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Carbophilic reactions of amines or methanol with thioaldehyde-*S*-oxides

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Summary — Reaction of primary aliphatic amines with γ-ethylenic thioaldehyde-*S*-oxides **1a,b** affords the corresponding imines **2a,b** via a carbophilic addition of amine. When treated with sodium methoxide (1 equiv) and an excess of a primary amine, some methyl sulfinates **3** or **6**, bearing a benzylic or allylic chain on the sulfur, are converted into imines **4** or **7**. Treatment of the methyl sulfinates **3** with methoxide anion in THF or methanol generally affords a mixture of aldehydes **9**, the corresponding dimethylacetals **14**, α,α'-dimethoxydisulfides **10**, esters **11**, thionoesters **12** and methyl α-methoxysulfinates **15**, whose ratios depend on the conditions. The formation of these compounds is best explained by a deprotonation–elimination of the methyl sulfinates into the corresponding thioaldehyde-*S*-oxides, which then undergo a carbophilic addition of methoxide anion or methanol. Several possible reaction paths from the so-formed α-methoxysulfenate anions IX are discussed for their conversion into the final compounds.

unsaturated sulfinic ester / elimination / thioaldehyde-S-oxide / imine / aldehyde / α,α'-dimethoxydisulfide / thionoester / methyl α-methoxysulfinate

Résumé — **Réactions carbophiles des amines ou du méthanol avec les S-oxydes de thioaldéhydes.** *Les réactions des amines aliphatiques primaires avec les* S*-oxydes de thioaldéhydes γ-éthyléniques* **1a,b** *donnent les imines* **2a,b** *par une addition carbophile de l'amine. Traités par 1 équiv de méthanolate de sodium et un excès d'amine primaire, quelques sulfinates de méthyle* **3** *ou* **6** *portant une chaîne benzylique ou allylique liée au soufre, sont transformés en imines* **4** *ou* **7**. *Les sulfinates* **3**, *traités par des anions méthanolates dans le THF ou le méthanol, donnent généralement des mélanges d'aldéhydes* **9**, *acétals diméthyliques correspondants* **14**, *disulfures α,α'-diméthoxylés* **10**, *esters* **11**, *thionoesters* **12** *et α-méthoxysulfinates de méthyle* **15**, *dont les proportions dépendent des conditions. La formation de ces composés serait bien expliquée par une déprotonation–élimination des sulfinates de méthyle* **3** *ou* **6** *conduisant aux* S*-oxydes de thioaldéhydes qui subissent ensuite une addition carbophile d'anion méthanolate ou de méthanol. Les anions α-méthoxysulfénates IX ainsi formés peuvent suivre plusieurs voies réactionnelles qui sont discutées.*

ester sulfinique insaturé / élimination / S-oxyde de thioaldéhyde / imine / aldéhyde / disulfure α,α'-diméthoxylé / thionoester / α-méthoxysulfinate de méthyle

In a previous communication [1], we reported a novel preparation of indoles VI by heating the *N*-arylalk-1-ene sulfinamides I in various solvents between 85 and 135 °C. The transformation probably occurs via several intermediates. First, a hetero-Cope-like [3.3]-sigmatropic rearrangement gives iminosulfines II and then the corresponding aminosulfines III, which cyclize by a carbophilic addition to give the indolinesulfenic acids IV whose aromatization yields the corresponding indole derivatives VI. In the course of the numerous examples investigated for our study, we have never obtained the sulfinamides V from the thiophilic addition of the amine on the neighboring thioaldehyde-*S*-oxides (fig 1).

We could not prove the formation of intermediates II or III because of their great intramolecular reactivity. We have therefore examined the poorly known reactivity of amines towards some authentic samples of sulfines or samples generated in situ. We now report the results of this study, which demonstrates that primary or secondary aliphatic amines can react with thioaldehyde-*S*-oxides in a carbophilic manner. During this work, we have also observed a novel carbophilic reaction of methanol or methoxide anions with thioaldehyde-*S*-oxides.

Reaction of thioaldehyde-*S*-oxides with amines

Recent reviews [2] on the chemistry of sulfines indicated that the reactivity of simple sulfines with amines was virtually unknown; however, our literature search,

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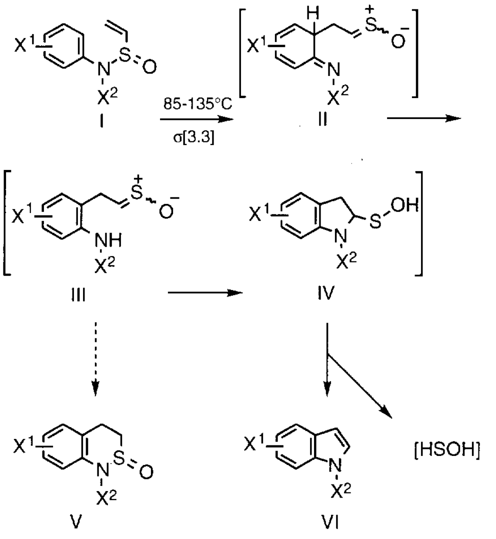


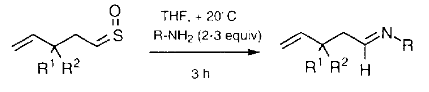
Fig 1

which was as thorough as possible, gave us the following information. Some thiophilic additions were established after reaction of lithium diisopropylamide with 9-fluorenethione- or substituted thiobenzophenone-*S*-oxides [3, 4]. Meanwhile, some carbophilic additions of amines to sulfines should be mentioned. Two publications from the 1960s [5, 6] reported the transformation of two arenecarbothioaldehyde-*S*-oxides by an acidic solution of 2,4-dinitrophenylhydrazine into 2,4-dinitrophenylhydrazones of the corresponding aldehydes. The Metzner group recorded the efficient transformation of 1,1,7-trimethylbicyclo[2.2.1]heptane-2-thione-*S*-oxide by primary aliphatic amines into the corresponding imines [7].

We started our study by using authentic samples of γ-ethylenic thioaldehyde-*S*-oxides prepared via a convergent synthesis from vinylmagnesium bromide and methyl sulfinates bearing a β,γ-ethylenic chain on the sulfur atom [8] (see fig 11 below).

A preliminary attempt was conducted according to the conditions of the transformation III → IV → VI, ie, the sulfine **1a** was refluxed with 4-methoxybenzenamine in toluene including an azeotropic distillation of the solvent for 2 h. The crude product analysis (^{1}H NMR) displayed the absence of both the starting sulfine and the corresponding imine while the 4-methoxybenzenamine (76%) was obtained after flash chromatography. Two other reactions involving primary aliphatic amines and sulfines **1a,b**, according to Metzner and coworkers' mild conditions for imination of a thioketone-*S*-oxide [7], yielded the corresponding imines **2a,b**, which were fully characterized by proton NMR spectroscopy (fig 2).

Generally, thioaldehyde-*S*-oxides must be reacted rapidly after their preparation and are not practical starting materials for an exhaustive study of their reactivity. We have therefore investigated their preparation in situ, from stable and accessible materials and in the presence of an appropriate nucleophile. Among the different routes developed for the preparation of sulfines, some eliminations recorded in figure 3 have been reported.



1a R^1 = nC$_5$H$_{11}$; R^2 = H

1b R^1, R^2 = -(CH$_2$)$_5$-

2a R^1 = nC$_5$H$_{11}$; R^2 = H ; R = CH$_2$-C$_6$H$_5$ (50%)

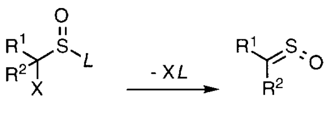
2b R^1, R^2 = -(CH$_2$)$_5$- ; R = i.C$_3$H$_7$ (64%)

Fig 2

- Using triethylamine, the elimination of hydrogen chloride from sulfinyl chlorides (VIIa) bearing an α-hydrogen atom was one of the first methods used to prepare some thioaldehyde-*S*-oxides [5, 6, 9].
- The elimination of trimethylsilanolate from α-silylsulfinate anions (VIIb) was a route to various sulfines but not thioaldehyde-*S*-oxides [2].
- The amine-induced β-elimination of chloroform from allylic or benzylic trichloromethylsulfoxides (VIIc) has recently been reported to afford smoothly the corresponding α,β-unsaturated thioaldehyde-*S*-oxides [10].
- When treated with methoxide anion in CD$_3$OD, the methyl diarylmethanesulfinates (VIId) can undergo elimination to yield the corresponding thioketone-*S*-oxides [11]. Moreover, the rates of elimination of some methyl substituted 1-naphthylmethanesulfinates (VIIe) have been determined [12].

The next substrates that came to our attention were the methyl arenemethanesulfinates **3** on account of their stability and easy access. They were conveniently prepared from the corresponding disulfides [13] and methanol using *N*-bromosuccinimide [14]. When treated with dry sodium methoxide and a slight excess of a primary aliphatic amine in the conditions summarized in figure 4, the methyl sulfinates **3a–e** afforded smoothly the imines **4a–e** isolated by filtration of the reaction mixture on a short path of basic alumina. The experiment starting with the *para*-chloro derivative **3e** also gave a small amount of the thioamide **5a** (7%).

