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O-Sulfinylation of Alcohols with Methanesulfonyl Cyanide or p-Toluenesulfonyl Cyanide.

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Abstract: Reaction of p-toluenesulfonyl cyanide or methanesulfonyl cyanide with alcohols in the presence of 1,8-diazabicyclo[5 4 0]undec-7-ene (DBU) or 1,4-diazabicyclo[2 2 2]octane (DABCO) gives sulfinates in good yield A mechanistic scheme involving sulfinyl cyanates **9** and **21** is suggested

Introduction

Transformation of alcohols to the corresponding imidates in a base-catalyzed reaction with various nitriles is an important reaction in synthetic organic chemistry This reaction has been known for almost a hundred years[1] (Nef, 1895) and it has found application for several synthetic purposes One major application is the use of imidates in glycoside and oligosaccharide synthesis[2] We have employed this method for the transformation of alcohols *via* their imidates to radicophilic thio- and selenocarbonyl derivatives for radical deoxygenation reactions[3] In an attempt to obtain tosyl imidates of various alcohols from the base-catalyzed reaction with the corresponding alcohol **2** and tosyl cyanide **1a** we have found that the corresponding sulfinates **4** were formed instead of the desired imidates (**3**) This prompted us to study this new reaction in detail and attempt to prove the mechanism

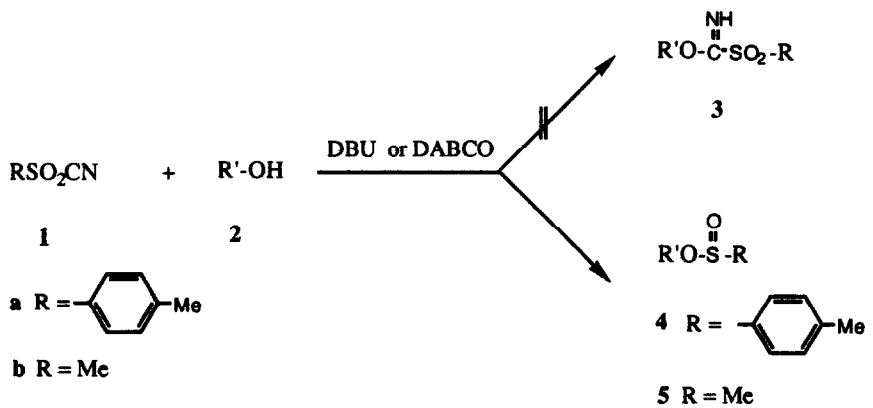
We have extended this new reaction by using methanesulfonyl cyanide **1b** instead of p-toluenesulfonyl cyanide We found that **1b** gave methanesulfinates **5** in high yield. The yields of this reaction were comparable to or higher than those of the corresponding p-toluenesulfinates[4,5]

O-Sulfinylation

Known methods for the synthesis of sulfinate esters require the activation[6,7] of sulfinic acids, or the use of the corresponding sulfinyl chlorides[8,9] A recent report describes a one-pot synthesis of sulfinates from alcohols with sulfonyl chlorides and trimethyl phosphite[10] The latter method, however, gives methanesulfinates in a lower yield[4].

Radical deoxygenation of alcohols[11] (the Barton-McCombie reaction) can be carried out on derivatives of alcohols containing a thio- or selenocarbonyl moiety. In most systems this functionality is the most radicophilic, thereby directing the attack of the radical reagent to the derivatized alcohol There are numerous reagents[12] for the transformation of alcohols to thiocarbonyl derivatives suitable for this radical process As a continuation of our research in this field we reacted various alcohols with tosyl cyanide **1a** (**Scheme 1**) in the presence of a base (DBU) to form the imidates **3** However, sulfinates **4** have been obtained in high yield, instead of **3** The sulphinates (**4**) formed in our reactions have been identified (in addition to physical methods) by comparison with authentic compounds and also by oxidizing them to the known sulfonates (tosylates)

