Photocyclization Reactions. Part 3 [1]. Synthesis of Naphtho[1,8-*bc*]-furans and Cyclohepta[*cd*]benzofurans Using Photocyclization of 8-Alkoxy-1,2,3,4-tetrahydro-1-naphthalenones and 4-Alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ones

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Photocyclization reactions were carried out on 8-alkoxy-1,2,3,4-tetrahydro-1-naphthalenones (six-membered ring ketones) **4a-g** and 4-alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ones (seven-membered ring ketones) **5a-e** in acetonitrile. Irradiation of **4a-f** gave rearranged naphthyl alcohols **8a-f** as major products. In the case of **4g**, 2a,3,4,5-tetrahydronaphtho[1,8-*bc*]furan-2a-ol **6g** was obtained. In contrast, irradiation of **5a-e** afforded 2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2a-ols **9a-e** in good yields. The difference in reactivities between **4a-g** and **5a-e** is attributed to the conformation of six- and seven-membered rings. Conformational and substituent effects in cyclization step of 1,5-biradicals are discussed along with reaction pathways.

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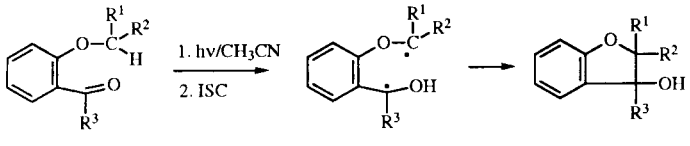
Introduction.

It is well-known that carbonyl compounds which possess γ-hydrogen atoms undergo a very facile photoelimination under irradiation, called a Norrish type II reaction, to produce alkenes and smaller carbonyl compounds [2]. In the reactions cyclobutanols are also formed by intramolecular cyclization of intermediate 1,4-biradicals. By using this type of photocyclization, benzofurans [3,4] have been synthesized from carbonyl compounds having δ-hydrogen. The reaction proceeds through 1,5-biradicals formed from δ-hydrogen abstraction by the carbonyl group [4]. For example, irradiation of 2-benzyloxybenzophenone affords *cis* and *trans* isomers of 2,3-diphenyl-2,3-dihydro-3-benzofuranol [3g]. On the other hand, photoreaction of 2'-benzyloxyacetophenone gives rearranged 2'-benzoylacetophenone as a major product [3g]. Thus, both carbonyl compounds afford different type of products according to benzoyl or acetyl groups. In the previous papers [1], we reported photocyclization reactions of 2-alkoxybenzaldehydes, 2'-alkoxyacetophenones, 2-formylphenoxyacetic acids, 2-acetylphenoxyacetic acids, ethyl 2-formylphenoxyacetates and ethyl 2-acetylphenoxyacetates, and discussed substituent effects on cyclization step of 1,5-biradicals (Scheme 1).

Scheme 1

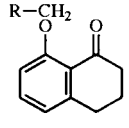


1 **2** **3**

1,5-biradical intermediate

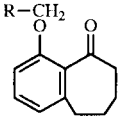
R^1 = H, Me, Et, *i*-Pr, Ph
R^2 = H, CO_2H, CO_2Et
R^3 = H, Me

In this paper [5], we report synthesis of naphtho[1,8-*bc*]furans and cyclohepta[*cd*]benzofurans from ether compounds of six- and seven-membered ring ketones **4**, **5** and discuss conformational effects of six- and seven-membered rings and substituent effects in the cyclization step of 1,5-biradicals.



4

a, R = H
b, R = Me
c, R = Et
d, R = *i*-Pr
e, R = Ph
f, R = *p*-Cl-C_6H_4
g, R = CN



5

a, R = H
b, R = Me
c, R = Et
d, R = *i*-Pr
e, R = Ph

Figure 1

Results and Discussion.

8-Alkoxy-1,2,3,4-tetrahydro-1-naphthalenones **4a-g** for photocyclization reactions were prepared by the reactions of 8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone with methyl iodide, ethyl iodide, propyl iodide, isobutyl bromide, benzyl chloride, *p*-chlorobenzyl chloride or bromoacetonitrile. Similarly, 4-alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ones **5a-e** were prepared from the reaction of 4-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one and the corresponding alkyl halides. The results are summarized in Scheme 2 and Table 1.

Irradiation of six-membered ring ketone **4a** (R = H) with high-pressure mercury lamp in acetonitrile gave naphtho[1,8-*bc*]furanol **6a** and rearranged naphthyl alco-

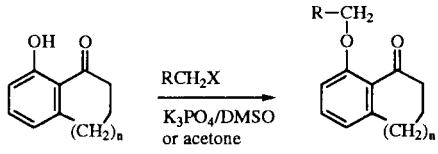
Table 1

Synthesis of 8-Alkoxy-1,2,3,4-tetrahydro-1-naphthalenones **4a-g** and 4-Alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ones **5a-e**

Starting material [a]	Reagent	Base	Solvent	Temperature (°C)	Time (minutes)	R	Product [b]	Yield (%)
N	MeI	K_3PO_4	DMSO	60	20	H	**4a**	82
N	EtI	K_3PO_4	DMSO	60	20	Me	**4b**	81
N	PrI	K_3PO_4	DMSO	60	20	Et	**4c**	79
N	*i*-BuBr	K_3PO_4	DMSO	60	120	*i*-Pr	**4d**	70
N	$PhCH_2Cl$	K_3PO_4	DMSO	60	20	Ph	**4e**	93
N	*p*-Cl-C_6H_4	K_3PO_4	Acetone	60	240	*p*-Cl-C_6H_4	**4f**	89
N	$BrCH_2CN$	K_3PO_4	Acetone	60	240	CH_2CN	**4g**	44
B	EtI	K_3PO_4	DMSO	60	10	Me	**5b**	90
B	PrI	K_3PO_4	DMSO	60	30	Et	**5c**	86
B	*i*-BuBr	K_3PO_4	DMSO	60	90	*i*-Pr	**5d**	87
B	$PhCH_2Cl$	K_3PO_4	DMSO	60	15	Ph	**5e**	76

[a] N and B are 8-hydroxy-5,6,7,8-tetrahydro-1-naphthalenone and 4-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one respectively. [b] 4-Methoxy-6,7,8,9-tetrahydrobenzocyclohepten-5-one **5a** was prepared by catalytic reduction of the corresponding 1-bromo derivative with hydrogen/Pd-C (see Experimental).

