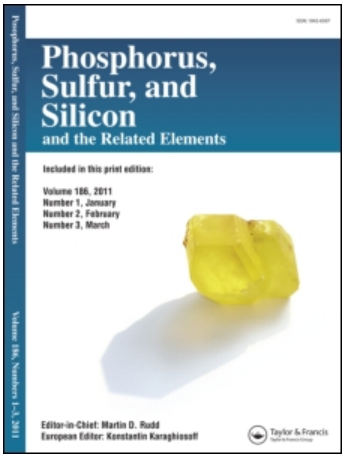


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

DIASTEREOSELECTIVE SYNTHESIS OF 2,2'-THIOBIS- AND 2,2'-SULFONYLBIS- (1,3-DIARYLPROP-2-EN-1-ONES)—AN OXIDATIVE CONFIGURATIONAL SWITCH

M. Gnanadeebam[a]; S. Renuga[a]; S. Selvaraj[b]; S. Perumal[b]; A. Dhanabalan[b]; M. J. E. Hewlins[c]
[a] Department of Chemistry, Fatima College, Madurai, India [b] School of Chemistry, Madurai Kamaraj University, Madurai, India [c] Department of Chemistry, Cardiff University, United Kingdom

Online publication date: 11 August 2010

To cite this Article Gnanadeebam, M. , Renuga, S. , Selvaraj, S. , Perumal, S. , Dhanabalan, A. and Hewlins, M. J. E.(2004) 'DIASTEREOSELECTIVE SYNTHESIS OF 2,2'-THIOBIS- AND 2,2'-SULFONYLBIS- (1,3-DIARYLPROP-2-EN-1-ONES)—AN OXIDATIVE CONFIGURATIONAL SWITCH', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 2, 203 — 214
To link to this Article: DOI: 10.1080/10426500490274637
URL: http://dx.doi.org/10.1080/10426500490274637

Phosphorus, Sulfur, and Silicon, 179:203–214, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490274637

Taylor & Francis
Taylor & Francis Group

DIASTEREOSELECTIVE SYNTHESIS OF 2,2′-THIOBIS- AND 2,2′-SULFONYLBIS-(1,3-DIARYLPROP-2-EN-1-ONES)—AN OXIDATIVE CONFIGURATIONAL SWITCH

M. Gnanadeebam,[a] *S. Renuga,*[a] *S. Selvaraj,*[b] *S. Perumal,*[b] *A. Dhanabalan,*[b] *and M. J. E. Hewlins*[c]
Department of Chemistry, Fatima College, Madurai 625018, India;[a] *School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India;*[b] *and Department of Chemistry, Cardiff University, CFI 3TB, United Kingdom*[c]

(Received February 17, 2002; accepted April 12, 2002)

Synthesis of some heretofore unknown 2,2′-thiobis(1,3-diarylprop-2-en-1-ones) and their oxidation to new 2,2′-sulfonylbis(1,3-diarylprop-2-en-1-ones) are reported. The stereochemistry of the sulfides and sulfones assigned as (Z,Z)- and (E,E)- respectively by X-ray diffraction studies reveals a configurational switch from (Z,Z)- to (E,E)-during oxidation.

Keywords: 2,2′-Sulfonylbis(1,3-diarylprop-2-en-1-ones); 2,2′-thiobis-(1,3-diarylprop-2-en-1-ones); bis(aroylmethyl) sulfides/sulfones; nmr spectroscopic data; stereochemistry

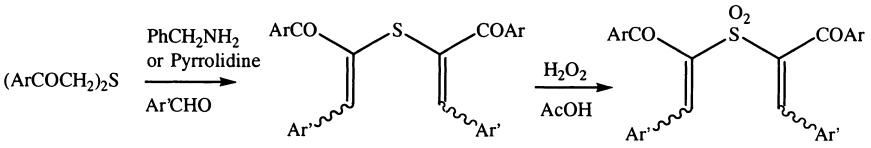
2,2′-Thiobis(1,3-diarylprop-2-en-1-ones) are highly useful synthons because of the presence of 1,5-dicarbonyl, α,β-unsaturated carbonyl and α,β-unsaturated sulfide functionalities as evident from the synthesis of several heterocycles from them. The corresponding sulfonyl derivatives are more reactive and hence are also very useful in organic synthesis.[1–5] Perusal of literature revealed that the reactions of β-ketosulfones with aromatic aldehydes and amines yielded the unsaturated sulfones or their Michael adducts or both depending on the reaction conditions.[6–8] But such studies on β,β'-diketosulfides leading to α,β-unsaturated compounds are meager.[9] Further, though the chemistry of 3,3′-thiobis(1,3-diarylprop-2-en-1-ones) has been reported,[10,11] synthetic

Address correspondence to S. Selvaraj, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India. E-mail: selvaraj-s@eth.net

studies on its position isomer 2,2′-thiobis(1,3-diarylprop-2-en-1-ones) are absent.

