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Research Article

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Synthesis and characterisation of some isomeric unsaturated (E)- and (Z)-sulfide-sulfones and bis-sulfones

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ABSTRACT

A pair of (E)- and (Z)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methylphenyl)sulfonyl] ethylenes were synthesised by the nucleophilic displacement of halogens with sodium salt of p-methylbenzenethiol from corresponding halo compounds. Oxidation of these two (E) and (Z)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methylphenyl)sulfonyl] ethylene gave the corresponding pair of (E)- and (Z)-1,2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methylphenyl)-2-phenyl ethylenes. The structures of these compounds were confirmed by IR, ^{1}H NMR and MASS spectral analysis.

Keywords: (*E*)- and (*Z*)-isomers, Sulfide-Sulfones; Disulfones.

INTRODUCTION

Biological studies carried out on vinyl sulfonyl compounds[1], mercapto halo ethylene sulfone derivatives[2] and bis(organosulfonyl)ethylenes[3, 4] revealed that they can be used as effective fungicides to protect seeds. The biological activities of these compounds depend mainly on their stereo chemical configurations (*cis* and *trans*) and their substituents present in them. Further more vinyl sulfones have been known for their synthetic utility in organic chemistry, easily participating in 1,4-addition reactions. This functional group has also recently been shown to potently inhibit a variety of enzymatic processes, providing unique properties for drug design and medicinal chemistry[5]. Divinyl sulfones and hydroxydiethyl sulfones are used to give crease-resistant finishes, while other sulfones are used as fuel additives and antibacterial agents , plasticizers,agiculture and anti-icing additives[6-9]. The most common method employed for the preparation of unsaturated disulfones is by the nucleophilic displacement[8,10] of halogens with thiols from halo ethylene sulfone derivatives. The present note describes the preparation of a mixture (*E*) - and (*Z*)-1-(4-methylphenyl)-2-phenyl-1-(4-methyl phenyl)thio ethylenes and its conversion in to (*E*)– and (*Z*)-1,2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methylphenyl)-2-phenyl ethylenes. Although some reports'[11-18] have appeared on the synthesis of cis and trans sulphide-sulfones and di sulfones, the data available is scanty.

EXPERIMENTAL SECTION

Melting points were determined in open capillaries on Mel-Temp apparatus, Laboratory devices, Cambridge, U.S.A and are uncorrected. IR spectra were recorded using KBr pellets on Perkin-Elmer SPECTRUM 100 FT-IR spectrophotometer. ^{1}HNMR spectra were recorded at 400 MHz on a BRUKER-400 spectrometer and their chemical shifts are reported in δ ppm with respect to TMS as an internal standard. Mass spectra were recorded on Micro Mass ESI-TOF Mass Spectrometer.

(*E*)- and (*Z*) -2-[(4-methylphenyl)]-1-phenyl-1-[(4-methylphenyl)thio]ethylenes (1)
A solution of 18.63 g (0.15 moles) of p-methylbenzenethiol and 12.6 g (0.06moles) of phenyl *p*-methylbenzyl ketone in dichloromethane (150 ml) was taken in a 500 ml conical flask fitted with an air condenser protected with a calcium chloride guard tube. The solution was stirred with a magnetic stirrer at room temperature and 3 g (0.023moles) of anhydrous aluminium chloride was added in small portions over a period of 15 minutes. The reaction mixture turned turbid as the reaction proceeds. After the addition, the mixture was further stirred for another 45 minutes and was then poured into 100 ml of water. The resulting mixture was extracted with 150 ml of dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was evaporated to give light yellow oil which solidified on cooling weighed 22.1 g. The solid was subjected to recrystallization in 95% ethanol.

(*E*)– and (*Z*)– 2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylenes (2a & **2b)**
About 7.91 g (0.025 moles) of a mixture of (*E*)-and (*Z*)-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylene **(1)** was dissolved in 150 ml of glacial acetic acid and the solution was taken in a 500 ml conical flask fitted with a magnetic stirrer. The stirrer was set in motion and a solution of 4 g (0.025 moles) of bromine in 25 ml of glacial acetic acid was added drop wise. During addition decolourisation was observed with immediate precipitation. The addition took about 15 minutes and stirring was continued for an additional thirty minutes. The solid separated was filtered to yield 6g (60.7%) of (*Z*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylene **(2b).** It was purified by recrystallisation from 95% ethanol to give an analytical sample, m.p. 114-116°C.

