Monatshefte für Chemie 136, 543–551 (2005)
DOI 10.1007/s00706-004-0245-z

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Carbon *vs.* Sulfur Addition of Nucleophiles to Sulfines. Part I. The Case of Sulfinates

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Received June 8, 2004; accepted (revised) July 22, 2004
Published online November 24, 2004

Summary. The nucleophilic substitution of chlorine in chlorosulfines with arylsulfinates leads to sulfonylsulfines with complete inversion of configuration within the starting sulfines. A mechanism for this displacement reaction is proposed. The sulfonylsulfines show good reactivity as heterodienophiles and the reaction with acyclic 1,3-dienes is surprisingly regio- and diastereoselective. The stereochemical details were established by X-ray crystallography and the competitive dienophilic properties were examined.

Keywords. Sulfines; *Ab initio* calculations; Hetero-*Diels-Alder*; 1,3-Dienes; Thiopyran-*S*-oxides.

Introduction

Sulfines with the general formula **1** are attractive heterocumulenes that participate in the thioepoxidation of alkenes [1], in nucleophilic additions [2], and in cycloaddition reactions [3]. Several routes have been developed for the synthesis of sulfines. The most important routes to these sulfur-centered heterocumulenes are oxidation of thiocarbonyl compounds with peracids [3], ozone [4], or singlet oxygen [5]. The reactions of sulfines with nucleophiles have attracted considerable interest because the attack of the nucleophiles can either occur in a thiophilic or carbophilic fashion (path a or b, *cf.* Scheme 1), depending on the structures of both sulfines and nucleophiles [2]. Nucleophilic reactions at the sulfine carbon atom (path b) occur only when the sulfine carbon atom bears a potential leaving group [6]. Therefore, chlorosulfines are expected to be the substrates of choice for carbophilic reactions. Displacement of chlorine in these sulfines would provide a new synthetic route to substituted sulfines with either retention or inversion of

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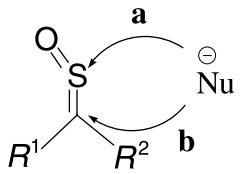

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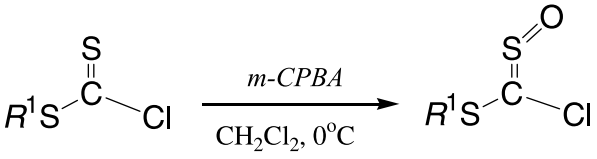
Scheme 1



2 **(Z)-3**

Scheme 2

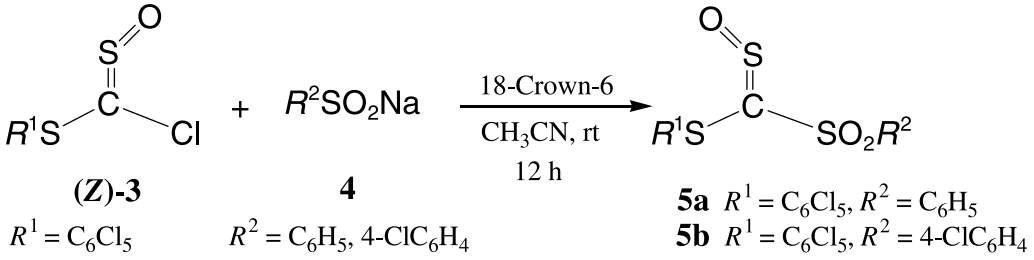
configuration at the sulfine moiety. In a previous paper [7] we have shown that the oxidation of aryl chlorodithioformates by *meta*-chloroperbenzoic acid (*m-CPBA*) leads to a stereoselective synthesis of the corresponding chlorosulfines with (*Z*)-geometry (*cf.* Scheme 2). As part of our ongoing studies of the synthesis and reactivity of sulfines [7–9], we were interested in the stereochemical pathway in which the nucleophiles attack chlorosulfines **3** (path a or b).

