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## CONDENSATION OF SOME AROMATIC ALDEHYDES WITH DIMETHYL SULFONE

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Condensation of some aromatic aldehydes with dimethyl sulfone using sodium amide has been studied. Majority of the aldehydes afforded *cis*-2,6-diaryl-1,4-oxathian-4,4-dioxides as the exclusive product. 4-Methoxybenzaldehyde, in addition, provided the bis  $\alpha,\beta$ -unsaturated sulfone as the major product while 4-nitrobenzaldehyde yielded only the Tischenko product by self-condensation. The products have been characterised by elemental analysis and spectral data.

**Key words:** Condensation, aromatic aldehydes, dimethyl sulfone, sodium amide, 2,6-diaryl-1,4-oxathian-4,4-dioxides, stereochemistry.

### CLARIFICATION FOR REFEREE'S COMMENTS

The  $^1\text{H}$  NMR spectra of 2,6-diaryl-1,4-oxathian-4,4-dioxides reveal that the methylene and methine protons constitute an ABX pattern. But only for compound **3c**, all eight peaks of AB part can be recognised. Analysis of the ABX system gave the *J* values,  $J_{\text{AX}}$  and  $J_{\text{BX}}$ . Such analysis, though not rigorous, is good approximation. Though such an analysis is not possible for other 2,6-diaryl-1,4-oxathian-4,4-dioxides (since all eight peaks of AB are not clearly recognisable), the large  $W_{1/2}$  of  $\text{C}_2$  &  $\text{C}_6$  protons ( $\sim 18$  Hz) inescapably indicates the axial nature of protons and hence the *cis* orientation of aryl groups.

### INTRODUCTION

The condensation of aromatic aldehydes with carbonyl compounds has been thoroughly studied and frequently employed synthetically. In contrast, a search of literature reveals that such condensations with sulfones have received little attention despite the extensive work carried out on carbanions produced from sulfones.<sup>1</sup> Russell, Becker and Schoeb<sup>2</sup> reported the condensation of 4-methoxybenzaldehyde with dimethyl sulfone in the presence of potassium *t*-butoxide. The reaction of aromatic aldehydes other than 4-methoxybenzaldehyde is conspicuously absent in the literature. Moreover, this reaction is also of interest as a potential synthetic method for 2,6-diaryl-1,4-oxathian-4,4-dioxides. It is pertinent to note that the chemistry of 2,6-diaryl-1,4-oxathian-4,4-dioxides is almost unexplored.<sup>3</sup> Herein we report the condensation of a few aromatic aldehydes with dimethyl sulfone.

## RESULTS

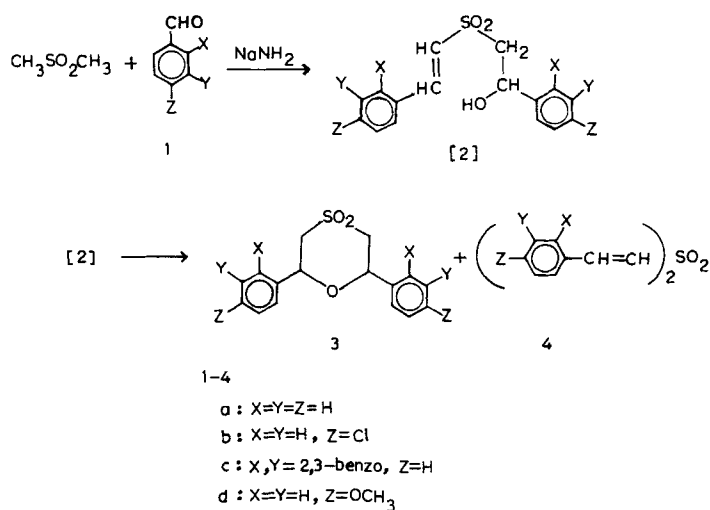
The reaction of aromatic aldehydes with dimethyl sulfone in the presence of sodium hydroxide yielded resinous product which could not be identified as reported earlier.<sup>4</sup> However, we have found that the condensation is successful when sodium amide is used as the base.

A mixture of dimethyl sulfone (20 mmole) and sodium amide (25 mmole) in dry DMF (20 mL) was stirred for 3 h. The aldehyde (40 mmole) in dry DMF (10 mL) was added dropwise with stirring and the reaction mixture was kept overnight. It was worked out by pouring the reaction mixture into ice-water. The results are presented in Table I.

