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Abstract

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AZOBENZENE–AN ACCEPTOR OF HYDRIDE HYDROGEN

In attempting to elucidate the specifically favorable role of acetone in the reaction for obtaining onium and organometallic compounds from aryldiazonium borofluorides, we investigated the behavior of phenyldiazonium borofluoride in ketones and found that, along with the usual decomposition with evolution of nitrogen, in certain cases there occurs, surprisingly, a reduction of the phenyldiazonium ion and formation of the phenylhydrazone of the ketone, which rearranges into the corresponding indole. We shall report separately on this reaction. Extending the study of this unusual reduction of two bonded nitrogen atoms to the case of azobenzene, we carried out the reaction of azobenzene in the presence of boron trifluoride as catalyst.

In the case of the same ketones which, for example cyclohexanone, give indole ring closure under the action of diazonium borofluoride, we also obtained the corresponding indole from azobenzene. Thus, from cyclohexanone the same tetrahydrocarbazole was obtained. In this case, instead of the elimination of ammonia in the ordinary Fischer synthesis, in our case aniline was eliminated from azobenzene. This cycle of reactions will be discussed separately in the near future.

Along with this reaction, the benzidine rearrangement of azobenzene almost always occurred. We replaced boron trifluoride by concentrated sulfuric acid. It turned out that not only in ketones, but in almost all organic solvents, azobenzene, abstracting hydrogen from the latter, rearranges into benzidine. Thus, azobenzene reacts with ketones: acetone (at b.p.; 74.6%)*, cyclohexanone (100°; 51.6%); acids: formic (b.p.; 74.6%), acetic (b.p.; 10.7%), succinic**; benzaldehyde (b.p.; 81%), dibutyl ether (100°; 77%), benzene (b.p.; 79%), thiophene (b.p.; 76%), nitrobenzene (140-150°; 64%), cyclohexane (b.p.; 7.5%), *n*-hexane (b.p.; 22%), benzyl alcohol (18°; 47%), cycloheptatriene (18°; 70%). The reactions were carried out in an excess of the organic compound. In the case of formic acid, benzaldehyde, cycloheptatriene, and benzyl alcohol, the reaction products were benzidine with an admixture of diphenylamine and products of dehydrogenation of the reagent, respectively, CO_2, benzoic acid, tropylium cation, and benzaldehyde.

In the case of all the other organic solvents, which under these conditions likewise form benzidine with azobenzene, they themselves were converted into resin–a black, infusible, finely dispersed powder containing carbon (54-65%), hydrogen (3-4%), nitrogen (3-9%), sulfur (2-3%, and in the case of thiophene–21%), and ash in the form of sodium sulfate (0.5–11%). The reaction time, depending on the organic compound, varies within wide limits: from 30 min in benzaldehyde to 10 h in the case of benzene. The reaction also proceeds if sulfuric acid is replaced by pyrophosphoric or borofluorohydric acid, but as catalysts they are weaker than sulfuric acid.

* The temperature of the reaction and the yield of benzidine with diphenyline, calculated on the reacted azobenzene, are indicated in parentheses.
** The reaction with succinic acid was carried out in carbon tetrachloride as solvent.

It is interesting that, in the reaction of azobenzene with acetone, in addition to benzidine and diphenyline, phenylisonitrile was detected. A small amount of phenylisonitrile is also obtained in the interaction of azobenzene with boiling acetic acid. A statement that, on boiling azobenzene, zinc chloride, and acetone, considerable amounts of benzidine are formed is found in the work of Engler and Schestopal ([1]).

