Diene–dienophile dual reactivity of conjugated vinyl sulfines

Samuel Braverman,* Dan Grinstein and Hugo E. Gottlieb

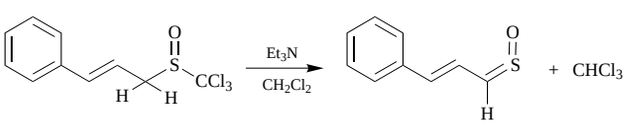
Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel

The discovery of a new and facile synthesis of α,β-unsaturated thioaldehyde *S*-oxides has enabled the exploration of the diene–dienophile reactivity of these novel heterocumulenes. Unlike some previous reports, the addition of (*Z*)-β,β-dimethylvinyl and (*Z*)-β-styryl sulfines to either cyclic or acyclic dienes proceeds in a non-stereospecific manner, yielding three stereoisomers. In contrast, the latter sulfine reacts as a diene with norbornene and other dienophiles to give a single product.

Introduction

Allylic trichloromethyl sulfoxides are readily prepared by the well known [2,3]-sigmatropic rearrangement of the corresponding sulfenates and have played a central role in the discovery and elucidation of the mechanism of this rearrangement.[1] Due to its high stereoselectivity and efficiency, this rearrangement[2] has received extensive applications in organic synthesis and has been used as a key reaction in the total synthesis of various natural products including prostaglandins and leukotrienes.[3]

More than a quarter century after their discovery, the same allylic trichloromethyl sulfoxides have become the source of another significant and striking observation. We have found that these sulfoxides undergo a facile and unexpected base-induced β-elimination of chloroform to afford conjugated vinyl sulfines (Scheme 1).[4] The reaction proceeds smoothly under



Scheme 1

mild conditions. In view of the well known haloform reaction and the α-elimination of chloroform, the lack of previous documented examples of β-elimination of chloroform is rather surprising.

During the past three decades a large variety of substituted sulfines have been reported.[5] However, thus far, conjugated vinyl sulfines have received scarce attention in the literature. They have been prepared by oxidation of the corresponding α,β-unsaturated thiones,[6] by arrangement of vinylsulfinyl carbenes,[7] by oxidation of 2,5-dimethylthiophene with singlet oxygen,[8] and as intermediates in a thermal fragmentation of their formal dimers.[9] A novel synthesis of thiophenes from allenic sulfones involving α,β-unsaturated sulfines as intermediates has also been reported.[10] However, all these routes have a limited scope, and yield disubstituted sulfines only.

Although oxidation of thiocarbonyl compounds is the most general route to sulfines, this method cannot be applied to the synthesis of thioaldehyde *S*-oxides, because the former are not stable. For this reason, this type of sulfine has been studied to a much lesser extent, and their synthesis involves alternative methods.[11,12] For example, Bonini and co-workers[12] have recently demonstrated that silyl thioketones can serve as synthetic equivalents of thioaldehydes, as the silicon substitution can be easily replaced by a proton at a later stage. By application of this concept, the synthesis of various thioaldehyde *S*-oxides, including some aromatic derivatives, could be accomplished. However, as pointed out above, the method reported by us[4] provides an easy and direct access to α,β-unsaturated thioaldehyde *S*-oxides.

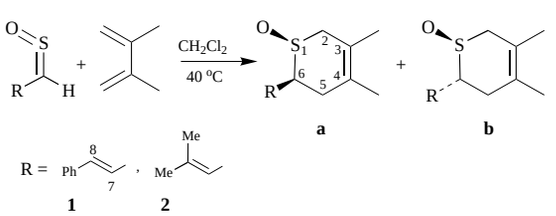
Some of our results on the dual diene–dienophilic reactivity of the novel conjugated vinyl thioaldehyde *S*-oxides are described below.

Results and discussion

Sulfines as dienophiles

Cycloaddition of sulfines with dienes, and especially with 2,3-dimethylbuta-1,3-diene is an important and well-documented reaction[5] which is used to trap sulfines to afford dihydrothiopyran *S*-oxides. For a long time, this reaction has been known to proceed in a stereospecific manner, with full retention of configuration of the sulfine.[5] However, recently Bonini and co-workers[12] have shown that for monosubstituted sulfines such as phenyl sulfine the [4+2] cycloaddition is not stereospecific. The authors rationalized the deviant results by invoking a *Z* to *E* interconversion of sulfines under the conditions of the cycloaddition reaction, and a faster reaction of one of the two stereoisomers, a typical example of the Curtin–Hammett principle. Our results are in full agreement with the observations of Bonini.

We have thus found that heating of γ,γ-dimethylallyl trichloromethyl sulfoxide with 2,3-dimethylbuta-1,3-diene in the presence of Et_3N results in the formation of the *cis*- and *trans*-cycloadducts **2a**,**b** in the ratio of 1:4.5 (Scheme 2). A great



Scheme 2

preference for the more stable *trans* isomer is thus observed, similar to the results obtained by Bonini. In order to rule out the possibility that the initial cycloadduct undergoes epimerization in the presence of base after cycloaddition, we performed a control experiment where each pure stereoisomer of **2** was independently subjected to the initial reaction conditions. Since no further reaction was observed, the stereochemistry is clearly established prior to, and not after, the cyclization.

