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The Invention of Radical Reactions. Part XXVII. Modified Julia Synthesis of Olefins Using Radical Deoxygenation.

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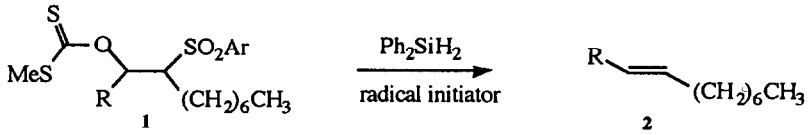
Abstract: *Xanthate derivatives of β-hydroxy sulfones react with methyl radicals generated from the photolysis of N-acetyloxy-2-thiopyridone to give the corresponding olefin. Under identical conditions a secondary alcohol is transformed into its thiopyridyl derivative.*

The Julia olefination procedure[1] based on the reductive elimination of β-hydroxy sulfone derivatives with sodium amalgam was shown to give essentially trans olefins[2]. One advantage of this method over the Wittig reaction is the facile preparation of the β-hydroxy sulfones formed by the condensation of an aryl sulfone and an aldehyde or a ketone. However the reductive step is more difficult to realize and poor yields are often reported when applied to complex natural product syntheses[3].

Lythgoe and Waterhouse[4] were the first to use the Barton McCombie radical deoxygenation[5] to effect the second part of this olefination process. Later, Williams *et al*[6] reported high yield olefination employing this method starting from methyl xanthate derivatives of β-hydroxy sulfones. This latest variation has been also successfully applied by Barrish *et al.*[7]. Recently Kende and Mendoza reported a new modification of the Julia olefin synthesis which consist in treating a β-hydroxyimidazolyl sulfone with samarium iodide[8].

In a preliminary communication[9] we have summarized our results bearing on the improvement of this reaction using new radical processes with the objective of avoiding tin hydride reagents. We wish now to report further experiments as well as some new results in the field of radical deoxygenation.

We have recently shown that diphenylsilane can replace efficiently tributyl tin hydride in the deoxygenation of primary and secondary alcohols[10]. It has also been used in a high-yielding transformation of dixanthates, formed from *vic*-diol, into their corresponding olefins[11]. We initially considered the possibility of performing the reductive elimination of the methyl xanthate **1** with Ph_2SiH_2 in a similar type of radical reaction (Scheme 1). We carried out this olefination using triethylboron-oxygen, azobisisobutyronitrile (AIBN) and benzoylperoxide as radical initiators. The results are summarized in Table 1.



1 **2**

Scheme 1

Good yields of olefin were obtained when compounds of type **1** were treated with Ph_2SiH_2 (2 eq.) and $(PhCOO)_2$ (2 eq.) in refluxing toluene. (Table 1, entry 5). Benzoylperoxide alone can also effect this transformation, however in moderate yield (Table 1, entry 7). Improvement of this reaction by decreasing the amount of reagent and initiator used was not successful.

Table 1: Radical olefination with Ph_2SiH_2

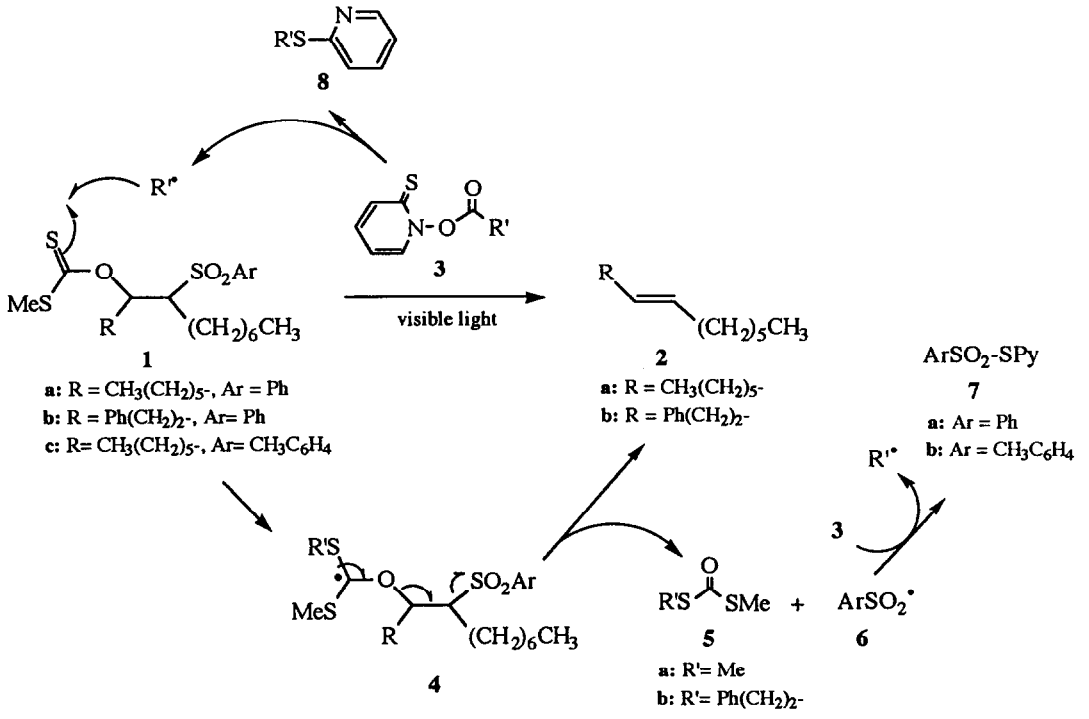
Entry	Starting Compound	Ph_2SiH_2 (eq.)	Initiator	(eq.)	Solvent	Temp (°C)	**2** Yield*(%)
1	**1a** R = $CH_3(CH_2)_5$- Ar = Ph	1.1	AIBN	5.5	toluene	110	75
2		2.0	AIBN	5.0	toluene	110	73
3		1.1	Et_3B-O_2	5.0	benzene	25	42
4		1.1	Et_3B-O_2	5.0	benzene	80	55
5	**1b** R= $Ph(CH_2)_2$- Ar= Ph	2.0	$(PhCOO)_2$	2.0	toluene	110	81
6		1.0	$(PhCOO)_2$	2.5	toluene	110	78
7		—	$(PhCOO)_2$	2.0	toluene	110	55

