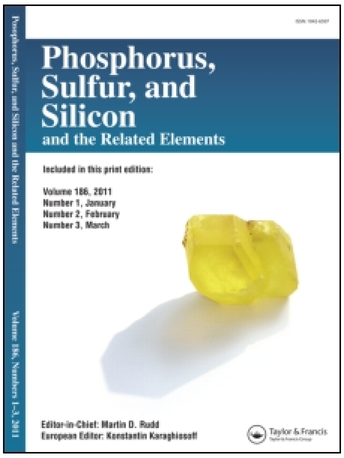

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CHLOROSULFONATION OF $\alpha\beta$-UNSATURATED ARYLIDENE KETONES

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CHLOROSULFONATION OF α,β-UNSATURATED ARYLIDENE KETONES

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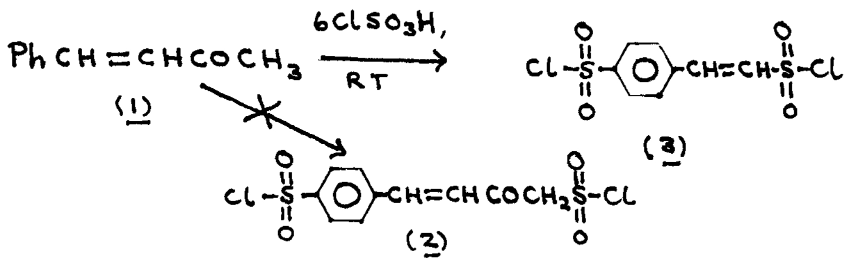
2-Thienylideneacetone (4), and the benzylidene derivatives of ethyl methyl ketone (19) and diethyl ketone (20) were reacted with excess chlorosulfonic acid to give the thienylidene 5,β-disulfonyl chloride (5) and the styrene disulfonyl chlorides (21 and 22). These were characterized by preparation of the sulfonamides (6–9, 23 and 24) required for screening as pest control agents. Benzylidene acetone (1) was condensed with aryl aldehydes to give the corresponding 1,5-diaryl-1,4-dien-3-ones (25–28), but the condensation failed with *p*-anisaldehyde and *o*-vanillin. Attempted chlorosulfonation of compounds (25 and 28) was unsuccessful and the products could not be characterised as sulfonamide derivatives. The ^{1}H NMR spectra of selected compounds are briefly discussed.

Key words: Chlorosulfonation of α,β-unsatured arylidene ketones; thienylidene 5,β-disulfonyl chloride; styrene disulfonyl chlorides

Previous work at Hatfield[1] demonstrated that dibenzylideneacetone reacted with a large excess of chlorosulfonic acid (10 molar equivalents) to give the 4,4′-bis-sulfonyl chloride (65%), but with less of the reagent (5 molar equivalents) a high yield (85%) of the monosulfonyl chloride was obtained. In contrast, we have shown[2,3] that benzylideneacetone (1) with excess chlorosulfonic acid did not afford the expected 4,ω-disulfonyl chloride (2), but rather styrene-4,β-disulfonyl chloride (3) (Scheme I).

The sulfonation of the terminal α-hydrogen of the methyl group in benzylidenacetone (1) would be anticipated from previous work[4] carried out on the sulfonation of acetophenone; indeed we proposed[2] that the mechanism for the conversion of (1) to (3) involves the formation of an intermediate containing the α-CH_2SO_2Cl moiety.

In view of these interesting results, we decided to examine the reaction of other αβ-unsaturated arylidene ketones with chlorosulfonic acid. 2-Thienylideneacetone (4) was prepared as previously described.[5] Treatment of 4 with excess chlorosul-



SCHEME I

fonic acid (8 molar equivalents) afforded the 5,β-disulfonyl chloride (5) in moderate yield (52%); the product was characterized as the sulfonamides (6–9) (Chart I).

