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A New Reaction of α-Chloro-α-chlorosulfenyl Ketones: Facile Syntheses of 3,3-Dichloro- and 3-Chloro-Chroman-4-ones and Thiochroman-4-ones

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Abstract: 3-Chloro-3-chlorosulfenylchroman-4-ones are efficiently obtained from chroman-4-ones by treatment with thionyl chloride. Direct oxidation affords 3,3-dichlorochroman-4-ones, whilst conversion to the sulfenamides prior to oxidation provides a facile route to 3-chlorochroman-4-ones.

INTRODUCTION

Chroman-4-ones undergo ready halogenation at the 3-position. Thus, reaction with bromine in carbon tetrachloride leads to good yields of 3-bromochroman-4-ones.[1] The use of an excess of the halogen results in both 3,3-disubstitution and bromination in the aromatic ring. In some instances all three products are formed, whilst variation of the solvent can lead to exclusive aromatic substitution.[2] The bromination of thiochroman-4-ones is not straightforward. Whereas 6-methylthiochroman-4-one gives a perbromide which is converted by water to the sulfoxide, or on standing gives the 3-bromo-6-methylthiochroman-4-one,[3] bromination of 2,2-dimethylthiochroman-4-one proceeds smoothly to afford a mixture of 3-bromo- and 3,3-dibromothiochroman-4-ones. However, attempts to separate the mixture by elution from silica affords a multicomponent mixture of ring contracted products.[4] Direct chlorination of ketones is less convenient[5] and sulfuryl chloride has been successfully used as an alternative reagent,[6] although dichlorination is sometimes the major reaction. 3-Chloro- and 3,3-dichloro- flavanones have been obtained from flavones using $CuCl_2$ as the chlorinating reagent.[7] Flavone reacts with thionyl chloride in refluxing benzene to give 3-chloroflavone in good yield,[8] whilst reaction of 2-methylchromone under similar conditions yields the 2-trichloromethyl analogue, as a consequence of side chain halogenation.[9]

The reaction of thionyl chloride with aromatic aldehydes in the presence of a catalytic amount of DMF results in formation of the dichloromethyl compound,[10] but α-methylene ketones react at the methylene function in the presence of pyridine.[11] The resulting α-chloro-α-chlorosulfenylketones are versatile intermediates for the formation of α-chlorosulfenamides,[12,13] 1,2-diketones,[13,14] α-ketothiones,[15]

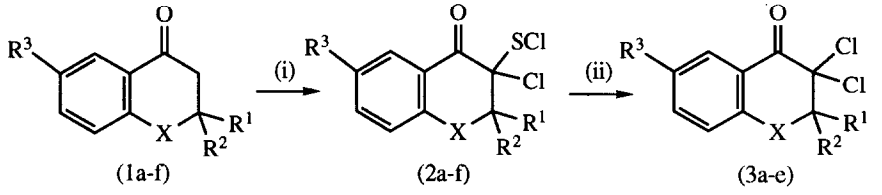
α-iminoketones,[16] thione *S*-imides[17] and thione *S*-ylides.[18] Some chemistry of this functional group has appeared in a general review on the application of thionyl chloride in organic synthesis.[19]

For our studies of benzopyran chemistry, we required quantities of 3-chlorochroman-4-ones and the corresponding thiochroman-4-ones and we now report the behaviour of both α-chlorosulfenyl chlorides (2), obtained from chroman-4-ones and thiochroman-4-ones (1), and the derived sulfenamides (4) towards oxidation. This new aspect of α-chloro-α-sulfenyl ketone chemistry offers a facile and selective route to 3-chloro- and 3,3-dichloro- chroman-4-ones and thiochroman-4-ones.

DISCUSSION

Stirring a solution of a 2,2-disubstituted chroman-4-one (1) overnight in an excess of thionyl chloride gave, on removal of the unreacted $SOCl_2$, the α-chlorosulfenyl chlorides (2) in high yield, without the need for the pyridine catalyst.[11] A more rapid conversion of the chromanones (1) to the α-chlorosulfenyl chlorides (2) could be achieved by heating the reaction mixtures at 50 °C for ~7 hours, but the products obtained from this procedure were accompanied by some tarry material which resulted in a decrease in the overall yield of the α-chlorosulfenyl chlorides.

