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Reaction of Sulfonium Salts of Formaldehyde Dithioacetals with Aromatic Aldehydes and Rearrangements of the Produced Thioalkyl Oxiranes

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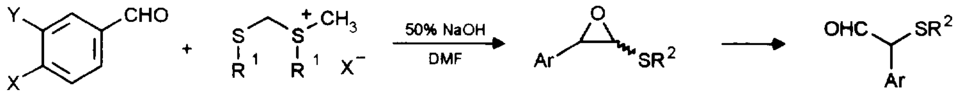
Abstract Aromatic aldehydes react with sulfur ylides generated from sulfonium salts of formaldehyde dithioacetals to give corresponding 2-thioalkyl-3-aryloxiranes. Depending on substituents in aromatic rings the oxiranes undergo rearrangements or are sufficiently stable to be isolated.

The reaction of sulfonium ylides with aldehydes or ketones to produce oxiranes is a common method in the repertoire of organic synthesis.[1] In spite of many papers in which such a process has been reported, to our knowledge nothing is known on reactions in which sulfonium ylides containing thioalkyl substituents are participating.

In our preliminary communication[2] we reported that the reaction of sulfonium ylides generated from sulfonium salts of formaldehyde dithioacetals with some aromatic aldehydes, carried out in two-phase system (DMF - concentrated aqueous NaOH) conditions which mimic phase transfer catalysis PTC, gave (alkylthio)arylacetaldehydes as the only products. The substituted oxiranes which were the initial products of this reaction were unstable and underwent rapid isomerization so they were not isolated nor observed in the mixture after the reaction was completed.

Extension of this reaction to other aromatic aldehydes gave rather surprising results as, depending on the substituents in the aromatic rings, some of the oxiranes were fairly stable. However there was a discontinuity of the electronic effects of substituents in aromatic rings on stability of the oxiranes (Scheme 1).



1 a-h

2 R^1= $-(CH_2)_3-$
3 R^1= $-CH_3$

4 a-h R^2=$(CH_2)_3SCH_3$
5 a-h R^2=CH_3

6 a, f-h R^2=$(CH_2)_3SCH_3$
7 a, f-h R^2=CH_3

	1a	1b	1c	1d	1e	1f	1g	1h
X	$-NO_2$	-CN	-Cl	-H	$-CH_3$	$-OCH_3$	$-OCH_3$	$-N(CH_3)_2$
Y	-H	-H	-H	-H	-H	-H	$-OCH_3$	-H

Scheme 1

Results of these experiments are shown in Table1.

Table 1

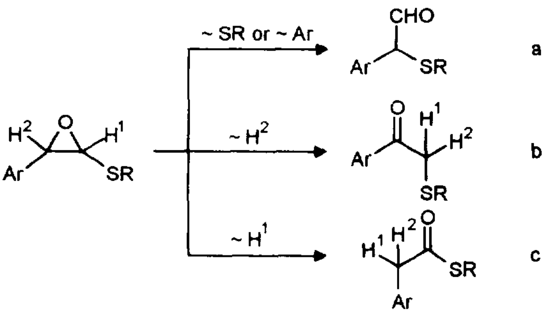
Aldehyde	Sulfonium salt	Oxirane, yield % procedure: A C	(alkylthio)arylacetaldehydes, Yield % procedure A	Aldehyde	Sulfonium salt	Oxirane, yield % procedure: A C	(alkylthio)arylacetaldehydes, Yield % procedure A
1a	**2**	- -	**6a** 69	**1e**	**2**	**4e** 90[a] 65	-
1a	**3**	- -	7a 81	**1e**	**3**	**5e** - 85	-
1b	**3**	**5b** 64 -	-	**1f**	**2**	- -	**6f** 67
1c	**2**	**4c** 90[a] 50	-	**1f**	**3**	- -	**7f** 70
1c	**3**	**5c** - 82	-	**1g**	**2**	- -	**6g** 70
1d	**2**	**4d** 90[a] 64	-	**1h**	**2**	- -	**6h** 84
1d	**3**	**5d** - 84	-	**1h**	**3**	- -	**7h** 57

[a] Yields estimated on basis of NMR spectra

As we have already reported in our preliminary communication the aldehydes **6a, f-h** and 7**a, f-h** exist as mixtures of aldehyde and enol tautomers. In the NMR spectrum of such a mixture, features characteristic for both of the forms are present and can be identified. At room temperature the equilibration is slow on the NMR time scale hence the obtained spectra are superpositions of both forms.

