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Note

Synthesis, structural and antimicrobial studies of some novel 1-(aroyl)-1-(arylsulphonyl)-2-[4-oxo-4*H*-1-benzopyran-3-yl]ethenes

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A series of new unsaturated ketosulphones, 1-(aroyl)-1-(arylsulphonyl)-2- [4-oxo-4*H*-1-benzopyran-3-yl]ethenes **3**, have been prepared by the condensation of pheacyl aryl sulphones with 3-formylchromones. The geometry of these compounds have been assigned by IR, ^{1}H NMR and mass spectral data. Their antimicrobial activity has also been studied.

In search of new antimicrobial agents, we have undertaken the synthesis of a series of new unsaturated ketosulphones[1]. As benzopyrans are of considerable biological importance, the introduction of benzopyran unit into α, β-unsaturated ketosulphones may stimulate the biological activity of the resultant compounds **3**. In connection with our current investigation on aroyl(cyclopropyl) sulphones with benzopyran moiety, we were also interested in preparing a series of unsaturated ketosulphones **3** as intermediates. The condensation of phenacyl aryl sulphones **2** with substituted 3-formylchromones **1** in acetic anhydride/gl. acetic acid in the presence of benzylamine as catalyst, yielded 1-(aroyl)-1-(arylsulphonyl)-2-[4-oxo-4*H*-1-benzopyran-3-yl]ethenes **3**. The physical and spectral data of these compounds are given in Table I.

The ^{1}H NMR spectra of **3** showed a signal in the region δ 7.80-8.00 (1H, s) for a vinylic proton. It is reported[2] that when the proton is *cis* to a sulphonyl group the chemical shift for vinylic proton occurs in the range δ 7.40-8.15. For similar type of compounds Uma[3] also reported the chemical shifts of the vinylic protons in the region 7.97-8.86. From this it may be inferred that in these compounds the vinylic protons may lie *cis* to sulphonyl group as shown in structure **3**. Baliah and Natarajan[4] assigned the same coinfiguration for similar type of compounds by dipole moment studies. The ^{1}H NMR spectra of **3** showed sharp singlets integrating for one proton in the region δ 8.00-8.69 characteristic of 2‴-H of chromone moiety. The chemical shift values of 2‴-H corroborate with the chemical shift values (8.20-9.00) reported[5] for 2-H of chromones in various chromone derivatives.

The mass spectrum of **3o** did not show any molecular ion (M^+). The major fragmentation of the molecular ion showed the loss of chlorobenzenesulphonyl radical [$C_6H_4ClSO_4$] with the formation of the cation, $C_{19}H_{12}ClO_4^+$, at m/z 339 (68%). This cation on further loss of neutral molecules, $C_{12}H_8O_3$ and CO, successively, gave the ions at m/z 139 (94%) $[ClC_6H_4CO]^+$ and 111 (100%) $[C_6H_4Cl]^+$, respectively.

Experimental Section

Melting points reported are uncorrected. IR spectra were recorded as KBr discs on a Perkin-Elmer Infrared 683 spectrometer, ^{1}H NMR spectra on a Bruker WH 300 or a Varian FT 80A (200 MHz, 80 MHz) instrument in $CDCl_3$/ $CDCl_3$ + d_6-DMSO using TMS as internal standard, and mass spectra on a CEC, 21-110B unit at 70 eV. Elemental analyses were performed at the University of Poona, Pune. 2′-Hydroxyacetophenones were prepared according to the procedure of Norris[6]. Benzopyrancarboxyaldehydes **1** were prepared by subjecting various *o*-hydroxyacetophenones to Vilsmeier-Haack reaction[7]. Phena-