Scheme 2

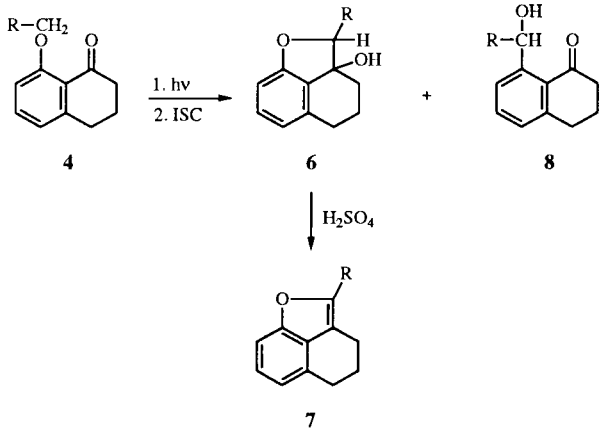


n = 1,2

4 (n = 1)
5 (n = 2)

hol **8a**. It was difficult to isolate **6a** and **8a** in a pure state because **6a** was easily dehydrated to **7a**. Therefore, the reaction mixture was treated with dilute sulfuric acid to give naphthofuran **7a** (34%) and rearranged naphthyl alcohol **8a** (36%). Similarly, when **4b-f** (R = Me, Et, *i*-Pr, Ph, *p*-Cl-C_6H_4) were irradiated followed by treatment with dilute sulfuric acid, rearranged naphthyl alcohols **8b-f** (48-71%) were obtained as major products along with naphtho[1,8-*bc*]furans **7b-f** (5-15%). In the case of **4g** (R = CN), 2-cyano-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2a-ol **6g** (39%) was isolated as a main product along with the dehydrated 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carbonitrile **7g** (12%). The stereochemistry of **6g** was assigned to be *cis* as shown below. The results are summarized in Scheme 3 and Table 2.

Scheme 3



4 **6** **8**

7

Table 2

Photocyclization Reactions of 8-Alkoxy-1,2,3,4-tetrahydro-1-naphthalenones **4a-g** [a] and Subsequent Treatment with Dilute Sulfuric Acid [b]

Starting material	R	Irradiation time (minutes)	Product Yields (%) **6**	**7**	**8**
4a	H	60	-	34	36
4b	Me	20	-	5	62
4c	Et	15	-	8	48
4d	*i*-Pr	15	-	11	60
4e	Ph	30	-	9	71
4f	*p*-Cl-C_6H_4	27	-	15	49
4g	CN	43	42	12	0

[a] An acetonitrile solution (500 ml) of **4a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] Photoreaction mixtures of **4a-g** were treated with 0.4 *M* sulfuric acid.

When **4f** (R = *p*-Cl-C_6H_4) was irradiated in acetonitrile (no subsequent treatment with sulfuric acid), naphtho[1,8-*bc*]furanol **6f** (14%) was isolated along with its dehydrated product **7f** (3%) and rearranged naphthyl alcohol **8f** (76%). Compound **7f** would be formed by dehydration of **6f** during isolation procedure after irradiation. Though *cis* and *trans* isomers were possible for **6f**, only one stereoisomer was obtained, showing stereoselectivity in the cyclization step. However, stereochemistry of **6f** is not clear. In contrast, when **4g** (R = CN) was irradiated in acetonitrile *cis* and *trans* isomers (with regard to cyano and hydroxyl groups) of naphtho[1,8-*bc*]furanol **6g** were isolated in good yield (74%). The *cis/trans* ratio was 11:1

judging from the ^1H nmr spectra in which the methylene group at C_3 in **6g** deshielded C_2-H at the *trans* position by an anisotropic effect [6]. The results are shown in Table 3.

Table 3

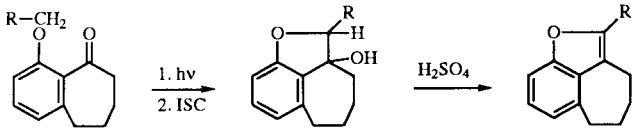
Photocyclization Reactions of 8-Alkoxy-1,2,3,4-tetrahydro-1-naphthalenones **4f-g** [a]

Starting material	R	Irradiation time (minutes)	Product **6** (*cis:trans*) [b]	Yields (%) **7**	**8**
4f	*p*-Cl-C_6H_4	27	14 [c]	3	76
4g	CN	43	74 (11:1)	0	0

[a] An acetonitrile solution (500 ml) of **4a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] *Cis* and *trans* isomers with regard to *p*-chlorophenyl or cyano and hydroxyl groups. [c] Only one isomer was obtained and the stereochemistry was not determined.

On the other hand, irradiation of seven-membered ring ketones **5a-e** afforded only cyclohepta[*cd*]benzofuranols **9a-e** in high yield (72-93%) and no rearranged alcohols were obtained. In each experiment only one stereoisomer of cyclohepta[*cd*]benzofuranols **9a-e** was produced. However, stereochemistry of **9a-e** is not clear. The results are summarized in Scheme 4 and Table 4.

