Photoamination of 2-Alkoxynaphthalenes with Alkylamines via Electron Transfer and Its Application to Synthesis of 1-Alkylamino-2-tetralones

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(Received September 1, 1993)

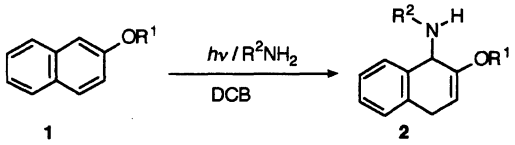
Photoaminations of 2-alkoxynaphthalenes (**1**) with ammonia and primary alkylamines were performed by irradiating an acetonitrile–water solution containing **1**, an amine, and *m*-dicyanobenzene to give 1-alkylamino-2-alkoxy-1,4-dihydronaphthalene (**2**) in relatively good yields. The conversion of **2** to *N*-acetyl-1-alkylamino-2-tetralones was performed by acetylation with Ac_2O followed by a treatment with $BF_3{\cdot}OEt_2$.

Nucleophilic additions induced by a photochemical electron transfer have been extensively investigated and have become a useful tool to introduce certain functional groups to aromatic nuclei and olefins.[1] We have investigated the photoinduced nucleophilic addition of ammonia and amines to arenes,[2] stilbenes,[3] 1,1-diarylalkenes,[4] and 1-arylpropenes.[5] It was found that the photoamination of naphthalene derivatives[2] readily gave 1-amino-1,4-dihydronaphthalenes, the synthesis of which by other methods has not been previously reported. Especially, the photoamination of 2-methoxynaphthalene occurred most efficiently and most selectively among the naphthalene derivatives investigated.[2] In part of our studies concerning the synthetic application of photoamination,[5,6] therefore, our attention was given to the preparation of a variety of 1-amino-1,4-dihydronaphthalenes by the photoamination of 2-alkoxynaphthalenes and their synthetic application. We preliminarily reported on the synthesis of 1-alkylamino-2-tetralone derivatives from 1-alkylamino-2-methoxy-1,4-dihydronaphthalene.[7]

Here, we wish to report on the details concerning the photoamination of several 2-alkoxynapthalenes with ammonia and alkylamines and of its application to the synthesis of 1-amino-2-tetralones.

Results and Discussion

Photoamination. The photoaminations of 2-alkoxynaphthalenes (**1**) with ammonia and alkylamines (RNH_2) were carried out by irradiating a deaerated acetonitrile–water (9 : 1) solution containing **1**, *m*-dicyanobenzene (DCB), and an amine by a high-pressure mercury lamp through a Pyrex filter. The photoamination of 2-methoxynaphthalene (**1a**), 2-ethoxynaphthalene (**1b**), 2-isobutoxynaphthalene (**1c**), and 2-(benzyloxy)naphthalene (**1d**) with RNH_2 gave the corresponding 1-alkylamino-2-alkoxy-1,4-dihydronaphthalene (**2**) as an exclusive product (Scheme 1). Compound **2** was slowly decomposed into intractable materials by long-time exposure under an oxygen atmosphere and was dehydroaminated into parent 2-alkoxynaphthalene when passed through a gas chromatograph over about 200 °C of injection temperature. However, they were easily isolated by the following procedure: After evaporation of acetonitrile, the photolysates were dissolved in benzene and then extracted with dilute aq HCl. The aqueous layer was neutralized with aq $NaHCO_3$ and extracted with Et_2O to give aminated products. DCB was almost recovered from the benzene solution. The results are summarized in Table 1. It was confirmed that no photoamination occurred in the absence of DCB. Moreover, it should be noted that the amino group was selectively introduced into the C-1 position of the naphthalene ring, and no other isomers, such as 1-amino-2-alkoxy-1,2-dihydronaphthalenes, were formed at all.



1 2

	R1		R1	R2		R1	R2
1a	Me	**2a**	Me	H	**2i**	Et	Et
1b	Et	**2b**	Me	Me	**2j**	Et	i-Pr
1c	i-Bu	**2c**	Me	Et	**2k**	i-Bu	Me
1d	CH_2Ph	**2d**	Me	n-Pr	**2l**	CH_2Ph	Me
		2e	Me	i-Pr	**2m**	CH_2Ph	Et
		2f	Me	$CH_2CH{=}CH_2$	**2n**	CH_2Ph	n-Pr
		2g	Et	H	**2o**	CH_2Ph	i-Pr
		2h	Et	Me			

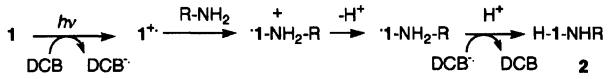
Scheme 1.

