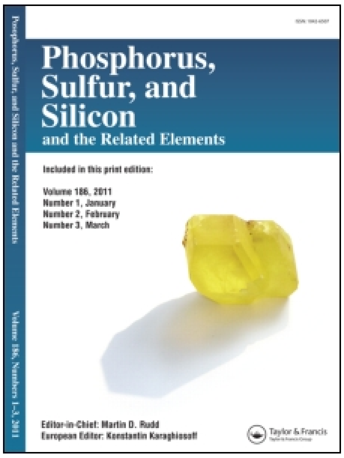

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A CONVENIENT HIGH YIELD SYNTHESIS OF FUNCTIONAL METHACRYLATES *VIA* DETHIOACETALIZATION. SYNTHESIS OF METHACRYLATE S,S-ACETAL DERIVATIVES AS INTERMEDIATES

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A CONVENIENT HIGH YIELD SYNTHESIS OF FUNCTIONAL METHACRYLATES *VIA* DETHIOACETALIZATION. SYNTHESIS OF METHACRYLATE S,S-ACETAL DERIVATIVES AS INTERMEDIATES

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(Received 03 November, 1998)

We describe a selective and efficient synthesis of a whole new class of functional methacrylates starting from S,S-acetals. Carbonyl compounds were regenerated from corresponding S,S-acetals using mercury (II) salts. According to this method, methacrylic sensitive group (possible polymerization), is not affected.

Keywords: acrylic monomers; carbonyl acrylic derivatives; S,S-acetals; hydroxyalkylated 1,3 dithianes; dethioacetalisation; mercury (II) salts

INTRODUCTION

In recent years, there has been a significant interest in the chemistry of (meth)acrylic ester monomers.

As part of our program aiming at the synthesis of functionalized acrylic monomers, we have considered the dethioacetalization of S,S-acetal acrylic monomers as an entry to a new type of acrylic ester derivatives (formula **1**) of potential utility as reticulants in polymer chemistry.

For preparation of methacrylate alkanone, we first considered the condensation of methacryloyl chloride with hydroxy ketone, but polymerization couldn't be avoided during the isolation of the monomer on silica gel.

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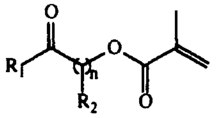
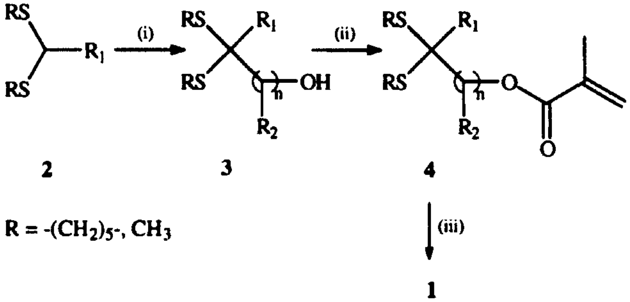
* Correspondence Author.



1

R_1 = H, alkyl, SCH_3, OH, Oalkyl
R_2 = alkyl
n = 1, 3

That's why we propose in this paper a convenient and selective route for the preparation of functional methacrylates of formula **1** starting from S,S-acetals. Our synthetic plan is shown in scheme 1 :



(i) a) n-BuLi, THF, -40°C, 2hr. b) aldehydes, oxiranes, oxetane, -78°C
(ii) methacryloyl chloride, Et_3N, $CHCl_3$, 48hr., r.t. (iii) dethioacetalization

SCHEME 1

RESULTS

As a further development of possible synthetic applications of S,S-acetal, our first goal was to synthesize the methacrylate S,S-acetal through reaction of methacryloyl chloride with alcohols.

The hydroxyalkylated 1,3-dithiane and hydroxyalkylated 2-alkyl-1,3-dithiane of formula **3** were prepared by the method of Seebach, *et al* [1,2].

Tables I and II list a number of products obtained by hydroxyalkylation of lithio-1,3-dithiane or lithio-2-alkyl-1,3-dithiane with aldehydes, oxiranes and oxetanes.

TABLE I hydroxyalkylation of 2-lithio-1,3-dithiane and 2-lithio-2-alkyl-1,3-dithiane with aldehydes and oxetanes

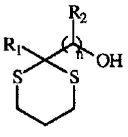
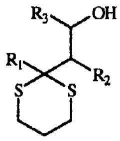
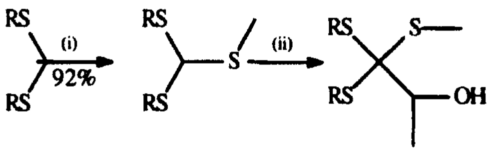
products	n°	R_1	R_2	n	yield (%)
	**3a**	H	CH_3	1	96
	3b	H	C_2H_5	1	98
	3c	H	Ph	1	88
	3d	CH_3	CH_3	1	82
	3e	CH_3	H	3	80
	3f	C_2H_5	CH_3	1	78

TABLE II hydroxyalkylation of 2-lithio-1,3-dithiane and 2-lithio-2-alkyl-1,3-dithiane with oxiranes

products	n°	R_1	R_2	R_3	yield (%)
	**3g**	H	H	CH_3	72
	3h	H	$-(CH_2)_4-$		91
	3i	H	H	CH_2OH	50
	3j	CH_3	$-(CH_2)_4-$		89

All of these compounds were obtained in good yields, varying between 50% and 98%, without any purification. Treatment of 2-lithio-1,3-dithiane in tetrahydrofuran with 1 equivalent of methyl disulfide[3] gave high yield of the corresponding orthothioformates **2a** ($R = -(CH_2)_3-$, $R_1 = SCH_3$) (scheme 2). **2a** was converted in similar yield to the corresponding α-hydroxyalkylated orthothioformate by using the method of Seebach, *et al* [3,4] at low temperature.

Conversion of the hydroxyalkylated S,S-acetals to the corresponding methacrylate derivative was carried out as shown in scheme 3. Reaction of an alcohol with 1.1 equivalents of methacryloyl chloride in the presence of triethylamine in chloroform affords **4** in yield varying between 71% and 14% after purification on silica gel (table III and IV).



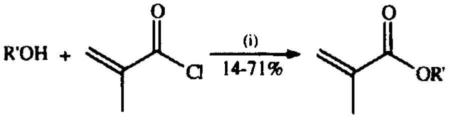
R = -$(CH_2)_3$-, **2a**
R = CH_3, commercial

R = -$(CH_2)_3$-, **3k**
R = CH_3, **3l**

product	R	yield
3k	-$(CH_2)_3$-	88%
3l	CH_3	97%

(i) a) n-BuLi, THF, -40°, 2 hr. b) CH_3SSCH_3, -78°C
(ii) a) n-BuLi, THF, -78°C, 1 hr. b) CH_3CHO, -78°C

SCHEME 2



(i) Et_3N, $CHCl_3$, r.t., 48hr.