* All the yields were determined by ^{1}H-NMR (200 MHz) analysis

In parallel with these studies we found that the *O*-acyl derivatives of *N*-hydroxy-2-thiopyridone **3** could be employed as reagents in this olefination process. The radical chemistry associated with this type of compounds has been extensively used since a decade for the mild generation of carbon[12], nitrogen[13] and oxygen centered radicals[14]. A new method of radical synthesis involves exchange of (say) a methyl radical for an R radical on an aryl-R telluride[15].

In a further extention of this approach the olefin **2**, essentially the trans isomer, was produced in good yields during the photolysis of **3** in the presence of **1** (Scheme 2). We have examined several *O*-acyl *N*-hydroxy-2-thiopyridones **3** in this system (Table 2) and found that the *O*-acetyl **3a** (R'=Me) is the most suitable.

In addition to giving high yields of olefin, this procedure has other advantages: **3a** is readily available from *N*-Hydroxy-2-thiopyridone and acetyl chloride and the by-product **5a** (R'=CH_3) is quite volatile and easily removed from the reaction mixture. Also we have another way to avoid the use of tin hydrides and of silanes.



Scheme 2

As shown in Table 2, the reaction can be carried out at higher temperature in refluxing benzene or toluene, but also at lower temperature in refluxing dichloromethane. From the crude mixture, in addition to the expected olefin **2** and the known by-product **8**, we also isolated the dithiocarbonate **5** and the sulfide **7**. Compound **5a** is difficult to obtain after work up of the reaction due to its volatility (lit.[16] b.p. 61-62°C/ 17 mm) however it is easily detected in the crude ^{1}H-NMR ($CDCl_3$, 200 MHz) and gives a singlet at 2.44 ppm. The structure of **5** was further determined from the derivative **5b** (R'= $Ph(CH_2)_2$-)[17]. Careful analysis of the ^{1}H-NMR of the crude mixtures allowed us to define the mechanism of this olefination. For example, when **1c** (Ar=$CH_3C_6H_4$, R=$(CH_2)_5CH_3$) was photolysed with **3a** (3 eq) in refluxing dichloromethane (Table 2, entry 9), the olefin **2a** was obtained in 78% yield among with 80% of **5a**, 75% of **7b**[18] and 22% of the starting methylxanthate **1c** was recovered.

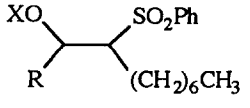
As shown in Scheme 2, the carbon radical R'• generated from **3** reacts with the thiocarbonyl of **1** to give the intermediate radical **4**. This radical then fragments to form, after loss of the sulfonyl radical **6**, the olefin **2** and the dithiocarbonate **5**. The sulfonyl radical **6** then carried the chain by further reacting with the thiocarbonyl of **3** to finally produce **7** and generate a new radical R'•. In this process R'• can also react with **3** to give the rearranged product **8**.

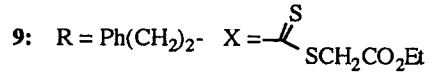
Table 2: Radical olefination with the *O*-acyl *N*-hydroxy-2-thiopyridones **3**.

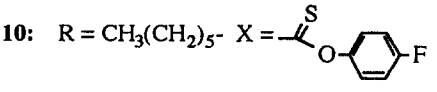
Entry	Starting Compound	3	R'	(eq.)	Solvent	Temp (°C)	2 yield (%)
1	**1a**	**3a**	CH_3	4.4	benzene	25	85[a]
2				1.1	benzene	80	50[a]
3				1.1	$CDCl_3$	0	31[b]
4				3.0	benzene	80	84[a]
5	**1b**			3.0	CH_2Cl_2	40	75[a]
6				3.0	acetone	60	67[a]
7				3.0	cyclohexane	80	50[a]
8				3.0	toluene	110	85[a]
9	**1c**			3.0	CH_2Cl_2	40	78[a]
10	**9**			3.0	CH_2Cl_2	40	50[b]
11	**10**			1.1	$CDCl_3$	0	13[b]
12	**11**			1.1	$CDCl_3$	0	0[b]
13	**13**			1.2	benzene	80	75[a]
14	**1a**	**3b**	$Ph(CH_2)_2$	1.1	benzene	80	48[a]
15		**3c**	cyclobutyl	1.1	benzene	80	37[a]
16	**1b**	**3d**	cyclopropyl	3.0	toluene	110	58[a]

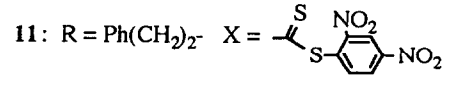
a, yield of the isolated product; b, determined by ^{1}H-NMR (200 MHz).