In addition, the same product ratio was also obtained when the reaction was performed with the isolated, pure (*Z*)-β,β-dimethylvinyl sulfine. This result can be explained by either a fast thermal *Z* to *E* interconversion of the sulfines prior to cycloaddition, or by a non-concerted reaction mechanism, or both.

In the case of (*Z*)-β-styryl sulfine there is again no difference between the products obtained either with isolated (*Z*)-sulfine

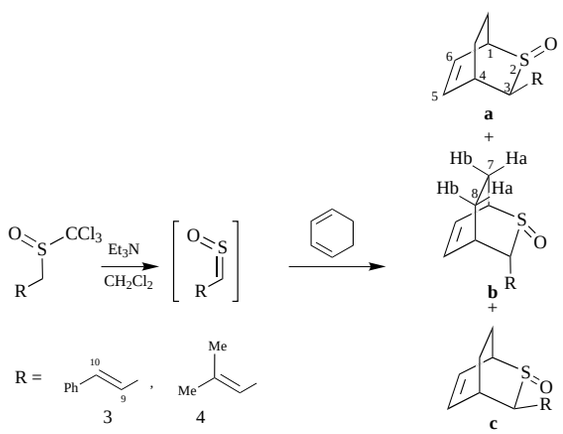
Table 1 ^{1}H and ^{13}C NMR Chemical shifts for compounds **3** and **4**

Proton	**3a**	**4a**	**3b**	**4b**	**3c**	**4c**
1	3.99	3.95	4.24	4.20	4.13	4.07
3	3.37	3.38	3.71	3.73	2.95	2.99
4	2.91	2.75	3.03	2.91	2.98	2.79
5	6.65	6.62	6.74	6.70	6.88	6.85
6	6.17	6.13	6.36	6.32	6.30	6.24
7a	2.71	2.60	1.57	1.51	1.52	1.45
7b	1.56	1.48	1.71	1.70	1.79	1.75
8a	2.14	2.05	1.50	1.47	1.70	1.64
8b	1.36	1.30	1.28	1.24	1.17	1.09
9	6.43	5.39	6.01	4.97	6.18	5.16
10	6.64		6.67		6.81	
Me		1.71		1.76		1.78
Me		1.86		1.80		1.81
o-ArH	7.45		7.39		7.39	
m-ArH	7.31		7.27		7.33	
p-ArH	7.26		7.23		7.27	
Carbon						
1	52.06	51.86[a]	51.67	51.47	52.00	51.78
3	56.38	51.77[a]	66.49	62.16	75.60	70.92
4	36.17	35.00	36.84	36.31	35.78	35.45
5	141.17	141.57	135.60[b]	135.66	138.56	138.22
6	125.67	125.56	126.65	126.63	125.04	124.53
7	13.08	13.02	17.08	17.33	17.47	17.33
8	18.98	18.81	23.72	23.91	17.99	17.88
9	136.58	115.41	135.20[b]	116.95	135.42	117.32
10	128.83	135.01	123.18	138.88	122.73	139.20
Me		18.76		19.06		18.78
Me		26.34		25.93		26.06
i-ArC	136.58		136.43		136.45	
o-ArC	126.74		126.65		126.65	
m-ArC	128.50		128.38		128.81	
p-ArC	127.96		127.80		128.25	

[a] Assignments for these values may be interchanged. [b] Assignments for these values may be interchanged.

or the sulfine generated *in situ* from cinnamyl trichloromethyl sulfoxide. Both cycloadditions to 2,3-dimethylbuta-1,3-diene (DMB) give a ratio of 1 : 1.5 for the *cis*- and *trans*-cycloadducts **1a**,**b** (Scheme 2). The behaviour of this sulfine is therefore analogous to the (*Z*)-β,β-dimethylvinyl sulfine.

In order to check the generality of the non-stereospecific cycloaddition reported above, the reaction with cyclohexa-1,3-diene was also examined. We have thus found that heating either cinnamyl or β,β-dimethylallyl trichloromethyl sulfoxide with cyclohexa-1,3-diene in the presence of Et_3N results in the formation of three stereoisomers of the expected 2-thiabicyclo-[2.2.2]octane *S*-oxide system, namely *exo*,*exo*-, *endo*,*endo*- and *endo*,*exo*- (see Scheme 3). The proportions of the three stereo-



Scheme 3

isomers were *ca*. 10, 60 and 30% respectively, for both vinyl sulfines. These results provide further proof that the cycloaddition reaction is not stereospecific.

