

## Synthese of Nitro-compounds By Means of Oxidation of Accylamino-compounds. (IV)

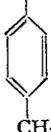
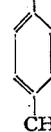
### Syntheses of Nitro-compounds by the Oxidation of General Acylaminocompounds and the Mechanism of this Reaction.

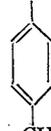
By Tkuo Kosuge<sup>1)</sup>

In the preceeding paper<sup>2)</sup> it was reported that acetyl amino compounds of aromatic series were oxidized to nitro-compounds with hydrogen peroxide. Further studied on the oxidation was undertaken in order to examine the variation of the yield when acetyl radical of the acetoluidide is replaced by other acyl radicals.

As acyl amino-compounds, thio-acettouluidide, formyl toluidie, butyl toluidide, benzoyl toluidide and p-nitro benzoyl toluidide were used.

The oxidation procdure was approximately the same described before (III). The results were shown in the following table.

$\text{NHCOC}_3\text{H}_7$ 	$\text{NO}_2$ 	12.8%
$\text{NH-CO-}$  	"	1.58%
$\text{NH-CO-}$  $\text{-NO}_2$ 	"	under 0.01%

Materials	Product	Yield
$\text{NHCOC}_3\text{H}_7$ 	$\text{NO}_2$ 	18.7%
$\text{NHCSCH}_3$ 	"	10%
$\text{NHCHO}$ 	"	47%

The results obtained above show that the yield of nitro-compounds was especially increased in the case where acetyl amino radical was replaced by formyl amino radical which can afford to weaken the C-N bond. And the fact that the yield afforded by acetanilide was better than that of benzanilide may be owing to the situation that C-N bond of benzanilide is stabilized by resonance.

It seems probable that p-nitrobenzoate weakens too much degree the C-N bond than benzoate, but the later weakens to much degree because the resonance system of p-nitro benzoate is longer than that of benzoate and C-N bond of benzoate is more weak.

It is generally accepted that C-N

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2) This annual report.

bond of the thioacetanilide is weaker than that of acetanilide. but the former produced the nitro compounds in worse yield than the latter. That will be due to the situation that thioacetanilide was decomposed to acetanilide with hydrogen

peroxide. In the case of formylanilid, excellent result was obtained.

This fact will be utilized when compounds having electron relasing groups are prepared.

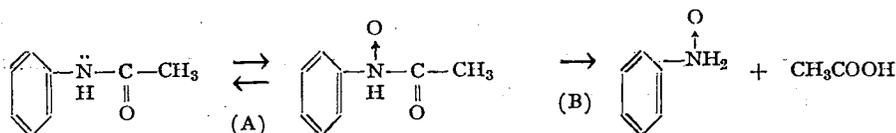
### Consideration of the Mechanism of the Reaction

In this place, the present author should like to consider the mechanism of this reaction, based on the results obtained.

It will be natural reasonable that the reaction is proceeded by way of N-oxide.

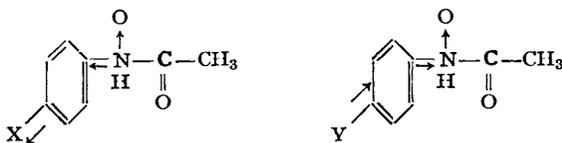
By the formation of N-oxide, electron density of nitrogen atom remakably decreases and N-C bond is weakened and then acetyl amino radical is apt to be split even in the absence of acid or base.

See the following table.



The stage (A) will proceed very easy, because this stage can be inrate-determining one from the fact that the yield increases even in the presence of electron attracting groups which are well known to hinder the formation of N-oxide and this stage may be reversible, because from the reaction solution acetyl amino compounds are recovered.

It may be inferred that the stage (B) is rate determining one of this reaction, from the fact that the yield decrease in the presence of electron releasing group, because electron density of nitrogen atom increases and C-N bond of the acylamino radical is strengthened by the presence of the electrong releasing groups.



X : Electron attracting group

Y : Electron releasing group

2) Kirpal, Bohm and R. H. Wiley<sup>3)</sup> found that 2- and 4-amino pyridine were oxidized to 2- and 4-nitro pyridine with hydrogen peroxide, but 3-amino pyridine was oxidized to azo-compounds. That is, amino having small electron density was oxidized to nitroradical, but amino having

comparatively large electron density was oxidized to azo compound with hydrogen peroxide. In consideration of this fact, in our case, too, by the formation of amine N-oxide electron density of nitrogen of amine decrease extremely and the amide becomes susceptible to hydrolyzation.

Thus the amine-N-oxide is oxidized to nitro-compound through the same course along which 2-amino and 4-amino pyridine are oxidized to nitro-compound respectively.



### Summary

1) Effects of the acyl radicals were

examined and it was found that formyl radical can afford good results.

2) Consideration was made about the mechanism of this reaction: the reaction will proceed by way of the following steps:

- a) N-atom of acetyl amino radical is oxidized to N-oxide.
- b) Acetyl radical is removed.
- c) Amino-N-oxide is oxidized to nitro radical.

### Experimental

A mixture of 4.6g. of p-formyl toluide, 60cc. of 30% hydrogen peroxide and 40cc. of glacial acetic acid was heated on the water bath for 9 hrs.

The reaction solution was neutralized

with ammoniak. The steam distillation produced 47% yield (1.78g.) of p-nitro-toluene. Other acetylamino compounds were prepared by similar procedure.

Acyl radical (g)	Hydrogen peroxide	Glacial acetic acid	Reaction time	Yield		
				g.	%	
Thioacetyl	4.6g	60cc.	40cc.	9 hrs.	0.38g.	10%
Butyl	5				0.48	12.8
Benzoate	5.9				0.06	1.58
p-Nitro benzoate	7.1				under 0.01	

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