The ^{1}H NMR spectrum of the dimethylsulfonamide (7) showed one AB splitting pattern in the aromatic region (δ 7.40, 7.25, J 3.2 Hz) indicative of coupling between the thiophene 3 and 4 protons hence implying 5-sulfonation. There was another AB pattern at δ 7.50, 6.50, J 15.3 Hz representing the two *trans* alkenic protons; the mass spectrum showed the molecular ion (M^+, 324). The reaction of thienylideneacetone (4) with less chlorosulfonic acid (4 molar equivalents) was investigated in our attempt to prepare the mono-sulphonyl chloride. After 5 days at room temperature, a product (24%) was obtained which was condensed with dimethylamine. TLC of the product showed two spots and the mass spectrum showed the molecular ion for both the mono- (M^+, 216) and the disulfonamide (7; M^+ 324). The ^{1}H NMR spectrum showed two AB splitting patterns for the *trans*-alkenic protons in an approximate ratio of 1:5. The microanalytical data was in reasonable agreement with this ratio of products (Found: C, 38.3; H, 5.0; N, 7.6. The disulfonamide (7) $C_{10}H_{16}N_2O_4S_3$ requires C, 37.0; H, 5.0; N, 8.6. The monosulfonamide (10), $C_8H_{11}NO_2S_2$ requires C, 44.2; H, 5.1; N, 6.45%).

The monosulfonamide could be either the structure (10) or (11) (Chart I); however the IR spectrum of the mixture did not show a carbonyl absorption band which suggests that sulfonation occurred preferentially in the side chain and therefore favours structure (10). Other attempts to obtain the mono-sulfonyl chloride by treatment of 4 with chlorosulfonic acid (2 molar equivalents) in thionyl chloride gave a black tar which did not yield a pure dimethylamide derivative.

Di-(2-thienylidene) acetone (12) was prepared by base-catalysed condensation of thiophen-2-carboxaldehyde with acetone as previously described.[6] The reaction of 12 with chlorosulfonic acid was examined under various conditions; the optimum

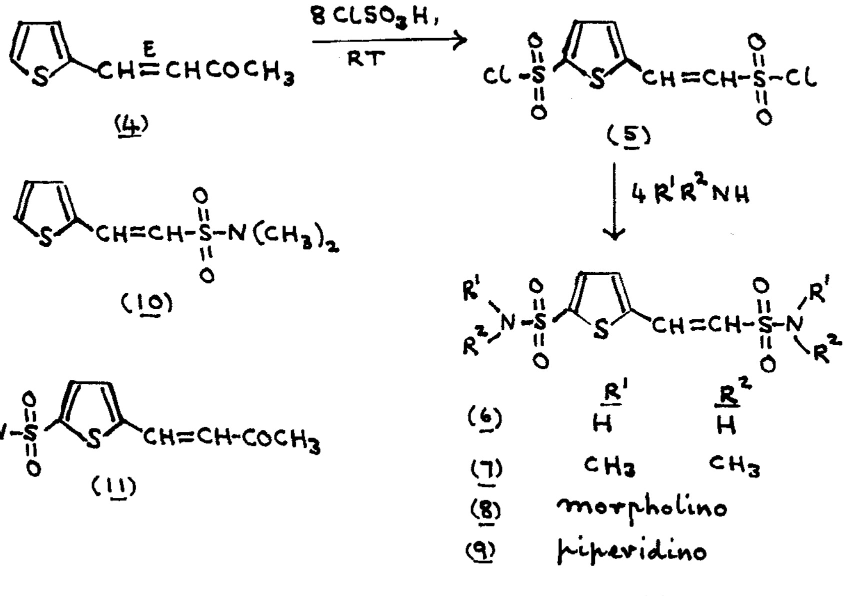


CHART I Sulfonyl derivatives of 2-thienylideneacetone (4).

yield (85%) of disulfonyl chloride (13) was obtained using a large excess of the reagent (12 molar equivalents) at room temperature (Chart II).