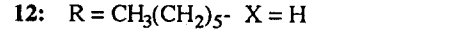
In order to compete with this non-desired pathway, other substrates were examined with a view to decreasing the amount of **8** formed by increasing the electrophilicity of the thiocarbonyl of **1**.

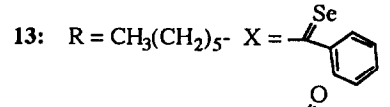


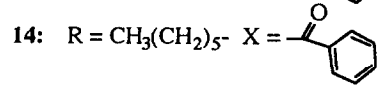






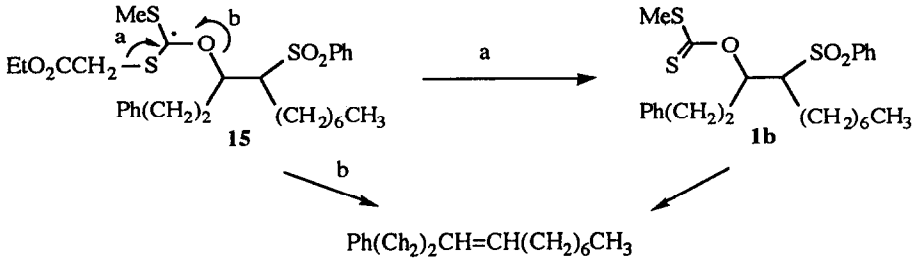






When the xanthate **9** was treated with 3 eq of **3a** in refluxing dichloromethane, the olefin **2b** was obtained in 50% yield (Table 2, entry 10). The methyl xanthate **1b** was also formed in 50% yield. In this experiment the starting compound **9** was totally consumed. This result showed that the thiocarbonyl of **9** was more reactive toward the radical methyl than its corresponding methyl xanthate derivative**1b**. However the intermediate radical **15** can now fragment in two different ways, leading to the formation of **2b** or to the

formation of the methyl xanthate **1b**. This later will then react with another radical methyl to give also the olefin **2b** (Scheme 3).



Scheme 3

The thionocarbonate **10** gave a poor yield of olefin in this system (Table 2, entry 11) compared to the methylxanthate derivative **1a** (Table 2, entry 3) and no formation of olefin was observed when the dinitrophenyl derivative **11** was used under the same conditions of photolysis (Table 2, entry 12). The selenobenzoate **13**, prepared[5] from the alcohol **12**, gave a good yield of olefin. Photolysis of **13** with only 1.2 eq of **3a** in refluxing benzene afford **2b** in 75% yield. From the reaction mixture we also isolated the benzoate **14**[2b] in 15% yield as well as **$CH_3SeCOPh$**[19] in comparable yield to the olefin. However all the attempts at reducing the amount of the benzoate derivative formed during the reaction were unsuccessful.

The results obtained from all these experiments showed that the methyl xanthates derivatives are still the substrates of choice in this olefination process.

To conclude this work, we decided to treat a secondary alcohol under the same conditions and see if one could effectuate a radical deoxygenation without a subsequent elimination of the sulfonyl radical. Thus when the methyl xanthate **18**[20] was photolysed in presence of **3a** (2 eq) in refluxing dichloromethane the thiopyridyl **19**[21] was obtained in 60% yield (Table 3, entry 2).

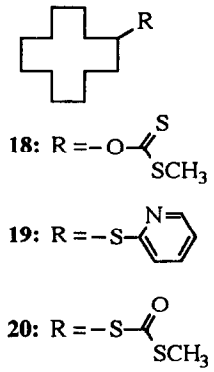


Table 3: Comparative photolytic studies[a] of methylxanthates **1c** and **18**.

Entry	Starting Compound	Products	Yield[b](%)	Start. Comp. Left[b] (%)	
1	**1c**	**2a**	63	**1c**	36
2	**18**	**19**	60	**18**	12
3	**1c + 18**	**2a**	54	**1c**	45
		19	36	**18**	59

a, Photolysis: 270 W tungsten lamp, 40°C, CH_2Cl_2, **3a** (2 eq.) added by portion
b, determined by ^{1}H-NMR (200 MHz).

The photolysis of **18** led also to the formation of other products identified as **20**[22] (12%), cyclododecene (5%) and cyclododecane (10%). If **3a** was added at one time to the reaction mixture these compounds were not formed; however the yield of **19** (45%) decreased and 45% of **18** remained unchanged. Under an identical photolytic procedure the β-hydroxysulfone derivative **1c** gave 63% of the olefin **2a** (Table 3, entry 1). Finally the photolysis of the mixture (1:1) of the two methyl xanthates **1c** and **18** in presence of **3a** (2 eq) resulted in the formation of 54% of the olefin **2a** for 36% of the thiopyridyl **19** (table 3, entry 3). This demonstrated that the radical deoxygenation associated with the olefination process is slightly faster.

