Lewis acid mediated elimination and rearrangement reactions of α-chlorosulfides derived from phenylthio-substituted 4,5-dihydrofuran-3(2*H*)-ones.

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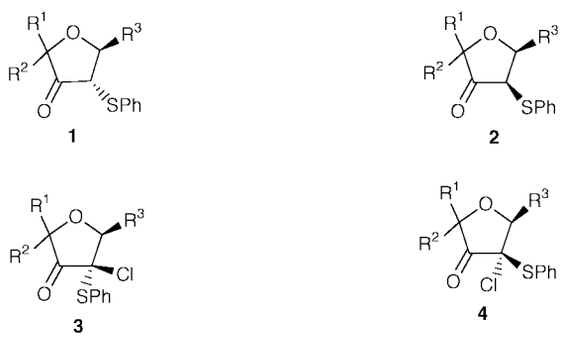
Phenylthio-substituted 4,5-dihydrofuran-3(2*H*)-ones were converted into α-chlorosulfides in a highly diastereoselective manner with sulfuryl chloride. Treatment of the chlorides with stoichiometric amounts of Lewis acids gave furan-3(2*H*)-one products resulting from elimination and aryl group migrations. Similar behaviour was observed with an α-acetoxy sulfide derivative. The X-ray crystal structures of a representative α-chlorosulfide and of a novel, ring sulfenylated product were determined.

Introduction

Phenylthio substituted-4,5-dihydrofuran-3(2*H*)-ones **1** and **2** are readily available in a highly stereoselective manner through silica gel or zinc bromide mediated cyclisations of silyloxyenone–benzenesulfenyl chloride adducts.[1] In the course of developing the chemistry of the heterocycles **1**, we converted the compounds into their α-chlorosulfide[2] derivatives **3** and **4**, and investigated Lewis acid catalysed C–C bond forming reactions of the latter with carbon nucleophiles.[3] These reactions were not successful but some novel chemistry derived from interactions of the chlorides with certain Lewis acids alone emerged from this work. Details of these studies, together with the single crystal X-ray structure determination of a furanone derived α-chlorosulfide and of a novel reaction product resulting from interaction of the compound with $SnCl_4$ and $TiCl_4$, and related work are presented in this paper.



a $R^1 = R^2 = Me$, $R^3 = Ph$
b $R^1 = R^2 = Me$, $R^3 = 4\text{-}MeOC_6H_4$
c $R^1 = R^2 = Me$, $R^3 = 3,4\text{-}(MeO)_2C_6H_3$
d $R^1 = R^2 = -(CH_2)_5-$, $R^3 = 3,4\text{-}(MeO)_2C_6H_3$
e $R^1 = R^2 = Me$, $R^3 = Pr^i$

a $R^1 = R^2 = Me$, $R^3 = Ph$
b $R^1 = R^2 = Me$, $R^3 = 4\text{-}MeOC_6H_4$
c $R^1 = R^2 = Me$, $R^3 = 3,4\text{-}(MeO)_2C_6H_3$
d $R^1 = R^2 = -(CH_2)_5-$, $R^3 = 3,4\text{-}(MeO)_2C_6H_3$

Results and discussion

Enones **5** were prepared[4] by aldol condensation of the requisite hydroxyketones with arene carbaldehydes in ethanolic KOH and converted into silyloxyenones **6** by standard methods.[5] An alternative route was employed for enone **7**: Horner–Wadsworth–Emmons condensation of **8** with isobutyraldehyde under Masamune–Roush conditions[6] gave **7**. Phosphonate **8** was prepared by conversion of methyl 2-hydroxyisobutyrate into its TBS ether using *tert*-butylchlorodimethylsilane (TBSCl), imidazole and a catalytic amount of 4-dimethylaminopyridine (DMAP) under forcing conditions in dimethylformamide (DMF), followed by condensation of the silyloxyester with an excess of dimethyl lithiomethylphosphonate in tetrahydrofuran (THF).[7] Cyclisation of substrates **6** and **7** according to our recently described procedure[1] gave the furanone products as mixtures of diastereomers **1** and **2** (ratio **1**:**2** >92:8) from which the major isomer **1** could be isolated by dry-flash or radial chromatography on silica gel followed, in certain cases (**1d** and **1e**) by recrystallisation.

Reaction of the furanones either as the *trans*-isomers, *i.e.* **1**, or as a mixture of isomers in the case of **1a** and **2a**, with sulfuryl chloride [chlorinations with *N*-chlorosuccinimide (NCS) were problematic for these substrates] in refluxing dichloromethane produced the α-chlorosulfides as mixtures of diastereomers **3** and **4**. Recrystallisation of the individual mixtures from ethyl acetate–hexane solutions yielded the chlorosulfides as single diastereomers, assigned structure **4** in each case.

The chlorosulfide structures **4a**–**d** were supported by characteristic dihydrofuranone infrared carbonyl absorptions[8] in the 1755–1765 cm^{-1} region and proton NMR chemical shifts in the range 5.4–5.5 ppm for the methine proton at C-5 in the heterocyclic ring (3.89 ppm for **4e**). With the exception of the latter where the furanone C-4 and C-5 carbon-13 resonances were coincidental (88.3 ppm), signals betweeen 81 and 84 ppm were observed for the furanone C-4 and C-5 ring carbons in the other chlorosulfides. The relative stereochemistry at these

† Corresponding author for X-ray crystallography.

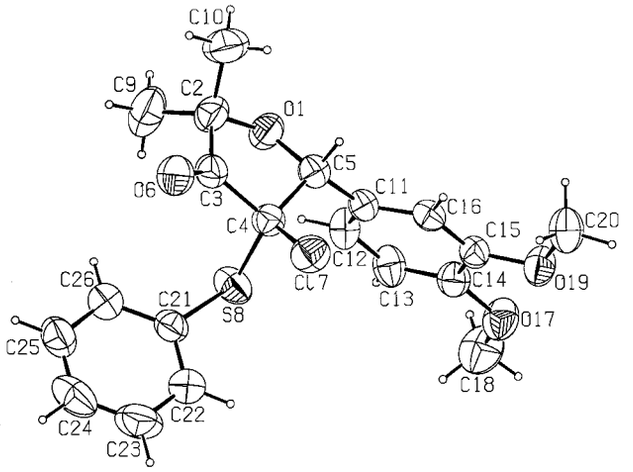


Fig. 1 Single crystal X-ray structure of compound **4c** showing the crystallographic numbering scheme.

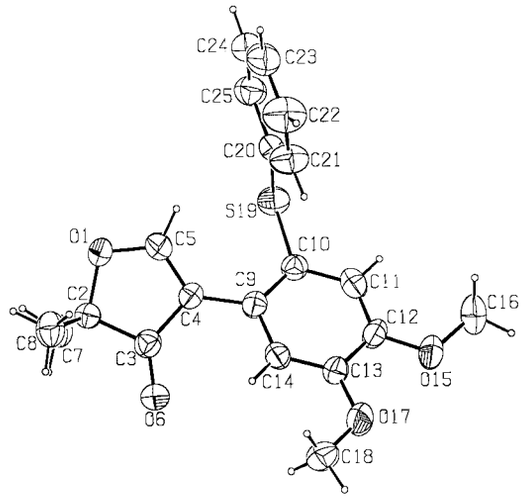


Fig. 2 Single crystal X-ray structure of compound **13** showing the crystallographic numbering scheme.

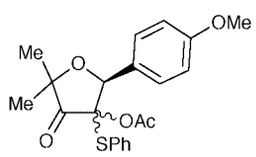
positions in a representative chloride **4c** was established by single crystal X-ray analysis and not surprisingly revealed that the 3,4-dimethoxyphenyl and phenylthio substituents were positioned on the same face of the dihydrofuranone ring (Fig. 1) in the thermodynamically more stable chlorosulfide. Since the ^{1}H NMR chemical shifts of the furanone C-5 ring protons in the structurally related compounds **4a**, **4b** and **4d** were similar to that in **4c** (5.44 ppm), these chlorides were assigned the same relative stereochemistry as **4c** and, by analogy, **4e** also.

Following the precedent of Trost and Massiot, treatment of furanone **1b** with lead tetraacetate[9] in CH_2Cl_2 produced the acetoxysulfide **9** (ν_{CO} = 1760 and 1740 cm^{-1}) in 80% yield as a mixture of diastereomers (ratio *ca.* 3:2) which were not separated.

