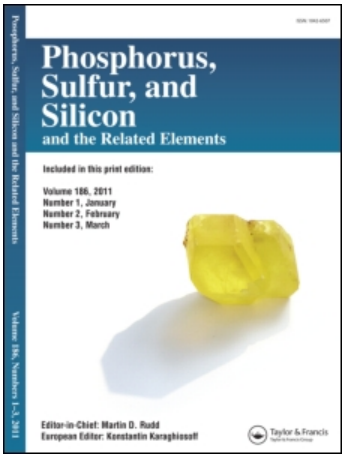

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SYNTHESIS OF CYCLIC FUNCTIONALIZED DISULFIDES AND THEIR OLIGOMERS

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SYNTHESIS OF CYCLIC FUNCTIONALIZED DISULFIDES AND THEIR OLIGOMERS

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In order to obtain comonomers for the free-radical polymerization of acrylic or vinylic monomers, cyclic disufides were synthesized. Ester or amide functions were introduced in these cyclic molecules in order to afford easily degradable centers in the copolymers chains. Looking for disulfide esters or disulfide amides from commercial materials, we have selected the synthesis of ten-membered cyclic disulfide-containing diamides and diesters. As it could be expected, competitive oligomerization – by step-growth polymerization – was observed in the synthetic course but some of the so-obtained oligomers could be also suitable comonomers for our purpose. The cyclic disulfide diesters or diamides and their oligomers were separated and characterized. Owing to their higher solubility in organic solvents and monomers, disulfide diesters afford the most convenient comonomers.

Keywords: Cyclic disulfides; 1,4,7,8 – dioxadithiecane- 5,10- dione; perhydro 1,2,5,8 -dithiadiazecine-4,9-dione

INTRODUCTION

The synthesis of biodegradable polymers is an important economic challenge[1] but most industrial vinylic polymers are known to resist for long times because only a few degradative processes could be taken into account[2]. In order to obtain more easily degradable vinylic polymers some biodegradable chemical groups like ester or amide functions might be introduced in the main chains of these polymers. Free-radical copolym-

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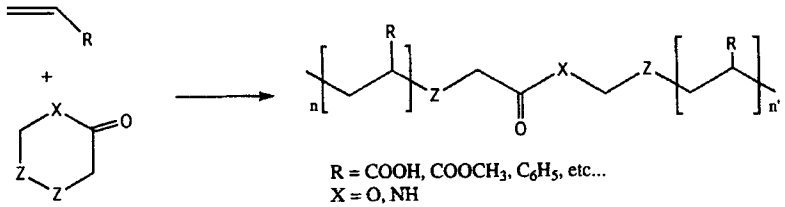
erization of vinylic monomers with cyclic comonomers containing biodegradable functions could represent a possible way to fit this requirement if ring-opening of these comonomers is made possible in free-radical chain growth (Scheme 1).



