Furan Derivatives. V. The Syntheses of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans Using Strong Bases

Takaaki HORAGUCHI,* Hidetaka NARITA, and Tsuneo SUZUKI†

Department of Chemistry, Faculty of Science, Niigata University, Ikarashi, Niigata 950-21

† *Nippon Dental University, Niigata, 1-8, Hamaura-cho, Niigata 950*

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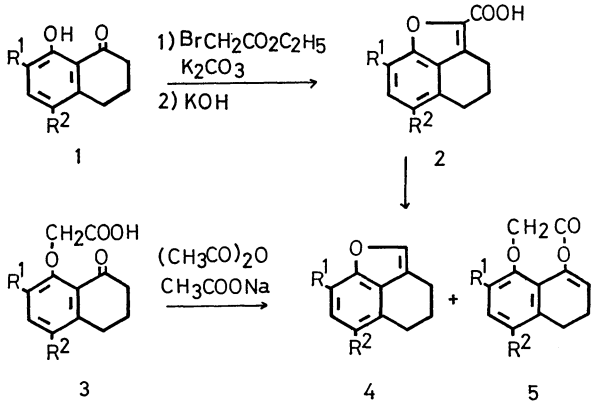
The reaction of ethyl (4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate and potassium hydroxide gave a mixture of 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan and 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylic acid in total yield above 90%. The mechanisms of formation of two products were examined, and potassium 2a-hydroxy-6-methoxy-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2-carboxylate was isolated as a precursor of 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan. It has become apparent that strong bases such as sodium hydroxide, sodium ethoxide, and sodium hydride were also useful for syntheses of 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan derivatives.

4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**4**) are important intermediates to prepare phenanthro[4,5-*bcd*]-furans,[1-4] and unique molecules which have strain[5-8] introduced by condensation of the furan and naphthalene rings at *peri*-positions. Two methods have been employed to synthesize 4,5-dihydro-3*H*-naphtho-[1,8-*bc*]furans (**4**) as shown in Scheme 1. In the first method[9-18] 8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone (**1**) reacted with ethyl bromoacetate in the presence of potassium carbonate followed by saponification and decarboxylation to give 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**4**).[19] The yields of **2** were below 50% for various kinds of substituents (R^1 and R^2) though decarboxylation reaction of **2** proceeded smoothly in good yields. In the second method[20-28] (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids (**3**) were treated with acetic anhydride and sodium acetate to give a mixture of 4,5-dihydro-3*H*-naphtho-[1,8-*bc*]furans (**4**) and lactones (**5**).[7,19] The yields of **4** were near 50% because of the formation of lactones (**5**). It seems that these low yields result from the strain[7] in the fused ring system of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans. Accordingly, we attempted to improve the yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]-furans by using strong bases instead of weak bases. The mechanisms of formation of the furan ring is discussed.

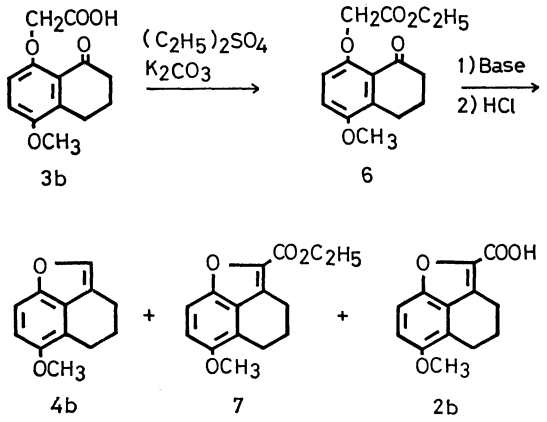


a) R^1=H; R^2=H
b) R^1=H; R^2=OCH_3
c) R^1=OCH_3; R^2=H
d) R^1=OCH_3; R^2=Cl

Scheme 1.

Results and Discussion

Ethyl (4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate (**6**) was obtained in an 88% yield by esterification of (4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acid (**3b**)[19] with diethyl sulfate[39] and potassium carbonate as shown in Scheme 2.



Scheme 2.

