Photochemical Reaction of 2,3-Dichloro-1,4-naphthoquinone with Enol Silyl Ethers

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2-Oxoalkylated 1,4-naphthoquinones were obtained in the photochemical reactions of 2,3-dichloro-1,4-naphthoquinone with 2-trimethylsiloxy-1-alkenes. Application of this method afforded a wide variety of functionalized 2-oxoalkylated 1,4-naphthoquinones. The photochemical reactions of 2,3-dichloro-1,4-naphthoquinone with 1-alkyl-2-(trimethylsiloxy)ethylenes gave naphthol derivatives. However, 1,1-dialkyl-2-(trimethylsiloxy)ethylenes gave none of products.

The photochemistry of quinones with olefins is one of the most important fields of study because quinones exist widely in nature and play an important role. The photochemical reactions of 2,3-disubstituted 1,4-naphthoquinones with 2-methoxy-1-alkenes and subsequent hydrolysis were found to yield 2-oxoalkylated 1,4-naphthoquinones.[1,2)] These quinones have possibilities to serve as precursors of naturally occurring and/or antitumor antibiotic quinonoid compounds. However, despite many studies on acylation[3—5)] and allylation[3,4,6—10)] of quinones, direct 2-oxoalkylation of quinones has never been reported.

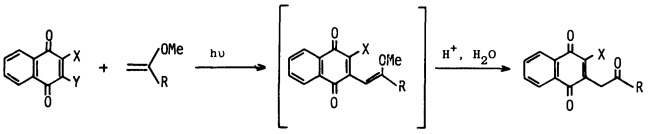


Fig. 1.

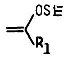
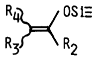
In this paper the photochemical reactions of 2,3-dichloro-1,4-naphthoquinone (**1**) with 2-trimethylsiloxy-1-alkenes **2** as well as other substituted enol silyl ethers **3** are discussed.

Results and Discussion

A benzene solution of quinone **1** and a mixture of 2-trimethylsiloxy-1-alkene **2** and its isomer **3** was irradiated with a high-pressure Hg arc lamp in the presence of pyridine at room temperature. Because **2** synthesized from 2-alkanone is contaminated with **3**, it is difficult to isolate **2** from the mixture of **2** and **3**. Then, the mixture of **2** and **3** was used for the reaction. Composite ratios of enol silyl ethers **2** and **3** in the mixture were summarized in Table 1. After hydrolysis of the reaction mixture, purification of products by column chromatography on silica gel gave two discrete classes of final products; 2-chloro-3-(2-oxoalkyl)-1,4-naphthoquinones **4** and 2,3-dichloro-4-(2-oxoalkoxy)-1-naphthols **5**. The results of the photochemical reactions of **1** with the mixture of **2** and **3** were summarized in Table 2. 2-Oxoalkylated 1,4-naphthoquinones **4** were obtained in good yields. In addition naphthol derivatives **5** were obtained. Products **5a**—**e** were obtained in yields of 10—30%, but **5f** was obtained only a little. On the other hand **4a**—**g** were obtained constantly as major products. From these results **5** were supposed to be derived from alkenes **3**, and **4** from **2**. To prove this pure enol silyl ethers **3** were synthesized from symmetrical ketones and an aldehyde, and were subjected to the photochemical reactions with quinone **1**. The results of the photochemical reactions of quinone **1** with substituted enol silyl ethers **3** were summarized in Table 2. Actually naphthol derivatives **5** were obtained from the photochemical reactions of quinone **1** with substituted enol silyl ethers **3m**—**n** and none of 2-oxoalkylated 1,4-naphthoquinones **4** were obtained at all.

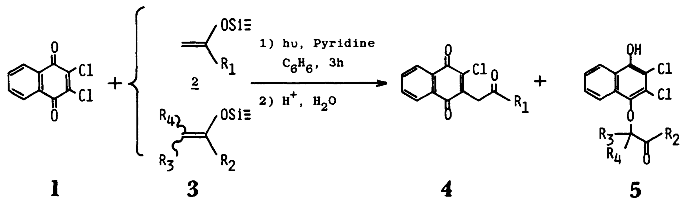
These selectivities of products are attributed to the difference of steric effect between **2** and **3**. We have demonstrated that these reactions occur via photoinduced electron transfer and ion radical pair or exciplex exists as an intermediate.[2)] In the reaction of **1** with **2**, radical cation **2**$^{+}$ can easily attack the carbon atom at 2 or 3 site of radical anion **1**$^{\overline{\cdot}}$ because of little steric effect and **4** is produced. But in the reaction of **1** with **3** (R_3=H, R_4=alkyl group), **3**$^{+}$ is hard to approach to the carbon atom at 2 or 3 site of **1**$^{\overline{\cdot}}$ owing to

