solution inactivation of the enzyme becomes more pronounced.

6. The inactivation of the enzyme appears to be brought about by the earlier oxidation product of the catechol (possibly *o*-quinone).

7. The inactivation of the enzyme appears to be offset either by further oxidation of the initial oxidation product of the catechol in acid solutions or by the removal of the early oxidation product of the catechol by secondary reactions in more alkaline solutions.

8. Evidence that no hydrogen peroxide is formed as an initial reaction product of this enzymatic oxidation of catechol was also obtained but is being withheld for a later publication.

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Brominations with Iodine Monobromide

BY WALTER MILITZER

In the course of some iodine number determinations on certain oils, the effect of the iodine monobromide solution as a substituting reagent was observed. In contrast to iodine monochloride, which is an iodinating reagent,[1] iodine bromide proved to be a brominating agent. Thus, phenol was brominated readily in carbon tetrachloride solution to give good yields of *p*-bromophenol, according to the equation

$$C_6H_5OH + IBr \longrightarrow p\text{-Br-}C_6H_4OH + HI$$
$$HI + IBr \longrightarrow I_2 + HBr$$

The greater part of the iodine precipitated from solution and could be recovered by filtration. The mechanism of the above reactions is substantiated by the reaction with aniline in which the *p*-bromoaniline hydroiodide precipitates from solution as follows

$$C_6H_5NH_2 + IBr \longrightarrow p\text{-}BrC_6H_4NH_2HI + HBr$$

The theoretical aspect of the reaction is of interest in view of the fact that substitution is quite often considered an addition of halogen and subsequent removal of hydrohalogen. The iodine bromide reaction apparently does not follow this mechanism. The addition of iodine bromide to double bonds is quite slow and selective, whereas its substitution reaction is very rapid. It will not add to cyclic double bonds such as are found in cholesterol and adds only slowly to cyclohexene. Furthermore, the iodine in iodine bromide is positive and the bromine negative, as shown by electrolysis studies.[2] Any subsequent elimination of hydrohalogen would, therefore, tend toward the elimination of hydrogen bromide rather than of hydrogen iodide. These facts seem to contradict the addition–elimination hypothesis.

As a preparative method for *p*-bromophenol and *p*-bromoaniline, iodine bromide cannot be recommended in preference to the existing methods for brominating and, indeed, is inferior; but for certain other compounds it possesses decided advantages over bromine. Thus, in the bromination of α-naphthol iodine bromide brominates quickly and smoothly to give good yields of 4-bromo-1-naphthol, whereas bromine is not applicable to the reaction. Iodine bromide is a milder reagent than bromine and is more easily handled. It can be made quickly in solution just prior to use.

In the preparation of α-bromonaphthalene, iodine bromide presents an advantage over bromine. The usual method of brominating naphthalene[3] with bromine involves a time consuming reaction; the iodine bromide method is rapid. In the action of bromine on naphthalene a by-product is formed which slowly liberates hydrogen bromide and in order to remove this by-product a four-hour heating of the intermediate with sodium hydroxide is necessary. With iodine bromide a similar by-product is formed which slowly liberates iodine, but its removal is accomplished by refluxing the original solution for thirty minutes with a small quantity of zinc dust.

Due to the sluggish addition of iodine bromide to olefinic linkages, it should prove a valuable brominating reagent for aromatic substances containing unsaturated side chains. Its effect in this respect is being investigated.

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(1) Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., 1936, p. 293.

(2) Finkelstein, *Z. physik. Chem.*, **124**, 285 (1926).

(3) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 116.

Experimental

4-Bromo-1-naphthol.—Twenty-six grams of finely divided iodine was placed in 60 cc. of glacial acetic acid and 5 cc. of bromine added. In order to facilitate formation of the iodine monobromide the solution was warmed to 50°. All of the iodine dissolved upon shaking except a trace. After the solution had cooled somewhat, it was introduced within ten minutes by means of a dropping funnel into a solution containing 14 g. of α-naphthol in 45 cc. of glacial acetic acid, kept cool by immersion in tap water. The reaction was allowed to stand for one hour during which time as much hydrogen bromide as possible was removed from the flask by a gentle air blast. The mixture was now poured into 700 cc. of water containing 16 g. of sodium bisulfite; 160 g. of sodium bicarbonate suspended in water was then added to neutralize the acetic acid and most of the hydrobromic acid. This led to a more complete precipitation of the product, which was now filtered, washed with water, and dried. The filtrate was saved for the recovery of iodine. The 20 g. of crude product was warmed with 1100 cc. of 33% alcohol, filtered, and allowed to crystallize. The yield after filtering and drying was 12 g. of a reasonably pure product (63%). After several recrystallizations from 33% alcohol (45 cc. per g.) the m. p. was 121–122°; Boudroux, 121°,[4] Reverdin and Kaufmann, 127–128°;[5] picrate, m. p. 169–170°, Boudroux 169°, Reverdin and Kaufmann 167°; acetyl derivative, m. p. 49–51°, R. and K. −51°.