As has been reported concerning the photoamination of **1a** with ammonia,[2] the photoamination of **1** with RNH_2 was certainly initiated by an electron transfer from the excited state of **1** to DCB, since no photoamination of **1** in the absence of DCB occurred, and since the oxidation potentials of **1** were relatively low (Table 1). The nucleophilic addition of RNH_2 to the resulting cation radial of **1** afforded the aminated cation radicals. A reduction of the aminated neutral radicals by the anion radical of DCB gave the final products (**2**) after protonation, as shown in Scheme 2. Therefore, the regioselective amination on the C-1 position of the naphthalene ring can be attributed to the distribution of positive charge on the cation radicals of **1**. Although the steric repulsion between the alkylamino group and the alkoxyl group has been predicted, the

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

ArH ($E_{1/2}^{ox}$/V)[b]	R^2NH_2	Irradn time (h)	Yield (%)[c]		Recov. of ArH (%)	Recov. of DCB (%)
1a (1.07)	NH_3	7	**2a**	69[d]	8	100
	$MeNH_2$	9	**2b**	67	9	67
	$EtNH_2$	9	**2c**	67	2	88
	n-$PrNH_2$	9	**2d**	40	5	74
	i-$PrNH_2$	9	**2e**	56	16	79
	CH_2=$CHCH_2NH_2$	8	**2f**	83	2	66
1b (1.08)	NH_3	8	**2g**	62	1	89
	$MeNH_2$	7	**2h**	59	12	90
	$EtNH_2$	10	**2i**	55	25	82
	i-$PrNH_2$	7	**2j**	61	33	98
1c (1.04)	$MeNH_2$	10	**2k**	64	7	78
1d (1.09)	$MeNH_2$	10	**2l**	60	7	83
	$EtNH_2$	12	**2m**	76	6	81
	n-$PrNH_2$	10	**2n**	68	4	87
	i-$PrNH_2$	10	**2o**	71	6	87

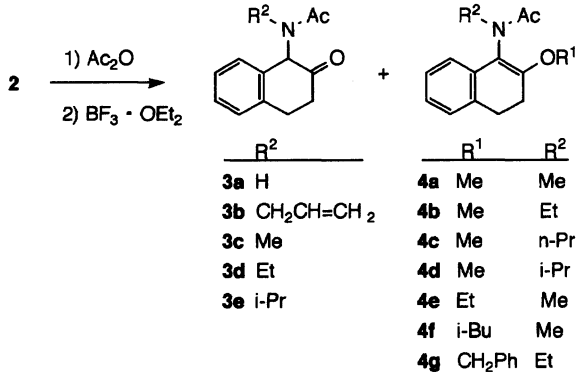
a) For an acetonitrile–water (9 : 1, 100 ml) solution containing ArH (10 mmol), DCB (5 mmol), and an amine (100 mmol). b) Half-peak oxidation potentials vs. $Ag/AgNO_3$. c) Isolated yields based on ArH used. d) Values from Ref. 2.



Scheme 2.

alkylamines selectively attack at C-1 where the highest positive charge might develop. This is in accord with the addition of CN^-,[8] BH_4^-,[9] and ammonia[2] which took place at the C-1 position of the cation radical of **1a**.

Preparation of 1-Amino-2-tretralones. If the dealkylation of the vinyl ether group of **2** takes place easily in a similar manner to the case of 2-ethoxy-1,4-dihydronaphthalene, which was converted to 2-tetralone by hydrolysis,[10] **2** could be a precursor for the syntheses of 1-alkylamino-2-tetralones. The dealkylation reactions were performed at room temperature, since **2** decomposed to the parent alkoxynaphthalenes at elevated temperature, as reported concerning the 9-amino-9,10-dihydrophenanthrene derivatives.[11] Dealkylation by mineral acids, such as H_2SO_4, H_3PO_4, and CF_3SO_3H, did not occur at room temperature. 1-Amino-2-methoxy-1,4-dihydronaphthalene (**2a**) was acetylated with Ac_2O and then treated with excess BF_3·OEt_2 at room temperature to give 1-acetylamino-2-tetralone (**3a**) in 92% yield. BF_3·OEt_2 was most effective among the Lewis acids investigated (e.g. BF_3 gas and $AlCl_3$). However, a direct treatment of **2a** with BF_3·OEt_2 gave 2-naphthol and/or intractable materials. Also, the usual treatment of the benzyloxy compound (**2m**) with Pd/C under a hydrogen atmosphere did not cause debenzylation. Therefore, the method using acetylation and a subsequent treatment with BF_3·OEt_2 was used for the preparation of **3** throughout the present investigation (Scheme 3). Table 2 summarizes the successful results.