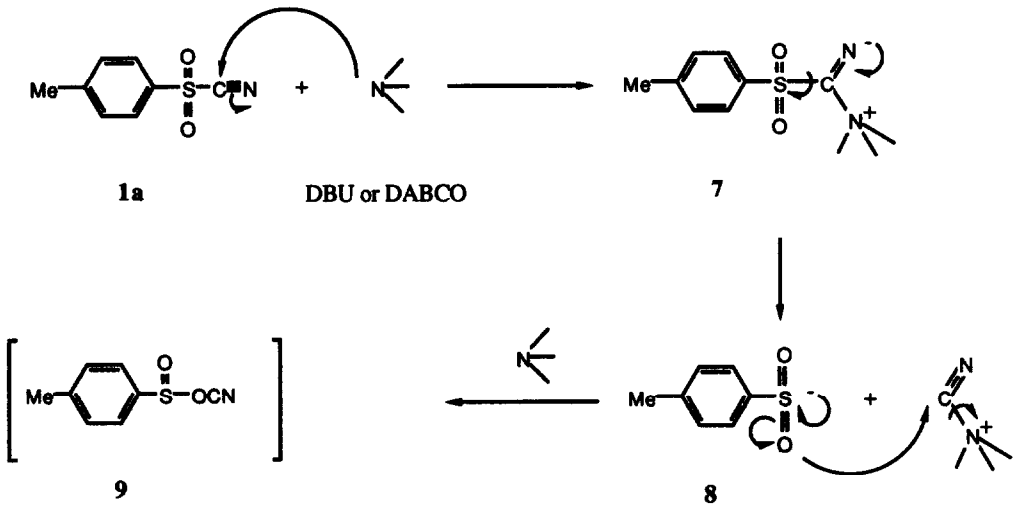
A thorough study showed that primary, secondary and tertiary alcohols furnish p-toluenesulfinates upon treatment with DBU or DABCO and **1a** Methanesulfonyl cyanide **1b** gave the corresponding methanesulfinates **5** in high yields (all the yields are given in the Experimental section)



Scheme 1

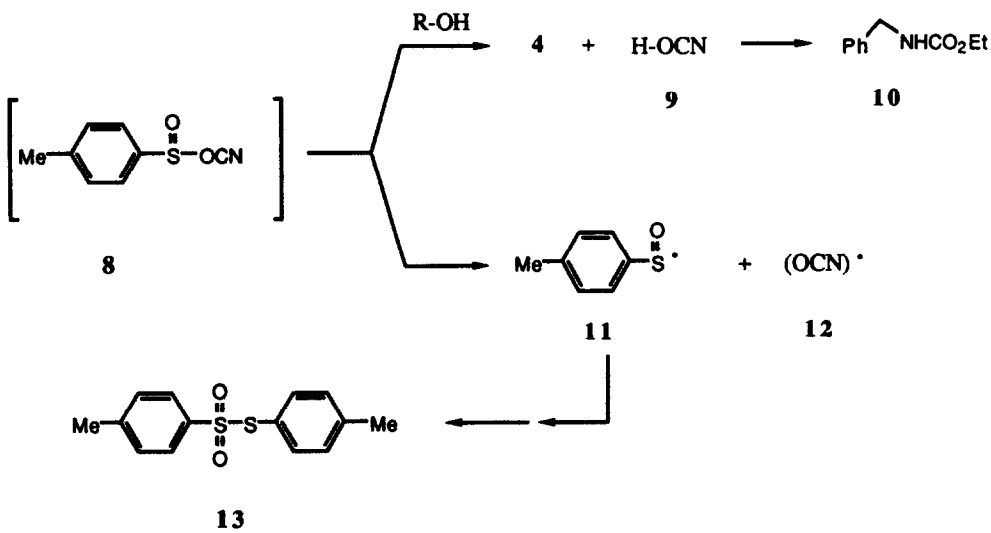
Tosyl cyanide is easily cleaved in homolytic[5,19,20,21] or heterolytic processes[13] With nucleophiles (ArO^-, RS^-, R_2N^-, ArMgX) it gives ArOCN, RSCN, R_2NCN, ArCN-type products. The only other product of our reactions is TsS-4Me-Ph[14] **13** This suggests a more complicated mechanism.