SCHEME 3

TABLE III reaction of 2-α and γ-hydroxyalkylated 1,3-dithiane and 2-α-hydroxyalkylated-2-alkyl-1,3-dithiane with methacryloyl chloride

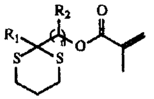
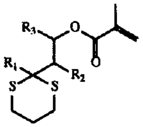
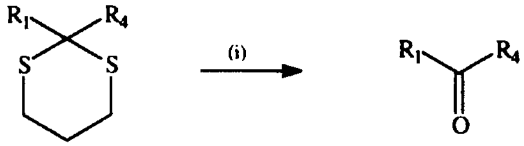
products	n°	R_1	R_2	n	yield (%)
	**4a**	H	CH_3	1	52
	4b	H	C_2H_5	1	56
	4c	H	Ph	1	48
	4d	CH_3	CH_3	1	48
	4e	CH_3	H	3	71
	4f	C_2H_5	CH_3	1	53

TABLE IV reaction of 2-β-hydroxyalkylated-1,3-dithiane and 2-β-hydroxyalkylated-2-alkyl-1,3-dithiane with methacryloyl chloride

products	n°	R_1	R_2	R_3	yield (%)
	**4g**	H	H	CH_3	41
	4h	H	$-(CH_2)_4-$		40
	4i	H	H	X	15
	4j	CH_3	$-(CH_2)_4-$		14

X : $CH_2OCOC(CH_3)=CH_2$

The last step consisted in dethioacetalization. The litterature reports many examples [5] for the conversion of 1,3-dithianes to the carbonyl products with the use of reagents such as heavy-metal salts (mercury (II) chloride[6], mercury (II) oxide-boron trifluoride etherate[7]), oxidizing reagents (N-halosuccinimide [6], halogen [6]), and alkylating reagents (methyl iodide [8]). After screening a number method of the usual reagents employed, we found the use of mercury (II) oxide/boron trifluoride etherate in aqueous tetrahydrofuran especially convenient (scheme 4).



R_1 = H, alkyl
R_4 = contain methacrylate

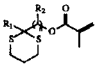
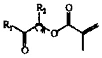
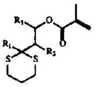
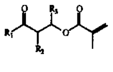
(i) HgO, BF_3 etherate, THF aq., reflux

SCHEME 4

By using this reagent, the hydrolysis is compatible with our sensitive methacrylic group and the dethioacetalization can be achieved selectively for many kinds of compounds without any by-products, any purification and in high yields.

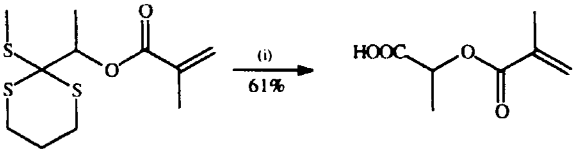
The table V lists a number of pure aldehydes and ketones obtained.

TABLE V dethioacetalization of methacrylate 2-α,β-hydroxyalkylated-1,3-dithiane and 2-α,β and γ -hydroxyalkylated-2-alkyl-1,3-dithiane

substrates	n°	R_1	R_2	R_3	n	products	n°	yield(%)
	**4a**	H	CH_3	-	1		**1a**	78
	4b	H	C_2H_5	-	1		**1b**	76
	4c	H	Ph	-	1		**1c**	81
	4d	CH_3	CH_3	-	1		**1d**	75
	4e	CH_3	H	-	3		**1e**	75
	4f	C_2H_5	CH_3	-	1		**1f**	86
	**4g**	H	H	CH_3	-		**1g**	89
	4h	H	$-(CH_2)_4-$		-		**1h**	96
	4i	H	H	X	-		**1i**	79
	4j	H	$-(CH_2)_4-$		-		**1j**	89

X : $CH_2OCOC(CH_3)=CH_2$

The hydrolysis and alcoholysis of orthothioesters **4k** to produce the carboxylic acids and esters has been well described[9,10,11] using a mixture of mercury (II) chloride and mercury (II) oxide. Methacrylic thiomethoxy-1,3-dithiane was converted to the corresponding carboxylic acid in a good yield by reaction of **4k** in refluxing 35% aqueous acetone for 24 hr with mercury (II) salts catalysis (scheme 5).



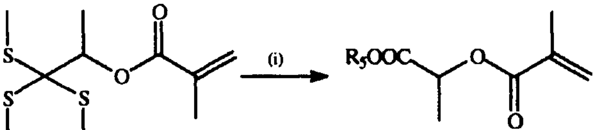
4k **1k**

(i) $HgCl_2$ / HgO BF_3 etherate, acetone aq., reflux 24 hr.

SCHEME 5

The corresponding esters were obtained in good yield by reaction of **4k** in refluxing aqueous alcohols in the presence of mercury (II) salts for periods of 4–5 hr (scheme 6).

The alcoholysis of **4k** in isopropyl alcohol proceeded less efficiently and in poorer yield than alcoholysis with ethanol ; this result suggests steric hindrance to the approach of the alcohol.



4k

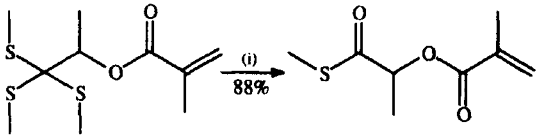
$R_5 = CH_2\text{-}CH_3$, **1l**
$R_5 = CH\text{-}(CH_3)_2$, **1m**

product	R_5	yield
1l	$CH_2\text{-}CH_3$	92%
1m	$CH\text{-}(CH_3)_2$	60%

(i) $HgCl_2$ / HgO BF_3 etherate, R_5OH, reflux, 4-5 hr.

SCHEME 6

The last type of functionalized methacrylate obtained by dethioacetalization was thioesters. The litterature reports only few examples[12,13,14] for the conversion of orthothioesters to thioesters. Traitment of **4l** with 1.7 equivalents of mercury oxide and boron trifluoride etherate in aqueous tetrahydrofuran at reflux for 30 minutes gave high yield of the corresponding thioester (scheme 7).



4l **1n**

(i) HgO BF_3 etherate, THF aq., reflux, 30 min.

SCHEME 7

Thus, here we have described a selective and efficient synthesis of a whole new class of functional methacrylate of formula **1** starting from S, S-acetals. We have shown that the procedure of dethioacetalization using mercury (II) salts is compatible with our substrate.

EXPERIMENTAL

All reagents were of commercial quality from freshly opened containers. Tris(methylthio)methane, mercury (II) chloride, mercury (II) oxid, n-butyllithium 1.6 M solution in hexane, were purchased from Aldrich Chemical Co. Tetrahydrofuran was dried by distillation from sodium-benzophenone.

Melting points were measured with a Tottoli apparatus. NMR spectra were recorded on a Brucker AC 250 MHz spectrometer and chemical shifts are reported in parts per million (δ) from internal tetramethylsilane. Mass spectra were recorded on a Hewlett-Packard spectrometer at 70 eV. Routine monitoring of reactions was performed using Merck 60 F 254 silica gel, aluminium-supported TLC plates.