Scheme 4



5 **9** **10**

Table 4

Photocyclization Reactions of 4-Alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ones **5a-g** [a]

Starting material	R	Irradiation time (minutes)	Product [b]	Yields (%)
5a	H	50	**9a**	79
5b	Me	30	**9b**	93
5c	Et	50	**9c**	73
5d	*i*-Pr	30	**9d**	72
5e	Ph	15	**9e**	79

[a] An acetonitrile solution (500 ml) of **5a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] Only one isomer was obtained and the stereochemistry was not determined.

Cyclohepta[*cd*]benzofuranols **9a-e** are readily converted to **10a-e** with sulfuric acid after irradiation. When photoreaction products of **5a-e** were treated with dilute sulfuric acid after irradiation, dehydrated cyclohepta[*cd*]benzofurans **10a-e** were obtained in good yields (73-87%). The results are shown in Table 5.

Table 5

Photocyclization Reactions of 4-Alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ones **5a-g** [a] and Subsequent Treatment with Dilute Sulfuric Acid [b]

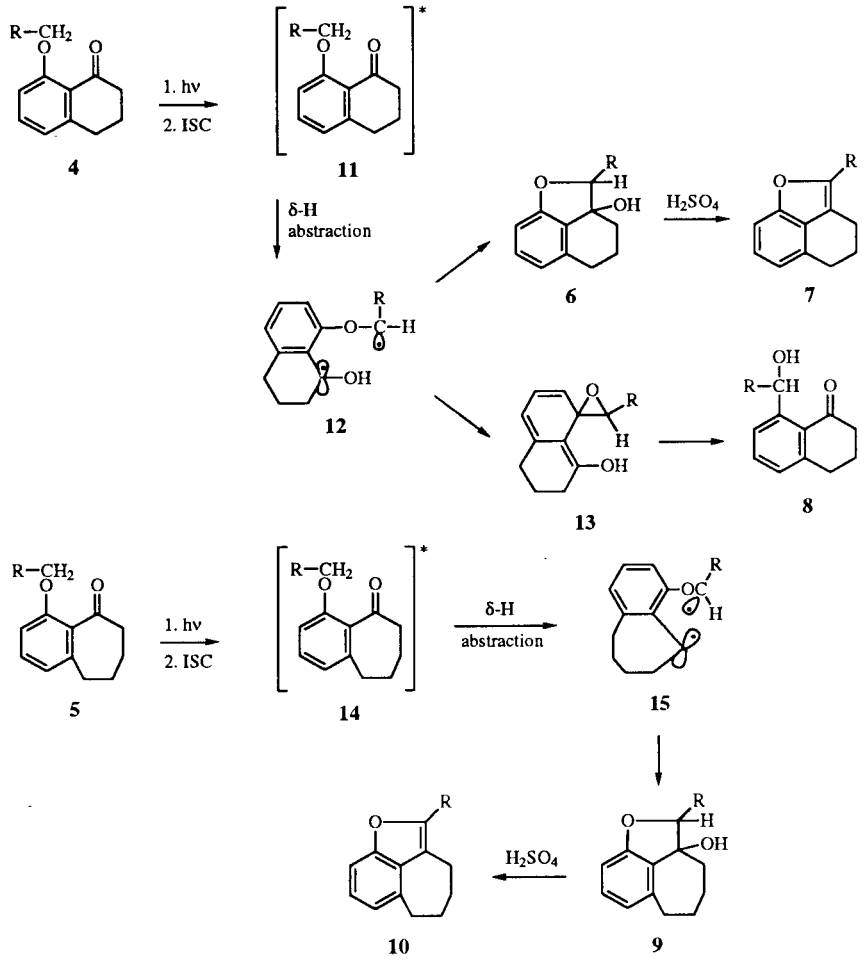
Starting material	R	Irradiation time (minutes)	Product	Yields (%)
5a	H	30	**10a**	80
5b	Me	20	**10b**	78
5c	Et	25	**10c**	73
5d	*i*-Pr	30	**10d**	79
5e	Ph	15	**10e**	87

[a] An acetonitrile solution (500 ml) of **5a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] Photoreaction mixtures of **5a-e** were treated with 0.4 *M* sulfuric acid.

All of our results would be explained by intramolecular cyclization of 1,5-biradical intermediates produced through δ-hydrogen abstraction. The mechanisms of photocyclization reactions through δ-hydrogen abstraction have been well studied [3,4]. The plausible mechanisms of photocyclization from 8-alkoxy-1,2,3,4-tetrahydro-1-naphthalenones **4a-g** and 4-alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ones **5a-e** are shown in Scheme 5.

Irradiation of ethers **4**, **5** produces (n, π*) excited triplet states **11**, **14** after intersystem crossing process (ISC). The carbonyl group of **11**, **14** abstracts δ-hydrogen to give 1,5-biradicals **12**, **15** which afford a variety of products. For example, intramolecular cyclization of **12**, **15** produces furanols **6**, **9** which readily undergo dehydration reactions with dilute sulfuric acid to give furans **7**, **10**. In contrast, novel rearrangement is necessary for the formation of rearranged naphthyl alcohols **8** from six-membered ring ketones **4**. The possible intermediates for rearranged alcohol formation are spiroenols **13** which were initially suggested by Wagner *et al.* [1a,3g]. The large difference in reactivities between six- and seven-membered ring ketones **4**, **5** could be explained by the conformation of the two ketones. In six-membered ring ketones having small dihedral angle between the carbonyl group and benzene ring [7], the *p*-orbital in the 1,5-biradicals **12** formed by δ-hydrogen abstraction would be nearly parallel to the π-orbitals of the benzene ring. Rotation by about 90° [3g] around the Ar-C bond is necessary for furan ring formation. However, such a rotation reduces benzylic conjugation between the *p*-orbital and benzene ring and accordingly causes strain in the six-membered ring. Therefore, spirocyclization of **12** to **13** occurs predominantly. Spiroenols **13** afford rearranged alcohols **8** by cleavage of the ether linkage. In contrast, seven-membered ring ketones **5** are flexible and have a large dihedral angle between the carbonyl group and benzene ring in the

Scheme 5



ground state [7]. The stable conformation of 1,5-biradicals **15** formed by δ-hydrogen abstraction would be similar to that of seven-membered ring ketones **5**. Therefore, the *p*-orbital in the 1,5-biradicals is not parallel to the π-orbitals of the benzene ring and not conjugated effectively. This conformation is desirable for cyclization to furan ring by rotation of the *p*-orbital along with flexibility of the seven-membered ring. Therefore, the 1,5-biradicals **15** cyclize readily to furanols **9**.