Table 2 Proton–proton coupling constants (J_{HH}) for compounds **3** and **4**

Protons	**3a**	**4a**	**3b**	**4b**	**3c**	**4c**
1–5	1.1	1.0	1.2	1.4	1.2	1.4
1–6	7.2	7.1	6.9	7.0	6.6	6.5
1–7a	1.9	2.0	1.5	1.5	1.8	1.3
1–7b	4.0	4.0	5.4	5.3	5.4	6.0
3–4	3.8	2.8	2.0	2.0	2.9	3.0
3–5			0.5	*a*		
3–7a			0.5	*a*		
3–8b	1.6	1.8			1.9	1.8
3–9	9.5	10.0	10.0	10.1	9.0	10.1
4–5	6.8	7.0	7.3	7.4	7.0	7.3
4–6	1.2	1.0	0.8	1.0	0.9	0.9
4–8a	2.7	2.8	2.5	*a*	2.7	3.0
4–8b	3.6	*a*	3.0	*a*	3.0	3.0
5–6	8.5	8.3	8.4	8.5	8.5	8.5
7a–7b	13.8	14.0			14.5	*a*
7a–8a	10.0	10.1	10.0	*a*	10.0	*a*
7a–8b	5.9	6.0			6.5	*a*
7b–8a	3.3	2.8	2.5	*a*	2.8	*a*
7b–8b	12.2	12.5	10.5	*a*	9.0	*a*
8a–8b	13.3	12.1	*a*	*a*	13.3	*a*
9–10	15.9		16.0		15.8	
9–Me		1.5		1.5		1.5
9–12		1.5		1.5		1.5

[a] Unknown because of peak superposition.

The determination of the stereochemistry of the above-mentioned isomers was not trivial and depended on a full analysis of the ^{1}H and ^{13}C NMR spectra (see Tables 1–2). Of great diagnostic value were $^{4}J_{HH}$ between the CH carrying the R side-chain (H_3) and one of the bridge methylene hydrogens (H_{8b}). When these two hydrogens are in a W relationship (and therefore R is *exo*) $J_{3,8b}$ is relatively large (1.6–1.9 Hz, see Table 2), otherwise it is ≤0.5 Hz. The ^{13}C chemical shifts (Table 1) are

Table 3 ^{1}H and ^{13}C NMR Chemical shifts for compounds **5** and **6**

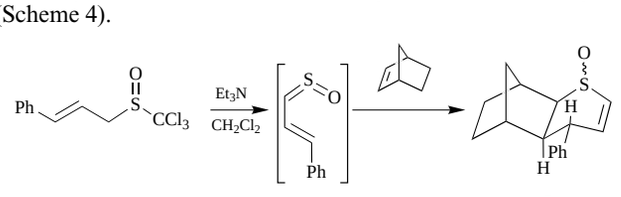
Proton	5	6a	6b
1	2.99	3.57	3.95
2	2.87	3.10	3.10
4	6.54	6.58	6.58
5	6.26	6.32	6.29
6	2.67	2.78	2.78
7	1.97	2.27	2.32
8	2.03	3.00	2.61
9*endo*	1.16		
9*exo*	1.54		
10*endo*	1.41		
10*exo*	1.77		
11a	1.73	1.88	1.91
11b	1.32	1.67	1.70
12a		5.43	4.95
12b		5.76	5.59
o-ArH	7.18	7.21	7.21
m-ArH	7.37	7.39	7.39
p-ArH	7.30	7.30	7.30
Carbon			
1	40.70	51.35	50.04
2	73.46	72.11	70.87
4	135.73	136.42	136.50
5	137.70	137.89	138.12
6	44.33	44.21	44.48
7	49.76	48.25	49.21
8	39.88	49.44	51.23
9	29.93	137.89	148.09
10	28.38	145.79	137.49
11	34.29	34.82	35.00
12		111.85	109.69
CCl_2		114.02	115.80
i-ArC	143.03	141.88	142.29
o-ArC	127.66	127.75	127.69
m-ArC	128.71	129.01	129.15
p-ArC	126.96	127.51	127.54

also very consistent; particularly informative are those of the bridgehead carbons. Thus, *endo* substituents have a shielding influence (a γ effect), *i.e.* the sulfoxide oxygen on C_7 and R on C_8.[13]

The picture thus obtained was fully self-consistent and indicates that in both series (R = β-styryl and R = β,β-dimethylvinyl) the same isomers are obtained. We should like to point out that we could find no precedent in the literature for a full analysis, by NMR spectroscopy, of this type of system, presumably in view of their relative spectral complexity.

Sulfines as dienes

As indicated above, our ability to prepare monosubstituted α,β-unsaturated sulfines gives the opportunity to investigate their reactivity as dienes in the Diels–Alder reaction. The only previous report on the use of sulfines as dienes is that by Motoki and Karakasa, who reacted a disubstituted α,β-unsaturated sulfine with norbornene.[9] However, no data was given regarding the stereochemistry, number of isomers and detailed ^{1}H and ^{13}C NMR spectral data. We have found that reaction of norbornene with β-styryl sulfine, generated *in situ* from cinnamyl trichloromethyl sulfoxide, in CH_2Cl_2 for 4 days at 40 °C, affords the tricyclic sulfoxide **5**, as the only product in 90% yield (Scheme 4).