A possible mechanistic pathway leading to this new reaction is depicted in **Scheme 2** and **3.**



1a **7** **9** **8**

Scheme 2



9 **10** **8** **11** **12** **13**

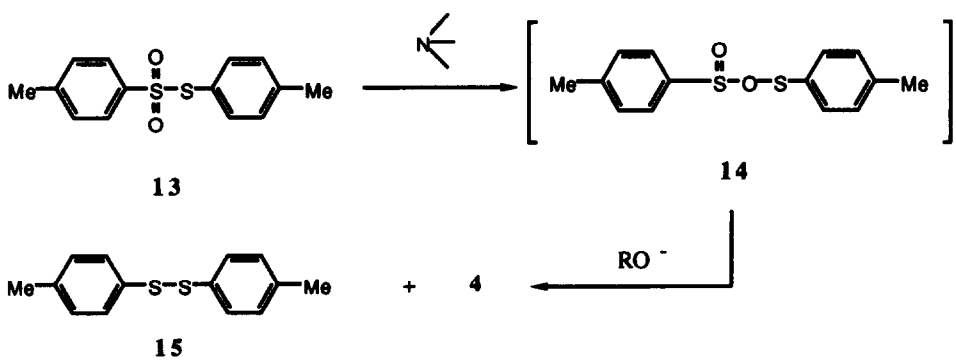
Scheme 3

Thus treatment of a sulfonyl cyanide (**1a**) with a strong, non-nucleophilic base (in this case DBU or DABCO) would give *via* intermediates **7** and **8** the cyanate **9** We assumed that this cyanate **9** was responsible for the sulfinate transfer to the given alcohols present resulting in the formation of the corresponding p-toluenesulfinates **4.** Blank experiments of tosyl cyanide and DBU or (DABCO) resulted in the formation of **13** (25%) most probably in accordance with **Scheme 3.**

In the presence of an alcohol the activated sulfinyl moiety of **9** can be transformed to sulfinates (**4**), or the weak S-O single bond may undergo homolytic cleavage giving sulfinyl radicals **11** In the absence of alcohols or radical traps the formation of the thiosulfonate (**13**) can be interpreted as a self termination of **11**[15] **(Scheme 3)**

One may suggest that **13** could possibly take part in the formation of sulfinates **4** in accordance with the **Scheme 4**

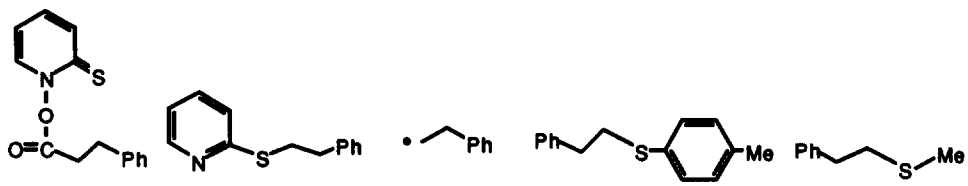
We have therefore studied the reaction of **13** and cyclododecanol (**2a**) in the presence of DBU However, reaction of 2 equivalents of **13** with 1 equivalents each of DBU and **2a** resulted in the formation of only 20% of cyclododecanol p-toluenesulfinate (**4a**) (24hr), and the known 4-tolyl-disulfide (**15**) (30%). This sulfinylation is much slower and gives much lower yields than the reaction of tosyl cyanide (**1a**) and alcohols in the presence of DBU (reaction time. 2hr). Moreover, we could not detect the disulfide (**15**) in the latter These findings suggest that O,S-sulfenyl-sulfinates of type **14** are not intermediates in the sulfinylation reaction of **1a** in the presence of DBU In order to corroborate our suggested mechanistic scheme of the sulfinylation reaction of **1a** (**Scheme 3**), we attempted to detect the other product HOCN (**6**) Therefore we attempted the known reaction[16] of the cyanate anion with benzyl chloride and ethyl alcohol in DMF Indeed, in the one-pot procedure (sulfinylation, followed by the addition of benzyl chloride and ethanol) we have obtained the benzyl urethane **10** (97% yield, g l c)



Scheme 4

In order to find further evidence of the radical cleavage of the suggested intermediate **9**, we have attempted to use mixed anhydrides of N-hydroxy-2-thiopyridone (like **16**), known thermal or photolytic sources of carbon radicals[17] When used alone in darkness, neither DABCO nor **1a** initiated the radical rearrangement of **16** to**17**

However, when **16** was treated in the dark with both DABCO and **1a**, **19** was isolated in 17% yield, undoubtedly formed from the phenylethyl radical **18**. In a similar reaction **1b** gave **20**.