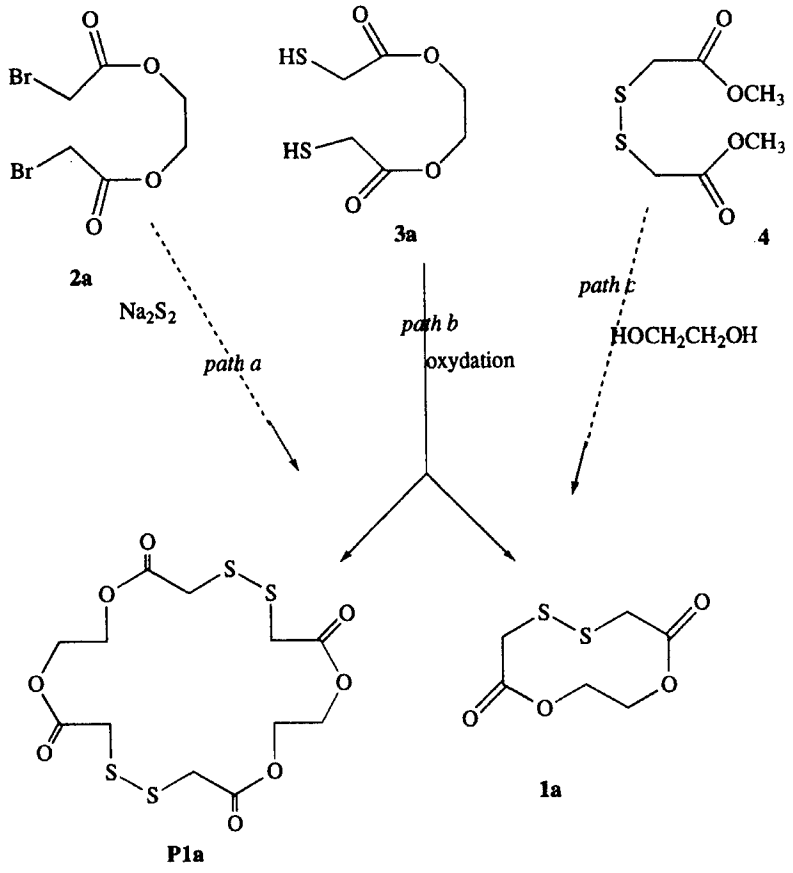
R = COOH, $COOCH_3$, C_6H_5, etc...
X = O, NH
Z-Z polymerizable group

SCHEME 1

Some studies dealing with this methodology are found in the literature. Thus, 2-methylene-1,3-dioxepane was copolymerized with ethylene and gave a biodegradable polyethylene although this cyclic ketene acetal was not a highly reactive monomer[3]. Various substituted 5-methylene-1,3-dioxan-4-ones were also synthesized for this purpose but the ring opening was incomplete[4]. More recently methylene-oxa-thia-cyclanones were prepared and have shown complete ring opening and high reactivity toward free radical copolymerization[5].

Owing to the good ability of sulfur compounds to act as transfer agents or free radical initiators [6–9] we have assumed that cyclic disulfides containing either ester or amide functions such as **1a** :1,4,7,8 – dioxadithiecane-5,10-dione and **1b:** perhydro 1,2,5,8-dithiadiazecine-4,9-dione (Schemes 2a and 2b) could be suitable comonomers for the synthesis of readily degradable copolymers.

Such ten-membered rings are thermodynamically difficult to obtain from acyclic compounds and investigations on their synthesis were undertaken mainly as they seemed readily accessible from simple commercial compounds. Symmetrical compounds were used leading to diester-or diamide-containing cyclic disulfides although only one isolated ester or amide function was theoretically needed in the degradation process. Moreover, although mercaptoacetic acid or its esters are commercial products, the synthesis of six-membered cyclic disulfides appeared difficult to achieve. For this first approach to test our hypothesis, the synthesis of symmetrical compounds seemed the most efficient way to introduce both the disulfide and the biodegradable functions in a cyclic molecule from easily accessible products. During the course of the cyclisation reaction,