Scheme 3.

Table 2. Treatment of *N*-Acetyl Derivatives of **2** with BF_3·OEt_2[a]

Entry	Acetamides of **2**		Products			
	R^1	R^2	yield (%)[b]			
1	Me	H	**3a**	92		
2	Me	Allyl	**3b**	55		
3	Me	Me	**3c**	80	**4a**	9
4	Me	Et	**3d**	49	**4b**	12
5	Me	*n*-Pr			**4c**	42
6	Me	*i*-Pr			**4d**	86
7	Et	Me	**3c**	75	**4e**	12
8	*i*-Bu	Me	**3c**	47	**4f**	40
9	CH_2Ph	Me	**3c**	77		
10	CH_2Ph	Et	**3d**	49	**4g**	42
11	CH_2Ph	*i*-Pr	**3e**	40		

a) Reaction of *N*-acetyl derivatives of **2** (2 mmol) with BF_3·OEt_2 (5—10 ml) at room temperature for 3—10 h. b) Isolated yields based on **2** used.

N-Acetyl-1-allylamino-2-tetralone (**3b**) was readily prepared by a treatment of the *N*-acetyl derivative of 1-allylamino-2-methoxy-1,4-dihydronaphthalene (**2f**)

without a reaction of the vinyl group (Entry 2). However, the treatment of the *N*-acetyl derivatives of **2b** and **2c** (R^1=Me and R^2=Me and Et) with BF_3·OEt_2 gave mixtures of *N*-acetyl-1-alkylamino-2-tetralones (**3c** and **3d**) and small amounts of the isomerized products, *N*-acetyl-1-alkylamino-2-methoxy-3,4-dihydronaphthalenes (**4a** and **4b**), respectively (Entries 3 and 4). In the cases of R^1=Me and R^2=*n*-Pr and *i*-Pr (**2d** and **2e**), only isomerization occurred, forming **4c** and **4d**, respectively (Entries 5 and 6). In order to improve the yields of *N*-acetyl-1-methylamino-2-tetralone (**3c**), *N*-acetyl derivatives of several **2** (R^1=Et, *i*-Bu, CH_2Ph, R^2=Me) were treated with BF_3·OEt_2. The treatment of *N*-acetyl derivatives of 2-ethoxy- and 2-isobutoxy-1-methylamino-1,4-dihydronaphthalenes (**2h** and **2k**) gave mixtures of **3c** and the isomerized product (**4e** and **4f**) (Entries 7 and 8), while the treatment of *N*-acetyl derivative of 2-benzyloxy-1-methylamino-1,4-dihydronaphthalene (**2l**) gave only compound **3c** in 77% yield (Entry 9).

Also, *N*-acetyl-1-isopropylamino-2-tetralone (**3e**) was prepared by the debenzylation of the *N*-acetyl derivative of 1-isopropylamino-2-benzyloxy-1,4-dihydronaphthalene (**2o**) (Entry 11), while the debenzylation of the *N*-acetyl derivative of 1-ethylamino-2-benzyloxy-1,4-dihydronaphthalene (**2m**) occurred along with the formation of an isomerized product (**4g**) (Entry 10). However, *N*-acetyl-1-propylamino-2-tertalone could not be prepared from the corresponding amides.

Although 1-amino-2-tetralones are pharmaceutically useful intermediates,[12] no convenient methods have been reported so far, compared with the case of the analogous 2-amino-1-tetralones.[13] Thus, the present procedure via photoamination and subsequent dealkylation will become a convenient method to prepare 1-amino-2-tetralones from commercially available starting materials.

Experimental

The melting points were measured on a Shibata MEL 270 melting-point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were taken for $CDCl_3$ solutions on a Bruker AC-250P spectrometer. A Hitachi M-2000A was used for analyzing the mass spectra. The oxidation potentials were measured in acetonitrile on a Hokuto Denko HA-501G potentiostat and a HB-105 function generator, using $Ag/AgNO_3$ as a reference electrode. GLC analyses were performed on a Shimadzu GC-14A using a capillary column (CBP1-M25-025).

