

24. Studies on Acetylene and its Derivatives. (X)

Studies on Polyvinylidenechloride (1)
Preparation of the Monomer.

Sango Kunichika and Susumu Hirase.

Vinylidenechloride was prepared by the dehydrochlorination of 1,1,2-trichloroethane, which had been obtained by the action of chlorine in the liquid phase (using trichloroethane as a solvent) upon vinylchloride containing 10-20 vol. % of acetylene. The results obtained on each reaction are as follow:

A) Trichloroethane

1. The higher the reaction temperature and also the higher the mol ratio of chlorine for vinylchloride, the more the formation of higher boiling products. The best yield (ca. 90%) of trichloroethane is obtained at lower temperature (0-20°), when the mol ratio of chlorine for vinylchloride is 1.2:1.

2. The rate of flow of the mixed gases and the height of the liquid layer do not largely effect on the yield.

3. Explosion, due to the presence of acetylene, does not occur when the content of vinylchloride is more than 70 vol. % in the gas.

B) Vinylidenechloride

1. Trichloroethane is easily dehydrochlorinated to vinylidenechloride in a yield of about 70% by the action of a slight excess of sodium-hydroxide solution (3.5-4%). When the concentration of sodium-hydroxide is higher, the reaction becomes difficult because of decrease of solubility of trichloroethane.

2. Vinylidenechloride is also obtained in a yield of 88% by using milk of lime as a dehydrochlorinating agent.

25. Alkylation of Dioxybenzenes by *p*-Toluolsulfonic Acid Ester.

Ryuzaburo Nodzu, Sango Kunichika and Sinsaburo Oka.

To study the bacteriostatic action on *Mycobacterium tuberculosis*, dioxybenzene monoalkyl ethers were prepared. As alkylating agent *p*-toluolsulfonic acid ester was used. Methyl, ethyl and butyl esters were prepared by adding 5N-sodium hydroxyde to a mixture of alcohol and *p*-toluolsulfonyl chloride with the yield: methyl ester 85%, ethyl ester 70% and butyl ester 56%.

Although butyl ester had been obtained by using pyridin instead of sodium hydroxyde aqueous solution we obtained it by using γ -picoline (B.P. 143-147°) with the yield: 85%. Hexyl ester was prepared also in an almost similar manner with the yield: 82%. Alklation was quite easily carried on as follows; 0.1 mol natrium

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 α, β -unsaturated Carbonyl compounds.

Hiroyoshi Akasi, Ryohei Oda and Koji Oki.

Continued from the preceeding 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 pigmeets 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 occured 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 occured between furfuryl-alcohol or nitrovinylfuran and diazonium salts.

We have also studied the reactions between diazonium salts and a few α, β -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 arylderivatives by the oxidation of reaction products and by the reduction of phenylmethylvinylketone to methyl- α -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 arylderivatives, (two of which were already reported by Kvalnes.) We have also obtained the reaction products between mesityloxide and four diazoniumsalts. By their oxidations, they were proved to be arylderivatives,