Thus, the dihedral angle between the carbonyl group and benzene ring of starting compounds play an important role in the cyclization step of 1,5-biradical intermediates. Electron-withdrawing substituent such as cyano group which stabilize 1,5-biradical intermediates suppresses spirocyclization reactions because the 1,5-biradicals are not reactive enough to form spiroenols with benzene ring. In summary, irradiation of seven-membered ring ketones **5** gave cyclohepta[*cd*]benzofurans in good yields. However, six-membered ring ketones **4** afforded rearranged naphthyl alcohols as major products.

EXPERIMENTAL

The melting points are uncorrected. Column choromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. Acetonitrile was dried by distillating over phosphorus pentoxide, then over potassium carbonate. Photoreactions were carried out with 400-W high-pressure mercury lamp (Riko UVL-400 HA) in a Pyrex cylinderical vessel equiped with a nitrogen inlet. The ir spectra were determined on a Hitachi Model 270-30 IR spectrometer. The ^1H and ^{13}C nmr spectra were determined at 90 MHz and 22.49 MHz on a JEOL-FX 90Q FT NMR spectrometer, using tetramethylsilane as the internal standard.

8-Methoxy-1,2,3,4-tetrahydro-1-naphthalenone **4a**.

A mixture of 8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone [8] (2.0 g, 12.3 mmoles), methyl iodide (1.9 g, 13.4 mmoles), tripotassium phosphate (5.1 g, 24.0 mmoles) and dimethyl sulfoxide (20 ml) was stirred at 60° for 20 minutes. After removal of insoluble materials by filteration the filterate was poured into water and extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted

with benzene (80)-ether (20) to give **4a** (1.8 g, 82%) as a colorless oil, bp 128° at 2.0 Torr; ir (neat): 1680 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 2.04 (tt, J = 6 and 6 Hz, 2H, 3-H_2), 2.62 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 2.92 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 3.90 (s, 3H, OCH_3), 6.82 (d, J = 7 Hz, 1H, 5-H), 6.82 (d, J = 7 Hz, 1H, 7-H), 7.38 (dd, J = 7 and 7 Hz, 1H, 6-H); ^{13}C nmr (deuteriochloroform): δ 22.9 (t), 30.8 (t), 41.0 (t), 55.9 (q), 110.1 (d), 120.7 (d), 122.3 (s), 133.9 (d), 147.0 (s), 160.4 (s), 197.0 (s).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.70; H, 7.01.

8-Ethoxy-1,2,3,4-tetrahydro-1-naphthalenone **4b**.

Compound **4b** (81%) was obtained as a colorless oil in a manner similar to the synthesis of **4a**, bp 108° at 0.6 Torr; ir (neat): 1680 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.49 (t, J = 7 Hz, 3H, OCH_2CH_3), 2.04 (tt, J = 6 and 6 Hz, 2H, 3-H_2), 2.62 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 2.91 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 4.11 (q, J = 7 Hz, 2H, OCH_2CH_3), 6.80 (d, J = 7 Hz, 1H, 5-H), 6.80 (d, J = 7 Hz, 1H, 7-H), 7.34 (dd, J = 7 and 7 Hz, 1H, 6-H); ^{13}C nmr (deuteriochloroform): δ 14.7 (q), 22.9 (t), 30.8 (t), 41.0 (t), 64.6 (t), 111.5 (d), 120.6 (d), 122.6 (s), 133.7 (d), 146.9 (s), 159.7 (s), 196.8 (s).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.52; H, 7.57.

8-Propoxy-1,2,3,4-tetrahydro-1-naphthalenone **4c**.

Compound **4c** (80%) was obtained as a colorless oil in a manner similar to the synthesis of **4a**, bp 134° at 2.0 Torr; ir (neat) 1680 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.09 (t, J = 7 Hz, 3H, $OCH_2CH_2CH_3$), 1.69-2.20 (m, 4H, $OCH_2CH_2CH_3$ and 3-H_2), 2.61 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 2.90 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 3.98 (t, J = 6 Hz, 2H, $OCH_2CH_2CH_3$), 6.79 (d, J = 7 Hz, 1H, 5-H), 6.79 (d, J = 7 Hz, 1H, 7-H), 7.33 (dd, J = 7 and 7 Hz, 1H, 6-H); ^{13}C nmr (deuteriochloroform): δ 10.6 (q), 22.6 (t), 23.0 (t), 30.8 (t), 41.0 (t), 70.5 (t), 111.3 (d), 120.5 (d), 122.6 (s), 133.7 (d), 146.9 (s), 160.0 (s), 196.7 (s).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.18; H, 7.81.

8-Isobutoxy-1,2,3,4-tetrahydro-1-naphthalenone **4d**.