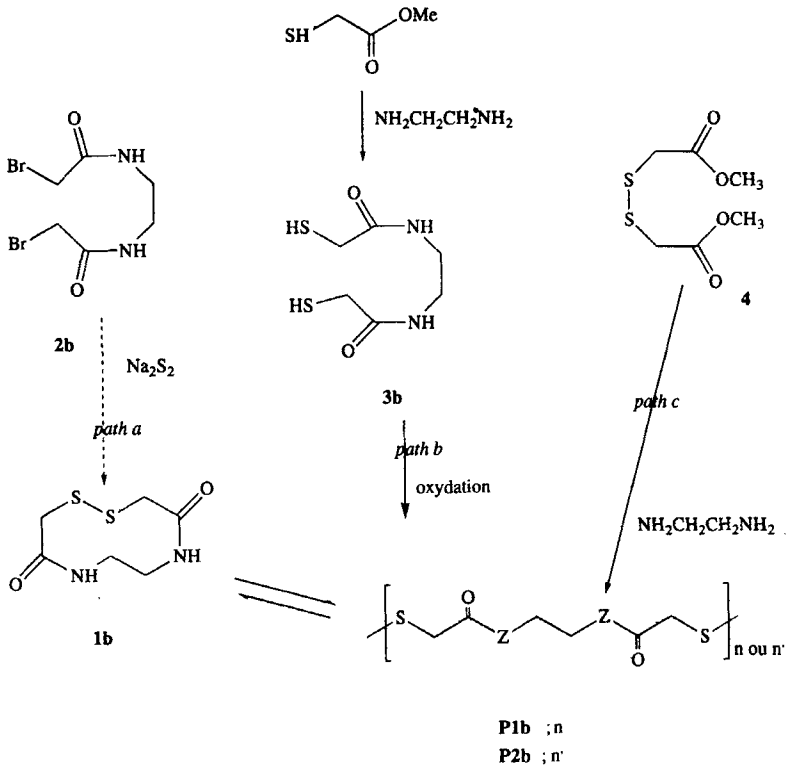


SCHEME 2a

we have expected to obtain – besides the cyclic product – large amounts of step-growth polymers and oligomers[10]. But these linear poly(disulfide)s could appear as efficient comonomers as the cyclic disulfides themselves.

Few functionalized cyclic disulfides are described in the literature. The diamide **1b** was previously prepared[11,12]. However, we have rapidly observed that the published identification data does not fit well with the proposed structure **1b**, but fit probably better with some polymeric compounds.

This paper reports the synthesis and characterization of some cyclic disulfides **1a, 1b** and their oligomers **P1a**, **P1b**, and **P2b** (Schemes 2a and



SCHEME 2b

2b). Both functional groups (ester and amide) were tested in this work as the physico-chemical behaviours of such derivatives are quite different. Their use as comonomers (or transfer agents) in free radical copolymerization will be published later[13].

RESULTS AND DISCUSSION

1 – Synthesis of 1,4,7,8-dioxadithiecane-5,10-dione 1a and its cyclic dimer P1a

Three synthetic paths were investigated to obtain **1a** from simple materials (scheme 2a).

Path a

An usual method to prepare cyclic disulfides is the treatment of bis(alkyl halide)s with alcaline disulfide salts[14]. The reaction is usually carried out in ethanol owing to the solubility of sodium disulfide.

Ethylene bis(bromoacetate) **2a** was readily prepared from bromoacetyl bromide and ethyleneglycol. First attempts to react **2a** with ethanolic sodium disulfide gave rise mainly to diethyl dithio-bis(acetate) through transesterification.

Other attempts to obtain **1a** were carried out in THF although sodium disulfide is obviously only poorly soluble in this solvent. Compound **1a,** identified by its ^{1}H NMR spectrum, was formed as a mixture with other unidentified products. Attempted optimization of the reaction (Table I) gave only low yields (≤ 16 %) and **1a** could not be isolated as a pure compound from these reaction mixtures. Therefore we discarded path a.

TABLE I Optimization of *path a* in the synthesis of **1a**

n°	*THF (ml)*	*reaction time h*	*overall yield %*	*% 2a* (recovered)*	*% 1a**
1	90	5	64.1	5	11
2	200	5	74.3	40	12
3	200	8.5	83.6	15.5	12
4	200	20	77.4	2.5	16
5	400	8.5	100	54	12
6	400	20	81.4	23	16

* determined from integrations of raw products ^{1}H NMR specta.

Path b

Oxydation is also a quite convenient method to prepare disulfides from thiols[15]. Ethylene glycol bis(thioglycolate) **3a** is a commercial material and the path b seemed an interesting alternative method to obtain **1a.**

Oxydation of the bis-thiol by hydrogen peroxide in high dilution conditions afforded in high yields a raw product which was constituted exclusively of **1a** and its cyclic dimer **P1a.** The later was present in large amounts. Traces of the starting material **3a** were also recovered.