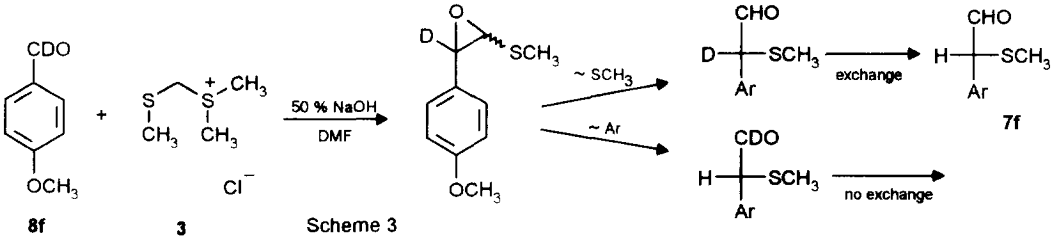
The oxiranes **4 c-e** and **5 b-e** having moderately electron withdrawing or donating substituents in the aromatic ring were sufficiently stable to be isolated from the reaction mixture and even purified *via* distillation under reduced pressure at temperatures not exceeding 130°C. These oxiranes were formed as mixtures of *cis-trans* isomers in ratios usually between 1:1 - 1:3. These mixtures were not separated, but gave correct elemental analyses and NMR spectra allowing estimation of the isomer ratios. Such high stability of **4c-e** and **5b-e** was very surprising because other similar oxiranes were very labile, it is also known that oxiranes can undergo thermal rearrangement.[3]

Looking for a rationalisation of this different behaviour of the oxiranes induced by the change of substituents in the aromatic ring, we have analysed possible mechanisms of the oxirane rearrangement. The studies of the mechanisms have been reported by a few authors.[4] In general there are three major rearrangement modes: migration of aryl or thioalkyl substituents (a), migration of benzylic hydrogen (b) or migration of hydrogen in the position α to SR substituents (c) (Scheme 2).



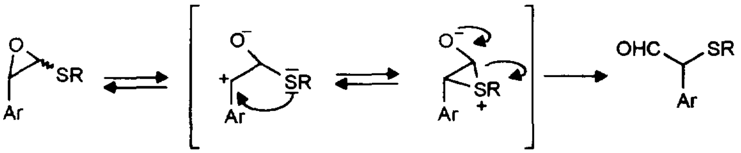
Scheme 2

First we have attempted to identify which substituent, Ar or SR, migrates in the rearrangement according to path (a) which was the major rearrangement pathway in our case. For this purpose **α-deuterio-4-methoxybenzaldehyde 8f** was synthesised and subjected to reaction with **3**. Since the product **7f**, does not contain deuterium in carbonyl group and, taking into account that under the reaction conditions the benzylic proton in **7f** is readily exchangeable, one can conclude that the SCH_3 group was the migrating substituent (Scheme 3). In model reaction of α-deuterio-4-methoxybenzaldehyde with trimethylsulfonium iodide 1-(4-methoxyphenyl)-1-deuteriooxirane was produced. It does not exchange deuterium under conditions of procedure A as it was confirmed by NMR spectroscopy.



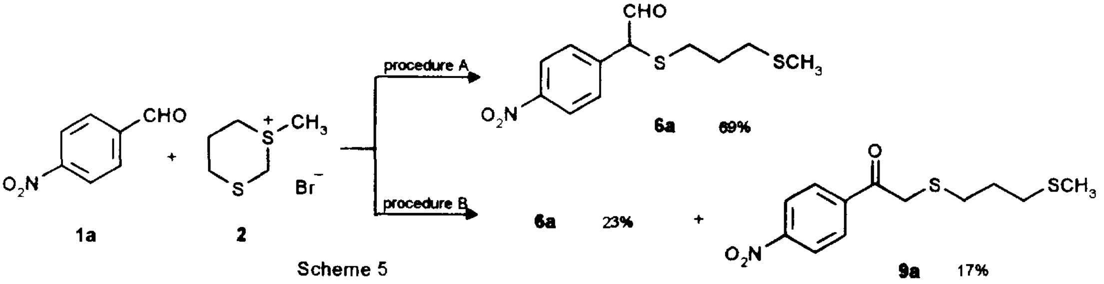
Scheme 3

Facile rearrangement of the oxiranes containing strong electron donating substituents in the aromatic rings proceeding with migration of the SR substituent, suggesting an S_N1 type of mechanism as shown on Scheme 4.