Compound **6** was treated with four kinds of strong bases (potassium hydroxide, sodium hydroxide, sodium ethoxide, and sodium hydride) in anhydrous dioxane. The results are summarized in Table 1.

When **6** was refluxed with five equivalents of potassium hydroxide in dioxane for 1 h followed by acidification with hydrochloric acid, two products, 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**4b**) and 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-car-

Table 1. The reactions of ethyl (4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate (**6**) and strong bases in dioxane

Base[a]	Products yield/%			Total yield/%
	4b	**7**	**2b**	
KOH	71	0	22	93
NaOH	47	0	45	92
C_2H_5ONa	44	0	50	94
NaH	24	49	19	92

a) Compound **6** (0.50 g; 1.80 mmol) was treated with 9.00 mmol of each base.

Table 2. The reactions of ethyl (4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate (**6**) and strong bases in benzene

Base[a]	Products yield/%				Total yield/%
	4b	**7**	**2b**	**3b**	
KOH	47	0	0	33	80
NaOH	39	0	0	47	86
C_2H_5ONa	42	0	55	0	97
NaH	42	43	10	0	95

a) Compound **6** (0.50 g; 1.80 mmol) was treated with 9.00 mmol of each base.

boxylic acid (**2b**), were obtained in 71 and 22% yields respectively. The total yield of **4b** and **2b** were 93%, and **2b** was smoothly converted to **4b** by decarboxylation.[19] However, the reaction of **6** with one equivalent of potassium hydroxide afforded **4b**, **2b**, and **3b** in 74, 7, and 12% yields respectively. In the presence of one equivalent of potassium hydroxide the yield of **2b** was reduced. The structures of **4b** and **2b** were confirmed by comparing the IR and ^{1}H NMR spectra and melting point with those of authentic samples.[19] Similarly, the reactions of **6** and other three bases gave 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**4b**, **7**, and **2b**) in total yield above 90%. The structure of **7** was confirmed by comparing the IR and ^{1}H NMR spectra and the melting point with those of an authentic sample.[19]

Nextly, the reactions of **6** with four strong bases were examined in anhydrous benzene. The results are summarized in Table 2.

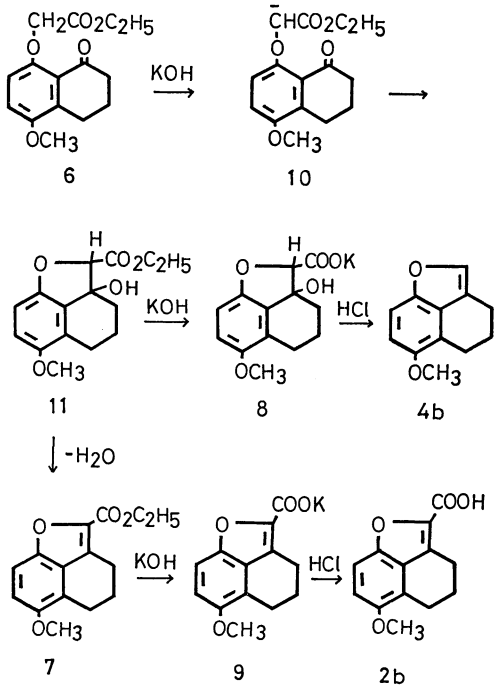
The reactions of **6** and sodium ethoxide or sodium hydride gave 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**4b**, **7**, and **2b**) in total yield above 90%. However, the reaction of **6** and potassium hydroxide or sodium hydroxide afforded **4b** in poor yields because of the ready saponification of **6** to the acid **3b**. Though ethanol was used as a solvent, favorable results were not obtained.

From the above results, strong bases are seen to be generally useful for synthesizing 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan derivatives in good yields. The methods seems to be applicable to syntheses of a variety of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans.

