Photochemically Induced Cyclisation of β-Keto Sulfides to Cycloalkanones

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On UV irradiation, β-keto sulfides $ArSCH_2COPh$ (Ar = C_6F_5, C_6Cl_5) cleaved to radicals ArS$^\bullet$ and $PhCOCH_2^\bullet$ which, in one case (Ar = C_6F_5), were trapped by 1,1-diphenylethylene as the adduct $PhCOCH_2CH_2C(Ph)_2SC_6F_5$. With diethyl ether as the solvent the major product was the monothioacetal $ArSCH(Me)OEt$. The keto sulfide $4\text{-}MeSO_2C_6H_4SCH_2COPh$ behaved similarly on irradiation in tetrahydrofuran. Irradiation of the unsaturated β-keto sulfides $CH_2{=}CH[CH_2]_2COCH_2SAr$ resulted in homolysis of the CH_2–S bond to give a 2-oxohex-5-enyl radical, which subsequently cyclised; 4-(pentafluorophenylsulfanyl)cyclohexanone (when Ar = C_6F_5) and cyclohexanone (when Ar = *p*-tolyl) were the major products. With β-keto sulfides containing an aryl substituent, ethyl 2-benzyl-2-methyl-3-oxo-4-(pentafluorophenylsulfanyl)butanoate and 1,3-bis(*p*-tolylsulfanyl)propan-one, irradiation resulted in cyclisation with loss of the sulfanyl substituent (probably involving electron transfer) to give 3-ethoxycarbonyl-3-methyl-1,2,3,4-tetrahydronaphthalen-2-one and 6-methylthiochroman-3-one, respectively, in high yield.

β-Keto sulfides are UV sensitive sources of free radicals, homolytic cleavage of the C_α–S bond being a typical consequence of irradiation.[1] This is illustrated by the photolysis of keto sulfide **1** (*e.g.* Ar = 4-X–C_6H_4; X = H, Cl, OH, OMe, Ph; R = *p*-tolyl, benzyl) to give a disulfide **2** and a diketone **3** and/or a ketone **4**.[1] In a search for keto sulfides which might be

$$\underset{\mathbf{1}}{ArCOCH_2SR} \xrightarrow{h\nu} ArCOCH_2^\bullet + {}^\bullet SR \longrightarrow$$

$$\underset{\mathbf{2}}{(RS)_2} + \underset{\mathbf{3}}{(ArCOCH_2)_2} + \text{/or } \underset{\mathbf{4}}{ArCOMe}$$

a Ar = Ph, R = *p*-tolyl

more efficient radical sources, we examined the photochemistry of β-keto sulfides **1** in which R was a phenyl group containing an electron-withdrawing substituent (or substituents). To this end, the keto sulfides **5** and **19** were prepared and irradiated. A significant change in the nature of the photoproducts was observed. As intramolecular reaction (cyclisation) of radicals containing unsaturated groups is now a useful procedure for the synthesis of cycloalkanes, we irradiated the keto sulfides **22** and **29**, which contain an alkenyl substituent, and **33** and **35**, which contain an aryl substituent, to determine whether cyclisation of the resulting 2-oxoalkyl radicals to give cycloalkanones would take place.

Results

Products, with yields, for all photoreactions are given in Table 1. Fission products, the disulfide **9** and acetophenone **10**, were produced on irradiation of the keto sulfide **5a** in benzene, chloroform or carbon tetrachloride (see also Scheme 1). With diethyl ether as the solvent, the major product was the monothioacetal **12a**. The monothioacetals **12b** and **21** were similarly the major photoproducts from the keto sulfides **5b** and **19** (irradiation in tetrahydrofuran), respectively. Fission products acetophenone **10**, the disulfide **20** (from **19**) and the thiol **8** (from **5b**) were also formed. When the keto sulfide **5a** was irradiated in the presence of 1,1-diphenylethylene, adducts **15** and **16** were obtained, along with small amounts of benzophenone **17** and the diketone **18**. The latter was formed in low yield on irradiation of the adduct **15** in benzene.

Irradiation of the unsaturated keto sulfides **22a** and **b** resulted in cyclisation to give the substituted cyclohexanone **26a** [ν_{max} 1713; signals for only 4 non-equivalent aliphatic carbon nuclei at δ 31.1, 38.9, 44.35 and 208.2 (CO) in the ^{13}C NMR spectrum] and cyclohexanone **28**, respectively. The disulfide **2a** and a little of the substituted cyclohexanone **26b** were also obtained from the keto sulfide **22b**. When the keto sulfide esters **29a** and **b** were irradiated, using a variety of solvents, complex mixtures were formed and no products were isolated.

Cyclisation in high yield to 1,2,3,4-tetrahydronaphthalen-2-one **34** and thiochromanone **36** followed irradiation of keto sulfides **33** and **35**, respectively.

The preparation of the β-keto sulfides **1a**, **5**, **19**, **22**, **29**, **33** and **35** and identification of the photoproducts are described in the Experimental section. The structures of the monothioacetals **12a** and **b** were confirmed by treating them with acidified 2,4-dinitrophenylhydrazine, when the 2,4-dinitrophenylhydrazone of acetaldehyde was obtained in each case.

