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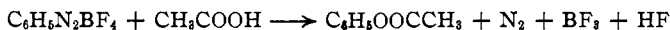
Replacement of the Diazo Group by the Acetoxy Group

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In the course of preparing some organic fluorine compounds by the excellent method of Balz and Schiemann,¹ which consists in the thermal decomposition of aryldiazonium borofluorides, it was found that *m*-chlorophenyldiazonium borofluoride interacts with acetic acid or acetic anhydride, with the elimination of nitrogen, to give *m*-chlorophenyl acetate in a yield of about 50%. *m*-Bromophenyldiazonium borofluoride behaved similarly and *p*-acetaminophenyldiazonium borofluoride with acetic anhydride gave diacetyl-*p*-aminophenol in a yield of about 52%.

The replacement of the amino group by the acetoxy group through the diazo reaction has been accomplished by the decomposition of dry diazo salts with glacial acetic acid,² or with acetic anhydride,³ and by the diazotization of an amine in warm glacial acetic acid.⁴ In either case the yield is poor. Moreover, when the dry diazo salts are employed, they are, as a rule, difficult to prepare and unstable. On the other hand, the aryl diazonium borofluorides have been shown¹ to be stable, easy to handle, and readily prepared.

The exact mechanism of the reaction is not known, but it probably takes place in the following manner



With *p*-acetaminophenyldiazonium borofluoride and acetic anhydride, the compound which is first obtained contains boron and fluorine. The product is probably a coordination compound of diacetyl *p*-aminophenol and boron trifluoride. On recrystallization from water or dilute alcohol the product loses boron and fluorine, and diacetyl-*p*-aminophenol is obtained.

As the aryl acetates are readily hydrolyzed to the corresponding phenols, the reaction provides a ready method of replacing the amino group by the hydroxy group when the normal decomposition of the diazo compound with water does not take place easily.

Experimental

***m*-Chlorophenyldiazonium Borofluoride.**—This compound was obtained from a solution of *m*-chlorophenyldiazonium chloride and a 40% solution of hydrofluoroboric acid in a yield of 93%. It decomposed at 157° (uncorr.).

***m*-Chlorophenyl Acetate.**—Twenty grams of *m*-chlorophenyldiazonium borofluoride was heated gently under reflux in 100 cc. of glacial acetic acid until nitrogen began to be evolved. After the vigorous reaction had subsided, the solution was boiled

(1) Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

(2) Orndorff, *Am. Chem. J.*, **10**, 368 (1888).

(3) Wallach, *Ann.*, **235**, 233 (1886).

(4) Meldola and East, *J. Chem. Soc.*, **53**, 460 (1888).

for five minutes, cooled and concentrated under reduced pressure to remove most of the acetic acid. Water was then added, and the solution was neutralized with solid sodium carbonate and extracted with ether. The ether extract was washed with water and dried over sodium sulfate. After the removal of the ether the remaining oil was distilled. It boiled at 84–86°, $p = 2$ mm.; at 108°, $p = 12$ mm. The yield was 7.5 g.

Anal. Calcd. for $C_8H_7O_2Cl$: Cl, 20.8. Found: Cl, 21.1.

***p*-Acetaminophenyldiazonium Borofluoride.**—This compound was obtained from a diazotized solution of *p*-acetaminoaniline and a 40% solution of hydrofluoroboric acid in a yield of 84%. It decomposed at 135° (corr.). It can be recrystallized from acetone-chloroform solution.

Diacetyl-*p*-aminophenol.—Twelve and a half grams of *p*-acetaminophenyldiazonium borofluoride in 65 cc. of acetic anhydride was heated under reflux until nitrogen was no longer given off. The reddish-brown solution deposited a crystalline product on cooling. This was filtered off and washed with acetic anhydride. It contained boron and fluorine, but it gradually lost them on heating. On recrystallization from water a product free from boron and fluorine was obtained. It melted at 151.5–152.5° (corr.). When mixed with an equal quantity of authentic diacetyl-*p*-aminophenol, there was no depression of the melting point.

Anal. Calcd. for $C_{10}H_{11}O_2N$: N, 7.25. Found: N, 7.23.

The acetic anhydride filtrate was concentrated under reduced pressure to remove most of the acetic anhydride. The concentrated solution was then worked up as described for the *m*-chlorophenylacetate. Two grams of diacetyl-*p*-aminophenol was obtained. The total yield of diacetyl-*p*-aminophenol was 5 g., 52%.

The *p*-acetaminophenyl diazonium borofluoride can also be converted to diacetyl-*p*-aminophenol by the use of acetic acid. In some experiments the crude diacetyl-*p*-aminophenol melted at 113–116° (uncorr.). A pure product was obtained only on sublimation.

Summary

m-Chlorophenyldiazonium borofluoride reacts with acetic acid to give *m*-chlorophenyl acetate.

p-Acetaminophenyldiazonium borofluoride interacts with acetic anhydride to give diacetyl-*p*-aminophenol.

Since the aryl acetates are readily hydrolyzed to the corresponding phenols, the reaction provides a ready method of replacing the amino group by the hydroxyl group when the normal decomposition of the diazo body with water does not take place.

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