RESULTS AND DISCUSSION

The reaction of bis(aroylmethyl) sulfides **1** with aromatic aldehydes in the presence of benzylamine or pyrrolidine afforded 2,2′-thiobis(1,3-diarylprop-2-en-1-ones) **2** in 62–78% and 74–89% yields respectively (Scheme 1).



1 **2** **10**

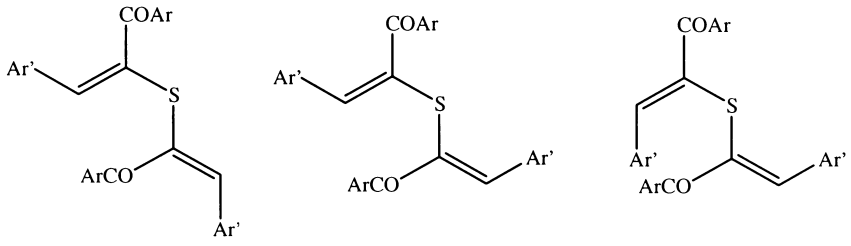
1, **2** and **10** (except **10c** and **10h**). **a:** Ar = C_6H_5, Ar′ = C_6H_5; **b:** Ar = C_6H_5, Ar′ = C_6H_4Cl-*p*; **c:** Ar = C_6H_5, Ar′ = $C_6H_4NO_2$-*p*; **d**: Ar = C_6H_4Cl-*p*, Ar′ = C_6H_4Cl-*p*; **e:** Ar = C_6H_4Cl-*p*, Ar′ = C_6H_4Me-*p*; **f:** Ar = C_6H_4Me-*p*, Ar′ = C_6H_5; **g:** Ar = C_6H_4Me-*p*, Ar′ = C_6H_4Cl-*p*; **h**: Ar = C_6H_4Me-*p*, Ar′ = $C_6H_4NO_2$-*p*

SCHEME 1

Pyrrolidine was found to be efficient in bringing out the condensation while other bases like sodium hydroxide and sodium ethoxide gave a resinous mass consisting of a complex mixture. The yields of various 2,2′-thiobis(1,3-diarylprop-2-en-1-ones) in benzylamine/pyrrolidine reactions are placed in Table I. Bis(aroylmethyl) sulfides upon condensation with aromatic aldehydes in the presence of either benzylamine or

TABLE I Yields of 2,2′-thiobis (1,3-Diarylprop-2-en-1-ones) 2

Compound	Yield (%) benzylamine	Pyrrolidine
2a	75	83
2b	63	74
2c	78	82
2d	70	83
2e	72	89
2f	70	85
2g	62	83
2h	65	79



(*E*,*E*) (*E*,*Z*) (*Z*,*Z*)

3 **4** **5**

FIGURE 1

pyrrolidine afforded only one diastereomer of 2,2′-thiobis(1,3-diarylprop-2-en-1-ones) whose configuration can be either (*E*,*E*) or (*E*,*Z*) or (*Z*,*Z*) (Figure 1).

The number of ^{1}H and ^{13}C NMR signals of the compounds point to the symmetrical structure **3** or **5** with either *s-cis* or *s-trans* configuration for both the α,β-unsaturated carbonyl groups. Complete configurational assignment was arrived at from an X-ray study (Figure 2) of **2b** to be (*Z*,*Z*)-*s-cis, s-cis* configuration (Figure 3).[12] NMR spectroscopic data show that **2a, 2c–2h**, also adopt the same configuration as **2b**.

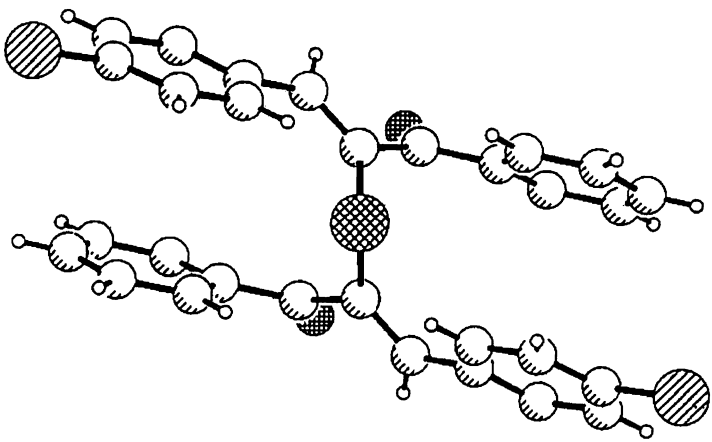
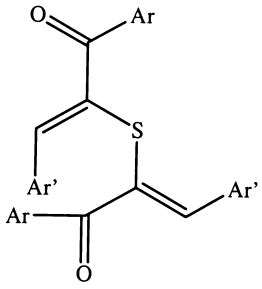


