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PHOTOCHEMICAL RING CLOSURE OF α,α-BISULFENYLATED CARBONYL COMPOUNDS

STEREOSELECTIVE FORMATION OF *CIS*-DIHYDROBENZOTHIOPHENES[1]

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Abstract—Photochemistry of α,α-bisulfenylated ketone has been investigated. Irradiation of 2-phenylthiodihydrothiophen-3-one (**1**) in benzene gave the radical recombination products **9** (63%) and **10** (49%). In a polar solvent, the ionic chemistry became predominant. Brief irradiation of **1** in acetonitrile and methanol gave the *cis*-fused dihydrothiophene **11** as the major product in 43% and 20% yields, respectively. The stereoselective photocyclization was generally observed for other ketones (**2–8**) in acetonitrile solution (Table 1). The photoproducts were easily dehydrated by treating with boron trifluoride etherate to give the corresponding benzothiophenes in high yields. Simple α-phenylthioketones are photoinert under the same conditions. The mechanism of this novel photocyclization of bisulfenylated ketones is also discussed.

Photochemistry of cyclic β-keto sulfides has been extensively studied in recent years.[2–6] Much of the interest in these systems stems from the unique UV characteristics due to the excited state interaction of the two groups[7–9] and the unusual photochemical behaviour of these compounds as a result of this interaction. In contrast, acyclic β-keto sulfides usually undergo photochemical reaction involving homolytic cleavage of the α-C–S bond to give none-S-containing products.[10,11] Recently, Schultz *et al.*[12] reported that 2-thioaryloxyenones (acyclic β-keto sulfides) photocyclize via thiocarbonyl ylide intermediates to afford dihydrothiophenes in high yield.

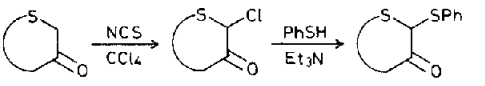
This report is concerned with the photochemistry of both cyclic and acyclic α-bisulfenylated carbonyl compounds. A S substituent α to a CO group enhances the thermodynamic acidity of an adjacent proton by $\sim 10^3$ over simple ketone and stabilizes an anion (enolate) at the carbon bearing sulfur.[13] Although this allows sulfur to be widely utilized in organic synthesis as a chemical control element,[14] the effect of a S substituent in photochemical reactions has received little attention. We describe herein a stereoselective photocyclization of S-phenyl β-keto sulfides to *cis*-fused dihydrothiophenes, and discuss the crucial role of α-S substituent.[15]

RESULTS AND DISCUSSION

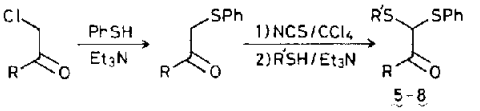
Preparation of α-bisulfenylated carbonyl compounds

Cyclic substrates **1–4** (Table 1) were prepared in good yield from the corresponding cyclic β-keto sulfides[16–19] by chlorination with NCS[20] followed by treatment with thiophenol in the presence of triethylamine (eqn 1). Acyclic substrates **5–8** (Table 1) were similarly prepared starting from the commercially available α-chloroketones (eqn 2).

Chlorination took place exclusively on α-carbon of β-keto sulfides at room temperature except for the case of tetrahydrothiopyran-3-one, for which the reaction was carried out at 5–10° in order to avoid the concurrent formation of dichlorinated products. These α-bisulfenylated ketones **1–8** showed a characteristic ^{1}H NMR



(1)

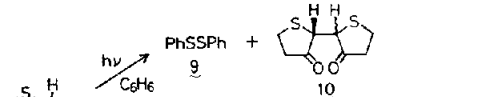


(2)

singlet at δ4.5–5.8 for an α-proton adjacent to two S atoms and normal IR CO bands (Experimental). Thus, these substrates are considered to exist exclusively in the keto form.

Photochemical cyclization

Irradiation of an argon-degassed benzene solution (5×10^{-3} M) of 2-phenylthio-dihydrothiophen-3-one (**1**) resulted in a rapid disappearance of **1** and afforded diphenyl disulfide (**9**) (63%) and a 3:4 diastereomeric mixture of **10** (49%) (eqn 3). These are considered to be the radical coupling products formed by the homolytic cleavage of the α-C–S bond.[10]



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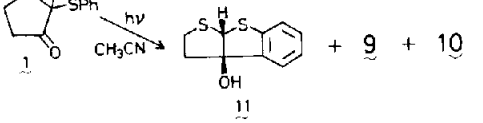
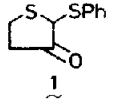
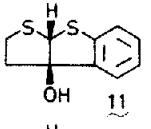
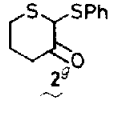
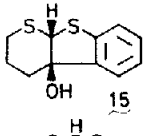
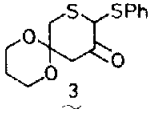
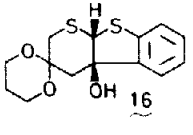
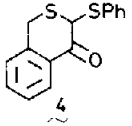
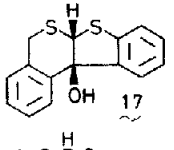
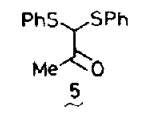
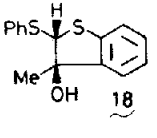
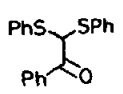
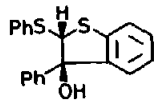
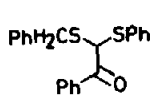
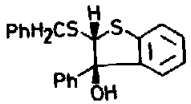
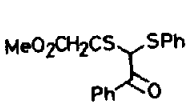
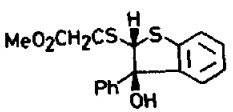


(4)

The similar irradiation (20 min) of **1** in acetonitrile gave dihydrothiophene **11** as the major product (43%) along with **9** (25%) and **10** (21%) (eqn 4). Compound **11** was also obtained as the sole product (20%) when methanol was used as a solvent.