Reaction of **4a** with a slight excess of $SnCl_4$ in CH_2Cl_2 at room temperature for 12 h resulted in an efficient dehydrochlorination reaction to produce the novel phenylthiofuranone **10a** in 69% yield. Structure **10a** (M^+ = 296) was supported by a characteristic furan-3(2*H*)-one carbonyl group absorption at 1705 cm^{-1} in its infrared spectrum[10] and heterocycle ^{13}C NMR signals at 87.7 (C-2), 102.9 (C-4), 184.3 (C-5) and 204.4 (C-3) ppm. Similarly, the 5-alkyl furanone **4e** gave **11** in high yield (87%). Interaction of **4b** with stannic chloride under the same conditions produced two compounds: furanone **10b** (12%) and the product of an aryl ring migration, **12b** (40%), as the only isolable reaction products. Acetoxyfuranone **9** which contains a poor leaving group behaved similarly and gave **10b** and **12b** in 11 and 30% yield respectively. The spectroscopic properties of the former were similar to those of **10a** and the identity of **12b** was confirmed through independent synthesis *via* oxidative cyclisation of hydroxyenone **5b** with thallium(III) nitrate in methanol according to the procedure of Nogradi and coworkers.[11]

Three products, the isomeric pair **10c** (7%) and **13** (35%) together with **14** (15%)—a novel ring chlorinated analogue of **10c**, were isolated from the reaction of stannic chloride with **4c**. The molecular structure of **13** was determined by single crystal X-ray analysis (Fig. 2) and that of **14** from its analytical and spectroscopic properties. Two one-proton singlets at 6.89 and 6.84 ppm in the ^{1}H NMR spectrum of the compound were important in establishing the presence of a 1,2,4,5-tetrasubstituted aryl group at the C-5 position in the furanone ring.

The same products were formed from **4c** and $SnCl_4$ in toluene with **10c** (44%) predominating; **13** and **14** were isolated in yields of 10 and 25% respectively. No compounds resulting from trapping of a chlorosulfide derived cationic intermediate by the aromatic solvent[12] were isolated or detected as products of these experiments. Further studies involving variation of the Lewis acid revealed that **4c** was unreactive towards $TiCl_4$ at



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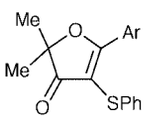
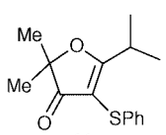


10

a Ar = Ph
b Ar = 4-MeOC$_6$H$_4$
c Ar = 3,4-(MeO)$_2$C$_6$H$_3$



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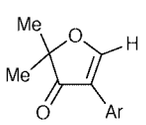
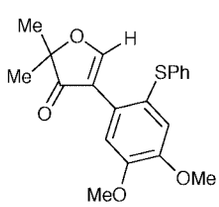


12

a Ar = Ph
b Ar = 4-MeOC$_6$H$_4$
c Ar = 3,4-(MeO)$_2$C$_6$H$_3$



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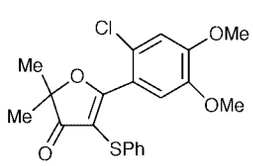

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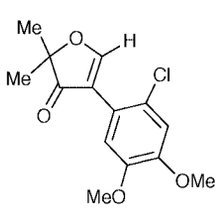

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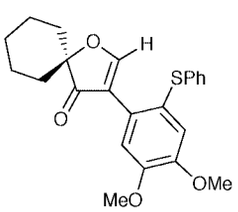

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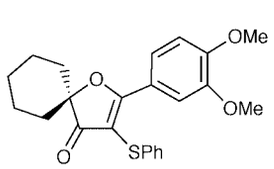

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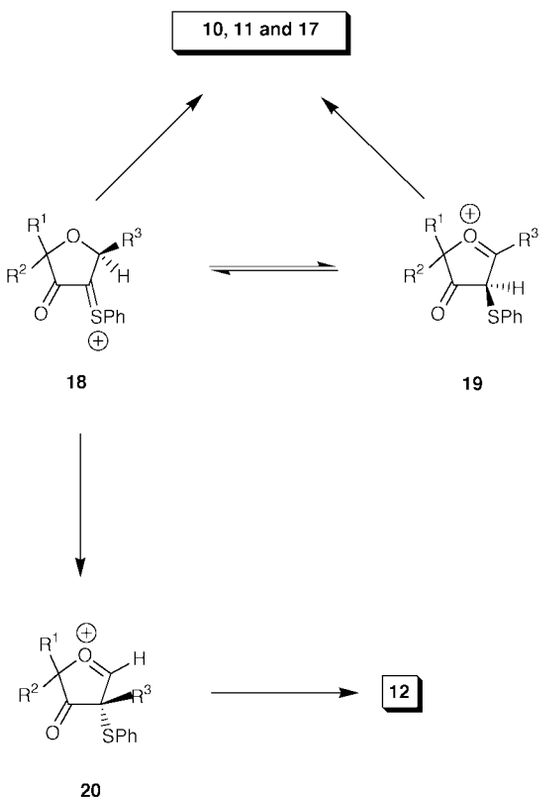
room temperature over a 24 h period, but produced the same products **10c** (5%), **13** (19%) and **14** (30%) upon heating with the reagent at reflux. A change in product distribution emerged from the interaction of **4c** with $ZnBr_2$. Furanone **10c** (49%) predominated and compound **13** was not detected in or isolated

from the reaction product mixture. Surprisingly, the chlorinated compound **14** rather than its bromo analogue was also a product of this reaction and was isolated in 11% yield. The presence of one chlorine substituent in the molecular structure was established from the mass spectrum of **14** which showed two ions in the expected ratio at m/z = 392/390 (M^+).

With $AlCl_3$ a further change in the behaviour of **4c** was observed: a new furanone, the chlorine containing compound **15**, emerged as the only product (28%) of a low yielding reaction. Structure **15** (M^+, m/z 284/282) was characterised by its furanone ring C-5 carbon-13 signal at 174.6 ppm and the corresponding attached proton resonance at 8.64 ppm, in particular.

Upon reaction with $SnCl_4$ under the conditions employed for **4c**, the related spiro-furanone **4d** yielded the isomeric structures **16** and **17** in 48% and 15% yields respectively. The corresponding ring chlorinated analogue of **14** was not detected or isolated as a reaction product.

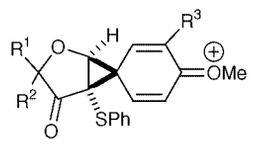
Formation of the phenylthiofuranones **10**, **11** and **17** can be rationalised (Scheme 1) through initial Lewis acid mediated



Scheme 1

loss of chloride ion from the α-chlorosulfides to produce furanone based acyl thionium ions **18** which can be further stabilised by a transannular resonance interaction with the furanone ring oxygen. Acyl thionium ions are commonly invoked as intermediates in the Pummerer reaction of α-sulfinyl carbonyl compounds[13] and are usually generated by treatment of these species with acids or their anhydrides.[14] Treatment of α-chlorosulfides with Lewis acids is also an effective source of acyl thionium ions.[12,15] It is interesting to note that reaction of a mixture of the isomeric chlorides **3c** and **4c** generated **10c**, **13** and **14** in a ratio similar to that observed with **4c** alone. Furthermore, it was found that **4c** equilibrated with **3c** in the presence of stannic chloride (*ca.* 7% after 30 min; the NMR spectra showed evidence for appearance of the final reaction products at this stage also) and consequently both isomers are likely sources of thionium ions **18**. Although α-acetoxysulfides are less effective than α-chlorosulfides as thionium ion precursors,[15c] formation of intermediate **18** from **9** is clearly favourable on the basis of the products isolated. Similar reactivity and compound distribution from the interaction of **4b** and **9** with $SnCl_4$ was observed in the present study.