Spectral-grade acetonitrile was distilled from P_2O_5 and then from CaH_2. 2-Methoxy-, 2-ethoxy-, and 2-isobutoxynaphthalenes (**1a**—**c**) and *m*-dicyanobenzene were commercially available. 2-(Benzyloxy)naphthalene (**1d**) was prepared by refluxing an aqueous solution of 2-naphthol with benzyl bromide in the presence of K_2CO_3 and tetrabutylammonium chloride. **1d**: Mp 96—98 °C (from methanol) (lit,[14] 101.5—102 °C); ^1H NMR δ=5.18 (2H, s), 7.22—7.50 (9H, m), 7.70—7.77 (3H, m); ^{13}C NMR δ= 70.01, 107.28, 119.04, 123.69, 126.36, 126.78, 127.57, 127.64, 128.00, 128.30, 128.50, 129.44, 135.02, 137.25, 157.65.

General Procedure of Photoamination. The photoaminations of 2-alkoxynaphthalenes (**1a**—**d**) were carried out by external irradiation of a deaerated acetonitrile–water (9:1 v/v; 100 ml) solution containing the arene (10 mmol), DCB (5 mmol), and an amine (100 mmol) by an Eikosha PIH-300 high-pressure mercury lamp through a Pyrex filter. The general procedure for isolation of **2** is as follows: After evaporation of acetonitrile, the photolysates were dissolved in benzene and then extracted with dilute HCl and neutralized with aq $NaHCO_3$. **2** were isolated from the aqueous layer after extraction of the solution with Et_2O. The starting arene and DCB were recovered from the benzene solution. The acetylation of **2** was performed with Ac_2O in pyridine.

1-Amino-2-methoxy-1,4-dihydronaphthalene (2a):[2] ^{13}C NMR δ=28.93, 50.62, 54.37, 91.38, 126.28, 126.72, 127.82, 128.73, 133.96, 137.56, 155.97.

2-Methoxy-1-methylamino-1,4-dihydronaphthalene (2b): Oil; ^1H NMR δ=2.06 (3H, s), 2.65 (1H, br s), 3.33—3.64 (2H, m), 3.64 (3H, s), 4.41 (1H, t, J=3.2 Hz), 5.08 (1H, dd, J=4.6 and 3.0 Hz), 7.15—7.26 (3H, m), 7.45 (1H, d, J=8.5 Hz); ^{13}C NMR δ=29.11, 29.65, 54.40, 57.07, 94.46, 126.16, 126.67, 127.58, 128.89, 135.06, 135.77, 152.66; MS *m/z* 189 (M^+). *N*-Acetyl derivative: Found: *m/z* 231.1224. Calcd for $C_{14}H_{17}NO_2$: M, 231.1258; MS *m/z* 231 (M^+), 188 (M−Ac), 158.

1-Ethylamino-2-methoxy-1,4-dihydronaphthalene (2c): Oil; ^1H NMR δ=0.96 (1H, br s), 1.04 (3H, t, J=7.1 Hz), 2.23 (1H, m), 2.46—2.59 (1H, m), 3.31—3.43 (1H, m), 3.50—3.71 (1H, m), 3.63 (3H, s), 4.48 (1H, s), 5.06 (1H, dd, J=4.6, 2.9 Hz), 7.15—7.30 (3H, m), 7.53 (1H, d, J=6.2 Hz); ^{13}C NMR δ=14.86, 29.13, 38.07, 54.46, 56.60, 94.62, 126.20, 126.88, 127.67, 129.07, 134.76, 135.79, 152.81; MS *m/z* 203 (M^+). *N*-Acetyl derivative: Found: *m/z* 245.1382. Calcd for $C_{15}H_{19}NO_2$: M, 245.1414; MS *m/z* 245 (M^+), 202 (M−Ac), 158.

2-Methoxy-1-propylamino-1,4-dihydronaphthalene (2d): Oil; ^1H NMR δ=0.81 (3H, t, J=7.4 Hz), 1.38 (2H, hex, J=7.3 Hz), 2.05—2.15 (1H, m), 2.20 (1H, br s), 2.31—2.41 (1H, m), 3.32—3.64 (2H, m), 3.64 (3H, s), 4.42 (1H, t, J=3.2 Hz), 5.04 (1H, t, J=3.1 Hz), 7.18—7.26 (3H, m), 7.46—7.49 (1H, m); ^{13}C NMR δ=11.86, 23.43, 29.12, 45.48, 54.28, 56.47, 93.80, 126.04, 126.50, 127.57, 128.85, 135.56, 135.95, 153.58; MS *m/z* 217 (M^+). *N*-Acetyl derivative: Found: *m/z* 259.1556. Calcd for $C_{16}H_{21}NO_2$: M, 259.1571; MS *m/z* 259 (M^+), 216 (M−Ac), 158.

