

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

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

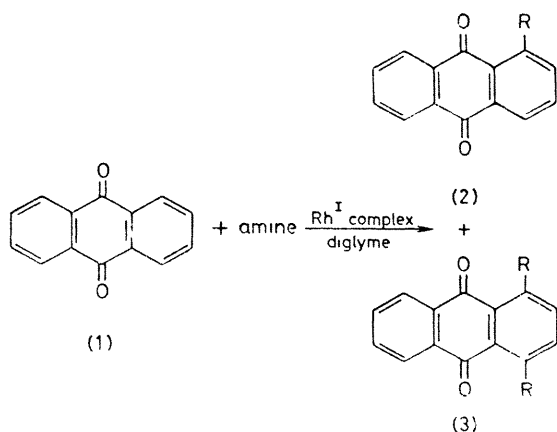
1-aminoanthraquinone to give 1-amino-4-n-butylaminoanthraquinone has been reported by Kitao and his co-workers.² Unsubstituted anthraquinone, however, gave no aminated product under their reaction conditions.

We report here a novel, direct amination of (**1**). In a typical experiment, a mixture of (**1**) ($5 \times 10^{-2} \text{ mol l}^{-1}$), n-butylamine (2.6 mol l^{-1}), and a rhodium(I) complex ($\text{Rh } 5 \times 10^{-3} \text{ g atom l}^{-1}$) 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/(I)	Reaction time/h		Yield/% ^a	
			Under N ₂	In air	(2a)	(3a)
1	—	0	0	34	0	0
2	RhCl·3H ₂ O	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 ₂ H ₄) ₂] ₂	0·10	30	0	2	0
7	"	0·11	3	30	100	18
8	[RhCl(C ₂ H 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 = NHBuⁿ
 b; R = NHBu^s
 c; R = NHBu^t
 d; R = NH(cyclo-C₆H₁₁)
 e; R = NHCH₂Ph
 f; R = NHSO₂C₆H₄Me-*p*
 g; R = NHCH₂CH₂OH
 h; R = NBuⁿ₂
 i; R = piperidin-1-yl
 j; R = N(Me)CH₂Ph

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 N₂ 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 N₂, 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(PPh₃)₂]₂, [RhCl(C₂H₄)₂]₂, [RhCl(C₂H₄)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(PPh₃)₃, RhCl(cod)(PPh₃), and RhCl(CO)(PPh₃)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(PPh₃)₂]₂ or [RhCl(C₂H₄)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 ⁿ NH ₂	10·64	a; 114	10
Bu ^s NH ₂	10·56	b; 74	0·8
Bu ^t NH ₂ ^c	10·45	c; 20	trace
cyclo-C ₆ H ₁₁ NH ₂	10·68	d; 141	3
PhCH ₂ NH ₂	9·35	e; 4 ^d	0
<i>p</i> -MeC ₆ H ₄ SO ₂ NH ₂ ^e	—	f; 0	0
HOCH ₂ CH ₂ NH ₂	9·50	g; 0	0
Bu ⁿ ₂ NH	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 N₂ for 3 h using [RhCl(PPh₃)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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