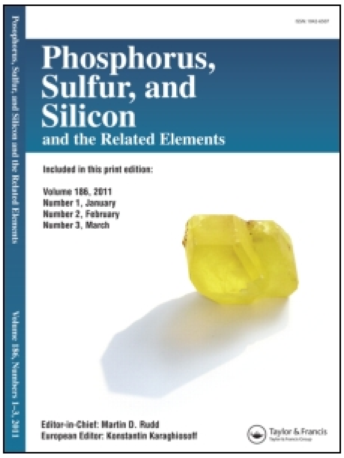

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SYNTHESIS AND NMR SPECTRAL STUDIES OF 2e,6e-DIAROYL-3e,5e-DIARYL -1,4-DITHIANE-1,1-DIOXIDES

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The synthesis of some 2,6-diaroyl-3,5-diaryl-1,4-dithiane-1,1-dioxides was carried out by the conjugate addition of hydrogen sulphide to 2,2′-sulphonylbis(1,3-diarylprop-2-en-1-ones) and the complete assignment of their ^{1}H and ^{13}C NMR chemical shifts made. The stereochemistry is found to be 2e,6e-diaroyl-3e,5e-diaryl-1,4-dithiane-1,1-dioxides from the NMR spectral data.

Keywords: 2e,6e-diaroyl-3e,5e-diaryl-1,4-dilhiane-1,1-dioxides; hydrogen sulphide; 2,2′-sulphonylbis(1,3-diarylprop-2-en-1-ones); NMR spectra; stereochemistry

INTRODUCTION

Though the 1,4-dithiane system has been extensively investigated, perusal of the literature reveals that there are only a very few reports on 1,4-dithiane-1,1-dioxides. Except for the synthesis and the spectral studies on 3,5-disubstituted-1,4-dithiane-1,1-dioxides [1–6] and a report on the use of the system in the extraction of gold[7], there is no work reported on the system. This lack of interest in this system which has the potential to be biologically active coupled with our interest in the synthesis and stereochemistry of new heterocycles prompted us to develop a method for the synthesis of 2,3,5,6-tetrasubstituted-1,4-dithiane-1,1-dioxides.

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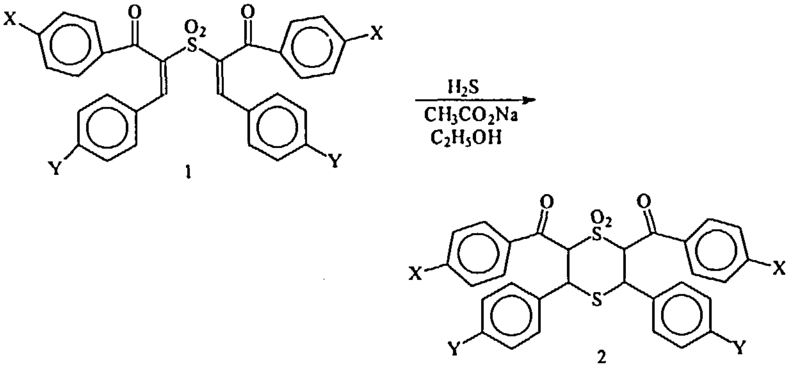
The presence of both sulfide and sulfone functions in the same heterocycle system requires the use of Michael addition of hydrogen sulfide to bis-styryl sulfone. The bis-styryl sulfones employed here are 2,2′-sulfonylbis(1,3-diarylprop-2-en-1-ones) obtained by the oxidation of the corresponding 2,2′-thiobis(1,3-diarylprop-2-en-1-ones)[8].

RESULTS AND DISCUSSION

In the present work, hydrogen sulfide was passed through a refluxing solution of **1** and NaOAc in EtOH for 30 min. The solid separated upon workup afforded 2,6-diaroyl-3,5-diaryl-1,4-dithiane-1,1-dioxides (Scheme 1).



1 and 2	X	Y
a	H	H
b	H	Cl
c	Cl	Cl
d	Cl	CH_3
e	CH_3	H

SCHEME 1

In all the cases the reaction goes to completion affording only **2**. The yield, m.p. and the elemental analyses for **2a-2e** are furnished in Table I. The yields of **2** given are after recrystallisation of the solids that separated from the reaction mixture. Analysis of the filtrate also showed only **2**.

TABLE I Physical data of compounds (2a-2e)

Comp.	*Yield (%)*	*m.p.*[a] *°C*	*Found (%)*		*Calcd(%)*	
			C	*H*	*C*	*H*
2a	73	301–4	70.35	4.65	70.31	4.69
2b	67	295–8	61.89	3.82	61.96	3.79
2c	67	300–3	55.45	3.13	55.38	3.07
2d	65	307–9	63.00	4.24	63.05	4.27
2e	92	296–9	71.20	5.15	71.11	5.19

[a] Decomposition takes place.

The absence of formation of any other stereoisomer in this reaction was concluded by monitoring the reaction from the initial stages to completion as well as by conducting the reaction in the absence of sodium acetate at refluxing and at room temperatures. This shows that **2** with all equatorial orientation (*vide infra*) is kinetically as well as thermodynamically controlled.

The ^{1}H and ^{13}C NMR spectral data of the compounds are presented in Tables II and III respectively. The stereochemical assignment of these compounds was deduced from the spectral data as discussed below for a representative case (**2a**).