Attention is also drawn to the procedure introduced in the Exprt. Section for using the alkoxyl anion resulting from the first step of the Julia reaction as normally practised. This anion can be reacted *in situ* with CS_2 and the derived thio-anion methylated with MeI without isolating any intermediate at all. So there are only two steps involved.

In conclusion, this work presents a new method for the formation of olefins from methylxanthate derivatives of β-hydroxysulfones as well as a new method for the radical deoxygenation of secondary alcohols. It has the advantage in using readily available materials. The methyl radical induced fragmentation of xanthates to give different radicals is a potentially useful reaction, especially when thiocarbonyl groups of thiohydroxamic acids less reactive than that of *N*-hydroxy-2-thiopyridone will have been prepared.

Experimental

Melting points were determined with a Kofler hot-stage melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 881 spectrophotometer. ^1H and ^{13}C NMR spectra were measured with a Varian Gemini 200 or a Varian XL 200E spectrometer for deuterochloroform solutions. Chemical Shifts are in p.p.m. downfield from tetramethylsilane used as an internal standard (δ values). Mass spectra were obtained on a V.G. Analytical 70s high-resolution double-focusing magnetic sector mass spectrometer with attached VG 11/250J data system in the EI mode. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Solvents were used either as purchased or dried and purified by standard methods. All the reactions were effected under an inert atmosphere of Argon. Flash Chromatography was performed using Kiessegel 60 (230-400 mesh, E. Merck). N-Hydroxy-2-thiopyridone was obtained from the 40% aqueous solution of its sodium salt (sodium Omadine®, kindly provided by the Olin Corp.)

Xanthate 1a:

A typical experiment:

To a solution of n-octyl phenyl sulfone[23] (1g, 3.94 mmoles) in dry THF (15 ml) was added 1.6M n-butyllithium in hexane (2.58 ml, 1.05 eq) under argon at -40°C. After a further 30 min. n-Heptanal (0.55 ml, 1 eq) was added dropwise at -40°C and the solution was stirred for one hour at this temperature. CS_2 (0.71 ml, 3 eq) was then added and stirring was continued for 5 hours, the temperature raising slowly to -20°C. Then the reaction mixture was cooled to -40°C and MeI (0.74 ml, 3 eq) was added. After a further hour at -40°C the mixture was quenched with a saturated aqueous ammonium chloride solution and allowed to come to room temperature. The mixture was poured into water and extracted with ether. The organic extracts were dried ($MgSO_4$) and evaporated. Purification of the residue by flash chromatography on silica gel (eluent EtOAc/

Hexane 0.5/9.5) gave **1a** (1.45 g, 81%, Threo/ Erythro ratio: 5:3). The first fractions gave the pure threo isomer. A mixture of the two isomers was then eluted from the column and finally the last fractions gave the pure erythro isomer. Erythro isomer (the more polar): **IR** (film): 1445-1305-1207-1144-1057 cm-1; **^{1}H** (δ) 0.9 (6H, m); 1.3 (16H, m); 1.6 to 1.9 (4H, m); 2.05 (2H, m); 2.4 (3H, s); 3.38 (1H, CHSO$_2$Ph, dt, J_1=2Hz, J_2=5.8Hz); 6.05 (1H, CH-O, dt, J_1=2Hz, J_2=6.9Hz); 7.55 (3H, m); 7.85 (2H, m); **^{13}C** (δ) 13.9 (CH_3); 14 (CH_3); 18.5 (CH_3S); 22.4 to 31.6 (CH_2); 66.5 (CHSO$_2$Ph); 80.4 (CH-O); 128.8 (CH), 129 (CH); 129.1 (CH); 133.6 (CH); 139.4 (Cq); 214.6 (C=S).Threo isomer: **IR** (film): 1445-1305-1207-1146-1085-1052 cm-1; **^{1}H** (δ) 0.9 (6H, m); 1.3 (18H, m); 1.7 to 2.1 (4H, m); 2.5 (3H, s); 3.62 (1H, CHSO$_2$Ph, m); 5.95 (1H, CH-O, dt, J_1=10.3Hz, J_2=2.7Hz); 7.6 (3H, m); 7.95 (3H, m); **^{13}C** (δ) 13.8 (CH_3); 18.6 (CH_3S); 22.4 to 31.5 (CH_2); 64.4 (CHSO$_2$Ph); 80.4 (CH-O); 128.5 (CH), 129 (CH); 133.6 (CH); 138.8 (Cq); 215 (C=S); **Anal.** Calcd. for $C_{23}H_{38}O_3S_3$ (Threo isomer); C, 60.21; H, 8.35; S, 20.97 Found C, 60.33; H, 8.37; S, 20.83.