General procedure for the preparation of 2-lithio-1,3-dithiane or 2-lithio-2-alkyl-1,3-dithiane. Solution in tetrahydrofuran

Dithiane are weighed into the flask prior to subsequent flushing with nitrogen. The reaction vessel is kept under positive inert gas pressure until work-up. Solvents, liquid reagents, and solutions of reagents are introduced, and samples are withdrawn through the serum cap by syringes. The amount of freshly distilled tetrahydrofuran necessary to obtain a 0.1–0.5 M solution of dithiane is added.

A 5% excess of n-butyllithium in n-hexane (1.5–2.5 M) is added at a rate of 3–5 mL / min. to the solution stirred at –40°C. After 1.5–2.5 hr. at –25 to –15°C, most dithianes are metalled quantitatively.

Hydroxyalkylations with carbonyl derivatives, oxiranes and oxetanes

A neat liquid carbonyl compound or the tetrahydrofuran solution of a solid carbonyl compound is added to the vigorously stirred solution of the anion at –70°C. In large-scale reactions the addition rate should be adjusted so that the temperature of the reaction mixture does not exceed –50°C. Many reactions of this type can also be carried out at higher temperatures (up to –20°C); however, the tendency of the highly nucleophilic lithio dithianes to abstract proton from enolizable carbonyls decreases with decreasing temperature.

With aldehydes the reaction is completed instantaneously. With oxiranes and / or with lithio-1,3-dithianes bearing bulky 2 substituents, subsequent storage of the reaction mixture at 0°C for 12–24 hr. is favorable.

The mixture is poured into three volumes of water. Several extractions with chloroform furnish an organic solution which is washed twice each with water, 7% aqueeous KOH, and again water and dried over sodium sulfate. The residue obtained after solvent removal is purified on silica gel.

2-(1'-hydroxyethyl-1')-1,3-dithiane (3a)

yield : 96%

^{1}HNMR ($CDCl_3$/TMS, 250 MHz) : δ : 4.03 (m, 1H) ; 3.77 (d, J = 6.9Hz, 1H) ; 2.91–2.73 (m, 4H) ; 2.01 (m, 1H) ; 2.01–1.96 (m, 2H) ; 1.35 (d, J = 6.1Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 68.09 (CH-OH) ; 53.1 (S-CH-S) ; 27.91 (S-CH_2) ; 27.55 (CH_2-S) ; 25.47 (CH_2) ; 20.2 (CH_3)

MS : m / z (%) = 164 (15) ; 119 (100) ; 75 (8) ; 59 (5) ; 45 (19)

2-(1'-hydroxypropyl-1')-1,3-dithiane (3b)

yield : 98%

^{13}CNMR ($CDCl_3$/TMS, 62.88 MHz) : δ : 67.9 (CH-OH) : 52.2 (S-CH-S) ; 28.9 (S-CH_2) ; 27.02 (CH_2-S) ; 24.8 (CH_2) ; 24.2 (CH_2) ; 9.6 (CH_3)

MS : m / z (%) = 178 (25) ; 160 (9) ; 119 (100) ; 59 (18)

2-(hydroxyphenylmethyl)-1,3-dithiane (3c)

yield : 88%, mp = 73°X

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 7.4 (m, 5H) ; 4.91 (m, 1H) ; 4.01 (d, J = 7Hz, 1H) ; 3.1 (ps, 1H) ; 2.97–2.92 (m, 2H) ; 2.90–2.88 (m, 2H) ; 1.83 (m, 2H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 140.12 (C_{aro}) ; 129.7 (CH_{aro}); 128.94 (CH_{aro}) ; 128.35 (CH_{aro}) ; 128.2 (CH_{aro}) ; 126.9 (CH_{aro}) ; 74.64 (CH-OH) ; 52.76 (S-CH-S) ; 27.58 (S-CH_2) ; 25.53 (CH_2-S) ; 25.26 (CH_2)

2-methyl, 2-(1'-hydroxyethyl-1')-1,3-dithiane (3d)

yield : 82%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 4.22 (q, J = 6.5Hz, 1H) ; 3.78 (m, 1H) ; 3.1–2.8 (m, 4H) ; 2.61–2.56 (m, 2H) ; 1.38 (s, 3H) ; 1.32 (d, J = 6.5Hz, 3H)

^{13}CNMR ($CDCl_3$/TMS, 62.88 MHz) : δ : 68.06 (H-C-O) ; 53.73 (S-C-S); 25.5 (CH_2) ; 24.27 (CH_2) ; 15.63 (CH_3) ; 14.01 (CH_3)

MS : m / Z (%) = 178 (8) ; 133 (100) ; 105 (2) ; 59 (22) ; 45 (9)

2-methyl, 2-(3'-hydroxypropyl-1')-1,3-dithiane (3e)

yield : 78%

^{1}HNMR ($CDCl_3$ /TMS, 250 MHz) : 6 : 3.63 (t, 2H) ; 2.80 (m, 4H) ; 2.08 (s, 1H, OH) ; 1.93 (m, 4H) ; 1.69 (m, 2H) ; 1.56 (s, 3H) ^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : 6 : 62.47 (CH_2OH) ; 48.75 (S-C-S) ; 37.56 (CH_2) ; 27.78 ($CH_{2dithiane}$) ; 27.72 ($CH_{2dithiane}$) ; 26.28 (CH_2) ; 27.6 (CH_3) ; 25.06 ($CH_{2dithiane}$)

MS : m / z (%) = 192 (14) ; 133 (40) ; 101 (8) ; 85 (100) ; 59 (40)

2-ethyl, 2-(1'-hydroxyethyl-1')-1,3-dithiane (3f)

yield : 78%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 4.23 (q, J = 7Hz, 1H) ; 3.71 (m, 1H) ; 2.98–2.81 (m, 4H) ; 2.15–2.02 (m, 1H) ; 1.95–1.6 (m, 3H) ; 1.33 (d, J = 7Hz, 3H) ; 1.07 (t, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ /TMS, 62.88 MHz) : δ : 67.8 (H-C-O) ; 59.58 (S-C-S); 26.7 (CH_2) ; 25.1 (CH_2) ; 24.4 (CH_2) ; 15.6 (CH_3) ; 9.1 (CH_3)

MS : m / z (%) = 192 (4) ; 147 (100) ; 106 (4) ; 73 (23) ; 45 (15)

2-(2 -hydroxypropyl-1')-1,3-dithiane (3g)

yield : 72%

^{1}HNMR ($CDCl_3$ /TMS, 250 MHz) : δ: 4.26 (m, 1H) ; 3.75 (m, 1H) ; 3.6–3.1 (m, 4H) ; 2.85 (t, J = 6Hz, 1H) ; 2.11–1.96 (m, 2H) ; 1.90–1.83 (m, 2H) ; 1.24 (m, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 64.85 (H-C-O) ; 44.23 (S-CH-S) ; 44.18 (CH_2) ; 30.20 (CH_2) ; 29.99 (CH_2) ; 29.81 (CH_2) ; 25.79 (CH_2) ; 23.47 (CH_3)

MS : m / z (%) = 178 (72) ; 145 (50) ; 119 (69) ; 85 (15) ; 74 (40) ; 45 (100)