Improvements of the experimental conditions (temperature, concentrations) (Table II) afforded **1a** and **P1a** in nearly quantitative yields. The cyclic product and its dimer were separated by chromatography on silica gel.

TABLE II Optimization of *path b* in the synthesis of **1a** (and **P1a**)

reaction time and T°C	*solvent (ml)*	*yield %*	***3a*** % recovered*	***1a*** %*	***P1a*** %*	***1a/P1a***
17 h/ 20	H_2O (80)	72	57	5	38	0.13
24 h / 40	H_2O (80)	79	43	4	53	0.07
48 h / 40	H_2O (80)	69	28	9	63	0.13
96 h / 50	H_2O (80)	41	3	0	97	0
72 h / 40	H_2O (225)	91.5	22	7	71	0.1
72 h / 40	H_2O (250)+THF (50)	87	14.5	6.5	79	0.08
96 h/40	H_2O (570)+THF (80)	96	5.6	12.3	82.1	0.15
12 days /40°C	H_2O (4300)+THF (125)	100	0	40	60	0.66

* determined from integrations of raw products ^1H NMR specta.

The assigned structures of **1a** and **P1a** are supported by spectroscopic and analytical data (experimental part). In size exclusion chromatography (SEC), **P1a** behaves like a dimer without any terminal group : so we have postulated that it was cyclic and this was confirmed by mass spectrometry. Chemical shifts and spin patterns in ^1H NMR spectra are different in these cyclic disulfides: monomer **1a** and its dimer **P1a.** In **1a** the methylene protons are not equivalent; so, an AB spin pattern is observed for CO-C$\underline{H}_2$-S groups and an A_2B_2 spin system is observed for O-C$\underline{H}_2$-C$\underline{H}_2$-O. On contrast, owing the flexibility of the 20-membered cycle in dimer **P1a,** the equivalent methylene protons appear as a singlet for each methylene group. ^{13}C NMR spectra are in accordance with the assigned cyclic structures of **1a** and **P1a**. As it appears in Table II, reaction in pure water affords mainly the cyclic dimer **P1a :** this unusual result must be related to the heterogeneous reaction conditions and reagent chain length. The monomeric cyclic disulfide yield becomes higher when THF is introduced to obtain homogeneous conditions. High dilution conditions, such as

required to prepare medium-sized cyclic compounds, allow the monomer yield to increase although the dimer remains the main product whatever the dilution used.

Attempts to depolymerize **P1a** in hot DMF, as it was efficiently realized for **P1b** *(see below)* led to decomposition of the product.

Path c

The transesterification of dimethyl dithiodiacetate **4** with 1,2-ethanediol (path c, scheme 2a) was also experimented. The disulfide **4** is readily prepared from methyl mercaptoacetate and a solution of hydrogen peroxide. But attempts to react **4** with ethylene glycol failed, giving very small amounts of **P1a** and no trace of **1a**.

2 – Synthesis of perhydro 1,2,5,8 -dithiadiazecine-4,9-dione 1b and its oligomers P1b et P2b

The synthesis of the cyclic diamide **1b** has been already described in the literature[11,12]. High yields were obtained according to path c (Scheme 2b) from bulk reaction between dimethyl dithio-diacetate **4** and ethylenediamine. Lower yields resulted from reaction in solution. Path b from N,N′-ethylene bis(mercaptoacetamide) **3b** gave also attractive yields.

Path c

We have first experimented the path c which gives quantitative yields according to Owen *et al.*[11]. These high yields in a transamidation for a ten-membered ring were explained by the postulated existence of intramolecular hydrogen bonding in this molecule – and more importantly – in the intermediate amino-ester : $H_2N\text{-}CH_2CH_2\text{-}NHCOCH_2S\text{-}SCH_2COOR$. The product isolated by Owen *et al.* was characterized, after crystallization from hot dimethylformamide, by mass spectrometry, analysis, IR spectroscopy and melting.