1-Isopropylamino-2-methoxy-1,4-dihydronaphthalene (2e): Oil, ^1H NMR δ=0.89 (3H, d, J=6.3 Hz), 1.02 (3H, d, J=6.3 Hz), 1.94 (1H, br s), 2.88 (1H, sept, J=6.3 Hz), 3.29—3.40 (1H, m), 3.50—3.60 (1H, m), 3.60 (3H, s), 4.33 (1H, t, J=2.8 Hz), 4.93—4.97 (1H, m), 7.06—7.26 (3H, m), 7.36—7.39 (1H, m); ^{13}C NMR δ=23.79, 23.89, 29.02, 45.18, 54.29, 55.41, 93.09, 125.89, 126.40, 127.74, 128.94, 135.40, 137.30, 155.92; MS *m/z* 217 (M^+). *N*-Acetyl derivative: Mp 119—120 °C. Found: C, 74.15; H, 8.34; N, 5.55%. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40%.

1-Allylamino-2-methyoxy-1,4-dihydronaphthalene (2f): Oil; ^1H NMR δ=2.00 (1H, br s), 2.82 (1H, dd, J=13.6 and 5.8 Hz), 3.05 (1H, dd, J=13.6 and 6.3 Hz), 3.34—3.62 (2H, m), 3.62 (3H, s), 4.42 (1H, t, J=3.2 Hz),

4.96—5.12 (3H, m), 5.74—5.90 (1H, m), 7.16—7.24 (3H, m), 7.44—7.48 (1H, m); ^{13}C NMR δ=29.11, 46.67, 54.34, 56.13, 93.88, 115.30, 126.08, 126.58, 127.58, 128.92, 135.56, 135.82, 137.41, 153.69. *N*-Acetyl derivative: Found: *m/z* 257.1414. Calcd for $C_{16}H_{19}NO_2$: M, 257.1384.

1-Amino-2-ethoxy-1,4-dihydronaphthalene (2g): *N*-acetyl derivative: Mp 174—176 °C (from methanol); ^{1}H NMR δ=1.31 (3H, t, *J*=6.9 Hz), 2.00 (3H, s), 3.38—3.59 (2H, m), 3.74—3.84 (2H, m), 5.00 (1H, t, *J*=3.5 Hz), 5.74—5.82 (2H, m), 7.17—7.30 (3H, m), 7.43—7.46 (1H, m); ^{13}C NMR δ=14.56, 23.40, 28.82, 47.91, 62.57, 94.98, 126.55, 127.11, 127.66, 128.90, 134.09, 135.70, 151.58, 169.83. Found: C, 72.40; H, 7.14; N, 5.82%. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06%.

2-Ethoxy-1-methylamino-1,4-dihydronaphthalene (2h): Oil; ^{1}H NMR δ=1.34 (3H, t, *J*=7.0 Hz), 2.07 (3H, s), 3.13 (1H, br s), 3.37 (1H, dt, *J*=21.0 and 3.7 Hz), 3.54 (1H, dt, *J*=21.0 and 3.1 Hz), 3.82 (2H, q, *J*=7.0 Hz), 4.40 (1H, t, *J*=3.3 Hz), 5.05 (1H, m), 7.12—7.25 (3H, m), 7.44—7.47 (1H, m); ^{13}C NMR δ=14.66, 29.20, 29.50, 57.13, 62.32, 94.97, 126.18, 126.73, 127.58, 129.00, 134.80, 135.89, 151.66; MS *m/z* 203 (M^+). *N*-Acetyl derivative: Found: *m/z* 245.1374. Calcd for $C_{15}H_{19}NO_2$: M, 245.1414 MS *m/z* 245 (M^+), 202 (M−Ac), 172.