Anal. calcd. for $C_{22}H_{19}BrS$**:** C, 66.83; H, 4.84; S, 8.11; Found: C, 66.65; H, 4.66; S, 8.02.; ν^{KBr} 1073 (S-aryl); 1628 (C=C); 2919 (C-H); 3021 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.18 (s, 3H, -CH_3), 2.22 (s, 3H, -CH_3), 6.9-7.3 (m, 13H, Ar-H). MS (70eV): m/z: 315, 192.

The filtrate from the above reaction mixture after separating the (*Z*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylene **(2b),** on dilution with water gave 2.17g (22%) of (*E*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylene **(2a),** as solid. This was purified from 95% ethanol to give an analytical sample, m.p.86-90° C.

Anal. calcd. for $C_{22}H_{19}BrS$**:** C, 66.83; H, 4.84; S, 8.11.; Found: C, 66.66; H, 4.72; S, 7.98; ν^{KBr} 1073 (S-aryl); 1673 (C=C); 2919 (C-H); 3021 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.15 (s, 3H, -CH_3), 2.2 (s, 3H, -CH_3), 6.9-7.5 (m, 13H, Ar-H). MS (70eV): m/z: 315, 192.

(*E*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylene (3a)
In a 250 ml round-bottomed flask fitted with a reflux condenser a solution of 1.97 g (0.005 moles) of (*E*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylene **(2a)** in 75 ml of acetic acid was taken. The solution was heated to boiling and 25 ml of 30% hydrogen peroxide was added and the solution was refluxed for two hours. The product separated on cooling was collected by filtration, yield 1.91 g (90%). Recrystallisation of the product from 95% ethanol gave an analytical sample of (*E*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylene **(3a),** m.p. 62-65°C.

Anal. calcd. for $C_{22}H_{19}Br\ O_2S$**:** C, 61.83; H, 4.48; S, 7.50; Found: C, 61.61; H, 4.39; S, 7.36.; ν^{KBr} 1084 (S-aryl); 1316, 1145 (SO_2-aryl); 1638 (C=C); 2920 (C-H); 3128 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.35 (s, 3H, -CH_3), 2.45 (s, 3H, -CH_3), 6.8-8.0 (m, 13H, Ar-H). MS (70eV): m/z: 271.

(*E*)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methylphenyl)sulfonyl] ethylene (4a).
To a hot solution of 1.06 g (0.0025 moles) of (*E*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylene **(3a)** in 40 ml of absolute ethanol taken in a 100 ml round-bottomed flask fitted with a reflux condenser protected with a calcium chloride guard tube, a solution of sodium 4-methylbenzenethiolate prepared from 60 mg (2.5 mg atom) of sodium, 10 ml of absolute ethanol and 0.31 g (0.0025 moles) of 4-methylbenzenethiol was added. The mixture was refluxed for 7 hours. The colourless product separated on cooling was collected by filtration on a buchner to yield 0.81 g (70%) of (*E*)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methyl phenyl)sulfonyl] ethylene **(4a).** Recrystallisation of the product from 95% ethanol gave an analytical sample, m.p. 132-134°C.

Anal. calcd. for $C_{29}H_{26}O_2S_2$**:** C, 74.01; H, 5.57; S, 13.63; Found: C, 73.86; H, 5.42; S, 13.49.; ν^{KBr} 1086 (S-aryl); 1300, 1142 (SO_2-aryl); 1638 (C=C); 2920 (C-H); 3130 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.15 (s, 3H, -CH_3), 2.2 (s, 6H, -2CH_3), 6.7-7.9 (m, 17H, Ar-H). MS (70eV): m/z: 315.

(*E*)-1,2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methylphenyl)-2-phenyl ethylene (5a)
A solution of 0.47 g (0.001moles) of (*E*)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methylphenyl)sulfonyl] ethylene **(4a)** in 30 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and added 8 ml of 30% hydrogen peroxide. The solution was refluxed for one hour and the colourless crystals separated on cooling were collected by filtration to yield 0.449 g (89.5%) of (*E*)-1,2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methylphenyl)-2-phenyl ethylene **(5a).** It was recrystallised from 95% ethanol to give an analytical sample, m.p. 190-194° C.