TABLE I  
Condensation products of aromatic aldehydes with dimethyl sulfone

Entry	Aldehydes	Products	Yield %
1	Benzaldehyde	2,6-Diphenyl-1,4-oxathian-4,4-dioxide	63
4	4-Chlorobenzaldehyde	2,6-Di-4-chlorophenyl-1,4-oxathian-4,4-dioxide	50
3	1-Naphthaldehyde	2,6-Di-1-naphthyl-1,4-oxathian-4,4-dioxide	62
4	4-Methoxybenzaldehyde	i) 2,6-Di-4-methoxyphenyl-1,4-oxathian-4,4-dioxide ii) Bis-(4-methoxy- $\beta$ -styryl)-sulfone	30 60
5	4-Nitrobenzaldehyde	4-Nitrophenylmethyl 4-nitrobenzoate	55
6	4-Methylbenzaldehyde	Resinous product	—

The reaction appears to proceed through the pathway (Scheme 1) suggested by Russell *et al.*<sup>2</sup>



SCHEME 1

A glance at Table I shows that 4-methoxybenzaldehyde **1d** yielded a mixture of products, 2,6-di-4-methoxyphenyl-1,4-oxathian-4,4-dioxide **3d** and bis (4-methoxy- $\beta$ -styryl) sulfone **4d** as reported earlier.<sup>2</sup> In contrast, benzaldehyde **1a**, 4-chlorobenzaldehyde **1b**, and 1-naphthaldehyde **1c** gave exclusively the 2,6-diaryl-1,4-oxathian-4,4-dioxides **3a**, **3b** and **3c** respectively.

The formation of a mixture of products during the condensation of 4-methoxybenzaldehyde may be attributed to the fact that the proposed intermediate (**2d**) prefers to undergo dehydration rather than conjugate addition as the electrophilicity of the  $\beta$ -carbon of the  $\alpha,\beta$ -unsaturated sulfone (**2d**) is less compared to that of **2a–2c** because of the presence of mesomerically electron releasing methoxyl group at para position.

4-Methylbenzaldehyde produced only a resinous product probably due to the generation of the carbanion from the methyl group of 4-methylbenzaldehyde complicating the course of the reaction. The behaviour of 4-nitrobenzaldehyde is entirely different. It did not undergo condensation with dimethyl sulfone at all. However, it produced 4-nitrophenylmethyl 4-nitrobenzoate by Tischenko reaction.

Attempts to isolate the intermediates such as  $\text{ArCH}=\text{CHSO}_2\text{CH}_3$  did not succeed. Use of excess of base, sodium amide, did not change the nature of the products contrary to the observations of Russell *et al.*<sup>2</sup>

The products obtained have been characterised by elemental analysis,  $^1\text{H}$  NMR and IR spectra.  $^1\text{H}$  NMR has also revealed that the two aryl groups have *cis* relationship with respect to each other in 2,6-diaryl-1,4-oxathian-4,4-dioxides. The  $\text{C}_2$  and  $\text{C}_6$  hydrogens appear as an ill-resolved doublet of doublet due to second order effects. The coupling constants for these protons have been deduced as,  $J = 2\text{ Hz}$ ,  $10\text{ Hz}$  for **3c**. For other oxathianes including **3c**, the large  $W_{1/2}$  of  $\text{C}_2$  and  $\text{C}_6$  protons ( $\sim 18\text{ Hz}$ ) indicates the *cis* orientation of the aryl groups.

## EXPERIMENTAL

Melting points are uncorrected.  $^1\text{H}$  NMR spectra were measured in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard on a R32 Perkin–Elmer instrument (90 MHz). IR spectra were recorded on Perkin–Elmer-577 instrument.

*General procedure for the condensation of aromatic aldehydes with dimethyl sulfone.* Sodium amide (25 mmole) was added to a solution of dimethyl sulfone (20 mmole) in dry DMF (20 mL) and stirred well for 3 h. A solution of the aromatic aldehyde (40 mmole) in dry DMF (10 mL) was added dropwise. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 24 h and then poured into ice-water. The separated solid was extracted repeatedly with ether. The combined ether extracts, after profuse washings with water were dried over anhydrous sodium sulfate and evaporated to give the desired product as a white solid.