Compound **4d** (70%) was obtained as a colorless oil in a manner similar to the synthesis of **4a**, bp 136° at 1.7 Torr; ir (neat): 1680 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.08 (d, J = 7 Hz, 6H, $OCH_2CH(CH_3)_2$), 1.80-2.32 (m, 3H, 3-H_2 and $OCH_2CH(CH_3)_2$), 2.59 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 2.88 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 3.76 (d, J = 7 Hz, 2H, $OCH_2CH(CH_3)_2$), 6.76 (d, J = 7 Hz, 1H, 5-H), 6.76 (d, J = 7 Hz, 1H, 7-H), 7.31 (dd, J = 7 and 7 Hz, 1H, 6-H); ^{13}C nmr (deuteriochloroform): δ 19.3 (q), 23.0 (t), 28.4 (d), 30.8 (t), 41.0 (t), 75.3 (t), 111.1 (d), 120.4 (d), 122.4 (s), 133.7 (d), 146.8 (s), 160.0 (s), 196.4 (s).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.81; H, 8.36.

8-Benzyloxy-1,2,3,4-tetrahydro-1-naphthalenone **4e**.

Compound **4e** (93%) was obtained as a colorless oil in a manner similar to the synthesis of **4a**, bp 158° at 0.3 Torr; ir (neat): 1680 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.94 (tt, J = 6 and 6 Hz, 2H, 3-H_2), 2.57 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 2.80 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 5.08 (s, 2H, OCH_2), 6.60-6.82 (m, 2H, 5-H and 7-H), 7.08-7.60 (m, 6H, 6-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 22.9 (t), 30.8 (t), 41.0 (t), 70.5 (t), 112.0 (d), 121.1 (d), 122.9 (s), 126.7 (d), 127.5 (d), 128.4 (d), 133.7 (d), 137.0 (s), 147.0 (s), 159.3 (s), 196.7 (s).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.78; H, 6.43.

8-(4-Chlorobenzyloxy)-1,2,3,4-tetrahydro-1-naphthalenone **4f**.

A mixture of 8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone [8] (3.0 g, 18.5 mmoles), *p*-chlorobenzyl chloride (4.0 g, 24.8 mmoles), tripotassium phosphate (7.8 g, 36.7 mmoles) and acetone (30 ml) was stirred at 60° for 240 minutes. After removal of insoluble materials by filteration the acetone was evaporated. The residue was chromatographed and eluted with benzene to give **4f** (4.7 g, 89%) as colorless crystals, mp 126-127° from benzene-hexane; ir (potassium bromide): 1670 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 2.06 (tt, J = 6 and 6 Hz, 2H, 3-H_2), 2.66 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 2.94 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 5.13 (s, 2H, OCH_2), 6.84 (d, J = 8 Hz, 1H, 5-H or 7-H), 6.84 (d, J = 8 Hz, 1H, 5-H or 7-H), 7.20-7.58 (m, 5H, 6-H and *p*-Cl-Ph-H_4); ^{13}C nmr (deuteriochloroform): δ 23.0 (t), 30.9 (t), 41.1 (t), 69.9 (t), 112.0 (d), 121.4 (d), 123.0 (s), 128.1 (d), 128.7 (d), 133.4 (s), 133.8 (d), 135.6 (s), 147.2 (s), 159.1 (s), 196.8 (s).

Anal. Calcd. for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27. Found: C, 70.98; H, 5.33.

8-Cyanomethoxy-1,2,3,4-tetrahydro-1-naphthalenone **4g**.

Compound **4g** (44%) was obtained as colorless crystals from benzene-hexane in a manner similar to the synthesis of **4f**, mp 78-79°; ir (potassium bromide): 1665 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 2.08 (tt, J = 6 and 6 Hz, 2H, 3-H_2), 2.65 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 2.97 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 4.85 (s, 2H, CH_2CN), 6.98 (d, J = 8 Hz, 1H, 5-H or 7-H), 7.05 (d, J = 8 Hz, 1H, 5-H or 7-H), 7.41 (dd, J = 8 and 8 Hz, 1H, 6-H); ^{13}C nmr (deuteriochloroform): δ 22.7 (t), 30.5 (t), 40.6 (t), 56.0 (t), 115.5 (d), 116.1 (s), 124.2 (s), 124.7 (d), 134.0 (d), 147.6 (s), 157.0 (s), 197.0 (s).

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.79; H, 5.67; N, 7.12.

4-Methoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **5a**.

Compound **5a** (96%) [9] was obtained from catalytic hydrogenation of the corresponding 1-bromo derivative as colorless crystals, mp 84-85° from methanol.

4-Ethoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **5b**.

A mixture of 4-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one [9] (2.0 g, 11.3 mmoles), methyl iodide (2.8 g, 17.9 mmoles), tripotassium phosfate (9.6 g, 45.2 mmoles) and dimethyl sulfoxide (20 ml) was stirred at 60° for 10 minutes. After removal of insoluble materials by filteration the filtrate was poured into water and extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene (90)-ether (10) to give **5b** (2.1 g, 90%) as a colorless oil, bp 123° at 1.7 Torr; ir (neat): 1695 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.35 (t, J = 7 Hz, 3H, OCH_2CH_3), 1.60-1.95 (m, 4H, 7-H_2 and 8-H_2), 2.43-2.85 (m, 4H, 6-H_2 and 9-H_2), 4.01 (q, J = 7 Hz, 2H, OCH_2CH_3), 6.69 (d, J = 7 Hz, 1H, 1-H or 3-H), 6.78 (d, J = 7 Hz, 1H, 1-H or 3-H), 7.21 (dd, J = 7 and 7 Hz, 1H, 2-H); ^{13}C nmr (deuteriochloroform): δ 14.7 (q), 23.5 (t), 25.8 (t), 32.7 (t), 42.5 (t), 64.5 (t), 111.3 (d), 121.0 (d), 130.5 (s), 130.8 (d), 139.1 (s), 155.3 (s),

206.9 (s).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.18; H, 7.72.

4-Propoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **5c**.