The same imination procedure has been carried out with allylic methyl sulfinates **6a,b**, sufficiently substituted, in order to keep the α,β-conjugated intermediate sulfines untouched by the alkaline medium (fig 5). Attempts with the sulfinates **6c,d** did not give good results. Finally, we note that this imination procedure is not appropriate by using the saturated sulfinate **8**, probably due to the low acidity of the protons next to



VIIa R^1 = Alkyle or Aryle;
R^2 = X = H ; *L* = Cl

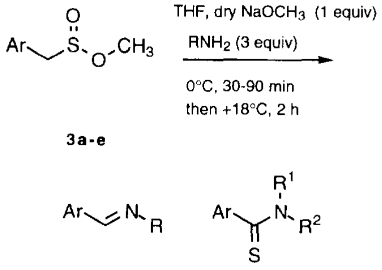
VIIb X = Si(CH$_3$)$_3$; *L* = O$^-$

VIIc R^2 = X = H ; *L* = CCl$_3$

VIId R^1 = R^2 = Aryle; X = H ; *L* = OCH$_3$

VIIe R^1 = substituted 1-naphthyl; R^2 = X = H ; *L* = OCH$_3$

Fig 3



3a-e

4

5

	Ar	R	Yield (%)
4a	1-naphthyl	$n.C_3H_7$	63
4b	$4.CH_3\text{-}C_6H_4$	$CH_2\text{-}Ph$	42
4c	$4.CH_3\text{-}C_6H_4$	$n.C_3H_7$	50
4d	$4.CH_3\text{-}C_6H_4$	$i.C_3H_7$	53
4e	$4.Cl\text{-}C_6H_4$	$n.C_3H_7$	41
5a	Ar = $4.Cl\text{-}C_6H_4$ $R^1 = n.C_3H_7$; $R^2 = H$		7%

Fig 4

the sulfinate group or the instability of the octanethial-S-oxide intermediate in basic conditions.

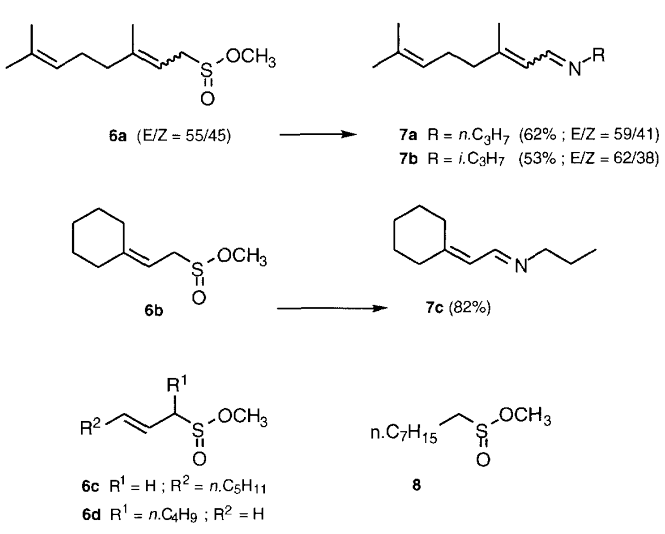
These results led us to investigate the study of the reactivity of arenecarbothioaldehyde-S-oxides prepared in situ with secondary aliphatic amines. Treatment of sulfinates **3a,c** with 1 equiv of anhydrous sodium methoxide in THF in the presence of 5 equiv of dimethylamine at 0 °C for 4.5 h followed by basic aqueous work-up yielded the predominant aldehydes **9a,c**. Starting from the sulfinate **3c**, a small amount of thioamide **5b** was also obtained. The similar reaction of sulfinates **3c,d** with sodium methoxide and morpholine (3 equiv) gave comparable results (fig 6; table I). In proton NMR spectra of crude products from entries 1 and 4 we observed very small amounts of compounds **10–12** generated by carbophilic addition of methanol on intermediate sulfines (see the following section).

Figure 7 displays some intermediates which appear to explain the formation of every compound mentioned above. Similarly to what Kice and coworkers [11, 12] pointed out for compounds VIId,e, the methyl arenemethanesulfinates **3** and the allylic methyl sulfinates **6a,b** have a labile benzylic (or allylic) proton, which may be removed easily using sodium methoxide leading in situ to methanol and the corresponding thioaldehyde-S-oxides VIIIa. In the presence of 1 equiv of methoxide anion and methanol or excess amine compound VIIIa would undergo a carbophilic addition of these nucleophiles to give the minor α-methoxysulfenic acid intermediates IX and the predominent α-aminosulfenic acid intermediates X which probably exist as their sodium salts [15].

The next section will deal with the results obtained for the reaction of sulfinates **3** with sodium methoxide yielding the compounds **9–12**, **14** and **15**, whose formation from α-methoxysulfenates IX will be discussed later.

The α-aminosulfenates X possess two apparently weak bonds: one binds the carbon to the sulfur atom and the other lies between the sulfur and the oxygen atom [16]. When R^1 = alkyl and R^2 = H, the cleavage of the first fragile bond can occur by the loss of the species NaOSH [17] to yield imines **4** and when $R^1 = R^2$ = alkyl, by the participation of the nitrogen lone pair which affords immonium salts XI. It is worth pointing out that no compound XII was formed by addition of methanol or amine. The cleavage of the S-O bond of compound X via a deprotonation in sequence with an elimination step [18] yielding the thioamides **5** seems to be unlikely on account of the hypothetical leaving group Na_2O.

Similar to the known dimerization of sulfenic acids or their salts [19], the α-aminosulfenate X could lead to the α,α'-diaminothiosulfinate intermediates XIII. The carbophilic reaction of a sulfenic acid to propanethial-S-oxide has been proposed to explain the formation of cepaenes in onion homogenates [20]. It is likely that a similar reaction involving the α-aminosulfenate X



6a (E/Z = 55/45)

6b

8

Fig 5

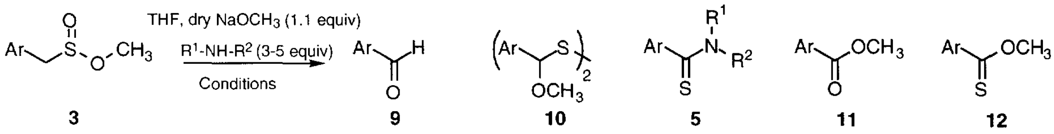


Fig 6

Table I. Reactions of compounds **3**.

Entry	*3*	*Substrate Ar*	*Conditions*	*Molar ratios of crude products*[a,b] 9	10	5	11	12
1	**3a**	1-Naphthyl	$(CH_3)_2NH$ (5 equiv); 0 °C; 4.5 h	95 (73)	5			
2	**3c**	4-ClC_6H_4	$(CH_3)_2NH$ (5 equiv); 0 °C; 4.5 h	72 (60)		**5b**: 28 (7)		
3	**3c**	4-ClC_6H_4	Morpholine (3 equiv); 0 °C; 2.5 h; +18 °C; 2 h[c]	77 (50)		**5c**: 23 (10)		
4	**3d**	2,4$(Cl)_2C_6H_3$	Morpholine (3 equiv); 0 °C; 2.5 h; +18 °C; 2 h[c]	70 (45)		**5d**: 17 (6)	9	4

[a] The ratios of compounds were determined by comparison of the integrations in the ^{1}H NMR spectra; [b] the yields (%) of compounds isolated after flash chromatography are in parentheses; [c] the reaction mixture was treated with dilute aqueous sulfuric acid and dichloromethane.

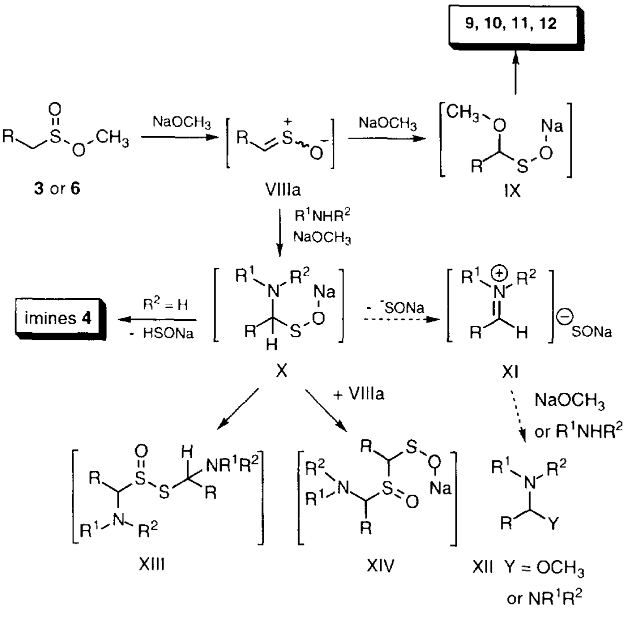


Fig 7

and thioaldehyde-*S*-oxide VIIIa could give the addition compounds XIV (fig 7).

The α,α'-diaminothiosulfinate intermediates XIII can then undergo a fragmentation [XIII′] to yield thioamides **5** and α-aminosulfenic acid either free or in the alkaline form X (fig 8). This transformation can be induced thermally, similar to some known cases [21], or can be caused by a deprotonation by methoxide anions present in the reaction mixture. The departure of sulfenate anion shown in formula XIII′ is known to occur easily for other compounds [22].

The addition compound XIV should, as shown in the formula XIV′, easily lead to the α-aminosulfenates X and the oxathiiranes XV followed by sulfur extrusion [23] yielding finally the aldehydes **9** (fig 9). It should be noted that the intermediates XIV experience a double instability factor due to the neighborhood of the sulfoxide group with the sulfur atom from the NaOS group [24] and the amino group [25].

