

Synthese of Nitro-compounds by Oxidation of Acylamino-compounds. (II)

Several Effects on the Yield of Nitro-compounds by the Oxidation of Acetylamino-compounds with Hydrogen Peroxide.

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The present author found that acetylaminobenzene sulfonamide was oxidized to nitrobenzene sulfonamide²⁾

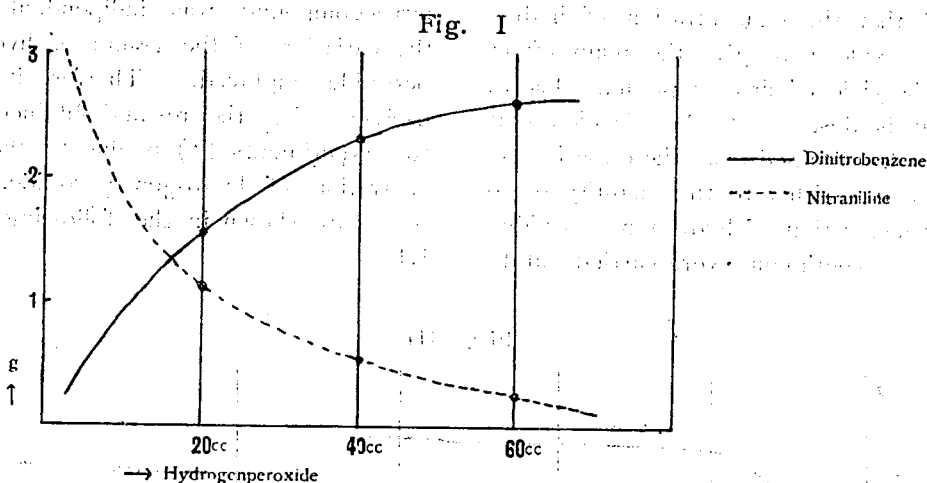
In the case of acetylamino-nitrobenzene, the same reaction was also effected to produce p-nitrobenzene in the yield of 51.5%.

Several effects upon the reaction were examined as follows.

1) The effect of the quantity of hydrogen peroxide,

As the large amounts of hydrogen-peroxide was used, the yield of dinitrobenzene increased. But the rate of increase diminished with further increase in quantity of hydrogen peroxide. Thus it is desirable to determine the optimal quantity to be employed in each reaction from the economical point of view.

The results obtained from the experiments are shown in the following figure 1.



2) The effect of the quantity of glacial acetic acid as solvent.

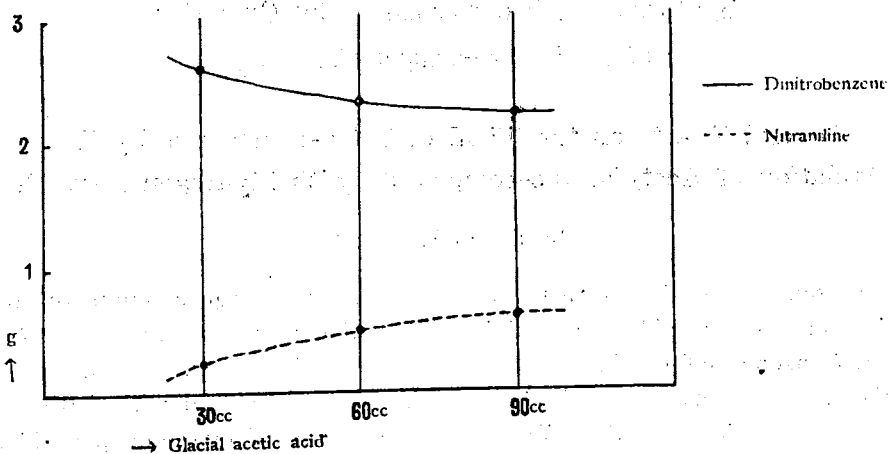
The increase in the amount of the solvent gave rise to decrease in the yield of the nitro-compound. This will be due to the fact that the concentration of

hydrogen peroxide was diluted by adding glacial acetic acid. Therefore it will be desirable to employ the minimum quantity of the solvent enough to dissolve the materials. The results are shown in the following figure II.