Discussion

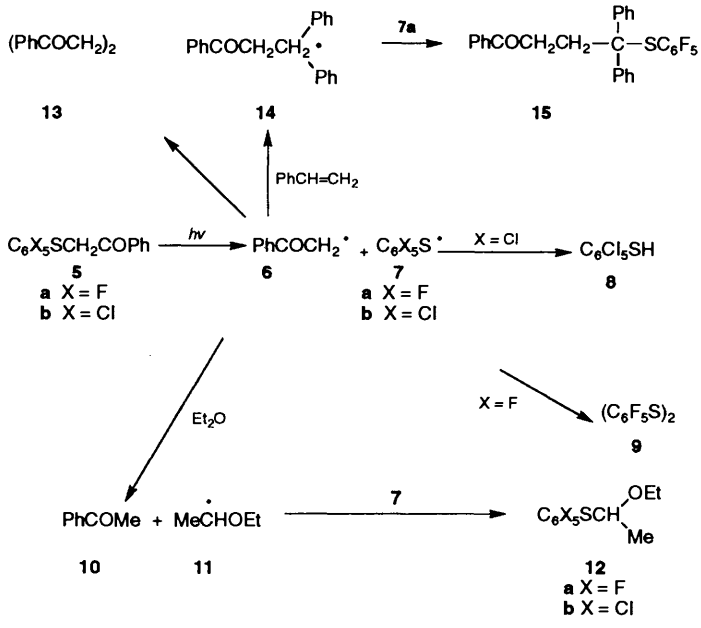
The pentafluorophenyl sulfide **5a** behaved similarly to the keto sulfides **1** (Ar = phenyl or *p*-substituted phenyl, R = *p*-tolyl or benzyl)[1] on irradiation in solvents other than an ether, giving a disulfide **9** and a ketone **10**, albeit in lower yields. However, on irradiation in diethyl ether, the yields of isolated products were much higher and the major product was the monothioacetal **12a** (59%), a type of photoproduct not observed previously on irradiation of β-keto sulfides. When the keto sulfide **1a** was irradiated in diethyl ether, only simple fission products **2a**, **3a** and **4a** were produced. The monothioacetals **12b** and **21** were also the major products from the keto sulfides **5b** and **19** (irradiation in THF), respectively.

The most likely route to the acetal **12a** is shown in Scheme 1. Cleavage to radicals $PhCOCH_2^\bullet$ **6** and $C_6F_5S^\bullet$ **7a** is followed by hydrogen abstraction from solvent by radical **6** to give the ethoxyethyl radical **11**, which combines with the sulfanyl radical **7a** to give the monothioacetal **12a**. Formation of the adduct **15** on irradiation of β-keto sulfide **5a** with 1,1-diphenylethylene demonstrates homolysis of **5a** to form radicals **6** and **7a**. The successful production of the acetal **12a** requires the rate of the reaction of the sulfanyl radical **7a** with radical **11** to be higher than that of the combination of two sulfanyl radicals to give the

Table 1 Irradiation of β-keto sulfides

β-Keto sulfide	Solvent	Light source[a]	Time (h)	Products (% Yield)
1a	Et_2O	C	4.5	**2a** (29), **3a** (5), **4a** (21)
5a	PhH	B	3.5	**9** (10), **10** (12), **5a** (15)
5a	CCl_4	B	3.5	**9** (14), **10** (16)
5a	$CHCl_3$	B	3	**9** (17), **10** (18)
5a	Et_2O	A	3	**9** (4), **10** (39), **12a** (59), **13** (3)
5a	PhH–PhCH=CH_2	B	4	**15** (21), **16** (11), **17** (6), **18** (2), **5a** (8)
5b	Et_2O	A	2	**10** (30), **13** (trace), **8** (16), **12b** (54)[b]
15	PhH	B	3	**18** (4), **15** (11)
19	THF	B	4	**10** (10), **19** (13), **20** (2), **21** (23)
22a	PhH	B	7.5	**26a** (50), **22a** (40)
22b	PhH	B	12	**2a** (26), **28** (34)[c], **26b** (2),[d] **22b** (32)[d]
33	$CHCl_3$	B	8	**34** (97)
35	$CHCl_3$	B	6	**2a** (6.5), **35** (5), **36** (85)

[a] A, 125-W medium pressure mercury-vapour lamp (see Experimental section); B, Rayonet RPR-100 photoreactor fitted with 300-nm lamps; C, 75-W medium pressure mercury-vapour lamp. [b] Structure consistent with IR, ^1H NMR and mass spectra. [c] GLC analysis. [d] Isolated as a 2,4-dinitrophenylhydrazone.



