Crosslinked sulphur-containing polymers: 2. Reaction of acetone with formaldehyde and bis-thiols*

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The polycondensation reaction of acetone with formaldehyde and bis-thiols, such as $HS–(CH_2)_n–SH$ ($n = 2$–6) as well as 2,2'-oxydiethanedithiol and 1,3-dimercaptobenzene, in alkaline medium, is investigated in order to obtain directly crosslinked poly(γ-ketosulphide)s. The correlation between the nature of the bis-thiol and the extent of crosslinking, the gelation time and the structure of the obtained polymer products is discussed in terms of bis-thiol nucleophilic character and chain length, as well as of the conformational requirements of the growing macromolecules.

INTRODUCTION

The present paper deals with the possibility of obtaining crosslinked poly(γ-ketosulphide)s by a three-component polycondensation of acetone, formaldehyde and bis-thiol.

Crosslinked products **II** possessing the γ-ketosulphide moiety were previously prepared[1] from linear poly(γ-ketosulphide)s **I**, formaldehyde and bis-thiols in alkaline conditions (*Scheme 1*).

Scheme 1

$R^1 \equiv, \text{or} \neq R^2 : (CH_2)_2, (CH_2)_4, (CH_2)_2O(CH_2)_2$
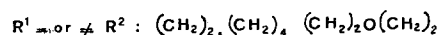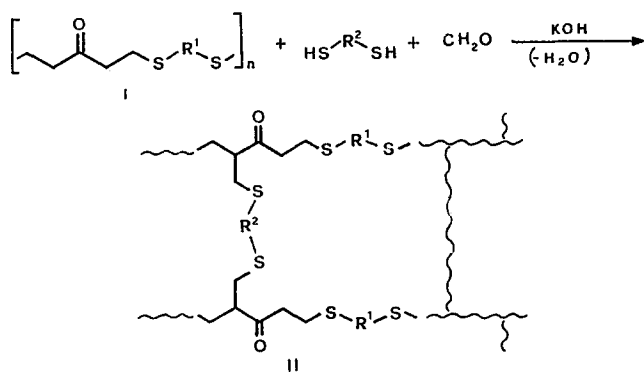
In particular, it was observed[1] that such reaction is successful when suitable polymeric substrates and bis-thiol reactants are employed. In fact, the substrate **I** must be sufficiently stable to the concurrent dethiolation reaction and the crosslinking agent has to be an aliphatic bis-thiol with proper chain length.

In principle, however, crosslinked products analogous to **II** may be obtained in one step by the above-mentioned

reaction of acetone, formaldehyde and a bifunctional thiol, thus avoiding the step of the synthesis of precursors **I** from ketonic bis-Mannich bases and bis-thiols[2].

The condensation reaction of alkylketones, formaldehyde and monofunctional thiols has been extensively studied[3], but, up to now, only ethanedithiol has been tested as bifunctional reagent in such a reaction, the linear polymer **III** being reported[3,4] to be produced when acetone, formaldehyde and ethanedithiol are allowed to react at room temperature in the presence of potassium hydroxide.
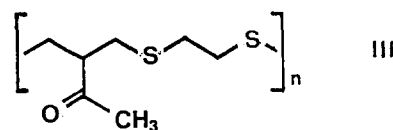

However, the effectiveness of ethanedithiol as crosslinking agent has proved to be very poor[1], due both to the shortness of its chain length, which prevents the macromolecular chains from becoming close enough together for crosslinking to occur, and to the low stability in alkaline medium of the macromolecules formed.

In this context, in addition to ethanedithiol (**1a**), (*Scheme 2*), we have examined a series of bis-thiols **1b–1e**, having progressively increasing chain lengths, as well as 2,2'-oxydiethanedithiol (**1f**) and 1,3-dimercaptobenzene (**1g**). In fact, on the basis of literature data[5–7], **1f** is expected to have similar reactivity as compared with **1a**, whereas **1g**, besides a more rigid structure, should display even less nucleophilicity.