16 **17** **18** **19** **20**

NMR experiments

^{13}C NMR experiments

The progress of the rearrangement of tosyl cyanide **1a** in the presence of an equimolar amount of DABCO was followed by ^{13}C NMR at low temperature DABCO was added into the tube containing the solution of **1a** at -60°C and ^{13}C NMR spectra were recorded at -60, -50, -40, -30, -20, -10, 0 and 20°C. We have found that the reaction between tosyl cyanide **1a** and the base takes place at temperatures higher than -50°C At -40°C the peaks of **1a** completely disappear and a new set of peaks appear corresponding to the cyanate **9** The most characteristic change is, as expected, the disappearance of the CN carbon at 113 6 ppm and the appearance of a new carbon at 152 5 ppm that is attributed to the OCN carbon of **9** This intermediate **9** is stable in the absence of alcohols up to -20°C At that temperature it disappears, due to the homolytic cleavage of **9**

The same experiment was repeated with methanesulfonyl cyanide **1b** In this case the rearrangement takes place upon the addition of DABCO at -60°C The carbon peaks of **1b** (45 6 and 112 6 ppm) change to those of the corresponding cyanate (42 4 and 156 6 ppm) This change is similar to that, observed in the case of **1a** We have found that this intermediate sulfinyl cyanate **21** is stable up to -50°C At -40°C this intermediate can no longer be detected The cyanate peak (152.5 ppm) disappears at -40°C The methyl signal of the intermediate methanesulfinyl cyanate **21** also disappears at -40°C, being replaced by that of the corresponding thiosulfonate **22**

21

22

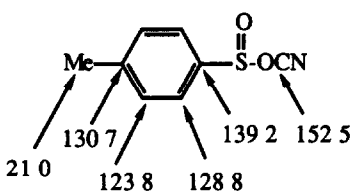
Low temperature ^{13}C NMR experiment in the presence of an alcohol.

DABCO (1 1 eq) was added carefully to methanesulfonyl cyanide **1b** (1 0 eq) in an NMR tube at -60°C The ^{13}C NMR spectrum showed the complete disappearance of **1b** and the appearance of the peaks of **21** as seen previously Cyclododecanol (0 8 eq) was then added at -60°C The ^{13}C NMR spectrum of the crude mixture showed clearly the peaks of the corresponding methanesulfinate **5a** The peaks of the intermediate methanesulfinyl cyanate **21** disappeared indicating that **5a** was indeed formed from **21**

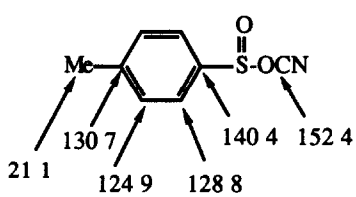
Independent preparation of p-toluenesulfinyl cyanate 9 and methanesulfinyl cyanate 21

p-Toluenesulfinic acid[6] was dissolved in $CDCl_3$ and the ^{13}C spectrum was recorded at -60°C This solution was then treated with DABCO, followed by cyanogen bromide The ^{13}C NMR spectra of this reaction mixture were then recorded at -60, -50, -40, -30, -20, -10, 0 and 20°C respectively The ^{13}C peaks of **9** (immediately appeared at -60°C and disappeared at -20°C) are in good agreement with those, seen in the p-toluenesulfonyl cyanide + DABCO reaction (**Scheme 5**)

A) **9** formed in the TsCN + DABCO reaction mixture

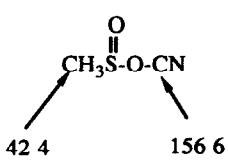


B) **9** formed in the 4-$MePhSO_2H$ + DABCO + BrCN reaction mixture

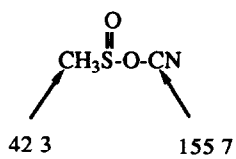


Scheme 5

A) **21** formed in the MsCN + DABCO reaction at -60°C



B) **21** formed in the $MeSO_2H$ + DABCO + BrCN reaction at -60°C



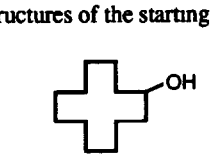
Scheme 6

Similarly, treatment of methanesulfinic[18] acid with DABCO and cyanogen bromide at -60°C we have observed the appearance of a peak in the ^{13}C NMR spectrum at 155 7 ppm. This can be attributed to the formation of the sulfinyl cyanate The corresponding value observed in the rearrangement of methanesulfinyl cyanide was 156 6 ppm. In both cases these peaks disappear above -40°C, indicating that these compounds are thermally unstable but can be made and used at - 60°C (**Scheme 6**).

