CHEMISTRY LETTERS, pp. 219-220, 1979. Published by the Chemical Society of Japan

A NOVEL 2-BUTYLAMINATION OF 1,4-DIHYDROXYANTHRAQUINONE PROMOTED BY METAL IONS

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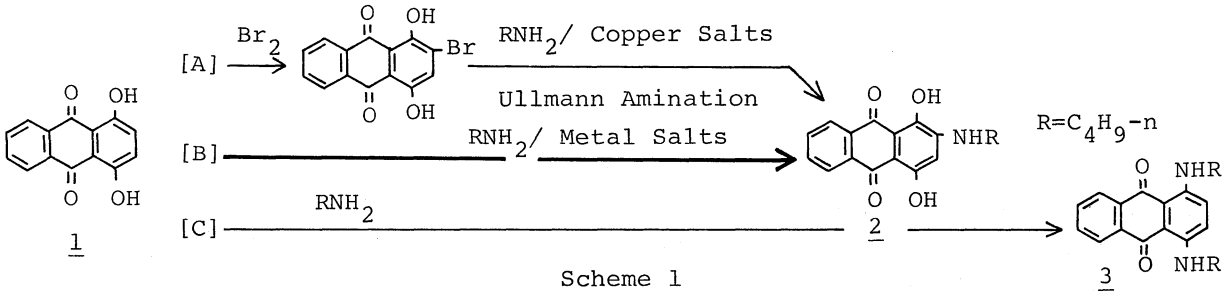
In the presence of cuprous or cupric chloride, 2-butylamino-1,4-dihydroxyanthraquinone was synthesized quantitatively from 1,4-dihydroxyanthraquinone and butylamine at ambient temperature.

In our previous paper[1,2], we reported a new metal-promoted amination between α-substituted anthraquinones and alkylamines. In the reaction, 1-amino-4-butylaminoanthraquinone was conveniently synthesized from 1-aminoanthraquinone and butylamine in the presence of various metal salts in a good yield under the mild conditions. In this communication, we examine the reaction between 1,4-dihydroxyanthraquinone 1 and butylamine in the presence of various metal salts (Scheme 1).



Scheme 1

Table 1. Butylamination of 1,4-dihydroxyanthraquinone under various conditions

Run[a]	Metal salt	Temp.(°C)	Time(hr)	Recovered 1(%)	Yield 2(%)	Yield 3(%)
1	$CuCl_2.2H_2O$	34	24	0	100	0
2[b]	"	34	24	0	100	0
3[b,c]	"	34	24	63.7	22.7	0
4[b,d]	CuCl	34	24	0	100	0
5	$CoCl_2$	34	24	70.5	24.0	0
6	"	34	120	64.4	29.2	0
7	"	70	24	0	70.9	0
8	$NiCl_2.6H_2O$	30	120	81.2	3,1	0
9	none	80	24	0	0	50.4[e]
10	Cu	80	24	0	0	37.3[e]

a) Reactant 1 (5 mmol) was stirred in butyl alcohol (7.5 ml) with butylamine (228 mmol, 46 times to 1) and metal salt (10 mmol).
b) Pyridine (25 ml) was used as solvent instead of butyl alcohol.
c) Butylamine (55.8 mmol, 11 times to 1) was used.
d) Deposition of metal copper was observed after the reaction.
e) Dealkylation of 3 was well known under these conditions[3] and the yield was depressed.

It was found that the reaction was proceeded smoothly at ambient temperature and 2 was obtained in a good yield. Cuprous and cupric chloride were the most effective salts and 2 was obtained quantitatively under the mild reaction conditions. Cobalt dichloride was moderately good but nickel dichloride has poor activity. This new synthetic method [B] is superior to usual Ullmann amination method [A] in the following points;

a) Halogenation does not necessary and one stage of process can be omitted.
b) The reaction proceed smoothly under the mild conditions comparing those of [A].
c) The yield is quantitative.

Without metal salts [C], usual nucleophilic butylamination at α-position was proceeded exclusively and 1,4-bisbutylaminoanthraquinone 3 was obtained in 50% yield (Run 9). Metal copper which can not form the metal complex with 1 also not effective at all on this amination (Run 10).

The formation of copper complex between quinone carbonyl group and α-hydroxyl group of 1 may play a great role on this amination as supposed for the similar 4-butylamination of 1-aminoanthraquinone[2]. The details of the mechanism are currently under investigation.

References

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(Received December 5, 1978)