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Synthesis of Mono- and Disubstituted Sulfines via β-Elimination of Chloroform from Trichloromethyl Sulfoxides

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Abstract: A new method for the synthesis of thioaldehyde and thioketone S-oxides by an unusual base-induced β-elimination of chloroform from readily available allylic and benzylic trichloromethyl sulfoxides is described. The reaction proceeds smoothly under mild conditions. The facile preparation of α,β-unsaturated sulfines by the new method is of special interest. A possible mechanism for this remarkable sulfine synthesis and apparently unprecedented β-elimination of chloroform is presented.

INTRODUCTION

Due to its high stereoselectivity and efficiency, the reversible [2,3]-sigmatropic rearrangement of allylic sulfenates to sulfoxides, also known as the Mislow-Braverman-Evans rearrangement,[1] has found extensive application in organic synthesis since its publication.[2] The process has been of particular interest since it was demonstrated as a key reaction for the stereospecific total synthesis of various natural products including prostaglandins and leukotrienes.[2] Allylic trichloromethyl sulfoxides have played an essential role in the discovery of this rearrangement and the elucidation of its mechanism since they enabled direct observation of the sulfenate-sulfoxide equilibrium and the isolation of the first stable allylic sulfenates.[3]

More than a quarter century later, the same allylic sulfoxides have become the source of another significant and striking observation which lies at the basis of the present study. Thus, we have recently found that these sulfoxides undergo an unexpected and apparently unprecedented β-elimination of chloroform at room temperature and afford the corresponding conjugated vinyl thioaldehyde S-oxides.[4]

In spite of the great variety of substituted sulfines previously reported,[5] the preparation of α,β-unsaturated sulfines has received relatively little attention so far.[6-10] Furthermore, all the routes employed for the preparation of such compounds have a limited scope and yield disubstituted sulfines only. On the other hand, our method is suitable for the preparation of both mono- and disubstituted α,β-unsaturated sulfines.

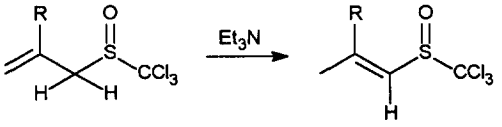
A second advantage of our method is its utility and efficiency for the preparation of both mono- and disubstituted sulfines in general. Comparable to the latter, the former type of sulfines, have been studied to a lesser extent because of the well-known lack of stability of the required thioaldehyde precursors. For this reason the usual thioacarbonyl oxidation route could not be applied, and, the synthesis of such sulfines in the past has

involved alternative methods.[11,12] However, the method described in this paper provides easy and direct access to thioaldehyde S-oxides.

The third significant feature of our article is its mechanistic novelty. The apparent lack of previous documented examples of β-elimination of chloroform is rather surprising, not only because of the leaving group ability of the trihalomethyl anion, which is well demonstrated by the old haloform reaction,[13] but also because of the α-elimination of chloroform which has been thoroughly studied and extensively used for the preparation of dichlorocarbene in the past.[14] We now wish to present a full report of our results on the preparation of thioaldehyde S-oxides,[4] as well as the extension of our new method for the preparation of thioketone S-oxides.

RESULTS AND DISCUSSION

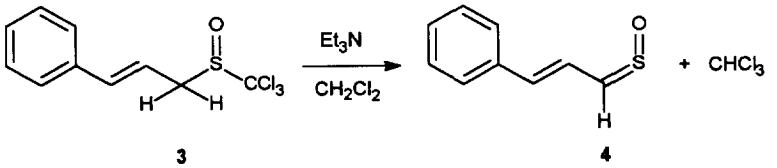
Because of the growing importance of vinyl sulfones in organic synthesis in recent years,[15] and due to our recent interest in allyl trichloromethyl sulfones,[16] we became interested in the preparation of the corresponding vinyl sulfones. The latter were expected to exhibit enhanced reactivity due to the powerful electron withdrawing ability of the trichloromethyl group. To our delight, we have found that unlike allylic aryl sulfones, these sulfones undergo an unusually fast isomerization to vinylic sulfones, even in the presence of weak bases such as triethylamine or 2,6-lutidine.[16] Interestingly, the reaction occurs readily even with cinnamyl trichloromethyl sulfone, in spite of the accompanying loss of conjugation of the double bond with the aromatic ring.



(1)

1a, b **2a, b**

Due to the potential synthetic utility of conjugated vinyl trichloromethyl sulfoxides, and as an obvious extension of the above-mentioned isomerization, we next investigated the analogous isomerization of the readily available allyl trichloromethyl sulfoxides.[3] To our surprise, we found that the reactivity of these compounds is quite different from the allylic sulfones and is highly dependent on substitution. For example, the isomerization of the unsubstituted allyl sulfoxide **1a** proceeds rather slowly and yields the corresponding vinyl sulfoxide **2a** on stirring overnight with one equivalent of Et_3N in CH_2Cl_2 at room temperature (eq. 1). We believe that the reduced rate of isomerization of sulfoxides *vs.* sulfones may be explained by the reduced acidity of the α-hydrogens in the former compounds. A similar explanation may be offered for the further reduction in rate of isomerization observed with the methallyl sulfoxide **1b** to **2b**, which proceeds only to ~50% when a solution of this compound in CH_2Cl_2 in the presence of Et_3N is refluxed overnight.