2-(2'-hydroxycyclohexyl- 1')-1,3-dithiane (3h)

yield : 91%, mp = 100°C

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 70.71 (H-C-O) ; 51.46 (S-CH-S) ; 50.55 (C-$H_{cyclohex}$) ; 31.25 (CH_2) ; 29.8 (CH_2) ; 27.61 (CH_2) ; 27. 1 (CH_2) ; 25.4 (CH_2) 24.32 (CH_2)

MS : m / z (%) = 218 (22) ; 132 (5) ; 119 (100) ; 73 (11) ; 41 (15)

2-(2',3'-dihydroxypropyl-1')-1,3-dithiane (3i)

yield : 50%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 4.15 (m, 1H) ; 3.9 (m, 1H) ; 3.8 (m, 1H) ; 3.7 (d, 2H) ; 3.6–3.3 (m, 4H) ; 2.9–2.8 (m, 2H) ; 2.72 (t, 1H) ; 1.9 (m, 2H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : 6: 69.03 (CH-OH) ; 66.71 (CH_2-OH) ; 43.98 (S-CH-S) ; 32.25 (CH_2) ; 30.20 (CH_2) ; 26.89 (CH_2)

2-methyl, 2-(2'-hydroxycyclohexyl-1')-1,3-dithiane (3j)

yield : 89%

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 72.4 (CHO) ; 51.8 (S-C-S) ; 50.3 ($CH_{cyclohex}$) ; 30.59 (CH_2) ; 27.7 (CH_2) ; 26.53 (CH_2) ; 26.2 (CH_2) ; 25.1 (CH_2) ; 24.32 (CH_2) ; 21.18 (CH_3)

MS : m / Z (%) = 232 (10) ; 207 (9) ; 133 (100) ; 107 (8) ; 59 (21) ; 41 (19)

Reaction of metallated 1,3-dithiane with methyldisulfide

A solution of 1,3-dithiane (8 g, 66.6 mmol) in 100 mL of tetrahydrofuran in a three-neck round-bottom flask equipped with magnetic stirring, nitrogen inlet and septum cap was cooled to –78°C, and 73.3 mmol (1.1 eq.) of 1.6 M n-butyllithium in hexane was injected to the solution stirred at –40°C. The stirring was maintained during 1,5–2.5 hr. at –25- –35°C.

6.89 g (73.3 mmol) of methyldisulfide was injected over a period of 10 min. at –78°C. The reaction mixture was allowed to warm to 25°C overnight, and then poured into a solution of 0.05 N hydrochloric acid. Tetrahydrofuran was removed by rotary evaporation and the remaining aqueous solution was extracted with chloroform. The organic layer was washed with 10% aqueous sodium bicarbonate, water, and saturated brine, dried over sodium sulfate, and evaporated *in vacuo* to yield 92% as a clear oil.

2-thiomethoxy-1,3-dithiane (2a)

crude yield : 92%

^{1}HNMR ($CDCl_3$/TMS, 250 MHz) : δ : 4.81 (s, 1H) ; 3.25 (m, 2H) ; 3.01 (t, J = 7Hz, 2H) ; 2.83 (t, J = 7Hz, 2H) ; 2.23 (d, 3H) ^{13}CNMR ($CDCl_3$/TMS, 62.88 MHz) : δ : 48.02 (S-CH-S) ; 29.26 (CH_2) ; 25.53 (CH_2) ; 23.58 (CH_2) ; 16.79 (CH_3)

MS : m / z (%) = 232 (10) ; 231 (60) ; 165 (16) ; 161 (12) ; 119 (10) ; 69 (100) ; 41 (42)

Hydroxyalkylations of metalled orthothioformate with aldehyde

Tris(methylthio)methane (7.7 g, 0.05 mol) or 2-thiomethoxy-1,3-dithiane (8.3 g, 0.05 mol) is dissolved in tetrahydrofuran (100 mL), and cooled to −78°C under nitrogen. A 1.6 M solution of n-butylithium in hexane (0.055 mol, 1. 1 eq.) is added over 1 hr. keeping the temperature of the solution below −70°C. A solution of aldehyde (0.055 mol, 1.1 eq.) in tetrahydrofuran is added dropwise and stirring is continued at −78°C for a further 45 min. The mixture is allowed to r.t. overnight. The resulting solution was poured into water. Tetrahydrofuran was removed by rotary evaporation and the remaining aqueous solution was extracted with chloroform. The organic layer was washed with 10% aqueous sodium bicarbonate, water and satured brine, dried over sodium sulfate, and evaporated *in vacuo* to afford **3k** and **3l.**

2-thiomethoxy, 2-(1'-hydroxyethyl-1') 1,3-dithiane (3k)

crude yield : 88%

^{1}HNMR ($CDCl_3$/ TMS, 250 MHz) : δ : 3.77 (m, 1H) ; 3.69 (s, 1H, OH) ; 3.3–2.5 (m, 6H) ; 2.09 (s, 3H) ; 1.44 (d, J = 6.3Hz, 3H)

^{13}CNMR ($CDCl_3$/TMS, 62.88 MHz) : δ : 71.70 (CH-OH) ; 69.52 (S-C-S) ; 31.89 (CH_2) ; 29.85 (CH_2) ; 24.93 (CH_2) ; 17.39 (CH_3) ; 15.57 (CH_3)

MS : m / z (%) = 192 (2) ; 165 (2) ; 118 (14) ; 74 (32) ; 45 (52)

1-trismethylthio, 2-hydroxypropane (3l)

crude yield : 97%

^{1}HNMR ($CDCl_3$/TMS, 250 MHz) : δ : 3.93 (q, J = 6.4 Hz, 1H) ; 2.9 (s large, 1H) ; 2.18 (m, 9H) ; 1.4 (d, J = 6.2 Hz, 3H)

^{13}CNMR ($CDCl_3$/ TMS, 62.88 MHz) : δ : 72.15 (CH-OH) ; 67.81 (S-C(S)-S) ; 18.39 (CH_3) ; 18.07 (CH_3) ; 14.65 (CH_3) ; 13.83 (CH_3)

MS : m / z (%) = 180 (100) ; 165 (24) ; 117 (77) ; 71 (12) ; 59 (22)

Esterification

Into a three-necked round-bottom flask fitted with a thermometer and magnetic stirrer, were added alcohol **3** (0.05 mol), 800ppm of EMHQ and triethylamine (0.05 mol) in chloroform. To this stirred and cooled (0°C) resulting mixture, was added dropwise a solution of methacryloyl chloride (0.055 mol, 1.1 eq.) in chloroform. Stirring was continued for an additional 24 hr. at r.t. The reaction mixture was washed successively with a solution of H_2SO_4 (6 M), 10% aqueous NaOH and water.

After drying the organic layer was evaporated to yield an oil which was purified by chromatography (EtOAc : light petroleum, 5 : 95).

