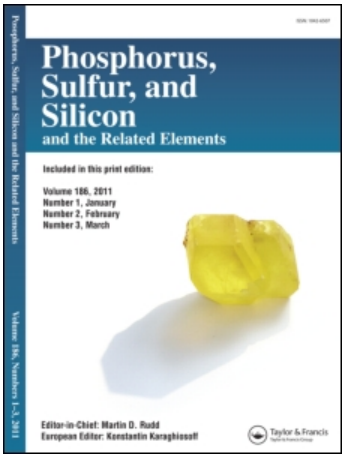

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A NOVEL REACTION OF BENZALACETONE WITH CHLOROSULFONIC ACID

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SHORT COMMUNICATION
A Novel Reaction of Benzalacetone with Chlorosulfonic Acid

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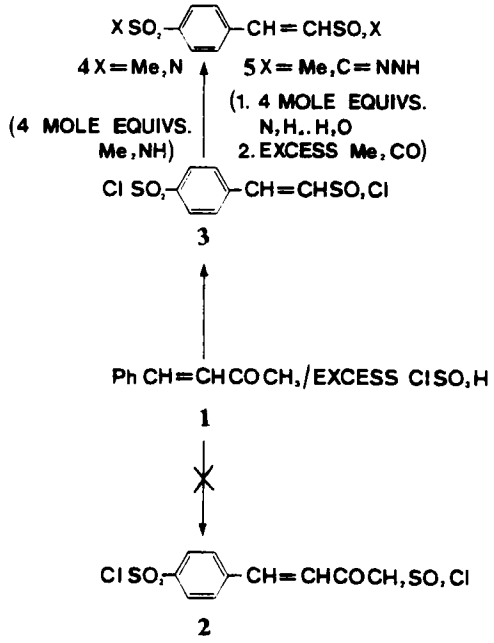
Benzalacetone **1** with an excess of chlorosulfonic acid did not give the expected 4,ω-disulfonyl dichloride **2**, but 4,β-dichlorosulfonylstyrene **3**, which was identified by microanalytical and spectral data, and characterised as the bis-N,N-dimethylsulfonamide **4** and the bis-acetone hydrazone **5**. A mechanism for the conversion of **1** into **3** is proposed.

Chlorosulfonation provides a useful route to a variety of sulfonyl derivatives by nucleophilic displacement of the chlorine atom in the resulting sulfonyl chloride. These compounds are of interest, as they have potential biocidal activity.[1–6] As part of our program concerned with the synthesis and biocidal evaluation of sulfonyl compounds, we are investigating the chlorosulfonation of ketones.[7–10] We now report the investigation of the reaction with benzalacetone.

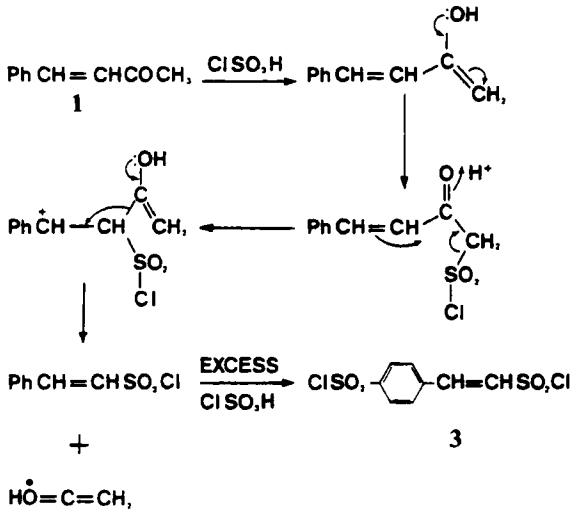
The product from the reaction of benzalacetone **1** (Scheme 1) with a large excess of chlorosulfonic acid, was identified by microanalytical and spectral data. The mass spectrum showed the molecular ion with two chlorine atoms present. The ^{1}H NMR spectrum indicated the absence of saturated C—H, *para*-substitution in the phenyl ring (AA′BB′ pattern), and the presence of an E-alkenyl group (AB pattern, J = 15.5 Hz). The structure of the product could therefore be assigned as **3**. The identity of **3** was confirmed by the reaction with dimethylamine to give the corresponding bis-*N*,*N*-dimethylsulfonamide **4**, and the bis-acetone hydrazone **5**. The ^{1}H NMR spectrum of **4** was similar to that of **3**, but in addition it contained the resonance signals due to the NMe_2 groups. However, $CHCl_3$-d was required as solvent in order to remove the accidental equivalence of the alkene hydrogen chemical shifts when the spectrum was determined in Me_2SO-d_6. Further confirmation was obtained from the ^{13}C NMR spectrum of **4**, which showed the presence of six chemical shifts. Two of these were due to the quaternary carbon atoms, and the remainder to the tertiary carbon atoms, on the basis of off-resonance decoupling and signal intensity. The ^{1}H NMR spectrum of **5** was also similar to that of **3**, but it contained in addition the resonance signals due to the NH and CMe_2 groups.

Weston and Suter[11] claimed that acetophenone with an excess of chlorosulfonic acid gave the 2,ω-disulfonyl dichloride. Enolisation would allow substitution both in the ring and in the side-chain. In the case of benzalacetone **1**, ring substitution almost certainly occurs without the direct intervention of the side-chain. However, electrophilic attack is expected at the *para* position, because of the directing influence of the π electrons of the alkenic side-chain. A similar result was observed with dibenzylideneacetone,[9] with chalcone[10] in the more activated ring, and with



SCHEME 1

cinnamic acid.[12] However, unlike **1** these compounds do not yield products involving attack on the side-chain. The reaction with the side-chain in **1** can be interpreted in terms of enolisation, followed by ω-chlorosulfonation and elimination of ketene (Scheme 2). The results with dibenzylideneacetone and chalcone are probably to be expected, particularly in view of steric factors. In the reaction with cinnamic acid, the oxygen analog of the enol of **1**, the absence of a similar reaction could be due to



SCHEME 2

initial protonation. This would cause deactivation to direct electrophilic attack and reduce the possibility of an interaction such as that proposed with **1**. It is likely that side-chain substitution precedes ring substitution with **1**, due to the additional activation provided by the styryl group.