The present investigation is therefore aimed at determining the best properties of the bis-thiol in terms of size, flexibility and nucleophilicity in order to perform the reaction reported in *Scheme 2*.

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*For Part 1, see reference 1

Scheme 2

2

$R = (CH_2)_n$, $n = 2$ (a) ; $R = (CH_2)_2O(CH_2)_2$ (f)
    3 (b)
    4 (c) $R = $ · (g)
    5 (d)
    6 (e)
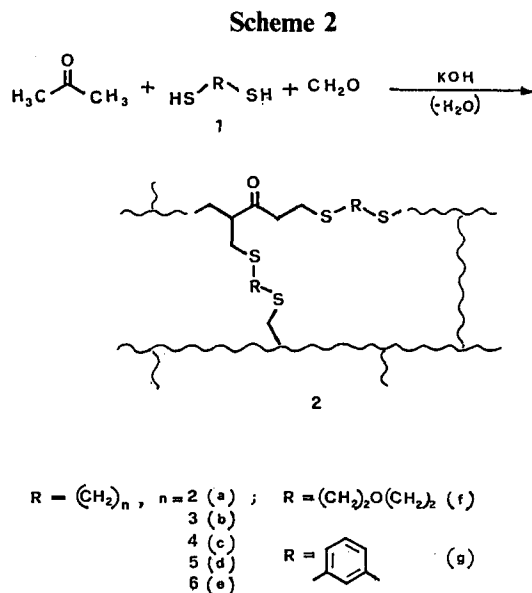
RESULTS AND DISCUSSION

When acetone, paraformaldehyde, bis-thiol and alcoholic potassium hydroxide in the molar ratio 1:2:1:1, in that order, are allowed to react at 40°C, under nitrogen atmosphere, gelation of the clear solution generally occurs after various reaction times, depending on the nature of the bis-thiol employed (*Table 1*). Only the reaction with **1g** does not produce any solid material.

The shortest gelation times are observed with bis-thiols **1b–1e**, which exhibit an even–odd effect related to the number of their carbon atoms (*Figure 1*).

The precipitated products **2** that result are gummy and behave as crosslinked materials, as they are insoluble in the common organic solvents, with the exception of **2a** (*Table 1*). Combined results from C, H, S elemental analysis (*Table 2*), *FT* i.r. spectroscopy and d.s.c. measurements confirm that the obtained products generally have the structure **2** (*Scheme 2*) but, at the same time, there is evidence of some relevant differences among **2a–2f**, thus one is able to get better insight of the reacting behaviour of the various bis-thiols employed.

The elemental analyses of products **2b**, **2d** and **2e** show (*Table 2*) intermediate values of carbon and sulphur contents with respect to those calculated for 1:1 and 1:2 ratios between acetone and $-CH_2S(CH_2)_nSCH_2-$ moieties, respectively, thus suggesting a lower degree of crosslinking

as compared with that represented in structure **2** (*Scheme 2*). *FT* i.r. spectra of **2b**, **2d** and **2e** (*Figure 2*) show similar patterns and are in agreement with the γ-ketosulphide structure proposed. In particular, bands around 1420 cm^{-1}, related to methylene groups adjacent

Table 1 Condensation products from the reaction of acetone with formaldehyde and bis-thiols **1a–1g** in ethanol solution at 40°C

		Precipitated product		
Bis-thiol	Type	Time[a] (h)	Yield[b] (%)	Solubility properties[c]
1a	**2a**[d]	2.8	25	G,I,L (s); D,E,H (p); A,B,C,F,M (i)
1b	**2b**	1.0	53	A–M (i)
1c	**2c**	0.4	75	A–M (i)
1d	**2d**	1.0	29	A–M (i)
1e	**2e**	0.8	33	A–M (i)
1f	**2f**	3.2	2 (57)[e]	A–M (i)
1g	—[f]	–	–	–