We have chosen the arylsulfinates as nucleophiles for the present study because the dienophilicity of sulfines strongly depends on the nature of the substituents at the sulfine carbon atom [10], and the introduction of the sulfonyl group adjacent to the sulfine moiety would enhance the reactivity of the resulting sulfines towards the cycloaddition reactions. Moreover, sulfonyl sulfines have scarcely been mentioned in literature despite their potential synthetic applications [9, 11]. In addition, we wished to examine the cycloaddition and regiochemistry of the reactions of the new sulfonylsulfines **5** with unsymmetrical 1,3-dienes as well as the competitive dieneophilicity of sulfines **5** compared to that of sulfines **3**.

Results and Discussion

The required chlorosulfine **3** used in this study was readily obtained in 92% yield by oxidation of the corresponding pentachlorophenyl chlorodithioformate **2** with *m-CPBA* [7] according to Scheme 2.

The displacement reaction was performed in acetonitrile by using crown ether (18-Crown-6) as solubilizing agent [12] for the sodium sulfinates **4**, the reaction with **3** could be accomplished at room temperature in a homogeneous reaction mixture after 12 hours to afford the sulfonylsulfines **5** in fairly good yields according to Scheme 3. To our delight the NMR and TLC analysis of the crude **5** showed that sulfines **5** were formed as a single stereoisomer and we have seen no evidence for two isomers. Moreover, the new sulfonylsulfines **5** are stable compounds under reaction conditions of the displacement. They could be isolated



Scheme 3

by chromatography as compared with the structurally related sulfenes reported by *Opitz et al.* [13].

However, when we tried the same reaction with a less bulky chlorosulfine, such as chloro(phenylthio)sulfine [*Ph*S(C=S=O)Cl], we were unable to isolate the corresponding sulfine, most likely due to the rapid reaction of the initially formed sulfine with sulfinate resulting in a reduction of the sulfine group. This observation is consistent with what had been observed earlier in analogous cases [3e]. Therefore, we believe that the presence of a bulky substituent at the sulfine moiety contributes significantly to the enhancement of the stability of **5**. Special attention was paid to the ^{13}C NMR spectroscopic characterization of **5** compared to **3**. A comparison of $\delta_{C=S=O}$ of **5** (182.13 ppm for **5a** and 181.93 for **5b**) and **3** (171.22 ppm) shows the effect of the strongly electron-withdrawing sulfonyl group of **5** on one hand and the shielding influence of the chlorine atom of **3** on the other hand. Furthermore, the IR spectra show strong bands at $\bar{\nu} = 1080$, 1145 cm^{-1} for **5a** and 1079, 1147 cm^{-1} for **5b** in the region for sulfines symmetric and asymmetric stretching. We were able to obtain pale yellow single crystals of sulfine **5b** and its structure and the non-linearity of the >C=S=O system were finally established by X-ray crystallographic analysis. It also confirmed that sulfine **5b** is the (*E*)-diastereomer, thus avoiding the steric and electronic repulsions expected for the (*Z*)-diastereomer (Fig. 1). The lengths of the >C=S and S=O