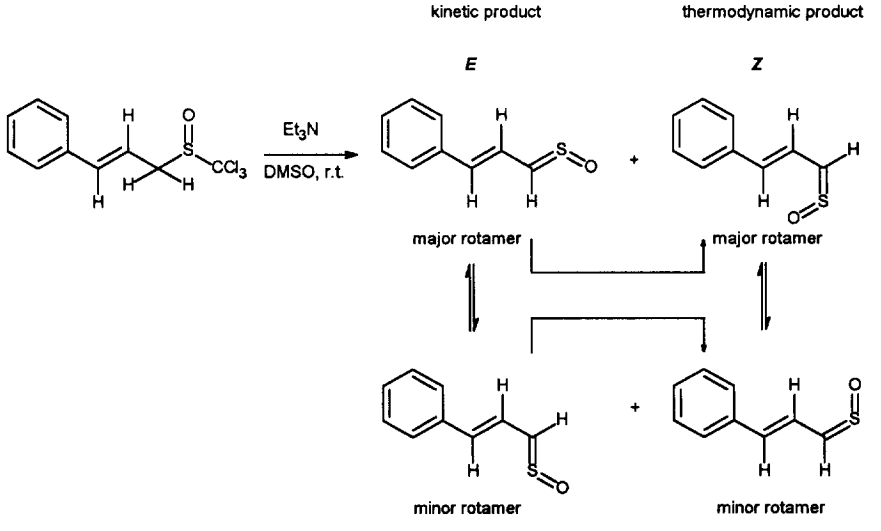
(2)

3 **4**

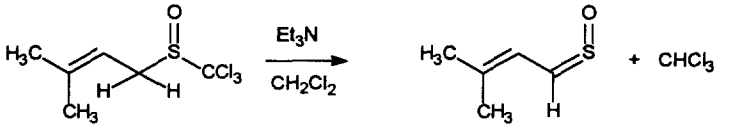
A remarkable effect of substitution has been detected when another allylic derivative, namely cinnamyl trichloromethyl sulfoxide was subjected to similar conditions. Unlike sulfoxides **1a** and **1b**, this sulfoxide (**3**) undergoes an apparently unprecedented β-elimination of chloroform and affords the corresponding thiocinnamaldehyde S-oxide (**4**, eq. 2). Sulfine **4**, the first published α,β-unsaturated thioaldehyde S-oxide, is readily identified by its characteristic ^{1}H NMR absorption at δ 8.71 and can be isolated by column chromatography in 90% yield as a yellow solid. When stored at low temperature, compound **4** is stable for extended periods of time.

As in sulfur dioxide, the CSO group in sulfines is expected to be bent at an angle of about 120°. Consequently, monosubstituted and unsymmetrically disubstituted sulfines should exist as geometrical isomers.[5a] ^{1}H NMR data allow assignment of the (*E*)-(*Z*) stereochemistry, provided that both diastereomers can be observed. To our delight, NMR spectra of **3** in DMSO with Et_3N present revealed the formation of both isomers. Addition of one equivalent of Et_3N results in the appearance of a red-brown solution whose ^{1}H and ^{13}C NMR spectra taken after 15 min indicated the presence of both *E* and *Z* isomers. We have thus been able to establish that sulfine **4** isolated as described above had the (*Z*)-configuration. With time, the NMR signals assigned to the (*E*)-isomer decrease and those assigned to the (*Z*) isomer increase. Due to the complexity of the NMR spectra of **4** in DMSO relative to $CDCl_3$ and due to the presence of both diastereomers, COSY and NOESY techniques had to be used. In the latter spectrum the major cross-peaks for the sulfine protons are due to NOE interactions with the proton β to the functional group (E isomer) or, alternatively with the α-proton (Z isomer). While we cannot see individual conformers due to fast equilibration, relative to the NMR time-scale, at room temperature, these results suggest that the major rotamer for each is as shown in Scheme 1. We belive that the conversion of the kinetic product to the thermodynamic isomer may be explained by an addition-elimination reaction of triethylamine, as previously suggested for arylsulfines.[12b-d]

Scheme 1

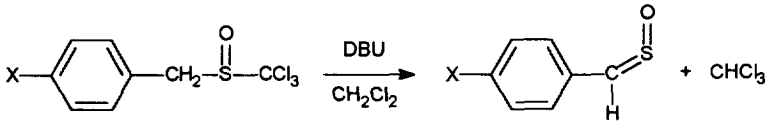


Prompted by these results, and in order to test the application of our new sulfine synthesis to the preparation of other α,β-unsaturated thioaldehyde-S-oxides, we next examined the reactivity of γ,γ-dimethylallyl trichloromethyl sulfoxide (**5**). This compounds, which is easily prepared by the reaction of α,α-dimethylallyl alcohol with Cl_3CSCl,[3b] also undergoes base induced β-elimination of chloroform and affords the corresponding conjugated vinyl sulfine **6**, as expected (eq. 3). Furthermore, by using a stronger base such as DBU instead of Et_3N and a more polar solvent such as DMSO, even allyl sulfoxides such as **1a** and **1b** undergo some elimination of chloroform (5-10%) along with isomerization of the double bond.