The ^1H and ^{13}C NMR spectra of these compounds are markedly different from those of the chromanones. The unsymmetrical substitution at C-3 confers diastereotopic properties on the geminal methyl groups of (2a,e and f) which now appear as individual signals shifted slightly downfied at ~δ 1.5 and δ 1.8. Of course the signals for the C-3 methylene protons are absent in all examples. The most noticeable feature in the ^{13}C NMR spectra of the α-chlorosulfenylchlorides is the considerable downfield shift of the C-3 signal, which now resonates in the range δ 85-92 as a consequence of the presence of the two electronegative substituents. In comparison, C-3 in 2,2-disubstituted chromanones absorbs typically at δ 46-51[20] and in 2,2-dimethylthiochromanone and its 1,1-dioxide at δ 54 and 50, respectively.[21] The C-2 unsymmetrically substituted chroman-4-ones (1c) and (1d) gave inseparable mixtures of diastereoisomeric α-chloro-α-chlorosulfenyl chlorides (2c) and (2d) on reaction with $SOCl_2$.



(1a-f) (2a-f) (3a-e)

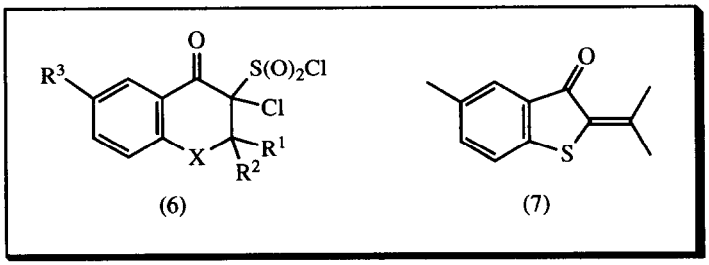
a: $R^1 = R^2$ = Me, R^3 = H, X = O; b: $R^1 = R^2$ = -$(CH_2)_5$-,R^3 = H, X = O;
c: R^1 = Me, R^2 = Et, R^3 = H, X = O; d: R^1 = Me, R^2 = Ph, R^3 = H, X = O;
e: $R^1 = R^2 = R^3$ = Me, X = SO_2; f: $R^1 = R^2 = R^3$ = Me, X = S.

Reagents and Conditions; (i) xs. $SOCl_2$, RT, 14h; (ii) xs.H_2O_2, AcOH, 50 °C, 3h.

Scheme 1

The oxidation of the α-chlorosulfenyl chlorides (2a-e) was accomplished using a 10 fold excess of hydrogen peroxide in glacial acetic acid at 50 °C, and was followed by elution of the crude reaction product from silica gel to afford the 3,3-dichlorochroman-4-ones (3a-e) in good yield. [**CAUTION**: The use of elevated reaction temperatures (> 60 °C) should be avoided as a vigorous exothermic decomposition of the proposed intermediate sulfonylchloride (6) occurs]. During several of the oxidation reactions, sulfur dioxide was detected in the reaction vessel by GC/MS.

A 15 fold excess of hydrogen peroxide was employed in the case of (2f) because of the presence of the sulfur heteroatom and this gave (3e) in which the heteroatom had been oxidised. It is noteworthy that the formation of this dichlorothiochromanone (3e) from (2f) was not accompanied by ring contraction to the benzo[*b*]thiophene (7), although such ring contractions are common for thiochromanones containing a suitably disposed 3-substituent,[4] and have been reported for the acidic hydrolysis of sulfenamides derived from 3-chloro-3-chlorosulfenyl-2,2-dimethylthiochroman-4-ones.[12]

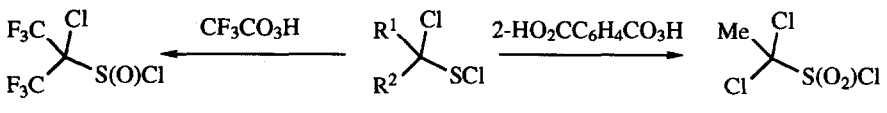


(6) (7)

The geminal methyl groups of the dichlorochromanones (3a and e) are equivalent and give rise to a broad signal at δ 1.70 (3a) and δ 1.82 (3e) in the ^{1}H NMR spectra. Recording the ^{1}H NMR spectrum of (3a) at 50 °C sharpened the signal appreciably. Conversely, cooling the sample of (3a) to - 20 °C resolved the signal into singlets at δ 1.49 and δ 1.83 for the pseudo axial and pseudo equatorial methyl groups. Similar loss of resolution of the ^{1}H NMR signals of the C-2 substituents was observed for the other dichlorochromanones (3b,c and d). This poor resolution can be attributed to the interconversion of the pyranone ring between two energetically similar half chair type conformers somewhat slowed by the presence of the bulky chlorine atoms at C-3.