Reactivity of thioaldehyde-*S*-oxides with methanol or methoxide anions

At the beginning of this study we reacted the sulfine **1a** with excess methanol at RT for 4 h to obtain a mixture of products whose proton NMR spectrum reveals the entire consumption of the starting sulfine and at

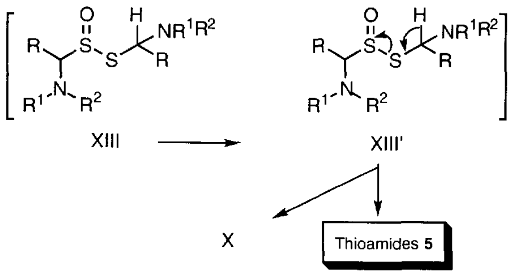


Fig 8

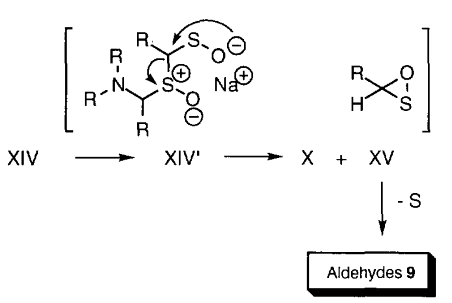


Fig 9

about 3.3 ppm the presence of ten peaks assigned to the methoxy groups. Unfortunately, attempts to separate the reaction products by flash chromatography failed. The treatment of the sulfine **1b** by methanol in the presence of 0.5 equiv of pyridinium *para*-toluenesulfonate at −18 °C for 2 days then at +5 °C for 2 days and finally at +18 °C for 12 h yielded, after column chromatography, a mixture of two isomers (30%) whose stucture can reasonably be **13** (fig 10). We have not continued with the study of the reactivity of γ-ethylenic thioaldehyde-*S*-oxides towards methanol in neutral or acidic conditions because of the numerous possibilities for evolution of δ-ethylenic-α-methoxysulfenic acids generated by a carbophilic addition of methanol to the sulfine group and yielding finally unstable products.

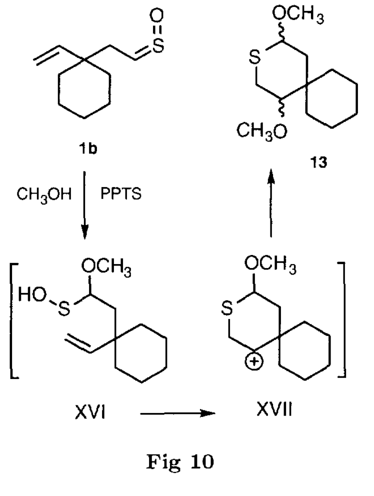


Fig 10

It is worth mentioning the experimental details of the reaction of vinylmagnesium bromide with methyl sulfinates bearing a β,γ-ethylenic chain on the sulfur atom [8] (fig 11). After 30 min of stirring at −78 °C, the reaction mixture (allyl vinylsulfoxide XVIII and methoxy magnesium bromide) was hydrolyzed at around −70 °C by addition of an aqueous solution of ammonium chloride. After ethereal dilution, the cooling bath was taken away and the reaction mixture allowed to rise to RT before regular work-up. It is reasonable to assume that the [3.3]-sigmatropic rearrangement occurred while the temperature rose from −70 °C to RT, and so the final sulfine was not in the presence of methoxy magnesium bromide; this point is essential for the success of the experiment.

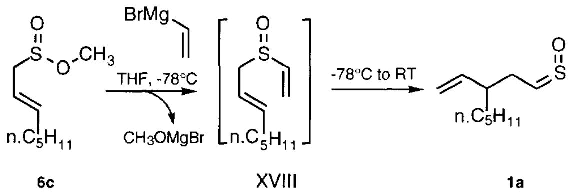


Fig 11

In a modified experimental procedure, the cooling bath was removed after 30 min of reaction at −78 °C of the sulfinate **6c** with the vinylmagnesium bromide thus allowing the temperature to rise to RT. Following the reaction by TLC, we could detect the presence of the sulfoxide XVIII near to the peak for sulfine **1a**. Finally, after 2.5 h of reaction at RT, hydrolysis and usual work-up procedure gave a very viscous residue in which proton NMR analysis indicated the absence of the sulfine **1a**, whose reaction with methoxy magnesium bromide had given a complex mixture of unidentifiable compounds.

As regards the reactivity of thioaldehyde-*S*-oxides with methoxide anions, we have recorded Kice and Lotey's [12] remark concerning the transformation illustrated in figure 12 from which yield and mechanistic details were not considered. It is noteworthy that the authors [12] indicated that the reaction did not yield the methyl (2-methoxy-1-naphthyl)methanesulfinate which could have resulted from thiophilic addition of methanol or methoxide anion on the sulfine.

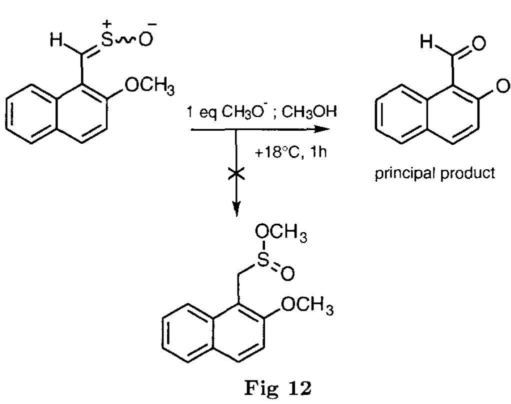


Fig 12

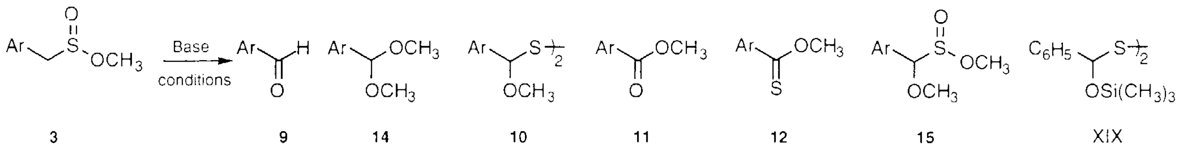


Fig 13

Table II. Reactions of compounds **3**.

Entry	**3**	*Substrate Ar*	*Conditions*			*Work-up*	*Ratios of crude products*[a,b]					
			Base	*Solvent*	*Temperature*		***9***	***14***	***10***	***11***	***12***	***15***
5	**3a**	1-Naphthyl	$LiOCH_3$ (1.1 equiv)	THF	+18 °C, 18 h	A	62 (42)	–	24	10 (3)	4	–
6	**3a**	1-Naphthyl	$NaOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 15 min then +18 °C, 3 h	B	73	–	20	7	–	–
7	**3b**	4-$CH_3C_6H_4$	$LiOCH_3$ (1.1 equiv)	THF	0 °C, 15 min then +18 °C, 1 h	B	70 (69)	–	25 (8)	3	2	–
8	**3b**	4-$CH_3C_6H_4$	$LiOCH_3$ (2 equiv)	THF	+18 °C, 3 h then reflux 2 h	B	17	–	54	13	16	–
9	**3b**	4-$CH_3C_6H_4$	$LiOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 15 min then +18 °C, 2.5 h	B	86 (52)	–	–	10 (7)	4 (2)	–
10	**3b**	4-$CH_3C_6H_4$	$LiOCH_3$ (3 equiv)	CH_3OH	0 °C, 15 min then +18 °C, 2.5 h	B	4	30	55	3	–	8
11	**3b**	4-$CH_3C_6H_4$	NaH (1 equiv)	DME	0 °C, 15 min then +18 °C, 45 min	B	61	–	30	–	9	–
12	**3b**	4-$CH_3C_6H_4$	$NaOCH_3$ (1.1 equiv)	THF	0 °C, 2 h	A	50	14	24	6	6	–
13	**3b**	4-$CH_3C_6H_4$	$NaOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 2 h	B	4	15	55	4	–	22
14	**3b**	4-$CH_3C_6H_4$	$NaOCH_3$ (1.1 equiv)	CH_3OH	+18 °C, 2 h then reflux 25 min	B	3	13	33 (22)	5	46 (26)	–
15	**3b**	4-$CH_3C_6H_4$	$NaOCH_3$ (1.1 equiv)	CH_3OH	+18 °C, 30 min then reflux 2 h	B	11	27	0	6	56 (31)	–
16	**3c**	4-ClC_6H_4	$LiOCH_3$ (1.1 equiv)	CH_3OH/THF (1:1)	0 °C, 15 min then +18 °C, 2 h	B	13	1	–	11	75 (41)	–
17	**3c**	4-ClC_6H_4	$LiOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 15 min then +18 °C, 2 h	B	22	–	41	24	13	–
18	**3c**	4-ClC_6H_4	$NaOCH_3$ (1.1 equiv)	THF	0 °C, 35 min	B	43 (19)	–	8	2	47 (15)	–
19	**3c**	4-ClC_6H_4	$NaOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 3 h	B	4	11	56 (32)	2	1	26
20	**3c**	4-ClC_6H_4	$NaOCH_3$ (1.1 equiv)	CH_3OH	+18 °C, 1 h then reflux 20 min	B	5	6	0	9	61	–[c]
21	**3d**	2,4-$Cl_2C_6H_3$	$LiOCH_3$ (1.1 equiv)	CH_3OH/THF (1:1)	0 °C, 30 min then +18 °C, 2 h	B	25 (11)	2	36 (14)	20	13	4
22	**3d**	2,4-$Cl_2C_6H_3$	$NaOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 3 h	B	10	1	46 (39)	–	–	43 (13)
23	**3d**	2,4-$Cl_2C_6H_3$	$NaOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 1 h	B	9	4	47 (58)	–	–	40 (25)
24	**3d**	2,4-$Cl_2C_6H_3$	$NaOCH_3$ (1.1 equiv)	CH_3OH	0 °C, 30 min, +18 °C, 90 min then reflux 30 min	B	10	7	3	10	70 (45)	–
25	**3e**	4-BrC_6H_4	$NaOCH_3$ (1.1 equiv)	THF	0 °C, 15 min	A	39	–	31	5	25	–
26	**3e**	4-BrC_6H_4	$NaOCH_3$ (1.1 equiv)	CH_3OH	+18 °C, 1 h then reflux 20 min	B	–	6	–	6	88 (35)	–

[a] The ratios of compounds were determined by ^1H NMR; [b] the yields (%) of compounds isolated after flash chromatography or preparative TLC on silica gel are in parentheses; [c] the ^1H NMR spectrum also showed a singlet at 4.67 ppm characterizing the presence of 4-chlorobenzyl alcohol (19%); A: work up with an aqueous solution of ammonium chloride and ether; B: work up with brine and ether.