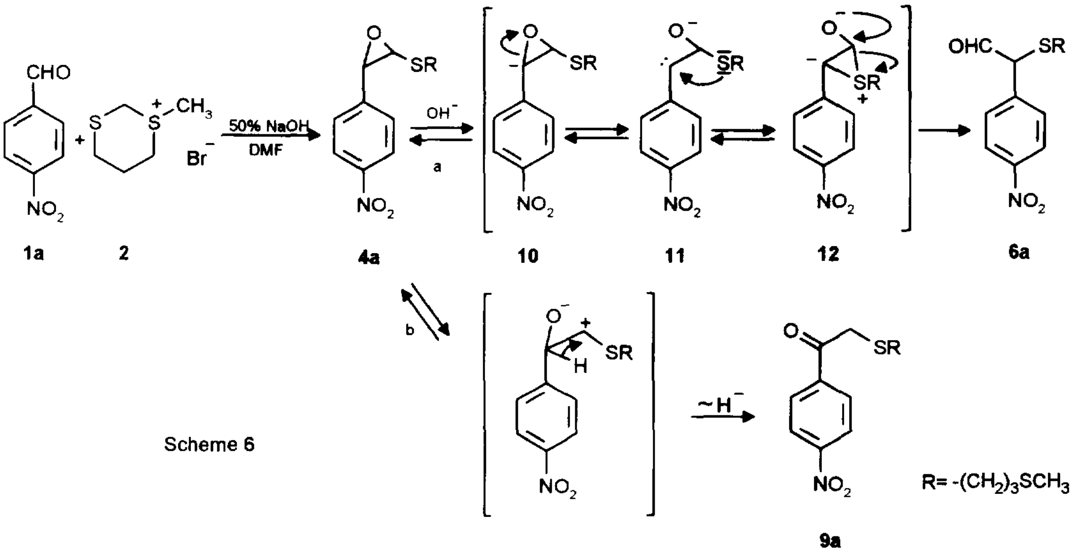
Scheme 4

The mechanistic scheme involving the S_N1 type process appears infeasible when Ar = *p*-nitrophenyl because it does not provide efficient stabilisation of carbocations. We have found that the rearrangement mode of **4a** is sensitive to the amount of base. In the presence of ca.100 fold excess of base - concentrated aqueous NaOH, (procedure A) the aldehyde **6a** was the sole product, whereas when NaOH was used in a slight excess (procedure B) two isomeric products **6a** and **9a** were formed (Scheme 5). The influence of a base on the rearrangement mode can be rationalised



Scheme 5

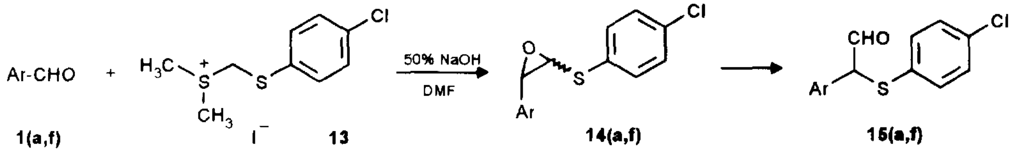
assuming that **6a** is formed *via* the following reaction sequence involving abstraction of the benzylic proton from the oxirane **4a**, C-O bond breaking in the resulting nitrobenzylic carbanion **10** gives a carbene type intermediate **11** which forms ylide **12** and finally the enolate of the aldehyde **6a** (pathway a on Scheme 6). When there is no base to promote this type of transformation the rearrangement occurs along an alternative pathway with migration of the benzylic hydrogen atom (path b, on Schemes 2 and 6). This reaction is apparently promoted by high stabilisation of the nitrobenzylic alkoxide anion.



Scheme 6

We were somewhat surprised that change of the procedure from A to B also affected the results of the reactions of aldehyde **1f** with **2**. When the reaction was carried out according to procedure B the main product **6f** contained some amounts of unnrearranged oxirane **4f** detected by NMR spectroscopy. Since in the case of **4f** the rearrangement proceeds apparently *via* S_N1 type of mechanism it was not reasonable to suppose that it is accelerated by deprotonation imposed by excess of base present in procedure A. Perhaps aqueous work-up of the reaction mixture produces electrolyte solution promoting the S_N1 type reactions. Indeed, when the reaction was carried out according to procedure B but the work-up was done in such a way that the solutions corresponded to those formed in procedure A were produced, we observed complete isomerization of the oxirane **4f** to aldehyde **6f**.

The mechanistic pathways of the rearrangement of oxiranes can be also tested by variation of nucelophilicity of the sulfur atom in SR. The rearrangement proceeding *via* classical S_N1 type mechanism (Scheme 4) should be insensitive to such changes whereas the reaction along path a and b (Scheme 6) should be somewhat inhibited. To use this criterion we prepared the sulfonium salt **13** and subjected it to reaction with **1a** and **1f** (Scheme 7).



Scheme 7

Indeed, as we expected, the reaction of 4-methoxybenzaldehyde **1f** with **13** according to procedure A gave only the aldehyde **15f**. On the other hand in the reaction of *p*-nitrobenzaldehyde **1a** with **13** besides aldehyde **15a** some amount of the oxirane **14a** was obtained, whereas in the procedure B only the unrearranged oxirane **14a** was obtained. Thus the spontaneous rearrangement of **14a** does not occur along path a or path b (Scheme 6). The lower tendency for the rearrangement along path b (Scheme 6) when RS = 4-Cl-C_6H_4-S as compared with RS = CH_3S is perhaps due to assistance by sulfur, the C-O bond breaking in the latter case. On the other hand, nucleophilicity of the sulfur atom plays an important role in the migration of the sulfur group to the carbene. The latter is the crucial step of the rearrangement *via* pathway a (Scheme 6). In the reaction of 4-methoxybenzaldehyde **1f** with **13** according to procedure B, the mixture of oxirane **14f** and aldehyde **15f** was produced. Its composition was estimated by NMR spectroscopy. Effects of changes of conditions and starting materials on the rearrangement are shown in Table 2.