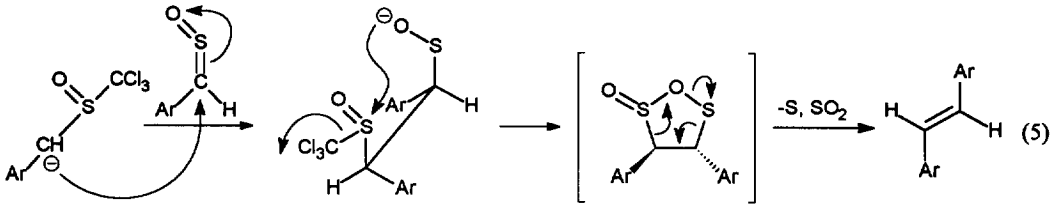
5 **6** (3)

In continuation, and in view of the above-mentioned difficulties involved in the synthesis of thioaldehyde-S-oxides in general, we have tested the reactivity of benzyl (**7a**) and *p*-methoxybenzyl (**7b**) trichloromethyl sulfoxides under basic conditions. Not unexpectedly, with these sulfoxides, Et_3N or DABCO are not sufficiently basic to bring about the elimination of chloroform. However, the use of a stronger base such as DBU results in a fast reaction at room temperature and affords the expected phenyl and *p*-methoxyphenyl sulfines (**8a** and **8b**) respectively, within less than 15 min (eq. 4). It is interesting to note that under ordinary conditions, only one isomer of the two possible stereoisomers could be detected. The Z stereochemistry of this isomer was



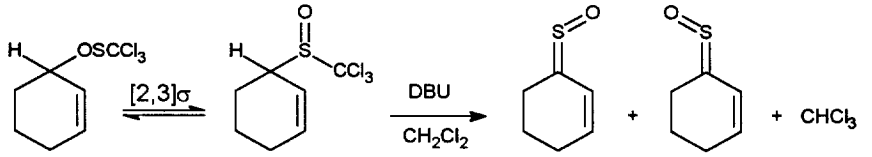
X = H, OMe **7a, b** **8a, b** (4)

determined by comparison of the NMR spectral data with those previously reported by Bonini, who obtained both isomers.[12] Occasionally, in the case of the *p*-methoxybenzyl sulfoxide (**7b**), the reaction with DBU also afforded *trans*-4,4'-dimethoxystilbene as a side product in 20% yield. Formation of the latter can be tentatively explained by a competing reaction of the α-sulfinyl carbanion with **8b**, followed by ring-closure to a five-membered heterocyclic system, with subsequently loss of SO_2 and S to yield the observed product (eq. 5). Attempts to increase the yield of this product by performing the reaction in the presence of added *p*-anisaldehyde has not led to positive results. Therefore we believe that an alternative explanation involving the reaction of the carbanion with an aldehyde moiety is unlikely. One should add that the formation of stilbene by decomposition of phenylsulfine has already been reported before.[12c]



(5)

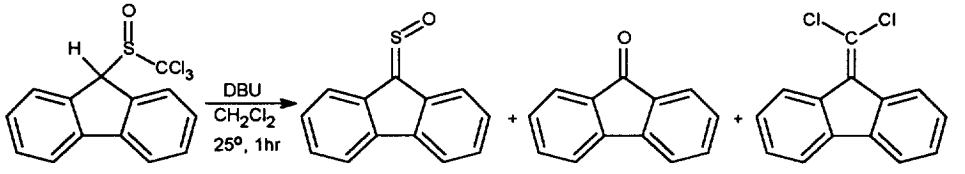
Disubstituted Sulfines: In order to extend the scope of the new method, the synthesis of disubstituted sulfines (thioketone S-oxides) by β-elimination of chloroform has also been investigated. We have thus found that both stereoisomers of 2-cyclohexenylsulfine are readily obtained from the reaction of 2-cyclohexenyl trichloromethyl sulfoxide **9** with DBU at room temperature. It is worthwhile noting that this sulfoxide is formed along with the corresponding sulfenate even if the esterification is carried out at -78° C. Furthermore, although this mixture contains only about 65% of sulfoxide, it can be used directly for the preparation of the sulfine because of the rapid sulfenate-sulfoxide equilibration (eq. 6). The ratio of the E/Z stereoisomers is about 1:1.8 by NMR integration. Synthesis of α,β-unsaturated sulfines, mainly methylated 2-cyclohexenyl sulfines was previously reported by Ramamurthy and coworkers,[17] but no ^{13}C NMR data was provided.



(6)

9 **Z-10** **E-10**

The behavior of 9-fluorenyl trichloromethyl sulfoxide (**11**) under basic conditions is of special interest, since this sulfoxide was found to undergo both β-elimination of chloroform and Ramberg-Bäcklund rearrangement. Thus, treatment of **11** with DBU at room temperature afforded, beside the expected fluorenylidenesulfine (**12**, 52%) and its oxidation product fluorenone (**13**, 36%), the Ramberg-Bäcklund rearrangement product 9-dichloromethylenefluorene (**14**, 12% eq. 7). In fact, the formation of the latter product,



(7)

11 **12** **13** **14**

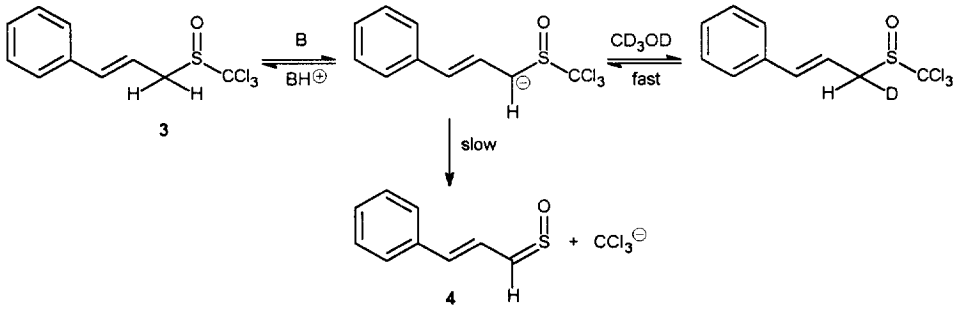
resulting from a competing 1,3-elimination, is not surprising for several reasons. The first one is the study reported by Venier and coworkers[18] on the reaction of the trichloromethyl anion generated by thermolysis of Cl_3CO_2Na with fluorenylidenesulfine in which 9-dichloromethylenefluorene (**14**) was produced in high yield. Formation of this compound has been explained by nucleophilic addition of the trichloromethyl anion to

fluorenylidenesulfine to give the 9-fluorenyl α-sulfinyl carbanion intermediate, followed by cyclization to the corresponding episulfoxide which then loses sulfur monoxide and affords the observed product[18].