Kice and Lotey [12] also reported the methanol elimination rate by reaction of methoxide anions with methyl (1-naphthyl)methanesulfinates variously substituted on the aromatic ring and established that the sulfine transformation occurred via an irreversible E_1CB-type mechanism. This leads us to believe that methyl arenemethanesulfinates **3a–e** treated solely with methoxide anions in a solvent should also give in situ the corresponding thioaldehyde-*S*-oxides, which can undergo some interesting transformations to yield a series of characterizable final products. The structural determination of these compounds would indeed help obtain information on the reactivity of arenecarbothioaldehyde-*S*-oxides towards methoxide anions.

Working on the system of parameters base/solvent/temperature, we have obtained the results summarized in figure 13 and table II. Thus, the methyl arenemethanesulfinates **3a–e** reacted with lithium or sodium methoxide in THF or methanol to yield the mixtures of products **9–12**, **14** and **15**, whose ratios depend on the reaction conditions and on the nature of the aryl group. The structures of some chromatographed non-separated products have been established by the presence of characteristic signals in the proton NMR spectra. The new α,α'-dimethoxydisulfides **10b,d** are obtained as a mixture of inseparable isomers *dl* and *meso* and have been fully characterized by their spectroscopic data, which match those of compound XIX (fig 13) prepared by another route [26]. The newly formed methyl α-methoxysulfinate **15d** (entries 22 and 23), isolated by column chromatography, was also a mixture of two inseparable isomers. Concerning the influence of the reaction conditions on the ratios of final products, the examination of the results exposed in table II leads to the following remarks.

- The aldehydes **9** are not always predominantly formed and the dimethylacetals **14** remain a minor component.
- Substantial amounts of α,α'-dimethoxydisulfides **10** are obtained after treatment at 0 °C (entries 12, 13, 19, 22, 23 and 25) or at RT (entries 5–7, 10, 11, 17 and 21). The comparison of entries 9 and 10 shows that the presence of 3 equiv of LiOMe lowers the yield in aldehyde **9** in favor of the acetal **14b** and disulfide **10b**.
- Increasing the temperature of the reaction causes the disappearance of the disulfide **10b** along with a greater proportion in the thionoester **12b** (entries 13–15). The same effect has been observed for experiments 19, 20 and 23, 24. We have checked that refluxing the pure α,α'-dimethoxydisulfides **10c** or **10d** with sodium or lithium methoxide in methanol indeed gave the thionoesters **12c** or **12d**.
- The methyl α-methoxysulfinates **15b–d** have been obtained in fair yields when the reactions were carried out in methanol at 0 °C (entries 13, 19, 22 and 23). The α-methoxysulfinate **15d** was found to be unstable (decomposition after a few hours at RT) and this instability is analogous to that already established for some α-methoxysulfoxides [27].

In order to explain the formation of this series of products, it was reasonable to suppose as above that the reaction of the sulfinates **3** proceeds firstly by an elimination giving in situ the corresponding arenecarbothioaldehyde-*S*-oxides VIIIa and secondly by the carbophilic addition of methoxide anion affording the α-methoxysulfenate anions IXa. Species IXa, and especially their lithium salts, could exist in a chelated form analogous to that of compounds XX [28] and be responsible for the following reactions (fig 14). The cleavage of the weak S-O bond of compound IXa via a deprotonation in sequence with an elimination step [29] yielding the thionoesters **12** seems to be unlikely on account of the hypothetical leaving group Na_2O. The α-methoxysulfenate intermediates IXa, on departure of $^-$SOM (IX′a), can give the carbocations XXI doubly stabilized by the neighboring aromatic ring and the ether group. These carbocations XXI would finally yield the dimethylacetals **14** in the presence of anhydrous methanol and methoxide anions [30].

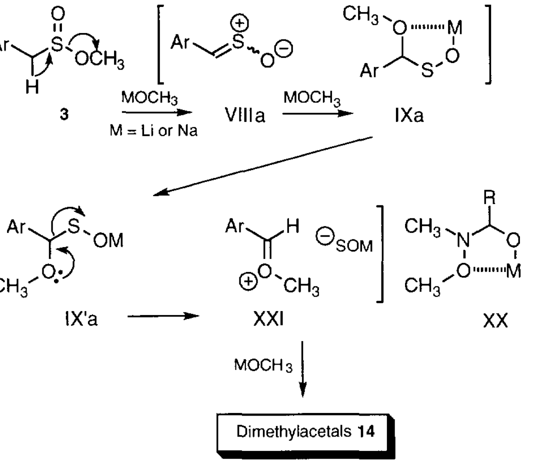


Fig 14

Sulfenic acids or their salts in aqueous solution are known to readily dimerize with the loss of water to form thiosulfinates [19]. Thus it seemed likely that the α-methoxysulfenate anions IX could similarly lead to the α,α'-dimethoxythiosulfinate intermediates XXII which can then undergo the following reactions (fig 15).

- The thiosulfinate XXII can undergo a fragmentation [XXII′] to yield thionoesters **12** and α-methoxyarenesulfenic acid either free or in the alkaline salt form IX. This transformation could be caused by a deprotonation by methoxide anions present in the reaction mixture or can be induced thermally similar to some known cases [21]. In our case, this reaction should be very easy due to the weakness of the thiosulfinate S-S bond together with the enhanced benzylic hydrogen acidity.
- A disproportionation reaction known to occur in basic conditions [31] yielding the α,α'-dimethoxydisulfides **10** and the α-methoxysulfinate anions, which were not isolated in our case.
- A base-catalyzed fragmentation [54] of the disulfides **10** affording the thionoesters **12** and the α-methoxythiolate anions XXIII. The disulfides **10** can be formed again by the reactions of XXIII with XXII or with IXa [32].

A rearrangement of thiosulfinate XXII into XXIV is possible, analogous to that already observed for other

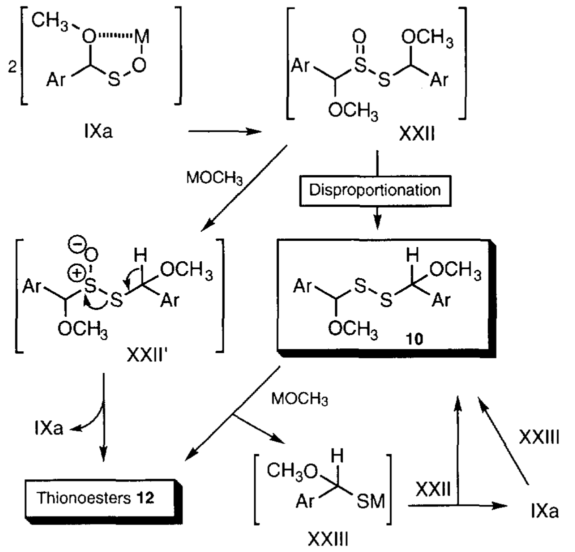


Fig 15

unstable α-methoxysulfoxides [27]. The base-catalyzed elimination shown in formula XXIV′ could then lead to aldehyde **9**, thionoester **12** and sulfur. The formation of methyl α-methoxysulfinates **15** may be explained by a nucleophilic attack of methoxide anions on the sulfinyl group of the thiosulfinate species XXII (fig 16).

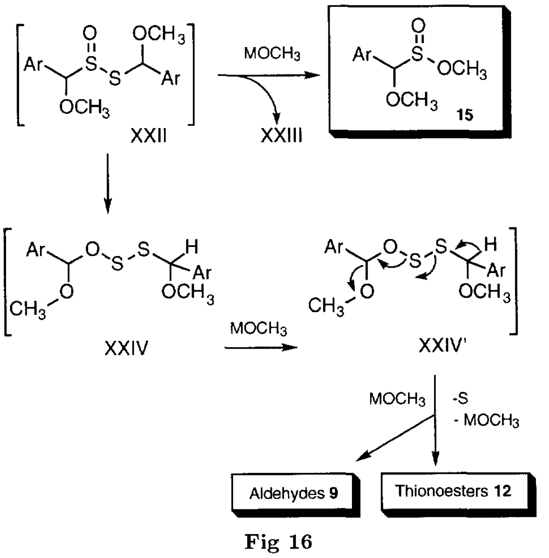


Fig 16

To the best of our knowledge, no literature data is available concerning the reactivity of thiosulfinates with methoxide anions. We have attempted this reaction in the case of two authentic thiosulfinates **16a,b**. The corresponding methyl arenesulfinates **17a,b** were obtained in modest yields due perhaps to the facile reaction of liberated thiolate anions Ar′-S⁻ with the starting thiosulfinates yielding the disulfides **18** (fig 17).

Similarly to the reaction of α-aminosulfenates X with sulfines VIIIa postulated above, it is likely that combination of α-methoxysulfenates IXa with VIIIa could lead to the intermediates XXV. The substitution step exposed in formula XXV′ would still give the oxathiiranes XV and then the aldehydes **9**. It must be understood that intermediates XXV are doubly unstable due to the neighboring sulfoxide group with the sulfur atom from the NaOS group [24] and the methoxy group [27]. This instability could be the source of aldehydes **9** formation (fig 18). On the subject of the sulfur extrusion proposed for the above-mentioned reactions, we must report that in the course of the experiments summarized in table II, we have indeed observed the formation of yellow-red coloration before aqueous work-up, as well as heterogeneous colloidal-like suspensions.

