

Tetrahedron Vol. 51, No. 38, pp. 10593-10600, 1995 Elsevier Science Ltd Printed in Great Britain 0040-4020/95 \$9.50+0.00

0040-4020(95)00632-X

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

Mieczysław Mąkosza* and Michał Sypniewski

Institute of Organic Chemistry, Polish Academy of Sciences ul. Kasprzaka 44, 01-224 Warsaw, Poland

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 communication² 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).



Results of these experiments are shown in Table 1.

Aldehyde	Sulfonium salt	Oxirane, yield % procedure: A C	(alkylthio)aryl- acetaldehydes, Yield % procedure A	Aldehyde	Sulfonium salt	Oxirane, yield % procedure: A C	(alkylthio)aryl- acetaldehydes, Yield % procedure A
la	2		6a 69	le	2	4e 90 ^a 65	-
1a	3		7 a 81	le	3	5e - 8 5	-
1b	3	5b 64 -	-	1 f	2		6f 67
1c	2	4c 90 ^a 50	-	1f	3		7f 70
lc	3	5c - 8 2	-	1g	2		6g 70
1d	2	4d 90° 64	-	1h	2		6h 84
1d	3	5d - 8 4	-	1h	3		7h 57

Table 1

^aYields estimated on basis of NMR spectra

As we have already reported in our preliminary communication the aldehydes **6a**, **f-h** and **7a**, **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 SCH₃ group was the migrating substituent (Scheme 3). In model reaction of α -deuterio-4-methoxybenzaldehyde with trimethylsulfonium iodide 1-(4-methoxybenzaldehyde-1)-deuteriooxirane was produced. It does not exchange deuterium under conditions of procedure A as it was confirmed by NMR spectroscopy.



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.



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



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.



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_N 1 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).



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-C₆H₄-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.

		l able 2					
Aldehyde	Sulfonium salt	Procedure	Proc	Products / Yield %			
1a	2	A	4 a	0	6a	69	
1a	13	А	14a 17 15a :		51		
la	la 2 B 6a an				nd 9a	id 9a ^a	
la	13	В	14a	63	15a	0	
1f	2	А	4f	0	6f	67	
lf	13	А	14f	0	1 5 f	50	
lf	2	В	4f	24 ^b	6f	43 ^b	
lf	13	В	14f	34 ^b	1 5 f	20 ^b	

^asee Scheme 5

^bYields 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



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

l adle 3						
Aldehyde Sulfonium salt Procedure Intermo oxir				nediate 2-Hydroxyacetophen rrane Yield %		
1c	3	С		16c	42	
1d	2	C	4d	16d	42	
le	3	C	5e	16e	56	
le	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 ₃ O- or (CH ₃) ₂ N- 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 CDCl₃. 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 procedures². Other starting materials were commercial. DCl/D₂SO₄ solution in D₂O was obtained by careful addition of freshly distilled SO₂Cl₂ (6 ml) to D₂O (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 (81): Reissert compound was prepared from quinoline and p-methoxybenzoyl chloride according to known procedure.⁶

Solution of DCl/D₂SO₄ in D₂O (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 % ¹H NMR: 7.37 (bs, 4H), 4.54 (s, 2H). Anal. calcd. for C₃H₆CIIS: C, 29.55; H, 2.13%; found: C, 29.42; H, 2.09%.

(4-Chlorophenylthiomethyl)-dimethylsulfonium iodide (13): lodomethyl 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 %. ¹H NMR: 7.67, 7.53 (AA'BB', 4H), 5.06, (s, 2H), 2.91 (s, 6H). Anal. Calcd. for: C₉H₁₂ClIS₂: C, 31.18; H, 3.49; found: C, 31.06; H, 3.50%.

2-(1,5-Dithiahexyl)-3-(4-chlorophenyl)axirane (4c), mixture of isomers (*cis-trans* ratio 1:2), oil; ¹H 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, -SCH₃, *cis-* isomer), 2.10 (s, -SCH₃, *cis-* isomer), 2.08-1.93 (m, aliphatic protons, both isomers). Anal. calcd. for C₁₂H₁₅ClOS₂: 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; ¹H 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, -SCH₃ *trans-* isomer), 2.10 (s, -SCH₃, *cis-* isomer), 2.08-1.94 (m, aliphatic protons, both isomers). Anal. calcd. for C₁₂H₁₆OS₂: 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; ¹H 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, -CH₃, both isomers), 2.12 (s, -SCH₃, *trans-* isomer), 2.10 (s, -SCH₃, *cis-* isomer), 2.08-1.94 (m, aliphatic protons, both isomers). Anal. calcd. for C₁₃H₁₈OS₂: C, 61.37: H, 7.13%; found: C, 61.39; H, 7.21%.

2-Methylthio-3-(4-cyanophenyl)oxirane (Sb), mixture of isomers (*cis-trans* ratio 1:3), oil; ¹H 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, -SCH₃, *trans-* isomer), 2.31 (s, -SCH₃, *cis-* isomer). Anal. calcd. for C₁₀H₉NOS: 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; ¹H 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, -SCH₃ trans- isomer), 2.30 (s, -SCH₃, *cis-* isomer). Anal. calcd. for C₉H₉ClOS: 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; ¹H 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, -SCH₃, *trans-* isomer), 2.30 (s, -SCH₃, *cis-* isomer). Anal. calcd. for C₉H₁₀OS: C, 65.02; H, 6.06%; found: C, 64.76; H, 5.96%.