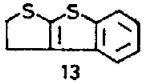
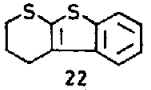
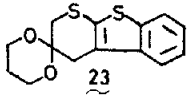
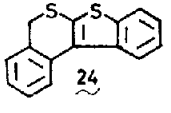
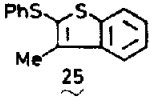
Table 1. Photocyclization of β-keto sulfides in acetonitrile and the spectral data of photoproducts[a]

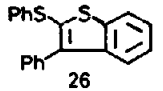
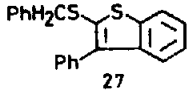
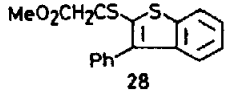
starting material	photoproduct[b,c]	% yield[d]	IR cm^{-1}	^{1}H NMR, δ(CDCl$_3$) methine[e]	OH[e,f]	others	MS, m/e	molecular formula	anal. calcd/found C	H
 1	 11	43	3380	4.77	3.10	2.45-3.40 (m,4H) 7.08-7.25 (m,4H)	210 (M$^+$) 192	$C_{10}H_{10}OS_2$	57.11 56.97	4.79 4.93
 2[g]	 15	37 (43)	3290	4.25	3.41	1.2-2.3 (m,6H) 6.9-7.5 (m,4H)	224 (M$^+$) 206	$C_{11}H_{12}OS_2$	58.89 58.87	5.39 5.46
 3	 16	26 (53)	3440	4.25	4.66	1.20-3.30 (m,6H) 3.70-4.15 (m,4H) 6.9-7.6 (m,4H)	296 (M$^+$) 278	$C_{14}H_{16}O_3S_2$	56.73 56.69	5.44 5.48
 4	 17	30[h]		4.63	3.43	4.11 (s,2H) 6.9-8.2 (m,8H)				
 5	 18	11[i] (19)	3420	4.68	3.72	1.89 (s,3H) 6.9-7.7 (m,9H)	274 (M$^+$) 256	$C_{15}H_{14}OS_2$	65.66 65.73	5.14 5.07

 6	 19	73 (80)	3440	5.12	3.88	7.11 (s,5H) 7.40-7.52 (m,7H) 7.55-7.85 (m,2H)	336 (M^+) 318	$C_{20}H_{16}OS_2$	71.39 71.66	4.79 4.83
 7	 20	31 (46)	3445	4.68	4.25	3.41 (s,2H) 7.05-7.55 (m,12H) 7.68-8.04 (m,2H)	350 (M^+) 332	$C_{21}H_{18}OS_2$	71.96 71.78	5.18 5.20
 8	 21	33[j] (36)	3450 1725	4.93	4.87	3.46,3.90(AB,2H)[k] 3.65 (s,3H) 7.12-7.63 (m,7H) 7.69-8.06 (m,2H)	332 (M^+) 314	$C_{17}H_{16}O_3S_2$	61.42 61.52	4.87 5.03

[a] All photolyses were carried out in acetonitrile (5×10^{-3} M) through a Pyrex filter. [b] Products are oil unless otherwise noted. [c] Diphenyl disulfides (9) was always obtained as the minor by-product. [d] Isolated yields. The yield in parentheses are based on the consumed starting materials. [e] Signals are all singlets. [f] Exchangeable by D_2O. [g] A quartz filter was used for photolysis. [h] Since 17 was easily dehydrated during isolation, the yield was estimated on the basis of the isolated dehydration product (24). [i] The major product was 1-phenylthiopropan-2-one (38%). [j] mp 97-98 °C. [k] J_{AB}= 15.0 Hz.

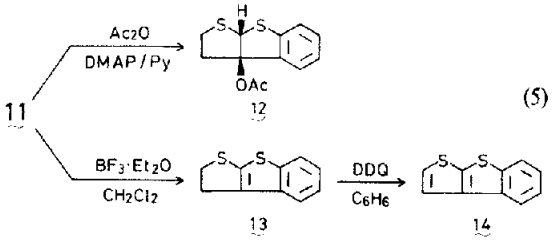
Table 2. Dehydration of the photoproducts by boron trifluoride etherate in methylene chloride

substrate	product	mp, °C	yield[d] (%)	IR cm^{-1}	^1H NMR, δ ($CDCl_3$)	MS[d], m/e	molecular found	anal. calcd/found C	H
11	 **13**	58-60	100	3000 2800 1425 1255 1150-980(br)	3.13-4.02 (A_2B_2, 4H) 7.15-7.97 (m, 4H)	192	$C_{10}H_8S_2$	62.46 62.41	4.19 4.24
15	 **22**	oil	97	3065 2930 1425 1260 1010	2.05-2.50 (m, 2H) 2.83-3.27 (m, 4H) 7.20-7.85 (m, 4H)	206	$C_{11}H_{10}S_2$	64.04 64.01	4.89 5.11
16	 **23**	125-126	96	3040 2950 2910 2880 1430 1305 1265	1.52-2.08 (m, 2H) 3.20 (s, 2H) 3.34 (s, 2H) 4.00 (t, 4H)[b] 7.20-7.74 (m, 8H)	278	$C_{14}H_{14}O_2S_2$	60.40 60.51	5.07 5.32
17	 **24**	oil	30[c]	2960 2940 1500 1460 1440 1030	4.06 (3, 2H) 7.20-7.97 (m, 4H)	254 253 (base)			
18	 **25**	oil	99	3080 2940 1585 1480 1440	2.63 (s, 3H) 7.02-7.45 (m, 7H) 7.65-7.84 (m, 2H)	256	$C_{15}H_{12}S_2$	70.27 70.01	4.72 4.93