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2) This annual report, page

Fig. II



3) The variation in the yield when the volum of hydrogen peroxide was varied, allowing the concentration unchanged.

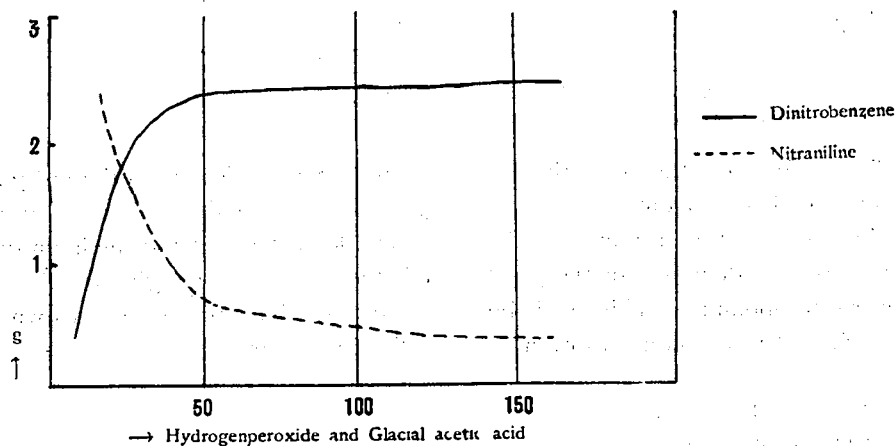
From the experimants (2) it is concluded that the concentration of hydrogen peroxide may give the main effect upon the yield of nitrocompound. Therefore, it is desirable to be clarified that the results obtained from the experimants (1) are due either to the quantity or to the concentration of hydrogen peroxide.

The experimants were carried out to

examine the variation in the yield when only the volum of hydrogen peroxide was varied.

From the experimants, the following points were made clear. The yield of nitro-compound was independent upon the variation of the volum of hydrogen peroxide employed. Therefore it seems probable that the results obtained from the experimants (1) is due to the concentration of hydrogen peroxide. The result are shown in the following figure III.

Fig. III



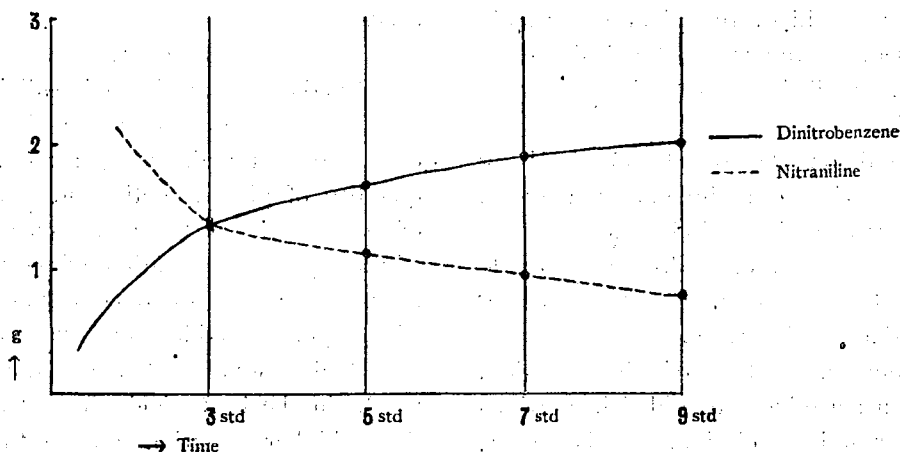
4) The effect of reaction-time.