Proton loss from species **18** would generate the phenylthio compounds **10**, **11** and **17** directly. However, intermediate **18** could undergo a 1,2-hydride shift[16] to give oxonium ion **19**; proton loss would then yield the phenylthiofuranones. Compounds derived from halide induced loss of the phenylthio group in **19**, *i.e.* 2,2-disubstituted-5-arylfuran-3(2*H*)-ones (analogues of the natural product bullatenone) which can be readily identified by characteristic furanone C-4 proton resonances in the region 6.0–6.4 ppm were not isolated nor detected as reaction products in our investigations.[4,17] An alternative 1,2-aryl group migration in **18** (R^3 = aryl) would generate oxonium ion **20** *via* the favourable phenonium ion[18] related spiro-dienone based structure **21** (R^3 = H or OMe). Species related to **21**



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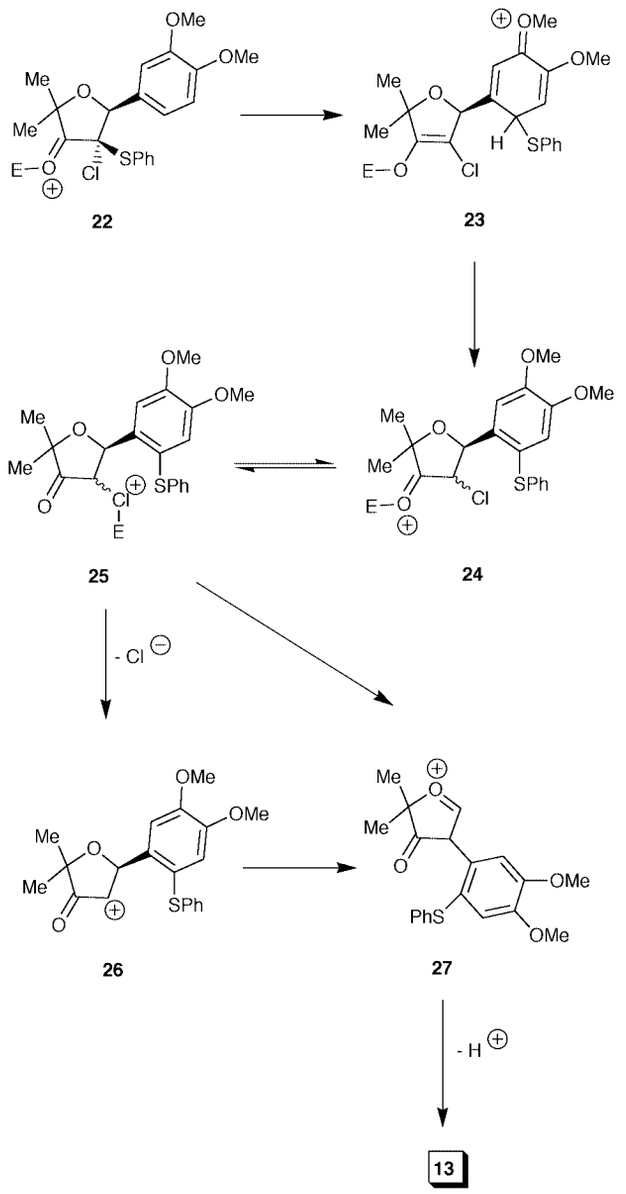
have been cited as intermediates in a range of transformations, for example the conversion of flavones into isoflavones with thallium(III) salts and under enzymatic conditions.[19] Loss of the phenylthio group from **20** would complete formation of the 4-aryl furanones **12**. Compounds **12a** and **12c** were not isolated as reaction products; the latter however is a potential source of **13**, **15** and **16**.

Under the reaction conditions employed in this study, compound **12c** could undergo Lewis acid induced electrophilic substitution with diphenyl disulfide or benzenesulfenyl chloride[20] generated from oxonium ion **20**, to produce **13**. This possibility could not be excluded since **12c**, prepared from **5c** and thallium(III) nitrate in methanol,[11] reacted slowly with both sulfur reagents over a 24 h period in the presence of an equimolar quantity of stannic chloride and produced **13** in 8 and 11% yields respectively. In contrast, furanone **12c** was stable to $AlCl_3$ in CH_2Cl_2 for 12 h. Compound **13** could arise by another mechanism which is outlined in Scheme 2. Thus, intramolecular electrophilic substitution of the reactive C-5 aryl ring in **22** (E = $SnCl_4$) *via* a Lewis acid–base adduct of **4c** with stannic chloride leads to the chlorofuranone complex **25**. Further reactions of this species *via* **26** would produce **13** (a concerted reaction: **25**→**27**, cannot be excluded). The feasibility of **25** as an intermediate could not be tested experimentally since α-chlorofuranones such as **30** are unknown. Although **26** is a destabilised carbocation,[21] interactions of its cationic site with the neighbouring furanone ring oxygen atom and sulfur of the phenylthio group render the structure more favourable as an intermediate; see structures **28** and **29**.

Significant quantities of the aryl ring chlorinated product **14** were isolated from reactions of **4c** with $SnCl_4$, $TiCl_4$ and $ZnBr_2$. Chlorination of the primary reaction product **10c** with an electrophilic chlorine species derived from or contained in the Lewis acids employed was thought to be a likely source of **14**. Surprisingly, **10c** was unreactive towards stannic chloride under the reaction conditions for 24 h and was recovered in 92% yield.

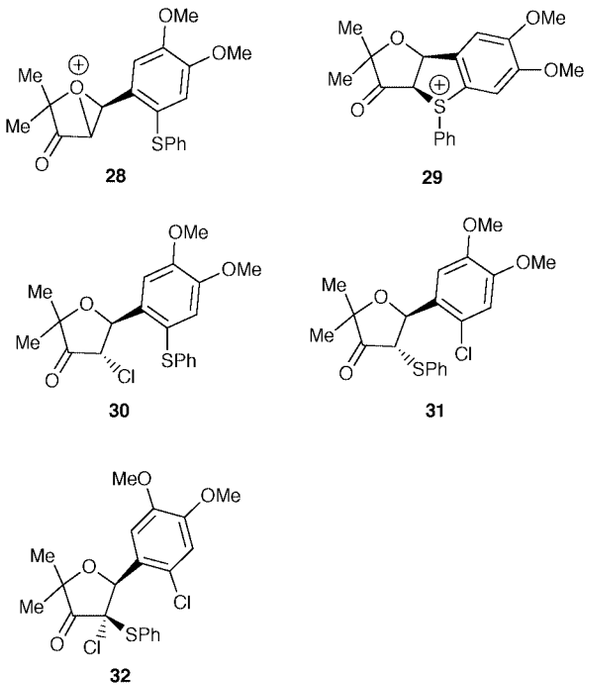
The mechanism outlined in Scheme 2 for the formation of **13** could accomodate formation of **14** also. Thus, intramolecular electrophilic chlorination of the 3,4-dimethoxyphenyl ring in the complex **22** would generate a Lewis acid-base complex of phenylthio dihydrofuranone **31** (analogous to **24**) as a reaction intermediate. Dehydrogenation of **31**, possibly induced by the Lewis acid, would complete formation of **14**. Furanone **1c** (a model for **31**) gave a complex mixture of compounds when treated with $SnCl_4$. Surprisingly, hydroxyenone **5c** was the



Scheme 2

major reaction product and was isolated in 46% yield. Analysis (TLC and NMR) of the remaining chromatographic fractions from this reaction failed to reveal any evidence for the presence of **10c**. Consequently the origin of **14** as a reaction product remains unclear. Isolation of **14** rather than a bromo analogue, albeit in low yield (12%), from interaction of **4c** with $ZnBr_2$ supports an intramolecular chlorination mechanism, however. We consider it unlikely that **14** arises from contamination of the starting chlorosulfide **4c** with the dichloride **32** since the former compound was used in an analytically pure state and its spectroscopic properties were in full agreement with its molecular structure. Significant quantities of a related dichloride were produced upon treatment of the 3,4-methylenedioxyphenyl analogue of **4c** with either *N*-chlorosuccinimide or sulfuryl chloride[22] and work with this particular substrate was discontinued. Halogenation of activated aromatic systems with *N*-halosuccinimides is well established.[23]

Aluminium trichloride induced loss of the phenyl group from intermediate **31**, concomitant with or preceding aryl group migration, could account for the formation of **15**. Upon reaction with $AlCl_3$, a model compound, furanone **1c**, gave a mixture of products from which **5c** was isolated as the only identifiable material in 39% yield; **12c** was not recognisable by TLC or ^{1}H NMR analysis of the reaction mixture.



In summary, interaction of dihydrofuran-3(2*H*)-ones bearing α-chlorosulfide functionality, with Lewis acids generates novel furanone structures resulting from elimination and aryl group migration reactions. The origin of furanones possessing phenylthio or chlorine substituted aryl groups at the 4- and 5-positions of the parent heterocycle remains to be established.