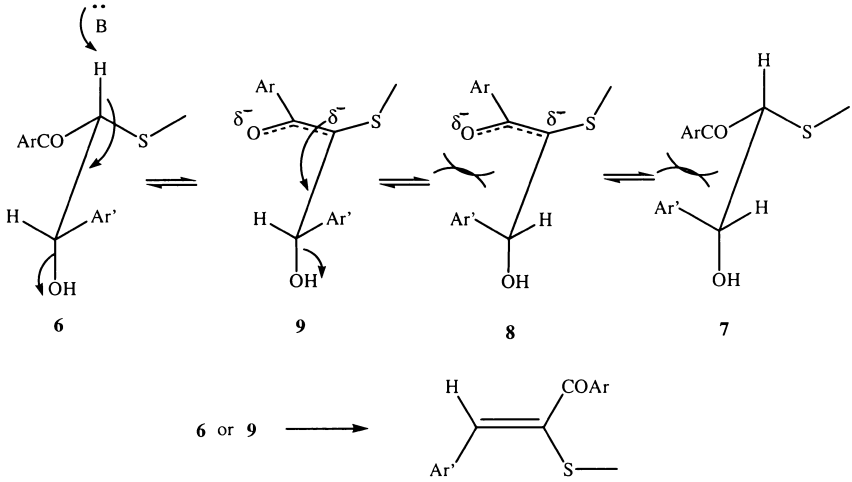
FIGURE 2 X-ray structure of **2b**.



(Z,Z)-s-cis, s-cis

FIGURE 3

The diastereoselective formation of 2,2′-thiobis(1,3-diarylprop-2-en-1-ones) is rationalized by considering the steric interactions between the various groups in the hydroxy sulfide at the elimination step (Scheme 2).



SCHEME 2

This reaction would proceed via the initial addition of the enolate from the bis(aroylmethyl) sulfides over the aldehydes affording the diastereomeric hydroxy sulfides **6** and **7** which can equilibrate via their enolates **8** and **9**. In the elimination of the hydroxyl group resulting in the formation of the C=C bond via either an E2 or an E1cB reaction, the steric interactions between the aryl and the aroyl groups would be more than that between the aryl and the sulfide functions. This would result in (*Z*,*Z*) configuration with respect to each alkenic bond in the product as the reaction would occur with less energy of activation from

either the hydroxy sulfide **6** or the enolate **9** in preference to the other diastereomeric hydroxy sulfide **7** or the enolate **8**.

Synthesis of 2,2′-Sulfonylbis(1,3-diarylprop-2-en-1-ones)

The synthesis of 2,2′-sulfonylbis(1,3-diarylprop-2-en-1-ones) **10** by condensation of bis(aroylmethyl) sulfones with various aromatic aldehydes in the presence of bases, did not succeed. Whilst amines such as ammonia[13] and methylamine[2] yielded only the 2,6-diaroyl-3,5-diaryltetrahydro-1,4-thiazine-1,1-dioxides by Mannich reaction, secondary amines like diethylamine, dibenzylamine, pyrrolidine and piperidine failed to produce the desired product. Alternatively, 2,2′-sulfonylbis(1,3-diarylprop-2-en-1-ones) **10** were obtained by the oxidation of the corresponding 2,2′-thiobis compounds **2** with hydrogen peroxide (30%) in glacial acetic acid (Scheme 1). The reactions afforded only one diastereomeric sulfone in all cases, except **2c** and **2h**, in good yield (80–87%). Poor solubility of the sulfides in acetic acid precluded the oxidation of **2c** and **2h**. All the sulfonylbis compounds were characterized using elemental analyses, IR, ^{1}H NMR and ^{13}C NMR spectroscopic data. The configuration of the sulfonylbis compounds was established unambiguously as *(E,E)-s-trans, s-trans* by a single crystal X-ray diffraction study [12] of **10a** (Figures 4 and 5).

