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DECARBOXYLATIVE RADICAL ADDITION TO VINYLSULPHONES AND VINYLPHOSPHONIUM BROMIDE: SOME FURTHER NOVEL TRANSFORMATIONS OF GEMINAL (PYRIDINE-2-THIYL) PHENYLSULPHONES.

Derek H. R Barton[a,b*], Jean Boivin[c], Elisabeth Crépon (née da Silva)[c], Jadab Sarma[a], Hideo Togo[b,d], and Samir Z. Zard[b,c*]

a) Department of Chemistry, Texas A&M University, College Station, Texas 77843, U S A
b) Institut de Chimie des Substances Naturelles, C N.R S , 91198 Gif-Sur-Yvette, France
c) Laboratoire de Synthèse Organique, Ecole Polytechnique, 91128 Palaiseau, France
d) Department of Chemistry, Chiba University, Chibashi 260, Japan.

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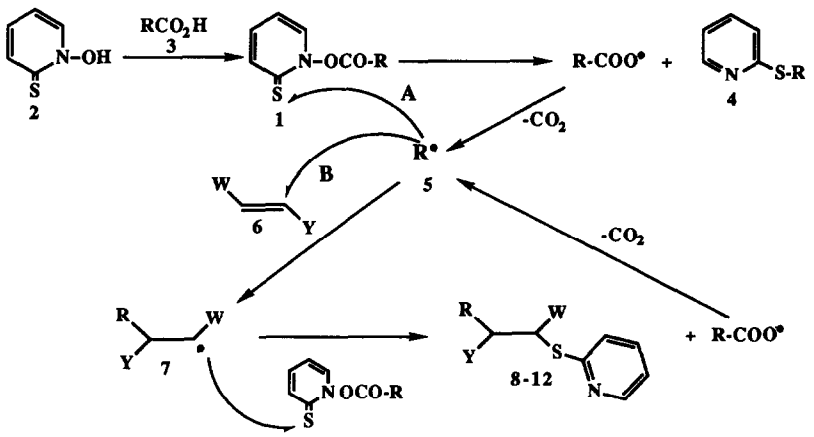
Summary *Irradiation of O-acyl derivatives 1 of N-hydroxy- 2-thiopyridone with visible light in the presence of phenyl vinyl sulphone or vinyl triphenylphosphonium bromide leads to the corresponding adducts 8 and 9 which can undergo a wide variety of further transformations*

Over the last decade, there has been an explosive growth in the use of radical reactions in organic synthesis[1] This is due in a large measure to the tremendous synthetic potential for creating new carbon carbon bonds through radical additions to unsaturated substrates as well as to the recent availability of a sizeable and rapidly growing body of kinetic data allowing, in many instances, fine control of the regio- and stereo-chemistry of such reactions Moreover, the relative insensitivity of radical processes to solvent effects and to steric factors (as far as the radical centre is concerned) provides the chemist with considerable predictive powers when applying these kinetic data in the design of a synthetic strategy

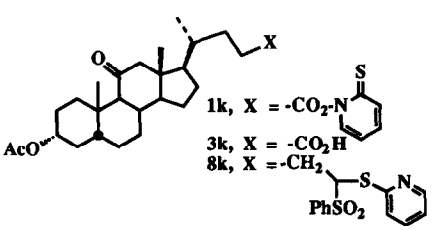
It is not surprising therefore that a great variety of inter- and intramolecular radical additions, or a combination of both, have found their way into the synthesis of highly complex targets The intermolecular variant, although usually more difficult to accomplish than the ring forming intramolecular process, offers the advantage of increasing both the functionality and the number of carbon atoms in the system As part of our ongoing exploratory study of the radical decarboxylation of carboxylic acids through their thiohydroxamate esters[2], we have found that vinyl sulphones and vinyl phosphonium are excellent partners in intermolecular radical additions Furthermore, the adducts in the case of the former, containing a geminal (phenylsulphonyl) pyridylsulphide group, constitute a springboard for hosts of selective transformations This work, which we now describe in detail, has been the subject of two preliminary communications[3]

A few years ago, we reported that esters **1** derived from N-hydroxy-2-thiopyridone **2** and aliphatic or alicyclic carboxylic acids **3** undergo, upon heating or, even better, upon irradiation with visible light from a tungsten lamp, a radical chain reaction leading to the corresponding pyridyl sulphides **4**, as shown in scheme 1 (path A)[2a]. This represents the radical decarboxylation process in its simplest expression It became immediately apparent, however, that we had in hand a general method for generating carbon radicals under exceptionally mild conditions and that the basic scheme can in fact be easily modified by adding various radical traps so as to capture the intermediate carbon radical **5** by other than the starting ester Instead of sulphide **4**, one can therefore obtain halides, chalcogenides, alcohols, etc , where the original acid function has been replaced by another group More importantly, it proved possible to intercept the carbon radical with an olefin **6** activated by one or more electron-withdrawing groups such as ketones, esters, or nitriles (**6**, W= -COR, -CN), as outlined in pathway B in scheme 1[2]



Scheme 1

6a ; 8, W = SO_2Ph; Y = H
6b ; 9, W = PPh_3^+ Br^-; Y = H
6c ; 10, W = SPh; Y = H
6d , 11, W = SOPh; Y = H
6e ; 12, W = SO_2Ph; Y= Me



For such modifications to be viable from a preparative standpoint, it is necessary that the route leading to the desired adducts (i e path B) prevails over the basic background reaction going through path A In practice, this is ensured by using an excess of the olefin. However, with some of the olefins which are known to polymerise under radical conditions, such as methyl acrylate or

acrylonitrile, this expedient favours the formation of telomers arising from further additions of the second carbon radical **7** onto the olefin A compromise must therefore be found in order to minimise all the unwanted competing pathways

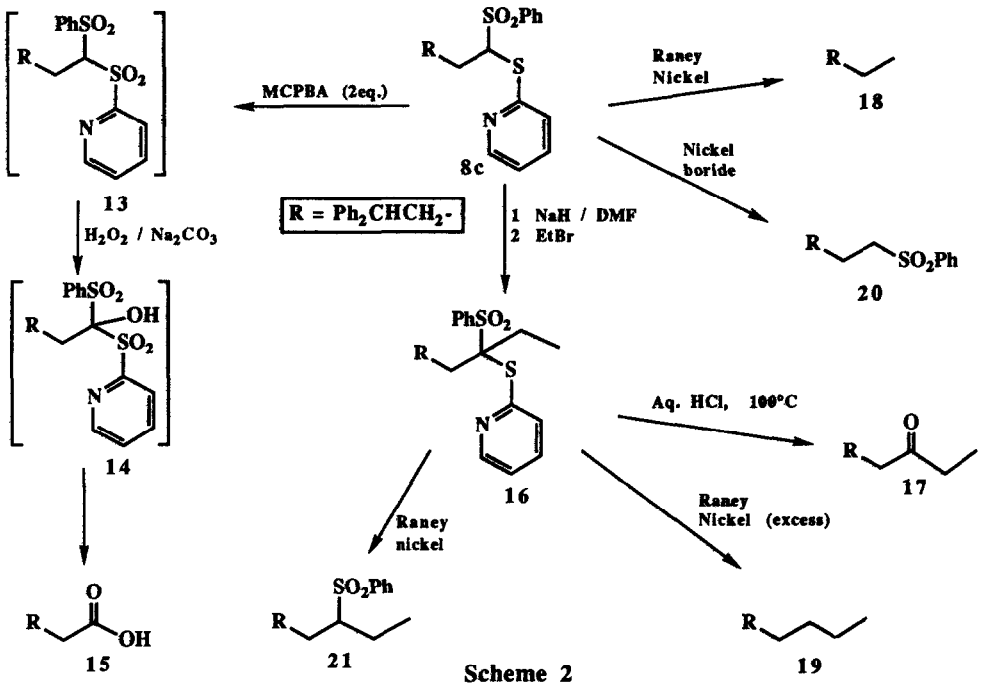
Clearly, an electrophilic, non polymerisable (under radical conditions) olefin would be ideally suited for our decarboxylation system We had earlier found that nitroolefins[4] were excellent traps for nucleophilic carbon centered radicals, but the simplest monomers are prone to base-catalysed polymerisation and are therefore difficult to handle Phenyl vinyl sulphone **6a** and vinyl phosphonium bromide **6b** (Schweizer's reagent), on the other hand, are both nicely crystalline compounds, easy to manipulate, and, not least of all, commercially available Moreover, and in contrast to methyl acrylate, we found that heating phenyl vinyl sulphone with AIBN did not lead to any noticeable telomerisation It is surprising that, until the present work, these electrophilic olefins have only been subjected to Michael type nucleophilic additions Their potential as partners in radical additions appears to have been neglected