Experimental

Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were determined in The Microanalysis Laboratory, University College, Cork, using a Perkin-Elmer 240 elemental analyser. Infrared spectra were recorded either on a Perkin-Elmer 682 or a Perkin-Elmer Paragon 1000 FTIR spectrometer. Solid samples were examined as KBr discs and liquids as thin films. Mass spectra were measured in electron impact mode using a Kratos Profile HV4 instrument. ^{1}H NMR spectra were recorded on JEOL PMX-60 Si (60 MHz) or JEOL JNM GSX-270 (270 MHz) spectrometers. Proton resonance multiplicities are documented as broad peaks (br), singlets (s), doublets (d), triplets (t), quartets (q), and multiplets (m). Proton decoupled ^{13}C NMR spectra were measured at 67.5 MHz on a JEOL JNM GSX-270 NMR spectrometer. For each carbon resonance, the number of attached protons was established from experiments run in the DEPT-90 and DEPT-135 modes. All spectra were run in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard unless otherwise specified. Chemical shifts are expressed in parts per million (ppm), positive shifts being downfield from TMS; *J* values are in Hz.

Thin layer chromatography (TLC) analysis was performed on precoated silica gel-60 HF_{254} plates (Merck 5554) and compounds were visualised using ultraviolet light or by iodine staining. 'Dry-flash' chromatography was carried out on silica gel-60 PF_{254} (Merck 7747). Preparative radial chromatography was performed on a Chromatotron (Model 7924, Harrison Research) using silica gel containing gypsum (Merck 7749) as the stationary phase, on 4 mm plates.

A Buchi GKR-50 apparatus was employed for bulb-to-bulb distillations and the oven temperature is quoted as the boiling point in each case. Organic extracts were dried over anhydrous magnesium sulfate. Solvents and reagents were dried and purified by standard methods.[24] All experiments involving the synthesis and reactions of dihydrofuranones including the

α-chlorosulfides **3** and **4** were conducted in dry solvents under a nitrogen atmosphere.

Hydroxyenones **5a**–**d** were prepared using literature procedures[4] and converted into their trimethylsilyl ethers with chlorotrimethylsilane and imidazole in CH_2Cl_2.[5]

(*E*)-2,6-Dimethyl-2-*tert*-butyldimethylsilyloxyhept-4-en-3-one 7

Methyl 2-hydroxyisobutyrate (4.73 g, 40 mmol), dry imidazole (4.35 g, 64 mmol), DMAP (0.5 g, 4 mmol) and TBSCl (7.25 g, 48 mmol) in dry DMF (20 cm^3) were heated at 100 °C for 16 h. Dilution of the cooled solution with ethyl acetate (200 cm^3), followed by washing with water (3 × 100 cm^3), brine (3 × 50 cm^3) and concentration of the dried organic extracts afforded a light oil. Bulb-to-bulb distillation gave *the silyl ether* (8.5 g, 90%), bp 80 °C at 10 mmHg; ν_{max}(film)/cm^{-1}: 1760; δ_H (60 MHz): 0.10 (6H, s), 0.9 (9H, s), 1.4 (6H, s), 3.73 (3H, s). This silyl ether (7.42 g, 32 mmol) in dry THF (80 cm^3) was added dropwise to a cold (−78 °C) solution of dimethyl lithiomethylphosphonate [prepared by addition of dimethyl methylphosphonate (17.34 cm^3, 0.16 mol) in dry THF (70 cm^3) to *n*-butyllithium (100 cm^3 of a 1.6 M solution in hexane) in dry THF (100 cm^3) at −78 °C]. The mixture was stirred at −78 °C for 1.5 h, then quenched at this temperature with saturated ammonium chloride solution (100 cm^3). The frozen mixture was allowed to warm to room temperature and diluted with ether (3 × 50 cm^3). Evaporation of the dried organic layer and kugelrohr distillation of the residue gave **8** (8.3 g, 80%), bp 100 °C at 0.1 mmHg; ν_{max}(film)/cm^{-1}: 1720; δ_H (60 MHz): 0.21 (6H, s), 0.91 (9H, s), 1.42 (6H, s), 3.20 (2H, d, J = 22), 3.65 (6H, d, J = 11).

Dried lithium chloride (0.968 g, 22 mmol) and dry triethylamine (3 cm^3, 21 mmol) were added in sequence, under nitrogen, to a solution of **8** (6.5 g, 20 mmol) in dry acetonitrile (50 cm^3). The resulting milky lithiophosphonate suspension was stirred at room temperature for 15 min and freshly distilled isobutyraldehyde (1.82 cm^3, 20 mmol) was slowly added by syringe. The mixture was stirred at ambient temperature for 5 days, then diluted with water (30 cm^3) and extracted with ether (5 × 50 cm^3). The extracts were washed with brine (3 × 50 cm^3), dried and concentrated *in vacuo.* Radial chromatography (5% ethyl acetate in heaxane) of the residue gave **7** (5.13 g, 95%) as a clear oil; ν_{max}(film)/cm^{-1}: 2957, 2873, 1704, 1634 and 1473; δ_H: 0.20 (6H, s), 0.83 (9H, s), 0.98 (6H, d, J = 6.3), 1.28 (6H, s), 2.40 (1H, m), 6.68 (1H, d, J = 15.6), 6.86 (1H, dd, J = 5.7 and 15.6); δ_C: −2.3, 21.2, 25.5, 27.0, 34.1, 79.1, 121.1, 154.3, 203.2.

Synthesis of furanones 1a, 2a and 1b–d

These were prepared using our published general procedure; analytical and spectroscopic data for **1b** is reported therein.[1]

cis- and *trans*-4-Phenylthio-2,2-dimethyl-5-phenyl-4,5-dihydrofuran-3(2*H*)-one 1a and 2a

Isolated in the form of a light yellow oil (0.4 g, 70%) as a mixture of diastereomers **1a** and **2a** in the ratio 95:5 from PhSCl[25] (0.33 g, 2.3 mmol) and enone **5a** (0.5 g, 1.8 mmol) following radial chromatography using 1:19 ethyl acetate–heptane as eluent (Found: C, 72.6; H, 6.3; S, 10.7. $C_{18}H_{18}SO_2$ requires C, 72.45; H, 6.1; S, 10.75%); ν_{max}(film)/cm^{-1}: 2970, 1750, 1430, 1375, 1160, 1075, 750; δ_H(**1a**): 0.99 (3H, s), 1.43 (3H, s), 3.57 (1H, d, J = 10.8), 4.87 (1H, d, J = 10.8), 7.15–7.60 (10H, m); δ_C(**1a**): 21.1, 24.4, 58.5, 78.4, 81.1, 126.5, 128.6, 128.8, 128.9, 129.4, 134.7, 131.2, 138.7, 213.2; *m*/*z*: 298 (M^+), 189, 164 (100%), 121, 102, 77, 51, 43. δ_H(**2a**): 1.35 (3H, s), 1.65 (3H, s), 3.90 (1H, d, J = 4.9), 5.52 (1H, d, J = 4.9), 7.20–7.50 (10H, m).

trans-4-Phenylthio-5-(3,4-dimethoxyphenyl)-2,2-dimethyl-4,5-dihydrofuran-3(2*H*)-one 1c

Isolated as a white crystalline solid (1.97 g, 55%) from PhSCl (1.73 g, 12 mmol) and **5c** (3.22 g, 10 mmol) following radial chromatography using 1:9 ethyl acetate–heptane as eluent; mp 103–104 °C (Found: C, 67.1; H, 6.25; S, 8.4. $C_{20}H_{22}SO_4$ requires C, 67.0; H, 6.2; S, 8.95%); ν_{max} (KBr)/cm^{-1}: 2900, 1760, 1590, 1570, 1460, 1260, 1230, 1140, 1086, 1025; δ_H: 1.05 (3H, s), 1.30 (3H, s), 3.59 (1H, d, J = 9.5), 3.89 (6H, s), 4.81 (1H, d, J = 9.5), 6.87 (1H, d, J = 7.2), 6.99 (1H, br s), 7.07 (1H, m), 7.20–7.30 (3H, m), 7.4–7.43 (2H, m); δ_C: 21.2, 24.5, 55.9, 56.0, 58.4, 78.6, 81.1, 109.4, 111.1, 119.2, 128.7, 129.05, 131.05, 131.4, 134.45, 149.2, 149.3, 213.3; *m*/*z*: 358 (M^+), 249, 164 (100%), 110, 91, 77, 43.