Compound **5c** (86%) was obtained as a colorless oil in a manner similar to the synthesis of **5b**, bp 130° at 2.0 Torr; ir (neat): 1695 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 0.99 (t, J = 7 Hz, 3H, $OCH_2CH_2CH_3$), 1.56-2.00 (m, 6H, $OCH_2CH_2CH_3$,7-H_2 and 8-H_2), 2.44-2.86 (m, 4H, 6-H_2 and 9-H_2), 3.92 (t, J = 7 Hz, 2H, $OCH_2CH_2CH_3$), 6.70 (d, J = 8 Hz, 1H, 1-H or 3-H), 6.78 (d, J = 8 Hz, 1H, 1-H or 3-H), 7.22 (dd, J = 8 and 8 Hz, 1H, 2-H); ^{13}C nmr (deuteriochloroform): δ 10.4 (q), 22.5 (t), 23.6 (t), 25.9 (t), 32.8 (t), 42.6 (t), 70.4 (t), 111.3 (d), 120.9 (d), 130.5 (s), 130.8 (d), 139.2 (s), 155.5 (s), 206.9 (s).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.83; H, 8.24.

4-Isobutoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **5d**.

Compound **5d** (87%) was obtained as colorless crystals from hexane in a manner similar to the synthesis of **5a**, mp 40-41°; ir (potassium bromide): 1695 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 0.98 (d, J = 7 Hz, 6H, $OCH_2CH(CH_3)_2$), 1.60-1.90 (m, 4H, 7-H_2 and 8-H_2), 1.90-2.32 (m, 1H, $OCH_2CH(CH_3)_2$), 2.42-2.84 (m, 4H, 6-H_2 and 9-H_2), 3.72 (d, J = 7 Hz, 2H, $OCH_2CH(CH_3)_2$), 6.70 (d, J = 7 Hz, 1H, 1-H or 3-H), 6.77 (d, J = 7 Hz, 1H, 1-H or 3-H), 7.22 (dd, J = 7 and 7 Hz, 1H, 2-H); ^{13}C nmr (deuteriochloroform): δ 19.1 (q), 23.7 (t), 26.0 (t), 28.3 (d), 32.8 (t), 42.6 (t), 75.3 (t), 111.2 (d), 120.9 (d), 130.5 (s), 130.8 (d), 139.2 (s), 155.7 (s), 206.8 (s).

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.53; H, 8.80.

4-Benzyloxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **5e**.

Compound **5e** (76%) was obtained as colorless crystals from benzene-hexane in a manner similar to the synthesis of **5a**, mp 76-77°; ir (potassium bromide): 1685 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.62-1.88 (m, 4H, 7-H_2 and 8-H_2), 2.44-2.82 (m, 4H, 6-H_2 and 9-H_2), 5.09 (s, 2H, OCH_2), 6.68 (d, J = 8 Hz, 1H, 1-H or 3-H), 6.80 (d, J = 8 Hz, 1H or 3-H), 7.08-7.44 (m, 6H, 2-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 23.4 (t), 25.8 (t), 32.7 (t), 42.5 (t), 70.9 (t), 112.2 (d), 121.6 (d), 127.0 (d), 127.7 (d), 128.3 (s), 128.5 (d), 131.0 (d), 137.0 (s), 139.5 (s), 155.1 (s), 207.1 (s).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.31; H, 6.95.

General Procedure for Photocyclization Reactions of Ethers **4a-g** and **5a-e**.

Method A.

An acetonitrile solution (500 ml) of the starting material (2.00 mmoles) was deoxygenated by bubbling nitrogen gas for 1 hour and then irradiated under monitoring by high performance liquid chromatography (hplc). The irradiation was stopped when the ether almost disappeared. After irradiation the acetonitrile was evaporated under reduced pressure below 40°. The residue was chromatographed and eluted with benzene-ether to give a variety of products.

Method B.

An acetonitrile solution (500 ml) of the starting material (2.00 mmoles) was deoxygenated by bubbling nitrogen gas for 1 hour and then irradiated under monitoring by high performance liquid chromatography (hplc). The irradiation was stopped when the ether almost disappeared. After irradiation the acetonitrile was evaporated under reduced pressure below 40°. The residue was dissolved in ethanol (20 ml) containing 0.4 *M* sulfuric acid (5 ml) and stirred for 30 minutes at room temperature. The solution was extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene-ether to give a variety of products.

4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furan **7a**.

Compound **7a** (34%, method B) was obtained as a colorless oil, bp 68° at 1.4 Torr and identical with an authentic sample [10] in the ir and ^1H nmr spectra.

8-Hydroxymethyl-1,2,3,4-tetrahydro-1-naphthalenone **8a**.

Compound **8a** (36%, method B) was obtained as a colorless oil; ir (neat): 3450 (OH), 1670 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 2.08 (tt, J = 7 and 7 Hz, 2H, 3-H_2), 2.68 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 2.96 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 4.32 (broad s, 1H, OH), 4.70 (s, 2H, OCH_2), 7.14-7.50 (m, 3H, 5-H, 6-H and 7-H); ^{13}C nmr (deuteriochloroform): δ 22.9 (t), 30.7 (t), 40.5 (t), 65.1 (t), 128.5 (d), 128.8 (d), 131.1 (s), 133.3 (d), 143.4 (s), 146.5 (s), 201.9 (s).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.22; H, 6.72.

2-Methyl-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan **7b**.

Compound **7b** (5%, method B) was obtained as a colorless oil, bp 76° at 0.4 Torr; ^1H nmr (deuteriochloroform): δ 1.97 (tt, J = 6 and 6 Hz, 2H, 4-H_2), 2.35 (s, 3H, CH_3), 2.67 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 2.83 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 6.74-7.16 (m, 3H, 6-H, 7-H and 8-H); ^{13}C nmr (deuteriochloroform): δ 12.1 (q), 20.3 (t), 24.2 (t), 26.7 (t), 107.5 (d), 111.5 (s), 119.0 (d), 123.3 (d), 129.1 (s), 131.9 (s), 147.0 (s), 152.5 (s).