Xanthate 1b:

This compound was prepared from n-octyl phenyl sulfone and hydrocinnamaldehyde following the method described for **1a** and was obtained after flash chromatography on silica gel (EtOAc / Hexane 1/9) in 85% yield (Threo / Erythro ratio: 5:4).Erythro isomer (the more polar):**IR** (film): 1446-1305-1204-1139-1083-1056 cm-1; **^{1}H** (δ) 0.85 (3H, t); 1.1 to 1.4 (10H, m); 1.7 (1H, m); 1.9 to 2.1 (2H, m); 2.4 (3H, s); 2.4 to 2.6 (2H, m); 2.6 to 2.8 (1H, m); 3.4 (1H, CHSO$_2$Ph, m, J_1=2.6Hz, J_2=5.5Hz); 6 (1H, CH-O, m, J_1=2.6Hz, J_2=5.7Hz); 7.1 (2H, m); 7.2 (3H, m); 7.5 to 7.7 (3H, m); 7.8 (2H, m); **^{13}C** (δ) 14. (CH_3); 18.7 (SCH_3); 22.5 to 32.5 (CH_2); 66.4 (CHSO$_2$Ph); 80 (CHO); 126.3 (CH), 128.4 (CH); 128.5 (CH); 128.6 (CH); 128.8 (CH); 129.1 (CH); 133.6 (CH); 138.7 (Cq); 140.1 (Cq); 214.7 (C=S).Threo isomer: **IR** (film): 1445-1305-1205-1147-1043 cm-1; **^{1}H** (δ) 0.85 (3H, t); 1.2 (8H, m); 1.4 (2H, m); 1.85 (1H, m); 2 to 2.3 (2H, m); 2.4 to 2.6 (5H, CH_2 and SCH_3, m); 2.8 (1H, m); 3.58 (1H, CHSO$_2$Ph, m); 5.7 (1H, CH-O, dt, J_1=10.6Hz, J_2=2.1Hz); 7.15 (2H, m); 7.25 (3H, m); 7.4 (2H, m); 7.6 (3H, m); **^{13}C** (δ) 14 (CH_3); 19 (CH_3S); 22.5 to 31.7 (CH_2); 64.4 (CHSO$_2$Ph); 79.5 (CH-O); 126.2 (CH), 128.5 (CH); 128.7 (CH); 128.8 (CH); 129.1 (CH); 133.6 (CH); 138.4 (Cq); 140.3 (Cq); 214.9 (C=S); **Anal.** Calcd. for $C_{25}H_{34}O_3S_3$ (Threo isomer); C, 62.71; H, 7.16; S, 20.09 Found C, 62.82; H, 7.20; S, 20.01.

Xanthate 1c:

This compound was prepared from n-octyl tolyl sulfone[24] and heptanal following the method described for **1a** and was obtained after flash chromatography on silica gel (Ether / Hexane 0.5/9.5) in 66% yield (Threo / Erythro ratio: 6:4).Erythro isomer (the more polar): **IR** (CH_2Cl_2): 1207-1136-1059 cm-1; **^{1}H** (δ) 0.8 (6H, m); 1.25 (18H, m); 1.5 to 2.1 (6H, m); 2.4 (3H, s); 2.44 (3H, s); 3.52 (1H, CHSO$_2$Ar, dt, J_1=2.1Hz, J_2=5.9Hz); 6.05 (1H, CH-O, dt, J_1=2.1Hz, J_2=6.8Hz); 7.34 (2H, d, J=8.5Hz); 7.78 (2H, d, J=8.5Hz); **^{13}C** (δ) 13.9 (CH_3); 14 (CH_3); 18.5 (SCH_3); 21.6 (CH_3); 22.4 to 31.6 (CH_2); 66.4 (CHSO$_2$Ar); 80.4 (CH-O); 128.8 (CH), 129,7 (CH); 135.3 (Cq); 144,6 (Cq); 214.5 (C=S).Threo isomer: **IR** (CH_2Cl_2): 1207-1142-1054 cm-1; **^{1}H** (δ) 0.88 (6H, m); 1.25 (18H, m); 1.7 to 2.2 (6H, m); 2,45 (3H, s); 2.5 (3H, s); 3.6 (1H, CHSO$_2$Ar, m); 5.9 (1H, CH-O, dt, J_1=10.3Hz, J_2=2.4Hz); 7.35 (2H, d, J=7.8Hz); 7.8 (2H, d, J=7.8Hz); 7.4 (2H, m); 7.6 (3H, m); **^{13}C** (δ) 14 (CH_3); 19 (CH_3S); 21.6 (CH_3); 22.5 to 31.6 (CH_2); 64.7 (CHSO$_2$Ar); 80.9 (CH-O); 128.7 (CH), 129.8 (CH); 136 (Cq); 144.8 (Cq); 215.2 (C=S); **Anal.** Calcd. for $C_{24}H_{40}O_3S_3$ (Threo isomer); C, 60.97; H, 8.52; S, 20.34 Found C, 61.07; H, 8.56; S, 20.25.