Another reason to expect the unusual Ramberg-Bäcklund rearrangement in the sulfoxide series, was our recent discovery of an exceptionally facile Ramberg-Bäcklund rearrangement of fluorenyl trichloromethyl sulfone which occurs at room temperature even in the presence of weak bases such as 2,6-lutidine, and affords dichloromethylenefluorene in quantitative yield.[19]

Reaction Mechanism. In order to establish the mechanistic details of the novel β-elimination of chloroform we first investigated whether the reaction proceeds by a stepwise and reversible E1cB mechanism or alternatively by a concerted E2 process. We have thus found, that on treatment of **3** with Et_3N in the presence of D_2O, the rate of hydrogen-deuterium exchange is faster than the rate of sulfine formation. Interestingly, deuteration of the two diastereopic α-methylene protons in CD_3OD with Et_3N as base proceeded at different rates. The $t_{½}$ of one such hydrogen exchange was *ca.* 11 min and of the other one was *ca.* 37 min, while $t_{½}$ for sulfine formation was *ca.* 80 min. From these results we can assume that the mechanism is (E1cB) rev as suggested in Scheme 3.

Scheme 3



Consistent with this mechanism are also the effects of the base strength and solvent polarity on the reaction rates. Thus, while only deuteration of **3** takes place after 4 days in $CDCl_3$ with a drop of D_2O using DABCO as base, and no elimination occurs even after 15 days in this solvent, sulfine formation is complete after 15 hrs in CH_2Cl_2. Although $CDCl_3$ is more polar than CH_2Cl_2, it forms hydrogen bonds with the base, which reduce the strength of the base. Using a stronger base such as Et_3N in $CDCl_3$, reaction is faster but only 24% sulfine is formed after 15 hours. The same base, however, induces complete conversion to sulfine after 6 hours in CH_2Cl_2 and after 15 minutes in DMSO as solvent. The remarkable effect of the polarity of the solvent provides further support of the E1cB mechanism, since the rate determining step of this mechanism is highly dependent on the carbanion concentration, which in turn is increased by the increase of solvent ionizing power in going from CH_2Cl_2 to DMSO. The use of a stronger base such as DBU may minimize the effect of the solvent considerably. With this base the reaction in CH_2Cl_2, $CDCl_3$ and DMSO takes place at similar rates and is complete within a few minutes in the case of sulfoxide **3**.

The importance of the stability of the carbanion intermediates is further demonstrated by the observed reduction in reaction rate in going from cinnamyl through γ,γ-dimethylallyl to benzyl sulfoxides. The results reported above on the reactivity of allylic and benzylic trichloromethyl sulfoxides under basic conditions also indicate a certain sensitivity of the β-elimination of chloroform to substituent effects and competing reactions. The contrasting results obtained with allyl and cinnamyl sulfoxides under similar conditions are rather remarkable, and may be assigned to thermodynamic factors related to the stability of the double bond in the product. Another competing process discovered in this study is the Ramberg-Bäcklund rearrangement observed with sulfoxide **11**. The enhanced stability of the well-known 9-fluorenyl carbanion is apparently responsible for the competing 1,3-elimination. Competition between 1,2- and 1,3-elimination reactions originating from the same carbanion is not very common.

EXPERIMENTAL

Melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet 60 SXB FTIR. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200, DPX-300 or DMX-600 spectrometers in either $CDCl_3$ or other deuterated solvents and using TMS as internal standard. Chemical shifts are reported in ppm units, and coupling constants are in Hz. High resolution mass spectra were obtained on a VG-Fison Autospec instrument and other mass spectra on a Finnigan GC/Ms 4021, by using either electronic (EI) or chemical ionization (CI). Column chromatography was performed with Merck silica gel 60 (230-400 mesh), and TLC was run on precoated Merck silica gel plates 60 F254. Dichloromethane was distilled from P_2O_5. Diethyl ether was dried over Na wires. Commercially available chemicals were used without further purification.

Trichloromethanesulfenates, General Procedure. Equimolar quantities of the corresponding alcohol and triethylamine were weighted into a round bottom flask. After addition of anhydrous ether, the flask was cooled in an ice bath, and an equivalent amount of trichloromethanesulfenyl chloride dissolved in dry ether was added gradually during 45 min with stirring. The reaction mixture was kept in the cooling bath for an additional hour, and then transferred to a separatory funnel. The organic layer was washed 3 times with 3% aqueous HCl, 3 times with 5% aqueous $NaHCO_3$, and again 3 times with water. After drying over anhydrous $MgSO_4$, filtration and evaporation of the ether, the desired product was obtained. In certain cases such as allyl and α,α-dimethylallyl esters, spontaneous [2,3]-sigmatropic rearrangement to the appropriate sulfoxide occurred.