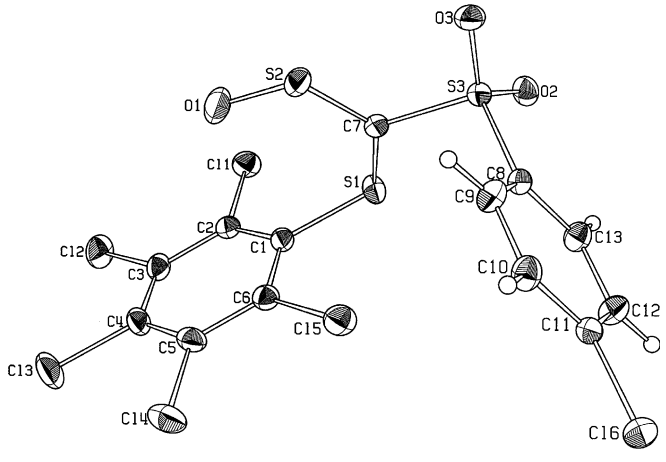
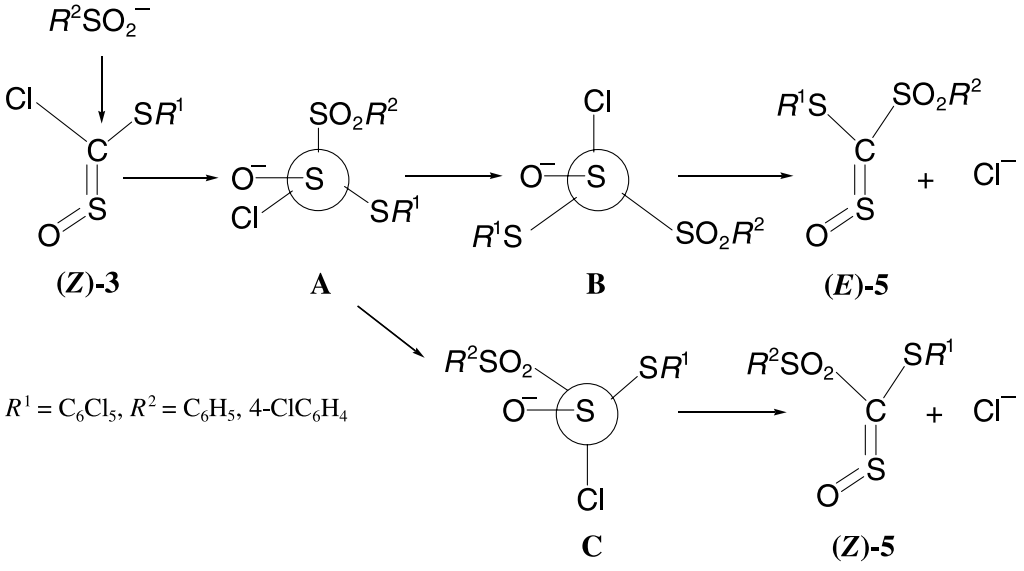


Fig. 1. Crystal structure of sulfine **5b** with 50% probability ellipsoids

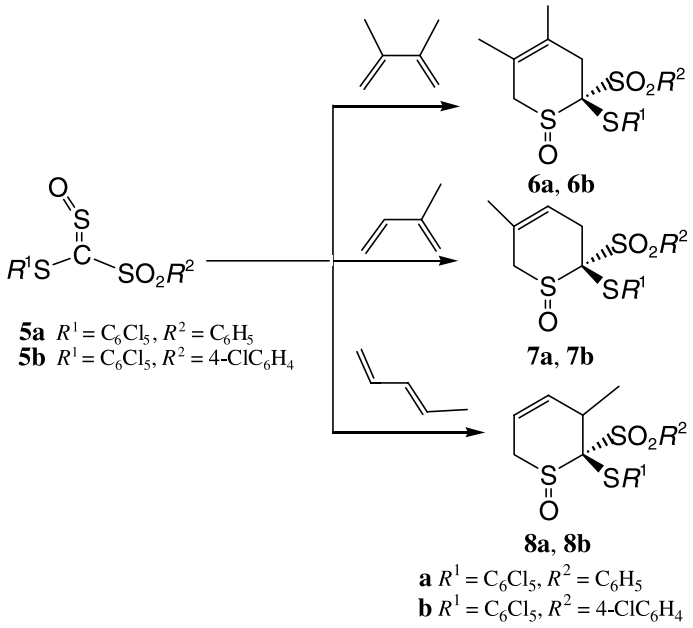
bonds were found to be 1.64 and 1.47 Å, they fall within the usual range for the analogues groups in sulfines [14]. In order to rationalize the observed (*E*)-selectivity we performed *ab initio* calculations with the G98W suite of programs [15]. The geometry of the (*Z*) and (*E*) diastereomers were optimized at the HF/3-21G(d) level. Single point energy calculations were performed at the HF/6-31 + G(d)/HF/3-21G(d) level. Indeed, the results obtained indicate that the (*E*)-diastereomer is thermodynamically more stable than the (*Z*)-diastereomer by 33.8 kJ mol^{-1}.