C-3 of the dichlorochromanones (3a-e) absorbs in the range δ 89-91 in the ^{13}C NMR spectra, shifted marginally downfield on replacement of the sulfenylchloride function by a chlorine atom. The conversion of (2f) to (3e) brought about a prominent downfield shift from δ 52.3 to δ 69.1 for C-2 as a consequence of the oxidation of the adjacent heteroatom. This value now compares well with that for C-2 of (2e) which absorbs at δ 68.9.

There are several examples known of oxidation of chlorosulfenyl chlorides in which no extrusion of SO_2 was observed. Reaction of (8a) with a slight excess of peroxytrifluoroacetic acid afforded the chlorosulfinyl chloride (9),[22] whilst oxidation of (8b) with 2 eq. of perphthalic acid gave the chlorosulfonyl chloride (10)[23] (Scheme 2).

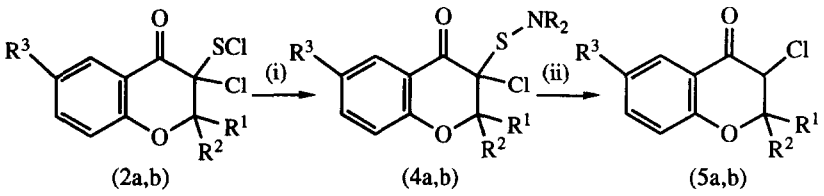


(9) (8a) $R^1 = R^2 = CF_3$ (10)

(8b) R^1 = Me, R^2 = Cl

Scheme 2

Treatment of a cold solution of the α-chlorosulfenyl chlorides (2a,b) in toluene with two equivalents of morpholine gave the sulfenamides (4a,b), respectively, in excellent yield. The ^1H and ^{13}C NMR spectra of (4a,b) compare favourably with those of the starting α-chlorosulfenyl chlorides, though with the obvious presence of signals associated with the morpholine function. Notably, the ^1H NMR signals of the amine group are broadened as a result of slow rotation of the amine moiety, and again sharpening of the signals was observed on recording the spectra at 50 °C.



(2a,b) (4a,b) (5a,b)

Reagents and Conditions; (i) 2 R_2NH, 5 °C-RT, 30m; (ii) xs. H_2O_2, AcOH, 50 °C, 3h.

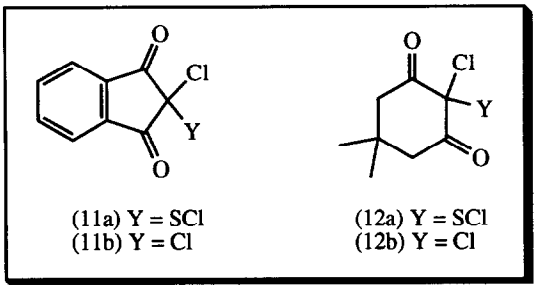
Scheme 3

Oxidation of the sulfenamides (4a,b) was achieved using an identical procedure to that described for the oxidation of the sulfenyl chlorides (2) (Scheme 3). The only isolatable products, 3-chlorochromanones, were obtained in high yield after elution of the crude reaction mixture from silica gel and distillation or recrystallisation.

The unsymmetrical substitution of C-3 in these chloroketones (5a,b) confers diastereotopic properties on the C-2 substituents. In the ^1H NMR spectra the geminal methyl group of (5a) affords signals at δ 1.53 and δ 1.56 and the signals for the spirocyclohexane ring of (5b) are much more complex compared with those of the chromanone (1b). H-3 appears as a singlet at ~ δ 4.35 and C-3 resonates at ~ δ 64 in these compounds.

The oxidation of (4a) with 2 equivalents of *m*-chloroperoxybenzoic acid (*m*-CPBA) was also investigated. The major product was characterised as the 3-chlorochroman-4-one (5a) albeit in a marginally lower yield (81%) than that obtained using H_2O_2/AcOH. The difficulty in the work-up of removing the *m*-chlorobenzoic acid, which is only sparingly soluble in the reaction mixture, by $NaHCO_3$ extractions and the

relative cost and hazard associated with *m*-CPBA render the use of 30% H_2O_2 in glacial acetic acid more attractive.