Table 1 Decarboxylative radical addition onto olefins **6a-e** The same R group applies to the products

Entry	Ester **1**	Olefin **6**	Equivalents	Products (yield %)
1	**1a**, R= 1-adamantyl-	**6a**	5	**8a** (100)
2	**1b**, R= cyclohexyl-	**6a**	4 8	**8b** (89)
3	**1c**, R= Ph_2CHCH_2-	**6a**	6	**8c** (75)
4	**1d**, R= Me_3C-	**6a**	5	**8d** (96)
5	**1e**, R= $PhCH_2CH_2$-	**6a**	5	**8e** (82)
6	**1f**, R= Me_2CH-	**6a**	2 9	**8f** (82)
7	**1g**, R= $PhOCH_2$-	**6a**	2 5	**8g** (84)
8	**1h**, R= 1-methylcyclohexyl	**6a**	5	**8h** (87)
9	**1i**, R= $(PhCH_2)_2CH$-	**6a**	5	**8i** (57)
10	**1j**, R= $CH_3(CH_2)_{14}$-	**6a**		**8j** (54)
11	**1k**, (steroid derivative)	**6a**	5 4	**8k** (70)
12	**1a**, R= 1-adamantyl-	**6d**	10	**11d** (43)
13	**1a**, R= 1-adamantyl-	**6e**	10	**12a** (27), **4a** (50%)
14	**1a**, R= 1-adamantyl-	**6b**	2	**37a** (88)
15	**1b**, R= cyclohexyl-	**6b**	2 5	**37b** (71)
16	**1c**, R= Ph_2CHCH_2-	**6b**	5	**37c** (82)

Our high hopes for these systems turned out to be well founded Irradiation of a mixture of adamantane carboxylic ester **1a** in the presence of an excess of phenyl vinyl sulphone **6a** gave a quantitative yield of the expected adduct **8a** Other thiohydroxamate esters derived from a variety of primary, secondary and tertiary carboxylic acids underwent the decarboxylative addition cleanly as shown by the results collected in Table 1 The excess olefin is destroyed by reaction with a slight excess of hydrazine, but it is possible to recover a fair amount back by mere recrystallisation from the crude reaction mixture

The high electrophilicity of the vinyl sulphone is crucial for the success of the reaction. For the sake of comparison, the less reactive phenyl vinyl sulphide **6c** and phenyl vinyl sulphoxide **6d** were briefly examined and found to behave quite poorly The former gave hardly any of the expected adducts whereas the best yield with the latter, even when using a ten-fold excess of the olefin, was only 43% of compound **11d** (derived from ester **1a**, entry 12). In both cases formation of rearranged sulphide **4** through path A was dominant Substitution in the β-position of the vinylic sulphone caused a marked decrease in the yield , as would be expected from ample literature precedent regarding other olefinic traps For example, irradiation of ester **1a** in the presence of excess of phenyl propenyl sulphone **6e** only produced 27% of adduct **12a** and 50% of unwanted sulphide **4a** (entry 13).



Scheme 2

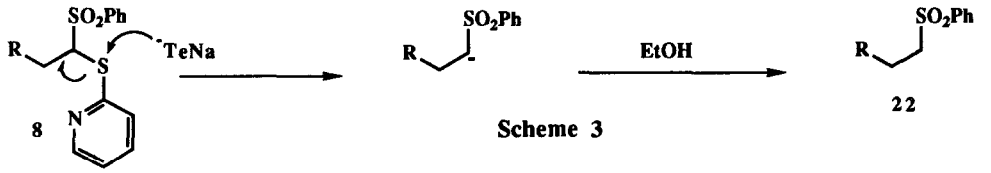
One of the attractive features of this decarboxylative radical addition to vinylic sulphones is that it provides derivatives with a sulphone and sulphide group in a geminal disposition Both groups influence each other's reactivity and, by exploiting their remarkably rich chemistry[5], a great variety of useful transformations can be conceived The following examples (Scheme 2) will hopefully give a glimpse of the wealth of possibilities

Taking compound **8c** as a typical adduct, oxidation of the sulphide group with two equivalents of peracid (MCPBA) followed by exposure of the intermediate bis(sulphone) **13** to hydrogen peroxide and sodium carbonate in methanol-tetrahydrofuran gave, after acidification, carboxylic acid **15** in 78%

overall yield This sequence in fact converts the starting carboxylic acid **3c** into its higher homologue **15** in what may be viewed as a useful alternative to the well known Arndt-Eistert[6] method Although we have not carried any further studies into the mechanism and scope of this apparently novel transformation, we believe that it could proceed through intermediate **14**, arising from the hydroxylation of the anion of **13** with hydrogen peroxide

Alkylation of the sodium salt of **8c**, easily generated with sodium hydride in DMF, with ethyl bromide afforded **16** in good yield (81%) Heating the latter with dilute hydrochloric acid resulted in a clean conversion (95%) to the corresponding ketone **17** The ease of the hydrolysis step is a direct consequence of the labilising effect the sulphide group exerts upon the sulphone (vide infra)

Both the sulphide and the sulphone groups may be reductively removed by treatment with Raney Nickel Alkanes **18** (82%) and the higher homologue **19** (78%) were thus obtained from **8c** and **16** respectively It is also possible to cleave off the sulphide group selectively using nickel boride as the reducing agent In this manner **8c** and **16** were converted into sulphones **20** and **21** in 83% and 72% yield respectively We later found that the same transformation could be accomplished quite conveniently using sodium telluride as can be seen from the examples collected in Table 2 Sodium telluride is readily prepared[7] *in situ* by reduction of tellurium powder with $NaBH_4$ followed by addition of ethanolic sodium hydroxide until pH 12 Air is bubbled at the end of the reaction to destroy excess reagent Elemental tellurium is thus precipitated and recovered quantitatively



Scheme 3

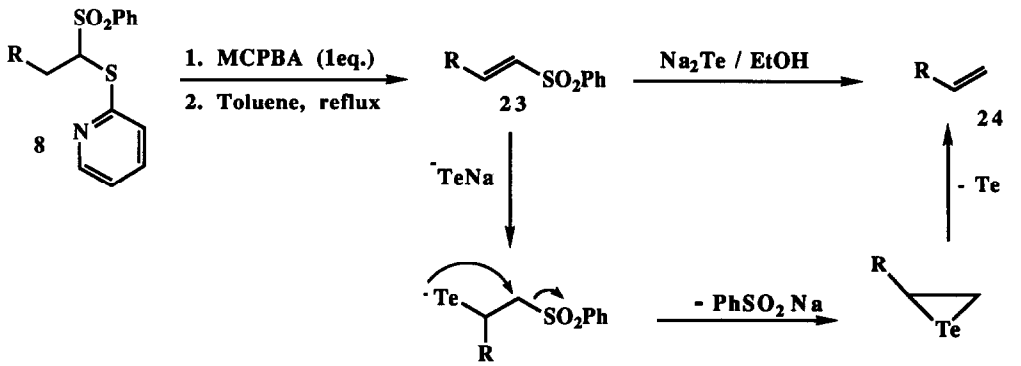
Presumably, the strongly nucleophilic telluride anion reacts at the sulphide sulphur with concomitant rupture of the carbon-sulphur bond (scheme 3) The negative charge in the leaving group is of course stabilised by the sulphone group Sodium telluride displays a wide range of mechanistic behaviour[8], reacting in some instances through electron transfer. This does not seem to be the case in this instance since electron transfer to the sulphone moiety would have resulted in overall desulphonylation

Another, perhaps synthetically more interesting, transformation mediated by sodium telluride concerns desulphonylation of vinylic sulphones **23**[9] These are easily prepared by oxidising the sulphide group in adducts **8** to the sulphoxide followed by thermolysis in toluene Exposure of the vinylic sulphones thus obtained to sodium telluride in ethanol resulted in a smooth conversion to the corresponding terminal alkenes **24** in generally high yields (Table 2)

