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A new class of heterocyclic system, **3a-f**, has been synthesized by reacting diazomethane with 4-styryl-1,2,3-benzoxathiazine 2,2-dioxides **1a-f**. Diazomethane adds to the $>C=S$ group of these compounds.

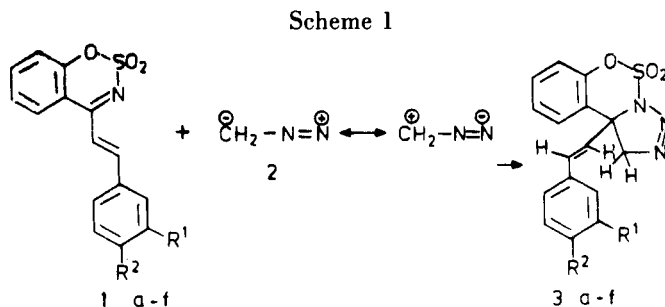
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Diazomethane is best represented as a resonance hybrid derived from linear resonating structures with opposing dipoles:



Under appropriate conditions diazomethane can behave either as an (i) electrophile (ii) nucleophile (iii) a 1,3-dipole or (iv) as a source of methylene. Thus diazomethane undergoes various reactions [1-4] depending upon reacting substrates. Compounds **1a-f** undergo smooth reaction with diazomethane in dichloromethane-ether mixture at room temperature, to furnish **3a-f** in 76-82% yield. The reaction is completed within a few minutes. The structures of the products were assigned unequivocally on the basis of spectral data. Thus, infrared absorption bands at 1380 and 1150 cm^{-1} indicate the presence of SO_2 group in these molecules. The mass spectrometric data clearly shows that only one molecule of diazomethane has been added up.

The pmr spectra show a quarter at δ 1.4 corresponding to two protons. The remaining protons show up as a complex multiplet in the aromatic region (δ 7.0-7.6). The methylene protons should have come around δ 3.0. An examination of the Drieding model shows that the two methylene protons lie in the shielding cone of the double bond and hence appear upfield at δ 1.4. Structure **3** is expected if the addition of diazomethane were to take place in the op-



- a: $\text{R}^1 = \text{R}^2 = \text{H}$
 b: $\text{R}^1 = \text{H}; \text{R}^2 = \text{Cl}$
 c: $\text{R}^1 = \text{H}; \text{R}^2 = \text{Br}$
 d: $\text{R}^1 = \text{H}; \text{R}^2 = \text{CH}_3$
 e: $\text{R}^1 = \text{H}; \text{R}^2 = \text{OCH}_3$
 f: $\text{R}^1 = \text{R}^2 = \text{OCH}_3$

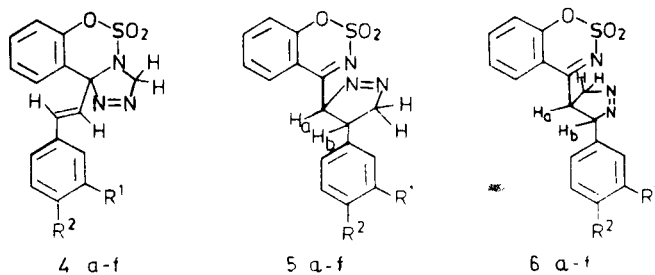


Table 1

Physical Properties of Compounds **3a-f**

Compound	R ¹	R ²	Yield (%)	MP (°C)	Molecular Formula	Calcd. %			Found %		
3a	H	H	82	150	C ₁₆ H ₁₃ N ₃ O ₃ S	58.71	3.97	12.84	58.78	3.84	12.93
3b	H	Cl	79	145	C ₁₆ H ₁₂ ClN ₃ O ₃ S	53.11	3.31	11.61	53.29	3.42	11.69
3c	H	Br	85	135	C ₁₆ H ₁₂ BrN ₃ O ₃ S	47.29	2.95	10.34	47.41	2.83	10.42
3d	H	CH ₃	76	140	C ₁₇ H ₁₅ N ₃ O ₃ S	59.82	4.39	12.31	59.91	4.50	12.49
3e	H	OCH ₃	78	150	C ₁₇ H ₁₅ N ₃ O ₄ S	57.14	4.20	11.76	57.29	4.08	11.81
3f	OCH ₃	OCH ₃	79	145	C ₁₈ H ₁₇ N ₃ O ₅ S	55.81	4.39	10.85	55.90	4.23	10.99

