Furan Derivatives. I. On the Methods of Synthesizing Some Naphtho[1,8-*bc*]furans

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Two kinds of methods of synthesizing naphtho[1,8-*bc*]furans (VIa–VId) are described. In the first method, naphtho[1,8-*bc*]furans (VIa–VId) were obtained by the decarboxylation of IIa–IId, which had previously been prepared from Ia–Id and ethyl bromoacetate. The yields of IIa–IId from Ia–Id were 45, 43, 49, and 46% respectively. In the second method, VIa–VId were obtained by heating Va–Vd with acetic anhydride and sodium acetate. The yields of VIa–VId were 34, 46, 46, and 70% respectively.

In previous papers,[1–3] we have reported on the syntheses of phenanthro[4,5-*bcd*]furans. In the course of the syntheses, naphtho[1,8-*bc*]furan derivatives (Xa–Xc) played an important part as the intermediate products, and the syntheses of the compounds Xa–Xc were attempted in the ways of A and B.

Attempts using Method B were all unsuccessful, however, resulting, for example, in the formation of the lactone (IX) rather than the expected naphtho[1,8-*bc*]furan (Xb). However, the syntheses of simple naphtho[1,8-*bc*]furans such as VI, which have no propionic acid residues, may be possible by this method. By Method A, naphtho[1,8-*bc*]furans (IIe—IIg) were obtained in relatively low yields (*ca.* 40%). One of the causes of the low yields may be the steric hindrance of the propionic acid residues, and it seems that Compounds Ia—Id, which have no propionic acid residues, are converted to IIa—IId in better yields. For these reasons, syntheses of naphtho[1,8-*bc*]furans (IIa—IId and VIa—VId) were attempted from Ia—Id and Va—Vd respectively using Methods A and B. Only a few articles[4–6] on naphtho[1,8-*bc*]furan derivatives have been published: for example, Royer *et al.* obtained naphtho[1,8-*bc*]furans in very poor yields by a method similar to A.

Results and Discussion

The syntheses of naphtho[1,8-*bc*]furans (IIa—IId and VIa—VId) were attempted from 8-hydroxy-1-tetralone derivatives (Ia—Id) by two kinds of methods. The first method is the same (A) as those used in the syntheses of IIe—IIg. Naphtho[1,8-*bc*]furans (IIa—IId) were obtained by the heating of Ia—Id, ethyl bromoacetate, and potassium carbonate at 120°C, followed by hydrolyses. From the reaction mixture before the hydrolyses, Compounds IIIa—IIId were also isolated. The carboxylic acids, IIa—IId, were decarboxylated with quinoline and copper to the expected naphto[1,8-*bc*]furans (VIa—VId). The yields of the reactions from tetralones (Ia—Id) to naphtho[1,8-*bc*]furans (IIa—IId) are shown in Table 1, along with those of IIe—IIg from Ie—Ig.

Table 1 shows that the yields of IIa—IId were comparable to one another and similar to those of IIe—IIg; the effects of the substituents (R_1, R_2, and R_3) on the yields did not appear, but in the presence of the propionic acid residues a higher reaction temperature (170—180 °C) was required to prepare IIe—IIg from Ie—Ig compared with that needed in the syntheses (120 °C) of IIa—IId. The yields of IIa—IId from Ia—Id did not vary at the reaction temperature of 150 °C. In the same way (150 °C), a benzofuran derivative (XII) was obtained in a yield of 76% from 2-acetyl-*p*-cresol (XI) and ethyl bromoacetate. It seems that the low yields of IIa—IId are a result of the inhibition of the free rotations of the carbonyl groups in Ia—Id, that is, to the difficult access of the