trans-3-Phenylthio-2-(3,4-dimethoxyphenyl)-1-oxaspiro[4.5]-decan-4-one 1d

Isolated as a white crystalline solid (1.64 g, 58%) from PhSCl (1.23 g, 8.51 mmol) and **5d** (2.57 g, 7.1 mmol) following dry-flash chromatography using 1:9 ethyl acetate–hexane as eluent and recrystallisation from the same solvent; mp 86–87 °C (Found: C, 68.9; H, 6.5; S, 7.7. $C_{23}H_{26}SO_4$ requires C, 69.3; H, 6.6; S, 8.05%); ν_{max}(KBr)/cm^{-1}: 3060, 2930, 1749, 1592, 1513, 1265, 1235, 1082; δ_H: 1.26–1.75 (10H, m), 3.58 (1H, d, J = 10), 3.88 (3H, s), 3.89 (3H, s), 4.81 (1H, d, J = 10), 6.88 (1H, d, J = 8.4), 7.01 (1H, s), 7.07 (1H, d, J = 8.1), 7.22–7.44 (5H, m); δ_C: 20.75, 21.3, 25.0, 29.1, 33.3, 55.9, 56.0, 58.9, 78.5, 82.5, 109.6, 111.25, 119.1, 128.45, 128.95, 131.1, 134.1, 149.2, 149.3, 212.9; *m*/*z*: 398 (M^+), 289, 272, 232, 204 (100%), 165, 150, 121, 109, 95, 77, 55.

trans-4-Phenylthio-2,2-dimethyl-5-isopropyl-4,5-dihydrofuran-3(2*H*)-one 1e

The furanone was prepared by addition of PhSCl (3.93 g, 28 mmol) in CH_2Cl_2 (10 cm^3) to **7** (7.02 g, 26 mmol) in the same solvent (40 cm^3). Fused zinc bromide (1.46 g, 6.5 mmol) was added in one portion after 1 h. The resulting black solution was stirred for 1 h, then filtered through a silica plug and the filtrate concentrated *in vacuo*. Radial chromatography of the residue (2% ethyl acetate in hexanes) gave *the furanone* (5.1 g, 74%), a viscous oil, as a mixture of diastereomers (94:6). The oil was mixed with pentane (5 ml) and stored at −10 °C for 24 h to give **1e** as large clear crystals, mp 47–48 °C (Found: C, 68.15; H, 7.7; S, 12.4. $C_{15}H_{20}SO_2$ requires C, 68.2; H, 7.6; S, 12.1%); ν_{max}(KBr)/cm^{-1}: 3072, 2974, 2872, 1760, 1582; δ_H: 0.92 (3H, s), 1.01 (3H, d, J = 6.8), 1.04 (3H, d, J = 6.8), 1.26 (3H, s), 2.01 (1H, septet of doublets, J = 5.7 and 6.8), 3.40 (1H, d, J = 10.2), 3.76 (1H, dd, J = 5.7 and 10.2), 7.32 (3H, m), 7.50 (2H, m); δ_C: 17.3, 18.9, 21.8, 24.3, 31.4, 52.5, 81.0, 81.3, 128.4, 128.9, 134.9, 132.2, 214.7; *m*/*z*: 264 (M^+), 192, 178, 164 (100%), 135, 109, 91, 84, 77, 69.

4-Phenylthio-4-chloro-2,2-dimethyl-5-phenyl-4,5-dihydrofuran-3(2*H*)-one 4a

A solution of SO_2Cl_2 (0.563 g, 4.17 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise over 10 min to a stirred mixture of furanones **1a** and **2a**, prepared as above (1.13 g, 3.79 mmol), in the same solvent (20 cm^3). The resulting solution was stirred at room temperature for 3 h, then washed successively with saturated sodium bicarbonate solution (3 × cm^3) and water (3 × 10 cm^3), dried and concentrated *in vacuo*. Radial chromatography of the resulting oil with 95:5 hexane–ethyl acetate as eluent gave a white solid (1.01 g, 80%) as a mixture of diastereomers. Recrystallisation of the solid from ethyl acetate–hexane gave a single diastereomer, mp 91–93 °C (Found: C, 65.2; H, 5.2; S, 9.9; Cl, 10.3. $C_{18}H_{17}ClSO_2$. requires C, 65.1; H, 5.1; S, 9.6; Cl, 10.35%); ν_{max}(KBr)/cm^{-1}: 2960, 1755, 1595, 15.80; δ_H: 1.40 (3H, s), 1.77 (3H, s), 5.49 (1H, s), 7.23–7.50 (8H, m), 7.69 (2H, d, J = 7.6); δ_C: 23.0, 26.9, 77.9, 80.6, 84.0, 127.2, 127.3, 128.2, 128.8, 129.2, 130.3, 133.1, 136.8, 202.1; *m*/*z*: 332 (^{35}Cl, M^+), 296, 246, 226, 198 (100%), 163, 129, 119, 105, 77, 69, 51.

The following compounds were prepared by the same general method.

4-Phenylthio-4-chloro-2,2-dimethyl-5-(4-methoxyphenyl)-4,5-dihydrofuran-3(2*H*)-one 4b

From SO_2Cl_2 (0.524 g, 3.88 mmol) in CH_2Cl_2 (20 cm^3) and furanone **1b** (1.16 g, 3.53 mmol) in the same solvent (40 cm^3). Radial chromatography of the resulting white residue using 95:5 hexane–ethyl acetate as eluent gave a white solid (1.05 g, 82%) which was recrystallised from ethyl acetate–hexane, mp 123–124 °C (Found: C, 63.0; H, 5.35; Cl, 10.0; S, 8.5. $C_{19}H_{19}ClSO_3$ requires C, 62.9; H, 5.2; Cl, 9.8; S, 8.8%); ν_{max} (KBr)/cm^{-1}: 3060, 2975, 2933, 1760, 1613, 1515, 1439, 1257, 1171, 1098, 1031; δ_H: 1.40 (3H, s), 1.76 (3H, s), 3.86 (3H, s), 5.45 (1H, s), 7.00 (2H, d, J = 10), 7.26–7.46 (5H, m), 7.64 (2H, d, J = 10); δ_C: 23.0, 26.8, 55.3, 78.3, 80.6, 83.9, 113.6, 125.0, 127.3, 128.5, 128.9, 130.35, 136.9, 160.3, 202.3; *m*/*z*: 362(^{35}Cl, M^+), 326, 253, 226, 198 (100%), 135, 119, 89, 77, 69, 43.

4-Phenylthio-4-chloro-5-(3,4-dimethoxyphenyl)-2,2-dimethyl-4,5-dihydrofuran-3(2*H*)-one 4c

From SO_2Cl_2 (0.83 g, 6.14 mmol) in CH_2Cl_2 (30 cm^3) and furanone **1c** (2.0 g, 5.58 mmol) in the same solvent (30 cm^3). Dry-flash chromatography of the resulting oil using 1:9 ethyl acetate–hexane as eluent gave a white solid (1.67 g, 76%) as a mixture of diastereomers (ratio, 1:1.2). Recrystallisation from ethyl acetate–hexane gave a single diastereomer, mp 126–128 °C (Found: C, 61.35; H, 5.6; S, 8.0, Cl, 9.1. $C_{20}H_{21}ClSO_4$ requires C, 61.2; H, 5.35; S, 8.2; Cl, 8.9%); ν_{max}(KBr)/cm^{-1}: 3056, 2976, 1761, 1593, 1518, 1260, 1163, 1098, 1029; δ_H 1.43 (3H, s), 1.78 (3H, s), 3.92 (3H, s), 3.97 (3H, s), 5.44 (1H, s), 6.96 (1H, d, J = 8.4), 7.21–7.45 (7H, m); δ_C 23.0, 26.8, 55.9, 56.0, 78.3, 80.6, 83.9, 110.5, 110.7, 119.8, 125.4, 127.2, 128.8, 130.4, 136.9, 148.8, 149.8, 202.0; *m*/*z*: 392(^{35}Cl, M^+), 355, 316, 183, 198, 164, 149, 110, 84, 49 (100%).

