

## REACTION OF PRIMARY AROMATIC AMINES WITH O-SULPHOBENZOIC ACID CYCLIC ANHYDRIDE

### Summary

Reaction of o-sulphobenzoic acid cyclic anhydride (16) with primary amines produced salts of 2-[(aryl amino)-carbonyl] benzene sulfonic acid<sup>(61)</sup>(66) and not the salts of 2-[(arylamino) sulfonyl] benzoic acid(65).

Contrary to earlier reports. It seems that the steric hindrance caused by the two oxygen atoms of the sulfone group prevent the attack of the nucleophilic amines on the sulfur atom despite the fact that sulfur atom is more polarized than the carbonyl in these compounds.

Attempts to prepare 2-[(aryl amino)- carbonyl] benzene sulfonic acid were not successful. For the reaction of one mole of the anhydride(16) with one mole or two moles or more of the primary arylamines, gave the salts of the corresponding acids(73) in each case.

The salts obtained from the reaction of one mole of the amine with one mole of the anhydride (16) at 5-10°C were not pure. However, when two moles or more of the amine were refluxed with one mole of the anhydride(16) pure salts(73) were obtained.

That the sulfonate salts of the type(73) were the products of these reactions and not the corresponding acids, indicate that the initially formed acids(66) are extremely strong acids. Once they are formed they combine with the rest of the amine to form the salts(73).

Emmiet Ried<sup>(16)</sup> claimed the preparation of 2-[(substituted amino) sulfonyl] benzoic acids(65) by the hydrolysis of N- substituted saccharin in the dioxane. However, with the exception of the report by Iyer and Muther<sup>(58,59)</sup>, no other report was found in the literature about preparation of 2-[(substituted amino) carbonyl]- benzene sulfonic acid(66).

Iyer and Muther(58,59)reported the preparation of the acids(66) from the reaction of the anhydride (16) with the amine in dioxane. Repeating these reactions during these studies gave the corresponding salts(73) and not the claimed acids (66). It is thus believed that the obtained salts have the structure (73) and not the structure(77).

Using of NMR or infrared spectroscopy to differentiate between structures(73) and(77) were not conclusive.

Attempts were made to prepare substituted saccharin from the prepared salts(73) using acetic anhydride-sodium acetate mixture as the dehydrating agent. However, the products were substituted acetanilides and not the corresponding substituted saccharin. A mechanism has been proposed to rationalize this reaction on page(125). On the other hand treatment of the salts(73) with thionyl chloride gave N-substituted saccharin in moderate yields.

Reaction of trifluoroacetic anhydride with salts like(73) did not form substituted isosaccharin nor the corresponding saccharin. A ratio of one mole of trifluoroacetic anhydride and one mole of the salts - (73) were allowed to react, forming trifluoroace anilide as the main product. N,N'-dicyclohexyl-carbodiimide(DCC), a powerful dehydrating agent used to prepare isoimides from amic acids, was allowed to react with salt(73) at room temperature. Dicyclohexylurea(DCU) was isolated from the

reaction mixture indicating that a reaction took place. The products in the organic solvent(dichloro methane) could not be purified completely from DCU .

The product which was believed to be N-substituted isosaccharin showed the presence of some DCU in its NMR spectrum. It seems that preparation of substituted isosaccharin using DCC requires further investigation and effective methods for purifying the product from DCU.