[a] Time required to obtain gelation
[b] Calculated on the basis of bis-thiol content in the product, as determined by elemental analysis
[c] Products **2a–2f** are insoluble in all the tested solvents at room temperature. Solubilities are reported for the following solvents at boiling point: ethanol (A), benzene (B), toluene (C), dioxane (D), tetrahydrofuran (E), diethylether (F), chloroform (G), methylene chloride (H), dimethylsulphoxide (I), dimethylformamide (L), water (M). Symbols: soluble (s), partially soluble (p) and insoluble (i)
[d] The structure of this product is not crosslinked
[e] At 60°C after ~0.5 h
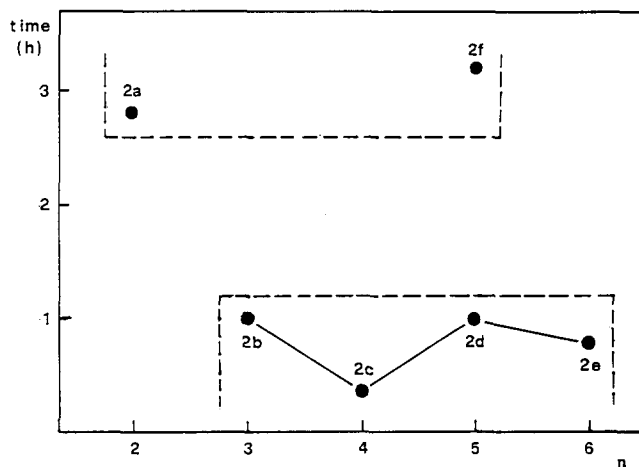[f] No precipitation occurs after 15 h of reaction

Figure 1 Time required for precipitation of products **2** vs. the number of atoms (*n*) separating the –SH groups of reactant bis-thiol

Table 2 Elemental analysis of products **2a–2f**

	Found (%)			Calculated[a] (%)					
				A			B		
Product	C	H	S	C	H	S	C	H	S
2a	44.9	6.6	43.9	47.7	6.9	36.4	44.9	6.2	43.5
2b	48.5	7.6	37.1	50.5	7.4	33.7	48.4	6.9	39.7
2c	54.8	7.7	29.5	52.9	7.9	31.4	51.4	7.5	36.5
2d	54.1	8.2	30.4	55.0	8.3	29.3	53.9	8.0	33.8
2e	56.4	9.3	28.6	56.9	8.7	27.6	56.1	8.4	31.5
2f	45.6	6.9	33.5	49.1	7.3	29.1	47.1	6.9	33.5

[a] Calculated for one (A) or two (B) $-CH_2-S-R-S-CH_2-$ groups for each acetone moiety, corresponding to linear poly(γ-ketosulphide) or to crosslinked structure of type **2**, respectively
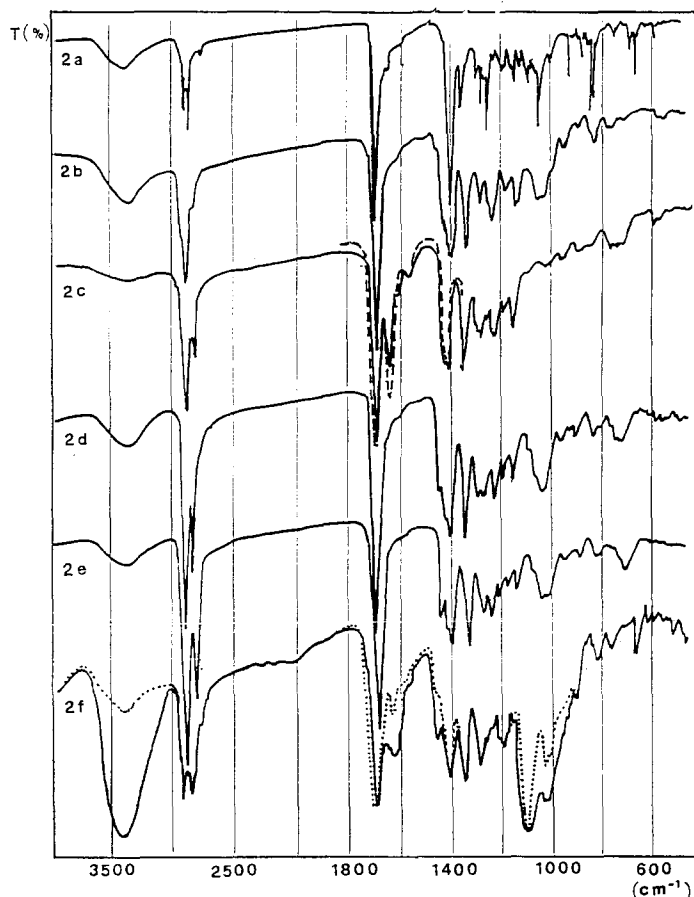
Figure 2 *FT*i.r. spectra of compounds **2a–2f**. The broken curve refers to the product **2c** obtained using a molar ratio acetone/bis-thiol 5:1; the dotted curve refers to the product **2f** obtained at 60°C