The yield of nitro-compounds are influenced by the reaction time. Thus, when the reaction time was lengthened, the better yield resulted. However, the reaction rate diminished with time. That

is probably due to the decrease of concentration of the oxidizing agent because of the self-decomposition of hydrogen peroxide.

The results are shown in the following figure IV.

Fig. IV



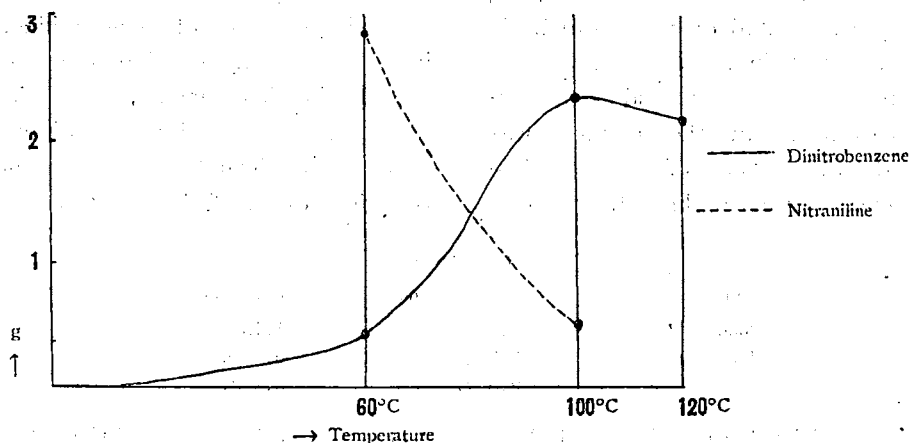
5) The effect of reaction temperature.

When the temperature below 100° was applied, the yield became better, as the temperature become higher. But above 100° the yield decreased on the

contrary. It seem probable that hydrogen peroxide was rapidly decomposed at the higher temperature, over 100° .

The results are shown in the following figure V.

Fig. V



6) The effects of decomposing agents of hydrogen peroxide.

As it is clear that effective decomposing agent for hydrogen peroxide is a deterrent to the present reaction, sodium acetate (the comparatively weak decomposing agent of hydrogen peroxide) was tried. When the sodium acetate was added, the yield remarkably decreased. And it will be desirable to use the stabilizing agent for hydrogen peroxide.

Based on the results obtained by the preceding experiments, it may be aduced that it is desirable to maintain the concentration of hydrogen peroxide throughtout the reaction, enough to proceed the oxidatiqn effectively.

From the outset of the reaction, hydrogen peroxide was added in portions to the reaction solution. However, unexpectedly the yield decreased. That may be due to the fact that the con-

centration of hydrogen peroxide can not be maintained at the optimal concentyation in the starting point of the reaction.

From the consideration of the results, it results that in order to obtain the best yield, longer reaction time, higher reaction temperature and higher concentration of hydrogen peroxide are necessary.

Summary

In the preparation of p-dinitrobenzene from p-nitroacetanilide the effects of quantity of hydrogen peroxide, of the quantity of glacial acetic acid as solvent, of the quantity of the hydrogen peroxide of the same concentration, of the reaction temperature and of decompsing agents of hydrgen peroxide were examined.

And it was concluded that in order to obtain the best yield, longer reaction time, higher reaction temperature and higher concentration of hydrogen peroxide are necessary.

Experimental

EFFECT OF THE QUANTITY OF HYDROGEN PEROXIDE: A mixture of 5 g. of p-acetylamino nitrobenzen, 60cc. of glacial acetic acid and a cc. of 30% hydrogenperoxide (a; 20, 40, 60cc.) was heated on the water bath. After heating 5 hrs. and cooling, the precipitate was filtrated and p-acetylaminonitrobenzene in the residue was hydrolized with 25 cc. of 30% hydrochloric acid. After boiling for 1 hour

and cooling, p-dinitrobenzene was filtrated and washed with 10 cc. of 30% hydrochloric acid. p-Dinitrobenzene was produced in the yields shown in the following table.

