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A Convenient Method for Synthesis of 1-Amino-2-tetralones by Photoamination of 2-Alkoxynaphthalenes with Alkylamines

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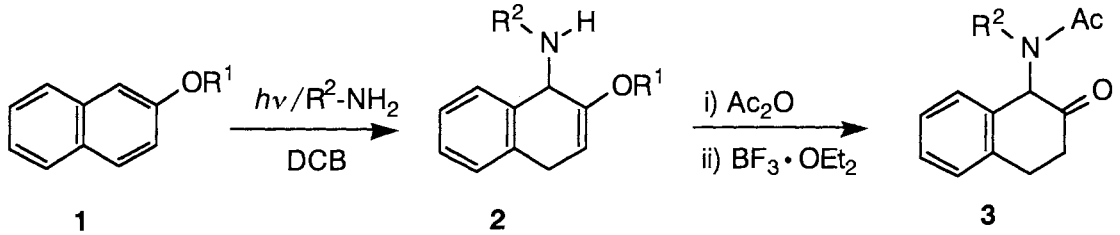
Irradiation of an acetonitrile-water solution containing 2-alkoxynaphthalene, an amine, and *m*-dicyanobenzene gave selectively 2-alkoxy-1-alkylamino-1,4-dihydronaphthalenes in relatively good yields. The aminodihydronaphthalenes were acetylated with Ac_2O and then treated with $BF_3 \cdot OEt_2$ to give *N*-acetyl-1-alkylamino-2-tetralones in good yields.

Much attention has been paid to the development of the photochemical electron-transfer reaction having synthetic potential.[1] Especially, nucleophilic addition to cation radicals generated by photochemical electron transfer to an electron acceptor has been extensively investigated to achieve the direct introduction of certain functional groups to electron-rich substrates.[2] We have studied direct amination of arenes,[3] stilbenes,[4] and 1,1-diarylalkenes[5] with ammonia and amines by photochemical electron transfer, thus offering useful procedure for organic synthesis. Synthetic application of photoamination has been achieved for the preparation of isoquinolines from stilbene and phenanthrene derivatives.[6] Here, we applied the photoamination of 2-alkoxynaphthalenes to the synthesis of 1-alkylamino-2-tetralones, since 1-amino-2-tetralones have medicinal interests[7] but there are no convenient methods to prepare from commercially available starting materials.



1 **2** **3**

R^1= Me, Et, i-Bu, CH_2Ph, R^2= H, Me, Et, allyl, n-Pr, i-Pr

Scheme 1.

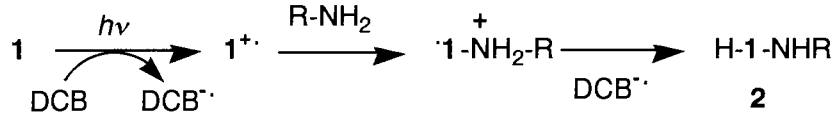
The photoaminations of 2-alkoxynaphthalene (**1**) were carried out by irradiating a deaerated acetonitrile-water (9:1) solution containing **1**, *m*-dicyanobenzene (DCB), and ammonia or an amine with high-pressure mercury lamp through Pyrex filter. A general procedure for isolation of **2** is as follows: After evaporation of

Table 1. The Photoamination of 2-Alkoxynaphthalenes (**1**)[a]

Entry	R^1	R^2	Irradn time/h	Yield of **2**[b] %	Recovery of **1**/%	Recovery of DCB/%
1	Me	H	7	69	8	100
2	Me	Me	9	67	9	67
3	Me	Et	11	67	2	88
4	Me	CH_2=$CHCH_2$	8	83	2	66
5	Me	n-Pr	7	80	5	76
6	Me	i-Pr	9	67	22	90
7	Et	Me	8	59	12	90
8	Et	Et	10	55	25	82
9	i-Bu	Me	10	64	7	78
10	CH_2Ph	Me	10	60	7	83

a) For an acetonitrile-water (9:1; 100 ml) solution containing **1** (10 mmol), DCB (5 mmol), and an amine (100 mmol). b) Isolated yields based on **1** used.

acetonitrile, the photolysates were dissolved in benzene and then extracted with dilute aq HCl and neutralized with aq $NaHCO_3$ to give an aminated product. Thus, 2-alkoxy-1-alkylamino-1,4-dihydronaphthalenes (**2**) were formed as an exclusive product. The results are summarized in Table 1. DCB was almostly recovered from the benzene solution. It was confirmed that no photoamination occurred in the absence of DCB. It should be noted that the amino group was selectively introduced into C-1 position of naphthalene moiety and no other isomers such as 1-amino-1,2-dihydronaphthalene were formed. Unfortunately, efficient photoamination did not occur with secondary alkylamines.



Scheme 2.

As has been reported for the photoamination of arenes,[3] the photoamination certainly proceeds via photochemical electron transfer from **1** to DCB and subsequent nucleophilic addition of an amine to the resulting cation radical of **1**, as shown in Scheme 2. Therefore, the selective photoamination on C1 position can be attributed to the distribution of positive charge on the cation radicals of **1**. Moreover, weak nucleophilic group such as vinyl group of allylamine as well as water used as co-solvent did not add to **1** at all.