The preference of the *(E,E)-s-trans, s-trans* configuration in the case of sulfonylbis compounds may also be understood in terms of the steric

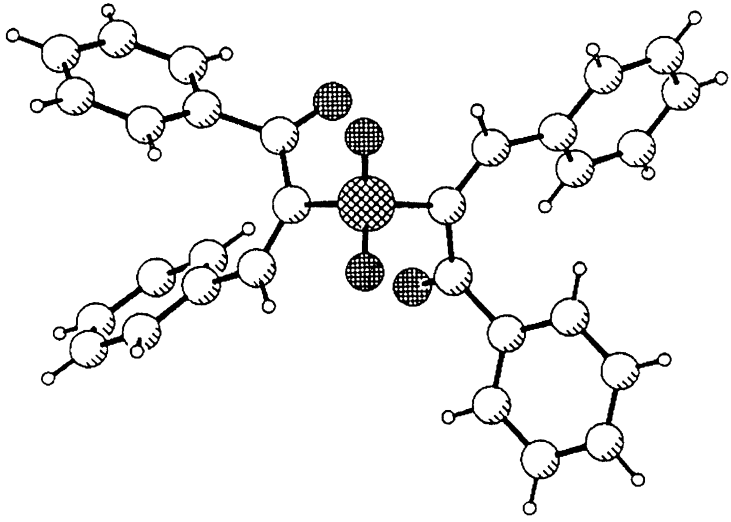
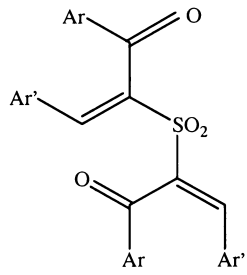


FIGURE 4 X-ray structure of **10a**.



(*E,E*)-*s-trans*, *s-trans*

FIGURE 5

requirements of aryl, aroyl, sulfonyl and sulfide groups viz. $-SO_2-$ > ArCO– > –S–. In sulfonylbis(1,3-diarylprop-2-en-1-ones), the steric interaction between the aryl and sulfonyl groups in cis relationship could be greater than that between aryl and aroyl groups in cis relationship rendering the (*E,E*) configurational isomer more stable. In contrast to this, in the case of thiobis(1,3-diarylprop-2-en-1-ones), the steric interaction between the aryl and sulfide groups in cis relationship is less than that between aryl and aroyl groups and hence the thiobis compounds assume (*Z,Z*) configuration (Figure 6).

The change in the configuration during oxidation can be rationalized by isomerisation of initially formed (*Z,Z*)-diastereomers of sulfonylbis compounds into the more stable (*E,E*)-diastereomers via an addition-elimination mechanism (Scheme 3).

As the sulfonylbis compounds could be very reactive towards conjugate addition (the reactivity of the C=C bond being enhanced by both the carbonyl and sulfonyl groups), the nucleophile (water) present in the medium during oxidation could add across the double bond resulting in the formation of hydroxy sulfones **11** and **12**. Similar observation of addition of water across α,β-unsaturated sulfone has been reported.[14] During elimination of the water molecule, the reaction could favorably

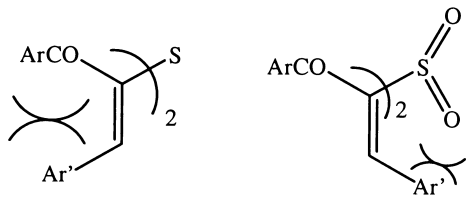
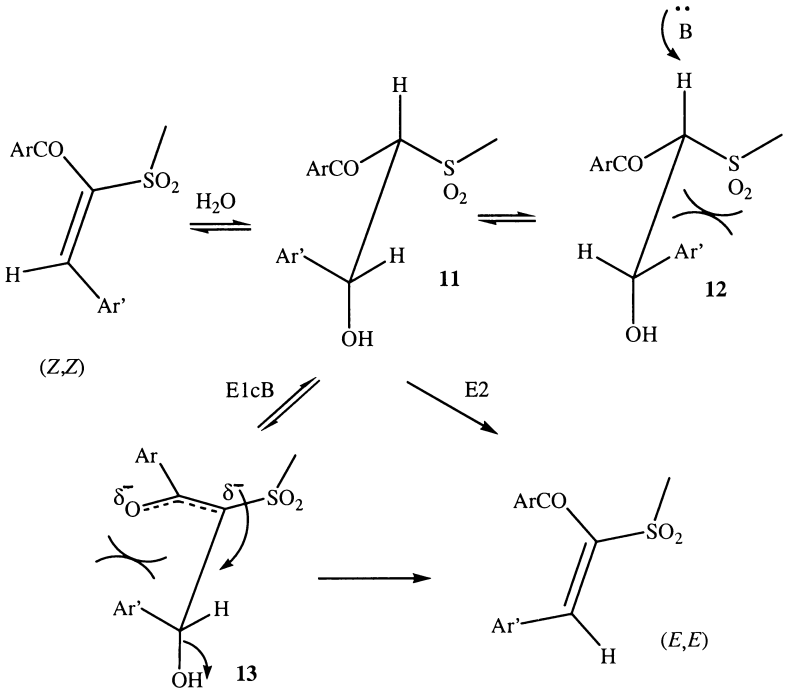


FIGURE 6



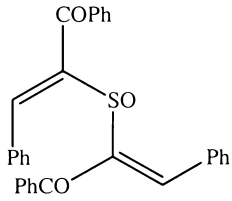
SCHEME 3

occur from either the hydroxy sulfone **11** or from the enolate **13** as these and the (*E*,*E*) sulfonylbis unsaturated systems are more stable than their respective diastereomeric analogs.

