The Wallach Rearrangement of Azoxybenzene by Trichloroacetic Acid

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Abstract

In boiling acetic anhydride, azoxybenzene was found to undergo the Wallach rearrangement with trichloroacetic acid catalyst which is less acidic than sulfuric and chlorosulfonic acid usually used for tne rearrangement. The yield of the products, *o*- and *p*- hydroxyazobenzene and a tarry material, is affected by the concentration of the catalyst and reaction time. The following three facts may be pointed out in comparison with sulfuric acid catalyst; (1) The yield of *o*-hydroxy-azobenzene is higher. (2) No azobenzene is detected. (3) *o*-hydroxyazobenzene is transformed into the para-isomer under the same condition as rearrangement.

1 Introduction

Sulfuric[1] and chlorosulfonic acid[2] have been used as the catalysts for the Wallach rearrangement. It was found that *o*-and *p*- hydroxyazobenzene was obtained as the rearrangement products in boiling trichloroacetic acid-acetic anhydride solution. Trichloroacetic acid is less acidic than sulfuric and chlorosulfonic acid and it was the first example of aliphatic acid containing chlorine to be able to use as the catalyst in the Wallach rearrangement. In this paper we authors report the reaction condition in the Wallach rearrangement with trichloroacetic acid as a catalyst.

2 Experimental

2.1 Synthesis of azoxybenzene

Azoxybenzene was synthesyzed by refluxing the mixture of nitrobenzene, methanol and sodium hydroxide for 3 hrs. The yellow needle crystal, m.p. 34.0 ~ 35.0°C*1, was obtained by recrystallization using ethanol.

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*1 Thermometer was uncorrected.

2.2 Wallach rearrangement by trichoroacetic acid

The solution of trichloroacetic acid and 5g(0.025mol.) azoxybenzene in 25 ml. acetic anhydride was refluxed. After the reaction completed, the reaction mixture was allowed to stand in an ice-water. Acetic and trichloroacetic acid were removed by decantation with water, and then residual black liquid material was boiled together with 50 ml. of 10% sodium hydroxide aqueous solution for about 20 min., After allowed to cool, the rearrangement product was separated from unchanged azoxybenzene by filtration, and then it was precipitated in the filtrated solution by acidification adding hydrochloric acid and volatile *o*-hydroxyazobenzene was distilled by steam distillation from precipitate. Crude *o*-hydroxyazobenzene was extracted with benzene and the benzene solution was dried with anhydrous calcium chloride. After the solution was filtrated to remove calcium chloride, benzene was distilled off to condense the solution and chromatography of the residue on silica gel with benzene afforded pure *o*-hydroxyazobenzene, m.p., 78.5~79.0°C. On the other hand, after residual crude *p*-hydroxyazobenzene was allowed to cool, it was filtered and dry *p*-hydroxyazobenzene was recrystallized with ethanol, m.p. being 151.5~152.0°C.

Measured results of the Rf value in thin layer chromatography and IR spectra were in accord with those of standard meterials synthesized by the coupling reaction between phenol and benzene diazonium chloride.[3] The *o*-hydroxyazobenzene copper salt was precipitated by the reaction with copper acetate in water-ethanol solution, m.p. being 199.0~200.0 °C, thereby *o*- and *p*-hydroxyazobenzene being also distinguished from each other. Unchanged azoxybenzene was also observed to be in accord with that of original azoxybenzene.

3 Results and Discussion

Changing the reaction time with the catalyst of 50 wt. % concentration, the yield of *o*-hydroxyazobenzene was 1.2% invariably, but that of *p*-hydroxyazobenzene increased in prolonged reaction time, reaching 50% at the reaction time 20 hrs. These results are shown in Fig. 1.

On discussing the effect of the catalyst concentration at the reaction time 20 hrs., the maximum yield of *p*-hydroxyazobenzene was obtained about 50% in 70 wt.% in the catalyst concentration and *o*-hydroxyazobenzene was 6.2% in 60 wt.% respectively as shown in Fig. 2.

Using sulfuric acid as a catalyst, appropriate sulfuric acid concentration in proceeding the Wallach rearrangement has been known to be from 80 to 98 wt.% in general case, whereas it was pointed out by Buncel, et.al.[4] that the reaction rate in 75.3 wt.% sulfuric acid was extremely slow. On the other hand, rearranegment was sufficiently carried out in 60 wt.% concentration in case of trichloroacetic acid.

Bamberger[5] reported that the yield of *o*-hydroxyazobenzene was only 0.6%, and

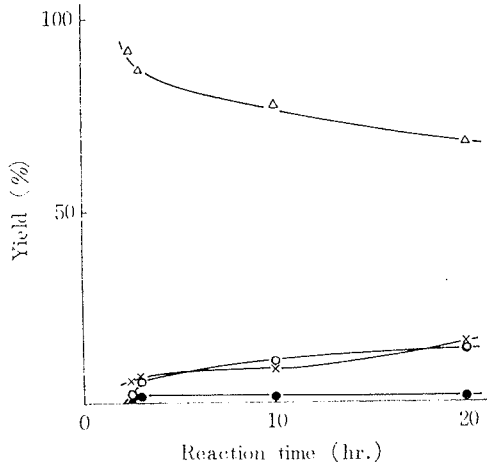

Fig. 1 Time dependence of the yield of rearrangement products in 50 wt. catalyst
—●— ; *o*-Hydroxyazobenzene,
—○— ; *p*-Hydroxyazobenzene,
—△— ; Unchanged azoxybenzene,
—×— ; Tarry products,