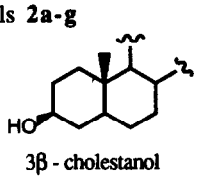
Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200E spectrometer for deuterochloroform solutions (δ scale, TMS as internal standard) Variable temperature ^{13}C NMR measurements were carried out on a Varian XL-200 spectrometer. Mass spectra (70 eV, electron impact) were obtained using a Hewlett-Packard 5995C quadrupole GC-MS instrument. IR spectra were measured with a Perkin-Elmer 881 spectrometer; only the most significant absorptions are listed Glc analyses were performed with a Chrompack 439 instrument equipped with a FID detector and a DB-5 (0 1 mm) fused silica capillary column (30m x 0 25 nm) using nitrogen as carrier gas, and napthalene as internal standard Microanalyses were performed by Atlantic Microlabs, Atlanta, GA Melting points were determined on a Kofler hot stage and are uncorrected N-Hydroxy-pyridine-2-thione was prepared from the 40% aqueous solution of its sodium salt (trade name sodium Omadine® a kind gift from the Olin Corporation)

Structures of the starting alcohols **2a-g**

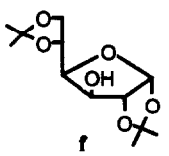


a

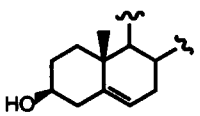


3β - cholestanol

c



f



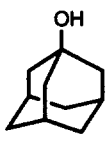
3β - cholesterol

b

d

CH_3-$(CH_2)_{17}$-OH

e



g

General procedure for the synthesis of sulfinates 4 from the tosyl cyanide **1a**.

To the solution of the starting alcohol **2** (2 mmol) in dry methylene dichloride (5-8 ml), DBU was added under argon at 0-5°C (ice bath), followed by the addition of tosyl cyanide (**1a**) in small portions Then the pale yellow solution was allowed to warm up to room temperature and the reaction monitored by t l c The reaction was complete in less than 2 hr Then the mixture was concentrated in vacuum and the title compounds isolated by column chromatography on silica gel (hexanes ether= 8 2)

Compound **4a**: Yield 89% (from methylene dichloride hexanes), mp 51-52°C, IR ($CHCl_3$) 1126 cm^{-1} (S=O), ^{1}H NMR (δ)· 1 1-1 9 (22 H, m, CH_2 groups), 2 4 (3 H, s, Me), 4 5 (1 H, m, H-1), 7 33 (2 H, d, J =

8Hz), 7 63 (2 H, d, J = 8Hz), ^{13}C NMR (δ) 20 0, 21 6, 23 5, 24 0, 24 2, 24 4, 30 9, 31 0, 78 2, 125 1, 129 7, 142 6, 143 2. m/z (%) 322 (0 3), 306 (1.6), 157 (100), HR-MS m/z = 322.1962,[calc. for $C_{25}H_{44}O_2S$ 322 1966]. Compound **4a** was identical with the product obtained by the reported procedure[10]

Compound **4b**[6] Yield 85% (from methylene dichloride hexanes), mp 130-131°C (lit.[6] 132-135°C, chloroform methanol), ^1H NMR (δ) 2 41 (6 H, s), 4 1-4 25 (2 H, m), 5 3 and 5 41 (2 H, m), 7 32 (4 H, d, J = 8Hz), 7 62 (4 H, d, J = 8Hz)

Compound **4c**[6] Yield. 91% (from methylene dichloride· hexanes), mp 118-120°C (lit.[6] 121-123°C, chloroform· methanol), ^1H (δ)· 2 42 (3 H, s), 4 2-4 35 (1 H, m), 7 32 (2 H, d, J = 8Hz), 7 61 (2 H, d, J = 8Hz)