Scheme 1

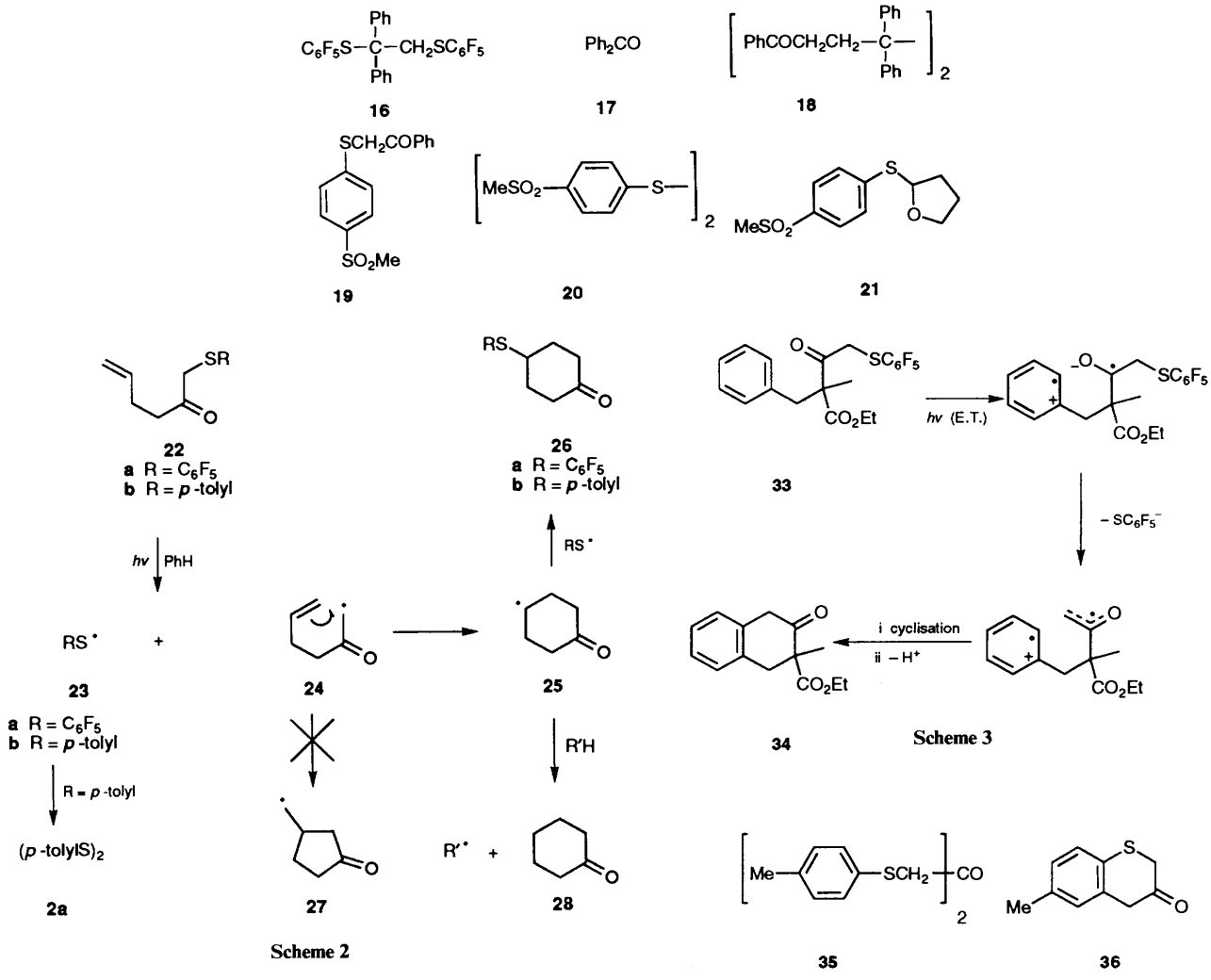
disulfide **9**. This situation will be more likely if the reactions of the radicals **6** and **7a** with diethyl ether, leading to **12a**, take place largely within a solvent cage, and also if the sulfanyl radical **7a** is sufficiently polar (electrophilic) for its rate of self-combination to be lower than that of reaction with a relatively nucleophilic alkyl radical such as **11**. Although the reactions of sulfanyl radicals RS$^\bullet$, particularly with unsaturated systems, have been well studied,[2] little attention has been focussed on how the structure of R might affect the reactions. The keto sulfides **5b** and **19**, which might be expected to produce relatively electrophilic sulfanyl radicals on photolysis, also yield monothioacetals as major photoproducts.

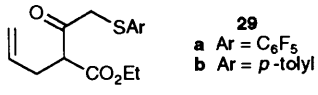
Since irradiation of β-keto sulfides was shown to produce radicals which could add to alkenes (this work and ref. 1),* we investigated the possibility of using the reaction as a method of radical cyclisation. If irradiation of the unsaturated β-keto sulfide **22** yielded radicals **23** and **24**, the latter could undergo cyclisation to a 5- or 6-membered ring. Reaction of the resulting cycloalkane radical with a hydrogen donor or with radical **23** would yield a cycloalkanone or substituted cycloalkanone, respectively. The keto sulfides **22a** and **b** were chosen since irradiation should give sulfanyl radicals which have differing reactivities and hence might lead to different products. Whereas the sulfanyl radical **23b** readily forms a disulfide **2a**, the more electrophilic sulfanyl radical **23a** may prefer to react with the relatively nucleophilic radical **25** or **27** to give a substituted cycloalkanone. Irradiation of the keto sulfide **22a** yielded the 4-substituted cyclohexanone **26a** as the only significant product and, as expected, irradiation of the keto sulfide **22b** gave mainly disulfide **2a** and cyclohexanone **28**, together with a little of the substituted cyclohexanone **26b**.

In contrast to the photocyclisation of the keto sulfides **22**, irradiation of the related keto sulfide esters **29a** and **b**, using a variety of solvents, led to complex mixtures from which no product was isolated. The presence of the ester group may hinder formation of the conformation (*cf.* **24**) required for radical cyclisation and it may also facilitate further reaction pathways.