(11a) Y = SCl
(11b) Y = Cl

(12a) Y = SCl
(12b) Y = Cl

In an attempt to extend the generality of this synthetic strategy, indane-1,3-dione, 5,5-dimethylcyclohexane-1,3-dione (dimedone) and ethyl benzoylacetate were used as substrates. The crude α-chloro-α-sulfenyl chlorides (11a) and (12a) derived from indane-1,3-dione and 5,5-dimethylcyclohexane-1,3-dione, respectively could not be induced to crystallise and hence were oxidised directly to their dichloro derivatives (11b) and (12b). The reaction of dimedone with several sulfur chlorides has been studied. Long reaction times with $SOCl_2$ in benzene at RT resulted in low yields of 2-chloro-5,5-dimethylcyclohexane-1,3-dione and 3-chloro-5,5-dimethylcyclohex-2-enone, whereas short reaction times favour the formation of a spiro-fused 1,3-oxathiole.[24] These features may contribute to the low overall yield of (12b). No products could be detected in the reaction mixture of ethyl benzoylacetate and thionyl chloride even after 33h at 50 °C.

EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. Infrared spectra were recorded on a Mattson-Polaris Fourier Transform spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM250 instrument for solutions in $CDCl_3$; coupling constants (*J*) are given in Hz. Flash chromatographic separations were performed on Crossfields Sorbsil C60 silica gel (M.P.D. 60Å, 40-60μ, activated) according to the published procedure.[25] The chroman-4-ones were prepared from 2'-hydroxyacetophenone and the requisite ketone according to the general procedure described by Kabbe.[26] 2,2,6-Trimethylthiochroman-4-one was obtained from 4-methylthiophenol and 3-methylbut-2-enoic acid.[27]

General Method for the Preparation of α-Chloro-α-chlorosulfenylketones

The ketone (20 mmol) was dissolved in thionyl chloride (140 mmol) and stirred overnight (14h). Removal of the excess thionyl chloride afforded a dark brown viscous oil which crystallised on standing. Recrystallisation (decolourising charcoal) afforded the following compounds:

1. *3-Chloro-3-chlorosulfenyl-2,2-dimethylchroman-4-one* (**2a**) from (**1a**) (88%) as bright yellow crystals from hexane and ethyl acetate; m.p. 84.5-85.5 °C; ν_{max}/Nujol cm^{-1} 1707; δ_H 1.51 (3H, s, 2-Me), 1.76 (3H, s, 2-Me),

6.96 (1H, dd, *J* 8.1, 1.2, 8-H), 7.11 (1H, m, 6-H), 7.56 (1H, m, 7-H), 7.99 (1H, dd, *J* 8.0, 1.2, 5-H); δ_C 22.5, 24.3, 85.8, 86.8, 118.0, 118.3, 122.4, 128.6, 136.6, 157.1, 180.2; (Found: C, 47.7; H, 3.6; Cl, 25.4, S, 11.4. $C_{11}H_{10}Cl_2O_2S$ requires C, 47.7; H, 3.6; Cl, 25.6, S, 11.6%).

2. *3-Chloro-3-chlorosulfenylspiro[chroman-2,1'-cyclohexane]-4-one* (**2b**) from (**1b**) (92%) as bright yellow needles from hexane and ethyl acetate; m.p. 150.0-150.5 °C; ν_{max}/Nujol cm^{-1} 1710; δ_H 1.23-2.22 (10H, m, cyclohexane ring), 7.01 (1H, d, *J* 8.1, 8-H), 7.10 (1H, m, 6-H), 7.57 (1H, m, 7-H), 7.97 (1H, dd, *J* 8.1, 1.4, 5-H); δ_C 21.6, 21.8, 25.1, 27.8, 31.8, 87.2, 88.1, 118.0, 119.1, 122.2, 128.7, 136.9, 156.9, 180.1; (Found: C, 53.1; H, 4.5; Cl, 22.2, S, 10.0. $C_{14}H_{14}Cl_2O_2S$ requires C, 53.0; H, 4.5; Cl, 22.4, S, 10.1%).