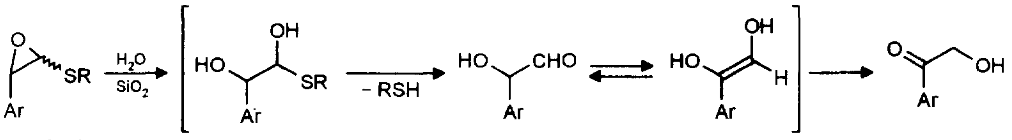
Table 2

Aldehyde	Sulfonium salt	Procedure	Products / Yield %			
1a	**2**	A	**4a**	0	**6a**	69
1a	**13**	A	**14a**	17	**15a**	51
1a	**2**	B	**6a** and **9a**^{a}			
1a	**13**	B	**14a**	63	**15a**	0
1f	**2**	A	**4f**	0	**6f**	67
1f	**13**	A	**14f**	0	**15f**	50
1f	**2**	B	**4f**	24^b	**6f**	43^b
1f	**13**	B	**14f**	34^b	**15f**	20^b

[a] see Scheme 5

[b] Yields estimated on basis of NMR spectra

Finally the most important question should be addressed: why the oxiranes **4c,d,e** and **5b,c,d,e** are much more stable than the analogues containing strong electron donating (-OCH_3, -$N(CH_3)_2$) or electron accepting (-NO_2) substituents. As it was already mentioned, independently of the procedure (A or B) these oxiranes did not rearrange during the isolation and could be purified by distillation under reduced pressure. However attempts at purification by column chromatography on silica gel resulted in rapid transformation of the oxiranes into corresponding substituted hydroxyacetophenones, apparently along the pathway including hydrolytic ring opening (Scheme 8). These epoxides did not rearrange to 2-thioalkyl-3-arylacetaldehydes upon contact with silica gel.[5]



Scheme 8

Yields of the formed 2-hydroxyacetophenones are shown in Table 3.

Table 3

Aldehyde	Sulfonium salt	Procedure	Intermediate oxirane	2-Hydroxyacetophenone Yield %	
1c	**3**	C	**5c**	**16c**	42
1d	**2**	C	**4d**	**16d**	42
1e	**3**	C	**5e**	**16e**	56
1e	**2**	C	**4e**	**16e**	43

Although epoxides **4c-e** and **5 b-e** are sensitive to hydrolytic ring opening on silica, they are very stable under neutral and basic conditions. They do not rearrange along the path shown in Scheme 4 because the aryl groups without CH_3O- or $(CH_3)_2N$- substituents provide less efficient stabilisation of the benzylic carbocations, they do not rearrange along path a, Scheme 6 because of low acidity of the benzylic protons, path b, Scheme 6 is also not available because the corresponding benzylic alkoxide anions are much less stabilised then nitrobenzylic alkoxide anion.

EXPERIMENTAL

Melting points are uncorrected. ^1H NMR spectra were taken on Varian Gemini 200 (200 MHz) spectrometer in $CDCl_3$. Chemical shifts are given in δ ppm referred to TMS. Silica gel (230-400 mesh, Merck) was used for column chromatography, or prepared according to the described procedures: Sulfonium salts **2** and **3** were prepared according to the known procedures[2]. Other starting materials were commercial. DCl/D_2SO_4 solution in D_2O was obtained by careful addition of freshly distilled SO_2Cl_2 (6 ml) to D_2O (24 ml).

Procedure A: To a vigorously stirred solution of an aldehyde (1 mmol) and sulfonium salt (1.1 mmol) in 6 ml DMF, under argon, 50% aqueous solution of NaOH (3 ml) was added. After 3-5 minutes the reaction mixture was poured into water (150 ml) and extracted with ethyl acetate (3x50 ml). In the case of *p*-nitrobenzaldehyde **1a**, the diluted reaction mixture was neutralised before extraction. The combined extracts were washed with water and dried. The solvent was evaporated to give the crude oxirane or its rearrangement product. Oxirane **5b** was purified by vacuum distillation (0.01 Torr.). Yields of oxiranes **4c,d,e** were estimated on basis of NMR spectra. Alkylthioarylacetaldehydes and arylthioarylacetaldehydes were purified by chromatography on silica gel using ethyl acetate-hexane as eluent.

Procedure B: To a vigorously stirred solution of an aldehyde (1 mmol) and sulfonium salt (1.1 mmol) in DMF (6 ml), under argon, 50% aqueous solution of NaOH (120 mg, ca.1.5 mmol) was added. After 3-5 minutes the reaction mixture was poured into water (150 ml). Further work-up was analogous to the procedure A.

Procedure C: To a vigorously stirred solution of an aldehyde (1 mmol) and sulfonium salt (1.1 mmol) in DMF (6 ml), under argon, 50% aqueous solution of NaOH (120 mg, ca. 1.5 mmol) was added. After 3-5 minutes the reaction mixture was poured into toluene (100 ml). A small piece of dry ice was added to the solution to convert traces of NaOH into carbonates. After warming up to room temperature, solution was filtered and solvents were evaporated under reduced pressure, to give almost pure oxiranes **4c,d,e** and **5c,d,e** which were purified by vacuum distillation (0.01 Torr.).