Alternatively, the resonance interaction between the C=C with C=O and SO_2 groups in the α,β-unsaturated sulfone (Scheme 3) can diminish the energy barrier for rotation around the C=C bond, facilitating configurational change as demanded by the steric interactions to stabilize the sulfonylbis compounds.

As the sulfides and the sulfones assume different configurations, it is interesting to study the configuration of the corresponding sulfoxides. Selective oxidation of the 2,2′-thiobis(1,3-diphenylprop-2-en-1-one) **2** by H_2O_2 in acetic acid gave mainly 2,2′-sulfinylbis(1,3-diphenylprop-2-en-1-one) **14** along with 2,2′-sulfonylbis(1,3-diphenylprop-2-en-1-one) **10a** from which the sulfinylbis compound was separated by column chromatography.

The ^{1}H NMR spectrum of sulfinylbis(1,3-diphenylprop-2-en-1-one) is consistent with the structure of the compound. As good crystals of the 2,2′-sulfinylbis(1,3-diphenylprop-2-en-1-one) could not be obtained, X-ray diffraction study of the compound was not carried out. The



14 *(Z,Z)*

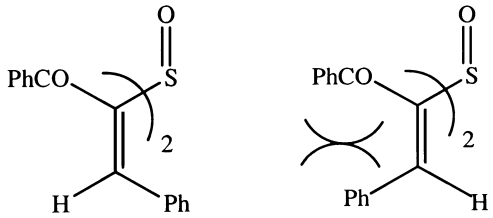
FIGURE 7

chemical shift of the *ortho* protons of the aryl group (H-*o*′) at 7.65 ppm is close to that found in 2,2′-thiobis(1,3-diphenylprop-2-en-1-one) suggesting (*Z*,*Z*)-configuration for the former also (Figure 7) in contrast to the chemical shift of the *ortho* protons (∼7.26 ppm) of the sulfonylbis compounds.

This assignment is also in consonance with the explanation given above as the steric interaction between the *cis*-sulfinyl and phenyl groups (Figure 8a) is likely to be less than that between the *cis*-phenyl and benzoyl groups (Figure 8b) as the sulfoxide group can adopt a conformation wherein the oxygen atom is oriented away from the cis phenyl group. Hence sulfinylbis compound **14** also adopts the (*Z*,*Z*)-configuration.

EXPERIMENTAL

The melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer IR-577 instrument with KBr pellets. NMR spectra of **2**



a (*Z*,*Z*) **b** (*E*,*E*)

FIGURE 8

were recorded on JEOL-GSX-400 instrument and those of compounds **10** and **14** were recorded on a Bruker AMX 360 instrument. The chemical shifts were referenced to TMS in all cases.

General procedure for the synthesis of 2,2′-thiobis (1,3-diarylprop-2-en-1-ones)-synthesis of 2,2′-thiobis-(1,3-diphenylprop-2-en-1-one) (2a). A mixture of bis(benzoylmethyl) sulfide (2.7 g, 10 mmol), benzaldehyde (2.2 g, 20 mmol) and benzylamine (0.5 ml) in ethanol (40 ml) was heated on a water-bath (60–80°C) for 5 min. The reaction mixture was kept aside for 24 h and the separated yellow solid was filtered and washed with ether affording a yellow solid consisting of a single entity (tlc). It was crystallized from ethanol-chloroform mixture. mp 137–38°C; IR (KBr) 1625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (4H, dd, $J = 8.0$, 1.5 Hz), 7.64 (4 H, d, $J = 7.2$ Hz), 7.41 (2H, t, $J = 7.2$ Hz), 7.28–7.40 (10H, m), 7.26 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 143.3, 137.4, 134.8, 134.6, 132.4, 130.8, 130.0, 129.7, 128.6, 128.3; Anal. Calcd for $C_{30}H_{22}O_2S$: C, 80.69; H, 4.97. Found: C, 80.79; H, 4.94.

The same procedure was followed for the condensation with pyrrolidine except for the reduced reaction time (4 h).