From X-ray and the *ab initio* calculations of the sulfine **5b**, it was concluded that the configuration of the starting sulfines is completely inverted in the products. Accordingly, given a displacement of chlorine with complete inversion of configuration we assume that an addition-elimination mechanism is operating. The generally accepted mechanism for this nucleophilic displacement reaction resembles that of the nucleophilic substitution of halogen at activated vinylic carbon [3e, 16]. The incoming sulfinate anion first approaches perpendicularly to the plane of the >C=S double bond of the sulfine group and the chloride anion departs in the same manner. The difference in energy barriers for the competitive rotations in the adduct anions (**A** to **B** *vs*. **A** to **C**, *cf*. Scheme 4), which are needed to move the chlorine into the desired leaving position are small, but apparently large enough to lead to a preference of one route over the other. However, we can not exclude the initial formation of (*Z*)-**5** followed by diastereomerization into the thermodynamically more stable (*E*)-**5** during the reaction and/or work-up. The stereo-chemical course may vary from one involving the formation of one or more anionic intermediates, such as that indicated in Scheme 4, to a concerted mechanism.

The hetero-*Diels-Alder* reaction between **5** and an excess (5 equiv.) of acyclic 1,3-dienes was carried out at room temperature in chloroform forming the



Scheme 4



Scheme 5

corresponding cycloadducts **6**, **7**, and **8** in quantitative yield after 2 hours (*cf.* Scheme 5). The NMR and TLC analysis of the crude materials showed that single diastereomers were obtained. As expected for *Diels-Alder* reactions, the sulfonyl group at the sulfine carbon atom of **5** enhanced the reactivity towards cycloaddition considerably. In addition to 2,3-dimethyl-1,3-butadiene, the unsymmetrical 1,3-dienes, such as 2-methyl-1,3-butadiene and (*E*)-1,3-pentadiene, were studied.

Formation of the single cycloadducts shows that the reaction is regioselective by more than 90%. Such a high degree of regioselectivity in hetero-*Diels-Alder* reactions of sulfines is surprising. It should be noted that, contrary to what was observed earlier in dihydrothiopyrane [17], adducts **6**, **7**, and **8** do not, at least during the work-up, eliminate sulfinic acid R^2SO_2H to any significant extent, nor do they isomerize by elimination-addition of sulfinic acid. In order to gain an insight into the steric course of the cycloaddition reaction, the structure of the crystalline cycloadduct **8b** was determined by X-ray analysis (Fig. 2). It showed that the sulfonyl group and sulfoxide oxygen are in a *trans* position to each other (*i.e.* the electrostatic interaction of the sulfone oxygen atoms and the sulfoxide oxygen will be minimized when these functions are placed in an *anti* position). This implies that during the cycloaddition reaction the stereochemistry present in the sulfine ((*E*)-geometry) is retained in the adduct.

In addition, the competitive dieneophilicity of sulfine **5a** was compared to that of **3** by preparing a mixture of one equivalent of sulfines **3** and **5a** in chloroform and letting them compete for 2,3-dimethyl-1,3-butadiene (one equivalent) at room temperature. The reaction, as monitored by NMR, revealed that the >C=S group of the resulting sulfine **5a** reacts selectively with the diene in the presence of the starting sulfine **3**. No evidence, however, was found for the cycloadduct from the