We have examined the reaction of **6** and potassium hydroxide in detail in order to explain the mechanisms of formation of 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**4b**, **7**, and **2b**), since the mechanism of formation of the furan ring had not been explored adequately for benzofuran derivatives.[40–46] When **6** was refluxed with one equivalent of potassium hydroxide in dioxane potassium 2a-hydroxy-6-methoxy-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2-carboxylate (**8**) was obtained as a precipitate in 76% yield. The structure of **8** was confirmed from the spectral properties. The IR spectrum of **8** showed absorption bands due to the carboxylate ion at 1420 and 1610 cm^{-1}. The ^{1}H NMR spectrum of **8** showed a peak due to a methine proton at 4.60 ppm (1H, s), but a hydroxyl group peak was not found because of an exchange reaction between the hydroxyl group and water. The ^{13}C NMR spectrum of **8** exhibited a peak due to a quaternary carbon (2a-position) at 76.8 ppm and a peak due to a tertiary carbon (2-position) at 96.6 ppm. However, the stereochemical relation between the methine proton and the hydroxyl group was not evident from the spectral properties.

In the reaction of **6** with five equivalents of potassium hydroxide in dioxane, compound **4b** was not present in the reaction mixture before acidification with hydrochloric acid judging from TLC analysis. Therefore, **4b** was produced by acidification of the reaction mixture. The ^{1}H and ^{13}C NMR spectra of the precipitates obtained from the reaction of **6** with five equivalents of potassium hydroxide showed that the precipitates consisted of **8** and potassium 6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylate (**9**), that is, potassium salt of **2b** was already present in the reaction mixture before acidification. Compound **8**, once produced, was stable and not converted to **4b** or **9** under the reaction conditions of **6** with potassium hydroxide.

When an aqueous solution of **8** was acidified with hydrochloric acid, **4b** was readily obtained in a 90% yield but the yield of **2b** was only 2%. Therefore, it is clear that **4b** was exclusively produced from the intermediate **8**. The reaction of **8** with diethyl sulfate in dioxane gave **4b** and **7** in 65 and 19% yields respectively. In the presence of potassium hydroxide the reaction of **8** with diethyl sulfate afforded **4b** and **2b** in 3 and 26% yields respectively. The results suggest that the ester **11** was unstable and converted easily to **4b** or **7** by elimination of ethyl hydrogen carbonate or water. In the presence of potassium hydroxide elimination of water was accelerated to give **2b**. Compound **8** was converted to **9** by heating at 240 °C for 2 h under reduced pressure in quantitative yield. From the above results the reaction mechanisms of formation of **4b**, **7**, and **2b** were



Scheme 3.

elucidated and are summarized in Scheme 3.

A proton of the active methylene group in **6** is removed by potassium hydroxide to give an anion **10**. The anion **10** cyclize to an ester **11** which reacts in two paths. Saponification of the ester **11** gives **8** which is stable under the reaction conditions and is converted to **4b** only by adding hydrochloric acid. Dehydration of the ester **11** affords **7** which can be saponified easily by excess potassium hydroxide to give **9**. Compound **9** is converted to **2b** by adding hydrochloric acid. Therefore, **11** is a precursor of **4b**, **7**, and **2b**, and **8** is a direct precursor of **4b**. The mechanisms of the reaction of **6** with potassium hydroxide will be applicable to the reactions of **6** and other strong bases. The reactivity and stereochemistry of **8** will be further investigated.

Experimental

All the melting points are uncorrected. The column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. The infrared absorption spectra (IR) were determined on a Hitachi EPI-G grating infrared spectrophotometer. The nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were determined at 90 MHz on a JEOL JNM-FX 90Q FT NMR spectrometer. Tetramethylsilane (TMS) was used as the internal standard in organic solvents. Methyl groups of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) were employed as the internal standard in deuterium oxide: The chemical shift of the methyl groups was taken as 0 ppm.

*A General Procedure for the Reactions of Ethyl (4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate (**6**) with Strong Bases.* A mixture of **6** (0.50 g; 1.80 mmol), potassium hydroxide (0.50 g; 9.00 mmol), and anhydrous dioxane (10 ml) was refluxed for 1 h. To the mixture water (20 ml) was added, and the solution was poured into 2 M** hydrochloric acid (100 ml). After 15 min the solution was extracted with ether. The ethereal solution was washed three times with a 1 M potassium carbonate solution (30 ml) and then with water, dried, and evaporated. The resulting oil was chromatographed and eluted with benzene to give 0.24 g (71%) of **4b** as colorless oil. The IR and ^{1}H NMR spectra of the oil are identical with those of an authentic sample.[19] Bp 102 °C at 0.7 Torr.*** ^{13}C NMR ($CDCl_3$): δ (TMS) 19.9, 21.7, 23.5, 56.7, 108.0, 109.4, 116.9, 128.8, 138.5, 148.4, 151.2.