3-Phenylthio-3-chloro-2-(3,4-dimethoxyphenyl)-1-oxaspiro[4.5]-decan-4-one 4d

From SO_2Cl_2 (0.414 g, 3.07 mmol) in CH_2Cl_2 (20 cm^3) and furanone **1d** (1.11 g, 2.79 mmol) in the same solvent (20 cm^3). Radial chromatography of the white reaction residue employing 95:5 hexane–ethyl acetate as eluent gave a white solid (0.966 g, 80%) which was recrystallised from ethyl acetate–hexane, mp 114.5–116.5 °C (Found: C, 64.1; H, 5.8; Cl, 8.3; S, 7.3. $C_{23}H_{25}ClSO_4$ requires C, 63.8; H, 5.8; Cl, 8.2; S, 7.45%); ν_{max} (KBr)/cm^{-1}: 2935, 2856, 1760, 1593, 1518, 1439, 1332, 1273, 1026; δ_H 1.59–2.22 (10H, m), 3.93 (3H, s), 3.97 (3H, s), 5.42 (1H, s), 6.96 (1H, d, J = 8.4), 7.24–7.42 (7H, m); δ_C: 21.0, 21.4, 24.8, 30.5, 35.6, 55.9, 56.0, 78.8, 82.1, 83.8, 110.6, 110.7, 119.9, 125.8, 127.4, 128.9, 130.3, 136.7, 148.7, 149.7, 201.7; *m*/*z*: 432 (^{35}Cl, M^+), 396, 306, 266, 238, 165, 121, 109, 77, 69, 55 (100%).

4-Phenylthio-4-chloro-2,2-dimethyl-5-isopropyl-4,5-dihydrofuran-3(2*H*)-one 4e

From SO_2Cl_2 (0.281 g, 2.08 mmol) in CH_2Cl_2 (10 cm^3) and **1e** (0.50 g, 1.89 mmol) in the same solvent (20 cm^3) at room temperature, for 14 h. Radial chromatography of the white reaction residue (eluent hexane) gave a white solid, mp 54–55 °C (Found: C, 59.95; H, 6.3; S, 10.4; Cl, 11.9. $C_{15}H_{19}ClSO_2$ requires C, 60.3; H, 6.4; S, 10.1; Cl, 11.9%); ν_{max}(KBr)/cm^{-1}: 2964, 2872, 1765, 1472, 1180, 1083, 1018; δ_H: 1.14 (3H, d, J = 6.5), 1.26 (3H, s), 1.30 (3H, d, J = 6.5), 1.60 (3H, s), 2.28 (1H, septet of doublets, J = 6.5 and 9.7), 3.89 (1H, d, J = 9.7), 7.33–7.51 (5H, m); δ_C: 19.1, 20.2, 22.9, 26.6, 29.8, 79.7, 88,3, 127.4, 128.6, 128.9, 136.8, 203.0; *m*/*z*: 298 (^{35}Cl, M^+), 264, 226, 212, 197, 163, 135, 119, 109, 91, 77, 65, 59, 43 (100%).

4-Acetoxy-4-phenylthio-2,2-dimethyl-5-(4-methoxyphenyl)-4,5-dihydrofuran-3(2*H*)-one 9

Lead tetraacetate (0.37 g, 0.83 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of **1b** (0.21 g, 0.64 mmol) in the same solvent (10 cm^3). The resulting mixture was stirred at room temperature under nitrogen until TLC analysis showed that all of the starting material had been consumed, then filtered and the solvent evaporated under reduced pressure to leave a yellow oil. Dry-flash chromatography using 1:19 ethyl acetate–hexane as eluent yielded **9** (0.198 g, 80%), a white oil, as a mixture of diastereomers in the ratio 1.4:1 (Found: M^+, 386.1189. $C_{21}H_{22}SO_5$ requires M, 386.1188); ν_{max} (film)/cm^{-1}: 2980, 1766, 1740, 1610, 1510, 1220; δ_H (major isomer): 1.52 (3H, s), 1.68 (3H, s), 2.19 (3H, s), 3.85 (3H, s), 5.85 (1H, s), 6.95 (2H, d, J = 9), 7.22–7.48 (7H, m); δ_H (minor isomer): 1.52–1.61 (6H, br s), 1.57 (3H, s), 3.81 (3H, s), 5.33 (1H, s), 6.86 (2H, d, J = 9), 7.22–7.48 (5H, m), 7.56 (2H, d, J = 9); δ_C: 19.7, 21.1, 24.3, 24.8, 25.2 (major), 27.0 (major), 55.3 (both isomers), 76.9 (major), 80.5, 80.75 (major), 82.4 (major), 85.2, 90.0 (major), 113.3 (major), 113.6, 126.5 (major), 127.5, 127.6, 128.2, 128.3, 128.7, 128.8, 129.9, 130.2, 136.6 (major), 136.8, 159.45, 160.0 (major), 168.7 (major), 169.3, 202.5, 205.8 (major); *m*/*z*: 386 (M^+), 326, 179, 141 (100%), 110, 77, 43.

Reactions of chlorosulfides 4a–e with $SnCl_4$

Compound 4a. A solution of $SnCl_4$ (0.659 g, 2.53 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise at ambient temperature to a solution of **4a** (0.765 g, 2.30 mmol) in the same solvent (15 cm^3). The mixture was stirred overnight at room temperature, then washed successively with water (3 × 15 cm^3), saturated sodium bicarbonate solution (3 × 15 cm^3) and water (3 × 15 cm^3), dried and concentrated under reduced pressure. Radial chromatography of the resulting brown oil using 95:5 hexane–ethyl acetate as eluent gave **10a** (0.47 g, 69%), mp 88–89 °C as a yellow solid (Found: C, 72.7; H, 5.5; S, 10.4. $C_{18}H_{16}SO_2$ requires C, 73.1; H, 5.4, S, 10.8%); ν_{max}(KBr)/cm^{-1}: 3067, 2980, 1705, 1582, 1546, 1350, 1178, 1072; δ_H: 1.56 (6H, s), 7.07–7.26 (5H, m), 7.42–7.58 (3H, m), 8.27 (2H, d, J = 7.5); δ_C: 23.2, 87.7, 102.9, 125.7, 126.6, 128.5, 128.8, 129.0, 129.2, 132.9, 135.8, 184.3, 204.4; *m*/*z*: 296 (M^+), 210, 165, 129, 121, 105 (100%), 91, 77, 51, 43.

Compounds **4b**–**e** were treated with $SnCl_4$ according to the same general procedure.

Compound 4b. $SnCl_4$ (0.703 g, 2.70 mmol) in CH_2Cl_2 (15 cm^3) and **4b** (0.89 g, 2.45 mmol) in the same solvent (15 cm^3) gave a dark green solution which was worked up in the usual way. Radial chromatography of the reaction residue (95:5 hexane–ethyl acetate) gave **10b** (0.098 g, 12%) as a white crystalline solid, mp 112–113 °C (Found: C, 69.65; H, 5.4; S, 9.5. $C_{19}H_{17}SO_3$ requires C, 69.9; H, 5.6; S, 9.8%); ν_{max}(KBr)/cm^{-1}: 2976, 1693, 1601, 1579, 1542, 1497, 1423, 1266, 1182; δ_H: 1.56 (6H, s), 3.86 (3H, s), 6.95 (2H, d, J = 8.9), 7.08–7.26 (5H, m), 8.31 (2H, d, J = 8.9); δ_C: 22.4, 55.5, 87.5, 100.9, 114.0, 121.8, 125.7, 126.3, 129.1, 131.1, 136.2, 163.5, 183.9, 204.3; *m*/*z*: 326 (M^+), 283, 240, 197, 159, 149, 135 (100%), 110, 77, 55.

Furanone **12b** (0.213 g, 40%) was isolated as a white crystalline solid, mp 83–85 °C (Found: C, 71.3; H, 6.5. $C_{13}H_{14}O_3$ requires C, 71.5; H, 6.5%); ν_{max}(KBr)/cm^{-1}: 3082, 2938, 1680, 1596, 1511, 1466, 1282, 1244; δ_H: 1.45 (6H, s), 3.84 (3H, s), 6.91 (2H, d, J = 8.9), 7.62 (2H, d, J = 8.9), 8.38 (1H, s); δ_C: 23.1, 55.3, 88.6, 114.2, 116.3, 121.5, 126.8, 159.0, 170.8, 205.0; *m*/*z*: 218 (M^+), 175, 148, 132, 117, 105, 89, 77, 63, 51, 43 (100%).

The compound was identified by comparison of its properties with those of authentic material, prepared from **5b** (0.485 g, 2.20 mmol) and thallium(III) nitrate[11] (1.08 g, 2.42 mmol) in methanol (20 cm^3), at room temperature, for 24 h. Neutralisation of the reaction mixture with 1 M NaOMe in MeOH, evaporation of the solvent *in vacuo* and dry-flash chromato-

graphy of the residue using 1:9 ethyl acetate–hexane as the mobile phase gave **12b** (0.192 g, 40%) as a white solid.