2-Hydroxyacetophenones: Crude epoxides from procedure C dissolved in a mixture of hexane (75 ml) and ethyl acetate (25 ml) were stirred with silica gel (10 g) for 12 h. The silica gel was filtered and washed with ethyl acetate, solvent was evaporated and crude 2-hydroxyacetophenones were purified by chromatography using ethyl acetate-hexane as eluent. Analytical samples were sublimed in vacuum.

***α-Deuterio-4-methoxybenzaldehyde* (8f):** Reissert compound was prepared from quinoline and *p*-methoxybenzoyl chloride according to known procedure.[6]

Solution of DCl/D_2SO_4 in D_2O (30 ml) and Reissert compound (2.9 g, 10 mmol) in dry THF (30 ml) were refluxed for 30 min. The reaction mixture was diluted with brine and extracted with ethyl acetate. The crude product was purified on short column giving α-deuterio-4-methoxybenzaldehyde **8f** containing more then 98% D. Yield 1.00 g, 73%.

Iodomethyl 4-chlorophenyl sulfide: Solution of the chloromethyl 4-chlorophenyl sulfide (3.86 g, 0.02 mol) in acetone (10 ml) was added dropwise to the solution of sodium iodide (4.5 g, 0.03 mol) in acetone (100 ml) and refluxed for 30 min. After cooling to room temperature, precipitated sodium chloride was filtered off, the filtrate was evaporated giving a brown oil. This was dissolved in ethyl acetate (100 ml), washed with water (2 x 30 ml), dried and after evaporation of the solvent was distilled from bulb to bulb under reduced pressure (10 Torr). Yield, 5.47 g, 96 %.^{1}H NMR: 7.37 (bs, 4H), 4.54 (s, 2H). Anal. calcd. for C_7H_6ClIS: C, 29.55; H, 2.13%; found: C, 29.42; H, 2.09%.

(4-Chlorophenylthiomethyl)-dimethylsulfonium iodide **(13)**: Iodomethyl 4-chlorophenyl sulfide (5.47 g, 0.019 mol) was dissolved in dimethylsulfide (10 ml). After 12 hr, solid of the sulfonium salt was filtered off, washed with ether and crystallised from MeOH-diethyl ether. Yield of **10**: 3.58 g, 53 %. ^{1}H NMR: 7.67, 7.53 (AA'BB', 4H), 5.06, (s, 2H), 2.91 (s, 6H). Anal. Calcd. for: $C_9H_{12}ClIS_2$: C, 31.18; H, 3.49; found: C, 31.06; H, 3.50%.

2-(1,5-Dithiahexyl)-3-(4-chlorophenyl)oxirane **(4c)**, mixture of isomers (*cis-trans* ratio 1:2), oil; ^{1}H NMR: 7.32, 7.21 (AA'BB', aromatic protons, *trans-* isomer), 7.32 (s, aromatic protons, *cis-* isomer), 4.46 (d, *J*=4.3 Hz, *cis-* isomer), 4.19 (d, *J*=4.3 Hz, *cis-* isomer), 4.11 (d, *J*=2.0 Hz, *trans-* isomer), 3.86 (d, *J*= 2.0 Hz, *trans-* isomer), 2.95-2.80, 2.72-2.57 (m, aliphatic protons, both isomers), 2.12 (s, -SC$\underline{H}_3$, *trans-* isomer), 2.10 (s, -SC$\underline{H}_3$, *cis-* isomer), 2.08-1.93 (m, aliphatic protons, both isomers). Anal. calcd. for $C_{12}H_{15}ClOS_2$: C, 52.44; H, 5.50%; found: C, 52.37, H, 5.70%.

2-(1,5-Dithiahexyl)-3-phenyloxirane **(4d)**, mixture of isomers (*cis-trans* ratio 1:2.6), oil; ^{1}H NMR: 7.42-7.23 (m, aromatic protons, both isomers), 4.41 (d, *J*=4.3 Hz, *cis-* isomer), 4.23 (d, *J* 4.3 Hz, *cis-* isomer), 4.16 (d, *J*=2.0 Hz, *trans-* isomer), 3.89 (d, *J*=2.0 Hz, *trans-* isomer), 2.94-2.80, 2.72-2.52 (m, aliphatic protons, both isomers), 2.12 (s, -SC$\underline{H}_3$ *trans-* isomer), 2.10 (s, -SC$\underline{H}_3$, *cis-* isomer), 2.08-1.94 (m, aliphatic protons, both isomers). Anal. calcd. for $C_{12}H_{16}OS_2$: C, 59.95; H, 6.71%; found; C, 59.77; H, 6.95%.