Table 2 Reaction of sodium telluride with gem (Pyridine-2-thiyl)- Phenylsulphones **8** and vinyl sulphones **23**

Entry	Adduct **8**	Sulphone **22** (Yield %)	Vinyl sulphone **23** (Yield %)	Alkene **24** (Yield %)
1	**8a**, R= 1-adamantyl-	**22a** (96)	**23a** (88)	**24a** (82)
2	**8b**, R= cyclohexyl-	**22b** (94)	—	—
3	**8c**, R= Ph_2CHCH_2-	—	**23c** (78)	—
4	**8d**, R= Me_3C-	**22d** (96)	—	—
5	**8e**, R= $PhCH_2CH_2$-	**22e** (96)	**23e** (85)	**24e** (75)
6	**8f**, R= Me_2CH-	**22f** (94)	—	—
7	**8g**, R= $PhOCH_2$-	—	**23g** (81)	**24g** (66)
8	**8j**, R= $CH_3(CH_2)_{14}$-	**22j** (95) (by n m r)	**23j** (80)	**24j** (94)

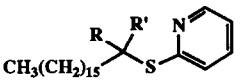
From a mechanistic standpoint, the exceptional nucleophilicity of the telluride anion can again be invoked to account for the reductive desulphonylation As outlined in scheme 4, Michael addition followed by nucleophilic displacement of the sulphone gives an episelenide which collapses into olefins and elemental tellurium. Such an extrusion of tellurium from episelenides has previously been postulated by Clive and Menchen[10]



Scheme 4

In another series of experiments, we have succeeded in replacing selectively the sulphone moiety with various groups through a Lewis acid catalysed nucleophilic displacement As in the acid catalysed hydrolysis of **16** to the corresponding ketone **17** described above, such a transformation is made possible by the presence of the pyridine sulphide group which stabilises the incipient carbocation resulting from complexation with the Lewis acid Observations of this nature on related systems, especially by the group of Trost[11], may be construed as precedent

After some experimentation, we found that ethylaluminum dichloride ($EtAlCl_2$) induced the reaction of **8j** with allyl trimethylsilane[12] to give homoallylic sulphide **25** in excellent yield (97%) Other common Lewis acids such as $TiCl_4$ or BF_3 were much less efficient Moreover, starting the reaction at low temperature was crucial for good and reproducible yields Oxidation with m-chloroperbenzoic acid of the homo-allylic sulphide thus obtained followed by sulphoxide thermolysis gave terminal diene **26** in 73% overall yield



8j, R = -SO_2Ph, R' = H

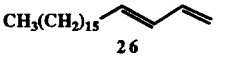
25, R = -$CH_2CH{=}CH_2$, R'= H

27, R = Me, R'= H

28, R = -SO_2Ph, R' = Me

29, R = R'= Me

34, R = R'= H



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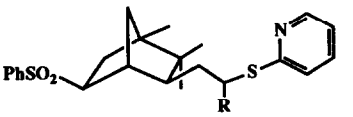
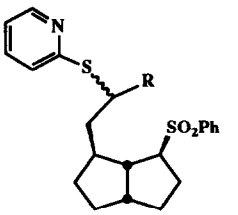


30, R = -SO_2Ph

32, R = Me



31, R = -SO_2Ph

33, R = Me

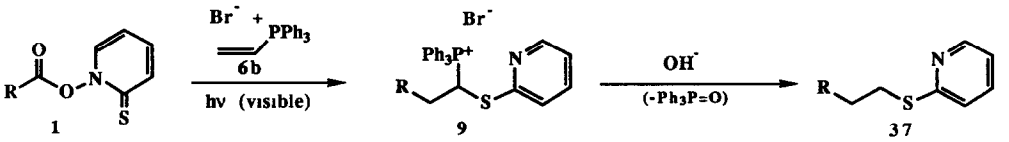
35, R = H

It is quite possible that an allyl aluminum complex[13] is involved rather than a simple Lewis acid complexation followed by nucleophilic displacement by the allyl trimethylsilane Indication that this could indeed be the case is provided by the observation that trimethyl aluminum reacts with **8j** to give sulphide **27** in 94% yield. An interesting example is provided by compound **28**, made in almost quantitative yield by alkylation with methyl iodide of the anion derived from **8j**, and which is converted into dimethylated sulphide **29** (80%) upon treatment with trimethyl aluminum This sequence leading to an isopropyl (or isopropenyl if the sulphide is eliminated via the sulphoxide) group is relevant to the terpene field where such subunits are frequently encountered. Moreover, this transformation is highly selective as illustrated by the transformation of compounds **30** and **31**[14] into methylated derivatives **32** and **33** in 88 and 80 % yield respectively Only the sulphone geminal to the pyridyl sulphide is substituted with a methyl group

To our initial surprise, exposure of adduct **8j** to ethylaluminum dichloride, in the absence of allyl trimethylsilane, resulted in the almost quantitative formation of sulphide **34** where the sulphone group has been replaced with a hydrogen To our knowledge, only in very rare instances has ethylaluminum dichloride been explicitly reported to act as a reducing agent, causing, for example, the reductive opening of certain lactones[15] The source of hydride is one of the ß-hydrogens of the ethyl group, with concomitant departure of ethylene This reaction is clearly related to the Meerwein-Pondorff-Verley reduction and to hydride transfers encountered with some organometallic reagents In the same way, **28** and **31** were desulphonylated into sulphides **27** (79%) and **35** (73%) respectively The clean obtention of the latter again underscores the selectivity of the process

The various transformations described in this exploratory study demonstrate the tremendous synthetic

potential of the decarboxylative radical addition to vinyl sulphones The rich chemistry embodied in the resulting adducts emerges beautifully as a consequence of the interplay between the sulphide and the sulphone groups



Scheme 5

In a brief complementary study of electrophilic, non polymerisable (under radical conditions) olefins, we examined the behaviour of vinylphosphonium bromide **6b** as a radical trap in the decarboxylation system We were gratified to find that capture of the transient carbon radicals was quite efficient (Table 1, entries 14-16) Due to their ionic nature, the primary adducts **9a-c** were converted, for isolation purposes, into sulphides **37a-c** by treatment with sodium hydroxide (scheme 5) The overall process leads therefore to the homologous sulphides (as compared to sulphides **4** resulting from simple decarboxylative rearrangement) similar to those prepared above by reductive desulphonylation using $EtAlCl_2$ In terms of synthetic utility, it is surely better to use adducts **9a-c** for what they are, namely Wittig reagents In view of the mild conditions and generality of the decarboxylation process, this approach should provide a wide variety of such Wittig reagents which are relatively inaccessible by other means

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Experimental Section

All reactions were performed under inert atmosphere (nitrogen or argon) Melting points were determined with a Köfler or a Reichert hot stage apparatus ^1H and ^{13}C n m r spectra are for deuteriochloroform solutions with tetramethylsilane as internal standard (δ ppm) Optical rotations are for chloroform solutions I.R spectra are of Nujol mulls unless otherwise stated Mass spectra (electron impact) were recorded on MS 50 or VG ZAB spectrometers MATREX 60 (35-70 μm) silica gel was used for column chromatography Solvents and reagents were purified according to standard laboratory techniques

2-(1-Adamantyl)-1-phenylsulphonyl-1-(pyridine-2-thiyl) ethane (8a). Ester **1a** was prepared according to reference[4] A solution of ester **1a** (580 mg, 2 mmol) and phenyl vinylsulphone **6a** (1 68 g, 10 mmol) in a mixture of benzene (8 ml) and dichloromethane (8 ml) was irradiated for 10 min (500 W, tungsten lamp) at 20-25°C under a nitrogen atmosphere The solvent was then evaporated under reduced pressure The residue was dissolved in tetrahydrofuran (16 ml) The solution was cooled to 0°C and hydrazinium hydroxide (1 5 g) was added. The reaction mixture was allowed to warm to

room temperature After 10 min the solvent was evaporated under reduced pressure. Chromatography of the crude residue (dichloromethane ether 9/1, v/v) afforded **8a** (830 mg) in quantitative yield, m.p 123-5°C (ether), ν_{max} (Nujol) 1145, 1300 cm^{-1}, m/z 272 (M^+ -$PhSO_2$), δ_H 8 4-8 7 (2H, m), 8 0-8.3 (2H, m), 7 4-7 8 (4H, m), 7 0-7 3 (2H, m), 6 0 (1H, dd, J= 10 2 Hz), 1 4-2 5 (17H, m), (Found C, 66 83, H, 6 58, N, 3 50 Calc for $C_{23}H_{27}NO_2S_2$ C, 66 79, H, 6 58, N, 3 39 %)

Typical Procedure for the Preparation of Esters 1 and Radical Addition to Phenyl vinyl sulphone 6a.