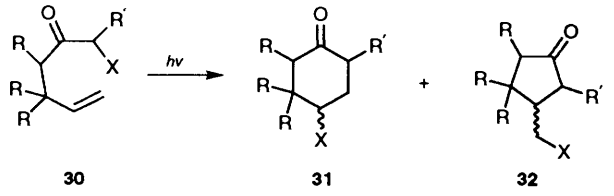
Cyclisation of the keto sulfide **22a** to cyclohexanone **26a** is similar to the photocyclisations of the keto selenide **30a** to cyclohexanone **31a**[4] and of the α-iodo ketone **30b** to the iodocyclohexanone **31b** (in the presence of hexamethylditin),[5]

* Radicals produced by irradiating β-keto sulfides, *e.g.* **1** (Ar = R = Ph), were used to initiate the polymerisation of alkenes.[3]



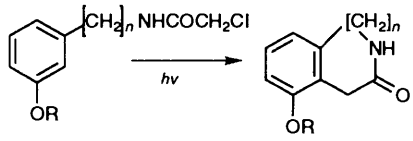


although in each case cyclopentanone **32** was a minor product.* No cyclopentanone derived from radical **27** was isolated from the photolysates from **22a** or **b**. This contrasts with the cyclisation of hex-5-enyl radicals, which generally cyclise to a 5- rather than a 6-membered ring.[9] It has been suggested that *endo*-cyclisation (*e.g.* **24** ⟶ **25**) is preferred to *exo*-cyclisation (*e.g.* **24** ⟶ **27**) when a carbonyl group is inside the ring formed.[5]



a R = H, R' = CO_2Me, X = SePH
b R = Me, R' = H, X = I

Irradiation of the keto sulfides **33** and **35** leads to high yields of the cyclisation products **34** and **36**, respectively. This reaction is somewhat similar to the photocyclisation of chloroacetamides **37** to lactams **38** for which an electron-transfer mechanism has been proposed.[10] A similar mechanism (see Scheme 3) is probably operative here. This could account for the high yields observed compared with the lower yields of radical-cyclisation products from the keto sulfides **22**.



Radical cyclisation of unsaturated β-keto sulfides may have limited value as a procedure for the synthesis of cycloalkanes, but the photocyclisation of aryl-substituted keto sulfides appears to be a promising method for the synthesis of 1,2,3,4-tetrahydronaphthalen-2-ones and related systems.

Experimental

Standard Procedures for Irradiation (*see Table* 1).—*Method A*. The solution was stirred under nitrogen and the light source, a 125-W medium-pressure mercury vapour lamp (Thorn Electric Kolorlux MBF with the outer glass envelope removed), was centrally situated in a water-cooled cold finger.

* In addition to the photocyclisation of **30a** and **b**, radical cyclisations leading to cyclohexanones include cyclisation of acyl radicals derived from unsaturated aldehydes[6] or seleno esters,[7] and the cyclisation of unsaturated 3-oxo esters in an electron-transfer reaction.[8]

Method B. The solution, purged with nitrogen, contained in a Pyrex tube, was irradiated in a Rayonet RPR-100 photoreactor fitted with 300-nm lamps.

Method C. As Method A, but using a 75-W medium-pressure mercury-vapour lamp.

Silica gel used for column chromatography was either MFC (Hopkin and Williams MFC) or 60H (Merck Kieselgel 60H, with pressure applied to the top of the column). Light petroleum refers to the fraction boiling in the range 60–80 °C. Ethereal solutions were dried over magnesium sulphate. IR spectra were recorded as Nujol mulls (for solids) or as liquid films; NMR spectra (δ_H) were recorded at 90 MHz in $CDCl_3$ with $SiMe_4$ as internal standard, unless otherwise stated, *J* values are given in Hz. In the mass spectra (EI), only *m/z* values for molecular and fragment ions containing ^{35}Cl are quoted for compounds containing chlorine; the expected isotope pattern of peaks was observed. Melting points were recorded on a Büchi 510 m.p. apparatus and are uncorrected. Where the same compound was obtained by different routes, identity was established by comparison of the IR spectra. DNPH = 2,4-dinitrophenylhydrazine.

Preparation of β-Keto Sulfides **1a**, **5**, **19**, **22**, **33** *and* **35**.—The appropriate α-bromo ketone (see below) was added over *ca.* 5 min to a cold solution of the appropriate potassium thiolate [1 equiv.; prepared from the thiol (see below) and potassium hydroxide (1 equiv.) in ethanol (75 cm^3 per 0.1 mol of thiol)]. After 1 h at room temp. the mixture was cooled and water was added to precipitate the keto sulfide. This was filtered off, washed with water, and crystallised from ethanol. The keto sulfides **22a**, **b** and **33** separated as oils, which were isolated by extraction into ether; **22a** and **b** were purified by bulb-to-bulb distillation under reduced pressure and **33** required purification by chromatography over silica gel 60H, eluting with light petroleum–ethyl acetate (3:1).

2-(Pentafluorophenylsulfanyl)-1-phenylethanone **5a** (80%), m.p. 66–67 °C (lit.,[11] m.p. 66–67 °C).