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.71; H, 7.26.

8-(1-Hydroxyethyl)-1,2,3,4-tetrahydro-1-naphthalenone **8b**.

Compound **8b** (62%, method B) was obtained as a colorless oil; ir (neat): 3440 (OH), 1675 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.52 (d, J = 7 Hz, 3H, CH_3CHOH), 2.07 (tt, J = 7 and 7 Hz, 2H, 3-H_2), 2.71 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 2.96 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 3.80 (broad s, 1H, OH), 5.25 (q, J = 7 Hz, 1H, CH_3CHOH), 7.04-7.50 (m, 3H, 5-H, 6-H and 7-H); ^{13}C nmr (deuteriochloroform): δ 22.5 (q), 22.8 (t), 31.0 (t), 40.9 (t), 67.8 (d), 125.4 (d), 128.3 (d), 131.0 (s), 133.3 (d), 146.4 (s), 147.9 (s), 202.0 (s).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.48; H, 7.54.

2-Ethyl-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan **7c**.

Compound **7c** (8%, method B) was obtained as a colorless oil, bp 86° at 0.6 Torr; ^1H nmr (deuteriochloroform): δ 1.30 (t, J = 8 Hz, 3H, CH_3CH_2), 2.00 (tt, J = 7 and 7 Hz, 2H, 4-H_2), 2.54-2.94 (m, 6H, CH_3CH_2, 3-H_2 and 5-H_2), 6.82-7.20 (m, 3H, 6-H, 7-H and 8-H); ^{13}C nmr (deuteriochloroform): δ 12.5 (q), 20.4 (t), 20.6 (t), 24.3 (t), 26.8 (t), 107.7 (d), 110.6 (s), 119.0 (d), 123.4 (d), 129.1 (s), 132.0 (s), 152.1 (s), 152.4 (s).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.53; H, 7.56.

8-(1-Hydroxypropyl)-1,2,3,4-tetrahydro-1-naphthalenone **8c**.

Compound **8c** (48%, method B) was obtained as a colorless oil; ir (neat): 3450 (OH), 1670 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.00 (t, J = 7 Hz, 3H, CH_3CH_2CHOH), 1.78 (qd, J = 7 and 7 Hz, 2H, CH_3CH_2CHOH), 2.06 (tt, J = 7 and 7 Hz, 2H, 3-H_2), 2.69 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 2.95 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 3.84 (broad s, 1H, OH), 4.97 (t, J = 7 Hz, 1H, CH_3CH_2CHOH), 7.00-7.46 (m, 3H, 5-H, 6-H and 7-H); ^{13}C nmr (deuteriochloroform): δ 11.1 (q), 22.8 (t), 30.0 (t), 31.0 (t), 40.9 (t), 73.8 (d), 126.2 (d), 128.1 (d), 130.7 (s), 133.1 (d), 146.3 (s), 147.4 (s), 201.9 (s).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.62; H, 8.03.

2-Isopropyl-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan **7d**.

Compound **7d** (11%, method B) was obtained as a colorless oil, bp 84° at 0.3 Torr; ^1H nmr (deuteriochloroform): δ 1.30 (d, J = 7 Hz, 6H, $CH(CH_3)_2$), 1.96 (tt, J = 6 and 6 Hz, 2H, 4-H_2), 2.74 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 2.81 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 3.08 (septet, J = 7 Hz, 1H, $CH(CH_3)_2$), 6.76-7.18 (m, 3H, 6-H, 7-H and 8-H); ^{13}C nmr (deuteriochloroform): δ 21.0 (t), 21.2 (q), 24.3 (t), 26.8 (t), 28.1 (d), 107.7 (d), 109.5 (s), 118.9 (d), 123.3 (d), 129.2 (s), 132.2 (s), 152.1 (s), 155.5 (s).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.80; H, 8.17.

8-(1-Hydroxy-2-methylpropyl)-1,2,3,4-tetrahydro-1-naphthalenone **8d**.

Compound **8d** (60%, method B) was obtained as a colorless oil; ir (neat): 3450 (OH), 1675 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 0.72 (d, J = 7 Hz, 3H, CH_3), 1.02 (d, J = 7 Hz, 3H, CH_3), 1.80-2.20 (m, 3H, $(CH_3)_2CHCHOH$, and 3-H_2), 2.68 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 2.93 (t, J = 7 Hz, 2H, 2-H_2 or 4-H_2), 4.40 (broad s, 1H, OH), 4.64 (d, J = 8 Hz, 1H, $(CH_3)_2CHCHOH$), 7.04-7.40 (m, 3H, 5-H, 6-H and 7-H); ^{13}C nmr (deuteriochloroform): δ 18.4 (q), 20.5 (q), 22.7 (t), 31.1 (t), 33.0 (d), 41.0 (t), 79.1 (d), 127.9 (d), 128.2 (d), 130.8 (s), 132.9 (d), 146.7 (s), 146.7 (s), 202.2 (s).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.81; H, 8.18.

2-Phenyl-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan **7e**.

Compound **7e** (9%, method B) was obtained as colorless crystals from benzene, mp 51.5-52.5°; ^1H nmr (deuteriochloroform): δ 2.06 (tt, J = 7 and 7 Hz, 2H, 4-H_2), 2.88 (t, J = 7 Hz, 2H, 3-H_2 or 5-H_2), 3.04 (t, J = 7 Hz, 2H, 3-H_2 or 5-H_2), 6.84-7.88 (m, 8H, 6-H, 7-H, 8-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 22.5 (t), 24.2 (t), 26.5 (t), 108.0 (d), 113.1 (s), 119.4 (d), 124.7 (d), 125.3 (d), 127.3 (d), 128.6 (d), 129.4 (s), 131.8 (s), 133.0 (s), 147.7 (s), 152.3 (s).