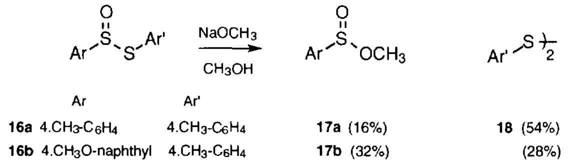


Fig 17

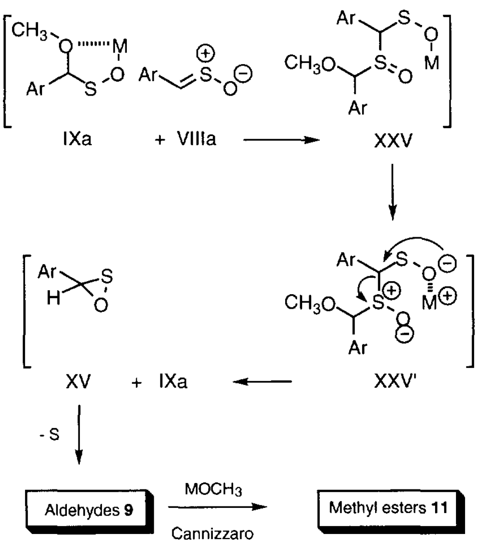


Fig 18

The formation of methyl esters **11** comes from a Cannizzaro-type reaction [33] of aldehydes with methoxide anions. In order to check, we reacted the authentic 4-chlorobenzaldehyde with a solution of sodium methoxide (1 equiv) in refluxing methanol for 2 h and found a mixture aldehyde **9c**/methyl 4-chlorobenzoate/4-chlorobenzyl alcohol in the ratio 80:9:11 (proton NMR titration).

We have examined the reactivity of some methyl allylic sulfinates, which could resemble that of benzylic sulfinates. The sulfinate **6b** treated with 1 equiv of sodium methoxide in methanol yielded the corresponding α,β-ethylenic aldehyde (34%). The poor yield obtained did not encourage us to go any further in that direction because of the aptitude of these conjugated aldehydes to give side reactions in a basic medium.

Conclusion

The results reported herein concerns the formation of imines by the reaction of primary aliphatic amines with some authentic γ-ethylenic thioaldehyde-S-oxides and several examples for the in situ formation of α-aromatic or α,β-ethylenic thioaldehyde-S-oxides starting from methyl arenemethanesulfinates or methyl alk-2-enesulfinates together with some new information about the reactivity of these sulfines towards amines or methoxide anion.

We must also underline the extreme complexity of the reactions given by the various intermediates that we have proposed and, in the present state of our work, it is difficult to specify the mechanism for the evolution of the α-amino- or α-methoxysulfenates X and IX intermediates. In any case, the intermediates IX and X seem to be, without any doubt, responsible for the formation of the final products [55].

Experimental section

The general experimental conditions have been described previously [34].

N-*(3-Ethenyloctylidene)benzenemethanamine* **2a**

Benzylamine (0.531 g; 0.54 mL; 4.96 mmol) was slowly added to a stirred solution of freshly prepared [8] sulfine **1a** (0.462 g; 2.48 mmol) in anhydrous THF (7.5 mL) under nitrogen at 0 °C. The yellow color of the solution deepened and the cooling bath was removed. The solution rapidly became turbid and a precipitate slowly appeared. The reaction mixture was stirred at room temperature for 3 h and then filtered on a short column of basic alumina. After evaporation of the solvent, the crude product was dissolved in pentane and purified by repeated filtrations on a column of basic alumina, affording the imine **2a** (0.300 g; 50% yield).

IR (film): 1 660, 1 450, 915 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.78–7.74 (m, 1H); 7.4–7.2 (m, 5H); 5.68–5.49 (m, 1H); 5.15–4.97 (m, 2H); 4.57 (s, 2H); 3.03–2.59 (m, 2H); 2.31–2.08 (m, 1H); 1.54–1.12 (m, 8H); 0.9 (t, J = 6.4 Hz, 3H) [35].

^{13}C NMR ($CDCl_3$, 62 MHz): δ 165.5 (d); 141.9 (d); 139.2 (s); 130.7 (s); 128.4 (d); 127.9 (d); 114.8 (t); 65.1 (t); 41.7 (d); 40.9 (t); 34.7 (t); 31.8 (t); 26.5 (t); 22.5 (t); 14.0 (q).

MS (CI, NH_3): m/z 244 (M^+ + 1, 100); 216 (2); 100 (12).

Imine **2b**

Prepared by the same procedure as above, using 3 equiv of isopropylamine and purified by a single filtration on basic alumina (64%).

IR (film): 1 650 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.60 (t, J = 5.5 Hz, 1H); 5.73 (dd, J = 17.5 Hz and 11 Hz, 1H); 5.12 (dd, J = 11 Hz and 1.1 Hz, 1H); 4.98 (dd, J = 17.5 Hz and 1.1 Hz, 1H); 3.23 (h, J = 6.5 Hz, 1H); 2.24 (d, J = 5.5 Hz, 2H); 1.75–1.20 (m, 10H); 1.13 (d, J = 6.5 Hz, 6H).

Methyl 1-naphthylmethanesulfinate **3a**

1-Naphthylmethanethiol [12] was converted by bromine and aqueous potassium hydrogen carbonate [36] into the corresponding disulfide (89%).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.0–7.92 (m, 2H); 7.86–7.74 (m, 4H); 7.57–7.44 (m, 4H); 7.38–7.28 (m, 2H); 7.11–7.07 (m, 2H); 3.93 (s, 4H).

Following a slightly modified procedure [14], the above disulfide was dissolved in dichloromethane and treated with N-bromosuccinimide (3 equiv) and methanol at 0 °C for 20 min, then at room temperature for 1 h. The crude product was purified by flash chromatography on silica gel affording the pure sulfinate **3a** (81% yield). Mp 110 °C (lit [12]: mp 106–108 °C).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.09–8.03 (m, 1H); 7.92–7.82 (m, 2H); 7.53–7.45 (m, 4H); 4.55 (d, J = 12.5 Hz, 1H); 4.42 (d, J = 12.5 Hz, 1H); 3.73 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 133.8 (s); 132.1 (s); 129.6 (d); 129.2 (d); 128.8 (d); 126.7 (d); 126.1 (d); 125.5 (d); 125.4 (s); 123.5 (d); 62.0 (q); 54.7 (t).

Methyl (4-methylphenyl)methanesulfinate **3b**

Following a previously described procedure [14], bis-[(4-methylphenyl)methyl]disulfide was converted into the title sulfinate (78%); $bp_{0.1}$ = 175 °C.

IR (film): 2 920, 1 510, 1 450, 1 405, 1 115, 995, 880, 820, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.22–7.18 (m, 4H); 4.02 (d, J = 13.2 Hz, 1H); 3.92 (d, J = 13.2 Hz, 1H); 3.74 (s, 3H); 2.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 138.2 (s); 132.0 (d); 129.5 (d); 125.4 (s); 63.5 (q); 54.8 (t); 21.6 (q).

MS (CI, NH_3): m/z 202 (M^+ + 18, 25); 185 (M^+ + 1, 11); 110 (100).

Anal calc for $C_9H_{12}O_2S$: C, 58.66; H, 6.56. Found: C, 58.52; H, 6.64.

1,1-Dimethylethyl (4-methylphenyl)methanesulfinate

Similarly to a previously described procedure [37], the reaction of (4-methylphenyl)methyl magnesium bromide with morpholine-4-sulfinyl chloride in THF/toluene at −60 °C then slowly warming to room temperature for 1 h, afforded 4-[(4-methylphenyl)methylsulfinyl]morpholine (71%); mp 93 °C.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.2–7.1 (m, 4H); 4.07–3.92 (m, 2H); 3.75–3.65 (m, 4H); 3.25–3.12 (m, 2H); 3.12–3.0 (m, 2H); 2.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 137.8 (s); 129.8 (d); 129.5 (d); 127.4 (s); 66.8 (t); 58.5 (t); 45.6 (t); 21.1 (q).

MS (CI, NH_3): m/z 240 (M^+ + 1, 12); 239 (M^+, 51); 191 (39); 134 (100).

Anal calc for $C_{12}H_{17}NO_2S$: C, 60.21; H, 7.16; N, 5.84. Found: C, 60.06; H, 7.03; N, 5.78.

When treated in dichloromethane with 2-methylpropan-2-ol (5 equiv) and boron trifluoride etherate (1.5 equiv) at 0 °C for 3 h and then at room temperature for 20 h, the above sulfinamide was converted into the corresponding 1,1-dimethylethyl sulfinate (74%).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.20–7.10 (m, 4H); 3.96 (d, J = 12.5 Hz, 1H); 3.88 (d, J = 12.5 Hz, 1H); 2.33 (s, 3H); 1.26 (s, 9H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 137.8 (s); 130.3 (d); 129.2 (d); 126.4 (s); 82.2 (s); 64.6 (t); 29.4 (q); 21.1 (q).

MS (CI, NH_3): m/z 244 (M^+ + 18, 65); 227 (M^+ + 1, 30); 216 (8); 188 (57); 127 (100).

Anal calc for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02. Found: C, 63.55; H, 8.12.