5

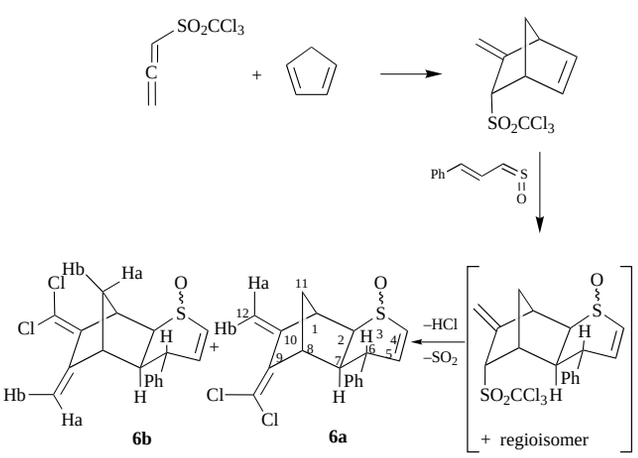
Scheme 4

Again, the stereochemistry of this product was derived from a full analysis of the NMR spectral data (see Tables 3–4; for the numbering of the carbon skeleton see compounds **6**, Scheme 5); the hydrogens at the ring junction (H_2 and H_7) were shown to be *endo* relative to the norbornane system by the observation of large (>1.5 Hz) coupling constants with one of the protons on the 11-methylene moiety (*vide supra*). The benzylic H_6 proton is *anti* to H_7 (the large value of $J_{6,7}$ indicates a dihedral angle of *ca.* 180°); in addition, we see that H_6 is approximately perpendicular to the plane of the 4,5 double bond from the fact that the vicinal coupling ($^{3}J_{5,6}$) is relatively small and the allylic coupling ($^{4}J_{4,6}$) is relatively large (see Table 4). This proton arrangement establishes a boat-shaped heterocyclic ring with a pseudo-equatorial phenyl substituent. We have simulated compound **5** using molecular mechanics calculations[14] and obtained excellent agreement with the experimental values of the vicinal coupling constants. We could not determine, however, the stereochemistry of the sulfoxide function, since it is not expected to significantly affect the coupling constants and we cannot compare chemical shifts of isomers as we did for compounds **3**–**4**, since only one was obtained. The predicted

Table 4 Proton–proton coupling constants (J_{HH}) for Compounds **5** and **6**

Protons	5	6a	6b
1–2		0.2	0.3
1–8	1.1		2.0
1–10$_{exo}$	4.5		
1–10$_{endo}$	0.2		
1–11a	2.0	1.4	1.5
1–11b	1.6	1.7	1.7
1–12a		0.4	0.8
1–12b		*a*	*a*
2–7	9.0	9.3	9.1
2–11b	2.1	2.2	2.2
4–5	9.8	9.8	9.7
4–6	3.0	3.0	3.0
5–6	4.0	4.0	4.0
6–7	10.5	10.6	10.6
7–8		0.2	0.3
7–11b	1.8	1.7	1.6
8–9$_{exo}$	4.4		
8–9$_{endo}$	0.2		
8–11a	2.0	1.6	1.5
8–11b	1.6	1.9	1.7
8–12a		0.8	0.3
9$_{endo}$–10$_{exo}$	4.2		
9$_{endo}$–10$_{endo}$	8.8		
9$_{endo}$–11a	2.2		
9$_{exo}$–9$_{endo}$	12.0		
9$_{exo}$–10$_{exo}$	12.0		
9$_{exo}$–10$_{endo}$	4.4		
10$_{endo}$–10$_{exo}$	12.0		
10$_{endo}$–11a	2.2		
11a–11b	10.9	11.0	10.9

[a] Unknown because of peak superposition.

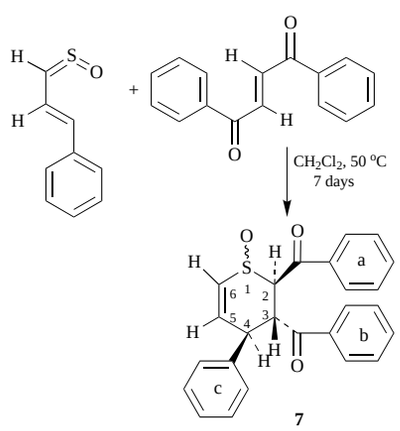


Scheme 5

difference in energy (PCModel[14]) is only 0.3 kcal mol^{-1} in favour of the isomer with the pseudo-equatorial (pointing in the α-direction) oxygen, a value we consider too small to be reliable.