The alkaline solution was acidified with 6M hydrochloric acid and the resulting precipitates were extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give 0.09 g (22%) of **2b** as crystals. Recrystallization from dioxane gave colorless needles; mp 229 °C (decomp). The IR spectrum and melting point of the needles are identical with those of an authentic sample.[19] ^{1}H NMR (CD_3COCD_3): δ (TMS) 1.88—2.16 (2H, m, $-CH_2-$), 2.83 (2H, t, J=6 Hz, $-CH_2-$), 3.07 (2H, t, J=6 Hz, $-CH_2-$), 3.88 (3H, s, Ar–OCH_3), 7.13 (1H, d, J=9 Hz, Ar–H), 7.30 (1H, d, J=9 Hz, Ar–H).

Similarly **6** was treated with sodium hydroxide, sodium ethoxide, or sodium hydride in dioxane. Isolation of **4b** and **7** was performed by chromatography using benzene followed by benzene(9)–ether(1) as developing solvents. The reactions of **6** and four kinds of bases in anhydrous benzene were carried out by a method similar to the reaction of **6** with potassium hydroxide in dioxane.

*A Reaction of **6** and One Equivalent of Potassium Hydroxide.* A mixture of **6** (0.500 g; 1.80 mmol) and potassium hydroxide (0.100 g; 1.80 mmol) was refluxed for 1 h in dioxane (10 ml). The reaction mixture was treated with 2 M hydrochloric acid by the method mentioned above. Thus, **4b** (0.250 g) was obtained in a 74% yield as a neutral product, and a mixture (0.085 g) of **2b** and **3b** was obtained as acidic products. The yields of **2b** and **3b** were determined to be 7 and 12% respectively by NMR analysis.

*Ethyl 6-Methoxy-4,5-dihydro-3H-naphtho[1,8-bc]furan-2-carboxylate (**7**).* Colorless needles from ethanol; mp 95—96 °C (lit,[19] 95—96 °C). The IR and ^{1}H NMR spectra of the needles were identical with those of an authentic sample.[19] ^{13}C NMR ($CDCl_3$): δ (TMS) 14.4, 21.4, 21.8, 23.3, 56.7, 60.8, 108.9, 113.3, 120.9, 126.9, 128.6, 139.3, 148.4, 151.5, 160.2.

*Ethyl (4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate (**6**).* A mixture of **3b**[19] (10.0 g), diethyl sulfate (20.0 g), potassium carbonate (40.0 g), and acetone (200 ml) was refluxed for 2 h. After removal of the acetone the mixture was extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The resulting oil was chromatographed and eluted with benzene(7)–ether(3) to give 7.60 g (88%) of **6**. Recrystallization from ethanol gave colorless needles; mp 72—73 °C. IR (KBr): ν_{max} 1680 (C=O), 1760 cm^{-1} ($COOC_2H_5$). ^{1}H NMR ($CDCl_3$): δ (TMS) 1.29 (3H, t, J=7 Hz, CH_3), 2.05 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.62 (2H, t, J=6 Hz, $-CH_2-$), 2.87 (2H, t, J=6 Hz, $-CH_2-$), 3.81 (3H, s, OCH_3), 4.24 (2H, q, J=7 Hz, $-OCH_2-$), 4.62 (2H, s, $-OCH_2CO-$), 6.81 (1H, d, J=9 Hz, Ar–H), 6.96 (1H, d, J=9 Hz, Ar–H). ^{13}C NMR ($CDCl_3$): δ (TMS) 14.2, 22.2, 23.6, 40.6, 55.9, 61.0, 68.4, 115.0, 115.2, 124.7, 135.1, 151.8, 152.0, 169.2, 197.2. Found: C, 64.63; H, 6.40%. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52%.