Table 1. Isomer Ratio of Enol Silyl Ethers **2** and **3** (%)[a)]

Enol silyl ether			 **2**		 **3**
2a	:	**3a**	80	:	20
2b	:	**3b**	94	:	6
2c	:	**3c**	90	:	10
2d	:	**3d**	91	:	9
2e	:	**3e**	79	:	21
2f	:	**3f**	99	:	1
2g	:	**3g**	99	:	1
2h	:	**3h**	100	:	0
2i	:	**3i**	100	:	0
2j	:	**3j**	100	:	0
2k	:	**3k**	73	:	27
2l	:	**3l**	94	:	6
2m	:	**3m**	—[b)]	:	100
2n	:	**3n**	—[b)]	:	100
2o	:	**3o**	—[b)]	:	100
2p	:	**3p**	—[b)]	:	100

a) The descriptions of **2a**—**p**, **3a**—**p** are listed in Table 2.
b) No **2** exist because enol silyl ethers are synthesized from symmetrical ketones and an aldehyde.

Table 2. Reaction of 2,3-Dichloro-1,4-naphthoquinone **1** with Enol Silyl Ether **2** and **3**



1 **3** **4** **5**

Alkene 2, 3		Quinone conversion/%	4 Yield/%[a]	5 Yield/%[a]
2a ; R_1=C_2H_5	**3a** ; R_2=CH_3, R_3=H, R_4=CH_3	43	**4a** ; 51	**5a** ; 19[b]
2b ; R_1=n-C_3H_7	**3b** ; R_2=CH_3, R_3=H, R_4=C_2H_5	33	**4b** ; 48	**5b** ; 18[b]
2c ; R_1=n-C_4H_9	**3c** ; R_2=CH_3, R_3=H, R_4=n-C_3H_7	34	**4c** ; 41	**5c** ; 18[b]
2d ; R_1=n-C_5H_{11}	**3d** ; R_2=CH_3, R_3=H, R_4=n-C_4H_9	26	**4d** ; 46	**5d** ; 19[b]
2e ; R_1=n-C_6H_{13}	**3e** ; R_2=CH_3, R_3=H, R_4=n-C_5H_{11}	26	**4e** ; 62	**5e** ; 31[b]
2f ; R_1=i-C_4H_9	**3f** ; R_2=CH_3, R_3=H, R_4=i-C_3H_7	37	**4f** ; 81	**5f** ; 5[b]
2g ; R_1=i-C_3H_7	**3g** ; R_2=R_3=R_4=CH_3	30	**4g** ; 63	**5g** ; 0[b]
2h ; R_1=CHC_2H_5 $CH_2OSi(CH_3)_3$	**3h** ; R_2=CH_3, R_3=C_2H_5, R_4=$CH_2OSi(CH_3)_3$	55	**4h** ; 68[c]	**5h** ; 0
2i ; R_1=CH-n-C_3H_7 $CH_2OSi(CH_3)_3$	**3i** ; R_2=CH_3, R_3=n-C_3H_7, R_4=$CH_2OSi(CH_3)_3$	64	**4i** ; 83[c]	**5i** ; 0
2j ; R_1=CH-n-C_5H_{11} $CH_2OSi(CH_3)_3$	**3j** ; R_2=CH_3, R_3=n-C_5H_{11}, R_4=$CH_2OSi(CH_3)_3$	32	**4j** ; 34[c]	**5j** ; 0
2k ; R_1=C_2H_4CH=CH_2	**3k** ; R_2=CH_3, R_3=H, R_4=CH_2CH=CH_2	52	**4k** ; 20	**5k** ; trace
2l ; R_1=C_2H_4CH=$C(CH_3)_2$	**3l** ; R_2=CH_3, R_3=H, R_4=CH_2CH=$C(CH_3)_2$	63	**4l** ; 24	**5l** ; 0
2m; —	**3m**; R_2=C_2H_5, R_3=H, R_4=CH_3	70(60)	**4m**; 0(0)	**5m**; 36(53)[d]
2n ; —	**3n** ; R_2=n-C_3H_7, R_3=H, R_4=C_2H_5	34	**4n** ; 0	**5n** ; 53
2o ; —	**3o** ; R_2=H, R_3=R_4=CH_3	19	**4o** ; 0	**5o** ; 0
2p ; —	**3p** ; R_2=i-C_3H_7, R_3=R_4=CH_3	59	**4p** ; 0	**5p** ; 0

a) Isolated yield based on starting quinone consumed. b) Irradiated for 2 h. c) R_1 contains a hydroxymethyl group. d) In the absence of pyridine.