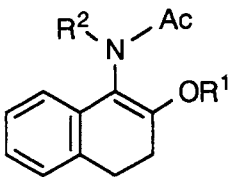
The synthesis of *N*-acetyl-1-alkylamino-2-tetralones (**3**) were performed by the acetylation of **2** with Ac_2O followed by the treatment with excess $BF_3 \cdot OEt_2$ at room temperature.[8] The results are shown in Table 2. The treatment of the acetamide of 1-amino-2-methoxy-1,4-dihydronaphthalene (**2**; R^1= Me, R^2= H) with $BF_3 \cdot OEt_2$ gave 1-acetylamino-2-tetralone (**3**; R^2= H) in 92% yield. But the direct treatment of **2** with $BF_3 \cdot OEt_2$ gave

Table 2. Preparation of *N*-Acetyl-1-alkylamino-2-tetralones (**3**) by Treatment of the Acetamides of **2** with $BF_3 \cdot OEt_2$[a)]

Entry	R^1	R^2	Yield/%[b)] **3**	**4**	Entry	R^1	R^2	Yield/%[b)] **3**	**4**
1	Me	H	92	0	6	Me	$CH_2CH=CH_2$	55	0
2	Me	Me	80	9	7	Me	Et	49	12
3	Et	Me	75	12	8	Me	n-Pr	0	42
4	i-Bu	Me	47	40	9	Me	i-Pr	0	86
5	CH_2Ph	Me	77	0	10	Et	Et	0	42

a) Reaction of the acetamides of **2** (2 mmol) with $BF_3 \cdot OEt_2$ (5-10 ml) at room temperature for 3-10 h. b) Isolated yields based on the acetamides of **2** used.

2-naphthol and/or intractable materials. Moreover, mineral acid (e.g. HBr, H_3PO_4, and CF_3SO_3H) and other Lewis acid (e.g. BF_3 and $AlCl_3$) were ineffective for the preparation of **3**, though the mineral acid was used for the dealkylation of 2-ethoxy-1,4-dihydronaphthalene in the preparation of 2-tetralone.[9)]



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Similarly *N*-acetyl-1-methylamino-2-tetralone (**3**; R^2= Me) was prepared from several acetamides of 2-alkoxy-1-methylamino-1,4-dihydronaphthalenes (**2**; R^1= Me, Et, i-Bu, CH_2Ph, R^2= Me): In the case of R^1= CH_2Ph **3** was exclusively formed, whereas in other cases **3** was formed along with *N*-acetyl-2-alkoxy-1-alkylamino-3,4-dihydronaphthalene (**4**). It is noteworthy that even when R^2 contains functional group such as vinyl group, **3** (R^2= allyl) could be prepared without the reaction of the vinyl group. In the cases of R^1= Me, R^2= n-Pr, i-Pr and R^1= R^2= Et, however, the treatment of the acetamides of **2** did not give the corresponding **3** at all, but gave **4** exclusively. Thus, bulky substituents on amino group would prevent the dealkylation.

The photochemical processes for the preparation of amino ketones have been designed in photochemical electron transfer between amines and enones.[10)] The present method provides a convenient method for the preparation of 1-amino-2-tetralones from 2-alkoxynaphthalenes which are commercially available and are easily prepared.

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8) The spectral data of **3** are as follows: *N*-Acetyl-1-amino-2-tetralone: mp 175-178 °C, ^{1}H NMR δ 2.22 (3H, s), 2.37-2.52 (1H, m), 2.75-2.86 (2H, m), 2.96-3.05 (1H, m), 3.21-3.31 (1H, m), 5.65 (1H, d, J= 12.0 Hz), 6.54 (1H, brs), 7.04-7.27 (4H, m). ^{13}C NMR δ 25.13, 27.11, 35.37, 59.47, 124.22, 127.29, 127.37, 127.70, 133.46, 136.27, 170.86, 206.41. Exact mass calcd for $C_{12}H_{13}NO_2$ 203.0946 found 203.0986. *N*-Acetyl-1-methylamino-2-tetralone: ^{1}H NMR δ 2.24 (3H, s), 2.37-2.59 (2H, m), 2.72-2.97 (4H, m), 2.84 (3H, s), 3.01-3.35 (1H, m), 6.32 (1H, s), 6.92-7.35 (4H, m). ^{13}C NMR δ 21.34, 28.34, 34.30, 37.79, 63.59, 125.96, 126.89, 127.60, 128.06, 133.34, 136.85, 172.31, 205.66. Exact mass calcd for $C_{13}H_{15}NO_2$ 217.1101 found 217.1143. *N*-Acetyl-1-ethylamino-2-tetralone: ^{1}H NMR δ 1.25 (3H, t, J= 7.1 Hz), 2.18 (3H, s), 2.54-3.44 (6H, m), 5.12 (1H, s), 6.94-7.53 (4H, m). ^{13}C NMR δ 14.72, 21.09, 28.28, 38.15, 45.32, 64.45, 125.91, 126.82, 127.02, 127.99, 134.88, 136.37, 173.60, 205.59. Exact mass calcd for $C_{14}H_{17}NO_2$ 231.1288 found 231.1246. *N*-Acetyl-1-allylamino-2-tetralone: ^{1}H NMR δ 2.20 (3H, s), 2.49-3.17 (4H, m), 3.83-4.15 (2H, m), 5.01-5.26 (2H, m), 5.43 (1H, m), 5.77-5.99 (1H, m),7.07-7.46 (4H, m). ^{13}C NMR δ 21.66, 28.32, 38.25, 52.84, 63.96, 118.41, 126.18, 126.91, 127.40, 128.02, 133.81, 134.84, 136.59, 171.27, 205.56. Exact mass calcd for $C_{15}H_{17}NO_2$ 243.1257 found 243.1217.
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