*Potassium 2a-Hydroxy-6-methoxy-2a,3,4,5-tetrahydro-2H-naphtho[1,8-bc]furan-2-carboxylate (**8**).* A mixture of **6** (1.00 g; 3.60 mmol), potassium hydroxide (0.20 g; 3.60 mmol), and anhydrous dioxane (20 ml) was refluxed for 1 h. After cooling the resulting precipitates were collected by filtration to give 0.84 g (76%) of **8**. Recrystallization from water–dioxane gave colorless needles, mp>250 °C. IR (KBr): ν_{max} 1420, 1610 (COO^-), 3250 cm^{-1} (OH). ^{1}H NMR (D_2O): δ (DSS) 1.38—2.98 (6H, m, $-CH_2-+-CH_2-+-CH_2-$), 3.77 (3H, s, Ar–OCH_3), 4.60 (1H, s, $-CH=$), 6.70 (1H, d, J=8 Hz, Ar–H), 6.75 (1H, d, J=8 Hz, Ar–H). ^{13}C NMR (D_2O): δ (DSS) 20.1, 22.8, 33.6, 59.0 76.8, 96.6, 109.5, 115.1, 127.3, 131.9, 153.8, 154.1, 176.6. Found: C, 51.20; H, 4.89%. Calcd for $C_{13}H_{13}O_5K\cdot H_2O$: C, 50.97; H, 4.94%.

*Potassium 6-Methoxy-4,5-dihydro-3H-naphtho[1,8-bc]furan-2-carboxylate (**9**).* Compound **2b** (0.50 g) was dissolved in an alkaline solution (30 ml) containing potassium hydroxide (0.12 g) and the water was removed under the reduced pressure to give 0.58 g (92%) as crystals. Recrystallization from water–dioxane gave colorless plates; mp 103—105 °C. The melting point of the plates after once melting was above 250 °C. IR (KBr): ν_{max} 1405, 1570 cm^{-1} (COO^-). ^{1}H NMR (D_2O): δ (DSS) 1.82 (2H, dt, J=6 Hz, $-CH_2-$), 2.56 (2H, t, J=6 Hz, $-CH_2-$), 2.83 (2H, t, J=6 Hz, $-CH_2-$), 3.80 (3H, s, Ar–OCH_3), 6.89 (1H, d, J=9 Hz, Ar–H), 7.11 (1H, d, J=9 Hz, Ar–H). ^{13}C NMR (D_2O): δ (DSS) 23.5, 24.0, 25.4, 59.6, 111.1, 115.2, 123.1, 125.2, 131.1, 146.7, 149.8, 152.7, 170.2. Found: C, 51.24; H, 4.98%. Calcd for $C_{13}H_{11}O_4K\cdot 2H_2O$: C, 50.97; H, 4.94%.

The Reaction of Potassium 2a-Hydroxy-6-methoxy-2a,3,4,5-tetra-

** 1 M=1 mol dm^{-3}.

*** 1 Torr≈133.322 Pa.

*hydro-2*H*-naphtho[1,8-*bc*]furan-2-carboxylate (8) and Hydrochloric Acid.* Compound **8** (0.100 g) was dissolved in water (10 ml) and the solution was poured into 2 M hydrochloric acid (100 ml). After 15 min the solution was extracted with ether. The ethereal solution was washed three times with a 1 M potassium carbonate solution and then with water, dried, and evaporated to give 0.55 g (90%) of **4b** as colorless oil. The alkaline solution was acidified with 6 M hydrochloric acid and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give 0.002 g (2%) of **2b** as colorless crystals.

*The Reaction of Potassium 2a-Hydroxy-6-methoxy-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2-carboxylate (8) and Diethyl Sulfate.* A mixture of **8** (0.100 g), diethyl sulfate (0.110 g), and dioxane (8 ml) was refluxed for 2 h. The mixture was extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The resulting oil was chromatographed and eluted with benzene. The first fraction gave 0.040 g (65%) of **4b** as colorless oil. The second fraction afforded 0.015 g (19%) of **7** as colorless crystals.

Similarly, **8** (0.100 g) was dealt with diethyl sulfate (0.110 g) in the presence of potassium hydroxide (0.100 g) to give **4b** and **2b** in 3 and 26% yields respectively. The total yield of **4b** and **2b** was low because unreacted **8** remained.

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