α-Bromonaphthalene.—Ten cc. of bromine (0.2 mol) was run into 100 cc. of carbon tetrachloride and 51 g. of iodine was added. To promote the formation of the iodine bromide the mixture was warmed to 50–60° and shaken until all of the iodine had dissolved. The warm solution of iodine bromide was now run into another containing 27 g. of naphthalene (slight excess of 0.1 mol) in 50 cc. of carbon tetrachloride. The apparatus was arranged to remove the hydrogen bromide which was evolved rapidly. Iodine began to precipitate from solution almost immediately. After the addition of iodine bromide was complete (ten minutes), the whole was warmed to 50–60° and allowed to stand for thirty to forty-five minutes, then filtered through glass wool into a separatory funnel. The solution was then shaken out with two portions of water to remove the remaining hydrobromic acid and with two portions of sodium hydroxide solution to remove the remaining iodine.[6] After a quick drying over calcium chloride, the carbon tetrachloride solution was refluxed for thirty minutes with 0.5 g. of zinc dust to remove compounds which slowly liberate iodine. After filtration, the carbon tetrachloride was distilled off. The remaining crude product contained naphthalene and α-bromonaphthalene. Fractionation of this at atmospheric pressure gave a fraction distilling over below 265°, and a second fraction of relatively pure α-bromonaphthalene boiling between 271 and 275° (uncorr.). The yield of the second fraction was 50–55% of the theoretical. The total yield may be increased by reworking the first fraction. The product was of a light straw color.

Summary

Iodine monobromide has been found to be a mild brominating agent for substitution on the aromatic ring.

In the preparation of 4-bromo-1-naphthol and α-bromonaphthalene, iodine monobromide presents advantages over the regular bromination procedures.

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(4) Boudroux, *Bull. soc. chim.*, [3] **31**, 35 (1904).

(5) Reverdin and Kaufmann, *Ber.*, **28**, 3054 (1895).

(6) The total recovery of iodine is almost quantitative.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Hydration of Diammonium Dihydrogen Pyrophosphite to Orthophosphite at 30°

BY SAMUEL J. KIEHL AND MANUEL FOSTER MOOSE

In 1888 Amat[1] discovered that pyrophosphites are unstable in aqueous solution and that they hydrate to orthophosphites. He followed the course of the hydration by titrating the solution by means of sodium hydroxide with phenolphthalein as an indicator. For justification of the method he says:

> "The monosodium phosphite is, in fact, neutral to methyl orange and acid to phenolphthalein; the pyrophosphite of sodium is neutral to these two reagents."

Since his researches no work has been published upon the hydration of pyrophosphites although for many years, from time to time, the hydration of pyrophosphate in aqueous solution has been investigated and conditions which prevent, retard or promote its occurrence have been partially established.[2] As yet, little is known concerning the conditions which effect the hydration of pyrophosphites. There is an analogy of

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(1) Amat, *Compt. rend.*, **106**, 1400 (1888).

(2) Graham, *Phil. Trans.*, **123**, 53 (1833); Sabatier, *Compt. rend.*, **106**, 63 (1888); Montemartini and Egidi, *Gazz. chim. ital.*, **31**, I, 394 (1901); Balareff, *Z. anorg. Chem.*, **67**, 234 (1909); *ibid.*, **68**, 288 (1910); *ibid.*, **96**, 103 (1916); Berthelot and André, *Compt. rend.*, **123**, 776 (1896); *ibid.*, **124**, 261 (1897); *ibid.*, **124**, 265 (1897); Giran, *ibid.*, **135**, 961–63, 1333–35 (1902); Holt and Meyers, *J. Chem. Soc.* **99**, 385 (1911); Abbott, THIS JOURNAL, **31**, 763 (1909); Kiehl and Hansen, *ibid.*, **48**, 2902 (1926); Kiehl and Coats, *ibid.*, **49**, 2180 (1927); Kiehl and Hill, *ibid.*, **54**, 1332 (1932); Kiehl and Claussen, *ibid.*, **57**, 2284 (1935).