We obtained, again in high yields, a raw product whose mass spectrometry and melting point however were not in accordance with Owen's data : the molecular ion is observed at 446 in the mass spectrum and no fragment could be observed above. Nevertheless, the "recrystallization process" in DMF, *i.-e.* warming to 110 – 115 °C for a long time, afforded in low yield an insoluble product whose characterization (mass spectroscopy, melting

point) was then in accordance with the structure **1b** and literature data. Its ^{1}H-NMR spectrum is even quite simple : two singlets exhibiting the equivalence of both protons in each methylene groups. Owing to the double bond character of the C-N bond in amide groups, the molecule **1b** presents a symmetry axis through the center of the S-S bond and the center of the ethylene group if the carbonyl groups are in an opposite position *i.e.* trans to each other and a symmetry plan if the carbonyl groups are in the same direction *i.e.* cis. The equivalence of the protons in the CH_2-groups arises from this symmetry. The ^{13}C NMR spectrum is consistent with the cyclic structure of **1b** with three peaks for three different carbons : 174.38 ppm for the carbonyl carbon and 40.45 and 42.19 ppm for the methylene carbons.

So, the first isolated raw product **P1b** looks like an oligomer of **1b** which depolymerizes partly in hot DMF. Such an equilibrium in a polar solvent between monomeric and dimeric bis(amide) disulfides was previously observed by other authors[16].

Attempts to depolymerize **P1b** in other solvents (water, acetonitrile, toluene) or in the bulk under vacuum, were not sucessfull, giving rise to a lot of unidentified products. The molecular ion observed in mass spectrometry on **P1b** at 446 does not fit with the formula of a cyclic dimer, such as observed in **P1a,** which would have given a molecular ion at 412 ; it could fit more with the formula of a open-chain dimer like the following formula:

$H_2NCH_2CH_2NHCOCH_2S\text{-}SCH_2CONHCH_2CH_2NHCOCH_2S\text{-}SCH_2\text{-}COOCH_3$

with one ^{34}S atome but the corresponding molecular ion at 444 (^{32}S) does not appear in the spectrum. Other attempts to measure the molecular weight either by SEC or by cryoscopy were unsuccessful because of the complete insolubility of **P1b** in suitable solvents. The ^{1}H NMR of **P1b** is quite different from the ^{1}H NMR of **1b**. It appears mainly as a singlet and does not allow any elucidation of the structure of **P1b**; a weak signal at 3.61 ppm could correspond to a methoxycarbonyl terminal group in a linear oligomer. The fact that **P1b** could be a linear oligomer of **1b** is supported by the presence of several signals, especially for carbonyl carbons in ^{13}C NMR corresponding to different chemical environments.

Path b

The path b was reported as a successfull way in the obtention of product **1b**. In this method N,N′-ethylene bis(mercaptoacetamide) **3b** is the start-

ing material. This compound **3b** was also prepared in high yields (82%) by Owen *et al.*[12] by aminolysis of methyl mercaptoacetate using ethylene diamine and characterized (analysis, ^{1}H NMR, m.p.). Their results must be accurately examined before the report of our results.

Owen *et al,* by oxydation of the bis-thiol **3b** into disulfide, obtained different results according to the type of oxydative agent used and pointed out the bis-thiol unusual sensitivity to air oxydation. Air oxydation of **3b** led to a product (m.p. 245°C) insoluble in usual solvents whose mass spectrum presents no peak above the isotopic pair at m/e = 206/208. So it is unlikely to be a dimer or oligomers. Iodine oxydation of **3b** led to the bis(amide) disulfide **1b**. Oxydation by hydrogen peroxide led to a mixture of **1b** and the product of melting point at 245°C. These products were regarded by Owen *et al.* as two diastereoisomeric structures of the ten-membered ring with cis or trans amide group.