Methyl (4-chlorophenyl)methanesulfinate **3c**

Obtained (82%) from bis[(4-chlorophenyl)methyl]disulfide; bp 0.02 = 100 °C.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.40–7.32 (m, 2H); 7.29–7.21 (m, 2H); 4.02 (d, J = 13.2 Hz, 1H); 3.93 (d, J = 13.2 Hz, 1H); 3.76 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 134.4 (s); 131.8 (d); 129.0 (d); 127.1 (s); 63.0 (q); 54.8 (t).

MS (CI, NH_3): m/z 244 (M^+ + 18, 40); 222 (M^+ + 18, 10); 207 (M^+ + 1, 2); 205 (M^+ + 1, 19); 125 (11).

Anal calc for $C_8H_9ClO_2S$: C, 46.95; H, 4.43. Found: C, 47.03; H, 4.39.

Methyl (2,4-dichlorophenyl)methanesulfinate **3d**

Obtained (91%) from bis[(2,4-dichlorophenyl)methyl]disulfide.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.46–7.42 (m, 1H); 7.33–7.24 (m, 2H); 4.20 (d, J = 13.2 Hz, 1H); 4.08 (d, J = 13.2 Hz, 1H); 3.77 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 135.5 (s); 135.1 (s); 133.5 (d); 129.4 (d); 127.5 (d); 126.1 (s); 61.1 (q); 54.8 (t).

MS (CI, NH_3): m/z 258 (M^+ + 18, 52); 256 (M^+ + 18, 100); 241 (M^+ + 1, 27); 239 (M^+ + 1, 45); 178 (22); 176 (35); 161 (34); 159 (55).

Anal calc for $C_8H_8Cl_2O_2S$: C, 40.18; H, 3.37. Found: C, 40.09; H, 3.41.

Methyl (4-bromophenyl)methanesulfinate **3e**

Obtained (73%) from bis[(4-bromophenyl)methyl]disulfide; bp 0.03 = 145 °C.

IR (film): 2 930, 1 705, 1 585, 1 480, 1 400, 1 115, 1 070, 990, 880, 840, 810, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.55–7.45 (m, 2H); 7.29–7.21 (m, 2H); 3.99 (d, J = 13.1 Hz, 1H); 3.90 (d, J = 13.1 Hz, 1H); 3.75 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 132.1 (d); 131.9 (d); 127.6 (s); 122.6 (s); 63.1 (q); 54.8 (t).

MS (CI, NH_3): m/z 268 (M^+ + 18, 68); 266 (M^+ + 18, 72); 251 (M^+ + 1, 64); 249 (M^+ + 1, 67); 188 (19); 186 (20); 171 (100); 169 (98).

Anal calc for $C_8H_9BrO_2S$: C, 38.57; H, 3.64. Found: C, 38.65; H, 3.59.

N-*(1-Naphthylmethylidene)propanamine* **4a**

- *General procedure*

A solution of methyl 1-naphthylmethanesulfinate **3a** (0.22 g; 1 mmol) in anhydrous THF (2 mL) was added to a solution of dry sodium methoxide (0.06 g; 1.1 equiv) and *n*-propylamine (0.177 g; 0.245 mL; 3 equiv) in THF (3 mL) at 0 °C. The yellow solution was stirred at 0 °C for 30 min then at room temperature for 2 h. The resulting yellow reddish heterogeneous mixture thus obtained was poured on a short column of basic alumina and the column was washed with anhydrous ether (50 mL). The combined filtrates were evaporated under reduced pressure affording a mixture of imine **4a** and naphthalene-1-carbaldehyde (91:9) (124 mg; 63%).

IR (film): 1 689, *1 643* cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.94 (s, 1H); 8.87 (d, J = 8.75 Hz, 1H); 7.93–7.85 (m, 3H); 7.62–7.47 (m, 3H); 3.71 (t, J = 7.5 Hz, 2H); 1.82 (tt, J = 7.5 Hz and 7.5 Hz, 2H); 1.02 (t, J = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 160.4 (d); 134.0 (s); 132.0 (s); 131.4 (s); 130.8 (d); 128.7 (d); 128.5 (d); 127.1 (d); 126.1 (d); 125.4 (d); 124.4 (d); 64.6 (t); 24.4 (t); 12.1 (q).

MS (CI, NH_3): m/z 199 (M^+ + 2, 40); 198 (M^+ + 1, 100); 173 (27); 171 (29).

- N-*[(4-Methylphenyl)methylidene]benzenemethanamine* **4b**

Following the above general procedure with 2 equiv of benzenemethanamine and stirring at room temperature for 3 h, the crude product could not be separated from benzenemethanamine by chromatography on a column of basic alumina, eluting with pentane. The two first fractions were mixtures of imine/amine in the ratio 84:16, and gave a ^{1}H NMR spectrum from which the following characteristic signals of the imine **4b** were extracted.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.35 (s, 1H); 7.67 (d, J = 8 Hz, 2H); 7.37–7.16 (m, 7H); 4.8 (s, 2H); 2.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 161.9 (d); 141.0 (s); 139.4 (s); 133.5 (s); 129.3 (d); 128.4 (d); 128.2 (d); 127.9 (d); 126.9 (d); 65.0 (t); 21.5 (q).

- N-*[(4-Methylphenyl)methylidene]propanamine* **4c**

IR (film): 1 640 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.25 (s, 1H); 7.62 (d, J = 8 Hz, 2H); 7.22 (d, J = 8 Hz, 2H); 3.57 (td, J = 7 Hz and 1.5 Hz, 2H); 2.37 (s, 3H); 1.72 (tq, J = 7.5 Hz and 7.5 Hz, 2H); 0.95 (t, J = 7.5 Hz, 3H).

- N-*[(4-Methylphenyl)methylidene]-1-methylethanamine* **4d**

IR (film): 1 635 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.27 (s, 1H); 7.62 (d, J = 8.2 Hz, 2H); 7.26 (d, J = 8.2 Hz, 2H); 3.51 (h, J = 6.3 Hz, 1H); 2.37 (s, 3H); 1.25 (d, J = 6.3 Hz, 6H).

- N-*[(4-Chlorophenyl)methylidene]propanamine* **4e**

The general procedure was slightly modified. A solution of methyl sulfinate **3c** and *n*-propylamine (3 equiv) in THF was added to a suspension of dry sodium methoxide in THF at 0 °C. After 15 min at 0 °C, the mixture was stirred at room temperature for 45 min. Filtration on a short column of basic alumina with ether as eluent afforded a mixture (85:15) of imine **4e** and thioamide **5a**.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.23 (s, 1H); 7.67 (d, J = 8.5 Hz, 2H); 7.38 (d, J = 8.5 Hz, 2H); 3.57 (td, J = 7 Hz and 1.2 Hz, 2H); 1.72 (tq, J = 7.5 Hz and 7.5 Hz, 2H); 0.95 (t, J = 7.5 Hz, 3H).

The thioamide **5a** showed the following characteristic signals: 7.66 (d, J = 8.75 Hz, 2H); 3.77 (td, J = 7.5 Hz and 5 Hz, 2H); 1.78 (tq, J = 7.5 Hz and 7.5 Hz, 2H); 1.05 (t, J = 7.5 Hz, 3H) identical to that of an authentic sample prepared following a described procedure [38].

- *4-Chloro-*N*-propylbenzenecarbothioamide* **5a**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.66 (d, J = 8.75 Hz, 2H); 7.34 (d, J = 8.75 Hz, 2H); 3.77 (td, J = 7.5 Hz and 5 Hz, 2H); 1.78 (tq, J = 7.5 Hz and 7.5 Hz, 2H); 1.05 (t, J = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 197.6 (s); 140.2 (s); 137.1 (s); 128.5 (d); 128.0 (d); 48.6 (t); 21.4 (t); 11.5 (q).

- *4-Chloro-*N,N*-dimethylbenzenecarbothioamide* **5b**

Mp 78 °C; lit [39]: mp 79–80 °C.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.39–7.21 (m, 4H); 3.59 (s, 3H); 3.17 (s, 3H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 199.9 (s); 141.7 (s); 134.6 (s); 128.6 (d); 127.3 (d); 44.1 (q); 43.3 (q).

- *4-[(4-Chlorophenyl)thioxomethyl]morpholine* **5c** *[40]*

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.42–7.17 (m, 4H); 4.47–4.36 (m, 2H); 3.96–3.84 (m, 2H); 3.72–3.56 (m, 4H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 199.4 (s); 140.6 (s); 134.8 (s); 128.7 (d); 127.3 (d); 66.5 (t); 66.4 (t); 52.5 (t); 49.5 (t).

MS (CI, NH_3): m/z 244 ($M^+ + 1$, 47); 242 ($M^+ + 1$, 100); 140 (24).

- *4-[(2,4-Dichlorophenyl)thioxomethyl]morpholine* **5d** *[41]*

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.43–7.36 (m, 1H); 7.43–7.20 (m, 2H); 4.53–4.32 (m, 2H); 3.98–3.80 (m, 2H); 3.83–3.35 (m, 4H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ 194.8 (s); 139.5 (s); 134.8 (s); 129.5 (d); 129.0 (s); 128.8 (d); 127.8 (d); 66.4 (t); 66.3 (t); 51.7 (t); 49.0 (t).

N-*[3,7-Dimethylocta-2,6-dienylidene]propanamine* **7a**

The starting material methyl 3,7-dimethylocta-2,6-diene-1-sulfinate was prepared following a described procedure [42].