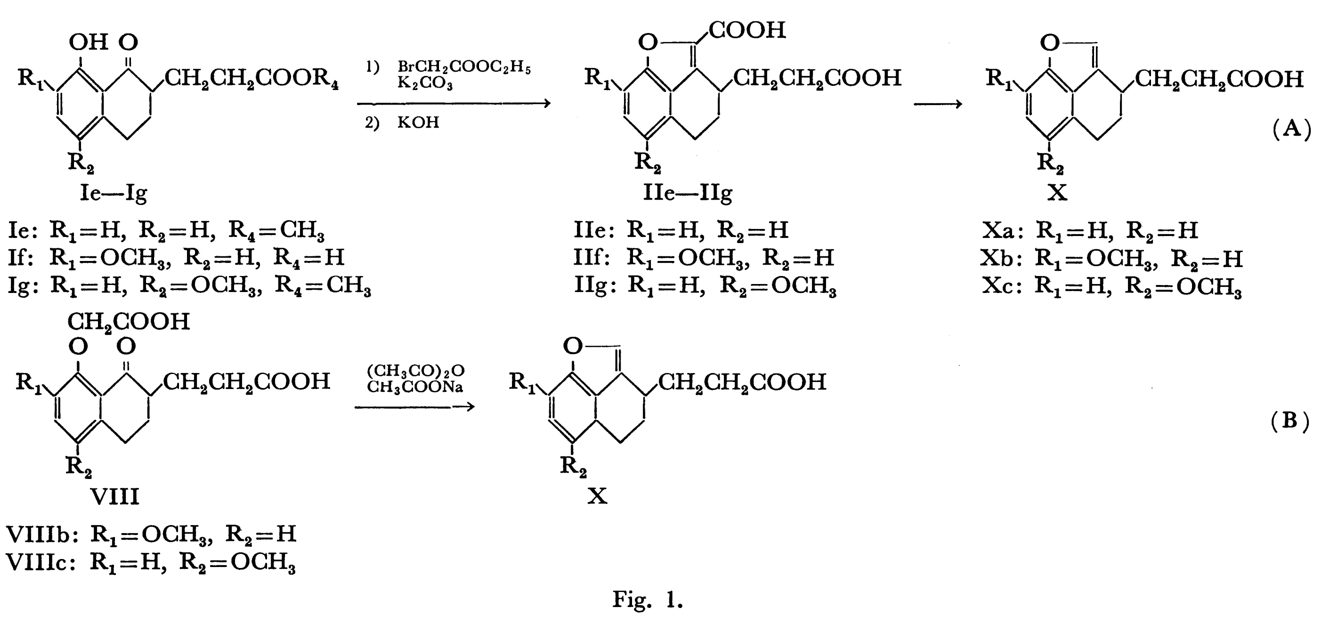
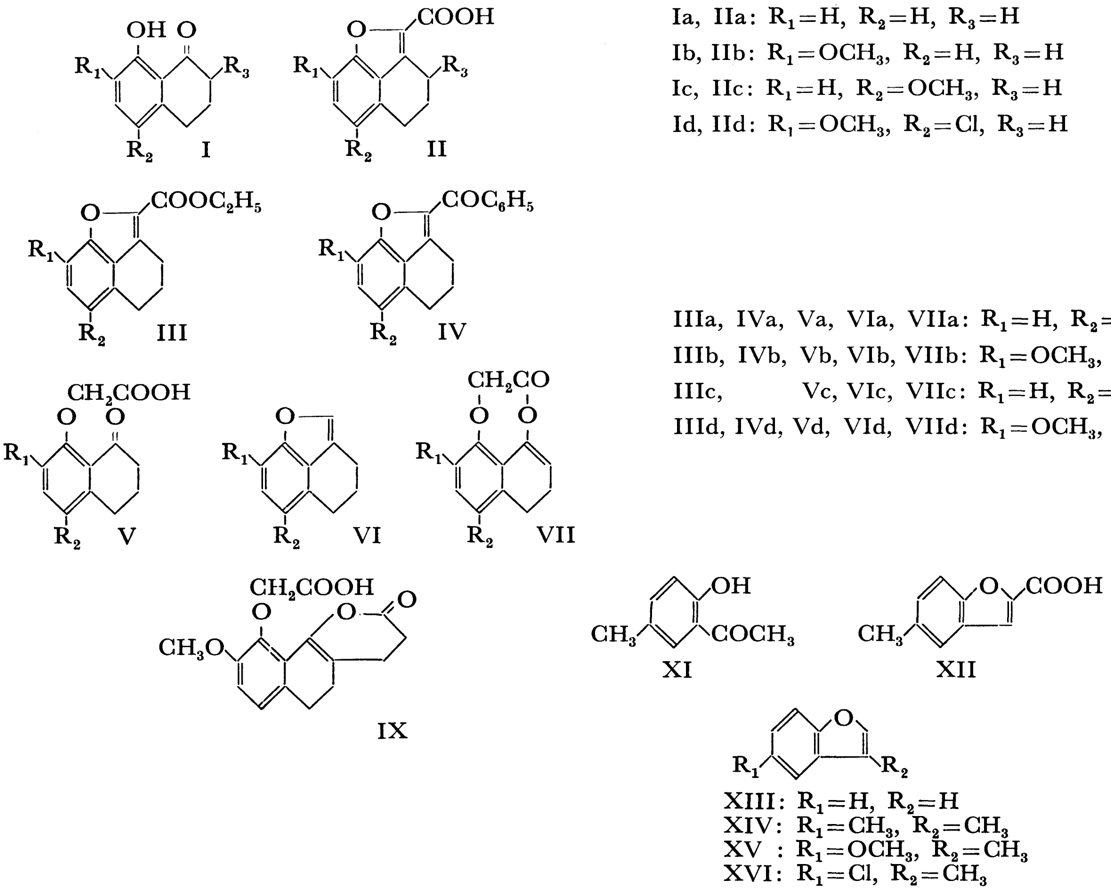


