmercaptan (50 mmol) is added under fast stirring at room temperature (if the solution obtained is too viscous, it is diluted with water and kept at 0°C). The thiolate is quickly poured into the solution of sodium hydroxyalkylthiosulfate and the mixture is treated with a saturated solution of sodium chloride and the temperature kept at 5°C. After separating the two phases, the aqueous phase is extracted with ether and the organic phases are washed with water and dried on Na_2SO_4. The solvent is removed and a yellow liquid is obtained (Table II).

Preparation of sulfoxides and sulfones **25–32**. *Sulfoxide*: To a solution of hydroxylated sulfide (20 mmol) is added dropwise 30% H_2O_2 (21 mmol) at 0°C. Stirring is continued at 0°C until getting a limpid solution. The mixture is warmed to 20°C and stirred for 12 hours. After separation of the two phases, extraction (chloroform) and elimination of the solvent, a colourless oil is isolated. The crude yields are quantitative.

^1H NMR and ^{13}C NMR show that the product obtained contains neither sulfide nor sulfone.

Sulfone: To a solution of hydroxylated sulfide (0,1 mol) is added dropwise 30% H_2O_2 (0,22 mol) at 7°C. The mixture is stirred at 18°C for 24 hours then warmed to 80°C for 2 hours. The mixture is extracted with chloroform, the organic phase is dried on Na_2SO_4 and the solvent is removed under reduced pressure. A viscous colourless oil is isolated (the crude yields are quantitative).

^1H NMR and ^{13}C NMR show that the product obtained contains neither sulfide nor sulfoxide.

Preparation of esters **33–42**. The procedure used is classical for a direct esterification. In a reactor equipped with a Dean-Stark separator 21 mmol of sulfurated alcohol, 26 mmol of propanoic (or lauric) acid, 40 mg of APTS and 17 ml of cyclohexane are mixed. The mixture is refluxed until the required quantity of water is distilled off. After cooling to room temperature the organic layer is washed with a saturated solution of sodium bicarbonate, with water and with a solution of saturated sodium chloride. After removing the solvent, a quite pure oil is isolated (no trace of alcohol in ^{1}H NMR). All these products are characterized by an IR band at 1740 cm^{-1}.

Preparation of chlorides **43–49**. To a solution of sulfurated alcohol (100 mmol) dissolved in chloroform, thionyl chloride (50 mmol) is added dropwise. The mixture is refluxed and the 2nd part of thionyl chloride (50 mmol) is added. The mixture is refluxed for 2 hours and the solvent is evaporated. The chlorides obtained can generally be distilled under reduced pressure.

Note: When R = $CH_2{=}C(Me){-}CH_2$, pyridine must be added to the reaction mixture in order to trap the HCl formed and avoid its condensation with the double bond.

Preparation of nitriles **50–56**. A solution of sodium cyanide (17 mmol) and dimethylsulfoxide (10 ml) is warmed at 90°C. Chloride derivative (14 mmol) is added (taking care that the maximum temperature is 155°C). The mixture is still stirred until the temperature reaches 40°C. The mixture is poured into 25 ml of water and extracted with chloroform. The crude product obtained is yellow. All the isolated produces have an IR band around 2100 cm^{-1}.

Preparation of sulfonates **57–58**. A mixture of chloride derivative (13 mmol), water (15 ml) and sodium sulfite (30 mmol) is warmed at 100°C and the temperature is maintained until getting a limpid solution (this may take quite some time). The water is then evaporated and a solid is isolated. This compound is dissolved in water and the solution is introduced into an ion exchange column equipped with Dowex 50X. The acid obtained is neutralized with 1N NaOH and the remaining water is evaporated under reduced pressure. The white solid is collected and dried ($T < 70°$).

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