Anal. calcd. for $C_{29}H_{26}O_4S_2$**:** C, 69.30; H, 5.21; S, 12.76; Found: C, 69.17; H, 5.11; S, 12.68; ν^{KBr} 1080 (S-aryl); 1285, 1180 (SO_2-aryl); 1685 (C=C); 2918 (C-H); 3090 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.2 (s, 3H, $-CH_3$), 2.25 (s, 6H, $-2CH_3$), 7.3-8.0 (m, 17H, Ar-H). MS (70eV): m/z: 503(M^++1), 347, 192, 139, 119.

(*Z*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylene (3b).
A solution of 5.93 g (0.015 moles) of (*Z*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylene **(2b)** in 200 ml of acetic acid was taken in a 500 ml round bottomed flask fitted with a reflux condenser. The solution was heated to boiling and 60 ml of 30% hydrogen peroxide was added and heated under reflux for two hours. The product separated on cooling was collected by filtration to yield 5.43 g (84.8%) of (*Z*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylene **(3b)**. Recrystallisation of the product from 95% ethanol gave an analytical sample, m.p. 152-154°C.

Anal. calcd. for $C_{22}H_{19}Br\ O_2S$**:** C, 61.83; H, 4.48; S, 7.50; Found: C, 61.78; H, 4.40; S, 7.39; ν^{KBr} 1083 (S-aryl); 1315, 1145 (SO_2-aryl); 1620 (C=C); 2919 (C-H); 3057 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.2 (s, 3H, $-CH_3$), 2.45 (s, 3H, $-CH_3$), 6.9-7.8 (m, 13H, Ar-H). MS (70eV): m/z: 428(M^++2), 426 (M^+), 347, 271, 192.

(*Z*)-2-(4-methylphenyl)-2-[(4-methyl phenyl)thio]-1-phenyl-1-[(4-methylphenyl)sulfonyl] ethylene (4b).
About 1.24 g (0.01 moles) of 4-methylbenzenethiol was added to an ethanolic solution of sodium ethoxide prepared from 230 mg (10 mg atom) of sodium dissolved in 30 ml of absolute ethanol. This solution was then added to a hot solution of 4.27 g (0.01moles) of (*Z*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylene **(3b)** in 160 ml of absolute ethanol contained in a 500 ml round-bottomed flask fitted with a reflux condenser and protected with a calcium chloride guard tube. The mixture was heated under reflux for 6 hours. The colourless product separated on cooling was filtered to yield 3.4 g (72.3%) of (*Z*)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylene **(4b).** On recrystallisation of the product from 95% ethanol gave an analytical sample, m.p. 156-158°C.