2-(1'-methacrylate of ethyl-1')-1,3-dithiane (4a)

yield : 52%, $n_D^{20} = 1.5295$

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.15 (s, 1H) ; 5.59 (ps, 1H) ; 5.26 (m, 1H) ; 4.12 (d, J = 6.4Hz, 1H) ; 2.9–2.7 (m, 4H) ; 2.09–1.93 (m, 2H) ; 1.94 (s, 3H) ; 1.43 (d, J = 6.4Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 166.5 (C=O) ; 136.13 (C=) ; 125.9 (=CH_2) ; 71.1 (CH-O) ; 50.96 (S-CH-S) ; 29.14 (S-CH_2) ; 28.79 (CH_2-S) ; 25.71 (CH_2) ; 18.27 (CH_3) ; 17.66 (CH_3)

GC / MS : m / z (%) = 146 (91) ; 119 (100) ; 69 (29) ; 41 (24)

2-(1'-methacrylate of propyl-1')-1,3-dithiane (4b)

yield : 56%, $n_D^{20} = 1.5203$

^{1}HNMR ($CDCl_3$/ TMS, 250 MHz) : δ: 6.16 (ps, 1H) ; 5.58 (ps, 1H) ; 5.16 (m, 1H) ; 4.11 (m, 1H) ; 2.88–2.86 (m, 2H) ; 2.78–2.75 (m, 2H) ; 2.04–1.92 (m, 4H) ; 1.96 (s, 3H) ; 0.93 (t, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 166.85 (C=O) ; 136.04 (C=) ; 125.94 (=CH_2) ; 75.28 (H-C-O) ; 49.52 (S-CH-S) ; 29.04 (CH_2) ; 28.81 (CH_2) ; 25.7 (CH_2) ; 24.81 (CH_2) ; 18.33 (CH_3acry) ; 9.73 (CH_3)

MS : m / z (%) = 246 (M^+, 2) ; 160 (74) ; 119 (100) ; 69 (21) ; 41 (19)

2-(methacrylate of phenylmethyl)-1,3-dithiane (4c)

yield : 48%, mp = 97°C

^{1}HNMR ($CDCl_3$/ TMS, 250 MHz) : δ: 7.43 (m, 5H) ; 6.27 (ps, 1H) ; 6.13 (d, J = 7.5Hz, 1H) ; 5.66 (ps, 1H) ; 4.36 (d, J = 7.5Hz, 1H) ; 2.78 (m, 4H) ; 2.06–2.01 (m, 2H) ; 2.01 (s, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 165.93 (C=O) ; 137.25 (C=) ; 135.84 (=CH_2) ; 128.64 (CH_{aro}) ; 128.23 (CH_{aro}) ; 127.08 (CH_{aro}) ; 126.29 (C_{aro}) ; 75.98 (CH-O) ; 50.30 (S-CH-S) ; 28.55 (S-CH_2) ; 25.28 (CH_2-S) ; 18.23 (CH_3)

MS : m / Z (%) = 294 (M^+, 2) ; 208 (21) ; 134 (10) ; 119 (100) ; 69 (29) ; 41 (39)

2-methyl, 2-(1'-methacrylate of ethyl-1')-1,3-dithiane (4d)

yield : 48%, n_D^{20} = 1.5300

^{1}HNMR ($CDCl_3$/ TMS, 250 MHz) : δ : 6.11 (ps, 1H) ; 5.63 (m, 2H) ; 3.18–2.96 (m, 2H) ; 2.52–2.75 (m, 2H) ; 2.15 (m, 1H) ; 1.95 (ps, 3H) ; 1.82 (m, 1H) ; 1.49 (s, 3H) ; 1.43 (d, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 166.6 (C=O) ; 135.42 (C=) ; 125.7 (=CH_2) ; 70.4 (H-C-O) ; 51.37 (S-C-S) ; 26.57 (CH_2-S) ; 26.25 (CH_2-S) ; 24.3 (CH_2) ; 22.29 (CH_3) ; 18.3 (CH_3) ; 15.3 (CH_3)

MS : m / z (%) = 246 (M^+, 6) ; 161 (4) ; 133 (100) ; 59 (22) ; 41 (21)

2-methyl, 2-(3'-methacrylate of propyl-1')-1,3-dithiane (4e)

yield : 71%, n_D^{20} = 1.5268

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.08 (ps, 1H) ; 5.54 (ps, 1H) ; 4.17 (t, J = 6.0Hz, 2H) ; 2.82 (m, 4H) ; 1.97–1.89 (m, 6H) ; 1.92 (s, 3H) ; 1.58 (s, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 167.3 (C=O) ; 136.23 (C=) ; 125.39 (=CH_2) ; 64.41 (CH_2O) ; 60.31 (S-C-S) ; 48.59 (CH_2) ; 37.66 (CH_2) ; 27.69 (CH_3) ; 26.41 (CH_2) ; 25.09 (CH_2) ; 24.12 (CH_2) ; 18.29 (CH_3)

MS : m / z (%) = 260 (51) ; 159 (9) ; 133 (91) ; 99 (100) ; 85 (38) ; 69 (38) ; 41 (61)

2-ethyl, 2-(1'-methacrylate of ethyl-1')-1,3-dithiane (4f)

yield : 53%, n_D^{20} = 1.5273

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.12 (ps, 1H) ; 5.58 (m, 2H) ; 3.08–2.98 (m, 2H) ; 2.71–2.57 (m, 2H) ; 1.96 (s, 3H) ; 1.97–1.87 (m, 4H) ; 1.45 (d, J = 7Hz, 3H) ; 1.11 (t, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 166.62 (C=O) ; 136.43 (C=) ; 125.75 (=CH_2) ; 71.22 (H-C-O) ; 57.02 (S-C-S) ; 28.29 (CH_2) ; 25.97 (CH_2) ; 25.89 (CH_2) ; 24.54 (CH_2) ; 18.44 (CH_3) ; 15.35 (CH_3) ; 9.2 (CH_3)

MS : m / z (%) = 260 (4) ; 147 (100) ; 106 (3) ; 69 (29) ; 41 (39)

2-(2'-methacrylate of propyl-1')-1,3-dithiane (4g)

yield : 41%, n_D^{20} = 1.5281

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.12 (ps, 1H) ; 5.57 (ps, 1H) ; 5.22 (m, 1H) ; 4.07 (m, 1H) ; 2.86 (m, 4H) ; 2.14 (m, 2H) ; 1.96 (s, 3H) ; 2.00–1.9 (m, 2H) ; 1.31 (d, J = 6.5Hz, 3H)

^{13}CNMR ($CDCl_3$/ TMS, 62.88 MHz) : δ : 166.71 (C=O) ; 136.54 (C=) ; 125.34 (=CH_2) ; 68.24 (H-C-O) ; 43.54 (S-CH-S) ; 41.52 (CH_2) ; 30.13 (CH_2) ; 29.93 (CH_2) ; 25.72 (CH_2) ; 20.14 (CH_3) 18.32 (CH_{3acry})

MS : m / z (%) = 246 (8) ; 145 (100) ; 133 (14) ; 119 (14) ; 85 (32) ; 69 (68) ; 41 (100)