4,4-Diphenyl-1-phenylsulphonyl-1-(pyridine-2-thiyl) butane (8c). To a solution of β,β-diphenylpropionic acid (452 mg, 2 mmol) in dry benzene (8 ml) oxalyl chloride (1 5 g) and a trace of DMF were added After 18 hr, excess of oxalyl chloride and solvent were removed by evaporation under reduced pressure The resulting acid chloride was dissolved in dry benzene (6 ml) in a flask protected from the light by an aluminium foil. After cooling to 0°C, N-hydroxypyridine-2-thione (280 mg, 2 mmol) was added A mixture of pyridine (400 mg, 5 mmol) and benzene (2 ml) was then slowly added. The ice-bath was removed and the stirring was continued for 30 min The reaction mixture was filtered Phenyl vinylsulphone **6a** (1 915 g, 10 2 mmol) and dichloromethane (3-5 ml) were added to the filtrate The irradiation was carried out for 30 min (500 W, tungsten lamp) at 20-25°C under nitrogen atmosphere After removal of the solvent, THF (15 ml) and hydrazinium hydroxide (1 6 g) were added and the reaction mixture was stirred for 15 min Evaporation under reduced pressure followed by column chromatography (eluent, dichloromethane) afforded the compound **8c** (676 mg, 74%), m p 98-101°C (ether-pentane), ν_{max} (neat) 1145, 1305 cm^{-1}, m/z 318 (M^+ -$PhSO_2$), δ_H 8 3-8 5 (1H, m), 7 9-8 1 (2H, m), 6 8-7 8 (16H, m), 5 95 (1H, m), 4 1 (1H, t, J= 8 Hz), 1 8-2 7 (4H, m), (Found C, 70 63, H, 5 54, N, 3 29 Calc for $C_{27}H_{25}NO_2S_2$ C, 70 56, H, 5 48, N, 3 05 %)

The following adducts were obtained by the same procedure

2-Cyclohexyl-1-phenylsulphonyl-1-(pyridine-2-thiyl) ethane (8b), yield 89% from **1b**, m p 76-8°C (ether-pentane), ν_{max} (neat) 1145, 1305 cm^{-1}, m/z 361, δ_H 8 4-8 6 (1H, m), 8 1-8 3 (2H, m), 7 4-7 8 (4H, m), 7 0-7 3 (2H, m), 6 05 (1H, dd, J=12 Hz), 2 4-0 7 (13H, m), (Found C, 63 06, H, 6 47, N, 3 87 Calc for $C_{19}H_{23}NO_2S_2$ C, 63 13, H, 6 41, N, 3 87 %)

3,3-Dimethyl-1-phenylsulphonyl-1-(pyridine-2-thiyl) butane (8d), yield 96% from **1d**, m.p 85-7°C, ν_{max} (chloroform) 1149, 1309 cm^{-1}, m/z 335, δ_H 8 21 (1H, d, J= 7 Hz), 7 87 (2H, dd, J= 2, J'= 7 Hz), 7 27-7 35 (5H, m), 6 91 (1H, dd, J= 2, J'= 7 Hz), 5 80 (1H, d, J= 9 6 Hz), 2 35 (1H, d), 1 81 (1H, dd), 0 99 (9H, s)

4-Phenyl-1-phenylsulphonyl-1-(pyridine-2-thiyl) butane (8e)[16], yield 82% from **1e**, ν_{max} (chloroform) 1145, 1308 cm^{-1}, m/z 383, δ_H 8 18 (1H, dd), 7 85 (2H, d), 7 0-7 7 (9H, m), 6 8-7 0 (2H, m), 5 75 (1H, dd), 2 55 (3H, m), 1 95 (3H, m)

3-Methyl-1-phenylsulphonyl-1-(pyridine-2-thiyl) butane (8f), yield 82% from **1f**, m p 97-8°C, ν_{max} (chloroform) 1149, 1309 cm^{-1}, m/z 321, δ_H 8 20 (1H, d), 7 91 (2H, d), 7 22-7 50 (4H, m), 6 80-7 02 (2H, m), 5 82 (1H, d), 1 73-2 20 (3H, m), 0 93 (3H, d), 0 95 (3H, d)

3-Phenoxy-1-phenylsulphonyl-1-(pyridine-2-thiyl) propane (8g), yield 95% from **1g**, m p 83-4°C, ν_{max} (chloroform) 1147, 1306 cm^{-1}, m/z 385, δ_H 8 14 (1H, d), 7 91 (2H, d), 7 30 (6H, m), 6 85 (5H, m), 6 03 (2H, dd, J= 4, J'= 11 Hz), 4.24 (2H, m), 2 92 (1H, m), 2 28 (1H, m)

2-(1-Methylcyclohexyl)-1-phenylsulphonyl-1-(pyridine-2-thiyl) ethane (8h), yield 87% from **1h**, m p 66-8°C (ether-pentane), ν_{max} (neat) 1150, 1305 cm^{-1}, m/z 234 (M^+ -$PhSO_2$), δ_H 8 4-8 6 (1H, m), 8 1-8 3 (2H, m), 7 4-7 8 (4H, m), 7 0-7 3 (2H, m), 6 0 (1H, dd, J=10 Hz), 2 50 (1H, dd, J= 16 Hz), 1 85 (1H, dd, J= 16 Hz), 0 7-2 0 (10H, m), 1 0 (3H, s), (Found C, 64 01, H, 6 78, N, 3 85 Calc for $C_{20}H_{25}NO_2S_2$ C, 63 97, H, 6 71, N, 3 73 %)

3,3-Dibenzyl-1-phenylsulphonyl-1-(pyridine-2-thiyl) propane (8i), yield 57% from **1i**, m p 108-110°C (ether-pentane), ν_{max} (neat) 1145, 1305 cm^{-1}, m/z 332 (M^+ -$PhSO_2$), δ_H 8 4-8 6 (1H, m), 8 0-8 2 (2H, m), 7 0-7 9 (16H, m), 6 10 (1H, m), 2.0-3 2 (1H, m), (Found C, 70 75, H, 5 84, N, 3 80 Calc for $C_{28}H_{27}NO_2S_2$ C, 71 00, H, 5 75, N, 2 96 %)

1-Phenylsulphonyl-1-(pyridine-2-thiyl) heptadecane (8j), yield 54% from **1j**, m p 79-80°C, ν_{max} (chloroform) 1149, 1310 cm^{-1}, m/z 348 (M^+ -$PhSO_2$), δ_H 8 20 (1H, d), 7 85 (2H, m), 7 2-7 5 (4H, m), 8 6-7 0 (2H, m), 5 70 (1H, dd), 2 2-2 5 (1H, m), 1 4-2 0 (3H, m), 1 26 (26H, m), 0 88 (3H, t)

3α-Acetoxy-25-phenylsulphonyl-25-(pyridine-2-thiyl)-11-oxo, 27-nor-5β-cholestane (8k), yield 70% from **1k**, m p 70-80°C (crude), $[\alpha]_D$ + 55° (c= 1, $CHCl_3$), ν_{max} (Nujol) 1730, 1700, 1305, 1145 cm^{-1}, m/z 524 (M^+ -$PhSO_2$), δ_H 8 4-8 6 (1H, m), 8 1-8 3 (2H, m), 7 4-7 8 (4H, m), 7 0-7 3 (2H, m), 5 75-6 05 (1H, m), 4 8 (1H, bs), 2 10 (3H, s), 1 20 (3H, s), 0 6 (3H, s), (Found C, 68 41, H, 7 72, N, 9 43 Calc for $C_{38}H_{51}NO_5S_2$ C, 68 54, H, 7 72, N, 9 63 %)

General Procedure for the Preparation of Vinylsulphones **23** from gem Phenylsulphonyl (Pyridine-2-thiyl) Derivatives **8**.