TABLE II PMR ($CDCl_3$) Spectral data of compounds (2a-2e)

Comp.	*X*	*Y*	*H-2,6*	*H-3,5*	*Aroyl*			*Aryl*			*Others*
					H-2′,6′	*H-3′,5′*	*H-4′*	*H-2″,6″*	*H-3″,5″*	*H-4″*	
2a	H	H	6.80	5.18	8.06	7.54	7.67	7.38	7.23	7.16	-
2b	H	Cl	6.79	5.23	8.06	7.56	7.68	7.42	7.32	-	
2c	Cl	Cl	6.78	5.22	8.07	7.66	-	7.34	7.39	-	-
2d	Cl	Me	6.76	5.11	8.07	7.65	-	7.23	7.09	-	2.14
2e	Me	H	6.74	5.15	7.97	7.39	-	7.37	7.22	-	2.27

The ^{1}H NMR spectrum of **2a** showed two doublets for the ring hydrogens apart from the aromatic signals between 7.16–8.06 ppm. The doublet at 5.18 ppm is assigned to C-3,5 hydrogens and the doublet at 6.80 pm is assigned C-2,6 hydrogens. These assignments are also supported by the nuclear Overhauser enchancements observed for the *ortho*-hydrogens of benzoyl (11%) and phenyl ring (4.5%) of **2a** upon irradiation of the doublet of H-2,6 at 6.80 ppm. Similar irradiation of the doublet of H-3,5 in **2a-2e** resulted in 2 – 4.5% enhancement of the intensity of the *ortho*-hydrogens of the phenyl ring which in turn forms the basis for the unambiguous assignment of the aryl protons.

The coupling constant of the doublets (J=11 Hz) of H-2,6 and H-3,5 indicates diaxial orientation of these protons and hence all the four substituents are assigned equatorial orientation. All the other compounds also exhibited similar spectral features (Table II). Thus the compounds are identified as 2e, 6e-diaroyl-3e,5e-diaryl-1,4-dithiane-1,1-dioxides.

The ^{13}C chemical shifts of these compounds have been assigned by multiplicity, substituent induced chemical shift considerations and ^{1}H-^{13}C two-dimensional correlation spectral measurements for two representative compounds (**2a** and **2b**). That only one signal for the carbonyl carbon and two signals for the dithiane ring carbons (one for C-2,6 and one for C-3,5) have been obtained for all these compounds also supports the all equatorial configurational assignment.

EXPERIMENTAL

The melting points are uncorrected. NMR spectra were recorded at 20° C on a Bruker AMX 360 instrument operating at 360 MHz for ^{1}H and at 90 MHz for ^{13}C. Solutions (in $CDCl_3$) were approximately 0.05M and chemical shifts were referenced internally to TMS in all cases. Standard Bruker software (UXNMR) was used throughout.

^{13}C NMR spectra were recorded with ^{1}H-decoupling (waltz-16) and by the DEPT-135 technique to establish the number of attached protons. Nuclear Overhauser enchancements (NOE) were determined by the difference method using low intensity pre-saturation pulses of 5s before each acquisition pulse. A sequence of 8 scans with selected irradiation followed by 8 scans with irradiation at a nearby blank position was repeated 12 times. The summed irradiated and blank free-induction decays were subtracted and transformed to give the difference spectra, and quantitative enchancements were taken from integral values, using TMS as internal standard and DMSO-d_6 as solvent. Approximately 0.05 M solutions of these compounds were used except for **2e** wherein a lower concentration was employed due to solubility considerations.

TABLE III CMR (DMSO-d_6) Spectral data of compounds (**2a-2e**)

Comp.	*C-2,6*	*C-3,5*	*Aroyl*					*Aryl*				*Others*
			C-1′	*C-2′,6′*	*C-3′,5′*	*C-4′*	*C=O*	*C-1″*	*C-2″,6″*	*C-3″,5″*	*C-4″*	
2a	69.5	49.7	137.2	129.3[a]	129.4[a]	135.1	189.7	136.2	128.6	129.3[a]	129.1[a]	-
2b	69.4	48.9	137.1	129.4	129.4	135.3	189.5	133.7	130.4	129.4	135.1	-
2c	69.5	48.7	135.4	131.3	129.8	141.1	188.5	133.7	130.3	129.8	134.9	-
2d	69.6	49.2	135.8	131.2	129.7[a]	140.4	188.7	133.1	128.4	129,9[a]	138.6	21.0, 21.3
2e	69.3	49.6	134.9	129.6	128.6	146.0	188.9	136.3	129.9	129.3	129.0	21.6, 22.0

[a] These assignments may be reversed.

2e,6e-Diaroyl-3e,5e-diaryl-1,4-dithiane-1, 1-dioxides (2a-2e): A typical procedure

To a refluxing ethanolic solution of 2,2′-sulphonylbis(1,3-diphenylprop-2-en-1-one) (0.005 mole) and anhydrous sodium acetate (1g), a stream of hydrogen sulphide was passed for 30 min. The reaction mixture was cooled to room temperature, the solid separated was filtered, washed successively with water and ether to give 2e,6e-dibenzoyl-3e,5e-diphenyl-1,4-dithiane-1,1-dioxide (2a) which crystallised from dioxane.

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