2-(2'-methacrylate of cyclohexyl-1')-1,3-dithiane (4h)

yield : 40%, n_D^{20} = 1.5288

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.13 (ps, 1H) ; 5.57 (ps, 1H) ; 4.98–4.82 (m, 1H) ; 4.37 (d, J = 7Hz, 1H) ; 2.96–2.79 (m, 5H) ; 1.96 (s, 3H) ; 2.13–1.25 (m, 10H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 166.53 (C=O) ; 136.61 (C=) ; 125.24 (=CH_2) ; 73.13 (H-C-O) ; 50.95 (S-CH-S) ; 47.34 (H-$C_{cyclohex}$) ; 31.63 (CH_2) ; 31.57 (CH_2) ; 31.13 (CH_2) ; 27.07 (CH_2) ; 26.35 (CH_2) ; 25.09 (CH_2) ; 24.06 (CH_2) ; 18.45 (CH_3) ;

MS : m / z (%) = 286 (24) ; 158 (9) ; 125 (30) ; 119(91) ; 69(42) ; 41(70)

2-(2', 3'-dimethacrylate of propyl-1')-1,3-dithiane (4i)

yield : 15%, n_D^{20} = 1.5048

^{1}HNMR ($CDCl_3$ /TMS, 250 MHz) : δ : 6.03 (ps, 1H) ; 6.02 (ps, 1H) ; 5.53 (ps, 1H) ; 5.51 (ps, 1H) ; 5.38 (m, 1H) ; 4.23 (m, 2H) ; 4.02 (m, 1H) ; 2.8 (m, 4H) ; 2.14 (m, 2H) ; 2.03 (m, 2H)

^{13}CNMR ($CDCl_3$ /TMS, 62.88 MHz) : δ : 167.01 (C=O) ; 166.99 (C=O); 136.8 (C=) ; 136.6 (C=) ; 126.01 (=CH_2) ; 125.99 (=CH_2) ; 68.8 (CH-O) ; 64.96 (CH_2-O) ; 43.8 (S-CH-S) ; 36.5 (CH_2) ; 30.44 (CH_2) ; 30.26 (CH_2) ; 26.02 (CH_2) ; 18.7 (CH_3)

MS : m / Z (%) = 330 (M^+, 2) ; 243 (2) ; 207 (4) ; 158 (81) ; 132 (16) ; 69 (100) ; 41 (69)

2-(2', 3'-dimethacrylate of propyl-1 ')-1,3-dithiane (4j)

yield : 15%, n_D^{20} = 1.5048

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.03 (ps, 1H) ; 6.02 (ps, 1H) ; 5.53 (ps, 1H) ; 5.51 (ps, 1H) ; 5.38 (m, 1H) ; 4.23 (m, 2H) ; 4.02 (m, 1H) ; 2.8 (m, 4H) ; 2.14 (m, 2H) ; 2.03 (m, 2H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 167.01 (C=O) ; 166.99 (C=O) ; 136.8 (C=) ; 136.6 (C=) ; 126.01 (=CH_2) ; 125.99 (=CH_2) ; 68.8 (CH-O) ; 64.96 (CH_2-O) ; 43.8 (S-CH-S) ; 36.5 (CH_2) ; 30.44 (CH_2) ; 30.26 (CH_2) ; 26.02 (CH_2) ; 18.7 (CH_3)

MS : m / Z (%) = 330 (M^+, 2) ; 243 (2) ; 207 (4) ; 158 (81) ; 132 (16) ; 69 (100) ; 41 (69)

2-thiomethoxy, 2-(1'-methacrylate of ethyl- 1')-1,3-dithiane (4k)

yield : 12%, n_D^{20} = 1.5521

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.16 (ps, 1H) ; 5.6 (ps, 1H) ; 5.39 (q, J = 7Hz, 1H) ; 3.24 (m, 2H) ; 2.75 (m, 2H) ; 2.14 (s, 3H) ; 1.95 (s, 3H) ; 1.52 (d, J = 6Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 166.27 (C=O) ; 136.05 (C=) ; 126.23 (=CH) ; 74.74 (CH-O) ; 66.28 (S-C-S) ; 27.11 (CH_2) ; 26.72 (CH_2); 24.62 (CH_2) ; 18.35 (CH_3) ; 16.78 (CH_3) ; 16.03 (CH_3)

(2-methacrylate of propanal)-tris(methylthio)methane (4l)

yield : 36%, n_D^{20} = 1.5394

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.13 (ps, 1H) ; 5.61 (ps, 1H) ; 5.28 (q, J = 6. 1 Hz, 1H) ; 2.21 (s, 9H) ; 1.89 (ps, 3H) ; 1.58 (d, J = 6Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 166.33 (C=O) ; 136.07 (C=) ; 126.09 (=CH_2) ; 75.27 (CH-O) ; 74.21 (S-C(S)-S) ; 18.91 (CH_3) ; 17.20 (CH_3) ; 14.30 (CH_3)

MS : m / z (%) = 219 (64) ; 171 (6) ; 153 (23) ; 118 (7) ; 69 (100) ; 41 (36)

Dethioacetalization of 1,3-dithiane derivatives

Red mercuric oxide (2 molar equivalent), 2 molar equivalent of boron trifluoride etherate, and 15% aqueous tetrahydrofuran (10 mL / g of dithiane) were stirred vigorously in a three-neck flask equipped with a dropping funnel and a nitrogen inlet tube. The dithiane (1 molar equivalent) was dissolved in the minimum of tetrahydrofuran and was added via the dropping funnel in the course of 10–15 minutes under nitrogen. Stirring was maintained for 10–20 minutes after addition was complete. In the course of this time, the red mercuric oxide gradually dissolved and a white precipitate appeared. All hydrolyses required 30 minutes at reflux to complete the reaction. Ethyl ether (2 volumes) was then added, the precipitated salts were filterd, and the ether was washed with water. The organic layer was washed to pH 10 with satured sodium carbonate and to neutrality with satured sodium chloride. After drying over sodium sulfate, the ether was evaporated under vacuum to yield crude and aldehyde or ketone. Analysis by nmr and MS spectroscopy indicated complete consumption of starting material and formation of aldehyde and ketone (>90% pure) in the yields reported in table V.