the steric effect between chlorine atom and R_4. Thus, it is probable that $\mathbf{3}^+$ is trapped on the oxygen atom in $\mathbf{1}^{\overline{\cdot}}$ and **5** is produced. In the reaction of **1** with **3** (R_3, R_4=alkyl group), $\mathbf{3}^+$ can approach to neither the carbon atom at 2 or 3 site of $\mathbf{1}^{\overline{\cdot}}$ nor the oxygen atom in $\mathbf{1}^{\overline{\cdot}}$ because of the large steric repulsion between the two reactive species. These are reflected in the fact that the chlorine atom is eliminated after coupling between radical cation and anion.

After all, the photochemical reactions of quinone **1** with enol silyl ethers **2** gave 2-oxoalkylated 1,4-naphthoquinones **4**. The reactions with enol silyl ethers **3a—f** and **3k—n** (R_3=H, R_4=alkyl group) gave naphthol derivatives **5a—f** and **5k—n**, respectively. However, the reactions with enol silyl ethers **3g,o,p** (R_3, R_4=alkyl group) gave no products.

Further, we introduced a hydroxyl group or a double bond into enol silyl ethers **2** as a functional group. The functionalized 2-trimethylsiloxy-1-alkenes **2** gave successfully the corresponding functionalized 2-oxoalkylated 1,4-naphthoquinones **3**. The results of the photochemical reactions of **1** with **2**, **3h—l** were summarized in Table 2.

In conclusion the photochemical reactions of quinone **1** with enol silyl ethers **2** and **3** afforded different products depending upon the substitution mode of enol silyl ethers.

Experimental

All melting points were determined with a Yanagimoto micro melting point apparatus and uncorrected. Mass spectra were taken on a JEOL JMS-DX300 mass spectrometer. ^{1}H NMR spectra were taken by using a JEOL PS-100 spectrometer and ^{13}C NMR were taken by using a JEOL FX-400 spectrometer. IR spectra were obtained by using a JASCO IRA-1 spectrometer on KBr pellets. Elemental analyses were performed at the Microanalysis Center of Kyoto University.

Material. Quinone **1** was used after recrystallization of commerical reagent. Enol silyl ethers **2** and **3** were synthesized according to the reported methods.[11–13]

General Procedures. Quinone **1** (1 mmol), enol silyl ether (2 mmol), and pyridine (2 mmol) were dissolved in benzene (25 ml) and irradiated in a Pyrex tube with a high-pressure Hg arc lamp for 2—3 h. After hydrolysis the reaction mixture was washed with brine, dried, concentrated, purified by chromatography on silica gel, and subjected to further examination for structure determination.

Identification of Products. 2-Chloro-3-(2-oxobutyl)-1,4-naphthoquinone (4a): Yellow needles from hexane–chloroform; mp 134—135 °C. MS; m/z 262 and 264 (M^+). Found: C, 63.74; H, 4.21; Cl, 13.58%. Calcd for $C_{14}H_{11}O_3Cl$: C, 64.01; H, 4.22; Cl, 13.50%. IR (KBr); 1705 and 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.18 (2H, m), 7.82 (2H, m), 4.03 (2H, s), 2.70 (2H, q, J=7.0 Hz), and 1.15 (3H, t, J=7.0 Hz).

2-Chloro-3-(2-oxopentyl)-1,4-naphthoquinone (4b): Yellow plates from hexane–chloroform; mp 108—109.5 °C. MS;

m/z 276 and 278 (M$^+$). Found: C, 65.09; H, 4.61; Cl, 12.96%. Calcd for $C_{15}H_{13}O_3Cl$: C, 65.11; H, 4.74; Cl, 12.81%. IR (KBr); 1705 and 1670 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.11 (2H, m), 7.78 (2H, m), 3.98 (2H, s), 2.63 (2H, t, J=7.0 Hz), 1.69 (2H, sextet, J=7.0 Hz), and 0.98 (3H, t, J=7.0 Hz).