***Trans* 2-(adamant-1-yl)-1-phenylsulphonyl ethene (23a)** MCPBA (110 mg, 85%, 0 53 mmol) was added portionwise to an ice-cooled solution of 2-(1-adamantyl)-1-phenylsulphonyl-1-(pyridine-2-thiyl) ethane **8a** (200 mg, 0 48 mmol.) in dichloromethane (8 ml) At the end of the addition the cooling bath was removed and the reaction mixture stirred for 4 hr at 20°C The reaction mixture was then poured into a saturated solution of aqueous sodium hydrogenocarbonate and extracted twice with dichloromethane The combined organic layers were dried ($MgSO_4$) and concentrated. Aqueous 1N hydrochloric acid (5 ml) was added to the residue and the reaction mixture was heated at 100°C for 1 5 hr Usual work-up followed by column chromatography (eluent dichloromethane) afforded compound **23a** (129 mg, 88%), m p 141-3°C (ether-pentane), ν_{max} (Nujol) 1145, 1300 cm^{-1}, m/z 302 (M^+), δ_H 8 0-8 3 (2H, m), 7 7-7 9 (3H, m), 7 1 (1H, d, J= 16 Hz), 6 3 (1H, d, J= 16 Hz), 1 5-2 3 (15H, m), (Found C, 71 36, H, 7 33, S, 10 70 Calc for $C_{18}H_{22}O_2S$ C, 71 49, H, 7 33, S, 10 60 %)

The following products were obtained by this procedure

***Trans* 4,4-Diphenyl-1-phenylsulphonyl but-1-ene (23c)**, yield 78% from **8c**, m p 101-3°C (ether), ν_{max} (Nujol) 1142, 1305 cm^{-1}, m/z 348 (M^+), δ_H 8 0-6 8 (16H, m), 6 4 (1H, d, J=16 Hz), 4 25 (1H, t, J= 8 Hz), 3 1

(2H, t, J= 8 Hz), (Found C, 75 92, H, 5 71, S, 9 28 Calc for $C_{22}H_{20}O_2S$ C, 75 83, H, 5 79, S, 9 20 %)

4-Phenyl 1-phenylsulphonyl but-1-ene (23e)[17], yield 85% from **8e**, ν_{max} (Chloroform) 1629, 1493, 1316, 1149 cm^{-1}, δ_H 7 91 (2H, d), 7 78 (2H, dd, J= 2, J'= 7 Hz), 7 53 (3H, m), 7 81-7 27 (5H, m), 6 95 (1H, dd, J= 7, J'= 14 Hz), 6 27 (1H,d, J= 14 Hz), 2 76 (2H, t, J= 7 Hz), 2 51 2H, m), m/z 272 (M^+), 131 (M^+-$PhSO_2$)

3-Phenoxy 1-phenylsulphonyl prop-1-ene (23g)[18], yield 81% from **8g**, m p 97-8°C, ν_{max} (Chloroform) 1640, 1599, 1563, 1497, 1320, 1149 cm^{-1}, δ_H 7 91 (2H, d), 7 41-7 68 (3H, m), 6 65-7 34 (7H, m), 4 70 (2H, dd, J= 2, J'= 6 Hz), m/z 274 (M^+)

1,1-Diphenyl butane (18). Excess of Raney-nickel (suspension in water) was added to a solution of **8c** (99 mg, 0 22 mmol) in ethanol (4 ml) containing one drop of water The reaction mixture was refluxed for 24 hr The catalyst was then removed by filtration and the filtrate evaporated to dryness The title compound **18** was obtained in 82% yield after column chromatography (eluent. dichloromethane-pentane 1 1), b p 120°C/3 mm Hg (Lit [19] b p, 116-7°C/2 mm Hg), m/z 210 (M^+), δ_H 7 5 (10H, s), 4 05 (1H, t, J=8 Hz), 1 9-2 3 (2H, m), 0 7-1 7 (5H, m)

4,4-Diphenyl-butanoic Acid (15). MCPBA (250 mg, 85%, 1 26 mmol) was added portionwise to an ice-cooled solution of **8c** (222 mg, 0 48 mmol) in dichloromethane (6 ml) At the end of the addition the cooling bath was removed and the reaction mixture stirred for 5 h at 20°C The reaction mixture was then poured into a saturated solution of aqueous sodium hydrogenocarbonate and extracted with dichloromethane(2 X 20 ml) The combined organic layers were dried ($MgSO_4$) and concentrated To the resulting disulphone residue, dissolved in a MeOH, THF, water mixture (1 ml, 6 4 1 v/v), potassium carbonate (1 1 g) and a few ml of 30% H_2O_2 were successively added The reaction mixture was heated at 60°C for 3 hr , during that time MeOH and 30% H_2O_2 were further added until the disulphone was consumed totally Extraction with ether and usual work-up followed by column chromatography (eluent dichloromethane-ether, 9 1, v/v) afforded the compound **15** (91 mg, 78%), m p 104-6°C (ether-pentane, lit[20] m p 104°C)

6,6-Diphenyl-3-phenylsulphonyl-3-(pyridine-2-thiyl) hexane (16). To a solution of **8c** (1g, 2 18 mmol) in dry DMF (4 ml) cooled at 0°C, sodium hydride (230 mg, 55%, 5 27 mmol) was added The reaction mixture was stirred for 10 min and ethylbromide (1g, 9 mmol) was added After 5 5 hr, the reaction was quenched by addition of water Extraction with ether and usual work-up gave a residue which was purified by column chromatography (eluent. dichloromethane) affording the title compound **16** (864 mg, 89%), ν_{max} (Nujol) 1140, 1300 cm^{-1}, m/z 346 (M^+ - $PhSO_2$), δ_H 8 5-8 7 (1H, m), 8 0-8 3 (2H, m), 7 1-8 0 (16H, m), 3 9 (1H, t, J= 7 Hz), 1 8-2 8 (6H, m),1 1 (3H, t, J= 7 Hz) This compound was used without further purification

6,6-Diphenyl-3-phenylsulphonyl hexane (21). Excess of Raney-nickel (4g, suspension in water) was added to a solution of **16** (192 mg, 0 39 mmol) in ethanol (10 ml) containing two drops of water The reaction mixture was refluxed for 18 hr The catalyst was then removed by filtration and the filtrate, poured into water, extracted with ether The usual work-up afforded the title compound **21** in 82% yield after column chromatography (eluent. dichloromethane-pentane 1 1), m p 88-90°C, ν_{max} (Nujol) 1300, 1145 cm^{-1}, m/z 378 (M^+), δ_H 8 7-7 6 (5H, m), 7 4 (10H, s), 3 90 (1H, t, J= 8 Hz), 2 70 3 20 (1H, m), 1 5-2 5 (6H, m), 1 95 (3H, t, J= 7 Hz), (Found C, 76 14, H, 6 92, S, 8 57

Calc for $C_{24}H_{26}O_2S$ C, 76 15, H, 6 92, S, 8 67%)

6,6-Diphenyl-3-hexanone (17). Compound **16** (200 mg, 0 41 mmol) was refluxed for 5 hr in a mixture of 36% hydrochloric acid (2 5 ml), water (2 ml), and methanol (7 ml) After further 12 hr at 60°C, the reaction mixture was worked-up as usually Column chromatography (eluent dichloromethane) afforded **17** in 95% yield, m p 66-68°C (pentane-ether, (lit.[21] m p 68-69°C), ν_{max} (Nujol) 1700 cm^{-1}, m/z 252 (M^+), δ_H 7 55 (10H, s), 4 05 (1H, m), 2 2-2 7 (6H, m), 1 05 (3H, t, J= 7 Hz)

1,1-Diphenyl hexane (19). Excess of Raney-nickel (suspension in water) was added to a solution of **16** (200 mg, 0 41 mmol.) in ethanol (10 ml) containing two drops of water. The reaction mixture was refluxed for 48 hr and monitored by T L C After completion the catalyst was removed by filtration and the filtrate, poured into water, extracted with ether The usual work-up afforded the title compound **19** in 78% yield after column chromatography (eluent. dichloromethane), b p 150°C/ 4 mm Hg, (Lit. [22], b p 162-6°C/ 12 mm Hg), m/z 238 (M^+), δ_H 7 5 (10H, s), 4 0 (1H, t, J= 8 Hz), 1 9-2 4 (2H, m), 1 6-1 0 (6H, m), 0 9 (3H, m)