3. *3-Chloro-3-chlorosulfenyl-2-ethyl-2-methylchroman-4-one* (**2c**) from (**1c**) as a mixture of diastereoisomers (~6:1)† (79%) as yellow crystals from hexane; m.p. 103.5-105.5 °C; ν_{max}/Nujol cm^{-1} 1704; δ_H major diastereoisomer 1.17 (3H, t, *J* 7.6, 2-$CH_2C\underline{H}_3$), 1.53 (3H, s, 2-Me), 2.21 (2H, m, 2-$C\underline{H}_2CH_3$), 6.96 (1H, dd, *J* 8.0, 1.3, 8-H), 7.15 (1H, m, 6-H), 7.57 (1H, m, 7-H), 8.01 (1H, dd, *J* 8.2, 1.4, 5-H); δ_C 7.27, 18.3, 29.2, 87.6, 87.8, 118.0, 118.4, 122.3, 128.5, 136.6, 157.1, 180.5; δ_H minor diastereoisomer 0.89 (3H, t, *J* 7.6, 2-$CH_2C\underline{H}_3$), 1.77 (3H, s, 2-Me), 1.97 (2H, m, 2-$C\underline{H}_2CH_3$), 6.99 (1H, dd, *J* 8.0, 1.3, 8-H), 7.17 (1H, m, 6-H), 7.58 (1H, m, 7-H), 8.03 (1H, d, *J* 8.1, 5-H); (Found: C, 49.7; H, 4.2; Cl, 24.2, S, 11.0. $C_{12}H_{12}Cl_2O_2S$ requires C, 49.5; H, 4.2; Cl, 24.4, S, 11.0%).

† Ratio based upon the relative integrals of the 2-Me signals (δ 1.53 and δ 1.77) in the ^1H NMR spectrum of the crude reaction mixture.

4. *3-Chloro-3-chlorosulfenyl-2-methyl-2-phenylchroman-4-one* (**2d**) from (**1d**) (77%) as a mixture of diastereoisomers (~17:1),† as pale yellow needles from light petroleum (b.p. 40-60 °C) and diethyl ether; m.p. 164.5-165.5 °C; ν_{max}/Nujol cm^{-1} 1712; δ_H 1.98 (3H, s, 2-Me), 7.15 (2H, m, Ar-H), 7.30 (3H, m, Ar-H), 7.62 (1H, m, Ar-H), 7.87 (2H, m, Ar-H), 8.09 (1H, d, *J* 8.1, 5-H); δ_C 21.7, 87.8, 88.0, 117.7, 118.4, 122.7, 126.9 (2 x C), 128.3 (2 x C), 129.6, 136.9, 137.2, 159.6, 179.9; (Found: C, 56.8; H, 3.5; Cl, 20.9, S, 9.3. $C_{16}H_{12}Cl_2O_2S$ requires C, 56.6; H, 3.6; Cl, 20.9, S, 9.5%).

† Ratio based upon the relative integrals of the 2-Me signals (δ 1.98 and δ 2.18) in the ^1H NMR spectrum of the crude reaction mixture.

5. *3-Chloro-3-chlorosulfenyl-2,2,6-trimethylthiochroman-4-one 1,1-dioxide* (**2e**) from (**1e**) (83%) as pale yellow microcrystals from ethyl acetate and hexane; m.p. 159.0-159.5 °C; ν_{max}/Nujol cm^{-1} 1705, 1298, 1151; δ_H 1.72 (3H, s, 2-Me), 1.92 (3H, s, 2-Me), 2.50 (3H, s, 6-Me), 7.71 (1H, dd, *J* 8.0, 1.2, 7-H), 7.92 (1H, d, *J* 7.9, 8-H), 8.12 (1H, d, *J* 0.9, 5-H); δ_C 16.6, 21.6, 23.5, 68.6, 89.1, 124.7, 126.0, 130.4, 133.8, 136.2, 145.2, 178.9; (Found: C, 42.6; H, 3.6; Cl, 20.8, S, 18.9. $C_{12}H_{12}Cl_2O_3S_2$ requires C, 42.5: H, 3.6; Cl, 20.9; S, 18.9%).