2-(1,5-Dithiahexyl)-3-(4-methylphenyl)oxirane **(4e)**, mixture of isomers (*cis-trans* ratio 1:2), oil; ^{1}H NMR: 7.31-7.12 (m, aromatic protons, both isomers), 4.45 (d, *J*= 4.3 Hz, *cis-* isomer), 4.20 (d, *J*=4.3 Hz, *cis-* isomer), 4.15 (d, *J*=2.0 Hz, *trans-* isomer), 3.85 (d, *J*=2.0 Hz, *trans-* isomer), 2.94-2.78 (m, aliphatic protons, both isomers), 2.34 (s, -C$\underline{H}_3$, both isomers), 2.12 (s, -SC$\underline{H}_3$, *trans-* isomer), 2.10 (s, -SC$\underline{H}_3$, *cis-* isomer), 2.08-1.94 (m, aliphatic protons, both isomers). Anal. calcd. for $C_{13}H_{18}OS_2$: C, 61.37: H, 7.13%; found: C, 61.39; H, 7.21%.

2-Methylthio-3-(4-cyanophenyl)oxirane **(5b)**, mixture of isomers (*cis-trans* ratio 1:3), oil; ^{1}H NMR: 7.75-7.20 (m, aromatic protons, both isomers), 4.48 (d, *J*=4.3 Hz, *cis-* isomer), 4.27 (d, *J*=4.3 Hz, *cis-* isomer), 4.08 (d, *J*=1.9 Hz, *trans-* isomer), 3.95 (d, *J*= 1.9 Hz, *trans-* isomer), 2.32 (s, -SC$\underline{H}_3$, *trans-* isomer), 2.31 (s, -SC$\underline{H}_3$, *cis-* isomer). Anal. calcd. for $C_{10}H_9NOS$: C, 62.80; H, 4.74; N, 7.32%; found: C, 62.62; H, 4.89; N, 7.18%.

2-Methylthio-3-(4-chlorophenyl)oxirane **(5c)**, mixture of isomers (*cis-trans* ratio 1:1.5), oil; ^{1}H NMR: 7.33, 7.23 (AA'BB', *trans-* isomer), 7.32 (s, *cis-* isomer), 4.42 (d, *J*=4.3 Hz, *cis-* isomer), 4.20 (d, *J*=4.3 Hz, *cis-* isomer), 4.08 (d, *J*=2.0 Hz, *trans-* isomer), 3.88 (d, *J*=2 Hz, *trans-* isomer), 2.31 (s, -SC$\underline{H}_3$ *trans-* isomer), 2.30 (s, -SC$\underline{H}_3$, *cis-* isomer). Anal. calcd. for C_9H_9ClOS: C, 53.86; H, 4.52%; found: C, 53.71; H, 4.68%.

2-Methylthio-3-phenyloxirane **(5d)**, mixture of isomers (*cis-trans* ratio 1:1.3), oil; ^{1}H NMR: 7.45-7.20 (m, aromatic protons, both isomers), 4.43 (d, *J*=4.3 Hz, *cis-* isomer), 4.24 (d, *J*= 4.3 Hz, *cis-* isomer), 4.12 (d, *J*=2.0 Hz, *trans-* isomer), 3.90 (d, *J*=2.0 Hz, *trans-* isomer), 2.31 (s, -SC$\underline{H}_3$, *trans-* isomer), 2.30 (s, -SC$\underline{H}_3$, *cis-* isomer). Anal. calcd. for $C_9H_{10}OS$: C, 65.02; H, 6.06%; found: C, 64.76; H, 5.96%.

2-Methylthio-3-(4-methylphenyl)oxirane **(5e)**, mixture of isomers (*cis-trans* ratio 1:1.2), oil; ^{1}H NMR 7.31-7.12 (m, aromatic protons, both isomers), 4.41 (d, *J*=4.3 Hz, *cis-* isomer), 4.21 (d, *J*=4.3 Hz, *cis-* isomer), 4.12 (d, *J*=2.0 Hz, *trans-* isomer), 3.87 (d, *J*=2.0 Hz, *trans-* isomer), 2.35 (s, -C$\underline{H}_3$ both isomers), 2.30 (s, -SC$\underline{H}_3$, *trans-* isomer), 2.29 (s, -SC$\underline{H}_3$, *cis-* isomer). Anal. calcd. for $C_{10}H_{12}OS_2$: C, 66.62; H, 6.71%; found: C, 66.49; H, 6.76%.

(1,5-Dithiahexyl)-(4-nitrophenyl)acetaldehyde **(6a)**, oil. ^{1}H NMR of carbonyl and enolic forms mixture: 9.46 (d, *J*= 4.2 Hz, -C$\underline{H}$O), 8.25, 7.55 (AA'XX', aromatic protons of carbonyl form), 8.19, 7.67 (AA'XX', aromatic protons of enolic form), 7.37 (d, *J*= 14.4 Hz, enolic form), 6.88 (d, *J*= 14.4 Hz, enolic form), 4.44 (d, *J*= 4.2 Hz, -C$\underline{H}$-CHO), 2.8-2.5 (m, aliphatic protons), 2.09 (s, -SC$\underline{H}_3$, both forms), 2.0-1.7 (m, aliphatic protons). Anal . calcd. for $C_{14}H_{20}NO_3S_2$: C, 50.50; H, 5.30; N, 4.91%; found: C, 50.28; H, 5.25; N, 4.91%.

