

was dissolved in 30 cc absolute methanol, 0.1 mol dioxybenzene and 0.1 mol sulfonic acid ester added and then heated on a water bath for two hours. The yields of monoalkyl ethers and dialkyl ethers were about 30-40% and 25-45%, respectively.

## 26. Reactions between Diazoniumsalts and $\alpha, \beta$ -unsaturated Carbonyl compounds.

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Continued from the preceding experiments, furancarboxylic-acid and various diazonium salts, prepared from aromatic amines, such as aniline, *p*-chloroaniline, *p*-nitroaniline, sulfanilic acid, 1-amino-2-naphthol-4-sulfonic acid, diaminostilbene-disulfonic acid, *p*-toluidine, and *p*-anisidine, were reacted similarly as arylfurfural synthesis. The yields attained to 35-39%. Benzoic acid and its derivative being obtained by oxidation of the reaction products with potassium-permanganate in alkaline solution, they were proved to be arylfurancarboxylic acids. The substituted position was difficult to determine. We have obtained new dyestuffs and pigments from arylfurancarboxylic acids by acid treatment as similar as in arylfurfural case.

Furylacrylic acid and diazonium salts prepared from aromatic amines, such as aniline, *p*-chloroaniline, *p*-nitroaniline, and sulfanilic-acid, were reacted. In this case the arylation occurred in the furan-nucleus: the reaction-products were proved to be quite identical with the compounds, which were prepared by Perkin's reaction from the arylfurfurals.

Furfuralacetone and *p*-nitrophenyldiazoniumchloride were reacted and the reaction product was proved to be arylfurfuralacetone, compared with the reaction-product prepared from *p*-nitrophenylfurfural and acetone.

On the other hand, we have found that no reactions occurred between furfuryl-alcohol or nitrovinylfuran and diazonium salts.

We have also studied the reactions between diazonium salts and a few  $\alpha, \beta$ -unsaturated carbonyl compounds besides furfural-derivatives.

We have obtained the corresponding aryl-derivatives by the reactions between methylvinylketone and diazoniumsalts. They were proved to be aryl-derivatives by the oxidation of reaction products and by the reduction of phenylmethylvinylketone to methyl- $\alpha$ -phenylacetone, (and synthesis of its semicarbazone, which has the same melting-point as stated in the literature.

By the reactions between benzoquinone and four diazonium salts, we have obtained corresponding aryl-derivatives, (two of which were already reported by Kvaines.) We have also obtained the reaction products between mesityloxide and four diazoniumsalts. By their oxidations, they were proved to be aryl-derivatives,

We could not succeed to obtain the reaction-product from *w*-nitrostyrol and diazonium salts:

## 27. A New Method to Replace the Diazonium-Salt Group with Halogen.

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Generally, the replacement of diazonium-salt group by halogen takes place in the presence of a cuprous salt (Sandmeyer) or copper powder (Gattermann).

We have discovered a new method of the replacement for the same purpose, as follows.

When the double salt of diazonium salt and zinc chloride is heated in such a suitable solvent as ether, benzene or toluene, the diazonium-salt group is replaced by a chlorine atom in good result.

Preparation of the double salt:

Aromatic amine is dissolved in hydrochloric acid solution and diazotised with sodium nitrite solution. After filtering, zinc chloride is added and then sodium chloride. The crystalline diazo-compound is collected, pressed and dried.

Reaction of the replacement:

To some suitable solvent contained in a round-bottomed flask with a reflux condenser is added the double salt. In this case the diazonium compound is insoluble in the solvent. And then warm the flask content gradually on a water bath with good shaking and the double salt begins to decompose with the evolution of nitrogen and goes into a clear solution. When the decomposition reaction is at an end, wash the reaction mixture with water and distil the layer of the solvent. According to this method, the diazonium salt is not hydrolyzed to the hydroxy compound, but the corresponding chloride is got as a reaction product with good yield.

We describe the results of our experiments hereunder.

In ether at 35°C for 5 hrs.

From benzene-diazoniumchloride, *m*-, *o*-toluene-diazoniumchloride.

Chlorbenzen 79% *m*-chlortoluene 85% *o*-chlortoluene 84%

In benzene at 80°C for 5 hrs.

From *p*-toluene-diazoniumchloride, *m*-, *p*-chlorbenzenediazoniumchloride, *p*-nitrobenzene-diazoniumchloride.

*p*-chlortoluene 75% *m*-dichlorbenzene 70%

*p*-dichlorbenzene 36% *p*-chlornitrobenzene 35%

In toluene at 100°C for 5 hrs.

From *p*-chlorbenzene-diazoniumchloride *p*-, *m*-, *o*-nitrobenzene-diazoniumchloride, *p*-, *o*-anisoldiazoniumchloride.