Compound 4c. *Method 1*. $SnCl_4$ (0.373 g, 1.43 mmol) in CH_2Cl_2 (10 cm^3) and **4c** (0.511 g, 1.3 mmol) in the same solvent (10 cm^3) gave a dark green coloured mixture which was worked up as for **4a** to give a brown oil. Repeated radial chromatography (eluent, 3% ethyl acetate in hexane) gave **13** (0.162 g, 35%) as a white solid, mp 99–100 °C (Found: C, 67.6; H, 5.7; S, 8.6. $C_{20}H_{20}SO_4$ requires C, 67.4; H, 5.7; S, 9.0%); ν_{max} (KBr)/cm^{-1}: 2984, 2928, 2846, 1699, 1591, 1508, 1374, 1253, 1142, 1038; δ_H: 1.32 (6H, s), 3.84 (3H, s), 3.92 (3H, s), 6.98–7.28 (7H, m), 8.52 (1H, s); δ_C: 22.8, 56.0, 87.7, 113.0, 115.0, 119.2, 121.4, 125.4, 126.0, 126.6, 129.0, 138.2, 148.5, 149.8, 174.5, 204.8; *m*/*z* 356 (M^+), 247, 225, 176, 121, 97, 81, 69, 55, 41 (100%).

The second product (0.032 g, 7%), a yellow oil, was identified as **10c** (Found: C, 67.4; H, 5.9; S, 8.55. $C_{20}H_{20}SO_4$ requires C, 67.4; H, 5.7; S, 9.0%); ν_{max}(film)/cm^{-1}: 2962, 1700, 1580, 1498, 1439, 1363, 1262, 1235, 1182, 1138, 1084; δ_H: 1.50 (6H, s), 3.70 (3H, s), 3.85 (3H, s), 6.84 (1H, d, J = 8.6), 7.02–7.19 (5H, m), 7.81 (1H, d, J = 2.0), 7.9 (1H, dd, J = 2.0, 8.6); δ_C: 23.3, 55.8, 55.9, 87.6, 100.7, 110.6, 111.4, 121.6, 123.2, 125.6, 126.1, 128.6, 136.1, 148.6, 153.2, 183.8, 204.3; *m*/*z*: 356 (M^+), 270, 207, 179, 165, 149, 109, 77, 69, 51, 43.

The third product (0.075 g, 15%) isolated as a white solid, was identified as **14**, mp 75–77 °C (Found: C, 61.8; H, 4.9; S, 8.3; Cl, 8.8. $C_{20}H_{19}SClO_4$ requires C, 61.5; H, 4.9; S, 8.2; Cl, 9.1%); ν_{max}(KBr)/cm^{-1}: 3060, 2977, 2933, 1710, 1603, 1582, 1500, 1439, 1403, 1217, 1182; δ_H: 1.61 (6H, s), 3.59 (3H, s), 3.90 (3H, s), 6.89 (1H, s), 6.94 (1H, s), 7.08–7.27 (5H, m); δ_C: 23.2, 55.9, 56.3, 89.4, 105.6, 113.2, 113.4, 120.3, 125.2, 125.8, 126.6, 129.0, 136.3, 147.5, 151.9, 186.9, 204.0; *m*/*z*: 390 (^{35}Cl, M^+), 355, 327, 304, 278, 223, 213, 199, 149, 139, 121, 109, 91, 77, 69, 51, 41 (100%).

Method 2. $SnCl_4$ (0.073 g, 0.28 mmol) in CH_2Cl_2 (5 cm^3) was added to a mixture (diastereomeric ratio 1:1.2) of **3c** and **4c** (0.1 g, 0.25 mmol) in the same solvent (5 cm^3). The solution was stirred at room temperature for 12 h and worked-up as above. ^1H NMR analysis of the residue involving integration of the methyl group resonances at 1.32, 1.50 and 1.61 ppm established the presence of **13**, **10c** and **14** in the ratio 7:2:6.

A second experiment on the same scale using isomerically pure **4c** was stopped after 30 min. ^1H NMR analysis showed that the product mixture contained 7% of the isomer **3c** (H-5 at 5.94 ppm).

Method 3. Repetition of the reaction on the same scale as in Method 1, in toluene at room temperature, overnight produced a yellow precipitate. This was isolated by filtration, washed with toluene (2 × 10 cm^3), dissolved in ethyl acetate (30 cm^3), washed with water (3 × 15 cm^3) and saturated sodium bicarbonate solution (3 × 15 cm^3), dried and concentrated *in vacuo* to yield a brown oil. The filtrate was treated in the same manner, combined with the oil and evaporated. Repeated radial chromatography of the residue using 5% ethyl acetate in hexanes as eluent gave **10c** (0.203 g, 44%), **13** (0.046 g, 10%) and **14** (0.129 g, 25%).

Method 4. A solution of **4c** (0.98 g, 2.5 mmol) and $TiCl_4$ (0.522 g, 2.75 mmol) in CH_2Cl_2 (20 cm^3) was refluxed under nitrogen for 24 h. The reaction mixture was worked-up and the products isolated and purified as in Method 1 to produce **10c** (0.045 g, 5%), **13** (0.17 g, 19%) and **14** (0.289 g, 30%).

Method 5. A mixture of **4c** (0.589 g, 1.50 mmol) and $AlCl_3$ (0.22 g, 1.65 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 12 h. The reaction was worked-up as in Method 1 and radial chromatography of the residue with 3% ethyl acetate in hexane as eluent gave **15** (0.12 g, 28%) as a white solid, mp 120–122 °C (Found: C, 59.6; H, 5.4; Cl, 13.0. $C_{14}H_{15}ClO_4$ requires C, 59.5; H, 5.35; Cl, 12.5%); ν_{max}(KBr)/cm^{-1}: 3082, 3000, 1685, 1593, 1516, 1383, 1250, 1205; δ_H: 1.41 (6H, s), 3.76 (3H, s), 3.84 (3H, s), 6.83 (1H, s), 7.20 (1H, s), 8.64 (1H, s); δ_C: 22.9, 56.1, 87.7, 112.5, 113.0, 114.1, 119.5, 123.4, 147.8, 148.6, 174.6, 204.8; *m*/*z*: 282 (^{35}Cl, M^+, 100%), 247, 219, 196, 181, 149, 135, 91, 77, 55, 43.

Method 6. A mixture of **4c** (0.588 g, 1.5 mmol) and $ZnBr_2$ (0.372 g, 1.65 mmol) in CH_2Cl_2 (15 cm^3) was stirred at room temperature for 24 h. Reaction work-up as in Method 1 and radial chromatography using 3% ethyl acetate in hexane gave **10c** (0.264 g, 49%) and **14** (0.063 g, 11%).

Compound 4d. $SnCl_4$ (0.628 g, 2.41 mmol) in CH_2Cl_2 (30 cm^3) and **4d** (0.95 g, 2.19 mmol) in the same solvent (30 cm^3), at room temperature, for 12 h gave a brown oil after the usual work-up. Radial chromatography (eluent, 5% ethyl acetate in hexanes) produced **16** (0.417 g, 48%) as a white solid, mp 155–157 °C (Found: C, 69.5; H, 6.35; S, 7.7. $C_{23}H_{24}SO_4$ requires C, 69.7, H, 6.1, S, 8.1%); ν_{max}(KBr)/cm^{-1}: 2936, 2854, 1687, 1613, 1589, 1502, 1440, 1244, 1211, 1180, 1036; δ_H: 1.36–1.76 (10H, m), 3.84 (3H, s), 3.95 (3H, s), 6.99–7.26 (7H, m) and 8.53 (1H, s); δ_C: 22.3, 24.7, 31.9, 56.3, 56.5, 90.0, 113.5, 115.9, 119.4, 121.5, 125.9, 126.5, 126.7, 129.3, 138.7, 148.7, 150.0, 175.1, 205.0; *m*/*z*: 396 (M^+), 307, 277, 262, 201, 183, 134, 123, 101, 77 (100%), 51, 41.