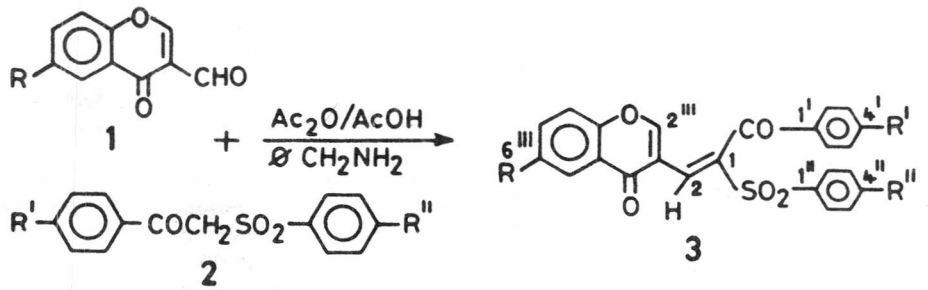

Table I—1-(aroyl)-1-(arylsulphonyl)-2-[4-oxo-4*H*-1-benzopyran-3-yl]ethenes **3**

Compd*	R	R′	R″	Yield (%)	m.p. (°C)	^{1}H NMR, δ (ppm) >C=CH–
3a	H	H	H	42	181-83	7.96
3b	H	NO_2	Br	18	234-36	—
3c	H	Cl	Cl	58	175-76	7.98
3d	H	CH_3	Cl	41	138-40	7.95
3e	Br	H	Cl	59	230-31	—
3f	Br	Cl	Cl	23	206-08	7.92
3g	Br	CH_3	Cl	60	231-33	7.95
3h	Br	NO_2	Cl	42	260-61	8.00
3i	Cl	H	Br	20	216-17	—
3j	Cl	H	Cl	58	221-22	—
3k	Cl	Cl	Cl	20	204-06	7.81
3l	Cl	NO_2	Cl	68	236-38	7.80
3m	Cl	NO_2	CH_3	38	250-51	8.00
3n	CH_3O	H	Cl	40	184-85	7.98
3o	CH_3O	Cl	Cl	31	195-96	7.92
3p	CH_3	H	H	41	204-06	7.98
3q	CH_3	H	Br	20	193-95	—
3r	CH_3	Cl	Br	37	205-06	7.93
3s	CH_3	NO_2	Br	20	236-37	—
3t	CH_3	CH_3	Cl	27	202-03	7.99
3u	CH_3	NO_2	CH_3	21	285-86	—

*Satisfactory chemical analyses were obtained: C ± 0.25; H ± 0.30.

cyl aryl sulphones[8] were prepared by the reaction of aryl sulphinates with phenacyl bromides.

1- (4-Chlorobenzoyl) -1- (4-chlorophenylsulphonyl) -2- [6-methoxy-4-oxo-4*H*-benzopyran-3-yl]ethane 3o (Table I). A mixture of 6-methoxy-4-oxo-4*H*-1-benzopyran-3-carboxaldehyde (2.05 g, 0.01 mole), 4-chlorophenacyl-4-chlorophenylsulphone (4.93 g, 0.01 mole) and benzylamine (0.2 mL) in acetic anhyride (25 mL) was heated on a water bath for 8 hr. The progress of the reaction was monitored by TLC. The product that separated on treatment of the reaction mixture with 50 mL of dry ether was recrystallised twice from gl. acetic acid, yielding 1.5 g (31%) of **3o** as colourless crystals, m.p. 195-97°.

This typical procedure was used for the preparation of other compounds **3a-u** (Table I).

Antimicrobial activity. The unsaturated ketosulphones **3a, c-j, l,n-r** and **t** were tested for their antibacterial activity *in vitro* against *S. aureus*, *B. subtillus* (gram +ve), *P. aeruginosa*, *E. coli* (gram −ve) and antifungal activity against *C. lunata*, *F. oxysporum* following the minimum inhibitory concentration[9] and Horsfall and Rich[10] methods, respectively, with slight modification. Compounds **3a, d, f, g, h, j** and **l** showed activity only against *B. subtillus* and *E. coli* while other compounds were inactive. As expected, chloro and bromo substituents on aromatic rings enhanced the antibacterial activity, and in general the compounds were more effective against *B. subtillus* compared to *E. coli*. However, all these unsaturated compounds potent antifungal activity.

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