***trans*-1-Propenyl Trichloromethyl Sulfoxide (2a).** A solution of 200 mg (1 mmole) of allyl trichloromethyl sulfoxide[3] in 10 mL CH_2Cl_2, was treated with 0.15 mL (1 mmole) triethylamine and allowed to react overnight. After 15 hours, the reaction mixture was transferred to a separatory funnel, and was washed 3 times with 5 mL portions of each 3% aqueous HCl, 5% aqueous $NaHCO_3$, and once with water and brine. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give 192 mg (96% yield) of *trans*-1-propenyl trichloromethyl sulfoxide (**2a**). IR (KBr): 1097 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$), δ 6.85 (dq, J = 15.2, 6.8 Hz, 1H, H_β), 6.45 (dq, J = 15.2, 1.5 Hz, 1H, H_α), 2.05 (dd, J = 6.8, 1.5 Hz, 3H, Me); ^{13}C

NMR (200 MHz, $CDCl_3$), δ 144.50 ($CH_3\underline{C}H$), 129.69 (CHS(O)), 107.22 (CCl_3), 18.28 (CH_3); MS (CI/CH_4): m/e 211 (MH^+, 32%), 209 (MH^+, 100%), 207 (MH^+, 97%), 90 (MH^+ -CCl_3, 10%), 74 (MH^+ -CCl_3, -O, 35%); HRMS (Elemental composition): calc. ($C_4H_6OSCl_3$, MH^+) 206.9204, obs., 206.9230.

2-Methyl 1-Propenyl Trichloromethyl Sulfoxide (2b). A solution of 200 mg (0.9 mmole) of methallyl trichloromethyl sulfoxide[3] in 10 mL CH_2Cl_2, was treated with 0.13 mL (0.9 mmole) triethylamine and heated under reflux for 3 days. Isolation of the product as described above for **2a** afforded 184 mg (92% yield) of 2-methyl 1-propenyl trichloromethyl sulfoxide **(2b)**. IR (KBr): 1090 cm^{-1} (S=O); ^1H NMR (200 MHz, $CDCl_3$), δ 6.04 (m, 1H, H_α), 2.13 (d, J = 0.65 Hz, 3H, Me), 2.03 (d, J = 0.56 Hz, 3H, Me); ^{13}C NMR (200 MHz, $CDCl_3$), δ 157.58 ($(CH_3)_2C$), 126.54 (=C), 108.23 (CCl_3), 26.42 (CH_3), 21.15 (CH_3); MS (EI): m/e 224 (M^+, 2.0%), 222 (M^+, 6.5%), 220 (M^+, 6.0%), 121 (CCl_3, 7.0%), 119 (CCl_3, 23.0%), 117 (CCl_3, 24.0%), 103 (M^+ -CCl_3, 100%); HRMS (Elemental composition): calc. ($C_5H_8OSCl_3$, MH^+) 220.9361, obs., 220.9400

***Z*-(*E*-Styryl)sulfine (4a).** A solution of 200 mg (0.7 mmole) of cinnamyl trichloromethyl sulfoxide[3] in 10 mL CH_2Cl_2, was treated with 160 mg (1.40 mmole) DABCO and allowed to react in the dark overnight. After 15 hours, the reaction mixture was transfered to a separatory funnel, and was washed 3 times with 5 mL portions of each 3% aqueous HCl, 5% aqueous $NaHCO_3$, and once with water and brine. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was separated by column chromatography (silica gel, ethyl acetate/hexane 5:95). Crystallization from chloroform/pentane gave the pure product (104 mg, 90% yield). M.p. 67-69 °C; IR (neat): 1076 cm^{-1} (S=O); ^1H NMR (300 MHz, $CDCl_3$): δ 8.71 (dd, J = 11.2, 0.8 Hz, 1H, CHSO), 7.77 (dd, J = 15.9, 11.2 Hz, 1H, H_α), 7.57 (m, 2H, *o*-H's), 7.38 (m, 3H, *m* + *p* - H's), 7.03 (bdd, J = 15.9, 0.8 Hz, 1H, C_β); ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.56 (C=S=O), 137.41 (C_β), 135.31 (ipso), 130.20 (C*m*), 129.05 (C*p*), 128.15 (C*o*), 118.0 (C_α); MS (CI/i-Bu): m/e 165 (MH^+, 100%); HRMS (Elemental composition): calc. (C_9H_8OS, M^+) 164.0295, obs., 164.0290.

***Z*-(*E*-Styryl)sulfine (4a) + *E*-(*E*-Styryl)sulfine (4b).** A solution of 25 mg (0.088 mmole) of cinnamyl trichloromethyl sulfoxide[3] dissolved in 1 mL DMSO-d_6, in an NMR tube, was treated with 12 μL (0.088 mmole) Et_3N. The color of the solution turned red, and the spectrum was taken after 15 minutes. The data assigned to each stereoisomer are as follows: **(4a)** ^1H NMR (600 MHz, DMSO): δ 9.42 (bd, J = 11.0 Hz, 1H of CHSO), 7.68 (m, 2H, *o*-H's), 7.67 (dd, J = 15.9, 11.0 Hz, 1H, Hα), 7.42 (m, 3H, *m* + *p* - H's), 7.28 (bd, J = 15.9, 1H, H_β); ^{13}C NMR (600 MHz, DMSO): δ 172.44 (C=S=O), 137.54 (C_β), 135.08 (ipso), 130.10 (C*m*), 129.07 (*p*), 128.12 (*o*), 117.63 (C_α); **(4b).** ^1H NMR (600 MHz, DMSO): δ 9.86 (bd, J = 12.9 Hz, 1H of CHSO), 7.63 (m, 2H, *o*-H's), 7.46 (dd, J = 15.0, 12.9 Hz, 1H, H_α) 7.39 (m, 3H, *m* + *p* - H's), 7.06 (bd, J = 15.0 Hz, 1H, H_β); ^{13}C NMR (600 MHz, DMSO): δ 182.57 (C=S=O), 137.59 (Cβ), 135.72 (ipso), 129.32 (C*m*), 128.91 (C*p*), 127.41 C*o*), 118.78 (Cα);