EXPERIMENTAL

The melting points are corrected. IR spectra were determined with a Perkin-Elmer 257 spectrophotometer. NMR spectra were recorded with a Bruker WP80 spectrometer, using tetramethylsilane as internal reference standard. Mass spectra were obtained with a VG Micromass V15 instrument. Microanalyses were by courtesy of Kodak Ltd., Harrow.

Benzalacetone **1** was prepared by the method of Vogel.[13]

4,β-Dichlorosulfonylstyrene **3**. Benzalacetone (4.96 g, 0.034 moles) in chloroform (50 ml) was cooled to −5°. Chlorosulfonic acid (39.6 g, 0.34 moles) was added dropwise with stirring. The reaction mixture was allowed to warm gradually to room temperature and then stirred for a week. It was added slowly to ice-water and the resulting sticky solid was extracted with chloroform (200 ml). The chloroform extract was dried ($MgSO_4$) and the solvent was removed by rotary film evaporation to give 7.8 g (94%) of a brown solid. Recrystallisation from methanol gave the product **3**, m.p. 147–149°; IR (KBr) ν_{max} 1610 (C=C stretch), 1390–1360, 1200–1160 (SO_2 stretch), 800 (out-of-plane bending, *para*-disubstitution) cm^{-1}; ^1H NMR ($CHCl_3$-d) δ 7.20–8.40 (AA'BB', 4 H, aromatic protons; AB, J = 15.5 Hz, E-CH=CH); MS m/z 300, 302, 304 (M^+ 18%, 12%, 2%), 265 (M—^{35}Cl, 56%), 267 (M—^{37}Cl, 19%), 201 (265-SO_2, 64%), 203 (267-SO_2, 21%), 102 (201-SO_2Cl, 203-SO_2Cl, 50%), 76 (102-HC≡CH, 20%).

Anal. Calcd. for $C_8H_6Cl_2O_4S_2$: C, 31.89; H, 1.99; Cl, 23.59; S, 21.26. Found: C, 31.87; H, 1.97; Cl, 23.42; S, 21.26.

Bis-4,β-N,N-dimethylsulfonamidostyrene **4**. A solution of **3** (3.01 g, 0.01 moles) in acetone (20 ml) was cooled to 0°. Dimethylamine (40% aq. solution, 2.25 g, 0.02 moles) was added dropwise with stirring, followed by triethylamine (2.02 g, 0.02 moles). The reaction mixture was allowed to warm to room temperature and then stirred for a week. It was poured into ice-water (200 ml). The product was isolated by vacuum filtration, and recrystallised from methanol to give **4**, 0.83 g (26%), m.p. 208–210°; IR (KBr) ν_{max} 1620 (C=C stretch), 1350–1320, 1190–1150 (SO_2 stretch), 795 (out-of-plane bending, *para*-disubstitution) cm^{-1}; ^1H NMR ($CHCl_3$-d) δ 7.70–7.95 (AA'BB', 4 H, aromatic protons; AB J = 15.5 Hz, E-CH=CH), 2.75, 2.88 (12 H, SO_2NMe_2); ^{13}C NMR ($CHCl_3$-d) δ 140.9 (C_β), 137.1, 138.0 (C1,4), 128.6, 128.8 (C2,3,5,6), 124.6 (C_α), 37.6, 37.9 (NMe_2); MS m/z 318 (M^+ 14%), 254 (M—SO_2, 87%), 211 (254-MeN=CH_2, 20%), 146 (254-Me_2NSO_2, 87%), 102 (146-Me_2N, 56%), 76 (102-HC≡CH, 31%), 44 (NMe_2, 100%).

Anal. Calcd. for $C_{12}H_{18}N_2O_4S_2$: C, 45.28; H, 5.66; N, 8.81; S, 20.13. Found: C, 45.34; H, 5.91; N, 8.61; S, 19.80.

Bis-4,β-propylidenehydrazinosulfonylstyrene **5**. A solution of the bis-hydrazide (0.7 g, 0.24 mmoles) in acetone (8 ml) was stirred at room temperature for 10 minutes, and decolorising charcoal (0.1 g) was added. The reaction mixture was warmed for 5 minutes, filtered, and the solvent removed by rotary film evaporation to give an orange solid. Recrystallisation from methanol gave **5** as a beige solid 0.3 g, (34%), m.p. 180–183°; IR (KBr) ν_{max} 1620 (C=C stretch), 1350–1320, 1190–1150 (SO_2 stretch), 800 (out-of-plane bending, *para*-disubstitution) cm^{-1}; ^1H NMR ($CHCl_3$-d) δ 9.40, 9.60 (2 H, SO_2NH, exchanged with H_2O-d), 6.90–8.10 (AA'BB', 4 H, aromatic protons; AB, J = 15.5 Hz, E-CH=CH), 1.87, 1.93, 2.00 (12 H, Me_2NSO_2); MS m/z 56 (N=CMe_2, 50%).

Anal. Calcd. for $C_{14}H_{20}N_4O_4S_2$: C, 45.16; H, 5.37; N, 15.05. Found: C, 45.12; H, 5.11; N, 14.56.

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