In order to check the generality of this reaction, we also treated β-styryl sulfine with the norbornene derivative shown in Scheme 5. The latter was previously prepared by us *via* the Diels–Alder reaction of allenyl trichloromethyl sulfone with cyclopentadiene.[15] As expected, two regioisomers could be isolated, but it turned out that the primary products had suffered a Ramberg–Bäcklund rearrangement with loss of SO_2 and HCI to give dichloromethylene derivatives. The regioisomers were identified by NOE interactions (enchancements of 3–5%) between one of the olefinic CH_2 hydrogens (H_{12a}) and the adjacent bridgehead proton (H_1 and H_8 for **6a** and **6b**, respectively). Otherwise the NMR spectral data (both ^1H and ^{13}C) for the heterocyclic ring of compounds **5** and **6** (see Tables 3–4) are virtually identical, indicating that they have the same stereochemistry, both at the ring junction and at the sulfoxide function.

Another substrate which reacted stereospecifically as a dienophile with β-styryl sulfine, leading to a single product **7**, was *trans*-1,2-dibenzoylethylene (Scheme 6). As in the previous



7

Scheme 6

cases (compounds **5**–**6**), the vicinal and allylic couplings involving the benzylic H_4 proton indicate a pseudo-equatorial phenyl substituent (for NMR spectral data, see Experimental). The other two vicinal coupling constants are both 11 Hz, indicating an all-*trans* stereochemistry with an *anti* arrangement of the ring hydrogens. Again, molecular mechanics calculations[14] reproduce the coupling constants well, but do not define the stereochemistry at the sulfoxide centre.

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. ^1H and ^{13}C NMR spectra were recorded at room temperature on Bruker AC-200, DPX-300 or DMX-600 spectrometers in either $CDCl_3$ or other deuterated solvents and using $SiMe_4$ as internal standard. Chemical shifts are reported in ppm units, and coupling constants (*J*) 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 electron impact (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 wire. Commercially available chemicals were used without further purification.

1,6-*cis*-5,6-Dihydro-3,4-dimethyl-6-[(2*E*)-styryl]-2*H*-thiapyran 1-oxide 1a and 1,6-*trans*-5,6-dihydro-3,4-dimethyl-6-[(2*E*)-styryl]-2*H*-thiapyran 1-oxide 1b

β-Styryl sulfine (250 mg, 1.5 mmol) and 2,3-dimethylbuta-1,3-diene (0.9 ml, 7.5 mmol) were dissolved in 10 ml CH_2Cl_2 under dry nitrogen in a Pyrex ampoule, and allowed to react at 40 °C in the dark. After 3 days, the crude mixture was concentrated under reduced pressure to give 351 mg (95%). The stereoisomers **1a** and **1b** were separated by column chromatography (silica gel, ethyl acetate–hexane 5:95). **1a**: ν_{max}/cm^{-1} 1046 (S=O); δ_H(200 MHz; $CDCl_3$) 7.35 (5H, m, Ph), 6.66 (1H, bd, *J* 16.0, H_8), 6.32 (1H, dd, *J* 16.0 and 8.0, H_7), 3.45 (1H, ddd, *J* 8.8, 8.0 and 5.3, H_6), 3.30 (2H, bs, H_2), 2.83 (1H, bdd, *J* 18.0 and 8.8, H_5), 2.33 (1H, bd, *J* 18.0, H_5), 1.75 (6H, bs, Me); δ_C(50 MHz; $CDCl_3$) 136.34 (*i*-Ph), 135.18 (C_8), 128,59 (*m*-ArH), 128.06 (*p*-ArH), 126.94 (C_4), 126.65 (*o*-ArH), 123.42 (C_7), 116.11 (C_3), 56.11 (C_6), 51.16 (C_2), 30.47 (C_5), 19.79 (Me), 19.79 (Me); *m*/*z* (CI) 247 (M^+, 44%), 197 ($MH - H_2SO$, 100), 91 ($PhCH_2^+$, 82) [HRMS (CI): MH^+, 247.1162. $C_{15}H_{19}OS$ requires MH^+, 247.1156]; **1b** δ_H(200 MHz; $CDCl_3$) 7.33 (5H, m, Ph), 6,73 (1H, d, *J* 15.9, H_8), 6.06 (1H, dd, *J* 15.9 and 8.1, H_7), 3.77 (1H, ddd, *J* 8.1, 6.6 and 4.3, H_6), 3.43 (1H, bd, *J* 16.2, H_2), 3.22 (1H, bd, *J* 16.2, H_2), 2.83 (1H, bd, *J* 17.0, H_5), 2.35 (1H, bdd, *J* 17.0 and 6.6, H_5), 1.76 (6H, bs, Me); δ_C(50 MHz; $CDCl_3$) 136.28 (*i*-Ph), 136.17 (C_8), 128.62 (*m*-ArC), 128.23 (*p*-ArC), 126.62 (*o*-ArC), 123.5 (C_4), 117.40 (C_3), 59.40 (C_6), 51.01 (C_2), 31.60 (C_5), 20.03 (Me), 20.03 (Me); *m*/*z* (CI/CH_4) 247 (MH^+, 62%), 197 ($MH^+ - H_2SO$, 100), 91 ($PhCH_2^+$, 34) [HRMS (CI): found MH^+, 247.1071. $C_{15}H_{19}OS$ requires MH^+, 247.1156].