4,4-Diphenyl-1-phenylsulphonyl butane (20). A solution of $NaBH_4$ (2g, 40 mmol) in water (20 ml) was added to a mixture of compound **16** (205 mg, 0 45 mmol), boric acid (10 g), and nickel chloride (hexahydrate, 4 8g, 20 mmol).The reaction mixture was refluxed for 21 hr The crude reaction mixture was filtrated and the filtrate, poured into water, extracted with ether The usual work-up afforded the title compound **20** (129 mg,83%) after column chromatography, m p 79-80°C, ν_{max} (Nujol) 1305, 1150 cm^{-1}, m/z 350 (M^+), δ_H 8 3-8 0 (2H, m), 8 0-7 7 (3H, m), 7 5 (10H, s), 3 95 (1H, t, J= 8 Hz), 3 20 (2H, t, J= 8 Hz), 1 5-2 4 (4H, m), (Found C, 74 78, H, 6 80, S, 8 51 Calc for $C_{22}H_{22}O_2S$ C, 75 40, H, 6 33, S, 9 15%)

Adamantyl Pyridyl Sulphide (4a) and 2-(Adamant-1-yl)-1-phenylsulphinyl-1-(pyridine-2-thiyl) ethane (11d).

Ester **1a** (145mg, 0 5 mmol) and vinyl phenyl sulphoxide **6d** (760 mg, 5 mmol) were dissolved in a mixture of dichloromethane (3 ml) and benzene (3 ml) and irradiated for 40 min at 15-20°C The solvent was removed by evaporation under reduced pressure and the residue purified by chromatography (eluent dichloromethane) to give **4a** (30 mg, 25%), m p 80-2°C (pentane), lit.[23] m p 78-80°C, m/z 245 (M^+), δ_H 8 7-8 9 (1H, m), 7 1-7 9 (3H, m,), 1 5-2 3 (15H, m), and **11d** (85 mg,43%, mixture of diastereomers), ν_{max} (Nujol) 1580, 1555 cm^{-1}, m/z 272 (M^+ -PhSO), δ_H 8 5-8 8 (1H, m), 7 0-8 1 (8H, m), 5 7 (1H, dd, J= 10 Hz), 5 3 (1H, dd, J= 9 2 Hz), 1 0-2 3 (17H, m)

Ester **1a** and vinyl phenyl sulphide **6c** under the same conditions as above (6 eq , 15-20°C, irradiation during 60 min) gave **4a** as the major product (70%)

2-(Adamant-1-yl)-1-phenylsulphonyl-1-(pyridine-2-thiyl) propane (12a)

Propenyl phenylsulphone **6e** was obtained by oxidation of the corresponding sulphide with hydrogen peroxide in AcOH (61%), m p 55-61°C (cis + trans), lit [24] m p 67-8°C (trans only), ν_{max} (Nujol) 1140, 1300 cm^{-1}, m/z 182 (M^+), δ_H 8 1-7 8 (2H, m), 7 8-7 5 (3H, m), 6.2-7 4 (2H, m), 2 2 (3H, d, J= 6 Hz, cis), 1 95 (3H, dd, J= 6 Hz, trans)

Ester **1a** and propenyl phenylsulphone **6e**, under the same conditions as in the preparation of **8a**, gave **4a** (50%) and

12a (27%), m p 162-5°C (dichloromethane-ether), ν_{max} (Nujol) 1145, 1303 cm^{-1}, m/z 286 (M^+ -$PhSO_2$), δ_H 8 4-8 2 (1H, m), 8 1-7 8 (2H, m), 7 3-7 7 (4H, m), 6 8-7 1 (2H, m), 6 2 (1H, s),2 45 (1H, q, J= 7 Hz), 1 4-2 3 (15H, m), 1 25 (3H, d, J= 7 Hz), (Found C, 67 17, H, 6 80, N, 3 38 Calc for $C_{24}H_{29}NO_2S_2$ C, 67 41, H, 6 84, N, 3 28 %)

Typical Procedure for the Preparation of Esters 1 and Radical Addition to Triphenyl vinylphosphonium bromide 6b.

4,4-Diphenylbutyl 2-pyridyl sulphide (37c) To a solution of β,β-diphenylpropionic acid (452 mg, 2 mmol) in dry benzene (8 ml), oxalyl chloride (1 7 g) and a trace of DMF were added. After 18 hr , excess of oxalyl chloride and solvent were removed by evaporation under reduced pressure The resulting acid chloride was dissolved in dry dichloromethane (6 ml) in a flask protected from the light by an aluminum foil After cooling to 0°C, N-hydroxypyridine-2-thione (280 mg, 2 mmol) was added. A mixture of pyridine (400 mg, 5 mmol) and dichloromethane (2 ml) was then slowly added. The ice-bath was removed and the stirring was continued for 30 min Triphenyl vinylphosphonium bromide **6b** (3 7 g, 10 mmol) and dichloromethane were added to the filtrate until it became homogeneous The irradiation was carried out for 20 min (500 w, tungsten lamp) at 10-15°C After removal of the solvent, methanol (50 ml) and diluted sodium hydroxide (2 9 g in 10 ml of water) were added and the reaction mixture was stirred for 4 hr at 37°C The reaction mixture was poured into water and extracted with ether Usual work-up followed by column chromatography (eluent dichloromethane) afforded the compound **37c** (524 mg, 82%), m p 57 9°C (ether-pentane), ν_{max} (neat) 3050, 3035, 1595, 1580, 1555 cm^{-1}, m/z 319 (M^+), δ_H 8 65 (1H, m), 7 0-7 8 (3H, m), 7 50 (10H, s), 4 0 (1H, t, J= 8 Hz), 3 25 (2H, t, J= 7 Hz), 2 0-2 5 (2H, m), 1 5-2 0 (2H, m), (Found C, 79 23, H, 6 67, N, 4 37 Calc for $C_{21}H_{21}NS$ C, 78 95, H, 6 63, N, 4 38 %)

The following adducts were obtained by the same procedure from the corresponding acids

2-Cyclohexylethyl 2-pyridyl sulphide (37b), yield 71%, b p 160-5°C/ 0 5 mm Hg (Kugelrohr), ν_{max} (neat) 1580, 1555 cm^{-1}, m/z 221, δ_H 8 55-8 75 (1H, m) 7 0-7 8 (3H, m), 3 2 (2H, t, J=7 5 Hz), 0 8-2 2 (13H, m), (Found C, 70 71, H, 8 73, N, 6 32 Calc for $C_{13}H_{19}NS$ C, 70 54, H, 8 65, N, 6 33 %)

2-(Adamant-1yl) ethyl 2-pyridyl sulphide (37a), yield 88%, b p 160-5°C/ 0 5 mm Hg (Kugelrohr), ν_{max} (neat) 1580, 1555 cm^{-1}, m/z 273, δ_H 8 65-8 85 (1H, m) 7 1-7 9 (3H, m), 3 0-3 4 (2H, m), 1 3-2 3 (17H, m), (Found C, 74 91, H, 8 56, N, 5 21 Calc for $C_{17}H_{23}NS$ C, 74 67, H, 8 48, N, 5 12 %)

2-Phenylsulphonyl-2-(pyridine-2-thiyl) octadecane (28). To a solution of **8j** (1g, 2 05 mmol) in dry DMF (8 ml) cooled at 0°C, sodium hydride (0 2 g, 60%, 5 mmol) was added The reaction mixture was stirred for 30 min and methyliodide (0 56 ml, 9 mmol) was added.The reaction mixture was allowed to warm to 20°C After 4 hr, the reaction was quenched by addition of water Extraction with ether and usual work-up gave a residue which was purified by column chromatography (eluent. petroleum ether-ether, 1/1, v/v) affording the title compound **28** (1 0 g mg, 97%), ν_{max} (neat) 1560, 1550, 1455, 1440, 1410, 1300, 1140 cm^{-1}, δ_H 8 49 (1H, m), 7 99 (2H, d, J= 8 7 Hz), 7 82 (1H, d, J= 7 8 Hz), 7 5-7 75 (4H, m), 7 1-7 3 (2H, m), 1 9-2 1 (2H, m), 1 57 (3H, s), 1-15-1 4 (28H, m), 0 88 (3H, t, J= 5 9 Hz)

General Procedure for the Reaction of gem Phenylsulphonyl (Pyridine-2-thiyl) Derivatives with Ethylaluminum Dichloride.

