

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

Effects of Radical upon Yield of Nitro-compounds. by the oxidation of Acetylamino-compounds with Hydrogen Peroxide

By Takuo Kosuge, Masami Sato and Shuichi Miyashita.

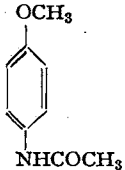
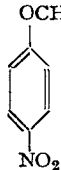
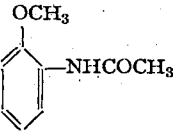
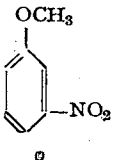
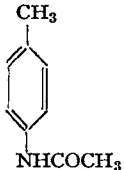
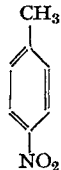
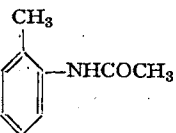
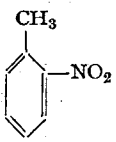
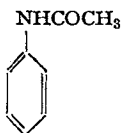
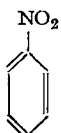
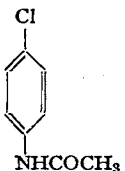

One of the present authors (T. Kosuge) found that acetylamino-nitrobenzene with hydrogen peroxide respectively.

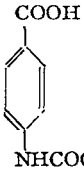
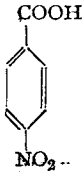
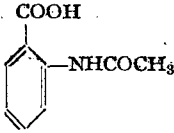
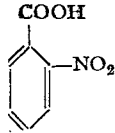
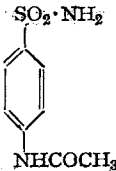
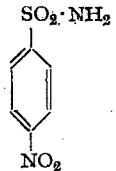
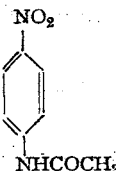
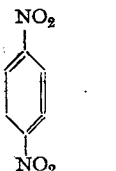
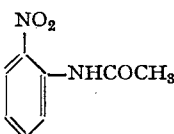
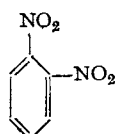
As a part of series of studies on effects of radicals introduced on benzene nucleus upon the yield of nitro-compounds are planned.

In the present investigation, it is our main concern to examine effects of substituents on the benzene nucleus upon the yield and to clarify the scope of our new procedure.

In the first place, mono-substituted acetanilides were employed as the starting materials.

Table I

Material	Product	Yield	Material	Product	Yield
		1%			4.1%
		18.7%			24.5%
		30.4%			
		32.2%			

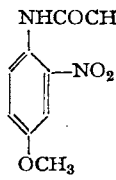
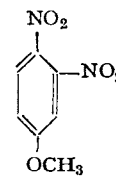
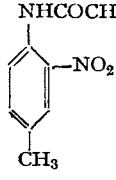
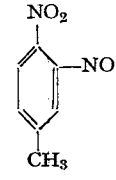
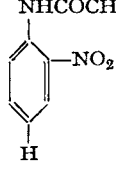
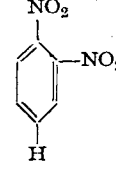
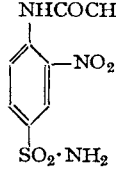
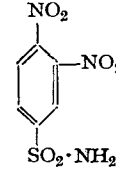
		66.2%			64.5%
		62%			
		51.5%			66.5%

As shown in the above table, better yields were obtained in the cases where electron attracting groups are introduced at the para or ortho position on the benzene nucleus. And the yields afforded by carboxylic acids and sulfonamide are exceptionally good.

We also notice that effect of the same substituent on the yield are different according to the position introduced, that is for example, the yield of o-nitroacetanilide is better than that of p-substituted one.

In the second place, di-substituted acetanilide were employed as materials. And studies on the superposed effects of the two substituents introduced simultaneously on the same benzene nucleus was made. The experiments were carried out in the same way described above. The results obtained are summarized in the following table.

Table II

Material	Product	Yield
		28.2%
		50.5%
		66.5%
		54.5%

As shown in the above table the better yield resulted in the case where another nitro group (strong electron attracting group) are introduced on the benzene.

Sulfonamide radical is also strong electron attracting group, but in this case, not so good result was obtained as the case of nitro radical.

This may be due to the situation that dinitro benzene sulfonamide could not be separated effectively from the reaction mixture.

It is well known that this type of dinitro-compounds can not be prepared or, if prepared, the yields are very poor according to the usual procedures. However, our procedure can afford to give

better and satisfactory results even in this case.

Summary

The effects of the radicals on the nitration by the oxidation of acetylamino compounds with hydrogenperoxide were studied. The yield increased in the case where radicals are electron attracting group.

As the compound were substituted in ortho-position, yields increase than the compound substituted in para position, as for as the same substituent is concerned. In the tri-substituted compound yields increase in the compounds having nitro radical, compared with the state having no nitro radical.

Experimental

A mixture of 4.5g. of p-methoxy acetanilide, 40cc. of glacial acetic acid and 60cc. of 30% hydrogenperoxide was heated on the water bath for 9 hrs. The reaction solution was neutralized with

ammoniak.

Steam distillation produced 1% yield (0.04g.) of p-nitroanisole, mp. 54°. Substituted acetanilides were prepared by similar procedure.

Material	Glacial acetic acid	Hydrogen peroxide	Reaction time	Yield		mp.
				0.15g.	4.1%	
o-Acetanilide	40cc.	60cc.	9hrs.	0.15g.	4.1%	52°
p-Acetanilide	"	"	"	0.71	18.7	54°
o- "	"	"	"	0.93	24.5	
p-Chloracetanilide	"	"	"	1.5	32.2	82-3°
Acetanilide	"	"	"	1.11	30.4	
p-Acetaminobenzoic acid	"	"	"	3.08	66.2	236°
o- "	"	"	"	3	64.5	145°
Acetsulfanilamide	"	"	"	3.5	62	116°
o-Nitroacetanilide	"	"	"	3.1	66.5	70°
2-Acetamino-5-methoxynitrobenzene	"	"	"	1.55	28.2	70°
2-Acetamino-5-methylnitrobenzene	"	"	"	2.27	50.5	61°
2-Acetamino-5-sulfonamide nitrobenzene	"	"	"	3.74	54.5	163-4°

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