1,6-*cis*-5,6-Dihydro-3,4-dimethyl-6-(2-methylpropenyl)-2*H*-thiapyran 1-oxide 2a and 1,6-*trans*-5,6-dihydro-3,4-dimethyl-6-(2-methylpropenyl)-2*H*-thiapyran 1-oxide 2b

β,β-Dimethylvinyl sulfine (250 mg, 2.1 mmol) and 2,3-dimethylbuta-1,3-diene (1.2 ml, 10.5 mmol) were dissolved in 10 ml CH_2C1_2 under dry nitrogen in a Pyrex ampoule, and allowed to react at 40 °C in the dark. After 3 days, the crude mixture was concentrated under reduced pressure to give 317 mg (93%). The stereoisomers **2a** and **2b** were separated by column chromatography (silica gel, ethyl acetate–hexane 5:95). **2a**: δ_H(200 MHz; $CDCl_3$) 5.17 (1H, dseptet, *J* 9.5 and 1.4, H_7), 3.38 (1H, ddd, *J* 10.0, 9.5 and 4.5, H_6), 3.20 (2H, bs, H_2), 2.54 (1H, dd, *J* 18.0 and 10.0, H_5), 2.09 (1H, dd, *J* 18.0 and 4.5, H_5), 1.73 (12H, m, Me); δ_C(50 MHz; $CDCl_3$) 139.02 (C_8), 127.11 (C_4), 119.05 (C_7), 115.65 (C_3), 51.75 (C_6), 51.08 (C_2), 30.55 (C_5), 25.93 (Me), 19.81 (Me_{ring}), 19.70 (Me_{ring}), 18.79 (Me); *m*/*z* (CI/CH_4) 199 (MH^+, 100%), 183 ($MH^+ - O$, 9), 149 ($MH^+ - H_2SO$, 57) [HRMS (CI): found MH^+, 199.1190. $C_{11}H_{19}OS$ requires MH^+, 199.1156]; **2b** δ_H(200 MHz; $CDCl_3$) 4.87 (1H, dseptet, *J* 9.0 and 1.3, H_7), 3.77 (1H, td, *J* 9.0 and 4.5, H_6), 3.22 (1H, bd, *J* 17.0, H_2), 3.03 (1H, bd, *J* 17.0, H_2), 2.73 (1H, bd, *J* 18.0, H_5), 2.00 (1H, dd, *J* 18.0 and 4.5, H_5), 1.65 (12H, m, Me); δ_C(50 MHz; $CDCl_3$) 141.53 (C_8), 125.90 (C_4), 117.68 (C_7), 116.58 (C_3), 53.74 (C_6), 49.17 (C_2), 30.63 (C_5), 25.95 (Me), 19.99 (Me_{ring}), 19.92 (Me_{ring}), 18.80 (Me); *m*/*z* CI/CH_4) 199 (MH^+, 50.5%), 183 ($MH^+ - O$, 45), 149 ($MH^+ - H_2SO$, 100) [HRMS (CI): found MH^+, 199.1100. $C_{11}H_{19}OS$ requires MH^+, 199.1156].

***exo*,*exo*-, *endo*,*endo*- and *endo*,*exo*-3-[(2*E*)-Styryl]-2-thiabicyclo[2.2.2]oct-5-ene 2-oxide 3a, b and c**

Cinnamyl trichloromethyl sulfoxide (150 mg, 0.5 mmol), triethylamine (70 μl, 0.5 mmol) and cyclohexa-1,3-diene (95 μl, 1.0 mmol) were dissolved in 10 ml CH_2Cl_2 under dry nitrogen in a Pyrex ampoule, and were allowed to react at 50 °C in the dark. After 12 days, the reaction mixture was transferred to a separatory funnel, and was washed separately three times with 5 ml portions of 3% aqueous HCl and 5% aqueous $NaHCO_3$, and once with water. The crude mixture was concentrated under reduced pressure to give 111 mg (91%), and was separated by

column chromatography (silica gel, ethyl acetate); *m*/*z* (CI) 245.1010 (**3a**), 245.1040 (**3b**), 245.0970 (**3c**). $C_{15}H_{17}OS$ requires MH^+, 245.1000); ^1H and ^{13}C NMR data: see Tables 1–2.

***exo*,*exo*-, *endo*,*endo*- and *endo*,*exo*-3-(2-methylpropenyl)-2-thiabicyclo[2.2.2]oct-5-ene-2-oxide (4a, b and c)**

γ,γ-Dimethylallyl trichloromethyl sulfoxide (160 mg, 0.7 mmol), triethylamine (0.1 ml, 0.7 mmol) and cyclohexa-1,3-diene (130 μl, 1.4 mmol) were dissolved in 10 ml CH_2Cl_2 under dry nitrogen in a Pyrex ampoule, and were allowed to react at 50 °C in the dark. After 12 days, the reaction mixture was transferred to a separatory funnel, and was washed separately three times with 5 ml portions of 3% aqueous HCl and 5% aqueous $NaHCO_3$, and once with water. The crude mixture was concentrated under reduced pressure to give 121 mg (88%), and was separated by silica column chromatography with a gradient of: (a) chloroform, (b) ethyl acetate and (c) CH_3CN, and then a preparative TLC plate with CH_3CN. *m*/*z* (CI) 197.0970 (**4a**), 197.1020 (**4b** and **c**, from a mixture). ($C_{11}H_{17}OS$ requires MH^+, 197.1000); ^1H and ^{13}C NMR data: see Tables 1–2.