6. *3-Chloro-3-chlorosulfenyl-2,2,6-trimethylthiochroman-4-one* (**2f**) from (**1f**) (96%) as bright yellow needles from ethyl acetate and hexane; m.p. 131.5-133.0 °C; ν_{max}/Nujol cm^{-1} 1693; δ_H 1.59 (3H, s, 2-Me), 1.83 (3H, s,

2-Me), 2.38 (3H, s, 6-Me), 7.12 (1H, d, *J* 8.1, 8-H), 7.29 (1H, dd, *J* 8.1, 1.2, 7-H), 8.10 (1H, d, *J* 1.0, 5-H); δ_C 20.9, 24.6, 26.1, 52.3, 92.3, 127.4, 128.4, 131.6, 133.3, 134.8, 136.9, 180.4; (Found: C, 47.1; H, 4.0; Cl, 22.9; S, 20.6. $C_{12}H_{12}Cl_2OS_2$ requires C, 46.9; H, 3.9; Cl, 23.1; S, 20.9%).

General Method for the Preparation of α,α-Dichloroketones

Hydrogen peroxide (30%, 50 mmol) was added to a stirred solution of the α-chlorosulfenyl chloride (**2**) (5 mmol) in glacial acetic acid (30 cm^3). The resulting solution was maintained at 50 °C **(CAUTION)** for 3h. The cooled solution was poured into water (400 cm^3) and extracted with ethyl acetate (5 x 50 cm^3). The combined ethyl acetate extracts were washed with water (2 x 100 cm^3) and aq. sat. $NaHCO_3$ solution (4 x 100 cm^3). Removal of the dried (Na_2SO_4) solvent gave the crude dichlorochromanones (**3**) which were further purified by elution from silica and recrystallisation or distillation.

The following compounds were obtained by this protocol:

1. *3,3-Dichloro-2,2-dimethylchroman-4-one* (**3a**) from (**2a**) (89%) as a low melting colourless solid on elution from silica with 15 % ethyl acetate in hexane and recrystallisation from light petroleum (b.p. below 40 °C); m.p. 83.0-84.0 °C; ν_{max}/Nujol cm^{-1} 1715; δ_H 1.70 (6H, vbs, 2-Me), 6.97 (1H, dd, *J* 8.2, 1.3, 8-H), 7.09 (1H, m, 6-H), 7.56 (1H, m, 7-H), 7.98 (1H, dd, *J* 8.1, 1.2, 5-H); δ_C 21.9 (broad, 2 x C), 85.1, 89.8, 116.9, 118.2, 122.1, 128.6, 137.0, 157.5, 180.1; (Found: M^+, 244.0058; C, 54.0; H, 4.1; Cl, 28.7. $C_{11}H_{10}Cl_2O_2$ requires M^+, 244.0057(9); C, 53.9; H, 4.1; Cl, 28.9%).

2. *3,3-Dichlorospiro[chroman-2,1'-cyclohexan]-4-one* (**3b**) from (**2b**) (81%) as a low melting solid on elution from silica with 10 % ethyl acetate in hexane and recrystalliisation from light petroleum (b.p. 40-60 °C); m.p. 63.0-65.0 °C; ν_{max}/Nujol cm^{-1} 1719; δ_H 1.21-2.40 (10H, bm, cyclohexane ring), 7.10 (2H, m, 6-H, 8-H), 7.59 (1H, m, 7-H), 7.99 (1H, dd, *J*, 8.1, 1.3, 5-H); δ_C 20.9 (2 x C), 24.8, 28.1(broad, 2 x C), 85.7, 90.6, 117.6, 118.2, 122.1, 128.7, 136.9, 156.9, 180.1; (Found: C, 58.9; H, 4.8; Cl, 24.9. $C_{14}H_{14}Cl_2O_2$ requires C, 59.0; H, 5.0; Cl, 24.9%).

3. *3,3-Dichloro-2-ethyl-2-methylchroman-4-one* (**3c**) from (**2c**) (91%) as a viscous yellow oil on elution from silica with 15 % ethyl acetate in hexane; b.p. 120-125 °C at 0.3 mmHg; ν_{max}/Nujol cm^{-1} 1717; δ_H 1.00 (3H, vbs, 2-$CH_2C\underline{H}_3$), 1.67 (3H, vbs, 2-Me), 1.93 (2H, vbs, 2-$C\underline{H}_2CH_3$), 6.99 (1H, dd, *J* 8.0, 1.3, 8-H), 7.10 (1H, m, 6-H), 7.57 (1H, m, 7-H), 7.97 (1H, dd, *J* 8.2, 1.4, 5-H); δ_C 7.49, 18.2, 25.2, 86.8, 90.6, 117.3, 118.1, 122.1, 128.6, 137.0, 157.3, 180.2; (Found: C, 55.5; H, 4.6; Cl, 27.2. $C_{12}H_{12}Cl_2O_2$ requires C, 55.6; H, 4.7; Cl, 27.4%).