19	 **26**	oil	95	3070 1580 1480 1435	7.05 (s, 5H) 7.12-7.45 (m, 5H) 7.57-7.90 (m, 4H)	318	$C_{20}H_{12}S_2$	75.43 75.62	4.43 4.66
20	 **27**	56-58	92	3055 3030 2935 1600 1500 1480	3.78 (s, 2H) 6.70-7.52 (m, 12H) 7.65-8.11 (m, 2H)	332 197 (base)	$C_{21}H_{16}S_2$	75.86 75.65	4.85 5.14
21	 **28**	oil	91	3080 2970 1725 1440 1275 1130	3.30 (s, 2H) 3.37 (s, 3H) 7.30-7.55 (m, 5H) 7.65-8.10 (m, 4H)	314 241 (base)	$C_{17}H_{14}O_2S_2$	64.84 64.87	4.49 4.66

[a] Isolated yield. [b] J = 6.0 Hz. [c] Over-all yield from 4. [d] Molecular ion peak with 100% rel intensity, unless otherwise noted.

The structure of **11** (oil) was assigned on the basis of the spectral data and chemical conversions. The mass spectrum (*m/e* 210 (parent)) and elemental analysis clearly indicate that **11** is an isomer of **1**. The IR spectrum showed an OH band at 3380 cm^{-1} and no CO band. The ^1H NMR spectrum ($CDCl_3$) exhibited two characteristic singlets of sulfur methine proton δ4.77 and OH proton at δ3.10 (exchangeable). The alcohol **11** was converted to acetate **12** by treating with acetic anhydride and 4-dimethylaminopyridine (DMAP) (eqn 5). The ^1H NMR spectrum of **12** (m.p. 135–137°) consists of signals at δ2.08 (s, 3 H), 2.6–3.7 (m, 4 H), 5.12 (s, 1 H), and 7.14–7.26 (m, 4 H). Treatment of **11** with BF_3-Et_2O gave a quantitative yield of benzothiophene **13** (m.p. 58–60°; ^1H NMR ($CDCl_3$) δ3.13–4.02 (A_2B_2, 4 H), 7.1–7.9 (m, 4 H)) which was further transformed to thieno[2,3-b]benzothiophene (**14**)[21] upon the treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (eqn 5).



(5)

The *cis* configuration of **11** was deduced on the basis of (a) the abnormally low chemical shift of the sulfur methine proton in ^1H NMR spectrum as a result of the van der Waals effect of a vicinal OH group,[22] (b) the strong shift of this methine signal (shift slope 1.03) besides the OH signal (5.02) in the Eu(fod)$_3$ study, and (c) the down field shift of the corresponding methine signal ($\Delta\delta = -0.35$ ppm) in acetate **12**.

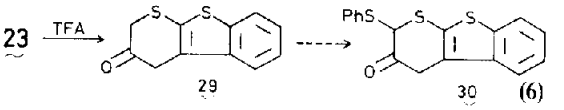
The generality of this photoreaction in acetonitrile solution was explored with substrates **2–8**. Both cyclic and acyclic β-keto sulfides underwent the stereoselective photocyclization (Table 1). In general, *cis*-dihydrobenzothiophene was formed as the sole product at the early stage of irradiation, whereas diphenyl disulfide (**9**) and polymeric substance gradually increased on prolonged irradiation.

It should be noted that the presence of the second S substituent is crucial for the above photoreaction, since simple α-(phenylthio)ketones are photoinert under the same conditions.

Dehydration of photoproducts

Dehydrative aromatization of **11** into **13** has been mentioned. All dihydrothiophenes obtained above were very slowly dehydrated to the corresponding benzothiophenes on leaving at room temperature. This transformation was rapidly performed by treating with BF_3-Et_2O. The results are summarized in Table 2.

The treatment of product **23** with aqueous trifluoro acetic acid (TFA) afforded ketone **29** (m.p. 115–118°) in quantitative yield. The conversion of **29** to the α-sulfenylated **30** was attempted, because **30** was considered to be a good model for another photocyclization to give interesting polycyclic heteroaromatic compounds. Unfortunately, all attempts of sulphenylation and chlorination of **29** were unsuccessful.

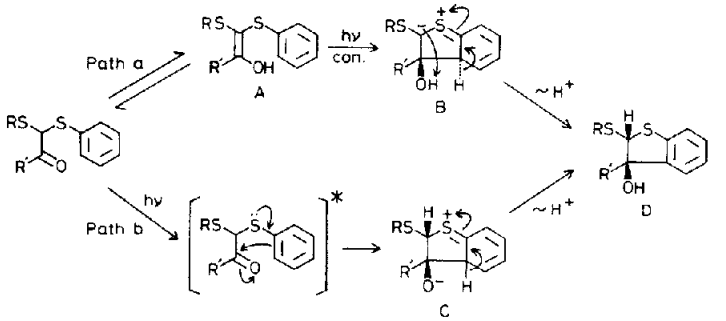


(6)