To a solution of gem phenylsulphonyl (pyridine-2-thiyl) derivative (X mmol) in dichloromethane (4 X ml), cooled to -78°C, was added slowly ethylaluminum dichloride (1 M solution in hexanes, Y ml, Y mmol) The cooling bath was then removed and the reaction mixture allowed to warm to room temperature Saturated sodium carbonate (5 ml) was then added, and the reaction mixture was extracted with dichloromethane After the usual work-up, the product was purified by column chromatography

The following products were obtained by this procedure

1-(Pyridine-2-thiyl) heptadecane (34), yield 89% from **8j**, (X= 0 29, Y= 0 9, eluent. petroleum ether-ether, 3/1), m p 35-7°C (methanol), ν_{max} (Nujol) 1580, 1555, 1415, 1120 cm^{-1}, δ_H 8 42 (1 H, d, J= 4 2 Hz), 7 47 (1 H, t, J= 8 1 Hz), 7 16 (1 H, d, J= 8 Hz), 6 96 (1 H, dd, J= 5 5 et 6 6 Hz), 3 16 (2 H, t, J= 7 3 Hz), 1 6-1 8 (2 H, m), 1 1-1 6 (28 H, m), 0 88 (3 H, t, J= 5 5 Hz), (Found C, 75 39, H, 11 08, N, 3 41 Calc for $C_{22}H_{39}NS$ C, 75 58, H, 11 24, N, 4 00 %)

2-(Pyridine-2-thiyl) octadecane (27), yield 79% from **28**, (X= 0 52, Y= 1 6, eluent petroleum ether ether, 3/1), colourless oil, ν_{max} (neat) 1580, 1555, 1410, 1120 cm^{-1}, δ_H 8 42 (1 H, d, J= 4 5 Hz), 7 45 (1 H, t, J= 7 9 Hz), 7 15 (1 H, d, J= 8 Hz), 6 94 (1 H, dd, J= 5 et 7 3 Hz), 3 90 (1 H, dd, J= 6 7 et 13 4 Hz), 1 5-1 8 (2 H, m), 1 39 (3 H, d, J= 6 2 Hz), 1 2-1 5 (28 H, m), 0 88 (3 H, t, J= 5 9 Hz), (Found C, 75 98, H, 11 30, N, 3 66 Calc for $C_{23}H_{41}NS$ C, 75 96, H, 11 36, N, 3 85 %)

2-[[2-[Octahydro-6-(phenylsulfonyl)-1-pentalenyl] ethyl] thio]-pyridine) (35), yield 73% from 31 [14] (mixture of epimers), (X= 0 62, Y= 2 5, eluent. petroleum ether-ether, 3/1 to 1/1), colourless oil, ν_{max} (neat) 1570, 1545, 1440, 1410, 1290, 1140 cm^{-1}, δ_H 8 41 (1 H, d, J= 4 1 Hz), 7 86 (2 H, d, J= 8 3 Hz), 7,4-7,6 (4 H, m), 7 14 (1 H, d, J= 8 Hz), 6 98 (1 H, dd, J= 5, J'= 6 3 Hz), 3 1-3 25 (1 H, m), 2 9-3 1 (2 H, m), 2,53-2,7 (1 H, m), 2 4-2 53 (1 H, m), 1 1-2 1 (11 H, m), δ_{13C} 159 31, 149 42, 138 72, 135 90, 133 50, 129 15, 128 59, 122 14, 119 27, 71 09, 50 98, 46 34, 43 96, 33 78, 32 23, 32 02, 31 71, 28 51, 27 93, m/z 387 (M^+), 247, 246 (M^+ - SO_2Ph), h r m s , Found 387 1330 Calc 387 13267

4-(Pyridine-2-thiyl) eicos-1-ene (25). To a solution of **8j** (245 mg, 0 5 mmol) and trimethyl allylsilane (0 4 ml, 2 5 mmol) in dichloromethane (2 ml), cooled at -78°C, dichloro ethylaluminum (1 M solution in hexanes, 1 5 ml, 1 5 mmol) was added dropwise The cooling bath was removed and the reaction mixture allowed to warm to room temperature The reaction mixture was poured into a solution of saturated potassium carbonate (5 ml), and extracted with dichloromethane Usual work-up followed by chromatography of the crude residue (eluent petroleum ether ether 3/1, v/v) afforded **25** (193 mg, 99%) as a colourless oil, ν_{max} (neat) 1640, 1580, 1555, 1415, 1125 cm^{-1}, δ_H 8 39 (1 H, d,

J= 5 Hz), 7 42 (1 H, t, J= 8 Hz), 7 14 (1 H, d, J= 8 Hz), 6 87 (1 H, dd, J= 4 9 Hz and J'= 7,3 Hz), 5 75-5 97 (1 H, m), 5 06 (2 H, t, J= 9 5 Hz), 3 96 (1 H, m, J= 6 5 Hz), 2 46 (2 H, t, J= 6 5 Hz), 1 5-1 7 (2 H, m), 1-1 5 (28 H, m), 0 86 (3 H , t, J= 6 Hz), (Found C, 77 31, H, 11 03, N, 3 56 Calc for $C_{24}H_{43}NS$ C, 77 05, H, 11 12, N, 3 59 %)

Eicosa-1,3-diene (26) To a solution of alkene **25** (300 mg, 0 77mmol) in toluene (3 ml), cooled at 0°C, MCPBA (156 mg, 85% purity, 0 77 mmol) was added portionwise After 30 min , triphenyl phosphine (204 mg, 0 78 mmol) was added. The reaction mixture was then heated under reflux for 1 5 hr Evaporation of the solvent under reduced pressure, followed by column chromatography (eluent petroleum ether) afforded the compound **26** (156 mg, 73%) as a colourless oil, ν_{max} (neat) 1640, 1590, 1450, 990 cm^{-1}, δ_H 6 2 à 6 45 (1 H, m), 5 95-6 15 (1 H, m), 5 1-5 3 (1 H, m), 4,9-5,15 (2H, m), 2 0-2 25 (2 H, m), 1 2-1 5 (28 H, m), 0 88 (3 H , t, J= 6 Hz), h r m s , Found 278 2970 Calc 278 2973

General Procedure for the Reaction of gem Phenylsulphonyl (Pyridine-2-thiyl) Derivatives with Trimethylaluminum.

To a solution of gem phenylsulphonyl (pyridine-2-thiyl) derivative (X mmol) in dichloromethane (4 X ml), cooled to -78°C, was added slowly trimethylaluminum (2 M solution in hexanes, Y ml, 2Y mmol) The cooling bath was then removed and the reaction mixture was allowed to warm to room temperature Saturated sodium carbonate (5 ml) was then added, and the reaction mixture was extracted with dichloromethane After the usual work-up, the product was purified by column chromatography

The following products were obtained by this procedure

2-(Pyridine-2-thiyl) octadecane (27), yield 94% from **8j**, (X= 0 50, Y= 0 75, eluent petroleum ether-ether, 3/1), colourless oil, identical to the sample prepared by methylation-reduction of **8j** (see above)

2-Methyl-2-(pyridine-2-thiyl) octadecane (29), yield 80% from **28**, (X= 0 50, Y= 0 75, eluent petroleum ether-ether, 9/1), colourless oil, ν_{max} (neat) 1580, 1555, 1415, 1125 cm^{-1}, δ_H 8 5 (1 H, d, J= 4 8 Hz), 7 51 (1 H, t, J= 7 6 Hz), 7 33 (1 H, d, J= 7 7 Hz), 7 07 (1 H, dd, J= 4 9 Hz, J'= 7 3 Hz), 1 74 (2 H, t, J= 5 8 Hz), 1 46 (6 H, s), 1 3-1 5 (28 H, m), 0 88 (3 H, t, J= 6 7 Hz), (Found C, 76 20, H, 11 26, N, 3 50 Calc for $C_{23}H_{43}NS$ C, 76 33, H, 11 48, N, 3 71 %)