2-(*Pentachlorophenylsulfanyl*)-1-*phenylethanone* **5b** (78%), m.p. 115 °C (Found: C, 42.0; H, 1.85. $C_{14}H_7Cl_5OS$ requires C, 42.0; H, 1.8%); ν_{max}/cm^{-1} 1680; δ_H 4.3 (2 H, s, CH_2), 7.3–7.7 (3 H, m, ArH) and 7.8–8.0 (2 H, m, ArH); *m/z* 398 (M^+, 6%), 105 (100) and 91 (11).

Methyl 4-(*benzoylmethylsulfanyl*)*benzenesulfinate* **19** (85%), m.p. 125–126 °C (Found: C, 58.8; H, 4.6. $C_{15}H_{14}O_3S_2$ requires C, 58.8; H, 4.6%); ν_{max}/cm^{-1} 1680; δ_H 3.03 (3 H, s, Me), 4.43 (2 H, s, CH_2) and 7.2–8.3 (9 H, m, ArH).

1-(*Pentafluorophenylsulfanyl*)*hex-5-en-2-one* **22a** (76%), distilled at 110–116 °C (oven temp.)/0.1 mmHg (Found: C, 48.7; H, 3.05. $C_{12}H_9F_5OS$ requires C, 48.6; H, 3.1%); δ_H(300 MHz) 2.25–2.32 (2 H, m, CH_2), 2.66–2.71 (2 H, m, CH_2), 3.58 (2 H, s, CH_2S), 4.93–5.03 (2 H, m, vinylic H) and 5.68–5.81 (1 H, m, vinylic H); *m/z* 296 (M^+, 0.3%), 83 (33) and 55 (100).

1-(p-*Tolylsulfanyl*)*hex-5-en-2-one* **22b** (59%), distilled at 130–134 °C (oven temp.)/1.0 mmHg (Found: M^+, 220.0899. $C_{13}H_{16}OS$ requires *M*, 220.0922); ν_{max}/cm^{-1} 1700 and 1640; δ_H(300 MHz) 2.24–2.27 (2 H, m, CH_2), 2.28 (3 H, s, Me), 2.63–2.65 (2 H, unsymmetrical t, CH_2CO), 3.58 (2 H, s, CH_2S), 4.91–5.01 (2 H, m, vinylic H), 5.67–5.81 (1 H, m, vinylic H), 7.05–7.08 and 7.20–7.24 (4 H, AA'BB' m, C_6H_4); *m/z* 220 (M^+, 40%), 137 (36), 91 (48) and 55 (100).

Ethyl 2-*benzyl*-2-*methyl*-3-*oxo*-4-(*pentafluorophenylsulfanyl*)*butanoate* **33** (85%), m.p. 64 °C (from ethanol) (Found: C, 55.6; H, 3.8. $C_{20}H_{17}F_5O_3S$ requires C, 55.6; H, 4.0%); ν_{max}/cm^{-1} 1735 and 1718; δ_H 1.22 (3 H, t, *J* 7.2, $MeCH_2$), 1.31 (3 H, s, Me), 3.05 and 3.22 (2 H, 2 d, *J* 13.7, CH_2Ph), 3.78 and 3.81 (2 H, 2 d, *J* 16.1, CH_2S), 4.15 (2 H, q, *J* 7.2, OCH_2) and 7.03–7.24 (5 H, m, Ph); *m/z* 432 (M^+, 12%), 173 (27), 145 (61), 135 (17), 117 (15), 91 (100) and 78 (12).

1-Phenyl-2-(*p*-tolylsulfanyl)ethanone **1a**,[1] 1,3-bis(*p*-tolylsulfanylpropanone **35**,[12] and 4-methylsulfonylbenzenethiol,[13] were prepared according to literature procedures. Apart from 1-bromohex-5-en-2-one and ethyl 2-benzyl-4-bromo-2-methyl-3-oxobutanoate (below), all other materials were commercially available.

1-*Bromohex-5-en-2-one*.—An ethereal solution of 1-diazohex-5-en-2-one[14] [prepared from pent-4-enoyl chloride (3.6 g)] was stirred at 0–5 °C with glacial acetic acid (10 cm^3) whilst 48% hydrobromic acid (6.8 cm^3) was added over 0.5 h. The mixture was stirred for 1 h at room temperature, water (50 cm^3) was added to it and the whole was extracted with ether. The ethereal extract was washed with aqueous sodium carbonate, dried and evaporated. Bulb-to-bulb distillation of the residue [102–105 °C (oven temperature)/12 mmHg] yielded the *title compound* (3.7 g, 70%) (Found: M^+, 175.9837. C_6H_9BrO requires *M*, 175.9815); ν_{max}/cm^{-1} 1720 and 900 (C–Br); δ_H 2.2–2.5 (2 H, m, $C{=}CCH_2$), 2.65–2.9 (2 H, m, $COCH_2$), 3.92 (2 H, s, CH_2Br), 4.9–5.2 (2 H, m, vinylic H) and 5.5-6.0 (1 H, m, vinylic H); *m/z* 178 and 176 (M^+, < 1%), 173 (52), 171 (41), 123 (37), 95 (58) and 83 (38).