2,2′-Thiobis(3-(*p*-chlorophenyl)-1-phenylprop-2-en-1-one) (2b). Crystallization from ethanol-chloroform mixture gave yellow crystals, mp 157–58°C; IR (KBr) 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (4H, d, $J = 8.4$ Hz), 7.66 (4H, d, $J = 7.5$ Hz), 7.45 (2H, t, $J = 7.5$ Hz), 7.30–7.39 (8H, m), 7.22 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 141.7, 137.0, 135.4, 134.8, 132.8, 132.4, 131.8, 129.8, 128.7, 128.2. Anal. Calcd for $C_{30}H_{20}Cl_2O_2S$: C, 69.90; H, 3.91. Found: C, 69.97; H, 3.93.

2,2′-Thiobis(3-(*p*-nitrophenyl)-1-phenylprop-2-en-1-one) (2c). Crystallization from ethanol-chloroform mixture gave yellow crystals, mp 238–40°C; IR (KBr) 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (4 H, d, $J = 8.2$ Hz), 7.95 (4H, d, $J = 8.2$ Hz), 7.75 (4H, d, $J = 8.0$ Hz), 7.20–7.60 (6H, m), 7.22 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 147.6, 140.6, 140.3, 137.5, 136.3, 133.0, 131.0, 129.9,128.4, 123.6. Anal. Calcd for $C_{30}H_{20}N_2O_6S$: C, 67.16; H, 3.76. Found: C, 67.09; H, 3.79.

2,2′-Thiobis(1,3-di(*p*-chlorophenyl)prop-2-en-1-one) (2d). Crystallization from ethanol-chloroform mixture gave yellow crystals, mp 175–77°C; IR (KBr) 1635 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (4H, d, $J = 7.5$ Hz), 7.65 (4H, d, $J = 7.2$ Hz), 7.28–7.46 (8H, m), 7.26 (2H, s). Anal. Calcd for $C_{30}H_{18}Cl_4O_2S$: C, 61.66; H, 3.10. Found: C, 61.58; H, 3.07.

2,2′-Thiobis(1-(*p*-chlorophenyl)-3-(*p*-methylphenyl)prop-2-en-1-one) (2e). Crystallization from ethanol-chloroform mixture gave yellow crystals, mp 196–97°C; IR (KBr) 1630 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$) δ 7.73 (4H, d, $J = 7.2$ Hz), 7.62 (4H, d, $J = 8.0$ Hz), 7.18–7.36 (8H, m), 7.22 (2H, s), 2.35 (6H, s). Anal. Calcd for $C_{32}H_{24}Cl_2O_2S$: C, 70.72; H, 4.45. Found: C, 70.79; H, 4.42.

2,2′-Thiobis(1-(*p*-methylphenyl)-3-phenylprop-2-en-1-one) (2f). Crystallization from ethanol-chloroform mixture gave yellow crystals, mp 152–54°C; IR (KBr) 1630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (4H, dd, $J = 7.7$, 1.1 Hz), 7.58 (4H, d, $J = 8.0$ Hz), 7.10 (4H, d, $J = 8.0$ Hz), 7.30–7.42 (6H, m), 7.24 (2H, s), 2.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 142.9, 142.4, 134.7, 134.5, 134.4, 130.5, 130.0, 129.3, 128.8, 128.3, 21.6. Anal. Calcd for $C_{32}H_{26}O_2S$: C, 80.98; H, 5.52. Found: C, 80.85; H, 5.56.

2,2′-Thiobis(3-(*p*-chlorophenyl)-1-(*p*-methylphenyl)prop-2-en-1-one) (2g). Crystallization from ethanol-chloroform mixture gave yellow crystals, mp 195–97°C; IR (KBr) 1630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (4H, d, $J = 8.6$ Hz), 7.58 (4H, d, $J = 8.2$ Hz), 7.34 (4H, d, $J = 8.6$ Hz), 7.10 (4H, d, $J = 8.2$ Hz), 7.18 (2H, s), 2.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 143.3, 141.2, 135.2, 134.7, 134.2, 132.9, 131.7, 130.0, 128.9, 128.6, 21.6. Anal. Calcd for $C_{32}H_{24}Cl_2O_2S$: C, 70.72; H, 4.45. Found: C, 70.64; H, 4.41.

2,2′-Thiobis(1-(*p*-methylphenyl)-3-(*p*-nitrophenyl)prop-2-en-1-one) (2h). Crystallization from ethanol-chloroform mixture gave yellow crystals, mp 223–25°C; IR (KBr) 1635 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (4H, d, $J = 8.2$ Hz), 7.95 (4H, d, $J = 8.2$ Hz), 7.65 (4H, d, $J = 7.6$ Hz), 7.15 (4H, d, $J = 7.6$ Hz), 7.22 (2H, s), 2.40 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 147.6, 144.0, 140.7, 139.7, 137.6, 130.9, 130.2, 129.1, 128.5, 123.4, 21.7. Anal. Calcd for $C_{32}H_{24}N_2O_6S$: C, 68.07; H, 4.28. Found: C, 68.13; H, 4.25.