The initial reaction was strongly exothermic and the mixture was cooled in ice during addition of 12 to the acid, a deep red colour was produced indicative of formation of a delocalized carbocation (cf. Reference 1). The disulfonyl chloride (13) did not melt <300°C and the mass spectrum exhibited the molecular ion cluster (M^+, 446, 444, 442) indicating the presence of two chlorine atoms. The product (13) was characterised by formation of the sulfonamides (14–18) (Chart II).

The sulfonamides were purified by recrystallization from ethanol and their structures established by ^1H NMR spectroscopy. For example, the dimethylsulfonamide derivative (14) showed an aliphatic to aromatic and alkenic proton ratio of 3:2; the alkenic protons resonated in the aromatic region due to the combined deshielding effects of the carbonyl group and the π-electrons of the aromatic ring. The alkenic proton adjacent to the >C=O group appears as a doublet at the lower field (δ 7.8) while the other alkenic proton is at higher field (δ 6.8) as a result of the shielding effect of the hetero sulfur atom. The coupling constant between these protons was 15.8 Hz indicating the expected *trans* configuration. The aromatic protons resonated as double doublets (δ 7.5–7.3) with a coupling constant of 3.5 Hz in good agreement with the literature value[7] for the coupling constant between the thiophene 3 and 4 protons.

Attempts to obtain dithienylidenacetone monosulfonyl chloride by reaction of 12 with chlorosulfonic acid (5 molar equivalents) or 2 molar equivalents in thionyl chloride were unsuccessful. A black product (multiple spots on TLC) resulted and