2-Chloro-3-(2-oxohexyl)-1,4-naphthoquinone (4c): Yellow plates from hexane–chloroform; mp 104—105.5 °C. MS; *m/z* 290 and 292 (M$^+$). Found: C, 66.04; H, 5.15; Cl, 12.23%. Calcd for $C_{16}H_{15}O_3Cl$: C, 66.10; H, 5.20; Cl, 12.19%. IR (KBr); 1705 and 1665 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.16 (2H, m), 7.80 (2H, m), 4.01 (2H, s), 2.66 (2H, t, J=7.0 Hz), 1.2—1.9 (4H, m), and 0.96 (3H, t, J=7.0 Hz).

2-Chloro-3-(2-oxoheptyl)-1,4-naphthoquinone (4d): Yellow needles from hexane–chloroform; mp 104—105 °C. MS; *m/z* 304 and 306 (M$^+$). Found: C, 66.77; H, 5.71; Cl, 11.70%. Calcd for $C_{17}H_{17}O_3Cl$: C, 67.00; H, 5.62; Cl, 11.63%. IR (KBr); 1710 and 1670 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.16 (2H, m), 7.77 (2H, m), 4.00 (2H, s), 2.66 (2H, t, J=7.0 Hz), 1.2—2.0 (6H, m), and 0.96 (3H, br-t, J=7.0 Hz).

2-Chloro-3-(2-oxooctyl)-1,4-naphthoquinone (4e): Yellow needles from hexane–chloroform; mp 107—108 °C. MS; *m/z* 318 and 320 (M$^+$). Found: C, 67.74; H, 6.04; Cl, 11.21%. Calcd for $C_{18}H_{19}O_3Cl$: C, 67.82; H, 6.01; Cl, 11.12%. IR (KBr); 1705 and 1670 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.18 (2H, m), 7.81 (2H, m), 4.01 (2H, s), 2.66 (2H, t, J=7.0 Hz), 1.1—1.9 (8H, m), and 0.92 (3H, br-t, J=7.0 Hz).

2-Chloro-3-(4-methyl-2-oxopentyl)-1,4-naphthoquinone (4f): Yellow needles from hexane–chloroform; mp 94—95.5 °C. MS; *m/z* 290 and 292 (M$^+$). Found: C, 65.86; H, 5.19; Cl, 12.17%. Calcd for $C_{16}H_{15}O_3Cl$: C, 66.10; H, 5.20; Cl, 12.19%. IR (KBr); 1705, 1675, and 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.16 (2H, m), 7.18 (2H, m), 4.00 (2H, s), 2.53 (2H, d, J=7.0 Hz), 2.24 (1H, nonet, J=7.0 Hz), and 1.00 (6H, d, J=7.0 Hz).

2-Chloro-3-(3-methyl-2-oxobutyl)-1,4-naphthoquinone (4g): Yellow needles from hexane–chloroform; mp 112—113 °C. MS; *m/z* 276 and 278 (M$^+$). Found: C, 64.84; H, 4.67; Cl, 12.76%. Calcd for $C_{15}H_{13}O_3Cl$: C, 65.11; H, 4.74; Cl, 12.81%. IR (KBr); 1695, 1675, and 1655 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.14 (2H, m), 7.78 (2H, m), 4.06 (2H, s), 2.86 (1H, septet, J=7.0 Hz), and 1.24 (6H, d, J=7.0 Hz).

2-Chloro-3-(3-hydroxymethyl-2-oxopentyl)-1,4-naphthoquinone (4h): Yellow needles from hexane–chloroform; mp 116—118 °C. MS; *m/z* 307, 308, and 309 (M$^+$). Found: C, 62.73; H, 4.77; Cl, 11.55%. Calcd for $C_{16}H_{15}O_4Cl$: C, 62.65; H, 4.93; Cl, 11.56%. IR (KBr); 3360 (OH), 1700, and 1650 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.05 (2H, m), 7.69 (2H, m), 4.05 (2H, s), 3.74 (2H, m), 2.85 (1H, br-s), 2.63 (1H, tt), 1.57 (2H, m), and 0.91 (3H, t, J=8.4 Hz).

2-Chloro-3-(3-hydroxymethyl-2-oxohexyl)-1,4-naphthoquinone (4i): Yellow needles from hexane–chloroform; mp 118—120 °C. MS; *m/z* 321, 322, and 323 (M$^+$). Found: C, 63.42; H, 5.29; Cl, 11.28%. Calcd for $C_{17}H_{17}O_4Cl$: C, 63.66; H, 5.34; Cl, 11.05%. IR (KBr); 3380 (OH), 1720, 1680, and 1670 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.01 (2H, m), 7.68 (2H, m), 4.04 (2H, s), 3.74 (2H, m), 3.20 (1H, br-s), 2.71 (1H, tt), 1.39 (4H, m), and 0.90 (3H, t, J=6.0 Hz).

