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Aspects of tautomerism. Part 16. Influence of the γ-keto function on the reactions of sulphonic acids

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Abstract. Reaction of sodium 2-formylbenzenesulphonate (1) with thionyl chloride or phosphorous pentachloride gives a mixture of pseudo (2) and normal (3) sulphonyl chlorides. Whereas ammonium 2-carboxybenzenesulphonate (6) gives only the normal sulphonyl chloride (7) on reaction with thionyl chloride, a mixture of normal (7) and pseudo (8) isomers are formed on reaction with phosphorous pentachloride. Sodium 2-benzoylbenzenesulphonate (15), on the other hand, gives the corresponding normal sulphonyl chloride (16) on reaction with both of the reagents mentioned above. Based on these observations it is concluded that γ-keto sulphonic acids are amenable to the influence of γ-carbonyl group as in the case of γ-keto carboxylic acids but to a lesser extent.

Keywords. Ring–chain tautomerism; neighbouring group effect; neighbouring group participation.

1. Introduction

It is customary in classical organic chemistry to discuss the properties of compounds in terms of their functional groups. In a multifunctional molecule, the properties of a particular functional group are affected by other functional groups present. Such changes have been described in terms of electronic, steric and field effects. Quantitative work carried out in the last fifty years or so has resulted in a fairly adequate description of these effects. When two or more functional groups are in close proximity, certain complex reactivity patterns – not displayed by the individual groups themselves – are observed. Not only are there quantitative changes of reactivity, but more often they are of a qualitative nature. A part of such reactivity patterns are referred to as neighbouring group participation. There exists a large body of observations wherein a functional group influences the reactivity patterns of its neighbour by mechanisms other than neighbouring group participation. We have designated these broader patterns of interaction of neighbouring groups as "neighbouring group effects". In the previous papers of this series, changes in reactivity patterns of a carboxylic acid derivative due to the presence of a neighbouring carbonyl group were studied.

The reactions of keto carboxylic acids with reagents like thionyl chloride, oxalyl chloride, phosphorous pentachloride etc. give rise to pseudo acid chloride and/or

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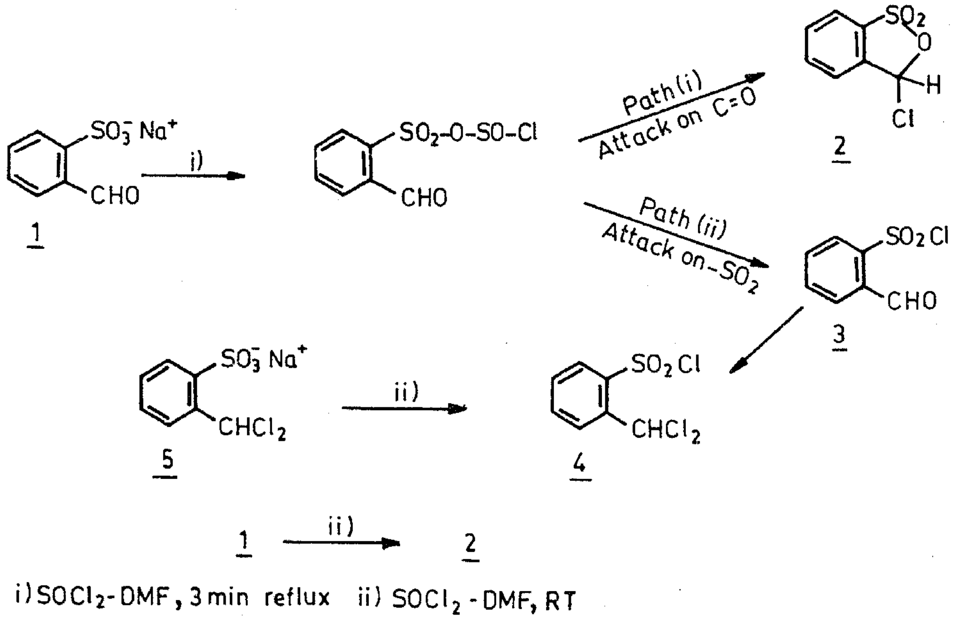
normal acid chlorides. Their formation from γ-keto carboxylic acids is fairly well understood. From a survey of available literature of γ-keto carboxylic acid chlorides, we have concluded (Bhatt *et al* 1980) that γ-keto acids, as a rule, give exclusively pseudo acid chlorides irrespective of the reagent used. There are very few exceptions to this rule. However, the situation with regard to γ-keto sulphonic acids is not defined. In the present paper we have examined this question and also the broader issue of change in the reactivity pattern of the sulphonic acid function, brought about by the presence of a carbonyl group in its neighbourhood.