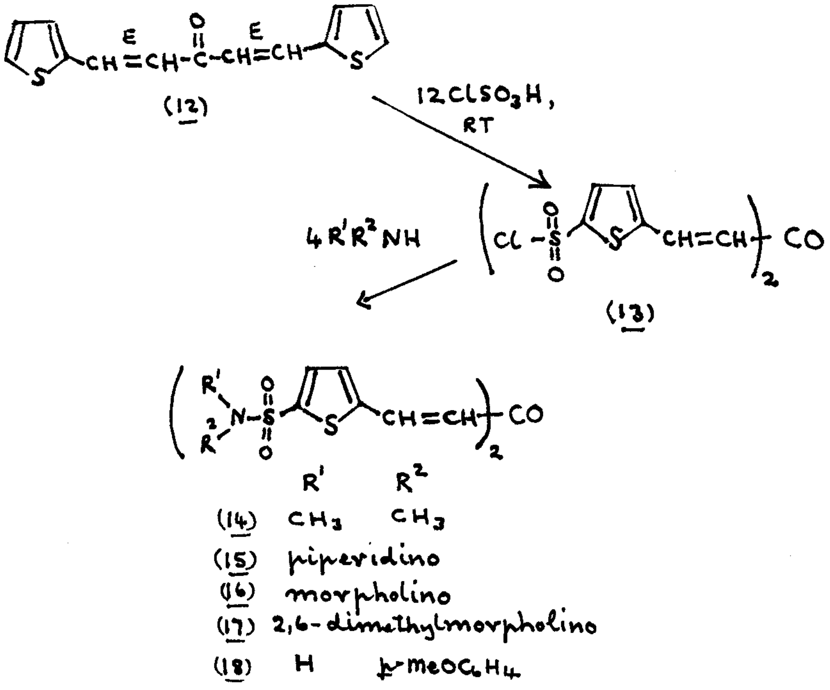


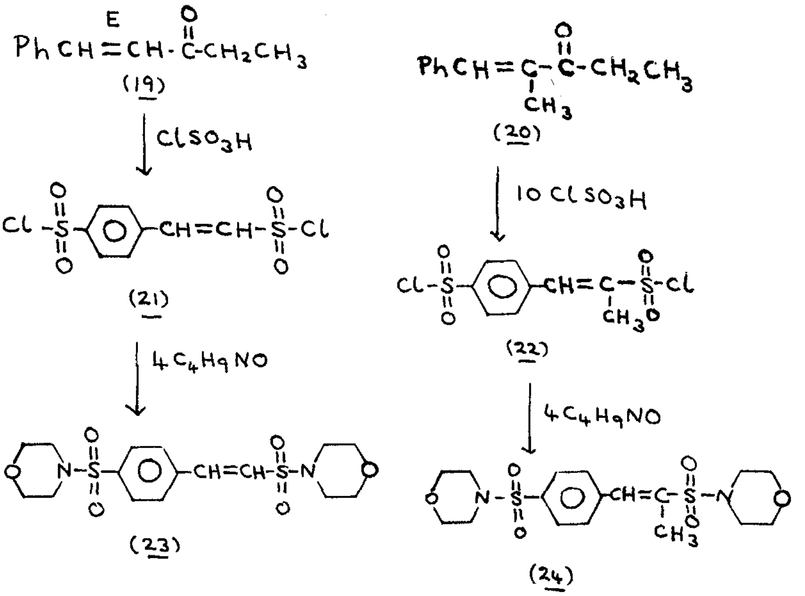
CHART II Sulfonyl derivatives of dithienylideneacetone (12).

this could not be purified by formation of the dimethyl sulfonamide derivative. This behaviour contrasts with the chlorosulfonation of dibenzylideneacetone[1] in which both the mono- and bis-sulfonyl derivatives were isolated. The failure to achieve monosulfonation is probably due to the presence of the more reactive thiophen nucleus not producing sufficient difference in the reactivity of the monosulfonyl chloride and the starting material (12) towards sulfonation.

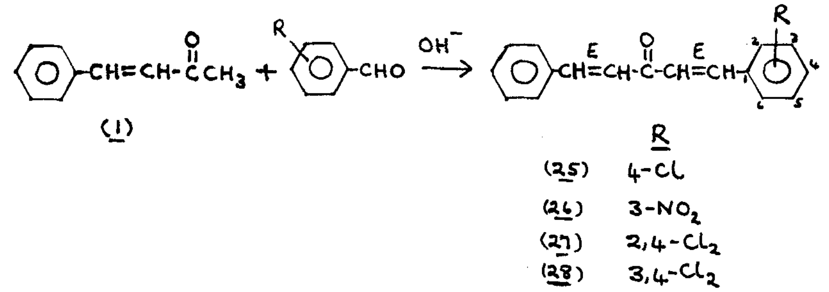
To examine the action of chlorosulfonic acid on some other monoarylidene ketones, the benzylidene derivatives of ethyl methyl ketone (19) and diethyl ketone (20) were prepared as previously described.[8,9] The thienylidene derivative of ethyl methyl ketone was obtained by the procedure[10] previously reported for the furan analogue.

In the reaction of diethyl ketone with benzylaldehyde, the formation of the mono benzylidene derivative (20) is favoured by the use of aqueous sodium hydroxide, whereas the use of ethanol as solvent increases the yield of the bis-benzylidene derivatives. Treatment of the benzylidene derivatives (19 and 20) with a large excess of chlorosulfonic acid (10 molar equivalents) in chloroform afforded the corresponding styrene bis-sulfonyl chlorides (21 and 22) respectively. The products were characterised by the preparation of the morpholidates (23, 24) (Scheme II).

The action of chlorosulfonic acid on benzylidene ethyl methyl ketone (19) gave styrene-4,β-disulfonyl chloride (21), the identical product to that previously obtained from analogous reactions with benzylideneacetone[2] and benzylidenepinacolone.[3] The identity was confirmed by preparation of the dimorpholidate derivative (23) for which the melting point and spectral data were in excellent agreement with those previously reported.[3]



SCHEME II Chlorosulfonation of the benzylidene derivatives of ethyl methyl ketone (19) and diethyl ketone (20).



SCHEME III Synthesis of 1,4-diarylpenta-1,4-dien-3-ones.

In the ^{1}H NMR spectrum of 23, the aromatic resonances showed the AA'BB' splitting pattern indicative of a *para*-disubstituted benzene and a doublet (δ 7.55, 7.34) with a coupling constant (*J*, 15.3 Hz) representing the *trans* alkenic protons.