2-Chloro-3-(3-hydroxymethyl-2-oxooctyl)-1,4-naphthoquinone (4j): Yellow plates from hexane–chloroform; mp 87—88 °C. MS; *m/z* 349, 350, and 351 (M$^+$). Found: C, 65.70; H, 6.03; Cl, 10.29%. Calcd for $C_{19}H_{21}O_4Cl$: C, 65.42; H, 6.07; Cl, 10.16%. IR (KBr); 3360 (OH), 1700, 1670, and 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.00 (2H, m), 7.66 (2H, m), 4.01 (2H, s), 3.79 (2H, d, J=6.0 Hz), 2.90 (1H, m), 2.38 (1H, br-s), 1.35 (8H, br-s), and 0.90 (3H, br-t).

2-Chloro-3-(2-oxo-5-hexenyl)-1,4-naphthoquinone (4k): Yellow needles from hexane–chloroform; mp 96—98 °C. MS; *m/z* 288 and 290 (M$^+$). Found: C, 66.82; H, 4.38; Cl, 12.56%. Calcd for $C_{16}H_{13}O_3Cl$: C, 66.56; H, 4.54; Cl, 12.28%. IR (KBr); 1700, 1670, and 1650 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.22 (2H, m), 7.86 (2H, m), 5.90 (1H, m), 5.15 (2H, dd, J=9.9 and 9.9 Hz), 4.04 (2H, s), 2.80 (2H, J=7.6 Hz), and 2.50 (2H, t, J=7.6 Hz).

2-Chloro-3-(6-methyl-2-oxo-5-heptenyl)-1,4-naphthoquinone (4l): Yellow needles from hexane–chloroform; mp 99—100.5 °C. MS; *m/z* 316 and 318 (M$^+$). Found: C, 67.97; H, 5.37; Cl, 11.29%. Calcd for $C_{18}H_{17}O_3Cl$: C, 68.25; H, 5.41; Cl, 11.19%. IR (KBr); 1700, 1660, and 1650 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.07 (2H, m), 7.72 (2H, m), 5.10 (1H, m), 3.94 (2H, s), 2.65 (2H, td, J=6.6 and 6.6 Hz), 2.38 (2H, t, J=6.6 Hz), 1.71 (3H, s), and 1.65 (3H, s).

2,3-Dichloro-4-(1-methyl-2-oxopropoxy)-1-naphthol (5a): Pink crystals from hexane–chloroform; mp 132.5—133.5 °C. MS; *m/z* 298, 300, and 302 (M$^+$). Found: C, 55.98; H, 3.77; Cl, 23.68%. Calcd for $C_{15}H_{14}O_3Cl_2$: C, 56.21; H, 4.04; Cl, 23.70%. IR (KBr); 3420 (OH) and 1730 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.11 (2H, m), 7.55 (2H, m), 6.30 (1H, br-s), 4.79 (1H, q, J=6.1 Hz), 2.53 (3H, s), and 1.39 (3H, d, J=7.0 Hz). ^{13}C NMR ($CDCl_3$) δ=208.3 (s), 145.1 (s), 143.5 (s), 128.3 (m), 127.4 (d), 126.6 (d), 122.8 (d), 122.2 (m), 122.1 (m), 121.2 (m), 112.4 (s), 84.2 (d), 26.0 (q), and 17.0 (q).

2,3-Dichloro-4-(1-ethyl-2-oxopropoxy)-1-naphthol (5b): Orange crystals from hexane–chloroform; mp 147—148 °C. MS; *m/z* 312, 314, and 316 (M$^+$). Found: C, 57.25; H, 4.43; Cl, 22.54%. Calcd for $C_{15}H_{14}O_3Cl_2$: C, 57.53; H, 4.51; Cl, 22.64%. IR (KBr); 3250 (OH) and 1690 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.17 (2H, m), 7.59 (2H, m), 6.14 (1H, br-s), 4.64 (1H, t, J=6.7 Hz), 2.48 (3H, s), 1.99 (2H, qd, J=6.7 and 7.0 Hz), and 0.99 (3H, t, J=7.0 Hz).