Compound **4d**[6]. Yield. 94%, mp (of the (S)-(-) menthyl p-toluenesulfinate) 102-104°C (lit.[6] 103-105°C), ^1H (δ) 2 42 (3 H, s), 3 95-4 4 (1 H, dt, J_{aa} = 10 5Hz, J_{ae} = 4Hz), 7 34 (2 H, d, J = 8Hz), 7 68 (2 H, d, J = 8Hz)

Compound **4e** Yield 92% (from ether· hexanes), mp 37-38°C, IR ($CHCL_3$) 1130 cm^{-1}(S=O), ^1H (δ) 0 8-1 8 (35 H, m), 2 41 (3 H, s, Me), 3 5-3 7 and 3 9-4 1 (2 H, dt, J_1 = 7Hz, J_2 = 10Hz), 7.32 (2 H, d, J = 8Hz), 7 61 (2 H, d, J = 8Hz), ^{13}C (δ) 14 2, 21 6, 22 8, 25 8, 29 3, 29 5, 29 6, 29 7, 29 8, 32 1, 64 6, 125 3, 129 8, 142 0, 142 6, m/z (%) 408 (0 3), 253 3), 157 (100), HR-MS m/z=408.3065, [calc for $C_{25}H_{44}O_2S$ 408 3062]

Compound **4f**[22] Yield 91%, IR ($CHCL_3$) 1130, 1140 cm^{-1}(S=O), ^1H (δ) (major) 1 2-1 6 (4 x 3 H, 4s), 2 44 (3 H, s), 3 9-4 3 (3 H, m), 4 76 (1 H, d, J = 3 6Hz), 4 95 (1 H, d, J = 3Hz), 5 85 (1 H, d, J = 3 6Hz), 7 37 (2 H, d, J = 8Hz), 7 68 (2 H, d, J = 8Hz), (minor) 1 2-1 6 (4 x 3 H, 4s), 2 44 (3 H, s), 3 9-4 3 (3 H, m), 4 51 (1 H, d, J = 2 4Hz), 4 82 (1 H, d, J = 3 5Hz), 5 92 (1 H, d, J = 3 3Hz), 7 35 (2 H, d, J = 8Hz), 7 65 (2H, d, J = Hz), m/z(%)· 399 (0 1), 383 (22), 139 (100)

Compound **4g**[6] Yield 87 5% (from methylene dichloride hexanes), mp 81-82°C (lit [6] 80-82°C), ^1H 1 7-2 3 (15 H, m), 2 45 (3 H, s), 7 30 (2 H, d, J = 8Hz), 7 60 (2 H, d, J = 8Hz)

p-Tolyl p-toluenethiosulfonate[14] **13** Yield 36%, mp 74-76°C (lit.[14] 74-76°C), ^1H (δ) 2 35 (3 H, s), 2 45 (3 H, s), 7 15 (2 H, d, J = 8Hz), 7 20 (2 H, d, J = 7Hz), 7 25 (2 H, d, J = 7Hz), 7 45 (2 H, d, J = 8Hz) An authentic specimen was prepared according to the literature procedure[14]

Oxidation of p-toluenesulfinates to p-toluenesulfonates *Typical procedure* To a solution of the appropriate p-toluenesulfinate **4** (0 5 mmol) in dry chloroform (5 ml) 60% mCPBA (0 210g, 1mmol) was added at 0°C in small portions The reaction was monitored by t l c When all the sulfinate was consumed, the reaction mixture was extracted with sat aqueous sodium bicarbonate and dichloromethane and the organic layer dried over anhydrous magnesium sulfate Removal of most of the solvents and dropwise addition of hexanes afforded the known tosylates in high yield.

Independent preparation of the p-toluenesulfonates *Typical procedure* The alcohol **2** (2 5 mmol) was dissolved in dry pyridine (20 ml) at 0°C and treated with tosyl chloride (1 42 g, 7 5 mmol) added in small portions After stirring overnight, the solvent was evaporated under vacuum and the residue was extracted with dichloromethane and water The organic layer was dried over magnesium sulfate and concentrated under vacum Gradual addition of hexanes afforded the known tosylates in high yield.

