

Syntheses of Nitro-compounds by Oxidation of Acetylamino-compounds. (V)

The Catalytic Action of Aromatic and Aliphatic carbonic acids

By Takuo Kosuge and Toshio Hoshiba

In our former paper, the finding that the yield increased exceptionally in acetylamino benzoic acid was described.

This results will be due to the fact that the acid had catalytic action for the oxidation.

In the synthesis of p-dinitrobenzene, when benzoic acid was added to the reaction mixture, the yield was increased by 8.5%.

In the synthesis of p-nitrotoluene, the effect of the quantity of benzoic acid upon the yield was studied. Except that the acid was added, the other procedure was the same described before.

The results are shown in the following table I.

Table I

Benzoic acid	Yield
none	18.7%
1 Teil	22.5%
2/3 Teil	22.7%
1/3 Teil	22.3%
1/6 Teil	22.7%
1/12 Teil	22.5%

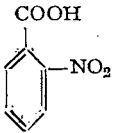
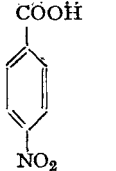
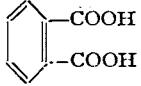
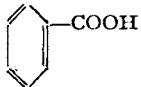
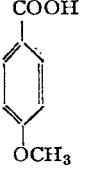
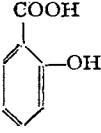
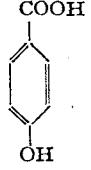
From the result obtained, it was found that benzoic acid has catalytic action upon the reaction.

Further experiments was done to examine the catalytic action of substituted benzoic acids. In the synthesis of p-nitrotoluene, the effect of 1/3 Teil of substituted benzoic acid on the yield was tested.

The results are shown in the follo-

wing table II.

Table II

Material	Increasing rate of yield	Disociation constant
	-1.5%	6.1×10^{-3}
	-1%	3.96×10^{-4}
	2%	1.3×10^{-3}
	4%	6.5×10^{-5}
	6%	3.38×10^{-5}
	3%	1.08×10^{-3}
	5%	3.3×10^{-5}

From the results obtained, it was found that benzoic acid derivatives containing electron releasing group had good catalytic action.

Therefore, it seems probable that this catalytic actions of benzoic acid derivatives have much to do with their dissociation constants, and acids of smaller dissociation constant, have stronger catalytic action.

Next we undertook the further studies on the catalytic action of aliphatic carbonic acid.

In the synthesis of p-nitrotoluene, the effects of one-thirds teil aliphatic carbonic acids on the yield was studied, employing the acid of one-third teil of acylamide.

The results are shown in the following table III.

Table III

acid	Increasing rate of yield
HCOOH	4%

Experimental

1) A mixture of 5g. of p-acetaminonitrobenzene, 3.4g. of benzoic acid 60cc. of 30% hydrogenperoxide and 40 cc. of glacial acetic acid was heated on the water bath for 9hrs.. Diluting with water produced 60% yield (2.82g.) of p-dinitrobenzene.

2) A mixture of 4.1g. of p-aceto-

C ₂ H ₅ COOH	3.5%
C ₃ H ₇ COOH	3.5%
C ₄ H ₁₀ COOH	8%

The results obtained show that higher members of the series have stronger catalytic action than lower ones.

It seems probable that the catalytic action of these carboxylic acids is due to the stabilizing power of hydrogenperoxide.

Summary

1) Substituted benzoic acids have catalytic action upon the oxidation of acylamino compound. The increasing rates of yield depends upon the strength of the acids employed and varied from -1.5 to 6%.

Better results were obtained when the acids of smaller dissociation constant was employed.

2) Aliphatic carbonic acid also had catalytic action and the increasing rate varied from 3.5 to 8%.

luidide, 1.1g. of benzoic acid, 60cc. of 30% hydrogenperoxide and 40cc. of glacial acetic acid was heated on the water bath for 9 hrs.. Neutralizing with ammoniak and steam distillation produced 22.3% yield (0.84g.) of p-dinitrotoluene.

Other catalysts were prepared by similar procedure.

Catalyst	Hydrogen peroxide	Glacial acetic acid	Reaction time	Yield	
				g.	%
o-Nitrobenzoic acid	60cc.	40cc.	9 hrs.	0.65g.	17.2%
p- " "	"	"	"	0.67g.	17.7%
phthalic acid	"	"	"	0.76g.	20.5%
p-methoxy benzoic acid	"	"	"	0.94g.	24.9%
p-oxy- "	"	"	"	0.9 g.	23.8%
o-Oxy- "	"	"	"	0.8 g.	21.5%
Formic acid	"	"	"	0.85g.	22.5%
propionic "	"	"	"	0.83g.	22 %
Butylic "	"	"	"	0.83g.	22 %
Caprylic "	"	"	"	1.01g.	26.8%

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(Faculty of Pharmacy, Kanazawa University)