The solution of p-nitraniline, obtained by the hydrolizing the unreacted acetylaminonitrobenzene, was concentrated, and neutralized with sodium hydroxide. p-Nitraniline was produced in the yield of the following table.

Table I

Hydroegenperoxide (a)	p-Dinitrobenzene	p-Nitraniline
20cc.	1.65g.	1.18g.
40cc.	2.38g.	0.53g.
60cc.	2.6 g.	0.27g.

THE EFFECT OF THE QUAN-

TITY OF GLACIAL ACETIC ACID

AS SOLVENT : A mixture of 5g. of p-acetaminonitrobenzene, 40cc. of 30% hydrogenperoxide and a cc. of glacial acetic acid was heated on the water bath

for 5 hrs. And p-Dinitrobenzene and p-nitraniline were produced in the yield shown in the following table II.

Table II

Glacial acetic acid (a)	p-Dinitrobenzene	p-Nitraniline
30cc.	2.65g.	0.22g.
60cc.	2.38g.	0.53g.
90cc.	2.38g.	0.57g.

THE VARIATION IN THE YIELD WHEN THE VOLUM OF HYDROGENPEROXIDE WAS VARIED ALLOWING THE CONCENTRATION UNCHANGED : A mixture of 5g. of acetylamino nitrobenzene was dissolved in a cc. of the mixture of 30

% hydrogenperoxide and glacial acetic acid in the ratio of 4:6, and was heated on the water bath for 5 hrs. And p-dinitrobenzene and p-nitraniline were produced in the yield shown in the following table III.

Table III

The mixture of glacial acetic acid and hydrogen peroxide (a)	p-Dinitrobenzene	p-Nitraniline
50cc.	2.4g.	0.72g.
100cc.	2.38g.	0.53g.
150cc.	2.43g.	0.42g.

THE EFFECT OF THE REACTION TIME : A mixture of 5g. of p-nitroacetanilide, 20cc. of 30% hydrogenperoxide and 60cc. of glacial acetic

acid was heated on the water bath for a hours. p-Dinitrobenzene and p-nitroaniline were produced in the yield shown in the following table IV.

Table IV

Reaction time (a)	p-Dinitrobenzene	p-Nitraniline
3 hrs.	1.48g.	1.49g.
5 hrs.	1.65g.	1.18g.
7 hrs.	1.97g.	0.99g.
9 hrs.	1.99g.	0.75g.

THE EFFECT OF REACTION TEMPERATURE : A mixture of 5g. of p-nitroacetanilide, 40 cc. of 30 % hydrogenperoxide and 60cc. of glacial

acetic acid was heated at a for 5 hrs. p-Dinitrobenzene and p-nitraniline were produced in the yield shown in the following table V.

Table V

Reaction temperature (a)	p-Dinitrobenzene	p-Nitraniline
60°	0.38g.	2.89g.
100°	2.38g.	0.53g.
120°	2.02g.	

THE EFFECT OF DECOMPOSING AGENTS OF HYDROGENPEROXIDE : A mixture of 5 g. of p-nitroacetanilide, 30cc. of glacial acetic acid, 40cc. of 30% hydrogenperoxide and 5g. of sodium acetate was heated on the water bath for 5 hrs.. And 1.35 g. of p-dinitrobenzene was produced.

THE METHOD OF PREPARING OF P-DINITROBENZENE AC-

CORDING TO THE BEST PROCEDURE FOUND FROM THE ABOVE EXPERIMENTS : A mixture of 5 g. of p-nitroacetanilide, 60cc. of 30% hydrogenperoxide and 40cc. of glacial acetic acid was heated on the water bath for 9 hrs.. From the reaction mixture diluted with water, 51.5% yield (2.75g.) of p-dinitrobenzene (mp. 127) was directly obtained.

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