Novel, Direct Amination of Anthraquinone by Rhodium(I) Complexes

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Summary In the presence of certain rhodium(I) complexes, anthraquinone was found to react with amines to give the 1-alkylaminoanthraquinones, along with small amounts of the 1,4-bis(alkylamino)anthraquinones, this direct amination characteristically occurs only at the α-position of anthraquinone

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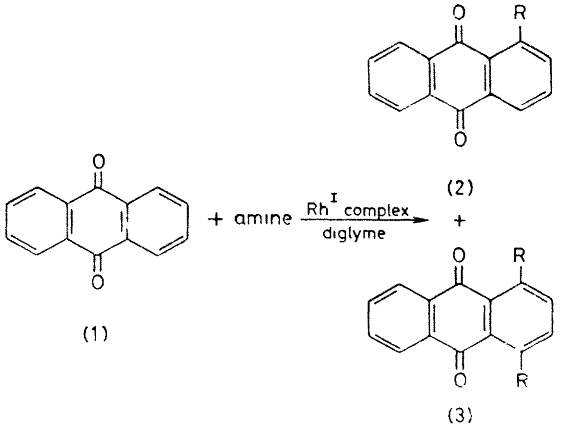
While studying the Ullmann condensation reaction of halogenoanthraquinones,[1] we found a novel reaction in which anthraquinone (**1**) was directly aminated in the presence of certain rhodium(I) complexes and n-butylamine to give 1-n-butylaminoanthraquinone (**2a**) along with only a small amount of 1,4-bis(n-butylamino)anthraquinone (**3a**) Recently cobalt- or copper-assisted amination of 1-aminoanthraquinone to give 1-amino-4-n-butylaminoanthraquinone has been reported by Kitao and his coworkers[2] Unsubstituted anthraquinone, however, gave no aminated product under their reaction conditions

We report here a novel, direct amination of (**1**) In a typical experiment, a mixture of (**1**) (5×10^{-2} mol l^{-1}), n-butylamine (2 6 mol l^{-1}), and a rhodium(I) complex (Rh 5×10^{-3} g atom l^{-1}) in diglyme (7·5 ml) was refluxed in air for 30 h after refluxing under N_2 for 3 h The products were separated by column chromatography on silica gel using benzene as eluant and identified by comparison with authentic samples In these reactions, amination occurred only at the α-position of (**1**) Disubstituted products, such as 1,5- and 1,4-bis(n-butyl-

TABLE 1. The direct amination of anthraquinone with n-butylamine using various rhodium(I) complexes.

Run	Rhodium complex	Rh/(**1**)	Reaction time/h Under N_2	In air	Yield/%[a] (**2a**)	(**3a**)
1	—	0	0	34	0	0
2	$RhCl\cdot 3H_2O$	0·10	3	36	0	0
3	$[RhCl(PPh_3)_2]_2$	0·11	30	0	7	0·1
4	,,	0·11	0	30	39	2
5	,,	0·11	3	30	136	26[b]
6	$[RhCl(C_2H_4)_2]_2$	0·10	30	0	2	0
7	,,	0·11	3	30	100	18
8	$[RhCl(C_2H_4)_2]_2$ + dpe[c]	0·11	0	30	48	9
9	,,	0·11	3	30	135	25[b]
10	$[RhCl(cod)]_2$	0·11	3	30	76	8
11	$RhCl(PPh_3)_3$	0·10	0	30	9	1
12	,,	0·10	3	30	64	5
13	$RhCl(cod)(PPh_3)$	0·11	3	30	18	trace
14	$RhCl(CO)(PPh_3)_2$	0·10	3	30	12	0·4

[a] Yield based on rhodium. [b] A trace of 1,5-bis(n-butylamino)anthraquinone was also formed. [c] dpe/Rh 1·0.



a; R = $NHBu^n$
b; R = $NHBu^s$
c; R = $NHBu^t$
d; R = $NH(cyclo\text{-}C_6H_{11})$
e; R = $NHCH_2Ph$
f; R = $NHSO_2C_6H_4Me\text{-}p$
g; R = $NHCH_2CH_2OH$
h; R = $NBu^n{}_2$
i; R = piperidin-1-yl
j; R = $N(Me)CH_2Ph$

amino)anthraquinone, were also observed in a small amount in some cases.†

Results of the amination in diglyme and n-butylamine using various rhodium complexes are summarized in Table 1. The yields are based on rhodium in order to estimate whether the metal complex could recycle as a catalyst. The amination does not proceed at all in the absence of rhodium(I) complexes (runs 1 and 2). The yields of reactions under N_2 are very low, even in the presence of rhodium(I) complexes (runs 3 and 6), showing that oxygen is necessary for this amination system. It is of interest, however, that refluxing under N_2, before the reaction in air, is favourable for the reaction (compare runs 4 and 5, 8 and 9, and 11 and 12). Among the rhodium(I) complexes examined the dimeric complexes, such as $[RhCl(PPh_3)_2]_2$, $[RhCl(C_2H_4)_2]_2$, $[RhCl(C_2H_4)_2]_2$ + 1,2-bis(diphenylphosphino)ethane (dpe) (dpe/Rh 1·0), and $[RhCl(cod)]_2$ (cod = cycloocta-1,5-diene), are more effective for the amination than are $RhCl(PPh_3)_3$, $RhCl(cod)(PPh_3)$, and $RhCl(CO)(PPh_3)_2$ (compare runs 5, 7, 9, and 10 and 12, 13, and 14). This seems to show that the formation of a co-ordinatively unsaturated monomeric rhodium(I) complex plays an important role in the production of active species. The use of $[RhCl(PPh_3)_2]_2$ or $[RhCl(C_2H_4)_2]_2$+dpe (dpe/Rh 1·0) gave yields of (**2**) $>$ 100%, based on rhodium (runs 5 and 9). This suggests that the rhodium(I) complexes can recycle as a catalyst, although inefficiently.

TABLE 2. Direct amination of anthraquinone with various amines.[a]

Amine	pK_{BH^+}	Yield/%[b] (**2**)	(**3**)
Bu^nNH_2	10·64	**a**; 114	10
Bu^sNH_2	10·56	**b**; 74	0·8
Bu^tNH_2[c]	10·45	**c**; 20	trace
$cyclo\text{-}C_6H_{11}NH_2$	10·68	**d**; 141	3
$PhCH_2NH_2$	9·35	**e**; 4[d]	0
$p\text{-}MeC_6H_4SO_2NH_2$[e]	—	**f**; 0	0
$HOCH_2CH_2NH_2$	9·50	**g**; 0	0
$Bu^n{}_2NH$	11·31	**h**; trace	0
Piperidine	11·12	**i**; 82	0
$PhCH_2(Me)NH$	9·58	**j**; 3	0

[a] Reactions were carried out at 110 °C in air for 30 h after reaction at 110 °C under N_2 for 3 h using $[RhCl(PPh_3)_2]_2$. [b] Yields based on the rhodium. [c] Reaction was carried out under reflux (*ca.* 100 °C). [d] 14% of 1-aminoanthraquinone was formed. [e] Concentration of amide was 1·3 mol l^{-1}.

The results given in Table 2 suggest that the stronger the basicity and the smaller the steric hindrance of the amine, the higher is the yield. In the cases of n-butylamine and cyclohexylamine, the yield based on rhodium exceeds 100%.

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† A trace amount of 1,5-bis(n-butylamino)anthraquinone was formed when the yield of (**2a**) was high.

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