***exo*-6-Phenyl-3-thiatricyclo[6.2.1.0^{2,7}]undec-4-ene 3-oxide 5**

Cinnamyl trichloromethyl sulfoxide (200 mg, 0.7 mmol), triethylamine (0.1 ml, 0.7 mmol) and norbornene (66 mg, 0.7 mmol) were dissolved in 10 ml CH_2Cl_2 under dry nitrogen in a Pyrex ampoule, and were allowed to react at 40 °C in the dark. After 4 days, the reaction mixture was transferred to a separatory funnel, and was washed separately three times with 5 ml portions of 3% aqueous HCl and 5% aqueous $NaHCO_3$, and once with water. The crude mixture was concentrated under reduced pressure and was separated by column chromatography (silica gel, ethyl acetate–hexane 5:95). Crystallization from chloroform–pentane gave the pure product (164 mg, 90%), mp 126–128 °C; ν_{max}(KBr)/cm^{-1} 1049 (S=O); *m*/*z* (CI/CH_4) 259 (MH^+, 100%), 193 ($MH^+ - C_5H_8$, 11), 165 [$Ph(CH)_3SOH^+$, 13] [HRMS (CI): found MH^+, 259.1142. $C_{16}H_{19}OS$ requires MH^+, 259.1156].

6-Phenyl-9-dichloromethylene-10-methylene-3-thiatricyclo-[6.2.1.0^{2,7}]undec-4-ene 3-oxide and 6-phenyl-9-methylene-10-dichloromethylene-3-thiatricyclo[6.2.1.0^{2,7}]undec-4-ene 3-oxide (6a and 6b)

Cinnamyl trichloromethyl sulfoxide (200 mg, 0.7 mmol), triethylamine (0.1 ml, 0,7 mmol) and *endo*-3-methylene-5-norbornen-2-yl trichloromethyl sulfone (203 mg, 0,7 mmol) were dissolved in 10 ml CH_2Cl_2 under dry nitrogen in a Pyrex ampoule, and were allowed to react at 40 °C in the dark. After four days, the reaction mixture was transferred to a separatory funnel, and was washed separately three times with 5 ml portions of 3% aqueous HCl and 5% aqueous $NaHCO_3$, and once with water. The crude mixture was concentrated under reduced pressure, and was separated by column chromatography (silica gel, ethyl acetate–hexane 5:95). Crystallization from chloroform–pentane gave the pure products (**6a**: 99 mg, 40%; **6b**: 119 mg, 48%) mp 145–147 °C (**6a**), 138–140 °C (**6b**) [HRMS (CI): MH^+, 351.0330 (**6a**), 351.0350 (**6b**). $C_{18}H_{17}Cl_2OS$ requires MH^+, 351.0377].

2,3-*trans*-3,4-*trans*-2,3-Dibenzoyl-4-phenyl-3,4-dihydro-2*H*-thiapyran-1-oxide 7

Cinnamyl trichloromethyl sulfoxide (340 mg, 1.2 mmol), triethylamine (0.2 ml, 1.2 mmol) and *trans*-1,2-dibenzoylethene (288 mg, 1.2 mmol) were dissolved in 10 ml CH_2Cl_2 under dry nitrogen in a Pyrex ampoule, and were allowed to react at 50 °C in the dark. After 7 days, the reaction mixture was transferred to a separatory funnel, and was washed separately three times with 5 ml portions of 3% aqueous HCl and 5% aqueous $NaHCO_3$, and once with water. The crude mixture was concentrated under reduced pressure and was separated by column chromatography (silica gel, ethyl acetate–hexane 5:95). Crystallization from chloroform–pentane gave the pure product (308 mg, 63%), mp 154–156 °C; ν_{max}(KBr)/cm^{-1} 1038 (S=O), 1670 (C=O); δ_H(300 MHz; $CDCl_3$) 8.00 (2H, m, *o*-Ar_AH), 7.64 (2H, m, *o*-Ar_BH), 7.63 (1H, m, *p*-Ar_AH), 7.49 (2H, m, *m*-Ar_AH), 7.34 (1H, m, *p*-Ar_BH), 7.17 (2H, m, *m*-Ar_BH), 7.10 ± 0.05 (5H, m, Ar_CH), 6.96 (1H, ddd, *J* 10.0, 2.5 and 0.5, H_6), 6.61 (1H, ddd, *J* 10.0, 2.5 and 0.3, H_5), 5.14 (1H, dd, *J* 11.0 and 0.5, H_2), 4.81 (1H, td, *J* 11.0 and 0.3, H_3), 3.80 (1H, dtd, *J* 11.0, 2.5 and 0.5 H_4); δ_C(75 MHz; $CDCl_3$) 203.83 (CO-B), 192.06 (CO-A), 141.06 (C_5), 138.70, 137.69, 135.17 (*i*-ArC-$_{A,B,C}$) 134.19 (*p*-ArC_A), 132.71 (*p*-ArC_B), 129.08, 128.86, 128.84, 128.53, 128.53, 127.87 (*o*-ArC, *m*-$ArC_{A,B,C}$), 127.87 (*p*-ArC_C), 127.65 (C_6), 65.68 (C_2), 49.11 (C_4), 40.17 (C_3); *m*/*z* (CI/CH_4) 401 (M^+, 35%), 237 ($PhCOCH_2CH^+COPh$, 100), 146 ($PhCHCHCHS^+$, 57) [HRMS (CI): found MH^+, 401.1240. $C_{25}H_{21}O_3S$ requires MH^+, 401.1211].