2-[[2-[Octahydro-6-(phenylsulfonyl)-1-pentalenyl]-1-(methyl) ethyl] thio]-pyridine (33), mixture of two isomers **a** and **b** (ratio 4 3), yield 79% from **31** (mixture of epimers)[14], (X= 0 55, Y= 1 8, eluent petroleum ether-ether, 3/2), colourless oil, ν_{max} (neat) 1570, 1545, 1435, 1405, 1295, 1280, 1135, 1115 cm^{-1}, δ_H 8 40 (1 H, m), **a** 7 91 and **b** 7 84 (2 H, d, Ja= 7 4 et Jb= 7 6 Hz), 7 4-7 7 (4 H, m), 7 15 (1 H, t, J= 6 8 Hz), 6 9-7 05 (1 H, m), 3 7 à 3 95 (1 H, m), **a** 3 25-3 4 and **b** 3 1-3 25 (1 H, m), 2 4 -2 75 (2 H, m), **a** 1 3 and **b** 1 22 (3 H, d, Ja= 6 7 and Jb= 6 7 Hz), (Found C, 65 58, H, 6 91, N, 3 34 Calc for $C_{22}H_{27}NO_2S_2$ C, 65 79, H, 6 78, N, 3 49 %)

2-[[1-(Methyl)-2-[3,3,4-trimethyl-6-(phenylsulfonyl) bicyclo[2.2.1] hept-2-yl] ethyl] thio-pyridine (32), mixture of two isomers **a** and **b** (ratio 7 3), yield 89% from **30** (mixture of epimers)[14], (X= 0 45, Y= 0 7, eluent petroleum ether-ether, 3/1), Crystallisation from methanol m p 97-107°C (mixture isomers **a** and **b** (ratio 3 1), ν_{max} (Nujol) 1570, 1545, 1410, 1300, 1275, 1140, 1120 cm^{-1}, δ_H 8 40-8 43 (1H, m), **a** 7 92 and **b** 7 79-7 87 (2H,

a d and **b** m, Ja= 7 1 Hz), 7 3-7 65 (4H, m), 6 9-7 13 (2H, m), 3 6- 3 8 (1H, m), 3 06 (1H, t, J= 7 6 Hz), **a** 2 56 and **b** 2 32 (1H, s), 1 9-2 15 (1H, m), 1 1-1 85 (9H, m) **a** 1 31 and **b** 1 16 (3H, d, Jb= 6 6 Hz and Ja= 6 8 Hz), **b** 0 99 and **a** 0 98 (3H, s), 0 83, 0 79 and 0 76 (6H, several s), (Found C, 67 13, H, 7 11, N, 3 40 Calc for $C_{23}H_{31}NO_2S_2$ C, 67 09, H, 7 27, N, 3 26 %)

General Procedure for the Reduction of *gem*-Phenylsulphonyl (Pyridine-2-thiyl) Derivatives **8**, into Sulphones **22** with Sodium Telluride.

A mixture of Tellurium powder (1 30 mg, 1 mmol) and sodium borohydride (152 mg, 4 mmol) in ethanol (10 ml) was heated to reflux under argon until disappearance of the tellurium The resulting solution was then cooled and its pH increased to greater than 12 by addition of 1N sodium hydroxide in ethanol (ca 15 ml) The *gem*-phenylsulphonyl (pyridine-2-thiyl) derivative (0 5 mmol) was then added and the mixture heated to reflux until all the starting material was consumed (ca 3 hours) Usual work up and purification by chromatography on silica gel provided the pure sulphide

The following products were obtained by this procedure

1-Phenylsulphonyl heptadecane (22j). yield 99% from **8j**, ν_{max} (Chloroform) 1456, 1307, 1149, 840, 680 cm^{-1}, δ_H 7 87 (2H, dd), 7 58 (3H, m), 3 5 (2H, m), 1 66 (2H, m), 1 22 (28 H), 0 85 (3H, t), m/z 380 (M^+), h m r s $C_{23}H_{40}O_2S$, Found 380 275, Calc , 380 274

1-Phenylsulphonyl-2-adamantyl ethane (22a). yield 96% from **8a**, m p 84-5°C, ν_{max} (Chloroform) 1448, 1305, 1151, 680 cm^{-1}, δ_H 7 90 (2H, dd), 7 47-7 73 (3H, m), 3 02-3 11(2H, m), 1 94 (3H, m), 1 30-1 78 (14 H, m), m/z 304 (M^+), h m r s $C_{18}H_{24}O_2S$, Found 304 1498, Calc , 304 1497

1-Phenylsulphonyl-3-methyl butane (22f)[25]. yield 95% from **8f**, ν_{max} (Chloroform) 1445, 1315, 1149, 735 cm^{-1}, δ_H 7 92 (2H, dd, J= 2, J'= 8 Hz), 7 48-7 76 (3H, m), 2 62-2 71(2H, m), 1 77-2 12 (1H, m), 1 48-1 76 (2 H, m), 0 87 (6H, d), m/z 212 (M^+)

1-Phenylsulphonyl-2-cyclohexyl ethane (22b). yield 94% from **8b**, ν_{max} (Chloroform) 1448, 1309, 1149, 700 cm^{-1}, δ_H 7 93 (2H, d, J= 8 Hz), 7 46-7 74 (3H, m), 3 10 (2H, m), 1 48-1 98 (7H, m), 1 40-1 03 (4 H, m), 0 72-1 01 (2H, m), m/z 252 (M^+), h m r s $C_8H_9O_2S$ M^+-C_6H_{11}, Found 169 0329, Calc , 169 0323

3,3-Dimethyl-1-phenylsulphonyl butane (22d)[26]. yield 96% from **8d**, m p 58-60 °C , ν_{max} (Chloroform) 1447, 1303, 1149, 720 cm^{-1}, δ_H 7.93 (2H, d, J= 8 Hz), 7 48-7 75 (3H, m), 2 95-3 20 (2H, m), 1 60 (2H, m), 0 87 (9H, s), m/z 226 (M^+)

4-Phenyl-1-phenylsulphonyl butane (22e)[11a]. yield 96% from **8e**, m p 62-3 °C , ν_{max} (Chloroform) 1448, 1309, 1149 cm^{-1}, δ_H 7 88 (2H, d, J= 8 Hz), 7 49-7 60 (3H, m), 7 15-7 24 (3H, m), 7 09 (2H, d, J= 8 Hz), 3 08 2H, t, J= 8 Hz), 2 57 (2H, t, J= 7 Hz), 1 70 (4H, m), m/z 274 (M^+)

General Procedure for the Reduction of Vinylsulphones **23** into Alkenes **24** with Sodium Telluride

A mixture of Tellurium powder (2 08 mg, 1 6 mmol) and sodium borohydride (243 mg, 6 4 mmol) in ethanol (10

ml) was heated to reflux under argon until disappearance of the tellurium The resulting solution was then cooled and its pH adjusted to about 12 by addition of 1N sodium hydroxide in ethanol (ca 6 ml) The vinyl sulphone (0 8 mmol) in THF (1 ml) was then added and the mixture heated to reflux until all the starting material was consumed (ca 2 hours) Usual work-up and purification by chromatography on silica gel provided the pure alkene

The following products were obtained by this procedure·

1-Heptadecene (24j)[27], yield 94% from 23j, colourless oil, ν_{max} (chloroform) 1635, 1466, 1378, 744, 668 cm^{-1}, δ_H 5 82 (1 H, m), 4 95 (2 H, m), 2 02 (2 H, m), 1.26 (26 H, bs), 0 88 (3 H, t Hz), m/z 238 (M^+)

4-Phenyl-1-butene (24e)[27], yield 75% from 23e, colourless oil, ν_{max} (chloroform) 1518, 1427, 927, 775 cm^{-1}, δ_H 7 08-7 34 (5H, m), 5 87 (1 H, m), 5 07 (2 H, m), 2 70 (2 H, m), 2 37 (2 H, m)

1-Ethenyl adamantane (24a)[28], yield 82% from 23a, δ_H 5 70 (1H, dd, J= 11, J'= 18 Hz), 4 88 (2H, dd, J= 11, J'= 18 Hz), 1.98 (3 H, bs), 1 81-1 84 (12 H, m)

3-Phenoxy-1-propene (24g)[27]; yield 66% from 23g, colourless oil, δ_H 7 29 (2H, d), 6 77-7 05 (3H, m), 5 92-6 20 (1H, m), 5 33 (2H, m), 4 55 (2H, d)

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