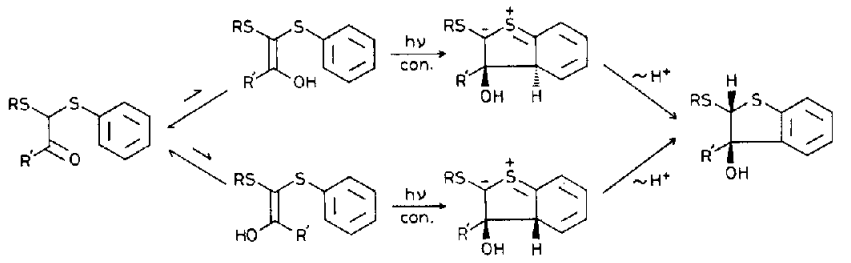
Reaction mechanism. S-Aryl vinyl sulfides are well known to photocyclize in a conrotatory fashion to give the thiocarbonyl ylide intermediate which in aprotic solvent undergoes suprafacial 1,4-H migration to give *trans*-dihydrothiophenes.[12,23,24] In the light of this mechanism, the above photoreaction is most reasonably considered to occur from the enol tautomer **A** (Scheme I). While the enol form of starting ketones was not detected by IR and ^1H NMR (CD_3CN, CD_3OD, and $CDCl_3$), small (nondetectable) amount of enol present in tautomeric equilibrium with the keto form is known to play an important role in the photochemical reactions.[25] But, also the photoenolization mechanism[26] cannot be ruled out for these S-activated ketones. The conrotatory photocyclization of enol **A** would give the thiocarbonyl ylide **B** (path a: Scheme I). The exclusive formation of *cis*-dihydrothiophenes may be attributed to the intramolecular protonation of the ylide **B** by the bridge-head OH group. The photochemically generated thiocarbonyl ylides are known to be sufficiently basic to be protonated by alcohol like methanol.[23] This intramolecular protonation-deprotonation mechanism can adequately explain the results of acyclic substrates **5–8**. In these cases, two stereochemically different ylide intermediates would be formed depending on the conformation of enols. However, the intramolecular protonation by the bridge-head OH proton leads both intermediates to only the *cis*-product (Scheme 2).

The alternative mechanism of the above photoreaction is a rather unprecedented direct cyclization of β-keto sulfide via the intermediate **C** (path b: Scheme I). In this case, the *cis* ring closure is sterically favored.

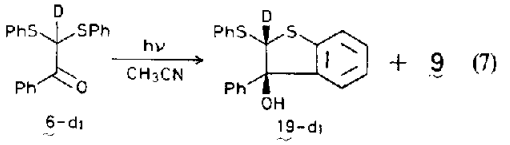
In order to gain more information about the reaction mechanism, the following experiments were undertaken. Irradiation of α-deuterated **6-d$_1$** under the same con-



Scheme I.

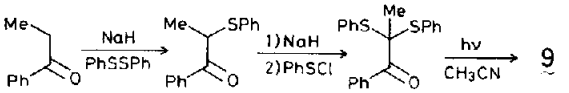


Scheme 2.



(7)

ditions gave **19**-d_1 (44.5%) and diphenyl disulfide (**9**) (46%). The product **19**-d_1 was completely deuterated at the sulfur methine position. The decreased formation of dihydrothiophene (**19**-d_1) and the increased yield of diphenyl disulfide (**9**) compared with the results in photolysis of **6** (Table 1) suggest the involvement of D-migration in the reaction (an isotope effect). This is only compatible with path a. Irradiation of **6**-d_1 in methanol afforded 26% yield of dihydrothiophene **19** with 90%-deuteration at the methine position along with **9** (56%). While a loss of D in the product implicates the transient formation of "exchangeable" species, the retention of D in major part of product supports the rapid intramolecular reaction mechanism. Furthermore, the more conclusive result was obtained in the photolysis of unenolizable substrate **31** prepared from propiophenone by two successive sulfenylations (eqn 8). Irradiation of **31** in acetonitrile under the same conditions gave only disulfide **9** in 79% yield. These results clearly indicate that the enol tautomer participates in the photochemical cyclization of α,α-bisulfenylated ketones, and path b is possibly ruled out.



(8)

The crucial effect of the second S substituent on the above photoreaction may be attributed to the S stabilization of the enol and/or ylide intermediate.[27]

EXPERIMENTAL[28]

2-Phenylthio-dihydrothiophen-3-one (**1**)

General procedure for preparation of cyclic 2,2-bisulfenylated keto compounds. To a soln of dihydrothiophen-3-one[16] (612 mg, 6 mmol) in CCl_4 (25 ml) was added powder of NCS (881 mg, 6.6 mmol) with vigorous stirring in an ice-bath. The resulting mixture was allowed to stir for 1–2 hr in which time the mixture was allowed to warm up to room temp. The insoluble solid was removed by filtration and the filtrate was treated with thiophenol (660 mg, 6 mmol) and Et_3N (652 mg, 6.45 mmol) at 0°. The mixture was stirred for several hrs at room temp. At the end of this time Et_2O (150 ml) was added and the resulting mixture was successively washed with water (3 × 40 ml) and brine (20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed by evaporation under the reduced pressure. The residuel oil was chromatographed on a silica gel column using n-hexane–ether (4:1) to give **1** (993 mg, 79%) as a colorless viscous oil, IR (neat) 3080, 2960, 1730, 1590, 1485, 1445, 1405, 1280 and 1140 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.4–3.3 (m, 4 H), 4.56 (s, 1 H) and 7.20–7.65 (m, 5 H), δ (C_6D_6-CD_3OD) 2.0–2.8 (m, 4 H), 4.47 (s, 1 H), 7.00–7.30 (m, 3 H) and 7.30–7.65 (m, 2 H), δ (CD_3CN) 2.4–3.2 (m, 4 H), 4.72 (s, 1 H) and 7.2–7.7 (m, 5 H); UV (EtOH) 244 (ε6200) and 310 (ε1000, sh). (Found: C, 56.91; H, 4.97. $C_{10}H_{10}OS_2$ requires: C, 57.11; H, 4.79%)

2-Phenylthio-thiacyclohexan-3-one (**2**). Thiacyclohexan-3-one[17] (468 mg, 4 mmol) was treated with NCS (587 mg, 4.4 mmol) in CCl_4 (10 ml) at 5–10° for 1 hr. The mixture was similarly worked up and allowed to react with thiophenol (440 mg, 4 mmol). Chromatography on a silica gel column using n-hexane–ether (4:1) gave **2** (714 mg, 80%) as colorless crystals, m.p. 65–72°; IR (KBr) 3070, 2920, 1685, 1475, 1420, 1320 and 1220 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.05–3.65 (m, 6 H), 4.53 (s, 1 H), and 7.2–7.6 (m, 5 H). (Found: C, 58.90; H, 5.38. $C_{11}H_{12}OS_2$ requires: C, 58.89; H, 5.39%).