General procedure for the synthesis of 2,2′-sulfonylbis (1,3-diarylprop-2-en-1-ones)-synthesis of 2,2′-sulfonylbis (1,3-diphenylprop-2-en-1-one) (10a). To a solution of 2,2′-thiobis(1,3-diphenylprop-2-en-1-one), (2.2 g., 5 mmol) in glacial acetic acid (25 mL), hydrogen peroxide (1 mL, 30%) was added in one lot. The reaction mixture was heated on a steam bath for about 1.5 h. and then kept at room temperature for 24 h. The solid separated out was filtered at the pump and washed well with water to give 2,2′-sulfonylbis(1,3-diphenylprop-2-en-1-one). Crystallization from ethanol-chloroform mixture gave 1.9 g. (81%) of colorless crystals, mp 180–82°C; IR (KBr) 1650, 1130, 1305 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.01 (4H, dd, $J = 7.2$, 1.0 Hz), 7.33 (4H, t, $J = 7.2$ Hz), 7.46 (2H, tt, $J = 7.2$, 1.0 Hz), 7.26 (6H, m), 7.19 (4H, t, $J = 7.0$ Hz), 7.80 (2H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ 191.8, 144.8, 137.0, 135.6, 134.3, 131.5, 131.2, 130.3, 129.9, 128.7, 128.6. Anal. Calcd for $C_{30}H_{22}O_4S$: C, 75.29; H, 4.63. Found: C, 75.14; H, 4.59.

The following compounds were prepared by the same procedure.

2,2′-Sulfonylbis(3-(*p*-chlorophenyl)-1-phenylprop-2-en-1-one) (10b). Crystallization from ethanol-chloroform mixture gave 2.3 g. (83%) of colorless crystals, mp 220–22°C; IR (KBr) 1635, 1130, 1310 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.98 (4H, dd, $J = 7.4, 1.1$ Hz), 7.33 (4H, t, $J = 7.4$ Hz), 7.45 (2H, t, $J = 7.4$ Hz), 7.05 (8H, m), 7.75 (2H, s). Anal. Calcd for $C_{30}H_{20}Cl_2O_4S$: C, 65.82; H, 3.68. Found: C, 65.75; H, 3.64.

2,2′-Sulfonylbis(1,3-di(*p*-chlorophenyl)prop-2-en-1-one) (10d). Crystallization from ethanol-chloroform mixture gave 2.5 g. (82%) of colorless crystals, mp 216–18°C; IR (KBr) 1640, 1125, 1310 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.92 (4H, d, $J = 8.6$ Hz), 7.35 (4H, d, $J = 8.6$ Hz), 7.20 (8H, m), 7.73 (2H, s). Anal. Calcd for $C_{30}H_{18}Cl_4O_4S$: C, 58.46; H, 2.94. Found: C, 58.34; H, 2.91.

2,2′-Sulfonylbis(1-(*p*-chlorophenyl)-3-(*p*-methylphenyl)prop-2-en-1-one) (10e). Crystallization from ethanol-chloroform mixture gave 2.5 g. (87%) of colorless crystals, mp 165–66°C; IR (KBr) 1645, 1145, 1295 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.94 (4H, d, $J = 8.5$ Hz), 7.31 (4H, d, $J = 8.5$ Hz), 7.12 (4H, d, $J = 8.1$ Hz), 7.02 (4H, d, $J = 8.1$ Hz), 7.75 (2H, s), 2.27 (6H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ 190.8, 144.8, 140.4, 138.6, 133.1, 131.5, 131.3, 130.4, 129.7, 129.2. Anal. Calcd for $C_{32}H_{24}Cl_2O_4S$: C, 66.79; H, 4.20. Found: C, 66.89; H, 4.23.

2,2′-Sulfonylbis(1-(*p*-methylphenyl)-3-phenylprop-2-en-1-one) (10f). Crystallization from ethanol-chloroform mixture gave 2.2 g. (86%) of colorless crystals, mp 215–17°C; IR (KBr) 1640, 1150, 1295 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.93 (4H, d, $J = 8.2$ Hz), 7.10 (4H, d, $J = 8.2$ Hz), 7.18–7.25 (10H, m), 7.75 (2H, s), 2.27 (6H, s). Anal. Calcd for $C_{32}H_{26}O_4S$: C, 75.87; H, 5.17. Found: C, 75.79; H, 5.20.

2,2′-Sulfonylbis(3-(*p*-chlorophenyl)-1-(*p*-methylphenyl)prop-2-en-1-one) (10g). Crystallization from ethanol-chloroform mixture gave 2.3 g. (80%) of colorless crystals, mp 186–88°C; IR (KBr) 1650, 1125, 1310 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.95 (4H, d, $J = 8.0$ Hz), 7.15–7.35 (12H, m), 7.80 (2H, s), 2.38 (6H, s). Anal. Calcd for $C_{32}H_{24}Cl_2O_4S$: C, 66.79; H, 4.20. Found: C, 66.84; H, 4.17.

