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A NOVEL SYNTHESIS OF 1-AMINO-4-BUTYLAMINOANTHRAQUINONE FROM 1-AMINOANTHRAQUINONE PROMOTED BY METAL IONS

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In the presence of cobalt salts, 1-amino-4-butylaminoanthraquinone was conveniently synthesized from 1-aminoanthraquinone and butylamine in a good yield under mild condition. Some of other metal ions were found to be effective on this amination. The yield was affected by both of the anion component of metal salt and the kind of solvent.

In our previous paper1), we reported a new copper-promoted amination between α-substituted anthraquinones and butylamine. In this reaction, however, 1-amino-4-butylaminoanthraquinone 2 was obtained from 1-aminoanthraquinone 1 in a low yield in the presence of various copper salts. In this communication, we examine the effect of some factors on the butylamination of 1 to improve the yield of 2.

Table 1. Effect of metal chlorides on the butylamination of 1-aminoanthraquinone

Runa)	Metal chloride	Recovered 1(%)	Yield 2(%)	Conversion(%)2)
1	none	99.0	0	-
2	$CuCl_2$	70.9	5.37	18.5
3	$NiCl_2$	57.2	11.1	22.2
4	$CoCl_2$	0	58.7	58.7
5	$AlCl_3$	65.9	3.1	9.2

a) Reactant 1(9 mmol) was heated in butyl alcohol(5 ml) with butylamine(15 ml) and metal salt(9 mmol) at 80-82°C for 24 hours3).

As shown in Table 1, the reaction does not proceed at all without metal salt. Cuprous and cupric salts have been already known as effective metal salts on this amination1). Another three metal chlorides, $NiCl_2$, $CoCl_2$ and $AlCl_3$, also were found to be effective but the other three, $MgCl_2$, $ZnCl_2$ and $FeCl_3$, were not effective. The order of activity was as follows; $Co^{2+} \gg Ni^{2+} > Cu^{2+} > Al^{3+}$. The activity of cobalt dichloride was particularly superior to those of others. When cobalt salt was used, the reaction was proceeded smoothly even at room temperature (Table 2).

The yield of 2 was affected markedly by the anion component of cobalt salts. Cobalt dichloride and dibromide were the good catalysts but difluoride has poor activity. Cobalt acetylacetonate has no activity at all because metal ion might be fixed strongly by acetylacetonate residue and could not act as a chelating agent to 1. Crystal water did not effect so much on the activity of cobalt salt (Run 2 and 3).

Table 2. Effect of anion component of cobalt salts on the butylamination of 1

Run a)	Cobalt salt	Time(hr)	Recovered 1(%)	Yield 2(%)	Conversion(%) 2)
1	$CoF_2 \cdot 3H_2O$	24	74.1	0.18	0.7
2	$CoCl_2$	8	0	66.1	66.1
3	$CoCl_2 \cdot 6H_2O$	8	6.0	53.5	56.9
4	$CoBr_2 \cdot 6H_2O$	8	5.3	63.5	67.1
5	$Co(OCOCH_3)_2 \cdot 4H_2O$	24	19.2	32.1	39.7
6	$Co(CH_3COCHCOCH_3)_2 \cdot 2H_2O$	24	91.2	0	-

a) Reactant 1(4.5 mmol) was stired in butyl alcohol (5 ml) with butylamine(15 ml) and cobalt salt(4.5 mmol) at 30±2°C 3).

It was supposed that the formation of metal chelate ring between 1-amino group and carbonyl group may play a great role on this amination. These ideas were supported by another experimental results; This amination was affected greatly by the N-alkyl substituent at 1-position. Aminated product was obtained only in a low yield when 1-methylamino- or 1-butylaminoanthraquinone was used as a reactant. Solvent effects were also observed and the yield of 2 was increased with the increase of polarity of solvents (Table 3). But in the cases of solvents having bi-dentate ligand, such as ethylene glycol and methyl cellosolve, the yield was depressed. Furthermore, an addition of small amount of ethylenediamine, which is known as an effective chelating agent, depressed completely the formation of 2 (Run 8). In these cases, the metal ion previously forms a complex with solvent and concequently its activity is reduced or depressed completely.

Table 3. Solvent effects on the butylamination of 1-aminoanthraquinone

Run a)	Solvent	Recovered 1(%)	Yield 2(%)	Conversion(%) 2)
1	Benzene	83.0	trace	-
2	Dioxane	87.1	1.81	14.1
3	Nitrobenzene	88.1	2.79	23.5
4	Dimethylformamide	78.7	5.30	25.4
5	Butyl alcohol	55.5	28.3	63.8
6	Methyl cellosolve	73.8	8.49	32.4
7	Ethylene glycol	79.3	4.56	22.0
8	Butyl alcohol + Ethylenediamine(5 ml)	89.4	0	-

a) Reactant 1(4.5 mmol) was heated in solvent(50 ml) with butylamine(15 ml) and anhydrous cupric acetate(9 mmol) at 80-82°C for 8 hours 3).

Reference and Notes

1) K.Yoshida, M.Matsuoka, T.Ueyama, Y.Yamashita, T.Kitao, Chem. Lett., 1978, 765.

2) The yields based on 1-aminoanthraquinone reacted.

3) The mixture was treated as same as that of earlier work 1).

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