The optimum amount of sulfuric acid was established in the reaction with formic acid from the amount of carbon dioxide evolved, which was determined as $BaCO_3$. The molar ratio of azobenzene to sulfuric acid is 1 : 2. At this ratio, the mixture of azobenzene with sulfuric acid is a yellow, apparently dry powder.*

The remarkable ability of azobenzene to tear hydrogen from such stable compounds as benzene, nitrobenzene, cyclohexane, *n*-hexane, and also the absence of reaction with chloroform and nitromethane, which possess mobile (readily protonated) hydrogen, allowed us to propose the following mechanism for the reduction reaction of azobenzene: an electrophilic reagent (H_2SO_4, H_3PO_4, HBF_4, $ZnCl_2$, HCl, HBr) gives a salt with azobenzene**

$$[C_6H_5{-}N{=}N{-}C_6H_5]^+HSO_4^-.$$

The cation formed tears hydrogen with an electron pair (hydride hydrogen) from the organic compound, forming as a result hydrazobenzene, which in turn rearranges to benzidine.

$$[C_6H_5{-}N{=}N{-}C_6H_5]^+HSO_4^- + H{:}C \longrightarrow C_6H_5NH{-}NH{-}C_6H_5 + C^+ + HSO_4^-.$$

The carbonium cation arising as a result from the organic hydride-ion donor is evidently, in most cases, stabilized by ejecting a proton and forming a multiple bond. The unsaturated compound readily polymerizes in the presence of sulfuric acid. Evidence for the reaction mechanism proposed by us is the particular ease of interaction of azobenzene at room temperature with tropilidene and benzyl alcohol, which, as is known, readily give up hydride hydrogen ([3]). Tropilidene thereby forms a tropylium salt, and benzyl alcohol—benzaldehyde.

The formation of benzoic acid and carbon dioxide in the interaction of azobenzene, respectively, with benzaldehyde and formic acid likewise testifies to the reduction of azobenzene by hydride hydrogen, since benzoic acid and carbon dioxide can be obtained only as a result of cleavage of hydride hydrogen ([4]).

The conversion of azobenzene into benzidine in inorganic acids (HCl, dil. H_2SO_4) was first observed by N. N. Zinin ([5]); later Werigo ([6]) showed that the reaction proceeds on boiling with hydrobromic acid. Tikhvinskii ([7]), and then Jacobsen ([8]), studied the mechanism of the reaction discovered by N. N. Zinin: Tikhvinskii carried out the reaction in glacial acetic acid at 100°, passing a stream of dry hydrogen chloride or hydrogen bromide; Jacobsen studied the reaction in methyl alcohol saturated with hydrogen chloride.

In both cases the authors noted the formation, along with benzidine, of mono- and dihaloanilines. We decided to check whether, on boiling azobenzene with hydrohalic acids, the reaction indeed proceeds differently than in the reactions with organic hydride-ion donors just described.

* On heating this mixture for 3 hours on a boiling water bath, azobenzene is recovered unchanged.

** Analogous salts of azobenzene with hydrochloric acid were isolated and studied by Jaffé ([2]).

Azobenzene reacts completely on boiling in 40% hydrobromic acid for 3 hours. From the reaction products we isolated benzidine and bromobenzidine, which, as was established chromatographically, contained an admixture of dibromobenzidine. On boiling azobenzene in concentrated hydrochloric acid, a portion of the azobenzene reacts (49%) and benzidine, chlorobenzidine, and dichlorobenzidine are formed. Neither in the case of hydrochloric acid nor with hydrobromic acid were mono- or dihaloanilines detected, although we also used the method described by Tikhvinskii; their absence was shown by paper chromatography ([9]).

It is evident that even from aqueous solutions of hydrogen halides the azobenzene salt abstracts the hydride anion, just as it does from organic substances, while the remaining positive halide ion halogenates benzidine. Thus, azobenzene salts with strong acids are the most powerful acceptors of hydride hydrogen, more powerful than carbonium cations. Of particular interest is the abstraction of the hydride anion from benzene, thiophene, and other aromatic compounds. One may suspect the formation of Wittig' s dehydrobenzene and its analogs, which polymerize in the presence of sulfuric acid into a resin. We are currently studying this aspect of the matter.

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