2-Ethoxy-1-ethylamino-1,4-dihydronaphthalene (2i): Oil; ^{1}H NMR δ=1.00 (3H, t, *J*=7.2 Hz), 1.34 (3H, t, *J*=7.0 Hz), 2.20—2.30 (1H, m), 2.44—2.57 (1H, m), 2.59 (1H, br s), 3.36 (1H, dt, *J*=21.1 and 4.5 Hz), 3.55 (1H, dt, *J*=21.1 and 3.2 Hz), 3.82 (2H, q, *J*=7.0 Hz), 4.39 (1H, t, *J*=3.3 Hz), 5.00 (1H, m), 7.16—7.25 (3H, m), 7.45—7.49 (1H, m); ^{13}C NMR δ=14.68, 15.48, 29.23, 38.20, 56.81, 62.28, 94.17, 126.03, 126.52, 127.06, 128.96, 135.67, 136.06, 153.00; MS *m/z* 217 (M^+). *N*-Acetyl derivative: Found: *m/z* 259.1558. Calcd for $C_{16}H_{21}NO_2$: M, 259.1570; MS *m/z* 259 (M^+), 216 (M−Ac), 188 (M−Ac−C_2H_4), 172.

2-Ethoxy-1-isopropylamino-1,4-dihydronaphthalene (2j): Oil; ^{1}H NMR δ=0.88 (3H, d, *J*=6.2 Hz), 1.04 (3H, d, *J*=6.2 Hz), 1.33 (3H, t, *J*=7.0 Hz), 2.06 (1H, br s), 2.93 (1H, sept, *J*=6.2 Hz), 3.34 (1H, ddd, *J*=20.9, 5.1, and 2.6 Hz), 3.56 (1H, dt, *J*=20.9 and 2.8 Hz), 3.79 (2H, q, *J*=7.0 Hz), 4.32 (1H, t, *J*=2.9 Hz), 4.93 (1H, dd, *J*=5.1 and 2.8 Hz), 7.13—7.23 (3H, m), 7.39—7.42 (1H, m); ^{13}C NMR δ=14.68, 23.85, 23.99, 29.10, 45.51, 55.56, 62.17, 93.38, 125.91, 126.36, 127.67, 129.03, 135.41, 137.52, 155.07; MS *m/z* 231 (M^+). *N*-Acetyl derivative: Found: *m/z* 273.1710. Calcd for $C_{17}H_{23}NO_2$: M, 273.1727.

2-Isobutoxy-1-methylamino-1,4-dihydronaphthalene (2k): Oil, ^{1}H NMR δ=0.98 (3H, d, *J*=6.6 Hz), 0.99 (3H, d, *J*=6.6 Hz), 2.06 (3H, s), 2.42 (1H, br s), 3.32—3.58 (5H, m), 4.40 (1H, t, *J*=3.4 Hz), 5.02 (1H, dd, *J*=4.5 and 3.2 Hz), 7.13—7.26 (3H, m), 7.45—7.49 (1H, m); ^{13}C NMR δ=19.39, 28.07, 29.21, 29.83, 57.12, 73.26, 94.40, 126.08, 126.53, 127.50, 129.00, 135.43, 135.77, 152.23; MS *m/z* 231 (M^+). *N*-Acetyl derivative: Found: *m/z* 273.1733. Calcd for $C_{17}H_{23}NO_2$: M, 273.1727.

2-Benzyloxy-1-methylamino-1,4-dihydronaphthalene (2l): Oil; ^{1}H NMR δ=2.07 (3H, s), 2.38 (1H, br s), 3.38 (1H, dt, *J*=21.2 and 4.0 Hz), 3.55 (1H, dt, *J*=21.2 and 3.2 Hz), 4.47 (1H, t, *J*=3.4 Hz), 4.84 (2H, s), 5.15 (1H, m), 7.12—7.48 (9H, m); ^{13}C NMR δ=29.16, 29.75, 57.04, 68.90, 95.71, 126.12, 126.58, 127.39, 127.47, 127.76, 128.44, 128.98, 135.24, 135.58, 137.28, 151.90; MS *m/z* 265 (M^+). *N*-Acetyl derivatives: Found: *m/z* 307.1549. Calcd for $C_{20}H_{21}NO_2$: M, 307.1570.

1-Ethylamino-2-benzyloxy-1,4-dihydronaphthalene (2m): Oil; ^{1}H NMR δ=0.99 (3H, t, *J*=7.1 Hz), 2.03—2.28 (1H, m), 2.33 (1H, br s), 2.44—2.54 (1H, m), 3.36 (1H, dt, *J*=21.1 and 4.2 Hz), 3.54 (1H, dt, *J*=21.0 and 3.1 Hz), 4.48 (1H, t, *J*=3.3 Hz), 4.83 (2H, s), 5.10 (1H, m), 6.95—7.50 (9H, m); ^{13}C NMR δ=15.67, 29.29, 38.13, 56.71, 69.98, 95.29, 126.18, 126.62, 127.47, 127.63, 127.86, 128.56, 129.06, 135.48, 136.06, 137.45, 152.86. *N*-Acetyl derivative: Found: *m/z* 321.1739. Calcd for $C_{21}H_{23}NO_2$: M, 321.1727.