2-methacrylate of propanal (1a)

yield : 78%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 9.56 (s, 1H) ; 6.21 (ps, 1H) ; 5.66 (ps, 1H) ; 5.28 (q, J = 6.3Hz, 1H) ; 1.97 (s, 3H) ; 1.42 (d, J = 6.7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 198.63 (H-C=O) ; 166.65 (C=O) ; 136.11 (C=) ; 126.82 (=CH_2) ; 74.77 (H-C-O) ; 18.24 (CH_3) ; 14.15 (CH_3)

MS : m / z (%) = 143 (3) ; 113 (25) ; 69 (100) ; 41 (59)

$C_7H_{10}O_3$	calc.	C 59.14	H 7.09
(142.15)	found	59.31	7.19

2-methacrylate of butanal (1b)

yield : 76%, n_D^{20} = 1.4595

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.24 (ps, 1H) ; 5.68 (ps, 1H) ; 4.98 (m, 1H) ; 1.96 (s, 3H) ; 1.83 (m, 2H) ; 1.03 (t, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 198.61 (HC=O) ; 166.85 (C=O) ; 135.37 (C=) ; 126.77 (=CH_2) ; 79.40 (H-C-O) ; 22.18 (CH_2) ; 18.15 (CH_3) ; 9.28 (CH_3)

MS : m / z (%) = 157(2) ; 127 (9) ; 113 (2) ; 69 (100) ; 41 (49)

$C_8H_{12}O_3$	calc.	C 61.52	H 7.74
(156.18)	found	61.39	7.61

2-phenyl, 2-methacrylate of ethanal (1c)

yield : 81%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 9.6 (s, 1H) ; 7.43 (m, 5H) ; 6.32 (ps, 1H) ; 6.10 (ps, 1H) ; 5.73 (d, J = 1.3Hz, 1H) ; 2.05 (s, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 194.07 (HC=O) ; 166.21 (C=O) ; 137.27 (C=) ; 126.33 (=CH_2) ; 135.20 (C_{aro}) ; 129.13 (CH_{aro}) ; 128.67 (CH_{aro}) ; 128.26 (CH_{aro}) ; 127.85 (CH_{aro}) ; 80.38 (H-C-O) ; 50.32 (CH) ; 18.13 (CH_3)

MS : m / z (%) = 175 (29) ; 105 (4) ; 69 (100) ; 41 (42)

$C_{12}H_{12}O_3$	calc.	C 70.57	H 5.92
(204.22)	found	70.39	5.79

2-methacrylate of butan-3-one (1d)

yield : 75%, n_D^{20} = 1.4377

^{1}HNMR ($CDCl_3$/ TMS, 250 MHz) : δ : 6.18 (ps, 1H) ; 5.63 (ps, 1H) ; 5.1 (q, J = 7Hz, 1H) ; 2.16 (s, 3H) ; 1.95 (s, 3H) ; 1.42 (d, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 205.88 (C=O) ; 166.59 (C=O) ; 135.52 (C=) ; 126.49 (=CH_2) ; 75. 1 (H-C-O) ; 25.58 (CH_3) ; 18.13 (CH_3) ; 15.95 (CH_3)

MS : m / z (%) = 156 (M^+, 5) ; 112 (28) ; 69 (100) ; 41 (59)

$C_8H_{12}O_3$	calc.	C 61.52	H 7.74
(156.18)	found	61.77	7.59

1-methacrylate of pentan-4-one (1e)

yield : 75%, n_D^{20} = 1.4492

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.01 (ps, 1H) ; 5.48 (ps, 1H) ; 4.09 (t, J = 6.3Hz, 2H) ; 2.47 (t, J = 7.23Hz, 2H) ; 2.09 (s, 3H) ; 1.89 (m, 2H) ; 1.85 (s, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ: 207.3 (C=O) ; 167.5 (C=O) ; 135.6 (C=) ; 125.2 (=CH_2) ; 63.5 (CH_2-O) ; 39.6 (CH_2-C=O) ; 29.4 (CH_3-C=O) ; 22.2 (CH_2) ; 18.03 (CH_3)

MS : m / z (%) = 127 (2) ; 101(21) ; 84 (39) ; 69 (90) ; 43 (100) ; 41 (50)

$C_9H_{14}O_3$	calc.	C 63.59	H 8.29
(170.21)	found	63.38	8.32

2-methacrylate of pentan-3-one (1f)

yield : 86%, n_D^{20} = 1.4431

^{1}HNMR ($CDCl_3$/ TMS, 250 MHz) : δ : 6.20 (ps, 1H) ; 5.65 (ps, 1H) ; 5.16 (q, J = 7Hz, 1H) ; 2.53 (m, 2H) ; 1.98 (s, 3H) ; 1.44 (d, J = 7Hz, 3H) ; 1.08 (t, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 208.59 (C=O) ; 166.66 (C=O) ; 135.6 (C=) ; 126.44 (=CH_2) ; 74.78 (H-C-O) ; 31.37 (CH_2) ; 18.18 (CH_3) ; 16.32 (CH_3) ; 7.11 (CH_3)

MS : m / z (%) = 170 (M^+, 5) ; 126 (22) ; 113 (4) ; 69 (100) ; 41 (39)

$C_9H_{16}O_3$	calc.	C 62.76	H 9.36
(172.22)	found	62.62	9.51

3-methacrylate of butanal (1g)

yield : 89%, n_D^{20} = 1.4428

^{1}HNMR ($CDCl_3$/ TMS, 250 MHz) : δ : 9.77 (d, J = 1.6Hz, 1H) ; 6.08 (ps, 1H) ; 5.57 (ps, 1H) ; 5.43 (m, 1H) ; 2.72 (m, 2H) ; 1.93 (s, 3H) ; 1.38 (d, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 199.37 (HC=O) ; 166.56 (C=O) ; 136.13 (C=) ; 125.71 (=CH_2) ; 66.21 (H-C-O) ; 49.52 (CH_2) ; 20.08 (CH_3) ; 18.16 (CH_3)

$C_8H_{12}O_3$	calc.	C 61.52	H 7.74
(156.18)	found	61.33	7.88

2-methacrylate of cyclohexanal (1h)

yield : 96%, n_D^{20} = 1.4729

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) ; δ : 9.59 (d, J = 2.6Hz, 1H) ; 6.06 (ps, 1H) ; 5.54 (ps, 1H) ; 5.06 (m, 1H) ; 2.46 (m, 1H) ; 2.12–1.3 (m, 8H) ; 1.9 (ps, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 202.14 (HC=O) ; 166.55 (C=O) ; 136.1 (C=) ; 125.71 (=CH_2) ; 71.41 (H-C-O) ; 54.61 ($CH_{cyclohex}$); 25.53 (CH_2) ; 24.7 (CH_2); 23.78 (CH_2) ; 23.45 (CH_2) ; 18.18 (CH_3)

MS : m / z (%) = 178 (3) ; 150 (2) ; 127 (7) ; 87 (92) ; 69 (100) ; 41 (94)

$C_{11}H_{16}O_3$	calc.	C 67.32	H 8.21
(196.24)	found	67.11	8.05

3-dimethacrylate of propanal (1i)

yield : 79%, n_D^{20} = 1.4698

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 9.75 (s, 1H) ; 6.08 (m, 2H) ; 5.60 (m, 2H) ; 4.34 (m, 2H) ; 3.71 (m, 1H) ; 2.81 (m, 1H) ; 1.96–1.86 (m, 2H) ; 1.84 (ps, 6H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 197.2 (CHO) ; 166.59 (C=O); 166.18 (C=O) ; 135.5 (C=) ; 135.22 (C=) ; 126.35 (=CH_2) ; 126.23 (=CH_2) ; 66.76 (H-C-O) ; 64.41 (CH_2O) ; 44.64 (CH_2) ; 18.09 (CH_3) ; 18.02 (CH_3)