Ethyl 2-*Benzyl*-4-*bromo*-2-*methyl*-3-*oxobutanoate*.—Bromine (2.7 g) in chloroform (10 cm^3) was added during 30 min to a stirred solution of ethyl 2-benzyl-2-methyl-3-oxobutanoate[15] (4.0 g) in chloroform (30 cm^3) and the solution was heated under reflux for 0.5 h. Water (*ca.* 50 cm^3) was added to the mixture which was then extracted with ether. Evaporation of the extract gave an oil which was chromatographed over silica gel 60H. Elution with light petroleum–ethyl acetate (3:1) yielded the *title compound* (4.1 g, 77%) as an oil (Found: C, 53.55; H, 5.4. $C_{14}H_{17}BrO_3$ requires C, 53.7; H, 5.5%); ν_{max}/cm^{-1} 1756 and 1725; δ_H 1.22 (3 H, t, *J* 7.2, $MeCH_2$), 1.38 (3 H, s, Me), 3.13 and 3.25 (2 H, 2 d, *J* 13.6, CH_2Ph), 4.02 and 4.07 (2 H, 2 d, *J* 14.1), CH_2Br), 4.05–4.25 (2 H, m, OCH_2), 7.05–7.09 (2 H, m, ArH) and 7.20–7.25 (3 H, m, ArH); *m/z* 314 and 312 (M^+, 15%), 233 (24), 191 (51), 145 (52), 117 (16), 91 (100), 84 (24) and 78 (16).

Ethyl 2-(*Pentafluorophenylsulfanyl*)*acetylpent-4-enoate* **29a**.—Ethyl 2-allylacetoacetate[16] (0.8 g, 4.7 mmol) was stirred for 10 min at room temp. with a 60% dispersion of sodium hydride in oil (0.22 g, 5.5 mmol) in dry tetrahydrofuran (10 cm^3). A 1.7 mol dm^{-3} solution of butyllithium in hexane (3.97 cm^3) and dry tetrahydrofuran (10 cm^3) were added at −15 °C to the mixture which was then stirred at −15 °C for 45 min. Bis(pentafluorophenyl) disulfide[17] (1.87 g, 4.7 mmol) in dry tetrahydrofuran (10 cm^3) was added to the mixture which was then stirred first at 0 °C for 90 min and then at room temp. for 2 h. 1 mol dm^{-3} Hydrochloric acid (10 cm^3) was added dropwise to the mixture, followed by water (*ca.* 30 cm^3) after which the whole was extracted with ether. Evaporation of the ethereal extract gave an oil, which was chromatographed over silica gel 60H eluting with light petroleum–dichloromethane (2:1) to give the *title compound* **29a** (0.82 g, 47%) as an oil [Found: $(M + NH_4)^+$ 386.0853. $C_{15}H_{17}F_5NO_3S$ requires $(M + NH_4)^+$, 386.0849]; ν_{max}/cm^{-1} 1749, 1729 and 1644; δ_H 1.23 (3 H, dt, *J* 3 and 7.1, $MeCH_2$), 2.46–2.64 (2 H, m, $C{=}CCH_2$), 3.78 (2 H, s, CH_2S), 3.8 (1 H, m, CHCO), 4.11–4.20 (2 H, m, OCH_2), 4.95–5.09 (2 H, m, $C{=}CH_2$) and 5.59–5.79 (1 H, m, C=CH); *m/z* 386 [$(M + NH_4)^+$, 51%] and 188 (100).

Ethyl 2-(p-*tolylsulfanyl*)*acetylpent-4-enoate* **29b**. Using the procedure above for the preparation of the keto sulfide **29a**, the dianion from ethyl 2-allylacetoacetate (0.6 g) was allowed to react with di-*p*-tolyl disulfide[18] (0.86 g). Elution of the crude product over silica gel 60H, using light petroleum–dichloromethane (2:1) yielded the title compound **29b** (0.65 g, 63%) as an oil (Found: M^+, 292.1133. $C_{16}H_{20}O_3S$ requires *M*, 292.1133); ν_{max}/cm^{-1} 1749, 1719 and 1647; δ_H 1.21 (3 H, t, *J* 7.1,

MeCH_2), 2.29 (3 H, s, Me), 2.46–2.60 (2 H, m, C=CCH_2), 3.75 and 3.76 (2 H, 2 d, *J* 15.1, SCH_2), 3.89 (1 H, apparent t, *J* 7.3, CHCO), 4.13 (2 H, q, *J* 7.1, OCH_2) 4.96–5.07 (2 H, m, C=CH_2), 5.61–5.73 (1 H, m, C=CH) and 7.06–7.09 and 7.22–7.24 (4 H, AA'BB' m, ArH); *m/z* 310 [$(M + NH_4)^+$, 100%], 293 [$(M + H)^+$, 23], 292 (M^+, 10), 202 (17) and 188 (23).

Irradiation of β-Keto Sulfides.—In general, a 1% solution of the β-keto sulfide (0.5–2.0 g) was irradiated [solvent, light source (A, B or C), time and product yields are given in Table 1]. Products were isolated by column chromatography of the residue left after removal of the solvent.