4. *3,3-Dichloro-2-methyl-2-phenylchroman-4-one* (**3d**) from (**2d**) (73%) as colourless crystals on elution from silica with 20 % ethyl acetate in hexane and recrystallisation from light petroleum (b.p. 40-60 °C); m.p. 101.0-101.5 °C; ν_{max}/Nujol cm^{-1} 1721; δ_H 1.97 (3H, bs, 2-Me), 7.16 (2H, m, Ar-H), 7.47 (3H, m, Ar-H), 7.63 (1H, m, Ar-H), 7.83 (2H, m, Ar-H), 8.05 (1H, dd, *J* 8.1, 1.7, 5-H); δ_C 20.8 (broad), 87.7, 89.5, 117.0, 118.5,

122.5, 127.6 (2 x C), 128.2 (2 x C), 128.8, 129.0, 137.2, 137.3, 157.5, 180.2; (Found: C, 62.7; H, 3.9; Cl, 23.3. $C_{16}H_{12}Cl_2O_2$ requires C, 62.7; H, 4.0; Cl, 23.1%).

5 (i). *3,3-Dichloro-2,2,6-trimethylthiochroman-4-one 1,1-dioxide* (**3e**) from (**2e**) (69%) as colourless crystals on elution from silica with 30 % ethyl acetate in hexane and recrystallisation from hexane; m.p. 150.0-152.0 °C; ν_{max}/Nujol cm^{-1} 1708, 1308, 1150; δ_H 1.82 (6H, bs, 2-Me), 2.55 (3H, s, 6-Me), 7.75 (1H, dd, *J* 8.1, 1.2, 7-H), 7.95 (1H, d, *J* 8.0, 8-H), 8.07 (1H, d, *J* 1.1, 5-H); δ_C 19.1 (2 x C), 21.5, 69.1, 90.9, 125.0 (2 x C), 130.3, 135.9, 137.0, 144.8, 180.0; (Found: M+NH_4^+, 324.0228; C, 47.0; H, 4.1; Cl, 23.3; S, 10.5. $C_{12}H_{12}Cl_2O_3S$ requires M+NH_4^+, 324.0228; C, 46.9; H, 4.0; Cl, 23.1; S, 10.4%).
(ii). *3,3-Dichloro-2,2,6-trimethylthiochroman-4-one 1,1-dioxide* (**3e**) from (**2f**) (51%) identical in all aspects to that prepared above.

The following compounds were obtained using the crude α-chloro-α-sulfenyl chlorides directly in the oxidation step.

6. *2,2-Dichloroindane-1,3-dione* (**8b**) from indane-1,3-dione (34%§) as pale yellow plates on elution from silica with 30% ethyl acetate in hexane and recrystallisation from ethyl acetate and hexane; m.p. 125.0-126.5 °C [lit. m.p. 126-128 °C[28]]; δ_H 8.05 (2H, m, Ar-H), 8.16 (2H, m, Ar-H); δ_C 72.8 (2-C), 125.7 (2 x Ar-CH), 137.0 (2 x Ar-C), 138.0 (2 x Ar-CH), 186.3 (2 x CO).

7. *2,2-Dichloro-5,5-dimethylcyclohexane-1,3-dione* (**9b**) from 5,5-dimethylcyclohexane-1,3-dione (26%§) as colourless needles on elution from silica with 20% ethyl acetate in hexane and recrystallisation from light petroleum (b.p. 30-40 °C); m.p. 110.5-111.5 °C [lit. m.p. 110-111 °C[29]]; δ_H 1.05 (6H, s, 5-Me), 2.97 (4H, s, 4-CH_2, 6-CH_2), δ_C 28.0 (5-Me_2), 30.4 (5-C), 48.9 (4-C, 6-C), 86.1 (2-C), 192.1 (2 x CO).

Note: § Percentage yield based on the amount of 1,3-diketone used.

General Method for the Preparation of α-Chloro-α-chlorosulfenamides (4)

A solution of the secondary amine (20 mmol) in dry toluene (40 cm^3) was added dropwise over a period of 10 minutes to a vigorously stirred solution of the 3-chloro-3-chlorosulfenyl derivative (10 mmol) in toluene (50 cm^3) cooled to 5 °C. The resulting viscous solution was allowed to warm to room temperature and was then filtered through a celite pad, which was washed well with toluene. Removal of the toluene gave the crude products which were recrystallised.