***Z*-β,β-Dimethylvinylsulfine (6a).** A solution of 200 mg (0.8 mmole) of γ,γ-dimethylallyl trichloromethyl sulfoxide[3] dissolved in 20 mL of CH_2Cl_2 was treated with 130 μL of DBU (0.8 mmole). The color of the solution turned red. After 15 hours, the reaction mixture was transfered to a separatory funnel, and was washed 3 times with 5 mL portions of each 3% aqueous HCl, 5% aqueous $NaHCO_3$, and once with water and brine. The crude mixture was separated by column chromatography (silica gel, ethyl acetate/hexane 5:95), to give 98 mg of a yellow liquid with a repulsive odor (88% yield). IR (neat): 1096 cm^{-1} (S=O); ^1H NMR (300 MHz, $CDCl_3$): δ

8.70 (bd, J = 11.8 Hz, 1H, CHSO), 6.99 (dspt, J = 11.8, 1.2 Hz, 1H, H_α), 1.95 (dqnt, J = 1.2, 0.6 Hz, 3H, Me), 1.89 (dqnt, J = 1.2, 0.6 Hz, 3H, Me); ^{13}C NMR (300 MHz, $CDCl_3$): δ 168.26 (C=S=O), 146.23 ($\underline{C}(CH_3)_2$), 116.86 (CH), 26.48 (CH_3), 20.30 (CH_3); MS (EI): m/e 116 (M^+, 69%), 99 (M^+ -OH, 100%), 101 (M^+ -CH_3, 76%), 67 (M^+ -HSO, 26%); HRMS (Elemental composition): calc. (C_5H_9OS, MH^+) 117.0374, obs., 117.028. In order to observe both isomers **6a** and **6b.** A solution of 10 mg (0.042 mmole) of γ,γ-dimethylallyl trichloromethyl sulfoxide[3b] dissolved in 1 mL DMSO-d_6, in an NMR tube, was treated with 3 μL (0.021 mmole) DBU. The color of the solution turned red, and spectrum was taken after 10 minutes. By NMR integration the mixture contained 90% of **6a** and 10% of **6b.** Consequently, some of the peaks of the latter compound could not be assigned. **(6a).** ^{1}H NMR (600 MHz, DMSO): δ 9.46 (bd, J = 11.8 Hz, 1H of CHSO), 6.82 (dspt, J = 11.8, 1.3 Hz, 1H, H_α), 1.92 (bs, 3H, Me), 1.90 (bs, 3H, Me); ^{13}C NMR (600 MHz, DMSO): δ 169.54 (C=S=O), 147.37 ($\underline{C}(CH_3)_2$), 116.13 (CH), 25.96 (CH_3), 18.89 (CH_3); **(6b).** ^{1}H NMR (600 MHz, DMSO): δ 9.95 (bd, J = 13.3 Hz, 1H of CHSO), 6.36 (dspt, J = 13.3, 1.2 Hz, 1H, H_α); ^{13}C NMR (600 MHz, DMSO): δ 179.71 (C=S=O), 118.06 (CH);

***Z*-Phenylsulfine (8a).** A solution of 200 mg (0.8 mmole) of benzyl trichloromethyl sulfoxide[20] in 10 mL CH_2Cl_2, was treated with 0.1 mL (0.8 mmole) DBU. The color of the solution turned yellow, and after one hour of sirrining at room temp., the reaction mixture was washed 3 times with 5 mL portions of each 3% aqueous HCl, 5% aqueous $NaHCO_3$, and once with water and brine. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. to give 104 mg of products. By NMR integration the mixture contained 90% of (8a) and 10% benzaldehyde. The spectral data of the former were consistent with the data published in the literature[12]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (s, 1H, CHSO), 8.08 (dd, J = 9.4, 2.0 Hz, 2H, *o*-H's), 7.35 (m, 3H, *m* + *p* - H's);

Reaction of *p*-Methoxybenzyl Trichloromethyl Sulfoxide with DBU. A solution of 25 mg (0.087 mmole) of *p*-methoxybenzyl trichloromethyl sulfoxide[20] dissolved in 1 mL CD_2Cl_2, in an NMR tube, was treated with 13 μL (0.087 mmole) DBU. The color of the solution turned yellow, and the spectrum was taken after 15 minutes. By NMR integration the mixture contained 52% of **8b**, 28% *p*-anisaldehyde and 20% of *trans-p*-methoxystilbene.