2-Phenylthio-thiacyclohexan-3-one-5-spiro-2'-1, 3-dioxane (**3**). Compound **3** was prepared from thiacyclohexan-3,5-dione monotrimethylene ketal[18] (376 mg, 2 mmol), NCS (294 mg, 2.2 mmol) and thiophenol (220 mg, 2 mmol) and chromatographed on a silica gel column using n-hexane–EtOAc (2:1) to give colorless crystals (436 mg, 74%), m.p. 120–122°; IR (KBr) 2960, 2890, 1690, 1580, 1480, 1430, 1415, 1320, 1240, 1210, 1100, 1070 and 1020 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.5–2.0 (m, 2 H), 2.75–3.15 (m, 4 H), 3.80–4.15 (m, 4 H), 4.53 (s, 1 H) and 7.2–7.6 (m, 5 H). (Found: C, 56.80; H, 5.44. $C_{14}H_{16}O_3S_2$ requies: C, 56.73; H, 5.44%).

3-Phenylthio-isothiochroman-4-one (**4**). Compound **4** was prepared from isothiochroman-4-one[19] (164 mg, 1 mmol), NCS (147 mg, 1.1 mmol) and thiophenol (110 mg, 1 mmol), and chromatographed on a silica gel column using n-hexane–ether (4:1) to give colorless crystals (237 mg, 87%), m.p. 89–90°; IR (KBr) 3070, 1670, 1600, 1450, 1405, 1280 and 1215 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.56 and 4.69 (ABq, J = 16.5 Hz, 2 H), 4.77 (s, 1 H), 7.06–7.65 (m, 8 H) and 7.92–8.15 (m, 1 H). (Found: C, 65.92; H, 4.65. $C_{15}H_{12}OS_2$ requires: C, 66.14; H, 4.44%)

2,2-Bis(phenylthio)acetone (**5**)

General procedure for preparation of acyclic 2,2-bisulfenylated keto compounds. 2-(phenylthio)acetone was prepared in quantitive yield from 2-chloroacetone and thiophenol by treating with Et_3N. To a stirred soln of 2-phenylthioacetone (1.0 g, 6.01 mmol) in CCl_4 (10 ml) was added NCS (845 mg, 6.31 mmol) at room temp and the resulting mixture was stirred for further 1–2 hr. The mixture was filtered to remove the ppt and the filtrate was combined with thiophenol (663 mg, 6.01 mmol). To this soln, Et_3N (640 mg, 6.3 mmol) was added and the resulting mixture was allowed to stir overnight at room temp. Then n-hexane (150 ml) was added and the mixture was washed with water (3 × 30 ml). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under the reduced pressure. The yellow residual oil was chromatographed on a silica gel column using n-hexane–EtOAc (8:1) to give **5** (1.31 g, 81%) as colorless crystals, m.p. 40–42° IR (neat) 3080, 1725, 1590, 1485, 1450, 1360 and 1230 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.35 (s, 3 H), 4.90 (s, 1H) and 7.25–7.65 (m, 10 H). (Found: C, 65.78; H, 5.23. $C_{15}H_{14}OS_2$ requires: C, 65.66; H, 5.14%).

2,2-*Bis(phenylthio)acetophenone* (**6**). Compound **6** was prepared in two steps from 2-(phenylthio)acetophenone (456 mg, 2.0 mmol) by successive treatment with NCS (295 mg, 2.2 mmol) and thiophenol (220 mg, 2.0 mmol) and chromatographed on a silica gel column using n-hexane–EtOAc (20:1) to give colorless prisms (432 mg, 64%), m.p. 99–100.5°; IR (KBr) 3060, 1660, 1575, 1435, 1260, 1150 and 990 cm^{-1}; ^1H NMR δ ($CDCl_3$) 5.72 (s, 1 H), 7.20–7.65 (m, 13 H) and 7.84–8.05 (m, 2 H). (Found: C, 71.20; H, 5.02. $C_{20}H_{16}OS_2$ requires: C, 71.39; 4.79%).

2-*Benzylthio-2-phenylthioacetophenone* (**7**). Compound **7** was prepared from 2-(phenylthio)acetophenone (715 mg, 3.13 mmol) by successive treatment with NCS (460 mg, 3.44 mmol) and benzyl-mercaptan (389 mg, 3.13 mmol) and chromatographed on a silica gel column using n-hexane–EtOAc (20:1) to give colorless prisms (650 mg, 59.3%), m.p. 75–76°; IR (KBr) 3100, 2960, 1665, 1610, 1590, 1510, 1485, 1645, 1450, 1335, 1285, 1200, and 1010 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.78 and 4.10 (ABq, J = 13.5 Hz, 2 H), 5.36 (s, 1 H), 7.20–7.56 (m, 13 H) and 7.70–7.90 (m, 2 H). (Found: C, 71.84; H, 5.23. $C_{21}H_{18}OS_2$ requires: c, 71.96; H, 5.18%).