2-Methylthio-3-(4-methylphenyl)oxirane (Se), mixture of isomers (*cis-trans* ratio 1:1.2), oil; ¹H 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, -CH₃, both isomers), 2.30 (s, -SCH₃, *trans-* isomer), 2.29 (s, -SCH₃, *cis-* isomer). Anal. calcd. for C₁₀H₁₂OS₂: C, 66.62; H, 6.71%; found: C, 66.49; H, 6.76%.

(1,5-Dithiahexyl)-(4-nitrophenyl)acetaldehyde (6a), oil. ¹H NMR of carbonyl and enolic forms mixture: 9.46 (d, J= 4.2 Hz, -CHO), 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, -CH-CHO), 2.8-2.5 (m, aliphatic protons), 2.09 (s, -SCH₃, both forms), 2.0-1.7 (m, aliphatic protons). Anal. calcd. for C₁₄H₂₀NO₃S₂: 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. ¹H NMR of carbonyl and enolic forms mixture: 9,36 (d, J= 5.0 Hz, -C<u>H</u>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<u>H</u>-CHO), 3.90 (s, -OC<u>H₃</u>, enolic form), 3.81 (s, -OC<u>H₃</u>, carbonyl form), 2.70-2.57 (m, aliphatic protons), 2.09 (s, -SC<u>H₃</u>, carbonyl form),). 2.06 (s, -SC<u>H₃</u>, enolic form), 2.1-1.8 (m, aliphatic protons). Anal. calcd. for C₁₃H₁₈O₂S₂: C, 57.74; H, 6.71%; found: C, 57.67; H, 6.66%.

(1,5-Dithiahexyl)-(3,4-dimethoxyphenyl)acetaldehyde (6g), oil. ¹H NMR of carbonyl and enolic forms mixture: 9.37 (d, J = 5.0 Hz, -CHO), 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, -CHO), 3.90 (s, -OCH₃, both forms), 3.88 (s, -OCH₃, both forms), 2.7-2.5 (m, aliphatic protons), 2.09 (s, -SCH₃, both forms), 2.0-1.8 (m, aliphatic protons). Anal. calcd. for C₁₄H₂/O₃S₂: C, 55.96; H, 6.71%; found: C, 55.70; H, 6.92%. (1,5-Dithiahexyl)-(N,N-dimethylaminophenyl)acetaldehyde (6h), oil. ¹H NMR: 9.35 (d, J= 5.1 Hz, 1H, -CHO), 7.21, 6.41 (AA^{XXX}, 4H, aromatic protons), 4.23 (d, J= 5.1 Hz, 1H, -CHO), 2.96 (s, 6H, -N(CH₃)₂), 2.7-2.5 (m, 4H), 2.08 (s, 3H, -SCH₃), 2.0-1.8 (m, 2H). Anal. calcd. for C₁₄H₂₁NOS₂: 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. ¹H 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, -SCH₃, carbonyl form), 2.09 (s, -SCH₃, enolic form). Anal. calcd. for C₉H₉NO₃S: 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. ¹H 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, -OCH₃), 2.08 (s, 3H, -SCH₃). Anal . calcd. for C₁₀H₁₂O₂S: C, 61.19; H, 6.17%; found: C, 61.06; H, 6.25%.

Methylthio-(N,N-dimethylaminophenyl) acetaldehyde (7h). oil. ¹H 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, -SCH₃). Anal. calcd. for C₁₁H₁₅NOS: 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. ¹H NMR: 8.32, 8.15 (AA'BB', 4H, aromatic protons), 3.80 (s, 2H, -CO-C<u>H</u>₂-S-), 2.72-2.50 (m, 4H, aliphatic protons), 2.09 (s, 3H, -SC<u>H</u>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). ¹H 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 C₁₄H₁₀ClNO₃S: 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). ¹H 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 C₁₄H₁₀CINO₃S: 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. ¹H NMR of carbonyl and enolic form mixture: 9.64 (d, J = 3.2 Hz, -C<u>H</u>O), 8.5-8.0, 7.8-6.9 (m, aromatic protons), 4.78 (d, J = 3.2 Hz, -C<u>H</u>-CHO). Anal. calcd. for C₁₄H₁₀ClNO₃S: 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. ¹H 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, -CH₃). Anal calcd. for C_1 -H₃ClO₂S: C, 61.53; H, 4.77%; found: C, 61.31; H, 4.39%.

(4-Chlorophenylthio)-(3,4-dimethoxyphenyl)acetaldehyde (15g), oil. ¹H 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, -OCH₃), 3.88 (s, 3H, -OCH₃). Anal. calcd. for C₁₆H₁₅ClO₃S: C, 59.53; H, 4.68%; found: C, 59.24; H, 4.62%.

4'-Chloro-2-hydroxyacetophenone (16c), Mp. 119-121°C ¹H 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 C₈H₇ClO₂: C, 56.32; H, 4.14%; found: C, 56.28; H, 4.07%.

2-Hydroxyacetophenone (13d), Mp. 83-85°C; ¹H 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 C₈H₈O₂: C, 70.58; H, 5.92%; found: C, 70.40; H, 5.97%.

J'-Methyl-2-hydroxyacetophenone (16e), Mp. 86-87°C; ¹H 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 C₉H₁₀O₂: C, 71.98; H, 6.71%; found: C, 71.85; H, 6.79%.

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(Received in UK 12 April 1995; revised 1 August 1995; accepted 4 August 1995)

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