Fig. 1.



Ia, IIa: R_1=H, R_2=H, R_3=H
Ib, IIb: R_1=OCH_3, R_2=H, R_3=H
Ic, IIc: R_1=H, R_2=OCH_3, R_3=H
Id, IId: R_1=OCH_3, R_2=Cl, R_3=H

IIIa, IVa, Va, VIa, VIIa: R_1=H, R_2=H
IIIb, IVb, Vb, VIb, VIIb: R_1=OCH_3, R_2=H
IIIc, Vc, VIc, VIIc: R_1=H, R_2=OCH_3
IIId, IVd, Vd, VId, VIId: R_1=OCH_3, R_2=Cl

XIII: R_1=H, R_2=H
XIV: R_1=CH_3, R_2=CH_3
XV : R_1=OCH_3, R_2=CH_3
XVI: R_1=Cl, R_2=CH_3

Fig. 2.

Table 1. The yields (%) of naphtho[1,8-*bc*]furans

Starting material	Product (%)	Starting material	Product (%)	Starting material	Product (%)
Ia	IIa (45)	Ie	IIe (41)	Ia	IVa (41)
Ib	IIb (43)	If[a]	IIf (39)	Ib	IVb (65)
Ic	IIc (49)	Ig	IIg (43)	—	—
Id	IId (46)	—	—	Id	IVd (71)

a) The corresponding acid was used as the starting material in place of ester.

active methylene to the carbonyl groups or, perhaps more likely, to ring strains in IIa—IId.

The acids IIa—IId showed absorptions corresponding to those of conjugated-carboxyl groups near 1680 cm^{-1} in the IR spectra and near 276 nm (ε 16000—20000) in the UV spectra. The naphtho[1,8-*bc*]furans (VIa—VId) exhibited signals due to hydrogens of the furan ring near δ 7.15 in the NMR spectra and absorptions characteristic of benzofurans near 253 nm in the UV spectra.

When phenacyl bromide was used in place of ethyl bromoacetate in the reactions from I to II, Compounds IV were obtained (Table 1). The yield (41%) of IVa was not good because of the difficulty of isolating IVa from the reaction mixture.

The second method of synthesizing naphtho[1,8-*bc*]-furans (VIa—VId) is a way (B) by which benzofurans are usually obtained.[7—10] 8-Hydroxy-1-tetralone derivatives (Ia—Id) reacted with ethyl bromoacetate to give the corresponding acids, Va—Vd, after hydrolyses. When the Va—Vd acids were treated with acetic anhydride and sodium acetate, two kinds of products, VIa—VId and VIIb—VIId, were obtained. The results are shown in Table 2.