2,2-*Bisulfenylated acetophenone* (**8**). Compound **8** was prepared from 2-chloro-2-(phenylthio)acetophenone (410 mg, 1.56 mmol) and methyl thioglycolate (165 mg, 1.56 mmol) and chromatographed on a silica gel column using n-hexane–EtOAc (4:1) to give colorless viscous oil (480 mg, 92.7%), IR (neat) 2960, 1720, 1665, 1600, 1585, 1440, 1270 and 1150 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.38 and 3.72 (ABq, J = 15 Hz, 2 H), 3.69 (s, 3 H), 5.84 (s, 1 H), 7.20–7.65 (m, 8 H), 7.84–8.10 (m, 2 H). (Found: C, 61.39; H, 4.92. $C_{17}H_{16}O_3S_2$ requires: C, 61.42; H, 4.87%).

Irradiation of **1**

General photochemical procedure. A soln of **1** (101 mg, 0.48 mmol) in benzene (100 ml) was placed in the preparative photoreactor and Ar was passed into the soln for 10 min prior to and during irradiation. The soln was irradiated with an Ushio 100-W high pressure mercury lamp placed in a water-cooled Pyrex well. After 30 min the solvent was evaporated under the reduced pressure and the residue was chromatographed on a silica gel column using n-hexane–ether (4:1) to give **9** (62 mg, 63%), **1** (23 mg, 23%) and **10** (24 mg, 49%) in the order of elution. Compound **10**: viscous oil, IR (neat) 3010, 2800, 1720, 1445, 1400, 1265 and 1130 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.5–3.4 (m, 4 H), 4.04 (s, 0.57 H) and 4.19 (s, 0.43 H); MS *m/e* (rel intensity) 202 (M^+, 11), 101 (M^+/2,100). Compound **1** (77 mg, 0.37 mmol) was irradiated in MeCN (80 ml) for 20 min under the same conditions. Chromatography of mixture gave **9** (10 mg, 25%), **11** (33 mg, 43%) and **10** (8 mg, 21%) in the order of elution. Compound **11**: colorless viscous oil, IR (neat) 3380, 3080, 2950, 1595, 1455, 1270 and 1055 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.5–3.5 (m, 4 H), 3.10 (s, 1 H, D_2O exchangeable), 4.78 (s, 1 H) and 7.08–7.25 MS *m/e* (rel intensity) 210 (M^+, 68), 192 (M^+-H_2O, 4), 182 (30), 177 (55), 153 (100), 121 (56), 77 (56). (Found: C, 56.97; H, 4.93. $C_{10}H_{10}OS_2$ requires: C, 57.11; H, 4.79%).

Compound **1** (105 mg, 0.5 mmol) was irradiated in MeOH (100 ml) for 1 hr to give **11** (21 mg, 20%).

Irradiation of **2**. **2** (224 mg, 1.0 mmol) was irradiated in MeCN (100 ml) for 30 min using a quartz well. Chromatography of the mixture gave **9** (16 mg, 15%), **22** (3 mg, 1.5%), **2** (29 mg, 13%) and **15** (83 mg, 37%) in the order of elution. Compound **15**: colorless viscous oil, IR (neat) 3390, 3070, 2930, 2860, 1590, 1445, 1325, 1280, 1270, 1235, 1185, 1160, 1100, 1075 and 1010 cm^{-1}; MS *m/e* (rel intensity) 224 (M^+, 99), 206 (M^+-H_2O, 100), 153 (93) and 135 (89). The ^1H NMR data was listed in Table 1. (Found: C, 58.87; H, 5.46. $C_{11}H_{12}OS_2$ requires: C, 58.89; H, 5.39%).

Irradiation of **3**. **3** (296 mg, 1.0 mmol) was irradiated in MeCN (100 ml) for 20 min. Chromatography of the mixture gave **9** (16 mg, 15%), **3** (150 mg, 51%) and **16** (77 mg, 26%) in the order of elution. Compound **16**: colorless semisolid, IR (neat) 3440, 3070, 2970, 2880, 1580, 1440, 1245 and 1100 cm^{-1}; MS *m/e* (rel intensity) 296 (M^+, 90), 278 (M^+-H_2O, 100) and 153 (97). The ^1H NMR data was listed in Table 1. (Found: C, 56.69; H, 5.48. $C_{14}H_{16}O_3S_2$ requires: C, 56.73; H, 5.44%).

Irradiation of **4**. **4** (272 mg, 1.0 mmol) was irradiated in MeCN (100 ml) for 30 min. Chromatography of the mixture gave **9** (32 mg, 29%) and **24** (76 mg, 30%) in the order of elution. Compound **24**: colorless viscous oil, ^1H NMR δ ($CDCl_3$) 4.06 (s, 2 H) and 7.2–8.0 (m, 8 H); MS *m/e* (rel intensity) 254 (M^+, 71), 253 (M^+-H, 100).

Compound **4** (80 mg, 0.29 mmol) was irradiated in MeCN (100 ml) for 10 min under the same conditions and then the solvent was removed carefully at 25° under the reduced pressure. The ^1H NMR spectra of the residual mixture indicated the presence of **17**, δ ($CDCl_3$) 3.43 (s, 1 H, D_2O exchangeable), 4.11 (s, 2 H), 4.63 (s, 1 H) and 6.9–8.2 (m, 8 H).

Irradiation of **5**. **5** (280 mg, 1.04 mmol) was irradiated in MeCN (100 ml) for 30 min. Chromatography of the mixture gave **9** (34 mg, 31%), **25** (8 mg, 3.1%), **5** (120 mg, 43%) and **18** (31 mg, 11%) in the order of elution. Compound **18**: colorless viscous oil, IR (neat) 3400, 3080, 2940, 1590, 1485, 1445, 1385 and 1360 cm^{-1}; MS *m/e* 274 (M^+), 256 (M^+-H_2O). The ^1H NMR data was listed in Table 1. (Found: C, 65.73; H, 5.07. $C_{15}H_{14}OS_2$ requires: C, 65.66; H, 5.14%).