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.19 and 8.13 (dt, J = 9.3 Hz and 1.2 Hz, 2H); 6.0 (broad d, J = 6 Hz, 2H); 5.17–5.02 (m, 2H); 3.47–3.33 (m, 4H); 2.39–2.28 (m, 2H Z); 2.23–2.06 (m, 2H Z + 4H E); 1.92 (d, J = 1.2 Hz, 3H E); 1.87 (d, J = 1.2 Hz, 3H Z); 1.73–1.54 (m, 16H); 0.92 (t, J = 7.4 Hz, 3H); 0.90 (t, J = 7.4 Hz, 3H). The spectrum is comparable to that described for *N*-(3,7-dimethylocta-2,6-dienylidene)prop-2-enamine [43].

- N-*[3,7-Dimethylocta-2,6-dienylidene]-1-methylethanamine* **7b**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.23 and 8.17 (d, J = 9.3 Hz, 2H); 6.0 (broad d, J = 9.3 Hz, 2H); 5.17–5.02 (m, 2H); 3.32 (h, J = 6.5 Hz, 2H); 2.38–2.28 (m, 2H Z); 2.24–2.09 (m, 4H E + 2H Z); 1.92 (d, J = 1 Hz, 3H); 1.88 (d, J = 1.2 Hz, 3H); 1.69 (broad s, 6H); 1.60 (broad s, 6H); 1.20 (d, J = 6.5 Hz, 6H); 1.18 (d, J = 6.5 Hz, 6H).

- N-*(2-Cyclohexylideneethylidene)propanamine* **7c**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.21 (broad d, J = 9.3 Hz, 1H); 5.94 (broad d, J = 9.3 Hz, 1H); 3.40 (td, J = 7.5 Hz, 2H); 2.50–2.38 (m, 2H); 2.30–2.16 (m, 2H); 1.73–1.52 (m, 8H); 0.92 (t, J = 7.5 Hz, 3H).

Methyl octane-1-sulfinate **8**

Following a slightly modified procedure [44], an ethereal solution of *n*-octylmagnesium bromide was slowly added to an ethereal solution of methyl chlorosulfinate (1.2 equiv) at −60 °C. After stirring at −60 °C for 2.5 h, the mixture was slowly allowed to warm to room temperature. The usual work-up afforded a crude product, which was distilled. Bp = 92–93 °C.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.78 (s, 3H); 2.85–2.60 (m, 2H); 1.75–1.60 (m, 2H); 1.46–1.20 (m, 12H); 0.93–0.84 (m, 3H).

MS (CI, NH_3): m/z 210 ($M^+ + 18$, 100); 193 ($M^+ + 1$, 97); 178 (5); 161 (10).

Representative procedure for the treatment of sulfinates **3** *with methoxide anions*

To a mixture of dry sodium (or lithium) methoxide (1.1 mmol) in anhydrous THF (3 mL) (or methanol, see table II) cooled at 0 °C was added a solution of sulfinate **3** (1 mmol) in THF (2 mL) (or methanol). The yellow suspension was stirred at the temperatures and for the number of times indicated in table II. The final work up were done either with aqueous NH_4Cl and ether (procedure A) or brine and ether (procedure B).

- *Naphthalene-1-carbaldehyde* **9a**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 10.4 (s, 1H); 9.26 (d, J = 8.75 Hz, 1H); 8.11 (d, J = 8.25 Hz, 1H); 8.03–7.90 (m, 2H); 7.93 (broad d, J = 8.75 Hz, 1H); 7.74–7.55 (m, 3H).

- *4-Methylbenzaldehyde* **9b**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.97 (s, 1H); 7.78 (d, J = 7.8 Hz, 2H); 7.33 (d, J = 7.8 Hz, 2H); 2.44 (s, 3H).

- *4-Chlorobenzaldehyde* **9c**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.99 (s, 1H); 7.83 (d, J = 8.4 Hz, 2H); 7.52 (d, J = 8.4 Hz, 2H).

- *2,4-Dichlorobenzaldehyde* **9d**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 10.42 (s, 1H); 7.87 (d, J = 8.4 Hz, 1H); 7.49 (d, J = 2 Hz, 1H); 7.42–7.35 (m, 1H).

- *4-Bromobenzaldehyde* **9e**

The following characteristic signals were extracted from the NMR spectrum of a chromatography fraction containing both **9e** and **10e**.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 10.0 (s, 1H); 7.77 (d, J = 8.5 Hz, 2H).

- *3,6-Di(1-naphthyl)-2,7-dioxa-4,5-dithiaoctane* **10a**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.19–8.08 (m, 2H); 7.91–7.77 (m, 4H); 7.58–7.34 (m, 8H); 5.89 (s, 2H); 5.81 (s, 2H); 3.56 (s, CH_3O); 3.44 (s, CH_3O).

- *3,6-Bis(4-methylphenyl)-2,7-dioxa-4,5-dithiaoctane* **10b**

Mixture of *dl* and *meso* isomers, mp 69–70 °C (pentane).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.34–7.12 (m, 16H); 5.28 (s, 2H); 5.25 (s, 2H); 3.53 (s, 6H); 3.46 (s, 6H); 2.37 (s, 6H); 2.36 (s, 6H).

^{13}C NMR ($CDCl_3$, 62 MHz): δ the italicized signals are that of the major isomer 138.0 (s); 136.2 (s); 135.3 (s); *129.0 (d)*; 128.9 (d); 126.41 (d); *126.38 (d)*; 94.0 (d); *93.6 (d)*; 57.6 (q); *57.4 (q)*; 21.2 (q).

MS (CI, NH_3): m/z 352 ($M^+ + 18$, 2); 335 ($M^+ + 1$, 2); 320 (12); 303 (100); 167 (46).

Anal calc for $C_{18}H_{22}O_2S_2$: C, 64.47; H, 6.59. Found: C, 64.66; H, 6.72.

- *3,6-Bis(4-chlorophenyl)-2,7-dioxa-4,5-dithiaoctane* **10c**

The following characteristic signals were taken from the NMR spectrum of a chromatography fraction containing both **9c** and **10c**.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.37–7.23 (m, 8H); 5.31 (s, 2H); 5.21 (s, 2H); 3.54 (s, 6H); 3.45 (s, 6H).

- *3,6-Bis(2,4-dichlorophenyl)-2,7-dioxa-4,5-dithiaoctane* **10d**

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.50–730 (m, 4H); 7.30–7.20 (m, 2H); 5.74 (s, 2H); 5.56 (s, 2H); 3.53 (s, 6H); 3.44 (s, 6H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 134.8 (s); 134.7 (s); 134.6 (s); 134.5 (s); 132.3 (s); 132.0 (s); 129.4 (d); 129.2 (d); 129.1 (d); 127.2 (d); 127.1 (d); 89.7 (d); 89.2 (d); 57.7 (q); 57.6 (q).

MS (CI, NH$_3$): m/z 464 (M$^+$ + 18, 4); 462 (M$^+$ + 18, 6); 460 (M$^+$ + 18, 4); 432 (29); 431 (17); 430 (55); 429 (23); 428 (37); 415 (59); 414 (48); 413 (100); 412 (44); 411 (69).

- *3,6-Bis(4-bromophenyl)-2,7-dioxa-4,5-dithiaoctane* **10e**

The following characteristic signals were taken from the NMR spectrum of a chromatography fraction.

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.54–7.40 (m, 8H); 7.30–7.12 (m, 8H); 5.30 (s, 2H); 5.20 (s, 2H); 3.55 (s, 6H); 3.45 (s, 6H).

- *Methyl naphthalene-1-carboxylate* **11a**

^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.92 (d, J = 8.75 Hz, 1H); 8.22–8.17 (m, 1H); 8.03 (broad d, J = 8.75 Hz, 1H); 7.92–7.87 (m, 1H); 7.65–7.47 (m, 4H); 4.02 (s, 3H).

- *Methyl 4-methylbenzoate* **11b**

The following characteristic signals were taken from the NMR spectrum of a crude mixture (entry 9) and were identical to that of an authentic sample.

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.95 (d, J = 8.2 Hz, 2H); 3.90 (s, 3H).

- *Methyl 4-chlorobenzoate* **11c**

^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.01–7.95 (m, 2H); 7.45–7.39 (m, 2H); 3.92 (s, 3H).

- *Methyl 2,4-dichlorobenzoate* **11d**

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.81 (d, J = 8.75 Hz, 1H); 7.48 (d, J = 2.25 Hz, 1H); 7.33–7.27 (m, 1H); 3.93 (s, 3H).

- *Methyl 4-bromobenzoate* **11e**

The following characteristic signals were taken from the NMR spectrum of a chromatography fraction.

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.94–7.88 (m, 2H); 3.92 (s, 3H).

- O-*Methyl naphthalene-1-carbothioate* **12a**

The following characteristic signal was taken from the NMR spectrum of a crude reaction mixture of products (entry 5).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 4.40 (s, 3H).

- O-*Methyl 4-methylbenzenecarbothioate* **12b** *[45]*

IR (KBr): 1 600, 1 440, 1 280, 1 225, 1 180, 1 155, 1 125, 820 cm^{-1}.

^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.16–8.10 (m, 2H); 7.24–7.16 (m, 2H); 4.3 (s, 3H); 2.4 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 212.2 (s); 134.6 (s); 135.8 (s); 129.0 (d); 128.8 (d); 59.1 (q); 21.5 (q).

MS (CI, NH$_3$): m/z 184 (M$^+$ + 18, 4); 167 (M$^+$ + 1, 100); 150 (2); 135 (9).

- O-*Methyl 4-chlorobenzenecarbothioate* **12c** *[45a]*

Mp 47 °C.

^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.18–8.12 (m, 2H); 7.4–7.32 (m, 2H); 4.28 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 210.6 (s); 139.3 (s); 136.5 (s); 130.0 (d); 128.3 (d); 59.4 (q).

MS (CI, NH$_3$): m/z 189 (M$^+$ + 1, 30); 188 (29); 187 (100); 186 (38); 155 (38).