*Condensation of benzaldehyde with dimethyl sulfone.* The solid product obtained as described in the general procedure on recrystallisation from ethyl alcohol gave *cis*-2,6-diphenyl-1,4-oxathian-4,4-dioxide (**3a**); m.p.  $147\text{--}9^\circ\text{C}$  (lit.<sup>3</sup> mp  $153\text{--}4^\circ\text{C}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.1–3.35 (m, 4H,  $\text{CH}_2$ ), 5.1–5.3 (dd, 2H, CH), 7.3–7.6 (m, 10 H, Ar–H); IR (KBr)  $1300, 1130\text{ cm}^{-1}$ , Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$ : C, 66.66; H, 5.55 Found: C, 66.52, H, 5.43.

*Condensation of 4-chlorobenzaldehyde with dimethyl sulfone.* The solid obtained as described in the general procedure on recrystallisation from ethyl alcohol yielded *cis*-2,6-di-4-chlorophenyl-1,4-oxathian-4,4-dioxide (**3b**); mp  $173\text{--}5^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.1–3.4 (m, 4H,  $\text{CH}_2$ ), 5.1–5.3

(dd, 2H, CH), 7.25–7.5 (m, 8H, Ar-H); IR (KBr) 1300, 1125  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_3\text{S}$ : C, 53.78; H, 3.92. Found: C, 53.81; H, 3.78.

**Condensation of 1-naphthaldehyde with dimethyl sulfone.** The product isolated as described in the general method on recrystallisation from ethyl alcohol gave *cis*-2,6-di-1-naphthyl-1,4-oxathian-4,4-dioxide (**3c**) mp 166–7°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.2–3.8 (m, 4H,  $\text{CH}_2$ ), 6.0–6.2 (dd, 2H, CH), 7.25–8.2 (m, 14H, Ar-H); IR (KBr) 1295, 1130  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{O}_3\text{S}$ : C, 74.23; H, 5.15. Found: C, 74.10; H, 5.06.

**Condensation of 4-methoxybenzaldehyde with dimethyl sulfone.** The reaction was conducted as described in the general method. During working-up the reaction mixture by pouring into ice-water, an ether-insoluble compound was obtained along with the usual ether-soluble product. The ether-soluble product was isolated as described above and recrystallised from ethyl alcohol to yield *cis*-2,6-di-4-methoxyphenyl-1,4-oxathian-4,4-dioxide (**3d**); mp 108–10°C. (lit.<sup>2</sup> mp 117–9°C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.1–3.3 (d, 4H,  $\text{CH}_2$ ), 3.8 (s, 6H,  $\text{OCH}_3$ ), 5.0–5.2 (t, 2H, CH), 6.8–7.5 (m, 8H, Ar-H); IR (KBr) 1300, 1125  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{O}_5\text{S}$ : C, 62.07; H, 5.75. Found: C, 62.01; H, 5.65.

The ether insoluble product on recrystallisation from ethyl alcohol-chloroform mixture gave bis(4-methoxy- $\beta$ -styryl) sulfone (**4d**); mp 158–60°C (lit.<sup>2</sup> mp. 158–60°C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.85 (s, 6H,  $\text{OCH}_3$ ), 6.7 (d, 2H,  $=\text{CHSO}_2$ ,  $J = 16$  Hz), 7.6 (d, 2H, Ar—CH=,  $J = 16$  Hz), 6.85–7.6 (m, 8H, Ar—H); IR (KBr) 1290, 1120  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_3\text{S}$ : C, 74.23; H, 5.15. Found: C, 74.10; H, 5.06.

**Condensation of 4-nitrobenzaldehyde with dimethyl sulfone.** The solid obtained as described in the general procedure on recrystallisation from ethyl alcohol-chloroform mixture gave 4-nitrophenylmethyl 4-nitrobenzoate; mp 157–9°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 5.5 (s, 2H, O— $\text{CH}_2$ —Ar), 7, 4–8.5 (m, 8H, Ar-H); IR (KBr) 1720, 1510, 1340  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_6$ : C, 55.63; H, 3.31. Found: C, 55.5; H, 3.10.

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