***Z*-*p*-Methoxyphenylsulfine (8b).** ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.24 (s, 1H of CHSO), 8.09 (d, J = 9.0 Hz, 2H, *o*-H's), 6.92 (d, J = 9.0 Hz, 2H, *m*-H's), 3.86 (s, 3H, methoxy); ^{13}C NMR (300 MHz, CD_2Cl_2): δ 166.05 (C=S=O), 162.20 (*p*), 131.63 (*o*), 114.35 (*m*), 126.89 (*ipso*), 55.48 (methoxy); MS (DCI/CH_4): m/e 169 (MH^+, 44%), 121 (MH^+-SO, 100%). HRMS (Elemental composition) calc. ($C_8H_9O_2S$) 169.0323, obs., 169.0300, ***trans*-*p*-Methoxystilbene.** ^{1}H NMR (300 MHz, CD_2Cl_2): 7.42 (d, J = 9.0 Hz, 4H, *o*-H's), 6.92 (s, 2H, olef. H), 6.88 (d, J = 9.0 Hz, 4H, *m*-H's), 3.82 (s, 6H, methoxy); ^{13}C NMR (300 MHz, CD_2Cl_2): δ 159.09 (*p* to the stilbene), 130.55 (ipso to the stilbene), 127.43 (C*o*), 126.25 (HC=CH), 114.16 (*m* to the stilbene), 55.33 (methoxy);

2-Cyclohexen-1-yl Trichloromethanesulfenate + 2-Cyclohexen-1-yl Trichloromethyl Sulfoxide (9). Starting from 2-Cyclohexen-1-ol (500 mg, 5.1 mmole), trichloromethanesulfenyl chloride (947 mg, 5.1 mmole) and triethylamine (0.7 mL, 5.1 mmole), and using the general procedure for the preparation of trichloromethanesulfenates, 1.084 g (86% yield) of 2-cyclohexen-1-yl trichloromethanesulfenate in equilibrium with 2-cyclohexen-1-yl trichloromethyl sulfoxide were obtained. By NMR integration the mixture contained 53%

ester and 47% sulfoxide. The spectral data of the ester are as follows: ^{1}H NMR (200 MHz, $CDCl_3$), δ 6.03 (dt, J = 10.0, 3.0 Hz, 1H, H_3), 5.97 (ddt, J = 10.0, 3.0, 1.5 Hz, 1H, H_2), 4.82 (m, 1H, H_1), 2.30-1.55 (m, 6H, H_4 + H_5 + H_6); ^{13}C NMR (200 MHz, $CDCl_3$), δ 133.71 (C_3), 125.68 (C_2), 101.35 (CCl_3), 83.91 (C_1), 29.44 (C_6), 25.10 (C_4), 18.14 (C_5); The spectral data for the sulfoxide are as follows: ^{1}H NMR (200 MHz, $CDCl_3$), δ 6.28 (dtd, J = 10.0, 3.5, 1.5 1H, H_3), 5.80 (ddt, J = 10.0, 4.5, 2.0 Hz, 1H, H_2), 3.95 (m, 1H, H_1), 2.30-1.55 (m, 6H, H_4 + H_5 + H_6); ^{13}C NMR (200 MHz, $CDCl_3$), δ 136.20 (C_3), 118.86 (C_2), 107.47 (CCl_3), 58.53 (C_1), 25.90 (C_6), 24.35 (C_4), 19.52 (C_5); MS (DCI/CH_4): m/e 211 (MH^+-HCl, 19%), 213 (13%), 175 (MH^+-Cl, -HCl, 9%), 177 (3%), 81 (MH^+-$HOSCCl_3$, 88%). HRMS (Elemental composition) calc. ($C_7H_9OSCl_2$, MH^+-HCl) 210.9751, obs., 210.9800.

***Z*-(2-Cyclohexen-1-yl)sulfine (*Z*-10) + *E*-(2-Cyclohexen-1-yl)sulfine (*E*-10).** A solution of 500 mg (2 mmole) of 2-cyclohexen-1-yl trichloromethyl sulfoxide in equilibrium with 2-cyclohexen-1-yl trichloromethanesulfenate dissolved in 10 mL CH_2Cl_2, was treated with 0.3 mL (2 mmole) DBU. The color of the solution turned red, and after one hour of sirrining at room temp., the reaction mixture was transfered to a separatory funnel, and was washed 3 times with 5 mL portions of each 3% aqueous HCl, 5% aqueous $NaHCO_3$, and once with water and brine. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. to give 215 mg (83% yield) of both isomeric sulfines. By NMR integration the mixture contained 65% of *Z*-(2-cyclohexen-1-yl)sulfine and 35% of *E*-(2-cyclohexen-1-yl)sulfine. H_5 could not be assigned due to the complexity of the spectrum. MS (CI/NH_3) (both isomers): m/e 145.9 (MNH_4^+, 100%), 128.9 (MH^+, 47%). HRMS (Elemental composition) calc. (C_6H_9SO) 129.0374, obs., 129.0420. **(Z-10).** ^{1}H NMR (200 MHz, $CDCl_3$), δ 7.28 (dt, J = 10.0, 2.0 Hz, 1H, H_2), 6.35 (dt, J = 10.0, 4.5 Hz, 1H, H_3), 2.56 (m, H_6), 2.25 (m, H_4); ^{13}C NMR (200 MHz, $CDCl_3$), δ 184.74 (C_1), 137.10 (C_3), 120.22 (C_2), 26.69 (C_4), 23.67 (C_6), 22.12 (C_5); **(E-10).** ^{1}H NMR (200 MHz, $CDCl_3$), δ 6.48 (dt, J = 10.0, 2.0 Hz, 1H, H_2), 6.16 (dt, J = 10.0, 4.5 Hz, 1H, H_3), 3.00 (m, 2H, C_6), 2.25 (m, 2H, H_4); ^{13}C NMR (200 MHz, $CDCl_3$), δ 191.13 (C_1), 134.85 (C_3), 119.81 (C_2), 25.90 (C_4), 24.28 (C_6), 20.34 (C_5);