Table 2. The yields (%) of naphtho[1,8-*bc*]furans and lactones

Starting material	Products (%)	
Va	VIa (34)	Va[a] (37)
Vb	VIb (46)	VIIb (32)
Vc	VIc (46)	VIIc (32)
Vd	VId (70)	VIIb (19)

a) Starting material (Va) recovered in place of a lactone (VIIa) because of hydrolysis during the working up.

The yields of VIa—VIc were low because of the formation of lactones, but the total yields of the naphtho-[1,8-*bc*]furans and lactones were good. The better

TABLE 3. THE ULTRAVIOLET ABSORPTION MAXIMA OF NAPHTHO[1,8-*bc*]FURANS (SOLVENT: ETHANOL)

Compound	λ nm (ε)				
VIa	283 (1100)	272 (1600)		250 (9800)	212 (26300)
VIb	290 (1600)	280 (1800)	255 (9200)	248 (9800)	216 (28500)
VIc	302 (2700)	290 (3200)		253 (10000)	213 (25500)
VId	294 (1600)	283 (1700)	255 (7700)	248 (8200)	217 (29200)

TABLE 4. THE ULTRAVIOLET ABSORPTION MAXIMA OF BENZOFURANS (SOLVENT: ETHANOL).

Compound	λ nm (ε)			
XIII[13]	281 (2800)	274 (2400)	243 (9800)	205 (21100)
XIV[12]	289 (3100)	282 (2600)	249 (9200)	209 (25000)
XV[14]	302 (3500)	293 (3900)	251 (9100)	211 (24800)
XVI[15]	292 (2800)	284 (1700)	251 (7800)	214 (30000)

yield (70%) of VId suggests that the inductive effect of the chlorine atom in Vd played an important role in the formation of the furan ring. As benzofurans are usually obtained from phenoxyacetic acid derivatives in good yields (*ca.* 80%)[7,8,10] by the same method, the generally low yields of naphtho[1,8-*bc*]furans may be due to the inhibition of the free rotations of the carbonyl groups in Va—Vd or, more likely, to ring strains in VIa—VId. For these reasons, the formation of seven-membered lactones is comparable to that of five-membered furan rings.

The VIa—VId products were identical with the compounds obtained by the decarboxylation of IIa—IId respectively. The VIIb—VIId products showed absorptions corresponding to those of lactone rings near 1765 cm^{-1} and to those of carbon-carbon double bonds near 1646 cm^{-1} in the IR spectra.

The UV absorption maxima of the naphtho[1,8-*bc*]furans (VIa—VId) and similar benzofurans (XIII—XVI) are shown in Table 3 and Table 4 respectively. The molecular extinction coefficients (ε) and wavelengths (λ) of naphtho[1,8-*bc*]furans and benzofurans are similar to one another except that the values of ε near 280 nm of the naphtho[1,8-*bc*]furans are lower than those of benzofurans. The differences in spectra may be due to the greater strain in the naphto[1,8-*bc*]furan rings.

The other synthetic methods and reactivities of the naphtho[1,8-*bc*]furans will be further investigated.

Experimental

All the melting points are uncorrected. The column chromatography was performed on silica gel (WACOGEL C-200). Unless otherwise stated, anhydrous sodium sulfate was employed as the drying agent. The infrared absorption spectra were determined with a JASCO Model DS 402G infrared spectrophotometer. The ultraviolet absorption spectra were determined with a Shimadzu Model UV-200 spectrophotometer. The nuclear magnetic resonance spectra were determined at 100 MHz with a JEOL Model 4H-100 NMR spectrometer, using tetramethylsilane as the internal standard.