Xanthate 9:

This compound was prepared in a manner analogous to that of **1a** starting from n-octyl phenyl sulfone and hydrocinnamaldehyde with the difference that ethylbromoacetate (1 eq) was added to the solution instead of methyliodide. Flash chromatography on silica gel (EtOAc/Hexane 1/9) gave **9** (Threo/ Erythro ratio: 6:4) in 70 % yield. Erythro isomer (the more polar): **IR** (film): 1733-1303-1217-1144-1051 cm-1;^{1}**H** (δ) 0.85 (3H, t); 1.1 to 1.4 (13H, m); 1.65 (1H, m); 1.8 to 2.1 (2H, m); 2.4 to 2.8 (3H, m); 3.38 (1H, CHSO$_2$Ph, m, J_1=2.5Hz, J_2=5.2Hz, J_3=7Hz); 3.7 (1H, CH$_2$CO$_2$Et, d, J=16.5Hz); 3.88 (1H, CH$_2$CO$_2$Et, d, J=16.5Hz); 4.2 (2H, q); 5.95 (1H, CH-O, m, J_1=2.5Hz, J_2=5Hz, J_3=7.4Hz); 7.1 to 7.4 (5H, m); 7.5 to 7.7 (3H, m); 7.82 (2H, m); ^{13}**C** (δ) 14 (CH_3); 14.1 (CH_3); 22 to 37.5 (CH_2); 61.9 (CH_2O); 66.1 (CHSO$_2$Ph); 80.6 (CH-O); 126.3 to 133.7 (CH); 138.5 (Cq); 139.2 (Cq); 167.5 (C=O); 211.4 (C=S); ·Threo isomer: **IR** (film): 1737-1305-1217-1147-1046 cm-1; ^{1}**H** (δ) 3.52 (1H, CHSO$_2$Ph, m); 3.85 (2H, CH$_2$CO$_2$Et, d); 4.18 (2H, CO$_2$CH$_2$, q); 5.65 (1H, CH-O, dt, J_1=10.9Hz, J_2=2.2Hz); 7.1 to 7.6 (10H, m).^{13}**C** (δ) 14.1 (CH_3); 22.5 to 38 (CH_2); 62 (CH_2O); 64.4 (CHSO$_2$Ph); 80.2 (CH-O); 126.1 to133.6 (CH); 140.1 (Cq); 167.3 (C=O); 211.7 (C=S).

4-Fluorobenzylthionocarbonate 10:

To a solution of n-octyl phenyl sulfone (300 mg, 1.18 mmoles) in THF (5 ml) was added at -40°C 1.6M n-butyl lithium (0.77ml) in hexane. After 30 min n-Heptanal (0.17 ml) was added and the reaction was stirred for one hour at -40°C, then 4-fluorobenzylchlorothionoformate[10c] (0.25 ml) was added at -40°C. After a further hour at -40°C the mixture was quenched with a saturated aqueous ammonium chloride solution and allowed to come to room temperature. The mixture was poured into water and extracted with ether. The organic extracts were dried ($MgSO_4$) and evaporated. Purification by flash chromatography on silica gel (EtOAc/Hexane 2/8) gave **10** (391 mg, 64%, Threo/Erythro ratio: 8:2) Erythro isomer (the more polar): ^{1}**H** (δ) 0.9 (6H, m); 1.2 to 1.5 (18 H, m); 1.6 to 1.9 (2H, m); 3.12 (1H, CHSO$_2$Ph, m, J_1=1.8Hz, J_2=5.8Hz); 5.75 (1H, CH-O, dt, J_1=1.8Hz, J_2=7Hz); 7 (4H, m); 7.75 (3H, m); 7.95 (2H, m); ^{13}**C** (δ) 14 (CH_3); 22.4 to 31.8 (CH_2); 66.2 (CHSO$_2$Ph); 81.4 (CH-O); 116 116.3 (CH, J_{C-F}=23.4Hz), 123.2 123.4 (CH, J_{C-F}=8.4Hz); 129 129.1 (CH, J_{C-F}=5.4Hz); 133.7 (Cq); 138.4 (Cq); 148 148.1 (Cq, J_{C-F}=2.8Hz); 193 (C=S).Threo isomer: ^{1}**H** (δ) 0.9 (6H, m); 1.2 to 1.5 (18 H, m); 1.7 to 2.2 (4H, m); 3.7 (1H, CHSO$_2$Ph, m); 5.6 (1H, CH-O, dt, J_1=10.5Hz, J_2=2.7Hz); 6.9 to 7.1 (4H, m); 7.6 (3H, m); 7.95 (2H, m); ^{13}**C** (δ) 14 (CH_3); 22.4 to 31.6 (CH_2); 64.5 (CHSO$_2$Ph); 82.2 (CH-O); 115.9 116.3 (CH, J_{C-F}=23.6Hz), 123.1 123.2 (CH, J_{C-F}=8.5Hz); 128.6 (CH); 129,1 (CH); 133.8 (Cq); 138.7 (Cq); 148.8 148.9 (Cq, J_{C-F}=2.8Hz); 158.1 162.9 (Cq, J_{C-F}=244.4Hz); 194 (C=S).