(1,5-Dithiahexyl)-(4-methoxyphenyl)acetaldehyde **(6f)**, oil. ^{1}H NMR of carbonyl and enolic forms mixture: 9.36 (d, *J*= 5.0 Hz, -C$\underline{H}$O), 8.04, 6.97 (AA'XX', aromatic protons of enolic form), 7.25, 6.92 (AA'XX', aromatic protons of carbonyl form), 6.10 (d, *J*= 8.5 Hz, enolic form), 4.44 (d, *J*= 8.5 Hz, enolic form), 4.27 (d, *J*= 5.0 Hz, -C$\underline{H}$-CHO), 3.90 (s, -OC$\underline{H}_3$, enolic form), 3.81 (s, -OC$\underline{H}_3$, carbonyl form), 2.70-2.57 (m, aliphatic protons), 2.09 (s, -SC$\underline{H}_3$, carbonyl form),), 2.06 (s, -SC$\underline{H}_3$, enolic form), 2.1-1.8 (m, aliphatic protons). Anal. calcd. for $C_{13}H_{18}O_2S_2$: C, 57.74; H, 6.71%; found: C, 57.67; H, 6.66%.

(1,5-Dithiahexyl)-(3,4-dimethoxyphenyl)acetaldehyde **(6g)**, oil. ^{1}H NMR of carbonyl and enolic forms mixture: 9.37 (d, *J*= 5.0 Hz, -C$\underline{H}$O), 7.72 (dd, *J*= 8.5 Hz, *J*= 2.0 Hz, aromatic proton of enolic form), 7.60 (d, *J*= 2.0 Hz, aromatic proton of enolic form), 6.92 (d, *J*= 8.5 Hz, aromatic proton of enolic form), 6.9-6.8 (m, aromatic protons of carbonyl form), 6.25 (d, *J*= 8.9 Hz, enolic form), 4.41 (d, *J*= 8.9 Hz, enolic form), 4.27 (d, *J*= 5.0 Hz, -C$\underline{H}$-CHO), 3.90 (s, -OC$\underline{H}_3$, both forms), 3.88 (s, -OC$\underline{H}_3$, both forms), 2.7-2.5 (m, aliphatic protons), 2.09 (s, -SC$\underline{H}_3$, both forms), 2.0-1.8 (m, aliphatic protons). Anal . calcd. for $C_{14}H_{20}O_3S_2$: C, 55.96; H, 6.71%; found: C, 55.70; H, 6.92%.

(1,5-Dithiahexyl)-(N,N-dimethylaminophenyl)acetaldehyde **(6h)**, oil. ^{1}H NMR: 9.35 (d, J= 5.1 Hz, 1H, -CHO), 7.21, 6.41 (AA'XX', 4H, aromatic protons), 4.23 (d, J= 5.1 Hz, 1H, -CH-CHO), 2.96 (s, 6H, -N(CH$_3$)$_2$), 2.7-2.5 (m, 4H), 2.08 (s, 3H, -SCH$_3$), 2.0-1.8 (m, 2H). Anal . calcd. for $C_{14}H_{21}NOS_2$: C, 59.32; H, 7.47; N, 4.94%; found: C, 59.23; H, 7.50; N, 5.02%.

Methylthio-(4-nitrophenyl)acetaldehyde **(7a)**, oil. ^{1}H NMR of carbonyl and enolic forms mixture: 9.45 (d, J= 4.1 Hz, -CHO), 8.25, 7.57 (AA'XX', aromatic protons of carbonyl form), 8.19, 7.67 (AA'XX', aromatic protons of enolic form), 7.33 (d, J= 14.4 Hz, enolic form), 6.88 (d, J= 14.4 Hz, enolic form), 4.34 (d, J= 4.1 Hz, -CH-CHO), 2.11 (s, -SCH$_3$, carbonyl form), 2.09 (s, -SCH$_3$, enolic form). Anal. calcd. for $C_9H_9NO_3S$: C, 51.17; H, 4.29; N, 6.63%; found: C, 51.07; H, 4.22; N, 6.47%.

Methylthio-(4-methoxyophenyl)acetaldehyde **(7f)**, oil. ^{1}H NMR: 9.35 (d, J= 4.9 Hz, 1H, -CHO), 7.26, 6.92 (AA'XX', 4H, aromatic protons), 4.16 (d, J= 4.9 Hz, 1H, -CH-CHO), 3.81 (s, 3H, -OCH$_3$), 2.08 (s, 3H, -SCH$_3$). Anal . calcd. for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17%; found: C, 61.06; H, 6.25%.

Methylthio-(N,N-dimethylaminophenyl) acetaldehyde **(7h)**, oil. ^{1}H NMR: 9.34 (d, J= 4.1 Hz, 1H, -CHO), 7.18, 6.72 (AA'XX', 4H, aromatic protons), 4.12 (d, J= 4.1 Hz, 1H, -CH-CHO), 2.96 (s, 6H, -N(CH$_3$)$_2$), 2.07 (s, 3H, -SCH$_3$). Anal . calcd. for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.96%; found: C, 62.89; H, 7.03; N, 6.56%.