to carbonyl or sulphide groups, as well as the ketone band at 1705 cm⁻¹ are present, and exhibit no substantial difference from the spectra of analogous crosslinked poly(γ-ketosulphide)s previously reported[1]. Moreover, the presence of a certain amount of methylol groups (bands at 3435 and near 1050 cm⁻¹) can be related to incomplete bis-thiol condensation, thus confirming the obtainment of partially crosslinked products.

The reaction with **1c** affords a yellow product having carbon and sulphur contents respectively higher and lower than the calculated ones (*Table 2*); in addition, the *FT*i.r. spectrum (*Figure 2*) reveals the presence of carbon–carbon double bonds conjugated with the carbonyl groups (band at 1661 cm⁻¹). In this case it is reasonable to hypothesize that acetone also gives, to some extent, aldol-type condensation reactions involving alkyl keto-groups and/or carbonyl groups of the polymer chains, as illustrated below. As a consequence, conjugated moieties responsible for the yellow colour of the product **2c** would be formed and by this route acetone would behave as a crosslinking agent.
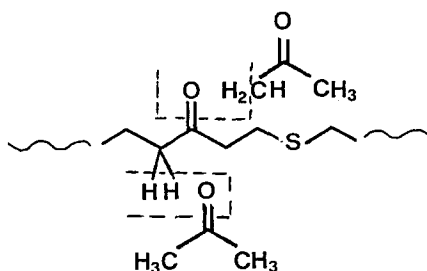
Accordingly, when the same reaction is carried out in the presence of an excess of acetone (see 'Experimental'), a relative increase of conjugated double bonds is observed in the crosslinked product (*Figure 2*), as checked by the increased intensity of the band at 1661 cm⁻¹ with respect to both the regular carbonyl band (1710 cm⁻¹) and the CH₂ bands (1436 and 1418 cm⁻¹).

The crosslinking behaviour of acetone, which is observed only in this case, can be explained by assuming that proper size and geometry of the network formed in the reaction with **1c** favour the participation of acetone molecules in the final steps of crosslinking.