Acknowledgments

We are grateful to the Israel Science Foundation for financial support of this study.

References

1 S. Braverman and Y. Stabinsky, *J. Chem. Soc., Chem. Commun.*, 1967, 270.
2 Also known as the Mislow–Braverman–Evans rearrangement, see A. Hassner and C. Stumer, in *Organic Syntheses Based on Name Reactions and Unnamed Reactions*, Pergamon, Oxford, 1994, p. 266.
3 S. Braverman, *Rearrangements of Sulfoxides in Chemistry of Sulfones and Sulfoxides*, eds. S. Patai, Z. Rappoport and C. J. M. Stirling, Wiley, New York, 1988, ch. 14.
4 S. Braverman, D. Grinstein and H. E. Gottlieb, *Tetrahedron Lett.*, 1994, **35**, 953; S. Braverman, D. Grinstein and H. E. Gottlieb, *Tetrahedron*, in press.
5 (*a*) B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 1; (*b*) B. Zwanenburg and B. G. Lenz, in *Houben-Weyl Methoden der Organischen Chemie*, *Band E 11/2*, *Organische Schwefelverbindugen*, Georg Thieme Verlag, Stuttgart, 1985, p. 911; (*c*) B. Zwanenburg, *Rev. Heteratom. Chem.*, 1988, **1**, 218; (*d*) B. Zwanenburg, *Phosphorus*, *Sulfur Silicon Relat. Elem.*, 1989, **43**, 1; (*e*) E. Block, in *Organic Sulfur Chemistry*, eds. R. Kh. Freidlina and A. E. Skorova, Pergamon, Oxford, 1981, p. 15.
6 B. Zwanenburg, unpublished results [*cf.* ref. 5(*a*)]; T. Saito, N. Shibahara and S. Motoki, *Tetrahedron Lett.*, 1983, **24**, 4435; D. H. R. Barton, L. S. L. Choi, R. H. Hesse, M. M. Pechet and C. Wilshire, *J. Chem. Soc.*, *Chem. Commun.*, 1977, 1529.
7 M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1979, 2397.
8 C. N. Skold and R. H. Schlessinger, *Tetrahedron Lett.*, 1970, 791; W. J. M. van Tilborg, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 140.
9 T. Karakasa and S. Motoki, *Tetrahedron Lett.*, 1979, 3961; T. Karakasa, H. Ohmura and S. Motoki, *Chem. Lett.*, 1980, 825.
10 S. Braverman, P. F. T. M. van Asten, J. B. van der Linden and B. Zwanenburg, *Tetrahedron Lett.*, 1991, **31**, 3867; J. B. van der Linden, P. F. T. M. van Asten, S. Braverman and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1995, **114**, 51.
11 J. Strating, L. Thijs and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 631; A. M. Hamid and S. Trippett, *J. Chem. Soc. C*, 1968, 1617; E. Block, L. K. Revelle and A. A. Bazzi, *Tetrahedron Lett.*, 1980, 1277.
12 B. F. Bonini, G. Mazzanti, P. Zani, G. Maccagnani, A. Battaglia and P. Giorgianni, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 964; G. Barbaro, A. Battaglia, P. Giorgianni, B. F. Bonini, G. Maccagnani and P. Zani, *J. Org. Chem.*, 1990, **55**, 3744; 1991, **56**, 2512; B. F. Bonini, *Phosphorus*, *Sulfur Silicon*, *Relat. Elem.*, 1993, **74**, 31.
13 J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith and J. D. Roberts, *J. Am. Chem. Soc.*, 1970, **92**, 7107.
14 PCModel, Serena Software, Box 3076, Bloomington, IN 47402-3076, USA.
15 S. Braverman and Z. Lior, *Tetrahedron Lett.*, 1994, **35**, 6725.

Paper 7/04473I
Received 25*th June* 1997
Accepted 4*th September* 1997