$C_{12}H_{16}O_3$	calc.	C 59.99	H 6.71
(240.25)	found	60.08	6.59

2-methacrylate of cyclohexane carboxaldehyde (1j)

yield : 89%, $n_D^{20} = 1.4784$

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.02 (ps, 1H) ; 5.51 (ps, 1H) ; 5.01 (m, 1H) ; 2.68 (m, 1H) ; 2.14 (ps, 3H) ; 1.88 (s, 3H) ; 2.01–1.75 (m, 4H) ; 1.51–1.10 (m, 4H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 209.69 (C=O) ; 166.32 (C=O) ; 136.34 (C=) ; 125.35 (=CH_2) ; 73.58 (H-C-O) ; 55.69 ($CH_{cyclohex}$) ; 30.78 (CH_2) ; 28.96 (CH_3) ; 27.91 (CH_2) ; 24.56 (CH_2) ; 23.82 (CH_2) ; 18.26 (CH_3)

MS : m / z (%) = 210 (M^+, 4) ; 150 (10) ; 124 (21) ; 109 (19) ; 69 (100) ; 43 (51) ; 41 (34)

$C_{12}H_{18}O_3$	calc.	C 68.54	H 8.62
(210.27)	found	68.66	8.85

Hydrolysis of 2-thiomethoxy-1,3-dithiane derivative 4k

3.58 mmol of **4k** was refluxed in 80 mL of 35% aqueous acetone with 4 g of mercuric chloride and 1.24 g of mercuric oxide for 24 hr. under nitrogen. The reaction was cooled and the mixture was filtered and the solid residue was washed with two 50 mL portions of methylene chloride. The methylene chloride extract was washed with 10% aqueous sodium carbonate. Acidification of the aqueous layer with diluted hydrochloride solution, followed by extraction with methylene chloride yielded 61% of acid 1k. This was pure in the nmr spectrum.

acid 2-methacrylate propanoïc (1k)

yield : 61%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 10.14 (s, 1H, OH) ; 6.18 (ps, 1H) ; 5.63 (ps, 1H) ; 5.13 (q, J = 7. 1 Hz, 1H) ; 1.94 (s, 3H) ; 1.55 (d, J=7. 1Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 208.24 (COOH) ; 166.65 (C=O) ; 135.31 (C=) ; 126.70 (=CH_2) ; 68.28 (CH-O) ; 18.02 (CH_3) ; 16.69 (CH_3)

$C_7H_{10}O_4$	calc.	C 53.16	H 6.37
(158.15)	found	53.29	6.11

Alcoholysis of 2-thiomethoxy-1,3-dithiane derivative 4k

3.58 mmol of **4k** was placed in a round-bottom flask with 80 mL of 95% alcohol, 4 g of mercuric chloride, and 1.24 g of mercuric oxide and refluxed for 4–5 hr. under nitrogen.

The mixture was filtered and the solid residue was washed with two 50 mL portions of methylene chloride. The filtrate was diluted with two 75 mL portions of methylene chloride. These extracts were combined, washed with 4 M aqueous ammonium chloride and saturated brine, dried over sodium sulfate, filtered, and evaporated in vacuo. Characterization by nmr spectroscopy indicated no significant impurities for **1l** and **1m.**

(2-methacrylate) of propanoate ethyl (1l)

yield : 92%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.13 (ps, 1H) ; 5.59 (ps, 1H) ; 5.07 (q, J = 7.2 Hz, 1H) ; 4.15 (q, J = 7.1 Hz, 2H) ; 1.93 (s, 3H) ; 1.49 (d, J = 7.2 Hz, 3H) ; 1.23 (t, J = 7. 1 Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 170.72 ($C{=}O_{ester}$) ; 166.58 ($C{=}O_{acry}$) ; 135.49 (C=) ; 126.29 ($=CH_2$) ; 68.76 (CH-O) ; 61.17 (CH_2) ; 18.04 (CH_3) ; 16.8 (CH_{3acry}) ; 13.95 (CH_3)

MS : m / z (%) = 186 (M^+, 3) ; 168 (2) ; 142 (22) ; 114 (18) ; 86 (4) ; 69 (100) ; 41 (30) ; 69 (100)

$C_9H_{14}O_4$	calc.	C 58.05	H 7.57
(186.20)	found	58.18	7.41

(2-methacrylate) of propanoate isopropyl (1m)

yield : 60%

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.18 (ps, 1H) ; 5.61 (ps, 1H) ; 5.05 (m, 2H) ; 1.95 (s, 3H) ; 1.5 (d, J = 7.1Hz, 3H) ; 1.23 (m, 6H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 170.28 (C=O) ; 166.64 ($C{=}O_{acry}$) ; 135.48 (C=) ; 126.27 ($=CH_2$) ; 76.48 (CH-O) ; 68.98 (CH-O) ; 21.55 (CH_3) ; 21.5 (CH_3) ; 18.20 (CH_3) ; 16.79 (CH_3)

MS : m / z (%) = 200 (M^+, 4) ; 158 (2) ; 141 (9) ; 114 (42) ; 86 (5) ; 69 (100) ; 56 (3) ; 41 (29)

$C_{10}H_{16}O_4$	calc.	C 59.98	H 8.05
(200.23)	found	59.88	7.98

Hydrolysis of 4l to obtain thiol ester

A solution of mercuric oxide (3.68 g, 17 mmol) in 35% aqueous HBF_4 (8.5 mL) was diluted with tetrahydrofuran (8 mL). A solution of trimethyltrithioester (10 mmol) in tetrahydrofuran (2 mL) was added in one portion with stirring under nitrogen. The reaction mixture became at once deep yellow. Stirring at room temperature was maintained for 2 hr. GC analyses showed incomplete consumption of starting material. The hydrolyses required 30 minutes at reflux to complete the reaction. KI (8.47 g, 51 mmol) was added. After stirring for a few minute, the mixture was diluted with hot ether (50 mL) and the organic layer was decanted. Then the mixture was exhaustively extracted, with stirring and heating, with the same solvent. The combined extracts were washed successively with a 5% aqueous $NaHCO_3$ solution and water, dried over sodium sulfate and evaporated under reduced pressure to afford the pure thiol ester **1n.**

1-((methyl sulfanyl) carbonyl)-1-methacrylate of ethyl (1n)

yield : 88%, n_D^{20} = 1.4801

^{1}HNMR ($CDCl_3$ / TMS, 250 MHz) : δ : 6.25 (ps, 1H) ; 5.68 (ps, 1H) ; 5.37 (q, J = 7Hz, 1H) ; 2.28 (s, 3H) ; 1.99 (ps, 3H) ; 1.5 (d, J = 7Hz, 3H)

^{13}CNMR ($CDCl_3$ / TMS, 62.88 MHz) : δ : 200.21 (S-C=O) ; 166.08 (C=O) ; 135.48 (C=) ; 126.94 (=CH_2) ; 75.00 (CH-O) ; 18.14 (CH_3) ; 17.90 (CH_3) ; 10.87 (CH_3)

MS : m / z (%) = 146(2) ; 141(38) ; 113(10) ; 75(3) ; 69 (100) ; 47 (4) ; 41(42)

$C_8H_{12}O_3S$	calc.	C 51.04	H 6.42
(188.24)	found	51.55	6.11

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