Photolysates from the keto sulfides **1a**, **5a** and **b** were chromatographed over silica gel MFC, eluting with light petroleum–toluene (1 : 1) (for products **2a**, **8**, **9**, **12a** and **b**) and with toluene–ethyl acetate (19 : 1) (for products **10** and **13**). Acetophenone **10** was extracted from mixtures with biphenacyl **13** using cold ethanol, and was characterised as its 2,4-dinitrophenylhydrazone. Similarly, the acetal **12b** was extracted from mixtures with the thiol **8** using light petroleum. Attempted distillation of **12b** at 0.5 mmHg led to decomposition with formation of the thiol **8**.

Photolysates from the keto sulfides **5a** (with 1,1-diphenylethylene), **19**, **22a**, **b**, **33**, **35** and ketone **15** were chromatographed over silica gel 60H. Solvent systems used for elution were chloroform and chloroform–ethyl acetate, light petroleum–ethyl acetate, and light petroleum–dichloromethane. The adduct **15** was purified further by chromatography, eluting with chloroform. Fractions containing products **15**, **17** and **18** were triturated with light petroleum to afford the solid products. The furan **21** was obtained as an unstable oil, which partly decomposed on attempted further purification. Products **22b**, **26b** and **28** were isolated, and products **26a** and **36** were, in part, characterised, as their 2,4-dinitrophenylhydrazones. A sample of the photolysate from the keto sulfide **22b** was shown to contain cyclohexanone (34%) by GLC analysis, using a 2% solution of cyclohexanone in benzene for comparison.

1-*Ethoxy*-1-*pentafluorophenylsulfanylethane* **12a**, b.p. 61 °C/0.5 mmHg (Found: C, 44.4; H, 3.1. $C_{10}H_9F_5OS$ requires C, 44.1; H, 3.3%); δ_H 1.18 (3 H, t, *J* 7, Me), 1.48 (3 H, d, *J* 6.5, Me), 3.49 (1 H, dq, *J* 7 and 9, OCH), 4.0 (1 H, dq, *J* 7 and 9, OCH) and 4.87 (1 H, q, *J* 6.5, SCH); *m/z* 227 (M − OEt, 11%), 200 (31), 199 (C_6F_5S, 20), 105 (14) and 73 (M − C_6F_5S, 100).

4-*Pentafluorophenylsulfanyl*-1,4,4-*triphenylbutan*-1-*one* **15**, m.p. 102–104 °C (from light petroleum) (Found: C, 66.8; H, 3.9. $C_{28}H_{19}F_5OS$ requires C, 67.5; H, 3.8%); ν_{max}/cm^{-1} 1685; δ_H 2.65–3.2 (4 H, A_2B_2 m centred at δ 2.91, CH_2CH_2), 7.7–8.15 (13 H, m, ArH) and 7.85 (2 H, dd, *J* 2 and 8, PhCO *ortho*-H).

1,2-Bis(*pentafluorophenylsulfanyl*)-1,1-*diphenylethane* **16**, m.p. 139–141 °C (from light petroleum) (Found: C, 54.4; H, 2.4. $C_{26}H_{12}F_{10}S_2$ requires C, 54.0; H, 2.1%); δ_H 4.05 (2 H, s, CH_2) and 7.0–7.4 (10 H, m, 2 × Ph).

2-(4-*Methylsulfonylphenylsulfanyl*)-2,3,4,5-*tetrahydrofuran* **21** m.p. 42–44 °C (Found: M^+, 258.0384. $C_{11}H_{14}O_3S_2$ requires *M*, 258.0383); δ_H 1.7–2.3 (4 H, m, CH_2CH_2), 3.07 (3 H, s, Me), 3.95–4.15 (2 H, m, OCH_2), 5.85 (1 H, dd, *J* 3.5 and 6, OCH) and *ca.* 7.0 (4 H, AA'BB' m, ArH); *m/z* 258 (M^+, 24%), 188 (M − dihydrofuran, 87), 173 (47), 125 (C_6H_5OS, 100), 109 (88) and 71 (C_4H_7O, 86).

4-(*Pentafluorophenylsulfanyl*)*cyclohexanone* **26a**, ν_{max}/cm^{-1} 1713; δ_H(300 MHz) 1.82–1.94 (2 H, m, 2 × CH), 2.13–2.26 (2 H, m, 2 × CH), 2.28–2.47 (2 H, m, 2 × CH), 2.52–2.61 (2 H, m, 2 × CH) and 3.56 (1 H, dt, *J* 3.7 and 8.6, 4-H); δ_C 31.1, 38.9, 44.35, 135.91–149.43 (C_6F_5) and 208.22 (CO).

4-(*Pentafluorophenylsulfanyl*)*cyclohexanone* 2,4-*dinitrophenylhydrazone* (Found: C, 45.75; H, 2.5; N, 12.0. $C_{18}H_{13}F_5N_4O_4S$ requires C, 45.4; H, 2.7; N, 11.8%); δ_H(300 MHz) 1.69–1.83 (2 H, m, 2 × CH), 2.10–2.20 (2 H, m, 2 × CH), 2.27–2.47 (2 H, m, 2 × CH), 2.70–2.88 (2 H, m, 2 × CH), 3.45–3.50 (1 H, m, CHS), 7.92 (1 H, d, *J* 9.6, ArH), 8.25–8.29 (1 H, m, ArH), 9.08 (1 H, d, *J* 2.6, ArH) and 11.14 (1 H, s, NH); *m/z* 476 (M^+, 53%), 276 (45), 200 (48), 199 (37) and 67 (100).