The benzylidene derivative of diethyl ketone (20) (Scheme II), similarly afforded the corresponding styrene disulfonyl chloride (22) and the morpholidate (24). The mass spectrum of the latter compound showed the molecular ion (M^+, 416) and in the ^{1}H NMR spectrum, the aromatic resonances (δ 7.8–7.6) exhibited the AA'BB splitting pattern. There was an additional singlet (δ 2.1) for the methyl protons which was not present in the NMR spectrum of 23; furthermore the spectrum of compound (24) did not indicate the presence of the *trans*-alkenic protons.

Several 1,5-diarylpenta-1,4-dien-3-ones (25–28) (Scheme III) were prepared by base-catalysed condensation of benzylideneacetone (1) with the appropriate aryl aldehyde.

Attempts to condense *p*-anisaldehyde and *o*-vanillin with benzylideneacetone, under similar conditions (aqueous ethanolic sodium hydroxide) were unsuccessful and in neither case could pure products be isolated. The condensation, therefore, only appears to be successful when the aryl aldehyde contains electron-withdrawing substituents, probably because these increase the reactivity of the carbonyl group towards nucleophilic attack.

Treatment of the diarylidene ketones (25 and 28) with chlorosulfonic acid (10 molar equivalents, room temperature, 1 week) gave impure products which on subsequent treatment with amines failed to give pure sulfonamides.

It is difficult to understand the failure of these reactions, since the closely analogous chalcones have been successfully converted into the sulfonyl chlorides and sulfonamide derivatives.[11,12]

The various sulfonamide derivatives have been submitted for biological screening for herbicidal, fungicidal and insecticidal activity.

EXPERIMENTAL

Melting points were determined with a Gallenkamp electric apparatus and are uncorrected. The ^{1}H NMR spectra were recorded with a Bruker AC 250 spectrometer using tetramethylsilane as internal standard and deuterochloroform as solvent unless otherwise stated; resonances indicated by an asterisk were reduced by D_2O treatment. IR spectra were recorded as Nujol mulls using a Perkin Elmer 237 spectrophotometer. Mass spectra were determined with a VG micromass V15 spectrometer operating at 70 ev. TLC was carried out using Camlab silica gel plates sensitized to UV 254 nm and cyclohexane-ethyl acetate (2:1) as eluant unless otherwise stated.

2-Thienylidene-5,β-disulfonyl chloride (5). Chlorosulfonic acid (30.4g, 0.26 mole) was added dropwise to a stirred ice-cold solution of 2-thienylideneacetone (4) (5g, 0.033 mole) in chloroform (10 ml). The black solution was stirred at room temperature (1 week) and was then gradually added to ice-water (200 ml); the resultant dark-green sticky solid was extracted with chloroform (2 × 100 ml). The extract was washed with water (3 × 20 ml), dried ($MgSO_4$) and evaporated under vacuum; the residue was recrystallized from petroleum ether (60–80°C) to give (5) (52%), m.p. 94–95°C. TLC showed one spot, R_F 0.65 (Found: C, 23.8; H, 1.3. $C_6H_4Cl_2O_4S_3$ requires C, 23.5; H, 1.3%). IR: υmax 1600 (Ar C=C), 1360, 1170 (SO_2) cm^{-1}.

MS: 310, 308, 306 (M^+), 273, 271 (M^+-Cl), 209, 207 (M^+-SO_2Cl), 108 (M^+-2 × SO_2Cl).

General procedure for preparation of sulfonamides. The bis-sulfonyl chloride (0.005 mole) was added portionwise to a stirred ice-cold solution of the appropriate amine (0.03 mole) in methanol (30 ml). After 12 hours, the suspension was poured onto ice-water and the product filtered off and dried by suction. The solid was purified by recrystallization from methanol to give the sulfonamide.