We have performed the amidation reaction between ethylenediamine and two equivalents of methyl mercaptoacetate according to literature's conditions. In this reaction, we obtained in fact two products and several attempts could not significantly modify their relative yields. The first one (~5%) presents a ^{1}H-NMR spectrum in accordance with the previously described bis-thiol **3b** but exhibits a higher melting point : 186°C instead of 138–139°C. The second one : **P2b** (yield: 80 %) presents a large melting zone from 210 to 230°C and is not soluble in usual solvents. Its formation occured even when the reaction was carried out under a nitrogen atmosphere. Its mass spectrum also shows a molecular ion at 446 (nothing at higher values) and the same scissions as **P1b** ; additional ions at 177 and 173 are also present for **P2b**. A weak singulet at 4.11 ppm is the main difference between the ^{1}H-NMR spectra of both products **P1b** and **P2b**. ^{13}C-NMR spectrum is more simple than the spectrum of **P1b**. It presents, like **1b**, three main signals, corresponding to carbonyl group carbon at 174.11 ppm and to the methylene carbons at 40.74 and 40.16 ppm but additional weak peaks at 176.75 and 26.45 ppm are also presents, as in the ^{13}C-NMR spectrum of **P1b**.

After stirring in hot DMF, **P2b**, as well as **P1b**, affords product **1b**, characterized by its ^{1}H NMR spectrum and melting point.

At the present time we think that **P1b** and **P2b** are oligomers of different degree of polymerization resulting from different step-growth polymerizations at different reaction rates. Owing to the multiplicity of carbonyl group signals in ^{13}C-NMR spectrum, we assume a larger degree of polym-

erization for **P1b** than for **P2b**. This assumption could be consistent with the synthesis conditions of both products: **P1b** in the bulk and **P2b** in solution. However, the results of the mass spectra remain inconsistent with these structures but we can assume depolymerization reactions and perhaps decompositions during the sample vapourization step before ionization.

Path a

As observed for **1a** and **P1a**, the bis(amide) **2b** was readily prepared from bromoacetyl bromide and ethylene diamine but we failed to provide **1b** through reaction of **2b** with sodium disulfide, probably because the bis-amide **2b** as well as sodium disulfide were insoluble in THF.

CONCLUSION

In conclusion, the cyclic disulfides **1a** and **1b** were synthesized, purified and characterized. Path b with optimization of the reaction in high dilution technique seems the best method to produce **1a** in suitable yield. The disulfide **1a** and its cyclic dimer **P1a** could be conveniently separated. Both are suitable molecules for our initial purpose and they will be checked as comonomers in radical vinylic polymerization.

Paths b and c produce mainly the oligomers **P1b** and **P2b**. As it was observed in the literature, warming them in DMF affords **1b**. The monomeric cyclic product and its oligomers were accurately differenciated and **1b** was fully identified. However, even if some data were obtained for products **P1b** and **P2b,** their low solubility did not allow more accurate differentiation.

Yields in **1b** remain low, but the equilibrium between **1b** and **P1b** might allow to use **P1b** for our purpose, if the rate of the free-radical copolymerization is slower than the depolymerization process. Nevertheless, the poor solubility of the amide compounds – cyclic disulfide as well as oligomers – will be a drawback for the considered copolymerizations.

EXPERIMENTAL

^{1}H and ^{13}C-NMR were recorded on BRUCKER DPX 200 spectrometer ; internal references : TMS for $CDCl_3$ and CF_3CO_2D and DSS for D_2O.

Mass spectra were registered on a NERMAG R 10.10 H (low resolution, electronic impact at 70 eV).

A Perkin-Elmer 1750 spectrophotometer was used for I.R. spectra.

Size Exclusion Chromatography was performed on Styragel columns calibrated with standard alcanes samples.

Ethylene bis(bromoacetate) : 2a

Ethylene glycol (5 g; 0.08 mol) and pyridine (12.75 g; 0.16 mol) were dissolved in a 50/50 mixture of dry ethylether and toluene. The solution was stirred and cooled in an ice bath. Bromoacetyl bromide (15 ml; 0.17 mol) was then added dropwise. Pyridinium bromide precipitated out as a white solid. The stirring was carried on over night at room temperature. The solid was filtered off, the organic phase washed with water, dried on magnesium sulfate and the solvent evaporated. The colorless liquid was distillated in the vacuum.