Irradiation of **6**. **6** (250 mg, 0.74 mmol) was irradiated in MeCN (70 ml) for 10 min. Chromatography of the mixture gave **9** (13 mg, 16%), **26** (trace), **6** (20 mg, 8%) and **19** (183 mg, 73%) in the order of elution. Compound **19**: colorless viscous oil, IR (neat) 3540, 3440, 3070, 1585, 1480, 1445, 1180 and 1055 cm^{-1}; MS *m/e* 336 (M^+), 318 (M^+-H_2O). The ^1H NMR data was listed in Table 1. (Found: C, 71.66; H, 4.85. $C_{20}H_{16}OS_2$ requires: C, 71.39; H, 4.79%).

Irradiation of **7**. **7** (280 mg, 0.80 mmol) was irradiated in MeCN (80 ml) for 15 min. Chromatography of the mixture gave **9** (41 mg, 47%), **7** (89 mg, 32%) and **20** (87 mg, 31%) in the order of elution. Compound **20**: colorless viscous oil, IR (neat) 3580, 3420, 3080, 1605, 1595, 1505 and 1460 cm^{-1}; MS *m/e* 350 (M^+), 332 (M^+-H_2O). The ^1H NMR data was listed in Table 1. (Found: C, 71.78; H, 5.20. $C_{21}H_{18}OS_2$ requires: C, 71.96; H, 5.18%).

Irradiation of **8**. **8** (300 mg, 0.90 mmol) was irradiated in MeCN (100 ml) for 25 min. Chromatography of the mixture gave **9** (8 mg, 8.1%), **28** (32 mg, 11%), **8** (28 mg, 9.3%) and **21** (97 mg, 32%) in the order of elution. Compound **21**: colorless needles, m.p. 97–98°; IR (neat) 3450, 3080, 2985, 1725, 1590, 1450 and 1300 cm^{-1}; MS *m/e* 332 (M^+), 314 (M^+-H_2O). The ^1H NMR data was listed in Table 1. (Found: C, 61.25; H, 5.03. $C_{17}H_{16}O_3S_2$ requires: C, 61.42; H, 4.87%).

Acetylation of **11**. To a soln of **11** (41 mg, 0.2 mmol) and DMAP (24 mg, 0.2 mmol) in pyridine (3 ml) was added Ac_2O (200 mg, 2.0 mmol) at room temp and the resulting mixture was allowed to stir for a day at this temp. The solvent and a excess Ac_2O was removed under the reduced pressure, and the residue was chromatographed on a silica gel column using n-hexane–ether (4:1) to give **12** (12 mg, 24%), as colorless crystals, m.p. 135–137°; IR (neat) 3080, 2960, 1740, 1440, 1360, 1220, 1200, 1170 and 980 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.08 (s, 3 H), 2.6–3.7 (m, 4 H), 5.12 (s, 1 H) and 7.14–7.26 (m, 4 H); M/S *m/e* (rel intensity (252^+, 4.5), 192 (M^+-CH_3CO_2H, 100) and 153 (55).

Dehydration of **11**

General procedure for dehydration of cis-fused dihydrobenzothiophenes **15–21**. A soln of **11** (39 mg, 0.19 mmol) in dry CH_2Cl_2 (10 ml) was added a CH_2Cl_2 soln. of BF_3-Et_2O (30 mg, 0.21 mmol) at room temp and the resulting mixture was allowed to stand at room temp for a few min. Then, the solvent was evaporated under the reduced pressure and the residue was chromatographed on a silica gel column using n-hexane to give **13** (35 mg, 100%), as colorless crystals, m.p. 58–60°; IR (KBr) 3000, 2800, 1425, 1255, 1150–980 (br.); MS *m/e* (rel intensity) 192 (M^+, 100), 191 (M^+-H, 79) and 190 (M^+-2 H, 30). The ^1H NMR data was listed in Table 2. (Found: C, 62.41; H, 4.24. $C_{10}H_8S_2$ requires: C, 62.46; H, 4.19%).

Compounds **15**, **16**, **18–21** were similarly dehydrated by treatment with BF_3-Et_2O to give **22**, **23**, **25–28**. The yield and physical data of those compounds were listed in Table 2.

Dehydrogenation of **13**. To a stirred soln of **13** (65 mg, 0.34 mmol) in dry benzene (10 ml) was added DDQ (77 mg, 0.34 mmol) under the Ar at room temp and the mixture was stirred for a few min at this temp. Then, the solvent was evaporated under the reduced pressure and the residue was

chromatographed on a silica gel column using n-hexane to give **14** (57 mg, 89%) as colorless crystals, m.p. 89–90.5° (Lit.[21a] m.p. 60–61°); IR (KBr) 3120–2910 (br), 1570, 1465, 1430, 1355, 1320, 1300, 1260, 1190, 1160, 1140–960 (br) cm^{-1}; ^1H NMR δ ($CDCl_3$) 7.23–7.60 (m, 4 H) and 7.70–7.93 (m, 2 H); MS *m/e* 190 (M^+, 100%). (Found: C, 63.06; H, 3.34. $C_{10}H_6S_2$ requires: C, 63.12; H, 3.18%).