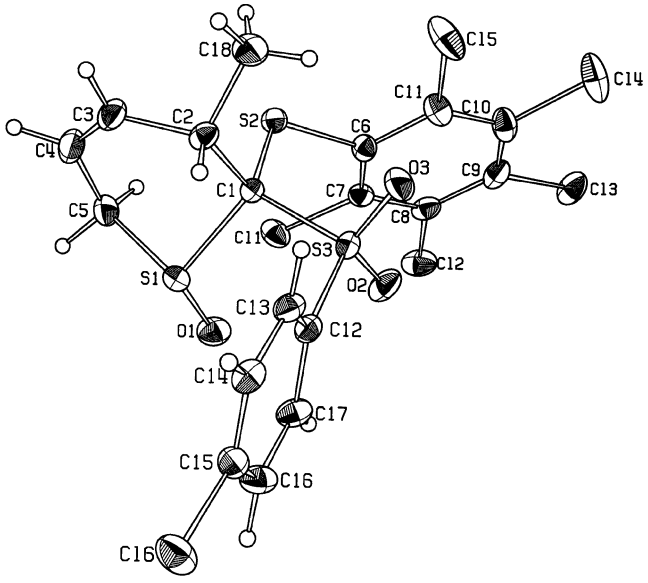


Fig. 2. Crystal structure of the cycloadduct **8b** with 50% probability ellipsoids

reaction between the sulfine **3** and 2,3-dimethyl-1,3-butadiene. This experiment confirms the higher dienophilic reactivity of the sulfonylsulfines **5** in [4 + 2] cycloaddition reactions as compared to the starting sulfines **3**.

In conclusion, the reaction of chlorosulfines with sulfinates provides easy access to new substituted sulfonylsulfines. Kinetic stabilization by sterically demanding groups is clearly a prerequisite. These results indicate that the displacement at the sp^2 carbon atom in the chlorosulfine occurs with complete inversion of configuration. Such substitution reactions at sp^2 centers are not frequently encountered. Sulfines react as dienophiles with 1,3-dienes in a [4 + 2] type cycloaddition reaction to give six-membered ring sulfoxides with high regio- and diastereoselectivity. The study also confirmed the higher reactivity of **5** as a dienophile compared to **3** in [4 + 2] cycloaddition reactions. Further work is underway to investigate the reactivity of sulfines **3** towards other nucleophiles and investigate sulfines **5** in 1,3-dipolar cycloadditions as well as to explore their synthetic utility especially in stereoselective synthesis.

Experimental

All ^1H and ^{13}C NMR experiments ($CDCl_3$) were carried out with a Varian Unity 400 MHz spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C). Chemical shifts are reported in ppm relative to *TMS* using appropriate solvent signals as internal standard. Mass spectra analysis was performed with a Kratos 50 tc spectrometer. The elemental analysis results agreed with the calculated values within experimental error. Melting points were recorded on a *Büchi* melting point apparatus and are uncorrected. TLC was done on Merck Kieselgel F_{254} precoated plates (Merck). Column chromatography was performed with silica gel 60 Fluka, particle size 0.035–0.070 mm (220–440 mesh ASTM) and the eluent is shown in parentheses. Solvents were dried/purified according to literature procedures. Single crystals suitable for X-ray studies from sulfine **5b** and the cycloadduct **8b** were grown in a mixture of CH_2Cl_2 and *n*-hexane (1/3), intensity data were measured at room temperature on a Siemens SMART

CCD diffractometer with a graphite-monochromator. Crystal data for sulfine **5b**; Mo Kα radiation, $\lambda = 0.71073$ Å, cell measurement temperature: 120 K, crystal color: light yellow, crystal system: triclinic, unit cell parameters: $a = 18.772(1)$, $b = 11.6329(8)$, $c = 20.470(1)$ Å, $\alpha = 71.718(1)$, $\beta = 81.993(1)$, $\gamma = 86.943(1)^\circ$, space group *P*-1, cell volume: 882.16(9) Å^3, R_{all}: 0.025, cell formula units *Z*: 2, absorption coefficient: 1.339 mm^{-1}, *F*(000): 512. Crystal data for the cycloadduct **8b**; Mo Kα radiation, $\lambda = 0.71073$ Å, cell measurement temperature: 120 K, crystal color: colourless, crystal shape: orthorhombic, unit cell parameters: $a = 18.772(1)$, $b = 11.6329(8)$, $c = 20.470(1)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90^\circ$, space group *Pbca*, cell volume: 4470(1) Å^3, R_{all}: 0.027, cell formula units *Z*: 2, absorption coefficient: 1.068 mm^{-1}, *F*(000): 2344. Complete X-ray data for compounds **5b** and **8b** were deposited at the Cambridge Crystallographic Data Center under the reference numbers CCDC 226257 and CCDC 226256, copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: int. code +44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk]. The starting pentachlorophenyl chlorodithioformate (**2**) and the corresponding chlorosulfine **3** were prepared according to Refs. [18] and [7].