2-Thienylidene-5,β-disulfonamide (6). (36%), m.p. 244–245°C. TLC showed one spot, R_F 0.36. (Found: C, 26.6; H, 3.1; N, 9.9, $C_6H_8N_2O_4S_3$ requires C, 26.9; H, 3.0; N, 10.4%). IR: υmax 3300, 3250 (NH_2), 1580 (Ar C=C), 1340, 1150 (SO_2) cm^{-1}.

MS: 268 (M^+), 252 (M^+-NH_2), 188 (M^+-SO_2NH_2), 108 (M^+-2 × SO_2NH_2).

The N,N-dimethylsulfonamide (7). (82%), m.p. 158–159°C. TLC showed one spot, R_F 0.62 (Found: C 36.9, H, 4.9; N, 8.8. $C_{10}H_{16}N_2O_4S_3$ requires C, 37.0; H, 5.0; N, 8.6%). IR: υmax 1600 (Ar C=C), 1350, 1140 (SO_2) cm^{-1}. NMR: δ 7.5–6.5 (m, 4H, ArH and alkenic H), 2.85 (s, 6H, NMe_2), 2.75 (s, 6H, NMe_2).

MS: 324 (M^+), 280 (M^+-NMe_2), 216 (M^+-SO_2NMe_2) 152 (M^+-SO_2NMe_2,SO_2), 108 (M^+-2 × SO_2NMe_2).

The morpholidate (8). (62%), m.p. 182°C. TLC showed one spot, R_F 0.47 (Found: C, 41.1; H, 5.0; N, 6.7. $C_{14}H_{20}H_2O_6S_3$ requires C, 41.2; H, 4.9; N, 6.9%). IR: υmax 1610 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. NMR δ 7.6–6.6 (m, 4H, ArH and alkenic H), 3.8–3.0 (m, 16H, morpholino H).

MS: 408 (M^+), 322 (M^+-C_4H_8NO), 258 (M^+-$SO_2C_6H_4NO$), 108 (M^+-2 × $SO_2C_6H_4NO$).

The piperidino derivative (9). (62%), m.p. 159–160°C. TLC showed one spot, R_F 0.65 (Found: C, 47.3; H, 6.0; N, 7.0. $C_{16}H_{24}N_2O_4S_3$ requires C, 47.5; H, 5.9; N, 6.9%). IR: υmax 1610 (Ar C=C), 1340, 1160 (SO_2) cm^{-1}. NMR: δ 7.8–6.8 (m, 4H, ArH, alkenic H), 3.2–3.0 (m, 8H, N-$C\underline{H}_2$), 1.8–1.4 (m, 12H, piperidino H).

Di-(2-Thienylidene) acetone-5,5′-disulfonyl chloride (13). Di-(2-Thienylidene) acetone (12) (5.0 g, 0.02 mol) was gradually added, with stirring to chlorosulfonic acid (29 g, 0.25 mole at 0°C). The solution was left for 1 week at room temperature and was then poured onto crushed ice (200 g). When all the ice had melted, the resultant precipitate was filtered off under suction, washed with ice-cold water (4 × 20 ml) and dried in a vacuum desiccator to give the disulfonyl chloride as a yellow solid (7.75 g, 85%), m.p. > 300°C. TLC showed one spot R_F 0.64. (Found: C, 34.9; H, 2.0. $C_{13}H_8Cl_2O_5S_4$ requires C, 35.2; H, 1.8%). IR: υmax 1720 (C=O), 1610 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}.

MS: 446, 444, 442 (M^+), 345, 343 (M^+-SO_2Cl), 246 (M^+-2 × SO_2Cl).

The dimethylamide derivative (14). (69%) brown crystals, m.p. 218–220°C (Found: C, 47.0; H, 4.8; N, 6.8. $C_{17}H_{20}N_2O_5S_4$ requires C, 47.4; H, 4.65; N, 6.5%). IR: υmax 1700 (C=O), 1610 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. ^1H NMR: δ 7.8–6.8 (m, 8H, ArH, alkenic H), 2.8 (s, 12H, NMe_2).