9-Fluorenyl Trichloromethanesulfenate. Using the general procedure for the preparation of trichloromethanesulfenates, except for allowing the reaction mixture to stir for 5 hours at room temperature, and starting with 9-hydroxyfluorene (1.00 g, 5.5 mmole), trichloromethanesulfenyl chloride (1.02 g, 5.5 mmole) and triethylamine (0.8 mL, 5.5 mmole), 1.56 g (86%) of 9-fluorenyl trichloromethanesulfenate were obtained. The latter was purified by chromatography (silica gel, ethyl acetate/hexane 10:90) and crystallized from CCl_4. M.p. 116-118 °C IR (neat) 935 cm^{-1} (O-S); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (dt, J = 7.2, 0.6 Hz, 2H, H_4+H_5), 7.68 (bd, J = 7.0 Hz, 2H, H_1+H_8), 7.38 (td, J = 7.4, 1.1 Hz, 2H, H_3+H_6), 7.29 (td, J = 7.4, 1.2 Hz, 2H, H_2+H_7), 6.29 (bs, 1H, H_9); ^{13}C NMR (300 MHz, $CDCl_3$): δ 141.62 (ipso α to C_4 and C_5), 140.59 (ipso α to C_1 and C_8), 130.11 (C_1 and C_8), 127.91 (C_3 and C_6), 125.59 (C_2 and C_7), 100.62 (CCl_3), 89.44 (C_9); MS (DCI/NH_3): m/e 354 (MNH_4^+, 3%), 352 (MNH_4^+, 37%), 350 (MNH_4^+, 95%), 348 (MNH_4^+, 100%), 165 (M^+-$OSCCl_3$, 67%); HRMS (Elemental composition): calc. ($C_{13}H_9^+$) 165.0704 obs., 165.0710. HRMS (Elemental composition): calc. (Cl_2CSOH^+) 130.9125 obs., 130.9120. These products are believed to arise by rearrangement of the obtained material, prior to fragmentation[20].

9-Fluorenyl Trichloromethyl Sulfoxide (11). A solution of 1.0 g, (3.015 mmole), of 9-fluorenyl trichloromethanesulfenate dissolved in 50 mL of CCl_4 was refluxed over anhydrous K_2CO_3 for 4 hours. Filtration

of the solution and evaporation of the solvent gave 0.92 g (92% yield) of 9-fluorenyl trichloromethyl sulfoxide. The latter was crystallized from CCl_4. M.p. 138-140 °C; IR (neat): 1100 cm^{-1} (S=O); ^1H NMR (300 MHz, $CDCl_3$): δ 7.80, 7.76, 7.74, 7.67 (m, 4H, H_1, H_4, H_5, H_8), 7.48, 7.46 (tm, J = 7.5 Hz, 2H, H_3, H_6), 7.37, 7.35 (td, J = 7.5, 1.5 Hz, 2H, H_2, H_7), 5.45 (bs, 1H, H_9); ^{13}C NMR (300 MHz, $CDCl_3$): δ 142.25 (ipso α to C_5), 142.02 (ipso α to C_4), 137.63 (ipso α to C_8), 133.73 (ipso α to C_1), 120.51 (C_5), 120.41 (C_4), 107.83 (CCl_3), 67.93 (C_9), 129.71, 129.43, 129.10, 127.83, 126.22, (C_1, C_2, C_3, C_6, C_7, C_8); MS (DCI/CH_4): m/e 202 (9-chlorofluorene, 3%), 200 (9-chlorofluorene, 8%), 165.07 (M-$SOCCl_3$, 100%), 131.90 (Cl_2CSO, 1%), 129.90 (Cl_2CSO, 2%). HRMS (Elemental composition) calc. ($C_{13}H_9Cl$) 200.0392, obs., 200.0390. HRMS (Elemental composition) calc. ($COSCl_2$) 129.9046, obs., 129.9030. These products are believed to arise by a thermal and unusual rearrangement of the obtained material, by a similar mechanism to the previously observed rearrangement of trichloromethanesulfenates[20]. This subject is now under further examination.

Reaction of 9-Fluorenyl Trichlorometyl Sulfoxide with DBU. A solution of 500 mg (1.5 mmole) of 9-fluorenyl trichlorometyl sulfoxide in 30 mL of CH_2Cl_2, was treated with 0.2 mL (1.5 mmole) of DBU. The color of the solution turned red. After one hour, the reaction mixture was transfered to a separatory funnel, and was washed 3 times with 15 mL portions of each 3% aqueous HCl, 5% aqueous $NaHCO_3$, and once with water and brine. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give 300 mg of products. By NMR integration the mixture contained 12% of dichloromethylenefluorene, 52% of fluorenylidensulfine and 36% fluorenone. The crude mixture was separated and purified by chromatography (silica gel, ethyl acetate/hexane 5:95) to give the three products mentioned above whose spectral were consistent with the data published in the literature e.g.: **Fluorenone.** M.p. 82-84 °C (lit[21] m.p. 84°C) **Fluorenylidensulfine.** M.p. 110-112 °C (lit[22] m.p. 111.0-111.8 °C); ^1H NMR (300 MHz, $CDCl_3$): δ 8.64 (dm, J = 7.6 Hz, 1H, H_1), 7.66 (dm, J = 7.6 Hz, 1H, H_8), 7.58, 7.56 (m, 2H, H_4, H_5), 7.43 (m, 1H, H_3), 7.36 (m, H_7), 7.30 (m, H_2), 7.17 (m, H_6); **Dichloromethylenefluorene.** M.p. 130-132 °C (lit[23] m.p. 130-132 °C); ^1H NMR (300 MHz, $CDCl_3$) :δ 8.3 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.3 (t, J = 7.2Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 140.1, 136.4, 134.1 (Ar_2C=), 129.0, 127.4, 125.7, 122.2 (=CCl_2), 119.5;

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