2,3-Dichloro-4-(1-propyl-2-oxopropoxy)-1-naphthol (5c): White needles from hexane–chloroform; mp 118—119 °C. MS; *m/z* 326, 328, and 330 (M$^+$). Found: C, 58.47; H, 4.92; Cl, 21.83%. Calcd for $C_{16}H_{16}O_3Cl_2$: C, 58.73; H, 4.93; Cl, 21.67%. IR (KBr); 3210 (OH) and 1700 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.12 (2H, m), 7.54 (2H, m), 6.11 (1H, br-s), 4.68 (1H, t, J=6.1 Hz), 2.44 (3H, s), 1.90 (2H, td), 1.48 (2H, qt), and 0.88 (3H, t, J=7.6 Hz).

4-(1-butyl-2-oxopropoxy)-2,3-dichloro-1-naphthol (5d): White crystals from hexane–chloroform; mp 103.5—104.5 °C. MS; *m/z* 340, 342, and 344 (M$^+$). Found: C, 59.99; H, 5.14; Cl, 20.85%. Calcd for $C_{17}H_{18}O_3Cl_2$: C, 59.84; H, 5.32; Cl, 20.78%. IR (KBr); 3200 (OH) and 1700 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.13 (2H, m), 7.55 (2H, m), 6.10 (1H, br-s), 4.67 (1H, t, J=5.8 Hz), 2.44 (3H, s), 1.91 (2H, td), 1.29 (4H, m), and 0.85 (3H, t, J=6.1 Hz).

2,3-Dichloro-4-(1-pentyl-2-oxopropoxy)-1-naphthol (5e): White crystals from hexane–chloroform; mp 52—54 °C. MS; *m/z* 354, 356, and 358 (M$^+$). Found: C, 60.68; H, 5.51; Cl, 19.75%. Calcd for $C_{18}H_{20}O_3Cl_2$: C, 60.86; H, 5.67; Cl, 19.96%. IR (KBr); 3520 (OH) and 1710 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.14 (2H, m), 7.55 (2H, m), 6.14 (1H, br-s), 4.68 (1H, t, J=6.1 Hz), 2.46 (3H, s), 1.88 (2H, td), 1.27 (6H, m), and 0.84 (3H, t, J=6.1 Hz).

2,3-Dichloro-4-(1-isopropyl-2-oxopropoxy)-1-naphthol (5f): White crystals from hexane–chloroform; mp 158—159 °C. MS; *m/z* 326, 328, and 330 (M$^+$). Found: C, 58.89; H, 4.82;

Cl, 21.92%. Calcd for $C_{16}H_{16}O_3Cl_2$: C, 58.73; H, 4.93; Cl, 21.67%. IR (KBr); 3290 (OH) and 1690 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.16 (2H, m), 7.55 (2H, m), 6.02 (1H, br-s), 4.65 (1H, d, J=4.2 Hz), 2.37 (3H, s), 1.68 (1H, m), and 1.08 (6H, d, J=6.7 Hz).

2,3-Dichloro-4-(1-methyl-2-oxobutoxy)-1-naphthol (5m): White needles from hexane–chloroform; mp 119—120 °C. MS; m/z 312, 314, and 316 (M$^+$). Found: C, 57.53; H, 4.51; Cl, 22.64%. Calcd for $C_{15}H_{14}O_3Cl_2$: C, 57.53; H, 4.51; Cl, 22.68%. IR (KBr); 3410 (OH) and 1690 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.05 (2H, m), 7.49 (2H, m), 6.24 (1H, br-s), 4.82 (1H, q, J=7.0 Hz), 2.93 (2H, q, J=7.3 Hz), 1.37 (3H, d, J=6.7 Hz), and 1.17 (3H, t, J=6.7 Hz).

2,3-Dichloro-4-(1-ethyl-2-oxopentyloxy)-1-naphthol (5n): White crystals from hexane–chloroform; mp 90.5—91.5 °C. MS; m/z 340, 342, and 344 (M$^+$). Found: C, 59.75; H, 5.32; Cl, 20.91%. Calcd for $C_{17}H_{18}O_3Cl_2$: C, 59.83; H, 5.32; Cl, 20.78%. IR (KBr); 3320 (OH) and 1690 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ=8.12 (2H, m), 7.54 (2H, m), 6.07 (1H, br-s), 4.67 (1H, t, J=6.0 Hz), 2.78 (2H, qd), 1.93 (2H, t, J=7.2 Hz), 1.70 (2H, qd, J=7.2 and 7.2 Hz), and 0.95 (3H, t, J=4.8 Hz).

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