Also isolated was **17** (0.166 g, 13%), mp 105–107 °C (Found: C, 69.6; H, 6.4, S, 7.7. $C_{23}H_{24}SO_4$ requires C, 69.7; H, 6.1; S, 8.1%); ν_{max}(KBr)/cm^{-1}: 2937, 1696, 1599, 1542, 1493, 1422, 1274, 1024; δ_H: 1.33–1.87 (10H, m), 3.69 (3H, s), 3.91 (3H, s), 6.86 (1H, d, J = 8.9), 7.00–7.20 (5H, m), 7.86–7.90 (2H, m); δ_C: 21.8, 24.5, 32.1, 55.8, 56.1, 89.5, 101.3, 110.7, 111.9, 121.9, 123.0, 125.6, 126.2, 129.1, 136.3, 148.7, 153.15, 183.9, 204.2; *m*/*z*: 396 (M^+), 341, 279, 253, 225, 179, 165, 149, 137, 107, 91 (100%), 73, 63, 43.

Compound 4e. $SnCl_4$ (0.344 g, 1.32 mmol) in CH_2Cl_2 (15 cm^3) and **4e** (0.359 g, 1.20 mmol) in the same solvent (15 cm^3) gave a dark brown oil. Radial chromatography using 5% ethyl acetate in hexane as eluent yielded **11** (0.274 g, 87%) as a white crystalline solid, mp 90–91 °C (Found: C, 68.7; H, 6.8; S, 12.0. $C_{15}H_{18}SO_2$ requires C, 68.7; H, 6.9; S, 12.2%); ν_{max}(KBr)/cm^{-1}: 2971, 2932, 2874, 1709, 1566, 1465; δ_H: 1.12 (6H, d, J = 7), 1.38 (6H, s), 3.36 (1H, septet, J = 7), 7.00–7.19 (5H, m); δ_C: 19.1, 23.0, 28.8, 88.6, 102.1, 125.6, 126.6, 128.9, 136.5, 199.4, 203.9; *m*/*z*: 262 (M^+), 247, 191, 163, 121, 99, 71, 51, 43 (100%).

Reaction of 9 with $SnCl_4$

A solution of $SnCl_4$ (0.373 g, 1.43 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to **9** (0.502 g, 1.3 mmol) in the same solvent (10 cm^3). The resulting mixture, which developed a dark green colour, was stirred at room temperature for 12 h and worked up as for **4a** to produce a brown oil. Radial chromatography using 5% ethyl acetate in hexane as eluent gave **10b** (0.047 g, 11%) and **12b** (0.085 g, 30%).

Reaction of 10c with $SnCl_4$

A solution of **10c** (0.25 g, 0.70 mmol) and $SnCl_4$ (0.20 g, 0.77 mmol) in CH_2Cl_2 (15 cm^3) was stirred at room temperature for 24 h, during which time a yellow precipitate formed; the mixture was then heated at reflux for 48 h. The starting material (0.23 g, 92%) was isolated following work-up of the reaction using the procedure employed for **4a**.

Reaction of 12c with diphenyl disulfide

Furanone **12c** was isolated as a white solid (0.153 g, 28%) from **5c** (0.551 g, 2.20 mmol) and thallium(III) nitrate[11] (1.08 g, 2.42 mmol) in methanol (20 cm^3) using the procedure employed for **12b**; mp 132–135 °C (Found: C, 67.2; H, 6.7. $C_{14}H_{16}O_4$ requires C, 67.7; H, 6.5%); ν_{max}(KBr)/cm^{-1}: 3061, 2968, 1680, 1614, 1594, 1517, 1358, 1258, 1136, 1026; δ_H: 1.46 (6H, s), 3.89 (3H, s), 3.92 (3H, s), 6.87 (1H, d, J = 8.2), 7.20 (1H, dd,

J = 8.2 and 2.0), 7.34 (1H, d, J = 2.0), 8.41 (1H, s); δ_C: 23.1, 55.6, 88.7, 109.2, 111.6, 116.3, 117.9, 121.95, 148.6, 149.2, 171.0, 205.0; *m*/*z*: 248 (M^+), 233, 205, 189, 178, 162, 147, 102, 91, 77.

A solution of **12c** (0.198 g, 0.8 mmol), diphenyl disulfide (0.174 g, 0.8 mmol) and $SnCl_4$ (0.260 g, 1 mmol) in CH_2Cl_2 (15 cm^3) was stirred at room temperature for 24 h and worked up as for **4a**. ^{1}H NMR analysis of the product mixture (0.155 g) involving integration of the characteristic furanone C-5 proton resonances at 8.41 and 8.52 ppm, for **12c** and **13** respectively, showed that the latter had been formed in 8% yield.

Reaction of 12c with benzenesulfenyl chloride

A solution of **12c** (0.094 g, 0.4 mmol), PhSCl (0.058 g, 0.4 mmol) and $SnCl_4$ (0.13 g, 0.44 mmol) in dry CH_2Cl_2 (5 cm^3) was stirred at room temperature for 24 h and worked up as for **4a**. ^{1}H NMR analysis of the product mixture (0.076 g) showed that **13** had been formed in 12% yield.

Reaction of 12c with $AlCl_3$

A solution of **12c** (9 mg, 0.036 mmol) in dry CH_2Cl_2 (2 cm^3) was added to a suspension of $AlCl_3$ (5.3 mg, 0.04 mmol) in the same solvent (2 cm^3). The mixture was stirred overnight and then filtered. Work-up of the organic filtrate as above gave a white solid (8 mg) identified as **12c**.

Reaction of 1c with $SnCl_4$ and $AlCl_3$

A solution of **1c** (0.15 g, 0.42 mmol) in dry CH_2Cl_2 (5 cm^3) was added to $SnCl_4$ (0.12 g, 0.46 mmol) in the same solvent (5 cm^3). The mixture was stirred overnight at ambient temperature, under nitrogen and worked up in the usual way. Dry-flash chromatography using 1 : 19 ethyl acetate–hexane as eluent gave two fractions. The first (61 mg) was a complex mixture of compounds and no evidence for the presence of **10c** either by TLC analysis with an authentic sample in various solvent systems or by comparison of its ^{1}HNMR spectrum with those of the mixture could be obtained. The second fraction contained a single compound identified as **5c** (62 mg, 46%) by comparison of its spectra with those of an authentic sample.

Similarly, reaction of **1c** with a suspension of $AlCl_3$ (0.061 g, 0.46 mmol) on the same scale gave a mixture of products from which **5c** (52 mg, 39%) was the only identifiable compound isolated. ^{1}H NMR examination of the reaction residue failed to reveal any evidence for the presence of **12c** (furanone H-5, 8.41 ppm).

X-Ray crystallographic analysis of 4c and 13

Crystal data. Compound **4c**. $C_{20}H_{21}O_4SCl$, M = 392.88, Monoclinic, a = 12.291(4), b = 11.696(2), c = 13.693(3) Å, β = 96.52(2)°, U = 1954.1(8) Å^3, $P2/n$ (alt. $P2/c$ No. 13), Z = 4, D_x = 1.335 g cm^{-3}. Colourless needles. Crystal dimensions 0.60 × 0.55 × 0.50 mm, μ(Mo-Kα) = 3.24 cm^{-1}.

Compound **13**. $C_{20}H_{21}O_4S$, M = 357.43, Monoclinic, a = 5.920(2), b = 16.419(5), c = 18.436(5) Å, β = 93.33(3)°, U = 1788.9(9)Å^3, $P2_1/n$ (alt. $P2_1/c$ No. 14), Z = 4, D_x = 1.327 g cm^{-3}. Colourless blocks. Crystal dimensions 0.70 × 0.60 × 0.40 mm, μ(Mo-Kα) = 2.02 cm^{-1}.

Both unit cells were obtained by least-squares refinement on diffractometer angles for 25 automatically centred reflections, Mo-Kα graphite monochromated radiation, λ = 0.71069 Å.

Data collection and processing. MACH-3 diffractometer, $\omega/2\theta$ mode.

For **4c**, 7280 reflections were measured up to θ = 25°, 3445 unique reflections (R_{int} = 0.044) giving 2362 observed reflections [$I > 2\sigma(I)$]. The data were corrected for decay (7.6%) during processing. For **13**, 6389 reflections were measured up to θ = 27.5°, 4044 unique reflections (R_{int} = 0.027) giving 1665 observed reflections [$I > 2\sigma(I)$]. The data were corrected for decay (1.8%) during processing.

Structure analysis and refinement. Both structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 with all non-H atoms anisotropic and hydrogen atoms allowed to ride on their parent atom. For **4c**, convergence was achieved with R = 0.036, wR_2 = 0.089. For **13**, convergence was achieved with R = 0.061, wR_2 = 0.104. Calculations were performed on a PC with the SHELXL,[26] PLATON[27] and maXus[28] suite of programs.‡

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