2-Benzyloxy-1-propylamino-1,4-dihydronaphthalene (2n): Oil; ^{1}H NMR δ=0.81 (3H, t, *J*=7.4 Hz), 1.35—1.47 (2H, m), 1.98 (1H, br s), 2.11—2.21 (1H, m), 2.35—2.46 (1H, m), 3.39 (1H, dt, *J*=21.3 and 3.7 Hz), 3.57 (1H, dt, *J*=27.7 and 3.3 Hz), 4.62 (1H, t, *J*=3.5 Hz), 4.86 (2H, s), 5.16 (1H, m), 7.16—7.54 (9H, m); ^{13}C NMR δ=11.83, 22.89, 29.20, 45.02, 56.12, 69.01, 96.08, 126.32, 126.90, 127.44, 127.66, 127.86, 128.52, 129.06, 134.60, 135.48, 137.20, 151.59; MS *m/z* 293 (M^+). *N*-Acetyl derivative: Found: *m/z* 335.1848. Calcd for $C_{22}H_{25}NO_2$: M, 335.1883.

2-Benzyloxy-1-isopropylamino-1,4-dihydronaphthalene (2o): Oil; ^{1}H NMR δ=0.86 (3H, d, *J*=6.2 Hz), 1.06 (3H, d, *J*=6.2 Hz), 2.00 (1H, br s), 2.90—3.06 (1H, m), 3.39 (1H, dt, *J*=20.1 and 2.2 Hz), 3.58 (1H, dt, *J*=20.0 and 2.1 Hz), 4.42 (1H, t, *J*=3.3 Hz), 4.86 (2H, s), 5.06 (1H, m), 7.15—7.43 (9H, m); ^{13}C NMR δ=23.58, 23.82, 28.80, 45.32, 55.14, 68.58, 94.17, 125.73, 126.13, 127.06, 127.38, 127.38, 128.13, 128.79, 134.17, 137.04, 137.18, 154.67; MS *m/z* 293 (M^+). *N*-Acetyl derivative: Found: *m/z* 335.1848. Calcd for $C_{22}H_{25}NO_2$: M, 335.1883.

Treatment of *N*-Acetyl Derivatives of 2a—f, h, k—o with BF_3·OEt_2. A solution of BF_3·Et_2O (10 ml) of *N*-acetyl derivative of **2** (2 mmol) was stirred at room temperature for 3—10 h. After neutralization with aqueous Na_2CO_3 solution, the solution was extracted with Et_2O. Then evaporation of the ether left the crude *N*-acetyl-1-alkylamino-2-tetralones and/or *N*-acetyl-2-alkoxy-1-alkylamino-3,4-dihydronaphthalenes. The isolation of *N*-acetyl-1-alkylamino-2-tetralones was preformed by column chromatography on silica gel. Since the isomerized products (**4a—e**) could not be purified, the spectral data were measured as mixture with the corresponding 1-amino-2-tetralones except for the cases of **4c** and **4d**.

1-Acetylamino-2-tetralone (3a): Mp 175—178 °C; ^{1}H NMR δ=2.22 (3H, s), 2.37—2.52 (1H, m), 2.75—2.86 (1H, m), 2.96—3.05 (1H, m), 3.21—3.31 (1H, m), 5.65 (1H, d, *J*=12.0 Hz), 6.54 (1H, br s), 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. Found: C, 71.07; H, 6.67; N, 6.97%. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; H, 6.89%.

***N*-Acetyl-1-allylamino-2-tetralone (3b):** Oil; ^{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, s), 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. Found: *m/z* 243.1217. Calcd for $C_{15}H_{17}NO_2$: M, 243.1257.

***N*-Acetyl-1-methylamino-2-tetralone (3c):** Oil; ^{1}H NMR δ=2.24 (3H, s), 2.37—2.59 (1H, m), 2.72—2.97 (2H, 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. Found: m/z 217.1143. Calcd for $C_{13}H_{15}NO_2$: M, 217.1101.

***N*-Acetyl-1-ethylamino-2-tetralone (3d):** Oil; ^{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. Found: m/z 231.1246. Calcd for $C_{14}H_{17}NO_2$: M, 231.1288.