Phenylsulfonyl(pentachlorophenylthio)sulfine (**5a**, $C_{13}H_5Cl_5O_3S_3$)

Sodium benzene sulfinate (**4a**, 153 mg, 0.93 mmol) was complexed with 18-crown-6 (246 mg, 0.93 mmol) by dissolving it in 25 cm^3 of methanol. After evaporation of the methanol, the complexed sulfinate was added to a solution of 350 mg of **3** (0.93 mmol) in 30 cm^3 of acetonitrile. The resulting solution was stirred for 12 h at room temperature. After concentration of the mixture, the product was passed through celite to remove the salts. The crude sulfine was purified by chromatography (CH_2Cl_2:*n*-hexane = 1:3) to give **5a** as a single isomer. Yellowish white crystals (300 mg, 67%), mp 199°C; IR (KBr): $\bar{\nu} = 1155$, 1343 (ν_{SO_2}), 1080, 1145 ($\nu_{C=S=O}$) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.62$ (m, 2H), 7.75 (m, 1H), 7.99 (d, $J = 8.00$ Hz, 2H); ^{13}C NMR ($CDCl_3$); $\delta = 128.52$, 128.80, 129.40, 129.57, 132.33, 135.05, 136.81, 137.78, 182.13 (>C=S=O) ppm; MS: m/z (%) = 339 (54, M–$C_6H_5SO_2$).

p-Chlorophenylsulfonyl(pentachlorophenylthio)sulfine (**5b**, $C_{13}H_4Cl_6O_3S_3$)

The procedure as given for **5a** was followed starting from 350 mg of **3** (0.93 mmol), 185 mg of sodium *p*-chlorobenzene sulfinate (**4b**, 0.93 mmol), and 246 mg of 18-crown-6 (0.93 mmol). The crude sulfine was purified by chromatography (CH_2Cl_2:*n*-hexane = 1:3) to give **5b** as a single isomer. Yellowish white crystals (295 mg, 61%), mp 232°C; IR (KBr): $\bar{\nu} = 1157$, 1345 (ν_{SO_2}), 1079, 1149 ($\nu_{C=S=O}$) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.59$ (d, $J = 8.40$ Hz, 2H), 7.91 (d, $J = 8.40$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 129.98$, 130.19, 131.15, 132.51, 136.32, 136.69, 136.84, 142.26, 181.93 (>C=S=O) ppm; MS: m/z (%) = 339 (67, M–*p*-$ClC_6H_5SO_2$).

3,6-Dihydro-4,5-dimethyl-2-(phenylsulfonyl)-2-(pentachlorophenylthio)-2H-thiopyran-S-oxide (**6a**, $C_{19}H_{15}Cl_5O_3S_3$)

