Novel Photochemical Syntheses of Amino- and Hydroxy-1,4-naphthoquinones with High Selectivity

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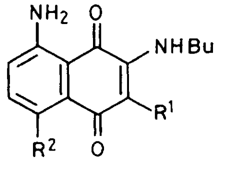
New routes to amino- and hydroxy-naphthoquinones have been developed by the photochemical reaction of 5-aminonaphthoquinones with alkylamines under nitrogen and aerated conditions, respectively.

Although photochemically induced nucleophilic substitution reactions of quinone systems are well documented,[1] few for aminonaphthoquinones are known. Some photochemical reactions of methoxynaphthoquinones with amines to give the corresponding aminonaphthoquinones and methoxyaminonaphthoquinones are known,[2] but not those of aminonaphthoquinones with amines.

We report the novel and regioselective photochemical syntheses of 8-alkylamino- (**2**) and 8-hydroxy-5-amino-naphthoquinones (**3**) by the reaction of 5-aminonaphthoquinones (**1**) with alkylamines under nitrogen and aerated conditions, respectively. The direct alkylamination and hydroxylation of (**1**) resulted in good yields under the conditions given in Table 1, and this is a very important selective synthetic method for these compounds which are formed in very low yields by thermal reactions. Compound (**2a**) has been prepared recently by the metal-promoted direct amination of (**1a**) in 22% yield.[3] Compound (**3**) may be synthesized by the reductive hydroxylation of 5-nitronaphthoquinones.[4] The photochemical reaction of (**1a**) with butylamine in aerated benzene gave (**2a**) and (**3a**) in low yields (Table 1, Run 1). Amination and hydroxylation were competing reactions under these conditions. Compound (**3a**) was not formed under a nitrogen atmosphere and (**2a**) was obtained selectively in 91% yield (Table 1, Run 2). A longer reaction time increased the isolated yield of (**2a**) but decreased the yield based on (**1a**) owing to the further photochemical decomposition of (**2a**) (Table 1, Run 3).

We propose that atmospheric oxygen co-operates with the amine in the direct hydroxylation of (**1a**). Hydroxylation did not proceed without amine. Selective syntheses of (**3**) were achieved using secondary or tertiary amines, which could not react with (**1**) because of steric hindrance (Table 1, Run 6), but the yield of (**3a**) was poor; 26% (diethylamine, Table 1, Run 6), 30% (piperidine), and 7% (triethylamine). On the other hand, the formation of (**2a**) was markedly decreased on addition of acetonitrile to the benzene solution and compound (**2a**) was not formed in benzene:acetonitrile (4:1) solution (Table 1, Run 5); however the yield of (**3a**) was low. Selective and the high yielding syntheses of (**3**) were achieved using tertiary butylamine under aerated conditions. Tertiary



(**1a**) R^1 = CN, R^2 = H
(**1b**) R^1 = Cl, R^2 = H
(**2a**) R^1 = CN, R^2 = NHBu
(**2b**) R^1 = CN, R^2 = NHPr
(**3a**) R^1 = CN, R^2 = OH
(**3b**) R^1 = Cl, R^2 = OH

Table 1. The reaction of (**1**) with amines.[a]

				Product (yield, %)[b]		
Run	Substrate	Amine	Atmosphere	(**1**)[c]	(**2**)	(**3**)
1	(**1a**)	$BuNH_2$	Air		(**2a**)(7)	(**3a**)(28)
2	(**1a**)	$BuNH_2$	N_2	(**1a**)(32)	(**2a**)(62,91[d])	
3[e]	(**1a**)	$BuNH_2$	N_2	(**1a**)(13)	(**2a**)(71,82[d])	
4	(**1a**)	$PrNH_2$	N_2	(**1a**)(56)	(**2b**)(43,98[d])	
5[f]	(**1a**)	$BuNH_2$	Air	(**1a**)(4)		(**3a**)(30)
6	(**1a**)	Et_2NH	Air			(**3a**)(26)
7	(**1a**)	Bu^tNH_2	Air	(**1a**)(2)		(**3a**)(81)
8	(**1b**)[g]	Bu^tNH_2	Air			(**3b**)(82)

[a] Irradiated with 100 W high pressure mercury lamp (400—500 nm); (**1**) (0.3 mmol) and amine (30 mmol) in benzene (300 ml) at 30 °C for 12 h. [b] Isolated yield after chromatography. All compounds gave spectral data (^1H n.m.r., mass) in agreement with the proposed structures and satisfactory analytical data. M.p. (**2b**) 188—189 °C, (**3a**) 217—217.5 °C, (**3b**) 146—147 °C. [c] Recovered (%). [d] Yield based on amount of (**1**) reacted. [e] Reaction time 48 h. [f] Solvent, benzene:acetonitrile = 4:1. [g] M.p. (**1b**) 127—129 °C.

butylamine could not react with (**1**) owing to steric hindrance and is a good oxygen-carrier for the formation of (**3**).

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