2,2′-Sulfinylbis(1,3-diphenylprop-2-en-1-one) (14). To a hot solution of 2,2′-thiobis(1,3-diphenylprop-2-en-1-one) (2.2 g., 5 mmol) in glacial acetic acid (100 mL), hydrogen peroxide (0.5 mL, 30%) was added and heated on a water bath at 60–70°C for 15 min. The reaction mixture was then poured into ice water and the separated solid was filtered and on chromatographic separation over silica gel with petroleum ether-chloroform (1:1 v/v) mixture as eluent gave 1.5 g. (66%) of colorless crystals, mp 143–44°C; IR (KBr) 1640, 1025 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.90 (4H, d, $J = 7.5$ Hz), 7.65 (4H, d, $J = 7.3$ Hz), 7.55 (2H,

t, $J = 7.5$ Hz), 7.45 (4H, t, $J = 7.5$ Hz), 7.38 (4H, t, $J = 7.3$ Hz), 7.25 (2H, t, $J = 7.3$ Hz), 7.59 (2H, s). Anal. Calcd for $C_{30}H_{22}O_3S$: C, 77.90; H, 4.79. Found: C, 77.81; H, 4.83.

ACKNOWLEDGEMENTS

M.G. and S. R. thank the Correspondent and the Principal, Fatima College, Madurai-18 for facilities. S. P thanks CSIR, New Delhi for a Major Research Project, S. S. and S. P. thank U. G. C, New Delhi for funds under UGC-DRS program, DST, New Delhi for funds under FIST program and for funds for the purchase of a high resolution NMR instrument under DST-IRHPA program.

REFERENCES

[1] S. Renuga, S. Selvaraj, S. Perumal, and M. J. E. Hewlins, *Tetrahedron*, **55,** 9309 (1999).
[2] M. Gnanadeepam, S. Selvaraj, S. Perumal, M. J. E. Hewlins, and A. Lycka, *Phosphorus, Sulfur and Silicon*, **155,** 167 (1999).
[3] M. Gnanadeepam, S. Renuga, S. Selvaraj, S. Perumal, and M. J. E. Hewlins, *Phosphorus, Sulfur and Silicon*, **134/135,** 171 (1998).
[4] S. Selvaraj, A. Dhanabalan, and N. Arumugam, *Sulf. Lett.*, **15,** 233 (1993).
[5] S. Renuga, S. Selvaraj, S. Perumal, and S. Sivakolunthu, *Indian J. Heterocycl. Chem.*, **8,** 81 (1998).
[6] M. Balasubramanian and V. Baliah, *J. Chem. Soc.*, 1844 (1954).
[7] M. Balasubramanian, V. Baliah, and T. Rangarajan, *J. Chem. Soc.*, 3296 (1955).
[8] V. Baliah and M. Sashapathirao Naidu, *J. Org. Chem.*, **24,** 867 (1959).
[9] V. Baliah and T. Rangarajan, *J. Chem. Soc.*, 3068 (1954).
[10] F. G. Baddar, F. H. Al-Hajjar, and N. R. El-Rayyes, *J. Heterocycl. Chem.*, **13,** 691 (1976).
[11] M. N. Basyouni and M. T. Omar, *Aust. J. Chem.*, **27,** 1585 (1974).
[12] M. Gnanadeepam, S. Selvaraj, A. M. M. Schreurs, J. Kroon, T. Steiner, and S. Perumal, *J. Chem. Cryst.* (in press); Compound **2b** forms monoclinic crystals, space group $C2/c$, $a = 14.275(3)$, $b = 6.280(1)$, $c = 26.533(5)$ Å, $\beta = 94.55(3)^\circ$, $Z' = 1/2$. The structure was solved from 4060 observed reflections (MoKα radiation) and refined to $R = 0.039$ and $R_w = 0.088$. Compound **10a** forms triclinic crystals, space group P-1, $a = 9.652(1)$, $b = 12.044(1)$, $c = 12.182(1)$ Å, $\alpha = 61.985(6)$, $b = 77.511(5)$, $c = 74.340(6)^\circ$, $Z' = 1$; The structure was solved from 7307 observed reflections (MoKα radiation) and refined to $R = 0.068$ and $R_w = 0.167$.
[13] V. Baliah and T. Rangarajan, *J. Org. Chem.*, **26,** 969 (1961).
[14] A. H. Ford-Moore, *J. Chem. Soc.*, 2433 (1954).