[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF TRINITY COLLEGE]

THE CONDENSATION OF AMINOANTIPYRINE. VII. HYDROLYSIS IN THE PRESENCE OF NITROUS ACID (1)[1]

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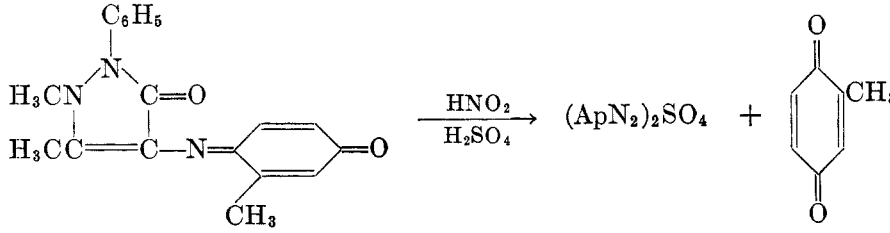
In the course of investigating the structure of some indophenol-type dyes formed by the interaction of 4-aminoantipyrine with phenols, difficulty was experienced in isolating the hydrolytic products. These products, 4-aminoantipyrine and quinone, react with each other at once to form anils in the same manner as aniline and quinone react.

It was thought that if the amine could be precipitated or otherwise removed from the reaction mixture as fast as it was formed during the hydrolysis, then the quinone could be isolated after the completion of the reaction. The presence of mercuric chloride, picric acid, or chloroplatinic acid failed to prevent anil formation.

Knorr (2) in 1896 reported that the diazonium salts of 4-aminoantipyrine were stable in hot aqueous solutions, and he also prepared and characterized a number of diazonium dyes made from aminoantipyrine. With these facts in mind, the hydrolysis of the antipyryl-indophenol dyes was carried out in the presence of sulfuric acid and nitrous acid. Apparently the amine liberated during the hydrolysis diazotizes faster than it reacts with the liberated quinone, because there is no apparent anil formation and because azo derivatives can be isolated in 94–95% yield and the pure quinone in 51% yield. While the yield of the quinone is low it is not inconsistent with quinone yields obtained by other methods.

A typical reaction may be summarized as:



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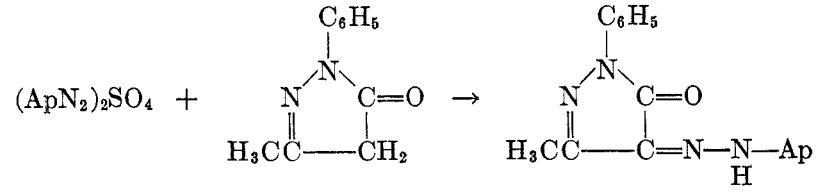

III IV

where Ap is the antipyryl radical.

[1] Taken from part of the work of J. Sagal in partial fulfillment of the requirements for the degree of Master of Science at Trinity College.

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On the basis of the results obtained with antipyrylquinoneimine dyes it is expected that other indophenol dyes can be hydrolyzed in the presence of nitrous acid to products which can be easily identified.

EXPERIMENTAL

The dye (I) 5.0 g. (0.016 mole) was partially dissolved in 50 cc. of acetone by gentle warming and to this solution was added 1.5 g. (0.022 mole) of sodium nitrite in 8 cc. of water and 13 cc. of 6 *N* sulfuric acid. At first the solution became opaque and purple but after twenty minutes of alternately heating to 60° and stirring the mixture became clear and red-brown at which time the hydrolysis was complete. Water, 50 cc., was then added and the resulting solution extracted with five 30-cc. portions of ether.

The ether extracts were combined in a distilling flask and the ether evaporated on a steam-bath. When all of the ether had been removed the remaining tarry mass was steam distilled. The distillate collected in an ice-cooled receiver soon deposited yellow plates from the canary-yellow liquid. These crystals after air drying weighed 1.0 g. (51% of theory), melted at 67–68°, and were identified as *p*-toluquinone. A mixture of Eastman Kodak *p*-toluquinone (m.p. 67–68.2°) and ours melted at 67–68°.