***N*-Acetyl-1-isopropylamino-2-tetralone (3e):** Oil; ^{1}H NMR δ=1.30 (3H, d, J=6.6 Hz), 1.35 (3H, d, J=6.6 Hz), 2.18 (3H, s), 2.42—3.08 (4H, m), 3.80—3.95 (1H, m), 4.43 (1H, s), 6.90—7.32 (4H, m); ^{13}C NMR δ=21.58, 21.66, 22.15, 27.92, 36.88, 47.46, 60.13, 126.36, 126.62, 127.09, 128.39, 132.41, 135.73, 173.35, 205.08. Found: m/z 245.1410. Calcd for $C_{15}H_{19}NO_2$: M, 245.1416.

***N*-Acetyl-1-methylamino-2-methoxy-3,4-dihydronaphthalene (4a):** ^{13}C NMR δ=20.99, 26.95, 27.12, 37.70, 55.28, 118.68, 126.92, 127.56, 127.64, 128.33, 132.99, 133.44, 152.36, 173.73; MS m/z 231 (M^+).

***N*-Acetyl-1-ethylamino-2-methoxy-3,4-dihydronaphthalene (4b):** ^{13}C NMR δ=12.88, 22.64, 27.85, 27.91, 43.19, 55.25, 120.08, 124.91, 126.80, 126.96, 127.02, 132.29, 133.11, 153.69, 172.31; MS m/z 245 (M^+).

***N*-Acetyl-2-methoxy-1-propylamino-3,4-dihydronaphthalene (4c):** Oil; ^{1}H NMR δ=0.87 (3H, t, J=7.4 Hz), 1.43—1.62 (2H, m), 1.90 (3H, s), 2.53—2.61 (1H, m), 2.66—2.71 (1H, m), 2.89—2.97 (2H, m), 3.72 (3H, s), 3.80—3.92 (2H, m), 6.95—7.28 (4H, m); ^{13}C NMR δ=11.51, 21.14, 21.24, 22.62, 26.90, 47.98, 55.19, 117.96, 121.07, 125.75, 126.98, 127.21, 132.37, 133.09, 153.58, 172.24. Found: m/z 259.1549. Calcd for $C_{16}H_{21}NO_2$: M, 259.1570.

***N*-Acetyl-2-methoxy-1-isopropylamino-3,4-dihydronaphthalene (4d):** Oil; ^{1}H NMR δ=0.95 (3H, d, J=6.8 Hz), 1.12 (3H, d, J=6.5 Hz), 1.84 (3H, s), 2.36—2.49 (1H, m), 2.71 (1H, ddd, J=16.6, 6.4, and 3.7 Hz), 2.87—3.03 (2H, m), 3.67 (3H, s), 4.62—4.73 (1H, m), 6.99—7.25 (4H, m); ^{13}C NMR δ=20.62, 20.73, 22.01, 22.91, 27.97, 47.24, 55.08, 115.29, 121.90, 125.46, 126.67, 126.89, 131.94, 135.03, 155.05, 172.18. Found: m/z 259.1620. Calcd for $C_{16}H_{21}NO_2$: M, 259.1572.

***N*-Acetyl-1-methylamino-2-ethoxy-3,4-dihydronaphthalene (4e):** ^{13}C NMR δ=14.81, 21.02, 23.42, 27.73, 27.90, 34.40, 118.96, 120.70, 126.68, 126.89, 127.07, 132.43, 133.05, 152.45, 173.69; MS m/z 245 (M^+).

***N*-Acetyl-1-methylamino-2-isobutyloxy-3,4-dihydronaphthalene (4f):** ^{13}C NMR δ=19.08, 19.08, 20.91, 23.51, 27.90, 28.83, 34.32, 74.59, 119.69, 121.34, 125.95, 127.06, 127.21, 132.15, 133.04, 152.83, 172.50; MS m/z 273 (M^+).

***N*-Acetyl-2-benzyloxy-1-ethylamino-3,4-dihydronaphthanlene (4g):** Oil; ^{13}C NMR δ=12.82, 21.55, 27.84, 28.22, 40.93, 65.01, 120.05, 124.91, 125.83, 126.80, 127.32, 127.42, 127.42, 128.02, 128.44, 128.44, 132.51, 133.47, 134.79, 153.32, 173.59. Found: m/z 321.1752. Calcd for $C_{21}H_{23}NO_2$: M, 321.1728.

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