Xanthate 11:

This compound was prepared in a manner analogous to that of **1a** starting from n-octyl phenyl sulfone and hydrocinnamaldehyde with the difference that 1-chloro-2,4-dinitrobenzene (1 eq) was added to the solution instead of methyliodide. Flash chromatography on silica gel (EtOAc/Hexane 3/7) gave **11** (1.5 g, 60%, Threo/ Erythro ratio: 7:3). Threo isomer: **IR** (CH_2Cl_2): 1533-1345-1217-1145-1020 cm-1; ^{1}**H** (δ) 0.9 (3H, t); 1.1 to 1.4 (9H, m); 1.7 (1H, m); 1.9 to 2.2 (2H, m); 2.5 (2H, m); 2.75 (1H, m); 3.35 (1H, CHSO$_2$Ph, m); 5.65 (1H, CH-O, dt, J_1=10.5Hz, J_2=1.7Hz); 7.1 to 7.7 (11H, m); 7.85 (1H, m); 8.42 (1H, dd), 8.8 (1H, dd); ^{13}**C** (δ) 14 (CH_3); 22.5 to 31.6 (CH_2);64.6 (CHSO$_2$Ph); 81.5 (CH-O); 120.4 to133.8 (CH); 138 (Cq); 139.3 (Cq); 139.8(Cq); 148.5 (Cq); 151.1 (Cq); 205.8 (C=S); **Anal.** Calcd. for $C_{30}H_{34}N_2O_7S_3$; C, 57.11; H, 5.43; S, 15.25 Found C, 57.49; H, 5.39; S, 15.77.

β-Hydroxysulfone 12[2b]:

n-Butyl lithium (2.6 ml of a 1.6M solution in hexane) was added dropwise to a solution of n-octyl phenyl sulfone (1g, 3.94 mmoles) in dry THF (20 ml) under argon at -40°C. After 30 min. n-Heptanal (0.55 ml) was added. The yellow color disappeared and after a further hour at -40°C, the mixture was quenched with saturated aqueous ammonium chloride and allowed to come to room temperature. The mixture was poured into water and extracted with ether. The organic extracts were dried ($MgSO_4$) and evaporated. Column chromatography of the residue on silica gel (EtOAc/Hexane 1/9) gave **12** (1.3g, 91%, Threo/Erythro ratio: 6:4).Erythro isomer (the more apolar): ^{1}**H** (δ) 0.88 (6H, t); 1.25 (16H, m); 1.7 (2H, m); 1.9 (2H, m); 2.9 (1H, CHSO$_2$Ph, dt, J_1=1Hz, J_2=5Hz); 3.1 (1H, OH, d, J=3.3Hz); 4.15 (1H, CHOH, m); 7.65 (3H, m); 7.95 (2H, m); ^{13}**C** (δ) 14 (CH_3); 22.5 to 34 (CH_2); 68.4 (CHSO$_2$Ph); 68.7 (CHOH); 128.6 (CH), 129.3 (CH); 133.9. (CH); 138.1 (Cq).Threo isomer: ^{1}**H** (δ) 0.89 (6H, m); 1.2 to 2 (22H, m); 3.1 (1H, CHSO$_2$Ph, q, J=7Hz); 3.35 (1H, OH, d, J=5Hz); 4.05 (1H, CHOH, m); 7.6 (3H, m); 7.9 (2H, m); ^{13}**C** (δ) 14 (CH_3); 22.5 to 34.2 (CH_2); 69.4 (CHSO$_2$Ph); 70.1 (CHOH); 128.5 (CH), 129.2 (CH); 133.7 (CH); 139 (Cq); **MS** (EI): 368 $(M)^{+\cdot}$.

Selenobenzoate 13

The reaction was carried on the threo derivative of the β-hydroxysulfone **12**. N,N-dimethylbenzamide (165mg, 1.1 eq) was kept for 24 hr. at room temperature in CH_2Cl_2 in presence of phosgene (2.2 mmoles). The solution was then evaporated in vacuum, and the imidoyl chloride was re dissolved in CH_2Cl_2. To this solution was added at -20°C a solution of the β-hydroxysulfone **12** (410 mg, 1.1 mmoles) in 4 ml of CH_2Cl_2. After stirring for 4hr at -20°C the mixture was warmed to 0°C and pyridine (225μl) was added and the solution stirred for 2hr at 0°C. Then the resulting mixture was added at -20°C to a solution of sodium hydrogen selenide [from selenium (87mg) and sodium borohydride (55 mg) in EtOH (3ml) followed by addition of acetic acid (46 μl)]. The solution was stirred 1hr at -20°C and 10 min. at room temperature then diluted with CH_2Cl_2 washed with water and brine. The organic layer was dried over $MgSO_4$ and evaporated. Flash chromatography of the residue on Silica gel (ether/Hexane 1/9) gave **13** (188mg, 35%) as a red oil. **IR** (film): 1446-1305-1250-1203-1146-908 cm-1; ^{1}**H** (δ) 0.8 (6H, m); 1 to 1.5 (18H, m); 1.9 to 2.3 (4H, m); 3.82 (1H, CHSO$_2$Ph, m); 6.25 (1H, CH-O, dt, J_1=9.5Hz, J_2=3.1Hz); 7.3 (2H, t, J=7.8Hz); 7.6 (4H, m), 7.95 (2H, dd, J_1=6.8Hz, J_1=1.6Hz); 8.1 (2H, dd, J_1=7.4Hz, J_1=1.2Hz); ^{13}**C** (δ) 14 (CH_3); 22.5 to 31.6 (CH_2); 64.6 (CHSO$_2$Ph); 83.2 (CH-O); 128.4 (CH), 128.7 (CH); 129.2 (CH); 132.9 (CH); 133.8 (CH);139.3 (Cq); 142.6 (Cq); 221 (C=Se). **Acc.Mass**: 535.96422 found 535.96423.