Cyclododecyl p-toluenesulphonate[23] Yield 89%, mp 88-89°C, ^{1}H (δ) 1 1-1 8 (23 H, m), 2 4 (3 H, s), 4 65 (1 H, m), 7 31 (2 H, d, J = 8Hz), 7 80 (2 H, d, J = 8Hz)

3β-cholestanyl p-toluenesulphonate Yield 85%, mp 135-136°C, ^{1}H (δ) 0 5-2 0 (m, cholest), 2 4 (3 H, s), 4 45 (1 H, m), 7 30 (2 H, d, J = 8Hz), 7 80 (2 H, d, J = 8Hz)

Reaction of the cyclododecanol **2a** with **13** in the presence of DBU To a solution of the alcohol **2a** (0 5 g, 2 7 mmol) in 20 ml dry dichloromethane were added DBU (0 42 g, 2 7 mmol) followed by compound **13** (1 5 g, 5 4 mmol) in small portions Stirring was continued at room temperature for 24 hr and the reaction was followed by t l c The solvent was then concentrated and the mixture separated on silica gel using hexanes ether (in gradient) as eluent The p-tolyl disulfide **15** has been isolated in 30% yield together with compounds **4a** (20%), **13** (52%) and **2a** (73%)

p-Tolyl disulfide **15**, mp 42-44°C The spectral data of this compound were identical to those reported for the commercial product (Aldrich, 98%)

Synthesis of the benzylurethane **10**. The title compound was synthesized according to the literature procedure[16] in 65% yield, mp 42-43°C (lit 41 5-42°C)

Synthesis of the benzylurethane **10** *in situ* The alcohol **2a** (0 1 g, 0 54 mmol) was dissolved in 4 ml dry dichloromethane at 0°C and treated with DBU (90 mg, 0 59 mmol) followed by tosyl cyanide **1a** (0 38 g, 2 1 mmol) in small portions The disappearance of the alcohol was followed by t l c After the end of the reaction 37 3 mg (0 81 mmol) of absolute ethanol and 82 mg (0 64 mmol) of freshly distilled benzyl chloride were added and the reaction mixture was kept boiling for 3 hr Glc analysis of the crude reaction mixture (an authentic sample was prepared and used for comparison) indicated a 97% yield of the *in situ* prepared benzylurethane **10**

Glc conditions 1µl samples were injected at once at an oven temperature of 80°C for one minute After the temperature was increased to 250°C at a rate of 15°C/min Retention times 5 80 min (int standard) and 8 75 min (urethane **10**)

Trapping experiments of the intermediate **9**.

a Using the acyl N-hydroxy-2-thiopyridone **16** Tosyl cyanide **1** (100 mg, 0 55 mmol) and compound **16** (0 43 g, 1 6 mmol) were placed in a flask covered with aluminum foil, under argon in 15 ml dry dichloromethane,

followed by addition of DABCO (30 mg, 0 28 mmol) in one portion The reaction mixture was stirred at 0°C for 3hr; then the solvent was distilled under vacuum The residue was purified on silica gel (hexanes. ether 80 20) to give the sulfide **19** in 17% yield as a pale yellow oil The indepedent preparation of the sulfide **19** was carried out according to the literature procedure[24] in 92% yield The same reaction of **1b** gave the sulfide **20** in 7% yield

b Using cyclohexene according to the known procedure[21] Tosyl cyanide **1a** (100 mg, 0.55 mmol), (0 82 g, 10 mmol) of freshly distilled cyclohexene and 2 ml of dry dichloromethane were placed in a flask under argon The flask was covered with aluminum foil to protect the reaction mixture from light DABCO (30 mg, 0 27 mmol) was then added and the reaction mixture was stirred at room temperature for 3 hr The solvent was removed in vacuum ^{1}H NMR analysis of the crude mixture showed no evidence of adducts containing the cyclohexyl moiety

Preparation of the mixed anhydride of *N*-hydroxy-2-thiopyridone **16** was carried out according to the literature procedures[25]

General procedure for the synthesis of methanesulfinates **5** from **1b** and **2**.