MS: 460 (M^+), 352 (M^+-SO_2NMe_2), 309 (M^+-SO_2NMe_2-NMe_2), 246 (M^+-2 × SO_2NMe_2), 217, 184, 162, 137, 109, 65, 57, 42.

The piperidino derivative (15). (64%) fawn solid, m.p. 250°C (Found: C, 51.4; H, 5.2; N, 5.3. $C_{23}H_{28}N_2O_5S_4$ requires C, 51.1; H, 5.1; N, 5.1%). ^1H NMR: δ 7.9–6.9 (m, 8H, ArH, alkenic H), 3.0 (s, 8H, N-$C\underline{H}_2$), 2.0–1.5 (m, 12H, piperidino H).

MS: 540 (M^+), 392 (M^+-$SO_2NC_5H_{10}$), 309 (M^+-$SO_2NC_5H_{10}$-NC_5H_{10}), 245 (M^+-2 × $SO_2NC_5H_{10}$), 151, 84, 64, 55, 42.

The morpholino compound (16). (47%) cream powder, m.p. 112–114°C. (Found: C, 46.1; 4.2; N, 5.4. $C_{21}H_{24}N_2O_7S_4$ requires C, 46.3; H, 4.4; N, 5.1%). ^1H NMR (DMSO-d_6): δ 7.8–6.9 (m, 8H, ArH, alkenic H), 3.9–3.5 (m, 4H, N-$C\underline{H}_2$), 3.0–2.5 (m, 4H, O-$C\underline{H}_2$).

MS: 544 (M^+), 394 (M^+-$SO_2C_4H_8NO$), 309, 245 (M^+-2 × $SO_2NC_4H_8NO$), 151, 86, 56, 42.

The 2,6-dimethylmorpholino compound (17). (36%), m.p. 125–126°C. (Found: C, 49.7; H, 5.2; N, 4.9. $C_{25}H_{32}N_2O_7S_4$ requires C, 50.0; H, 5.3; N, 4.7%). ^{1}H NMR (DMSO-d_6): δ 8.0–7.0 (m, 8H, ArH, alkenic H), 3.8–2.0 (m, 12H, morpholino H), 1.1 (s, 12H, Me).

MS: 600 (M^+), 423 (M^+-$SO_2C_6H_{12}NO$), 309, 245 (M^+-2 × $SO_2C_6H_{12}NO$), 215, 115, 71, 56.

The p-anisidino derivative (18). (58%) greenish crystals, m.p. 195°C. (Found: C, 52.5; H, 4.1; N, 4.8. $C_{27}H_{24}N_2O_7S_4$ requires C, 52.6; H, 3.9; N, 4.5%). IR: υmax 3225 (NH), 1700 (C=O), 1605 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 10.2* (s, 2H, NH), 7.9–6.9 (m, 16H, ArH, alkenic H), 3.8 (s, 6H, OMe).

MS: no M^+ ion at 616, but fragment ions at 536, 480, 430 (M^+-SO_2NH-C_6H_4OMe), 250 (M^+-2 × $SO_2NHC_6H_4OMe$), 203, 123 ($MeOC_6H_4NH_2$), 108, 80, 64, 48.

General procedure for chlorosulfonation of the benzylidene derivatives of ethyl methyl ketone (19) and diethyl ketone (20). The benzylidene ketone (0.025 mole) was dissolved in dry chloroform (50 ml) and cooled to 0°C. To this solution, chlorosulfonic acid (0.25 mole) was gradually added with stirring and the resulting brown solution was allowed to stand at room temperature for one week. The solution was poured onto crushed ice and the chloroform layer separated. The aqeuous layer was re-extracted with chloroform (2 × 30 ml) and the combined chloroform layer washed with 0.5 M aqueous sodium hydrogen carbonate solution (2 × 30 ml) and water (4 × 30 ml). The chloroform layer was evaporated under reduced pressure to give the crude sulfonyl chloride which was characterized by formation of the sulfonamides (23 and 24).