posite direction (*vide* Scheme-1). The pmr signals due to methylene protons, sandwiched between two nitrogen atoms (*vide* structure 4), should appear relatively at a lower field *i.e.* δ 5.0. The signal is actually observed at δ 1.4 and this, therefore, rules out the structure 4 for the cyclo-adduct. An addition of diazomethane across the C=C bond would give rise to two regio isomers 5 and 6. In structure 5 the benzyl protons should appear as a quartet at around δ 2.5. In structure 6 the benzyl protons should have appeared as a doublet $\sim \delta$ 5 in the pmr spectrum. Since these signals are lacking in the ^1H -nmr spectrum, therefore, the assignment of structures 5 and 6 to the cyclo-adducts is also ruled out.

Table 2
Spectroscopic Data of Compounds 3a-f

Compound	MS M ⁺ , m/z	IR (Potassium bromide) cm ⁻¹	^1NMR , ppm (Deuteriochloroform)
3a	327	2980, 1380, 1150	3.4 (q, 2H), 7.0-7.6 (m, 9H, + 2H)
3b	361	2975, 1385, 1165	1.6 (q, 2H), 7.1-7.7 (m, 8H, + 2H)
3c	406	2990, 1390, 1170	1.5 (q, 2H), 7.2-7.8 (m, 8H + 2H)
3d	341	2970, 1380, 1165	1.4 (q, 2H), 2.4 (s, 3H), 6.8-7.5 (m, 8H, + 2H)
3e	357	2980, 1380, 1170	1.5 (q, 2H), 3.7 (s, 3H), 6.8-7.4 (m, 8H + 2H)
3f	387	2985, 1385, 1175	1.5 (q, 2H), 3.7 (s, 3H), 3.8 (s, 3H), 7.1-7.8 (m, 7H + 2H)

EXPERIMENTAL

All melting points are uncorrected. The nmr spectra were recorded on a Varian EM-390 (90 MHz) instrument in deuteriochloroform using TMS as the internal standard. The ir spectra were measured on a Perkin-Elmer Model 580 spectrophotometer in potassium bromide. Diazomethane was generated *in situ* by the interaction of *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide with a base [5].

4-Styryl-1,2,3-benzoxathiazine 2,2-Dioxides 1a-f [6].

General Procedure.

Chlorosulphonyl isocyanate (4 ml, 0.046 mole) in toluene (5 ml) was added over a period of 20 minutes to a stirred solution of 2'-hydroxychalcone (0.046 mole) in toluene (40 ml) at 100-105°. Stirring was continued for 3 hours at this temperature. The toluene was distilled off *in vacuo* and the residue was added to cold water (50 ml). The solid thus obtained was filtered, washed with water and recrystallized from ethanol to yield the desired 4-styryl-1,2,3-benzoxathiazine 2,2-dioxides 1a-f.

Reaction of 4-Styryl-1,2,3-benzoxathiazine 2,2-Dioxides with Diazomethane.

Excess diazomethane was bubbled into a stirred solution of 1 (0.001 mole) in dichloromethane-ether mixture (1:1, 5 ml) at room temperature ($\sim 16^\circ$). The reaction mixture was allowed to stand for 30 minutes. The solvent was removed under reduced pressure. The silica gel chromatography of the residue, using benzene as an eluent, afforded the pure compound. The compounds prepared are listed in Table 1, 3a-f, along with their relevant data.

REFERENCES AND NOTES

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