In the reaction with **1f**, again, a distinctive behaviour is observed, as only a minor amount of white product **2f** precipitates from the solution in very low yield and after a long reaction time (*Table 1*). This is attributable to the likely formation of a large amount of soluble oligomeric molecules, which are not able to grow sufficiently to cause gelation of the whole reaction mixture. For this reason, only a limited amount of crosslinked polymer is formed and can precipitate. Accordingly, the *FT*i.r. spectrum of **2f** (*Figure 2*) shows the presence of a remarkable amount of side-chain and/or terminal methylol and α,β-unsaturated carbonyl groups (bands at 3433, 1038 and 1661–1631 cm⁻¹ respectively). Moreover, elemental analysis (*Table 2*) confirms a carbon content lower than that expected on the basis of the structure **2** reported in *Scheme 2*. Therefore, structure **2** would be better represented as follows:
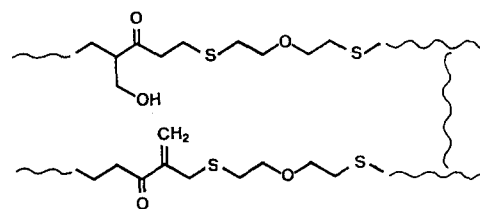
A confirmation of the above hypothesis comes from the data obtained by performing the same reaction at 60°C. In fact, **2f** is produced in a better yield (57%, *Table 1*) and the *FT*i.r. spectrum shows a significantly lower content of both methylol and α,β-unsaturated carbonyl groups (*Figure 2*). In such reaction conditions, the degree of crosslinking that results is higher and product **2f** resembles more strictly the general structure **2**.

As regards **1a** and **1g**, which do not give any crosslinked product, the following considerations can be drawn. Product **2a**, obtained in the reaction with ethanedithiol, shows elemental analysis (*Table 2*) and *FT*i.r. spectrum (*Figure 2*) in agreement with a structure having a –CH₂S(CH₂)₂SCH₂–/acetone molar ratio of 2:1. However, the solubility properties as well as the d.s.c. pattern (see below) prove that **2a** is not crosslinked and therefore it must actually be constituted by branched polymeric chains involving also cyclic structures of the type depicted below, as evidenced by ¹H n.m.r. investigation.
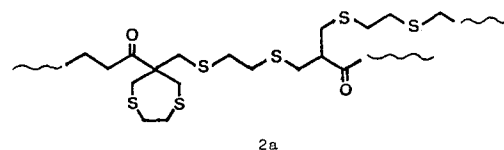
The presence of a signal at 3.2 ppm (see 'Experimental'), previously observed[1] also in analogous condensations of

poly(γ-ketosulphide)s I with ethanedithiol and formaldehyde, can in fact be attributed to the ring $-CH_2S-$ groups in β positions with respect to the carbonyl. The structure here proposed for 2a differs from that (III) reported in the literature for the same reaction, where a 1,1- enchainment of the acetone molecule is proposed[4]. Such a difference can be explained by taking into account the higher reaction temperature adopted in our experiments, which should favour more extensive condensation reactions leading to highly branched polymer chains. These data confirm that ethanedithiol is not convenient as a curing agent in this type of reaction.

Finally, in the reaction with 1,3-dimercaptobenzene (1g) no polymeric material at all is obtained, the only isolated product consisting of a mixture of mono- and bis-methylol derivatives of 1g (see 'Experimental').

The d.s.c. behaviour of 2a–2f (*Figure 3*) confirms the interpretation of the experimental data given above. With the only exception of 2a, all the compounds examined do not exhibit any melting peak, in agreement with a crosslinked structure. Most of them show a broad endothermic peak, at a temperature higher than 200°C, with concurrent emission of volatile bad-smelling thiol derivatives attributable to a degradation process. In fact, a second cycle of heating, after slow cooling of such samples, does not reproduce the original d.s.c. pattern, thus confirming the above mentioned hypothesis.