4-(p-*Tolylsulfanyl*)*cyclohexanone* **26b**, ν_{max}/cm^{-1} 1715; δ_H(300 MHz) 1.68–2.0 and 2.1–2.6 (8 H, m, 4 × CH_2), 2.31 (3 H, s, Me), 3.39–3.47 (1 H, m, CHS), 7.09–7.12 and 7.32–7.35 (4H, AA'BB'm, C_6H_4).

4-(p-*Tolylsulfanyl*)*cyclohexanone* 2,4-*dinitrophenylhydrazone* (Found: M^+, 400.1212. $C_{19}H_{20}N_4O_4S$ requires *M*, 400.1205); δ_H(300 MHz) 1.6–1.8, 2.1–2.45 and 2.65–2.8 (8 H, 3 m, 4 × CH_2), 2.32 (3 H, s, Me), 3.3–3.4 (1 H, m, CHS), 7.1–7.3 and 7.32–7.35 (4 H, AA'BB' m, C_6H_4), 7.92 (1 H, d, *J* 9.6, ArH), 8.25 (1 H, dd, *J* 3.5 and 9.6, ArH), 9.09 (1 H, d, *J* 2.5, ArH) and 11.1 (1 H, s, NH).

3-*Ethoxycarbonyl*-3-*methyl*-1,2,3,4-*tetrahydronaphthalen*-2-*one* **34** [Found: $(M + NH_4)^+$, 250.1446. $C_{14}H_{16}O_3$ requires $(M + NH_4)^+$, 250.1443]; ν_{max}/cm^{-1} 1738 and 1718; δ_H 1.01 (3 H, t, *J* 7.2 *Me*CH_2), 1.36 (3 H, s, Me), 2.92 and 3.44 (2 H, 2 d, *J* 15.4, $ArCH_2$), 3.59 and 3.78 (2 H, 2 d, *J* 20.1, CH_2CO), *ca.* 3.93–4.06 (2 H, m, OCH_2) and 7.07–7.31 (4 H, m, ArH); *m/z* 250 [$(M + NH_4)^+$, 100%] and 233 (19).

6-*Methylthiochroman*-3-*one* **36** (Found: M^+, 178.0456. $C_{10}H_{10}OS$ requires M^+, 178.0452); ν_{max}/cm^{-1} 1718; δ_H 2.31 (3 H, s, Me), 3.2 (2 H, s, $ArCH_2$), 3.6 (2 H, s, CH_2S) and 6.9–7.3 (3 H, m, ArH); *m/z* 178 (M^+, 97%), 150 (46), 149 (66), 136 (74), 135 (100), 134 (43), 91 (66) and 77 (36).

Treatment of 6-methylthiochroman-3-one with acidified DNPH yielded the corresponding 2,4-*dinitrophenylhydrazone*, m.p. 193–194 °C (from light petroleum–chloroform) (Found: C, 53.2; H, 4.0; N, 15.6. $C_{16}H_{14}N_4O_4S$ requires C, 53.6; H, 3.9; N, 15.6%); ν_{max}/cm^{-1} 3295; δ_H 2.32 (3 H, s, Me), 3.64 (2 H, s) and 3.76 (2 H, s) ($ArCH_2$ and SCH_2), 7.01 (1 H, d, *J* 7.8, 7- or 8-H), 7.10 (1 H, s, 5-H), 7.23 (1 H, d, *J* 7.8, 8- or 7-H), 7.99 (1 H, d, *J ca.* 9.5, dinitrophenyl 6-H), 8.33 (1 H, dd, *J ca.* 2.5 and 9.5, dinitrophenyl 5-H), 9.13 (1 H, d, *J ca.* 2.5, dinitrophenyl 3-H) and 11.15 (1 H, s, NH).

The structures assigned to the following were consistent with their spectroscopic properties: 1-ethoxy-1-pentachlorophenylsulfanylethane **12b**, δ_H 1.14 (3 H, t, *J* 7, Me), 1.6 (3 H, d, *J* 6, Me), 3.48 (1 H, dq, *J* 7 and 9, OCH), 3.82 (1 H, dq, *J* 7 and 9, OCH) and 5.16 (1 H, q, *J* 6, SCH); *m/z* 352 (M^+, 0.02%), 280 (C_6HCl_5S, 6), 73 (M − C_6Cl_5S 100%) and 45 (OEt, 89); 1,4,4,5,5,8-hexaphenyloctane-1,8-dione **18**, ν_{max}/cm^{-1} 1680; δ_H 2.4–3.0 (8 H, A_2B_2 m centred at δ 2.75, 2 × CH_2CH_2), 7.15–7.5 (26 H, m, ArH) and 7.82 (4 H, dd, *J* 2 and 8, PhCO *ortho*-H); *m/z* 299 [$PhCOCH_2CH_2C(Ph)_2$, 62%] and 105 (PhCO, 100).

Treatment of the thioacetals **12a** and **b** with acidified DNPH yielded acetaldehyde 2,4-dinitrophenylhydrazone, identical with a sample prepared from acetaldehyde. All other photoproducts were identical with commercially available materials or with samples prepared by literature procedures. The latter were disulfides **2a**,[18] **9**,[17] and biphenacyl **13**.[19]

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