To a solution of 250 mg of **5a** (0.52 mmol) in 3 cm^3 of chloroform was added an excess of 0.60 cm^3 of 2,3-dimethyl-1,3-butadiene (5.30 mmol). After stirring for 2 h at room temperature, the volatiles were evaporated *in vacuo* and the crude product was crystallized from CH_2Cl_2:diethyl ether (1:3) and cooling overnight gave analytically pure **6a** as colorless crystals (275 mg, 94%), mp 161°C; IR (KBr): $\bar{\nu} = 1150$, 1313 (ν_{SO_2}), 1086 ($\nu_{S=O}$) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.22$ (s, 3H), 1.60 (s, 3H), 2.62 and 3.00 (AB_q, $J = 18.60$ Hz, 2H), 3.72 and 3.96 (AB_q, $J = 15.80$ Hz, 2H), 7.58 (m, 2H), 7.70 (m, 1H), 8.20 (d, $J = 8.40$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.02$, 19.22, 33.92, 54.66, 96.03, 120.53, 126.02, 128.64, 128.80, 131.23, 132.26, 134.84, 135.47, 136.58, 141.26 ppm; MS: m/z (%) = 562 (44, M^+).

3,6-Dihydro-4,5-dimethyl-2-(p-chlorophenylsulfonyl)-2-(pentachlorophenylthio)-2H-thiopyran-S-oxide (**6b**, $C_{19}H_{14}Cl_6O_3S_3$)

The procedure as given for **6a** was followed starting from 250 mg of **5b** (0.48 mmol) and 0.54 cm^3 of 2,3-dimethyl-1,3-butadiene (4.80 mmol). The cycloadduct **6b** was obtained as colorless crystals (265 mg, 92%), mp 174°C; IR (KBr): $\bar{\nu} = 1147$, 1310 (ν_{SO_2}), 1089 ($\nu_{S=O}$) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.19$ (s, 3H), 1.60 (s, 3H), 2.63 and 3.02 (AB_q, $J = 18.60$ Hz, 2H), 3.74 and 4.01 (AB_q, $J = 16.20$ Hz, 2H), 7.55 (d, $J = 8.40$ Hz, 2H), 8.16 (d, $J = 8.40$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.91$, 19.19, 33.69, 54.71, 96.30, 120.77, 125.97, 128.64, 129.03, 129.42, 130.07, 132.77, 134.03, 136.79, 141.97 ppm; MS: m/z (%) = 596 (62, M^+).

3,6-Dihydro-5-methyl-2-(phenylsulfonyl)-2-(pentachlorophenylthio)-2H-thiopyran-S-oxide (**7a**, $C_{18}H_{13}Cl_5O_3S_3$)

The procedure as given for **6a** was followed starting from 250 mg of **5a** (0.52 mmol) and 0.52 cm^3 of 2-methyl-1,3-butadiene (5.20 mmol). After stirring for 2 h at room temperature, the volatiles were evaporated *in vacuo* and the crude product was crystallized from CH_2Cl_2:diethyl ether (1:3) and cooling gave **7a** as colorless crystals (257 mg, 90%), mp 138°C; IR (KBr): $\bar{\nu} = 1156$, 1315 (ν_{SO_2}) 1083 ($\nu_{S=O}$) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.68$ (s, 3H), 2.72 (m, 1H), 3.00 (part of AB_q, $J = 19.20$ Hz, 1H), 3.80 and 3.93 (AB_q, $J = 16.60$ Hz, 2H), 5.04 (m, 1H), 7.60 (m, 2H), 7.72 (m, 1H), 8.20 (d, $J = 7.60$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 23.32$, 27.93, 53.75, 94.81, 118.63, 128.27, 128.70, 131.10, 131.27, 132.42, 134.93, 135.55, 136.85, 141.30 ppm; MS: m/z (%) = 548 (24, M^+).