Preparation of antipyryl-4-azo-1-phenyl-3-methylpyrazolon-5. A. *From hydrolysis mixture.* The portion of the hydrolysis mixture remaining after the ether extraction was warmed to 50° on a steam-bath and a stream of air was passed over it to remove the final traces of ether. When the amber-colored solution had been cooled to room temperature 2.8 g. (0.016 mole) of 1-phenyl-3-methylpyrazolon-5 (III) in 5 cc. of glacial acetic acid was added followed by the addition of a saturated sodium carbonate solution until effervescence ceased. The red flocculent precipitate was brought on a Büchner funnel and washed with 200 cc. of cold water. After drying at 60° the crude dye (m.p. 180–198° d.) weighed 5.9 g., or 94% of theory. Recrystallized from 95% alcohol the sparkling red crystals (IV) melted in the range 200–204° d.

B. *From aminoantipyrine.* The azo dye was prepared from aminoantipyrine and 1-phenyl-3-methylpyrazolon-5 by the method described by Knorr and Stolz (2), and the compound melted at 200–205° d. as described in the literature. A mixture of the dyes prepared by the two methods also melted at 200–205° d.

Preparation of antipyryl-4-azo-β-naphthol. A. *From hydrolysis mixture.* The dye was prepared by the same method described under A above except that β-naphthol replaced the pyrazolon. When pure, the compound melted at 246–248° d.

B. *From aminoantipyrine.* Knorr and Geuther (3) coupled aminoantipyrine with β-naphthol, but failed to report the melting point of the compound. Their work was repeated and the compound was found to melt at 246–248° d. A mixture of this compound and ours obtained from the hydrolysis mixture melted at 246–248° d.

Preparation of ethyl-1-phenyl-2,3-dimethylpyrazolon-4-azoacetoacetate. A. *From hydrolysis mixture.* The dye (I) 2.0 g. was hydrolyzed and the quinone removed by extraction with ether as previously described. To the aqueous portion was added 0.87 cc. of ethyl acetoacetate in 10 cc. of alcohol, followed by the addition of 2 g. of sodium acetate. After 90 seconds a yellow ppt. formed in the red solution and the amount of ppt. was further increased by the addition of 3 g. more of sodium acetate in 5 cc. of water. The ppt. was brought on a filter, washed with 25 cc. of water and then by 5 cc. of cold alcohol. The residue, dissolved in 20 cc. of boiling alcohol, was filtered hot, and as the solution cooled yellow needles were deposited. After two further crystallizations the product had the constant melting point 174–175° without decomposition and weighed 0.39 g.

B. *From aminoantipyrine.* Morgan and Reilly (4) diazotized aminoantipyrine hydrochloride with ethyl nitrite and coupled the diazo compound with ethyl acetoacetate. In our work sodium nitrite was used as the diazotizing agent instead of ethyl nitrite.

To 5.0 cc. of water was added 0.20 g. of aminoantipyrine, 10 drops of 6 *N* HCl and 0.08 g. of $NaNO_2$. The addition of 1 cc. of ethyl acetoacetate in 5 cc. of alcohol to this mixture

produced a voluminous yellow ppt. 30 seconds after 0.5 g. of sodium acetate in 10 cc. of water was added. The product was washed with water, crystallized from alcohol, and was found to melt without decomposition at 174.5–176°. Morgan and Reilly reported the melting point as 174–175°, and a mixture of the products from A and B melted at 174.5–176°.

This hydrolysis procedure is being used successfully in the structure studies of other antipyrylquinone-imine dyes.

SUMMARY

1. The action of nitrous and sulfuric acids on certain indophenol-type dyes has been shown to inhibit anil formation during hydrolysis.

2. The hydrolytic products are readily identified.

3. It is expected that some other indophenol-type dyes will react in an analogous manner.

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REFERENCES

(1) Part VI, preceding paper.
(2) KNORR AND STOLZ, *Ann.*, **293**, 58, (1896).
(3) KNORR AND GEUTHER, *Ann.*, **293**, 55, (1896).
(4) MORGAN AND REILLY, *J. Chem. Soc.*, **103**, 808, (1913).