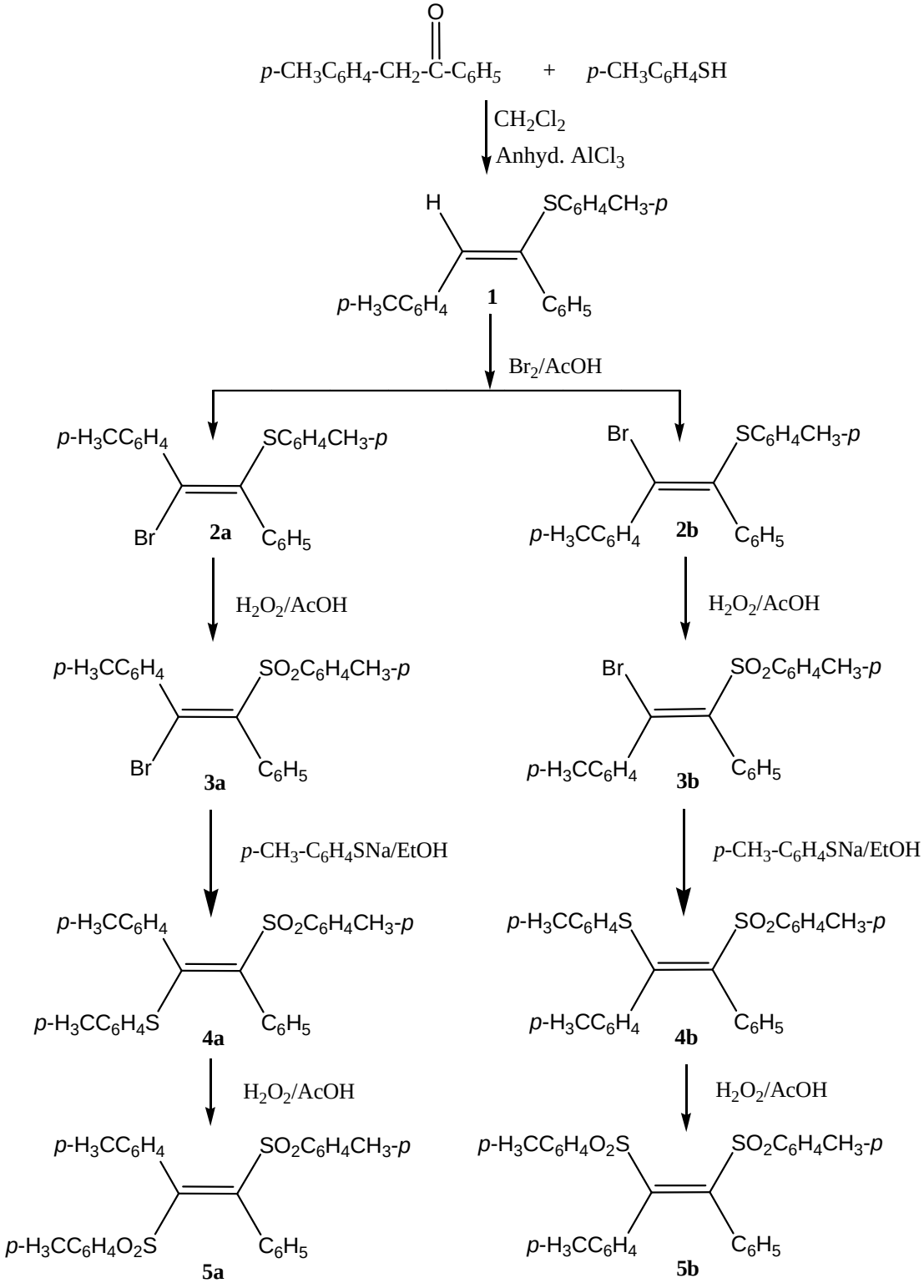
Anal. calcd. for $C_{29}H_{26}O_2S_2$**:** C, 74.01; H, 5.57; S, 13.63; Found: C, 73.92; H, 5.42; S, 13.55; ν^{KBr} 1083 (S-aryl); 1300, 1139 (SO_2-aryl); 1626 (C=C); 2849, 2917 (C-H); 3030 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.2 (s, 9H, $-3CH_3$), 6.55-7.9 (m, 17H, Ar-H). MS (70eV): m/z: 471(M^++1), 315.

(*Z*)-1,2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methylphenyl)-2-phenyl ethylene (5b).
A solution of 0.94 g (0.002moles) of (*Z*)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methylphenyl)sulfonyl] ethylene **(4b)** in 50 ml of glacial acetic acid was taken in 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and added 8 ml of 30% hydrogen peroxide. The solution was refluxed for one hour and the colourless crystals separated on cooling were collected by filtration to yield 0.79 g (79.3%) of (*Z*)-1,2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methylphenyl)-2-phenyl ethylene **(5b).** It was recrystallised from 95% ethanol to give crystalline solid, m.p. 175-177°C.

Anal. calcd. for $C_{29}H_{26}O_4S_2$**:** C, 69.30; H, 5.21; S, 12.76; Found: C, 69.19; H, 5.15; S, 12.59.; ν^{KBr} 1084 (S-aryl); 1308, 1150 (SO_2-aryl); 1632 (C=C); 2850, 2918 (C-H); 3025, 3062 cm^{-1} (Ar-H). ^{1}HNMR ($CDCl_3$, 400 MHz): 2.4 (s, 9H, $-3CH_3$), 6.7-7.7 (m, 17H, Ar-H). MS (70eV): m/z: 503(M^++1), 347, 283, 192, 139, 119, 105.