*4,5-Dihidro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylic Acid (IIa).* A mixture of 8-hydroxy-1-tetralone (Ia; 5.0 g),[11] ethyl bromoacetate (18.5 g), potassium carbonate (30.7 g), and ethyl methyl ketone (10 ml) was refluxed for 6 hr at 120 °C. The reaction mixture was then extracted with acetone, and the acetone was evaporated. The residue was dissolved in a small amount of ethanol and hydrolized with a 3 M potassium hydroxide solution. The alkaline solution was acidified with 6 M hydrochloric acid, and the resulting precipitates were extracted with ether. The ethereal layer was washed with water and dried, and then evaporated. When the residue was then washed with benzene, 2.8 g (45%) of IIa were obtained; mp 238 °C (decompn.). Recrystallization from tetrahydrofuran gave colorless prisms; mp 240 °C (decompn.). IR (KBr): 1675 (COOH), 778 cm^{-1} (three adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 282^{sh} (ε 18200), 275 (20100), 229^{sh} (13700), 224 nm (14800).

Found: C, 71.04; H, 5.06%. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99%.

*8-Methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylic Acid (IIb).* Colorless needles (from tetrahydrofuran; 43%): mp 229 °C (decompn.). IR (KBr): 1680 (COOH), 795 cm^{-1} (two adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 305^{sh} (ε 3300), 276 (16100), 234 nm (22000).

Found: C, 67.26; H, 5.31%. Calcd for $C_{13}H_{12}O_4$: C, 67.24; H, 5.21%.

*6-Methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylic Acid (IIc).* Colorless needles (from dioxane; 49%), mp 240—241 °C (decompn.). IR (KBr): 1675 (COOH), 802 cm^{-1} (two adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 275 (ε 20000), 218 nm (17100).

Found: C, 66.95; H, 5.23%. Calcd for $C_{13}H_{12}O_4$: C, 67.24; H, 5.21%.

*6-Chloro-8-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylic Acid (IId).* Colorless needles (from tetrahydrofuran; 46%): mp 249 °C (decompn.). IR (KBr): 1687 (COOH), 817 cm^{-1} (C-Cl). UV (EtOH): λ_{max} 310^{sh} (ε 2400), 276 (16400), 269^{sh} (15800), 235 nm (24700).

Found: C, 58.35; H, 4.25%. Calcd for $C_{13}H_{11}O_4Cl$: C, 58.55; H, 4.16%.

*Ethyl 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylate (IIIa).* A mixture of Ia (3.0 g), ethyl bromoacetate (11.1 g), potassium carbonate (18.4 g), and ethyl methyl ketone (10 ml was refluxed for 6 hr at 120 °C. The reaction mixture was then extracted with ether; the ethereal layer was washed with water and dried, and then evaporated. The residue was recrystallized from ethanol to give 1.5 g (35%) of IIIa as colorless needles; mp 85—86 °C. IR (KBr): 1720 (ester), 786 cm^{-1} (three adjacent aromatic hydrogen atoms). NMR (CCl_4): δ 7.30 (d, 1H, J=8 Hz, Ar-H), 7.20 (d, 1H, J= 8 Hz, Ar-H), 6.85—6.98 (m, 1H, Ar-H), 4.32 (q, 2H, J=

6 Hz, $-OCH_2-$), 3.03 (t, 2H, $J=6$ Hz, $-CH_2-$), 2.86 (t, 2H, $J=6$ Hz, $-CH_2-$), 1.91—2.17 (m, 2H, $-CH_2-$), 1.40 (t, 3H, $J=6$ Hz, CH_3). UV (EtOH): λ_{max} 281 (ε 23000), 231 (13600), 226 nm (13200).

Found: C, 72.77; H, 6.05%. Calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%.

*Ethyl 8-Methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylate (IIIb).* Colorless needles (from ethanol; 34%); mp 100—101 °C. IR (KBr): 1722 (ester), 809 cm^{-1} (two adjacent aromatic hydrogen atoms). NMR (CD_3COCD_3): δ 6.93 (s, 2H, Ar–H), 4.38 (q, 2H, $J=6$ Hz, $-OCH_2-$), 3.99 (s, 3H, OCH_3), 3.03 (t, 2H, $J=6$ Hz, $-CH_2-$), 2.83 (t, 2H, $J=6$ Hz, $-CH_2-$), 1.40 (t, 2H, $J=6$ Hz, CH_3). UV (EtOH): λ_{max} 305 (ε 4400), 283 (19200), 237 nm (23400).

Found: C, 68.96; H, 6.07%. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20%.