To the solution of the starting alcohol **2** (2 mmol) in dry methylene dichloride (8-10 ml) DBU (1 1 eq., 2 2 mmol, 0 33 g, 0 33 ml) was added under argon at 0°C followed by dropwise addition of methanesulfonyl cyanide (1 5 eq , 3 mmol, 0 32 g) The pale yellow solution was allowed to warm up to room temperature and monitored by tlc When the reaction was finished (tlc) the mixture was concentrated in vacuum and the products isolated by column chromatography on silica gel (hexanes ether = 8 2)

Compound **5a** Yield 92% (from hexanes), mp 26-27°C, IR ($CHCl_3$) 1114 cm^{-1} (S=O), ^{1}H NMR (δ) 1 3-1 9 (22 H, m, CH_2 groups), 2 60 (3 H, s, Me), 4 3-4 4 (1 H, m, H-1), ^{13}C NMR (δ) 20 7, 20 8, 23 1, 23 2, 23 3, 24 0, 24 3, 30 4, 30 8, 44 7, 79 1, m/z (%) 167 (8), 55 (100), calcd for $C_{13}H_{26}O_2S$ C 63 37, H 10 63, found C 63 46, H 10 67%

Compound **5b**[26] Yield 91% (from hexanes/ether), mp 111-115°C (lit mp 97-112°C), IR ($CHCl_3$) 1110 cm^{-1}(S=O), ^{1}H NMR (δ) 0 65-2 51 (43 H, m), 2 62 (3 H, s, Me), 4 0-4 2 (1 H, m), 5 39 (1H, m), ^{13}C NMR (δ) 44 8 (Me), 80 0 (C-3), m/z (%) 386 (25), 368 (100)

Compound **5c** Yield 98% (from ether/pentane), mp 83-85°C, IR ($CHCl_3$) 1119 cm^{-1} (S=O), ^{1}H NMR (δ) 0 6-2 1 (46 H, m), 2 60 (3 H, s, Me), 4 1-4 2 (1 H, m), ^{13}C NMR (δ) 44 7 and 44 9 (Me), 79 7, 79 9 (C-3), m/z (%) 264 (25), 55 (100), calcd for $C_{28}H_{50}O_2S$ C 74 61, H 11 18, found C 74 45, H 11 14%

Compound **5d**[10,27] Yield 93% , IR ($CHCl_3$) 1123 cm^{-1}(S=O), ^{1}H NMR (δ) 0 75-2 24 (18 H, m), 2 60 (3 H, s, Me), 2 62 (3H, s), 3 71-4 01 (2 H, m)

Compound **5e** Yield 91% (from ether/hexanes), mp 38-39°C, IR ($CHCl_3$) 1123 cm^{-1} (S=O), ^{1}H NMR (δ) 0 85-0 95 (t, 3H, J = 7Hz), 1 2-1 75 (32 H, m), 2 62 (3H, s), 3 95-4 05 (2 H, m), ^{13}C NMR (δ) 14 2,

22 8, 25.8, 29.3, 29.7, 29.8, 30.2, 32 0, 44 2, 68 5, m/z (%) 315 (10), 99 (30), 57 (100), calcd for $C_{19}H_{40}O_2S$ C· 68 62, H· 12.12, found C 68 69, H 12 06%

Compound **5f**. Yield. 84%, mp 79-82°C (from ether/pentane); IR ($CHCl_3$) 1074, 1135 cm^{-1} (S=O), ^1H NMR (δ) 0 85-0 95 (t, 3H, J = 7Hz), 1 31, 1 34, 1 43, 1 51(4 x 3H, s), 2.689, 2 693 (2 x 3H, s), 4 0-4 3 (4 H, m), 4 6 (1H, d, J = 3 5 Hz), 4 8 (d1H, d, J = 2 0 Hz), 5 9 (1H, d, J = 3 5 Hz), ^{13}C NMR (δ) 25 2, 25 3, 26 2, 26 3, 26 6, 26 7, 26 8, 26 9, 44 3, 44 8, 66 8, 67 6, 72 2, 72 3, 76 5, 77 2, 77 8, 78 2, 80 3, 80 7, 83 0, 83 8, 83 9, 105 0, 105.3, 109 3, 109.4, 112 4, m/z (%) 307 (50), 249 (20), 127 (25), 101 (100), calcd for $C_{13}H_{22}O_7S$ C· 48.44, H 6 88, found C 48 55, H 6 90%

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