RESULTS AND DISCUSSION

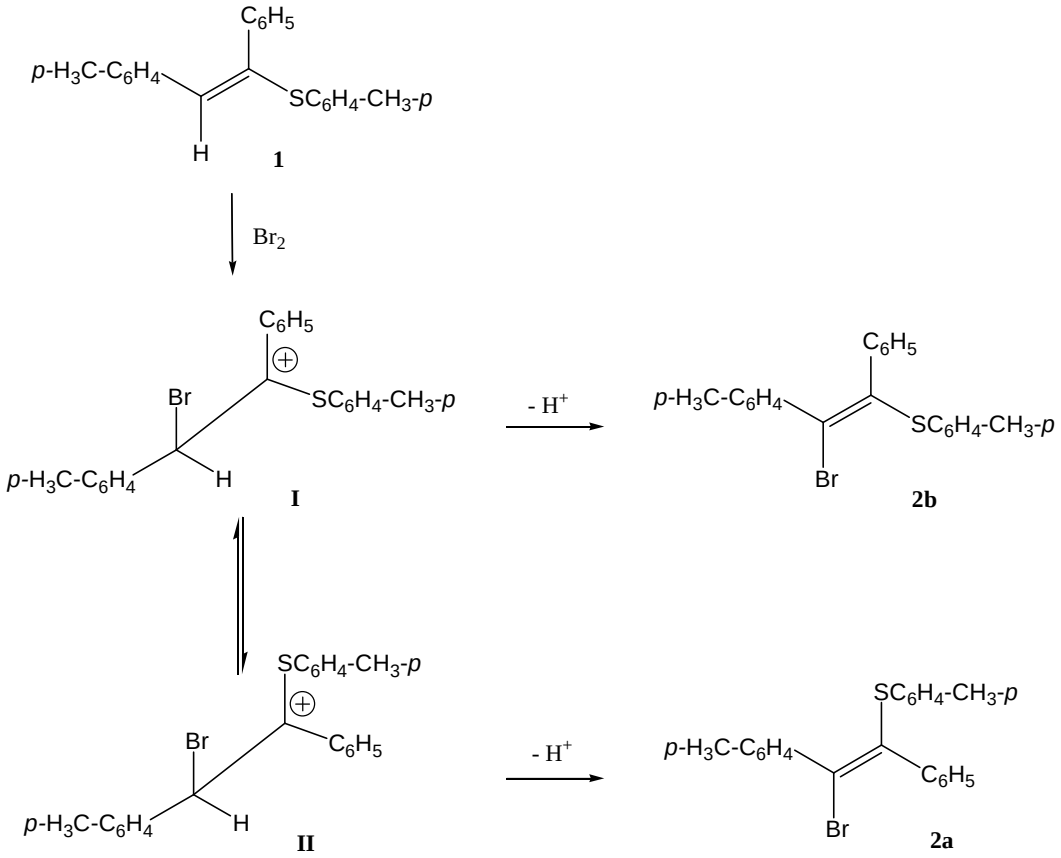
Phenyl *p*-methylbenzyl ketone[15] and *p*-methylbenzenethiol in dichloromethane led to the formation of a mixture of (*E*)- and (*Z*) -2-[(4-methylphenyl)]-1-phenyl-1-[(4-methylphenyl)thio]ethylenes **(1)**. Compounds (*E*)- and (*Z*)-1,2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methyl phenyl)-2-phenyl ethylenes were prepared **(5a** & **5b)** starting from (*E*)– and (*Z*)– 2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylenes **(2a** & **2b) (Scheme-1)** which in turn are obtained by the bromination of (*E*)- and (*Z*) -2-[(4-methylphenyl)]-1-phenyl-1-[(4-methylphenyl)thio]ethylenes **(1)**.



SCHEME-1

Compounds (*E*)– and (*Z*)– 2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylenes **(2a** & **2b)** are probably formed via a carbonium ion intermediate **(I) (Scheme-2)**. Rotation of C-C bond in carbonium ion intermediate **(I)** may give rise to the carbonium ion intermediate **(II) (Scheme-2)**. However **I** is expected to be more stable than **II** due to steric factor of the bulkier *p*-$CH_3C_6H_5S$. Expulsion of a proton from **I** leads to the formation of

2b where as **II** leads to the formation of **2a**. Since the formation of **2b** involves the formation of a more stable carbonium ion, they were obtained in major proportion.



SCHEME-2

Oxidation of **2a** & **2b** afforded (*E*) - and (*Z*)-2-bromo-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylenes **(3a** & **3b)** respectively. Compounds **(3a** & **3b)** when heated with sodium salt of *p*-methylbenzenethiol, nucleophilic displacement of bromine occurred resulting in the formation of (*E*) - and (*Z*)-2-(4-methylphenyl)-2-[(4-methylphenyl)thio]-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylenes **(4a** & **4b)** with the retention of configuration[7-9]. Oxidation of **(4a** & **4b)** afforded (*E*) – and (*Z*)-1, 2-Bis[(4-methylphenyl)sulfonyl]-1-(4-methylphenyl)-2-phenyl ethylenes **(5a** & **5b)** respectively.

CONCLUSION

A new series of unsaturated Sulfide-Sulfones and Bis-Sulfones were prepared. The synthesized compounds with chemical structure may serve as a very promising basis for the development of effective antibacterial and antifungal agents.

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