*Ethyl 6-Methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-3-carboxylate (IIIc).* Colorless needles (from ethanol; 44%); mp 95—96 °C. IR (KBr): 1702 (ester), 796 cm^{-1} (two adjacent aromatic hydrogen atoms). NMR (CD_3COCD_3): δ 6.99 (d, 1H, $J=9$ Hz, Ar–H), 6.72 (d, 1H, $J=9$ Hz, Ar–H), 4.38 (q, 2H, $J=8$ Hz, $-OCH_2-$), 3.88 (s, 3H, OCH_3), 3.02 (t, 2H, $J=6$ Hz, $-CH_2-$), 2.81 (t, 2H, $J=6$ Hz, $-CH_2-$), 1.40 (t, 3H, $J=8$ Hz, CH_3). UV (EtOH): λ_{max} 315 (ε 3400), 287 (21600), 279 (22000), 221 nm (14900).

Found: C, 69.28; H, 6.19%. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20%.

*Ethyl 6-Chloro-8-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylate (IIId).* Colorless needles (from ethanol; 36%); mp 117.5—119.5 °C. IR (KBr): 1704 (ester), 808 cm^{-1} (C–Cl). NMR (CD_3COCD_3): δ 6.93 (s, 1H, Ar–H), 4.40 (q, 2H, $J=8$ Hz, $-OCH_2-$), 4.02 (s, 3H, OCH_3), 3.00 (t, 2H, $J=6$ Hz, $-CH_2-$), 2.80 (t, 2H, $J=6$ Hz, $-CH_2-$), 1.40 (t, 3H, $J=6$ Hz, CH_3). UV (EtOH): λ_{max} 305 (ε 3300), 283 (19000), 276 (17800), 239 cm (25300).

Found: C, 60.88; H, 5.04%. Calcd for $C_{15}H_{15}O_4Cl$: C, 61.13; H, 5.13%.

*2-Benzoyl-8-methoxy-4,5-dihydro-3*H*-naphto[1,8-*bc*]furan (IVb).* A mixture of Ib (3.0 g), phenacyl bromide (4.6 g), potassium carbonate (7.0 g), and dioxane (10 ml) was refluxed for 8 hr at 120 °C. The reaction mixture was then extracted with ether; the ethereal layer was washed with water and dried, and then evaporated. The residue was recrystallized from ethanol to give 3.0 g (66%) of IVb as colorless needles; mp 80.5—81.5 °C. IR(KBr): 1625 (C=O), 815 (two adjacent aromatic hydrogen atoms), 702 cm^{-1} (five adjacent aromatic hydrogen atoms). UV(EtOH): λ_{max}313 (ε17000), 254 (16500), 205 nm (28700).

Found: C, 77.80; H, 5.35%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%.

*2-Benzoyl-3,4-dihydro-3*H*-naphtho[1,8-*bc*]furan (IVa).* Colorless needles (from ethanol; 41%); mp 51—52° C. IR (KBr): 1629 (C=O), 773 (three adjacent aromatic hydrogen atoms), 718 cm^{-1} (five adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 320 (ε 19100), 256^{sh} (8600), 240 (11000), 205 nm (29100).

Found: C, 82.18; H, 5.20%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%

*2-Benzoyl-6-chloro-8-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]-furan (IVd).* Colorless needles (from acetone; 71%); mp 114—115 °C. IR (KBr): 1628 (C=O), 810 (C–Cl), 720 cm^{-1} (five adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 314 (ε19800), 257 (16500), 210 nm (32700).

Found: C, 69.73; H, 4.66%. Calcd for $C_{19}H_{15}O_3Cl$: C, 69.89; H, 4.63%.

(2-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy) acetic Acid (Vb). A mixture of Ib (5.0 g), ethyl bromoacetate (18.5 g), potassium carbonate (30.0 g), and acetone (40 ml) was refluxed for 6 hr at 70 °C. The reaction mixture was subsequently extracted with acetone, and the acetone was evaporated. The residue was dissolved in a small amount of ethanol and hydrolyzed with a 3 M potassium hydroxide solution. The alkaline solution was acidified with 6 M hydrochloric acid, and the resulting precipitates were collected by filtration. Recrystallization from acetone gave 4.8 g (73%) of Vb as colorless needles; mp 176—178 °C. IR (KBr): 1750 (CO-OH), 1650 (C=O), 822 cm^{-1} (two adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 325 (ε 3200), 256 (8200), 216 nm (21600).