3,6-Dihydro-5-methyl-2-(p-chlorophenylsulfonyl)-2-(pentachlorophenylthio)-2H-thiopyran-S-oxide (**7b**, $C_{18}H_{12}Cl_6O_3S_3$)

The procedure as given for **6a** was followed starting from 250 mg of **5b** (0.48 mmol) and 0.48 cm^3 of 2-methyl-1,3-butadiene (5.20 mmol). After stirring for 2 h at room temperature, the volatiles were evaporated *in vacuo* and the crude product was crystallized from CH_2Cl_2:diethyl ether (1:3) and cooling gave **7b** as colorless crystals (255 mg, 91%), mp 152°C; IR (KBr): $\bar{\nu} = 1155$, 1313 (ν_{SO_2}), 1085 (ν_{SO}) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.68$ (s, 3H), 2.73 (m, 1H), 3.03 (d, part of AB_q, $J = 18.80$ Hz, 2H), 3.80 (d, part of AB_q, $J = 16.40$ Hz, 1H), 3.99 (d, part of AB_q, $J = 16.40$ Hz, 1H), 5.00 (m, 1H), 7.56 (d, $J = 8.40$ Hz, 1H), 8.16 (d, $J = 8.40$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 23.24$, 27.93, 53.80, 95.28, 118.63, 128.42, 128.60, 129.01, 129.40, 130.06, 132.76, 134.05, 138.45, 142.00 ppm; MS: m/z (%) = 582 (57, M^+).

3,6-Dihydro-3-methyl-2-(phenylsulfonyl)-2-(pentachlorophenylthio)-2H-thiopyran-S-oxide (**8a**, $C_{18}H_{13}Cl_5O_3S_3$)

The procedure as given for **6a** was followed starting from 300 mg of **5a** (0.62 mmol) and 0.62 cm^3 of *trans*-piperylene (6.20 mmol). After stirring for 2 h at room temperature, the volatiles were evaporated *in vacuo* and the crude product was crystallized from CH_2Cl_2:diethyl ether (1:3) to give **8a** as colorless crystals (325 mg, 95%), mp 119°C; IR (KBr): $\bar{\nu} = 1155$, 1311 (ν_{SO_2}), 1090 ($\nu_{S=O}$) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.82$ (d, $J = 7.20$ Hz, 3H), 3.08 (m, 1H), 3.73 (m, 1H), 4.27 (d, part of AB_q, $J = 16.40$ Hz, 1H), 5.52 (d, $J = 10.40$ Hz, 1H), 5.62 (m, 1H), 7.60 (m, 2H), 7.72 (m, 1H), 8.09 (d, $J = 7.60$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.41$, 38.14, 48.15, 96.47, 118.57, 124.75, 129.05, 131.18, 131.93, 133.85, 135.04, 135.61, 136.95, 142.43 ppm; MS: m/z (%) = 548 (45, M^+).

3,6-Dihydro-3-methyl-2-(p-chlorophenylsulfonyl)-2-(pentachlorophenylthio)-2H-thiopyran-S-oxide (**8b**, $C_{18}H_{12}Cl_6O_3S_3$)

The procedure as given for **6a** was followed starting from 250 mg of **5b** (0.48 mmol) and 0.48 cm^3 of *trans*-piperylene (4.80 mmol). After stirring for 2 h at room temperature, the volatiles were evaporated

in vacuo and the crude product was crystallized from CH_2Cl_2:diethyl ether (1:3) to give **8b** as colorless crystals (260 mg, 93%), mp 142°C; IR (KBr): $\bar{\nu} = 1153$, 1312 (ν_{SO_2}), 1089 (ν_{SO}) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.79$ (d, $J = 6.80$ Hz, 3H), 3.10 (m, 1H), 3.75 (m, 1H), 4.30 (d, $J = 15.60$ Hz, 1H), 5.51 (m, 1H), 5.62 (m, 1H), 7.55 (d, $J = 8.40$ Hz, 2H), 8.03 (d, $J = 8.40$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.37$, 28.20, 48.15, 96.65, 118.50, 123.71, 128.04, 129.33, 132.02 132.50, 133.62, 134.07, 142.12, 142.40 ppm; MS: m/z (%) = 582 (38, M^+).

Acknowledgements

The author thanks Prof. *R. Hazell*, Aarhus University, Denmark, for the X-ray structural analysis and Dr. *A. El-Nahas*, El Menoufiea University, Egypt, for performing the computation for sulfine **5**.

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