It is also noteworthy that 2c is the only material that does not show any pronounced degradation peak. This higher thermal stability suggests a larger crosslinking density of the sample, attributable to the presence of additional bridges originated by the condensation of acetone molecules, as proposed before.
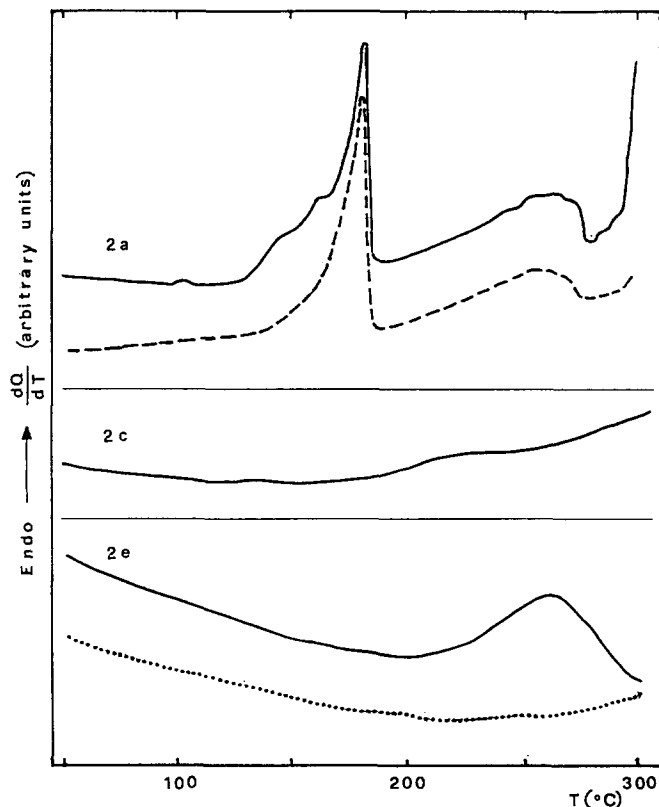
As expected, product 2a, on first heating, exhibits a multiple endothermic peak with a relative maximum at 180°C, which becomes a single peak when a pristine sample is submitted to a second heating cycle. This behaviour, typical of a melting transition, confirms that no crosslinking occurs in the synthesis of 2a.

In conclusion, all the data reported above allow one to make some final considerations, as follows.

The reaction of acetone, formaldehyde and bis-thiol in the presence of a stoichiometric amount of potassium hydroxide as catalyst generally gives crosslinked products, the structure of which depends on the nature of the bis-thiol employed. When the sulphur atoms of bis-thiol are separated by more than two aliphatic carbon atoms, crosslinking readily occurs. The time required to obtain gelation of the reaction mixture is related to the number of bis-thiol carbon atoms.

The even–odd effect observed in the reactions producing 2b–2e (*Figure 1*) can tentatively be attributed to a better availability of the growing γ-ketosulphide polymeric chains to crosslink when 'even' bis-thiol moieties are involved. In fact, in this case, the $CH_2-CO-CH_2$ groups display alternating opposite orientations along a linear chain section in the most stable conformation. As a consequence, the linking through $CH_2S(CH_2)_nSCH_2$ bridges of other analogous polymeric segments approaching from both sides of the reference chain is made possible, as illustrated below. By contrast, when the bis-thiol moiety is 'odd', only chain sections approaching from one side of the reference chain can be linked and conformational changes are therefore required in order to have extensive crosslinking.
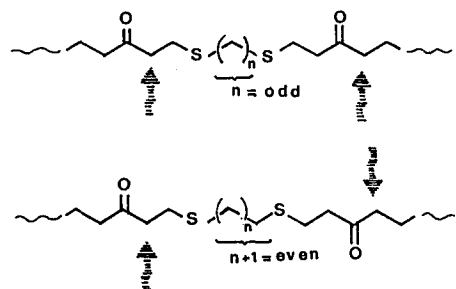
When ethanedithiol (1a) is used, crosslinking does not take place at all. This occurrence confirms that the shortness of 1a gives rise to excessively high steric repulsions between the macromolecular sections so as to prevent any crosslinking reaction. It cannot be excluded, however, that the nucleophilicity of ethanedithiol can play an important role in such a reaction. Indeed, the presence of an electron-attracting atom in the β position with respect to the sulphur atom reduces the nucleophilic character of 1a, thus depressing its reactivity in the adopted conditions. This is confirmed by the reaction with oxydiethanedithiol (1f), which has similar nucleophilicity but a higher chain length than 1a. In fact, in this case also, the reaction is remarkably slow (*Figure 1*) and only a minor amount of crosslinked product is obtained. Accordingly, dimercaptobenzene 1g, which has the lowest nucleophilic character, does not react at all with acetone, giving with formaldehyde only methylol derivatives.