- O-*Methyl 2,4-dichlorobenzenecarbothioate* **12d** *[46]*

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.61 (d, J = 8.25 Hz, 1H); 7.40 (d, J = 2.25 Hz, 1H); 7.25 (dd, J = 8.25 Hz and 2.25 Hz, 1H); 4.27 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 211.8 (s); 139.1 (s); 136.5 (s); 132.0 (d); 131.0 (s); 130.0 (d); 126.8 (d); 59.5 (q).

MS (CI, NH$_3$): m/z 225 (M$^+$ + 1, 12); 224 (M$^+$, 25); 223 (M$^+$ + 1, 64); 222 (M$^+$, 74); 221 (M$^+$ + 1, 94); 220 (M$^+$, 88); 191 (92); 189 (100).

- O-*Methyl 4-bromobenzenecarbothioate* **12e** *[47]*

^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.08–8.0 (m, 2H); 7.55–7.48 (m, 2H); 4.30 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 210.6 (s); 136.9 (s); 131.3 (d); 130.1 (d); 128.1 (s); 59.4 (q).

MS (CI, NH$_3$): m/z 250 (M$^+$ + 18, 66); 248 (M$^+$ + 18, 70); 232 (M$^+$ + 1, 60); 230 (M$^+$ + 1, 63); 152 (100); 150 (98).

- *2,5-Dimethoxy-3-thiaspiro[5.5]undecane* **13**

■ *Isomer A*

^{1}H NMR (CDCl$_3$, 250 MHz): δ 5.08 (dd, J = 3.6 Hz and 6.1 Hz, 1H); 3.72 (dd, J = 5.2 Hz and 9.2 Hz, 1H); 3.48–3.22 (m, 2H); 3.38 (s, 3H); 3.28 (s, 3H), 2.36 (dd, J = 3.6 Hz and 13.6 Hz, 1H); 1.98 (dd, J = 13.6 Hz and 6.1 Hz, 1H); 1.75–1.20 (m, 10H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 90.2 (d); 74.6 (t); 58.8 (q); 57.2 (q); 56.5 (d); 47.6 (s); 46.1 (t); 37.4 (t); 30.7 (t); 26.2 (t); 23.6 (t); 22.9 (t).

■ *Isomer B*

^{1}H NMR (CDCl$_3$, 250 MHz): δ 5.12 (dd, J = 3.7 Hz and 6.2 Hz, 1H); 3.62 (dd, J = 3.8 Hz and 8.6 Hz, 1H); 3.48-3.22 (m, 2H); 3.36 (s, 3H), 3.29 (s, 3H), 2.39 (dd, J = 6.2 Hz and 13.6 Hz, 1H); 1.94 (dd, J = 13.6 Hz and 3.7 Hz, 1H); 1.75–1.70 (m, 10H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 90.0 (d); 73.8 (t); 58.8 (q); 57.1 (q); 55.9 (d); 47.6 (s); 46.5 (t); 36.9 (t); 31.0 (t); 26.2 (t); 23.5 (t); 23.0 (t).

MS (EI): m/z on the mixture of the isomers 230 (M$^+$, 10); 193 (4); 185 (82); 172 (28); 153 (100).

- *1-(Dimethoxymethyl)-4-methylbenzene* **14b**

The following characteristic signals were taken from the NMR spectrum of a crude reaction mixture (entries 12 and 14) and were identical to that of an authentic sample.

^{1}H NMR (CDCl$_3$, 250 MHz): δ 5.36 (s, 1H); 3.32 (s, 6H).

- *4-Chloro-1-(dimethoxymethyl)benzene* **14c**

The following characteristic signals were taken from the NMR spectrum of a crude mixture of products (entry 19).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 5.37 (s, 1H); 3.31 (s, 6H).

- *2,4-Dichloro-1-(dimethoxymethyl)benzene* **14d**

The following characteristic signals were taken from the NMR spectrum of a chromatography fraction (entry 23).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 5.58 (s, 1H); 3.37 (s, 6H).

- *4-Bromo-1-(dimethoxymethyl)benzene* **14e**

The following characteristic signals were taken from the NMR spectrum of a crude mixture of products (entry 26).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 5.36 (s, 1H); 3.31 (s, 6H).

- *Methyl methoxy-(4-methylphenyl)methanesulfinate* **15b**

The following characteristic signals were taken from the NMR spectrum of a crude mixture of products (entry 10).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 4.83 and 4.76 (2s, 1H); 3.82, 3.68, 3.63 and 3.60 (4s, 6H).

- *Methyl methoxy-(4-chlorophenyl)methanesulfinate* **15c**

The following characteristic signals were taken from the NMR spectrum of a crude reaction mixture of products (entry 19).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 4.85 and 4.78 (2s, 1H); 3.82, 3.70, 3.67 and 3.62 (4s, 6H).

- *Methyl methoxy-(2,4-dichlorophenyl)methanesulfinate* **15d**

Isolated after flash chromatography on silica gel (last fractions) of the crude products (entries 22, 23) (two stereomers).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.50–7.41 (m, 2H); 7.37–7.28 (m, 1H); 5.52 (s, 1H); 5.40 (s, 1H); 3.78, 3.74, 3.73 and 3.65 (4s, 6H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 135.8 (s); 135.7 (s); 134.8 (s); 134.4 (s); 130.7 (d); 130.0 (d); 129.7 (s); 129.5 (d); 129.3 (d); 128.6 (s); 127.6 (d); 127.4 (d); 97.1 (d); 96.0 (d); 60.7 (q); 60.1 (q); 55.8 (q); 55.3 (q).

MS (CI, NH$_3$): m/z 290 (M$^+$ + 18, 13); 288 (M$^+$ + 18, 54); 286 (M$^+$ + 18, 83); 273 (M$^+$ + 1, 11); 271 (M$^+$ + 1, 65); 269 (M$^+$ + 1, 100); 208 (20); 206 (37).

- *4-Methylphenyl 4-methylbenzenethiosulfinate* **16a**

Prepared following a described procedure [49]; mp 101–102 °C (ether/pentane); lit [49]: mp 87 °C; [50]: mp 102 °C.

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.60–7.52 (m, 2H); 7.46–7.40 (m, 2H); 7.32–7.27 (m, 2H); 7.21–7.15 (m, 2H); 2.42 (s, 3H); 2.38 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 142.1 (s); 141.1 (s); 140.8 (s); 135.4 (d); 130.1 (d); 129.6 (d); 126.3 (s); 124.3 (d); 21.5 (q); 21.4 (q).

- *4-Methylphenyl 4-methoxynaphthalene-1-thiosulfinate* **16b**

Following a described procedure [51], the reaction of 4-methoxynaphthalene-1-sulfinyl chloride [52] with tributyl (4-methylphenylthio)stannane afforded a crude product which was purified by flash chromatography (22%).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.39–8.32 (m, 1H); 8.12–8.03 (m, 1H); 7.91 (d, J = 8.2 Hz, 1H); 7.78–7.52 (m, 2H); 7.42–7.37 (m, 2H); 7.21–7.16 (m, 2H); 6.88 (d, J = 8.2 Hz, 1H); 4.06 (s, 3H); 2.39 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 158.7 (s); 140.6 (s); 136.3 (s); 135.3 (d); 129.9 (d); 129.8 (s); 128.8 (s); 127.6 (d); 126.6 (s); 125.9 (d); 125.4 (d); 122.9 (d); 122.2 (d); 103.2 (d); 55.8 (q); 21.3 (q).

Methyl 4-methylbenzenesulfinate **17a**

To a cooled solution of the thiosulfinate **16a** (0.400 g; 1.52 mmol) in THF (5 mL) and methanol (2 mL) was added a solution of sodium methoxide in methanol (1 N; 1.5 mL; 1.5 mmol) and the mixture was stirred at 0 °C for 2 h. The usual work-up and flash chromatography gave firstly the disulfide **18** (0.2 g) and then the known sulfinate **17a** [52] (0.04 g; 16%).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.62–7.57 (m, 2H); 7.38–7.31 (m, 2H); 3.47 (s, 3H); 2.43 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 142.7 (s); 140.8 (s); 129.6 (d); 125.2 (d); 49.2 (q); 21.4 (q).

MS (EI): m/z 170 (M$^+$, 50); 139 (100); 91 (66); 84 (30).

- *Methyl 4-methoxynaphthalene-1-sulfinate* **17b** *[53]*

When similarly treated with sodium methoxide, the thiosulfinate **16b** (0.39 g; 1.19 mmol) afforded a mixture of sulfinate **17b**, disulfide **18** and some unsymmetrical disulfides. Flash chromatography yielded the pure compound **17b** (0.09 g; 32%).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.39–8.32 (m, 1H); 8.25–8.19 (m, 1H); 8.09 (d, J = 8.2 Hz, 1H); 7.69–7.52 (m, 2H); 6.95 (d, J = 8.2 Hz, 1H); 4.08 (s, 3H); 3.42 (s, 3H).

^{13}C NMR (CDCl$_3$, 62 MHz): δ 159.3 (s); 130.6 (s); 129.5 (s); 128.2 (d); 126.6 (d); 126.2 (d); 125.8 (s); 122.2 (d); 122.1 (d); 102.7 (d); 56.0 (q); 49.2 (q).

- *Cyclohexylideneacetaldehyde*

When treated with sodium methoxide (1 equiv) in methanol at 0 °C for 4 h then at 18 °C for 1 h, the methyl 2-cyclohexylideneethanesulfinate **6b** [42] afforded after usual work-up and chromatography the pure cyclohexylideneacetaldehyde (34%) with a ^{1}H NMR spectrum identical to that of an authentic sample [48].

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