2. Results and discussion

Reaction of sodium 2-formylbenzenesulphonate 1 with thionyl chloride and ambient temperature gave 3-chlorobenzoxathiole-1,1-dioxide 2 as the only product. However, when 1 was refluxed with thionyl chloride in the presence of dimethylformamide for three minutes, a mixture of 2-formylbenzenesulphonyl chloride 3 and its pseudo isomer 2 was formed in the ratio 4:7, along with 2-dichloromethylbenzenesulphonyl chloride 4 (use of longer reaction times, 1 h, gives 2 and 4 only). This is contrary to the earlier report (King *et al* 1971) that exclusively 3 is formed under the same reaction conditions. Formation of the pseudo sulphonyl chloride 2 in larger proportion must be due to the preference of path (i) over that of path (ii) (scheme 1).



Scheme 1.

When the normal sulphonyl chloride 3 was heated to 150–160° in a vacuum sealed tube, it was converted to the pseudo isomer 2. But 2 and 3 are stable and are not interconvertible at ambient temperature. That they do not display tautomerism is shown by their infrared and nuclear magnetic resonance spectra (see experimental section) which do not change.

Furthermore, the normal sulphonyl chloride 3 remained unaffected when stirred with thionyl chloride in the presence of dimethylformamide at ambient temperature. But when the reaction mixture was refluxed, the dichloride 4 was obtained. Also, 2 was not affected by thionyl chloride in the presence of dimethylformamide either at ambient temperature or under reflux. Thus pseudo 2 and normal 3 sulphonyl chlorides do not isomerise under the conditions used for their preparation.

The reaction of sodium 2-dichloromethylbenzenesulphonate 5 with thionyl chloride gave 4, without a trace of 2. This finding rules out the possibility of the formation of the pseudo isomer 2, by the intramolecular nucleophilic displacement of chlorine in 5.

From the foregoing it is seen that pseudo and normal isomers 2 and 3 are formed by two independent competing pathways. However, the fact that path (i) is preferred over path (ii) is shown by the exclusive formation of 2 at lower temperature and in larger proportion at higher temperatures. Previous studies (Shashidhar and Bhatt 1986; Newman and Courduvelis 1966) have established that the pseudo acid chlorides are formed from δ- and γ-keto acids by means of cyclic transition states and not by displacement of the chlorosulphite ester or its analogues by the chloride ion. This concerted reaction was originally described as a 3,2,1-bicyclic pathway (Newman and Courduvelis 1966; Newman *et al* 1966). We have designated it as a $2_\sigma + 2_\pi + 2_\sigma$ concerted pathway using modern terminology (Shashidhar and Bhatt 1986), path (i) is therefore by analogy with γ-keto-acids, in all probability a $2_\sigma + 2_\pi + 2_\sigma$ concerted reaction.

Formation (Goldberger 1916) of 2 by the action of phosphorous pentachloride on 1 has been attributed to the ring–chain tautomerism of 2-formylbenzenesulphonic acid (Freeman and Ritchie 1957). Its infrared spectrum shows the presence of carbonyl group (ν_{max} 1690 cm^{-1}) and ^{1}H NMR spectrum (D_2O) shows only the peaks due to aldehydic (10·7 δ) and aromatic hydrogens (7·6–8·2 δ). The putative tautomerism, therefore, does not exist. However, it is interesting to note that, 2-formylbenzenesulphinic acid by contrast, exists completely in the cyclic form (King *et al* 1971).

Heating dry potassium 2-carboxy benzene sulphonate with phosphorous pentachloride at 150° for about five hours, Remsen (1903) had obtained in good yield a mixture of 7 and the pseudo acid chloride 8 (scheme 2). They believed that the major product m.p. 40° (80–90% yield) was 8 and the minor product m.p. 79° (10–20% yield) was 7 (see also List and Stein 1898). These assignments were based on chemical reactions, which are unreliable methods of establishing structures of closely related compounds. Spectroscopic methods, particularly IR spectroscopy is useful for identification in the present case. The carbonyl stretching frequency at 1780 cm^{-1} (typical of a carboxylic acid chloride) for the 40° melting isomer and its absence in the 79° melting isomer makes it necessary to reverse Remsen's assignments. Other spectroscopic data fully corroborate this view.

When ammonium 2-carboxybenzenesulphonate 6 was refluxed with thionyl chloride (b.p. 79°) in the presence of dimethylformamide, 2-chlorocarbonylbenzenesulphonyl chloride 7 was obtained. On the other hand, when 6 was refluxed in phosphorous oxychloride (b.p. 105°) with phosphorous pentachloride, a mixture of 7 and its pseudo isomer 8 in the ratio 4:1 was obtained. When pure samples of 7 and 8 were independently refluxed with thionyl chloride in presence of dimethylformamide or with phosphorous pentachloride, in phosphorous oxychloride, they remained unaffected. Clearly 7 and 8 are not interconvertible under the conditions used for their preparation. In contrast to the 2-formyl derivative 1, formation of the normal isomer is preferred over the pseudo isomer.

The behaviour of 2-carboxybenzenesulphonic acid differs from that of γ-keto