2-(1,5-Dithiahexyl)-4'-nitroacetophenone **(9a)**, oil. ^{1}H NMR: 8.32, 8.15 (AA'BB', 4H, aromatic protons), 3.80 (s, 2H, -CO-CH$_2$-S-), 2.72-2.50 (m, 4H, aliphatic protons)., 2.09 (s, 3H, -SCH$_3$), 1.98-1.80 (m, 2H, aliphatic protons). Anal. calcd. for $C_{14}H_{20}NO_3S_2$: C, 50.50; H, 5.30; N, 4.91%; Found: C, 50.51; H, 5.33; N, 4.76%.

cis-2-(4-Chlorophenylthio)-3-(4-nitrophenyl)oxirane **(*cis*-14a)**, Mp. 109-112° (ethyl acetate-hexane). ^{1}H NMR: 8.25, 7.64 (AA'XX', 4H, aromatic protons), 7.41, 7.33 (AA'BB', 4H, aromatic protons), 4.74 (d, J= 4.3 Hz, 1H), 4.41 (d, J= 4.3 Hz, 1H). Anal. calcd. for $C_{14}H_{10}ClNO_3S$: C, 54.64; H, 3.28; N, 4.55%; found: C, 54.77; H, 3.12; N, 4.63%.

trans-2-(4-Chlorophenylthio)-3-(4-nitrophenyl)oxirane **(*trans*-14a)**, Mp. 114-117° (EtOH). ^{1}H NMR: 8.22, 7.46 (AA'XX', 4H, aromatic protons). 7.50, 7.37 (AA'BB', 4H, aromatic protons), 4.33 (d, J= 1.9 Hz, 1H), 3.68 (d, J= 1.9 Hz, 1H). Anal. calcd. for $C_{14}H_{10}ClNO_3S$: C, 54.64; H, 3.28; N, 4.55%; found: C, 54.67; H, 3.04; N, 4.60%.

(4-Chlorophenylthio)-(4-nitrophenyl)acetaldehyde **(15a)**, oil. ^{1}H NMR of carbonyl and enolic form mixture: 9.64 (d, J =3.2 Hz, -CHO), 8.5-8.0, 7.8-6.9 (m, aromatic protons), 4.78 (d, J= 3.2 Hz, -CH-CHO). Anal. calcd. for $C_{14}H_{10}ClNO_3S$: C, 54.64; H, 3.28; N, 4.55; found: C, 54.54; H, 3.13; N, 4.36%.

(4-Chlorophenylthio)-(4-methoxyphenyl)acetaldehyde **(15f)**, oil. ^{1}H NMR: 9.51 (d, J= 4.5 Hz, 1H, -CHO), 7.33, 7.27 (AA'BB', 4H, aromatic protons),7.24, 6.92 (AA'XX', 4H, aromatic protons), 4.66 (d, J= 4.5 Hz, 1H, -CH-CHO), 3,88 (s, 3H, -CH$_3$). Anal calcd. for $C_{15}H_{13}ClO_2S$: C, 61.53; H, 4.77%; found: C, 61.31; H, 4.39%.

(4-Chlorophenylthio)-(3,4-dimethoxyphenyl)acetaldehyde **(15g)**, oil. ^{1}H NMR: 9.52 (d, J= 4.4 Hz, -CHO), 7.34, 7.28 (AA'BB', 4H, aromatic protons), 6.90-6.78 (m, 3H, aromatic protons), 4.66 (d, J= 4.4 Hz, -CH-CHO), 3.89 (s, 3H, -OCH$_3$), 3.88 (s, 3H, -OCH$_3$). Anal. calcd. for $C_{16}H_{15}ClO_3S$: C, 59.53; H, 4.68%; found: C, 59.24; H, 4.62%.

4'-Chloro-2-hydroxyacetophenone **(16c)**, Mp. 119-121°C ^{1}H NMR: 7.87, 7.49 (AA'XX', 4H), 4.86 (d, J=4.7 Hz, 2H), 3.45 (t, J=4.7 Hz, 1H). Anal. calcd. for $C_8H_7ClO_2$: C, 56.32; H, 4.14%; found: C, 56.28; H, 4.07%.

2-Hydroxyacetophenone **(13d)**, Mp. 83-85°C; ^{1}H NMR: 7.98-7.88 (m, 2H), 7.70-7.45 (m, 3H), 4.89 (d, J=4.6 Hz, 2H), 3.53 (t, J=4.6 Hz, 1H). Anal. calcd. for $C_8H_8O_2$: C, 70.58; H, 5.92%; found: C, 70.40; H, 5.97%.

4'-Methyl-2-hydroxyacetophenone **(16e)**, Mp. 86-87°C; ^{1}H NMR: 7.82, 7.31 (AA'XX', 4H), 4.85 (d, J=4.7 Hz, 2H), 3.54 (t, J=4.7 Hz, 1H), 2.44 (s, 3H). Anal calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71%; found: C, 71.85; H, 6.79%.

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