Olefination Procedures:

Olefination with Ph_2SiH_2 and AIBN:

A typical experiment; xanthate **1a** (275 mg,0.6 mmoles) was dissolved in dry toluene (2ml) and heated to reflux. To this solution was added diphenysilane (123 μl, 1.1 eq) in one portion. AIBN (540 mg, 5.5 eq) was then added by portions (25 mg, 0.25 eq) at 20 min intervals and the solution was refluxed for a futher 30 min. The solvent was evaporated and the yield was measured by ^{1}H-NMR with an internal reference (cf Table 1, entry 1).

Olefination with Ph_2SiH_2 and Et_3B-O_2:

A typical experiment; xanthate **1a** (122.4 mg,0.267 mmoles) was dissolved in dry benzene (5ml). Diphenylsilane (55µl, 1.1 eq) and a 1M solution of triethylborane in hexane (1.33 ml, 5eq) were added and the solution was refluxed. Then dry air (170 ml) was bubbled through the reaction mixture for 3 hrs with a syringe pump. The solution was kept boiling for a futher 15 min. The solvent was then removed in vacuum and the yield was measured by ^{1}H-NMR with an internal reference (cf Table 1, entry 4).

Olefination with Ph_2SiH_2 and $Ph(COO)_2$:

A typical experiment; to the xanthate **1b** (310 mg, 0.66 mmoles) was added toluene (2ml) and diphenylsilane (245 µl, 2eq) under argon and the solution was brought to boil. To this mixture was added dropwise a solution of benzoyl peroxide (320 mg, 2 eq) in dry toluene (3 ml). The solvent was removed in vacuum and the yield was measured by ^{1}H-NMR with an internal reference (cf Table 1, entry 5).

Olefination with N-acetyloxy-2-thiopyridone 3a:

N-acetyloxy-2-thiopyridone 3a:

This compound was prepared by an improved method over the literature procedure[25]. To a solution of N-hydroxy-2-thiopyridone (10g) in dichloromethane (100 ml) was added, at 0°C and in the dark, pyridine (6.4 ml) and acetyl chloride (5.6 ml). The reaction mixture was stirred for 2 hrs and then washed quickly with water. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure at 20 °C in the dark. Recrystallisation of the crude from dichloromethane-hexane afforded the yellow **3a** (12g, 90%). m.p. 88-90°C; **^{1}H** (δ) 2.42 (3H, s); 6.64 (1H, dt, J_1= 1.8 Hz, J_2= 6.9 Hz); 7.21 (1H, m); 7.62 (2H, m);**^{13}C** (δ) 18.3 (CH_3); 112.6 (CH); 133.6 (CH); 137 (CH); 137.5 (CH); 165.8 (C=O); 175.6 (C=S).

Olefination :

A typical experiment, to a refluxing solution of the xanthate **1b** (500mg, 1.05 mmoles) in 3 ml of toluene was added by portion (ten times over a period of one hour) N-acetyloxy-2-thiopyridone **3a** (530 mg, 3.15 mmoles). The reaction mixture was at the same time photolysed with a tungsten lamp (270 W) . After evaporation of the solvent, the residue was chromatographied on silica gel (Hexane) and gave the olefin **2b** (205 mg, 85%, E/Z 4:1) (cf Table 2, entry 4).

7-Pentadecene (2a)[2, 26] (E/Z 4/1): **IR** (film): 1459-964-722 cm-1**^{1}H** δ 0.9 (6H, m); 1.3 (18 H, s); 2 (4H, m); 5.4 (2H, CH=, m).**^{13}C NMR** ($CDCl_3$) δ 14.1 (CH_3); 22.7 to 32.6 (CH_2); 129.9 (CH=, Z); 130.4 (CH=, E).

1-Phenyl-3-undecene (2b)[27] (E/Z 4/1): **IR** (film): 1451-966-696 cm-1 **^{1}H** δ 0.9 (3H, t); 1.3 (10 H, s); 1.97 (2H, m); 2.3 (2H, m); 2.65 (2H, m); 5.42 (2H, CH=, m); 7.1 to 7.3 (5H, m).**^{13}C** δ 14.1 (CH_3); 22.7, 27.3 (Z), 29.1, 29.2, 29.6, 29.7, 31.9, 32.6, 34.5, 36.1 (Z), 36.2 (CH_2); 125.6, 125.7 (E), 128.2, 128.4, 128.6 (Z), 129.3 (CH); 130.7 (Z), 131.3 (E) (CH=); 142.2(Cq). **MS** (EI): 230 $(M)^{+\cdot}$.

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