Found: C, 62.63; H, 5.65%. Calcd for $C_{13}H_{14}O_5$: C, 62.40; H, 5.64%.

(8-Oxo-5,6,7,8-tetrahydro-1-naphthoxy)acetic Acid (Va). Colorless plates (from acetone-*n*-hexane; 22%); mp 100—102 °C. IR (KBr): 1775, 1757 (COOH), 1645 (C=O), 798 cm^{-1} (three adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 313 (ε 3700), 254 (9000), 216 nm (18600).

Found: C, 65.35; H, 5.51%. Calcd for $C_{12}H_{12}O_4$: C, 65.45, H, 5.49%.

(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy) acetic Acid (Vc). Colorless plates (from acetone; 30%); mp 152—153 °C. IR (KBr): 1776, 1758 (COOH), 1650 (C=O), 827 cm^{-1} (two adjacent aromatic hydrogen atoms). UV (EtOH): λ_{max} 348 (ε 3500), 252 (6300), 229 nm (18200).

Found: C, 62.42; H, 5.68%. Calcd for $C_{13}H_{14}O_5$: C, 62.40; H, 5.64%.

(4-Chloro-2-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy) acetic Acid (Vd). Colorless needles (from acetone; 71%); mp 148—150 °C. IR (KBr): 1755 (COOH), 1657 (C=O), 802 cm^{-1} (C–Cl). UV (EtOH): λ_{max} 325 (ε 3300), 257 (5600), 220 nm (23100).

Found: C, 55.00; H, 4.75%. Calcd for $C_{13}H_{13}O_5Cl$: C, 54.85; H, 4.60%.

Decarboxylation of IIa–IId. A mixture of IIa (1.0 g), copper powder (1.0 g), and quinoline (10 g) was heated for 45 min at 160 °C. The reaction mixture was then extracted with ether; the etheral layer was acidified with 2 M hydrochloric acid and washed with 2 M hydrochloric acid, a 1 M potassium carbonate solution, and water, dried, and then evaporated. The residue was chromatographed on silica gel and eluted with benzene. A pale yellow fraction was collected to give 650 mg (83%) of VIa as a colorless oil. Bp 68 °C at 1.5 mmHg. IR (neat): 1627 (furan), 772 (three adjacent aromatic hydrogen atoms), 750 cm^{-1} (furan H). NMR (CCl_4): δ 6.80—7.20 (m, 3H, Ar–H), 7.13 (s, 1H, furan H), 2.82 (q, 4H, $J=6$ Hz, $-CH_2-+-CH_2-$), 2.00 (q, 2H, $J=6$ Hz, $-CH_2-$).

Found: C, 83.31; H, 6.19%. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37%.

VIb. Colorless oil (86%); bp 102 °C at 0.7 mmHg. IR (neat): 1638 (furan), 794 cm^{-1} (two adjacent aromatic hydrogen atoms, furan H). NMR (CCl_4): δ 7.18 (s, 1H, furan H), 6.73 (d, 1H, $J=8$ Hz, Ar–H), 6.55, (d, 1H, $J=8$ Hz, Ar–H), 5.96 (s, 3H, OCH_3), 2.75 (q, 4H, J=5 Hz, $-CH_2-+-CH_2-$), 1.98 (q, 2H, $J=5$ Hz, $-CH_2-$).

Found: C, 76.68; H, 6.29%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

VIc. Colorless oil (80%); bp 105 °C at 1.8 mmHg. IR (neat): 775, 765 cm^{-1} (two adjacent aromatic hydrogen atoms, furan H). NMR (CCl_4): δ 7.16 (s, 1H, furan H), 7.05 (d, 1H, $J=9$ Hz, Ar–H), 6.64 (d, 1H, $J=9$ Hz, Ar—H), 5.77 (s, 3H, OCH_3), 2.75 (q, 4H, $J=8$ Hz, $-CH_2-+-CH_2-$), 1.98 (q, 2H, $J=5$ Hz, $-CH_2-$).