Yield after distillation : 62%

b.p.: 150°C (5mmHg)

^{1}H-NMR ($CDCl_3$) : δ (ppm) = 3.82 (s, 4H, Br-CH_2-CO); 4.35 (s, 4H, CH_2O)

N,N′-ethylene bis(bromoacetamide) : 2b

Toluene (83 ml), diethyl ether (28 ml), water (20ml), ice (110 g), potassium carbonate (11.5 g; 0.083 mol) and ethylenediamine (5 g; 0.083 mol) were vigorously stirred. Bromoacetyl bromide (16.8 ml; 0.19 mol) was dropped in and the temperature was maintained between −2 and +4°C. Potassium bromide precipitated and carbon dioxide was evolved. The solution was still stirred for half an hour and then filtered. The solid was washed with diethyl ether, then the organic layers washed, dried, and concentrated to give a white solid. Recrystallisation from ethanol gave the pure sample as bright white spangles.

Yield after purification : 32%

m.p.: 147–148°C

^{1}H-NMR ($CDCl_3$) : δ (ppm)= 3.4 (d, 4H, NH-CH_2); 3.8 (s, 4H, Br-CH_2-CO); 6.9 (m, 2H, NH)

1, 4-Dioxa-7,8-dithiecane-5, 10-dione : 1a and P1a

Path a

Sodium disulfide nonahydrate (7.2 g; 30 mmol) was dissolved in refluxing ethanol (100ml). Sulfur (0.96 g; 15 mmol) was added. The orange-colored solution was refluxed for two hours. Ethanol was evaporated and THF was added to the orange colored solid. Ethylene bis(bromoacetate) (3.04 g; 10 mmol) was added dropwise in a suspension of sodium disulfide (1.65 g; 15 mmol) in THF. The mixture is refluxed for 6 hours. After cooling, the suspension was filtered and the solvent evaporated. The yellow oil was dissolved in a mixture of water/dichloromethane (50/50). The organic material was extracted several times with dichloromethane. The combined organic layers were washed with water and dried over anhydrous sodium sulfate. After evaporation a viscous yellow oil was recovered. The different attempts are collected in table I. **1a** could not be isolated.

Path b

Ethylene bis(mercaptoacetate) (2.94 g; 14 mmol) and water (80ml) were mixted under stirring. A 3% hydrogen peroxide solution (18 ml; 16 mmol) was added dropwise. The accurate experimental conditions are collected in table II. The white solution was extracted with dichloromethane according to the usual process and the combined extracts dried over anhydrous sodium sulfate. A white viscous liquid was obtained on concentration and analyzed by ^{1}H NMR spectroscopy. A silica gel chromatography (eluent : dichloromethane/cyclohexane) provided pure **1a** and **P1a.**

1a :m.p.: 55°C

mass (70eV) : m./e : 208

^{1}H-NMR ($CDCl_3$): δ (ppm)= 3.35 (AB, 4H, J = 13 Hz, S-CH_2-CO), 4.38–4.43 and 4.55–4.65 (A_2B_2, 4H, O-CH_2-CH_2-O)

^{13}C-NMR ($CDCl_3$): δ (ppm)= 169.3 ; 61.51 ; 40.9

I.R. (KBr) : ν (cm^{-1}) = 1734, 1261 cm^{-1}

P1a : m.p.: 118°C

mass (70eV) : m./e : 416

M_n in alcane equivalent : 14.5

^{1}H-NMR ($CDCl_3$): δ (ppm)= 3.64 (s, 4H, S-CH_2-CO), 4.43 (s, 4H, O-CH_2-CH_2-O) ^{13}C- NMR ($CDCl_3$): δ (ppm) = 169.2 ; 63.1 ; 41.7

Path c

Methyl bis(thioacetate) : 4

A 3% w/w-solution of hydrogen peroxide (2.3 g; 20 mmol) and methyl mercaptoacetate (3.2 g ; 30 mmol) were mixted and stirred for 48 hours at 40°C. The aqueous solution was extracted with dichloromethane. The organic phase was washed, dried and the solvent evaporated. A bad-smelling liquid was obtained ; it was used without purification.