Compound (23). (41%), m.p. 255–257°C. (Found: C, 47.4; H, 5.5; N, 6.8. $C_{16}H_{22}N_2O_6S_2$ requires C, 47.7; H, 5.5; N, 7.0%). IR: υmax 1600 (Ar C=C), 1320, 1180 (SO_2) cm^{-1}. ^{1}H NMR (($CD_3)_2CO$): δ 8.02–7.82 (m, 4H, ArH, AA'BB' pattern), 7.55, 7.34 (d, 2H, alkenic H, J 15.3 Hz), 3.8–3.6 (m, 8H, CH_2-O), 3.20–3.0 (m, 8H, CH_2-N).

MS: 402 (M^+), 338 (M^+-SO_2).

Compound (24). (21%), m.p. 201–202°C. (Found: C, 48.8; H, 5.8; N, 6.5. $C_{17}H_{24}N_2S_2O_6$ requires C, 49.0; H, 5.8; N, 6.7%. IR: υmax 1610 (Ar C=C), 1350, 1160 (SO_2), 785 (ArC-H) bending, *p*-disubstituted). ^{1}H NMR (($CD_3)_2CO$): δ 7.8–7.6 (m, 5H, ArH, alkenic H, AA'BB' pattern), 3.8–3.7 (m, 8H, OCH_2), 3.3–3.0 (m, 8H, CH_2-N), 2.1 (s, 3H, CH_3).

MS: 416 (M^+), 352 (M^+-SO_2), 266 (M^+-$SO_2NC_4H_8O$), 86 (C_4H_8NO).

General procedure for the preparation of 1,5-diarylpenta-1,4-dien-3-ones. Sodium hydroxide (2.56 g, 0.064 mole) was dissolved in water (23 ml) and ethanol (14 ml) and the solution was cooled to approximately 20°C with vigorous stirring while benzylideneacetone (7.3 g, 0.05 mole) was added, followed by the appropriate aryl aldehyde (0.05 mole). During the addition the temperature of the mixture increased slowly but it was kept <30°C. After about 30 minutes, the temperature started to fall and a precipitate formed; the mixture was left for 3 hours, cooled and the solid filtered off with suction. The products were purified by recrystallization from ethanol to give the pentadienones (25–28):

Compound (25). (54%), m.p. 132–134°C. (Found: C, 76.1; H, 5.0. $C_{17}H_{13}ClO$ requires C, 76.0; H, 4.9%).

MS: 268 (M^+), 165 (M^+-PhCH=CH), 131 (M^+-ClC_6H_4CH=CH).

Compound (26). (95%), m.p. 123–125°C. (Found: C, 73.1; H, 4.9; N, 4.6. $C_{17}H_{13}NO_3$ requires C, 73.1; H, 4.7; N, 5.0%). ^{1}H NMR: δ 8.5–7.0 (m, 9H, ArH), 8.2, 7.83 (dd, 4H, alkenic H).

MS: 279 (M^+), 278 (M^+-H), 262 (M^+-OH), 232 (M^+-NO_2).

Compound (27). (32%), m.p. 153–156°C. (Found: C, 67.5; H, 4.2. $C_{17}H_{12}Cl_2O$ requires C, 67.3; H, 4.0%).

MS: 302 (M^+), 301 (M^+-H), 267 (M^+-Cl), 199 (M^+-PhCH=CH), 171 (M^+-PhCH=CHCO).

Compound (28). (27%), m.p. 135–138°C. (Found: C, 66.8; H, 4.1. $C_{17}H_{12}Cl_2O$ requires C, 67.3; H, 4.0%). ^{1}H NMR: δ 7.8–7.2 (m, 8H, ArH), 7.08, 7.0 (dd, 4H, alkenic H).

MS: 302 (M^+), 274 (M^+-CO), 267 (M^+-Cl), 238 (M^+-CO, -HCl), 204 (M^+-CO, −2Cl), 199 (M^+-PhCH=CH).

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