Found: C, 76.44; H, 6.33%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

VId. Colorless oil (78%); bp 110 °C at 0.6 mmHg. IR (neat): 1638 (furan), 805 cm^{-1} (C–Cl). NMR (CCl$_4$): δ 7.21 (s, 1H, furan H), 6.60 (s, 1H, Ar–H), 3.95 (s, 3H, OCH$_3$), 2.73 (q, 4H, J=6 Hz, –CH$_2$–+–CH$_2$–), 1.90 (q, 2H, J=6 Hz, –CH$_2$–).

Found: C, 64.45; H, 4.94%. Calcd for C$_{12}$H$_{11}$O$_2$Cl: C, 64.73; H, 4.98%.

*8-Methoxy-4,5-dihydro-3*H*-naphtho[1.8-*bc*]furan (VIb) and Lactone (VIIb).* *VIb*: A mixture of Vb (1.0 g), sodium acetate (4.6 g), and acetic anhydride (15 ml) was heated for 1 hr at 145 °C and then for 10 min at 160 °C. The reaction mixture was poured into water, and the solution was extracted with ether. The ethereal layer was washed with a 1 M potassium carbonate solution and water, dried, and then evaporated. The residue was chromatographed on silica gel and eluted with benzene. The first fraction gave 350 mg (46%) of IVb as a colorless oil.

VIIb: A latter fraction gave 250 mg (32%) of colorless crystals. Recrystallization from benzene-*n*-hexane gave VIIb as colorless needles; mp 112—114 °C. IR (KBr): 1764 (lactone), 1642 (C=C), 810 cm^{-1} (two adjacent aromatic hydrogen atoms).

Found: C, 67.14; H, 5.35%. Calcd for C$_{13}$H$_{12}$O$_4$: C, 67.24; H, 5.21%.

*6-Methoxy-4,5-dihydro-3*H*-naphto[1,8-*bc*]furan (VIc) and Lactone (VIIc).* *VIc*: Colorless oil (46%).

VIIc: Colorless needles from benzene-*n*-hexane (32%); mp 102—103 °C. IR (KBr): 1759 (lactone), 1650 (C=O), 804 cm^{-1} (two adjacent aromatic hydrogen atoms).

Found: C, 67.13; H, 5.11%. Calcd for C$_{13}$H$_{12}$O$_4$: C, 67.24; H, 5.21%.

*6-Chloro-8-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (VId) and Lactone (VIId).* *VId*: Colorless oil (70%).

VIId: Colorless needles from benzene-*n*-hexane (19%); mp 153.5—155 °C. IR (KBr): 1771 (lactone), 1642 (C=C), 837 cm^{-1} (C–Cl).

Found: C, 58.33; H, 3.96%. Calcd for C$_{13}$H$_{13}$O$_5$Cl: C, 58.55; H, 4.16%.

*4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furan (VIa).* *VIa*: Colorless oil (34%).

Va: A latter fraction gave 450 mg (37%) of crystals; mp 96—98 °C. The compound was identical with Va in its infrared spectra. This suggests that the corresponding lactone should be hydrolyzed during the working-up.

3,5-Dimethylbenzofuran-2-carboxylic Acid (XII). A mixture of XI, ethyl bromoacetate (15.2 g), and potassium carbonate (12.3 g) was heated for 6 hr at 150 °C. The following procedures were done in the same way as the synthesis of IIa to give 1.9 g (76%) of XII; mp 220—222 °C (dec.). Recrystallization from acetone-tetrahydrofuran gave colorless prisms; mp 222—223 °C (decompn.) (lit,12) mp 224—225 °C). IR (KBr): 1670 (COOH), 815 cm^{-1} (two adjacent aromatic hydrogen atoms). UV (EtOH): $\lambda_{\max}$ 300$^{\mathrm{sh}}$ (ε 5600), 273 (18700), 214 nm (17600).

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