Deketalization of **23**. A soln of **23** (63 mg, 0.29 mmol) in aqueous trifluoroacetic acid (4 ml) was stirred at room temp for 30 min and then the soln was neutralized with a sat $NaHCO_3$aq. The resulting mixture was extracted with CH_2Cl_2 (4 × 80 ml) and the organic layer was dried over Na_2SO_4. The solvent was evaporated under the reduced pressure and the residual yellow solid was recrystallized from EtOH to give **29** (50 mg, 100%) as colorless plates, m.p. 115–118°; IR (KBr) 2975, 1720, 1590, 1440, 1400, 1260, 1100 and 1010 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.50 (s, 2 H), 3.80 (s, 2 H), 7.23–7.50 (m, 2 H) and 7.50–7.78 (m, 2 H); MS *m/e* 220 (M^+). (Found: C, 59.92; H, 3.75. $C_{11}H_8OS_2$ requires: C, 59.97; H, 3.66%).

Preparation of **6**-d_1. A soln of **6** (672 mg, 2.0 mmol) and catalytic amount of NaOMe in dry dioxane (3 ml) and D_2O (1 ml) was placed in a sealed tube and heated at 70–80° for 4 hr. The mixture was cooled to room temp and extracted with dry Et_2O (3 × 5 ml). The organic layer was dried over $MgSO_4$ and the solvent was evaporated under the reduced pressure. The residual pale yellow solid was washed with small portions of ether to give colorless solid (610 mg, 91%), IR (KBr) 3120–2900 (br), 1665, 1585, 1475, 1440, 1315, 1245, 1180 and 1160 cm^{-1}; ^1H NMR δ ($CDCl_3$) 5.74 (s, 0.08 H), 7.20–7.65 (m, 13 H) and 7.85–8.10 (m, 2 H).

Irradiation of **6**-d_1. A soln of **6**-d_1 (175 mg, 0.52 mmol) in MeCN (100 ml) was irradiated for 10 min under the same conditions as the above photochemical reaction. Chromatography of the mixture gave **9** (26 mg, 46%), **26** (16 mg, 10%), **6**-d_1 (27 mg, 15%) and **19**-d_1 (66 mg, 38%) in the order of elution.

Compound **19**-d_1: colorless viscous oil, ^1H NMR δ ($CDCl_3$) 3.91 (s, 1 H, D_2O exchangeable), 5.14 (s, 0.08 H), 6.95–7.55 (m, 12 H) and 7.65–7.90 (m, 2 H); MS *m/e* 337 (M^+).

Irradiation of **6**-d_1 (194 mg, 0.58 mmol) in MeOH (100 ml) for 11 min under the same conditions gave **9** (35 mg, 56%), **26** (30 mg, 16%) and **19**-d_1 (50 mg, 26%).

Compound **19**-d_1: colorless viscous oil, ^1H NMR δ ($CDCl_3$) 3.92 (s, 1 H, D_2O exchangeable), 5.13 (s, 0.18 H), 6.90–7.60 (m, 12 H) and 7.65–7.95 (m, 2 H).

Preparation of 2,2-*bis*(*phenylthio*)*propiophenone* (**31**). To a suspension of NaH (120 mg, 60% oil suspension, 3.0 mmol) in dry THF (8 ml) was added propiophenone (402 mg, 3 mmol) dropwise with stirring at room temp and the mixture was stirred at this temp until evolution of H_2 gas ceased. Then, hexamethylphosphoramide (2 ml) and diphenyldisulfide (719 mg, 3.3 mmol) and the resulting mixture was stirred for further 1.5 hr at room temp. Then water (20 ml) was added and the mixture extracted with Et_2O (3 × 20 ml). The organic layer was successively washed with water (2 × 10 ml) and brine (10 ml), and dried over $MgSO_4$. The solvent was evaporated under the reduced pressure and the residual oil was evaporated under the reduced pressure and the residual oil was chromatographed on a silica gel column using n-hexane–ether (20:1) to give 2-(phenylthio)propiophenone (512 mg, 71%) as colorless oil, IR (neat) 3120–2800 (br), 1665, 1585, 1480, 1445, 1375, 1330, 1240 and 1180 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.52 (d, 3 H), 4.62 (q, 1 H), 7.20–7.35 (m, 5 H), 7.35–7.60 (m, 3 H) and 7.8–8.1 (m, 2 H). (Found: C, 74.25; H, 5.91. $C_{15}H_{14}OS$ requires: C, 74.35; H, 5.82%).

To a soln of 2-(phenylthio)propiophenone (242 mg, 1.0 mmol) in dry THF (2 ml) was added NaH (40 mg, 60% oil suspension, 1.0 mmol) with stirring, and the mixture was stirred at room temp. When the evolution of H_2 gas stopped, hexamethylphosphoramide (1 ml) and a soln of phenylsulfenylchloride in CH_2Cl_2, which was prepared from NCS (150 mg, 1.1 mmol) and thiophenol (110 mg, 1.0 mmol),[29] was added with stirring in an ice-bath. The resulting mixture was stirred for 3 hr at room temp. Then Et_2O (50 ml) was added and the mixture successively washed with water (3 × 15 ml) and brine (10 ml), and the organic layer was dried over $MgSO_4$. The solvent was evaporated under the reduced pressure and the residual oil was chromatographed on a silica gel column using n-hexane–benzene (2:1) to give **31** (175 mg, 50%) and 2-(phenylthio)propiophenone (96 mg, 40%).

Compound **31**: colorless viscous oil, IR (neat) 3120–2880 (br), 1660, 1580, 1470, 1440, 1370, 1300, 1235 and 1180 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.38 (S, 3 H), 7.1–7.6 (m, 13 H) and 8.3–8.6 (m, 2 H). (Found: C, 71.82; H, 5.32. $C_{21}H_{18}OS_2$ requires: C, 71.96; H, 5.18%).

Irradiation of **31**. Irradiation of **31** (158 mg, 0.45 mmol) in MeCN (100 ml) under the same conditions followed by the same work-up to give **9** (39 mg, 80%) together with a polymeric substance.

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