Yield : 91%

^{1}H-NMR ($CDCl_3$): δ (ppm) =3.60 (s, 4H, SCH_2); 3.77 (s, 6H, OCH_3)

Transesterification : The diester **4** (2.4 g; 11.4 mmol), ethylene glycol (0.71 g; 11.4 mmol) and p-toluenesulfonic acid (0.022 g; 1% mol) were stirred in toluene at 80°C for 52 hours. A distillation apparatus allowed the methyl alcohol to be removed as it formed but no methanol was collected. The diester **4** was recovered from the reaction mixture.

Perhydro 1, 2- dithia- 5,8-diazecine-4, 9-dione : 1b and P1b

The reaction was carried out according to reference 11. Equimolar quantities of ethylene diamine and methyl dithiodiglycolate were admixed. The reaction proceeded at room temperature for a night. The mixture became viscous and a pale yellow solid is recovered, washed with cold ethanol and dried : **P1b**

yield = 90 %

m.p. : 180 °C

mass (70 ev) : m./e = 446, 208 (^{34}S), 206 (^{32}S), 177, 173, 164, 160, 142, 133, 106, 104, 87, 84, 72

^{1}H-NMR (CF_3COOD) : δ (ppm)= 4.11 (s, weak), 3.80 (s, large), 3.61 (s, weak)

^{13}C-NMR ($CDCl_3$): δ (ppm)= 177.4 (weak), 176.2 (weak), 175.4 (weak), 175.2, 175.0 (weak), 42.7 (weak), 41.8, 41.2, 39.5 (weak)

P1b (3 g) was dissolved in hot DMF (70 ml, 110–115°C) ; on cooling a white product precipited; it was filtered and dried : **1b**

yield = 35–40 %

m.p.: 206–208°C (lit[12]: 205 °C)

mass (70 ev) : m./e = 208 (^{34}S), 206 (^{32}S), 164, 160, 142, 133, 106, 104, 87, 84, 72

^{1}H-NMR (CF_3COOD) : δ (ppm)= 3.80 (s, 4H) 3.86 (s, 4H)

^{13}C-NMR (CF_3COOD): δ (ppm)= 40.45, 42.19, 174.38

I.R. (KBr) : ν =3322, 3264, 1645 and 1533 cm^{-1}

N,N′ ethylene bis(mercaptoacetamide) : 3b

The reaction was carried out according to reference 12. Ethylene diamine (3.6 g; 60 mmol) was added slowly to stirred, ice-cooled methyl mercaptoacetate (12.8 g; 120 mmol) and the mixture was then heated at 100°C for 1.5 hr. Overnight the product solidified and a white solid is recovered from cold ethanol :

yield : 5 %

m.p. : 186°C (lit[12]: 138–139 °C)

^{1}H-NMR (D_2O): δ (ppm)= 3.25 (s, 4H,CH_2N), 3.4 (s, 4H, CH_2S) (lit[12] : 3.45 and 3.59)

Another white solid insoluble in ethanol and usual solvents is recovered by filtration : **P2b**

yield 81%

m.p. : 210–230°C (dec)

mass (70 eV) : m./e = 446, 208 (^{34}S), 206 (^{32}S), 164, 160, 142, 133, 106, 104, 87, 84, 72

^{1}H-NMR (CF_3COOD): δ (ppm)= 3.79 (s, 85–90%), 3.56 (s, 15–10)

^{13}C-NMR (CF_3COOD) : δ (ppm)= 176.75 (w), 174.11, 40.74, 40.16, 26.45 (w)

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