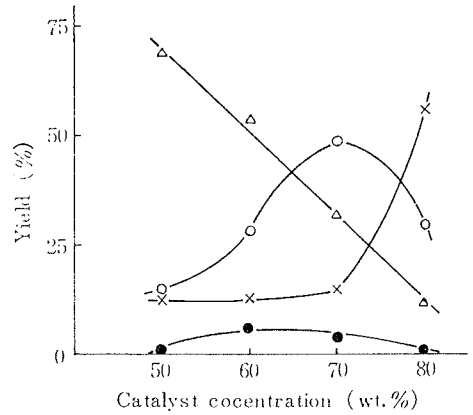

Fig. 2 Effect of catalyst concentration for rearrangement products
—●— ; *o*-Hydroxyazobenzene,
—○— ; *p*-Hydroxyazobenzene,
—△— ; Unchanged azoxybenzene,
—×— ; Tarry products,

Lachman[6] also reported as much as 2%.*2 Refluxing the *o*-hydroxyazobenzene in trichloroacetic acid-acetic anhydride solution regarded as possible to proceed the Wallach rearrangement, we could find *p*-hydroxyazobenzene in this reaction mixture. Therefore, this fact indicates that *p*-hydroxyazobenzene was produced both in direct formation by the Wallach rearrangement of azoxybenzene and in transformation via one of the rearrangement products, *o*-hydroxyazobenzene. Furthermore, considering the dependency of the reaction time on the yield with the catalyst cocentration 70 wt.%, we could obtain the yield of 4.4% *o*-hydroxyazobenzene and 51% *p*-hydroxyazobenzene at reaction time 30 hrs. respectively.

As increasing the reaction time and catalyst concentration, formation of the tarry products also increased as in the case when sulfuric acid was used as a catalyst.

This reaction seems to be not acid rearrangement but thermal rearrangement, although it was reported by Knipscheer[8] that 2% yield of *o*-hydroxyazobenzene was obtained in acetic anhydride at 200°C. As the azoxybenzene was recovered quantitatively in boiling acetic anhydride in the period of 20 hrs., it was concluded that the trichloroacetic acid was only concerned as a catalytic action. When azoxybenzene was refluxed in 0.1 mol. solution of mono- and dichloroacetic acid in 25 ml. acetic anhydride for 20 hrs., we recovered almost all azoxybenzene together with a

*2Though the yield for *o*-hydroxyazobenzene was cited to be 4% in the review,[7] it is not the yield but the ortho-para ratio. The yield should be accounted to be 2% by estimating raw azoxybenzene cited in the original paper.[6]

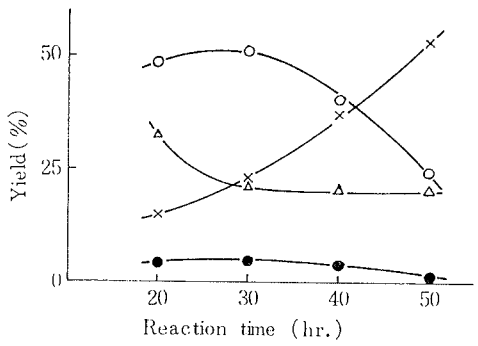

Fig. 3 Time dependence of the yield of rearrangement products in 70 wt. catalyst
—●— ; *o*-Hydroxyazobenzene,
—○— ; *p*-Hydroxyazobenzene,
—△— ; Unchanged azoxybenzene,
—×— ; Tarry products,

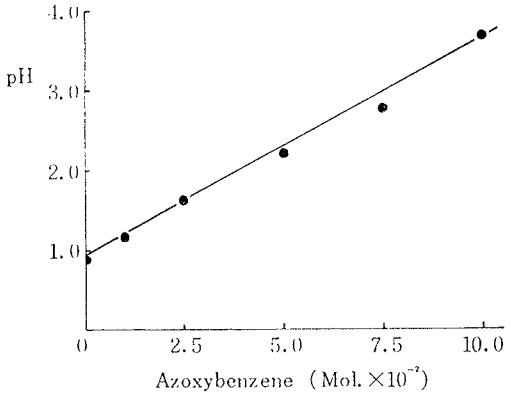

Fig. 4. pH change by added azoxybenzene in acetonitrile solution of trichloroacetic acid

trace of *p*-hydroxyazobenzene and some black materials. Also the rearrangement product was not obtained by using salycilic scid and benzene sulfonic acid as a catalyst.

Mechanism of the Wallach rearrangement has been described by various authors[9)10)11)] as addition of any proton to the oxygen atom of azoxy group in the first step and the same process also is likely to proceed in trichloroacetic acid as in sulfuric acid. When apparent pH change was measured in 50 ml. acetonirile solution with a trace of trichloroacetic acid by gradual addition of azoxybenzene, the elevation of pH in this solution was observed as increasing additive quantities of azoxybenzene as shown in Fig. 4. Based on the result of this experiment, we assumed that the protonation of azoxy group occured in the intial step of the Wallach rearrangement using trichloroacetic acid as a catalyst.

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