Figure 3 D.s.c. (heating rate, 20°C min^{-1}) of products 2a, 2c and 2e. The broken curve refers to pristine 2a recrystallized after melting at 185°C; the dotted curve refers to second heating cycle of sample 2e after slow cooling. Products 2b, 2d and 2f show curves similar to 2e

EXPERIMENTAL

FT i.r. spectra were recorded on a Perkin–Elmer 1750

spectrophotometer and ^{1}H n.m.r. spectra (in CDCl$_3$) on a Varian EM 360L spectrometer; chemical shifts are given as δ (ppm), using tetramethylsilane (TMS) as internal reference. Elemental analyses were obtained on a Carlo Erba CHN/S elemental analyser model 1106.

Calorimetric measurements were carried out on samples kept under a nitrogen atmosphere using a Perkin-Elmer differential scanning calorimeter model DSC-2C.

Acetone (Carlo Erba) and bis-thiols **1a**, **1f** (Merck), **1b**, **1c**, **1d** and **1e** (Aldrich) were purified by distillation (under vacuum for bis-thiols) just before use.

General reaction procedure

To a mixture of acetone (1 g, 17.2 mmol), the appropriate bis-thiol (17.2 mmol) and paraformaldehyde (1.04 g, 34.4 mmol), kept under a nitrogen atmosphere with stirring in a thermostated bath at 40°C, were added 17.2 mmol of KOH in absolute ethanol (9.7 ml of 1.78 M solution). The reaction was allowed to proceed up to gelation of the mixture, then transferred into an excess of water and thoroughly washed with dilute hydrochloric acid and finally with water. The gummy material obtained was dried under vacuum at 70°C. Reaction yields, gelation times, elemental analyses and solubility assays of the precipitated products are reported in *Tables 1* and *2*. *FT* i.r. spectra were recorded as KBr discs ($\sim 1\%$) and are reported in *Figure 2*.

The reaction with **1c** was also carried out with 86 mmol of acetone under the above conditions and afforded product **2c** (42% yield), the *FT* i.r. spectrum of which is partially reported in *Figure 2*.

The reaction with **1a** gave a product soluble on heating in several solvents (*Table 1*), the ^{1}H n.m.r. spectrum of which showed peaks from 2.6 to 3.3 ppm attributable to S–CH$_2$CH$_2$–S, CO–C–CH$_2$–S, CH$_2$–CO and CH–CO groups.

The reaction with **1g** (2.45 g, 17.2 mmol) did not give any precipitation of product after 15 h. Pouring of the solution into excess of water afforded a liquid material, which was extracted with dichloromethane and reprecipitated with petroleum ether (0.76 g). The *FT* i.r. spectrum of such product showed no carbonyl absorption at 1705 cm^{-1} and bands at 3400–3300 and 1020 cm^{-1} (C–OH), 2560 cm^{-1} (–SH), 1580 and 780 cm^{-1} (1,3-disubstituted aryl). The ^{1}H n.m.r. spectrum exhibited peaks at 3.5 ppm (m, OH and SH), 4.9 ppm (s, S–CH$_2$–O), 7.3 ppm (m, aryl H-4, H-5, H-6) and 7.6 ppm (m, aryl H-2). Analysis of peak areas was in agreement with the presence of a mixture of 1,3-C$_6$H$_4$(SH)(SCH$_2$OH) and 1,3-C$_6$H$_4$(SCH$_2$OH)$_2$ in the ratio 60/40. By evaporation to dryness of the petroleum ether solution, 1.54 g of material mainly constituted by 1,3-C$_6$H$_4$(SH)$_2$ (by n.m.r.) were recovered.

ACKNOWLEDGEMENTS

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