1. *3-Chloro-2,2-dimethyl-3-(morpholinosulfenyl)chroman-4-one* (**4a**) from (**2a**) (93%) as colourless crystals from light petroleum (b.p. 40-60 °C) and hexane m.p. 107.5-109.0 °C; ν_{max}/Nujol cm^{-1} 1695; δ_H 1.45 (3H, s, 2-Me), 1.73 (3H, s, 2-Me), 2.93 (4H, bm, -$N(CH_2)_2$-), 3.51 (4H, bm, -$O(CH_2)_2$-), 6.93 (1H, dd, *J* 8.0, 1.1, 8-H), 7.06 (1H, m, 6-H), 7.51 (1H, m, 7-H), 7.96 (1H, dd, *J* 8.2, 1.3, 5-H); δ_C 21.7, 23.9, 56.9 (broad, 2 x C), 67.7

(2 x C), 85.0, 88.5, 118.0, 119.7, 121.7, 127.7, 136.0, 157.5, 183.7; (Found: C, 55.1; H, 5.7; Cl, 11.0; N, 4.4; S, 9.7. $C_{15}H_{18}ClNO_3S$ requires C, 55.0; H, 5.6; Cl, 10.8; N, 4.3; S, 9.8%).

2. *3-Chloro-3-morpholinosulfenylspiro[chroman-2,1'-cyclohexane]-4-one* (**4b**) from (**2b**) (85% crude) as a viscous yellow oil/semisolid which could not be induced to crystallise and decomposed on distillation under reduced pressure; ν_{max}/Nujol cm^{-1} 1699; δ_H 1.28-2.06 (10H, m, cyclohexane ring), 2.90 (4H, bm, $-N(CH_2)_2-$), 3.52 (4H, bm, $-O(CH_2)_2-$), 7.04 (2H, m, 6-H, 8-H), 7.54 (1H, m, 7-H), 7.96 (1H, dd, *J* 8.2, 1.3, 5-H).

General Method for the Preparation of α-Chloroketones (5)

These compounds were obtained using an identical procedure to that employed for the 3,3-dichlorochromanones (**3**) above.

1. *3-Chloro-2,2-dimethylchroman-4-one* (**5a**) from (**4a**) (91%) as colourless crystals on elution from silica with 25 % ethyl acetate in hexane and recrystallisation from light petroleum (b.p. 30-40 °C) ; m.p. 37.5-39.0 °C [lit. m.p. 37.5-39.0 °C[12]; ν_{max}/Nujol cm^{-1} 1695; δ_H 1.53 (3H, s, 2-Me), 1.56 (3H, s, 2-Me), 4.40 (1H, s, 3-H), 6.97 (1H, dd, *J* 8.0, 1.2, 8-H), 7.04 (1H, m, 6-H), 7.52 (1H, m, 7-H), 7.90 (1H, dd, *J* 8.0, 1.3, 5-H); δ_C 22.1, 24.8, 64.6, 81.3, 118.2, 118.4, 121.5, 127.6, 136.6, 158.6, 186.1; (Found: M^+, 210.0448; C, 62.8; H, 5.2; Cl, 16.8. $C_{11}H_{11}ClO_2$ requires M^+, 210.0447(6); C, 62.7; H, 5.3; Cl, 16.8%).

2. *3-Chlorospiro[chroman-2,1'-cyclohexan]-4-one* (**5b**) from crude (**4b**) (78%) as a viscous green yellow oil on elution from silica with 20 % ethyl acetate in hexane; b.p. 85-90 °C at 0.5 mbar [lit. b.p. 120 °C at 11 mmHg °C[30]; ν_{max}/Nujol cm^{-1} 1702; δ_H 1.25-2.20 (10H, m, cyclohexane ring), 4.30 (1H, s, 3-H), 7.03 (2H, m, 6-H, 8-H), 7.53 (1H, m, 7-H), 7.89 (1H, dd, *J* 8.1, 1.2, 5-H); δ_C 20.7, 21.2, 24.9, 30.7, 31.5, 63.6, 81.3, 118.2, 118.6, 121.4, 127.6, 136.6, 158.2, 186.2; (Found: C, 67.0; H, 6.1; Cl, 14.2. $C_{14}H_{15}ClO_2$ requires C, 67.1; H, 6.0; Cl, 14.1%).

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