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.01; H, 5.94.

8-(1-Hydroxy-1-phenylmethyl)-1,2,3,4-tetrahydro-1-naphthalenone **8e**.

Compound **8e** (71%, method B) was obtained as a colorless oil; ir (neat): 3430 (OH), 1670 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 2.06 (tt, J = 6 and 6 Hz, 2H, 3-H_2), 2.58 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 2.96 (t, J = 6 Hz, 2H, 2-H_2 or 4-H_2), 5.10 (d, J = 7 Hz, 1H, OH), 6.15 (d, J = 7 Hz, 1H, PhCHOH), 7.02-7.50 (m, 8H, 5-H, 6-H, 7-H and Ph-H_5).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.65; H, 6.22.

2-(*p*-Chlorohenyl)-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan **7f**.

Compound **7f** (3%, method A and 15%, method B) was obtained as a colorless oil; ^1H nmr (deuteriochloroform): δ 2.04 (tt, J = 6 and 6 Hz, 2H, 4-H_2), 2.87 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 2.97 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 6.82-7.42 (m, 5H, 6-H, 7-H, 8-H and *p*-Cl-Ph-H_2), 7.50-7.74 (m, 2H, *p*-Cl-Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 22.5 (t), 24.3 (t), 26.5 (t), 107.8 (d), 113.7 (s), 119.6 (d), 125.1 (d), 126.5 (d), 128.4 (s), 128.9 (d), 129.4 (s), 130.4 (s), 133.1 (s), 146.7 (s), 152.5 (s).

Anal. Calcd. for $C_{17}H_{13}ClO$: C, 75.98; H, 4.88. Found: C, 76.25; H, 5.13.

8-{(1-Hydroxy-1-(4-chlorophenylmethyl)}-1,2,3,4-tetrahydro-1-naphthalenone **8f**.

Compound **8f** (76%, method A and 49%, method B) was obtained as a colorless oil; ir (neat): 3400 (OH), 1670 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.84-2.28 (m, 2H, 3-H_2), 2.44-2.70 (m, 2H, 2-H_2 or 4-H_2), 2.82-3.10 (m, 2H, 2-H_2 or 4-H_2), 5.16 (d, J = 6 Hz, 1H, OH), 6.10 (d, J = 6 Hz, 1H, *p*-Cl-PhCHOH), 7.04-7.68 (m, 7H, 5-H, 6-H, 7-H and *p*-Cl-Ph-H_4); ^{13}C nmr (deuteriochloroform): δ 22.5 (t), 30.7 (t), 40.4 (t), 73.4 (d), 127.9 (d), 128.0 (d), 128.2 (d), 128.8 (d), 131.1 (s), 132.4 (s), 133.1 (d), 141.8 (s), 145.4 (s), 146.8 (s), 201.8 (s).

Anal. Calcd. for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27. Found: C, 70.94; H, 5.47.

4, 5-Dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carbonitrile **7g**.

Compound **7g** (12%, method B) was obtained as a colorless oil; ir (neat): 2225 (CN) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.09 (tt, J = 6 and 6 Hz, 2H, 4-H_2), 2.91 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 2.95 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 7.07 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.25 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.40 (dd, J = 8 and 8 Hz, 1H, 7-H); ^{13}C nmr (deuteriochloroform): δ 20.6 (t), 23.6 (t), 26.1 (t), 109.0 (d), 112.1 (s), 120.7 (s), 120.8 (d), 125.8 (s), 129.1 (d), 131.1 (s), 134.7 (s), 153.7 (s).

Anal. Calcd. for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.48; H, 5.16; N, 7.87.

2-(*p*-Chlorophenyl)-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2a-ol **6f**.

Compound **6f** (14%, method A) was obtained as colorless crystals from benzene-hexane, mp 140°; ir (potassium bromide): 3295 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 1.39 (s, 1H, OH), 1.69-1.83 (m, 1H), 1.92-2.35 (m, 3H), 2.56-2.74 (m, 1H), 2.85-2.97 (m, 1H), 5.24 (s, 1H, 2-H), 6.77 (d, J = 8 Hz, 1H, 6-H or 8-H), 6.77 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.21 (dd, J = 8 and 8 Hz, 1H, 7-H), 7.36-7.50 (m, 4H, *p*-Cl-Ph-H_4); ^{13}C nmr (deuteriochloroform): δ 18.7 (t), 24.9 (t), 31.6 (t), 74.0 (s), 94.7 (d), 107.4 (d), 120.3 (d), 128.1 (d), 128.5 (d), 129.3 (s), 130.4 (d), 133.8 (s), 134.1 (s), 136.3 (s), 158.6 (s).

Anal. Calcd. for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27. Found: C, 71.12; H, 5.23.

Cis-2-cyano-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2a-ol *cis*-**6g**.

Compound *cis*-**6g** (68%, method A and 42%, method B) was obtained as colorless crystals from benzene-hexane, mp 113-114°; ir (potassium bromide): 3495 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 1.74-2.32 (m, 4H, 3-H_2 and 4-H_2), 2.54-2.88 (m, 2H, 5-H_2), 3.00 (s, 1H, OH), 5.16 (s, 1H, 2-H), 6.68 (d, J = 8 Hz, 1H, 6-H or 8-H), 6.76 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.22 (dd, J = 8 and 8 Hz, 1H, 7-H); ^{13}C nmr (deuteriodimethyl

sulfoxide): δ 18.2 (t), 24.2 (t), 30.3 (t), 75.6 (s), 81.7 (d), 107.5 (d), 116.6 (s), 121.1 (d), 127.3 (s), 130.6 (d), 136.5 (s), 157.2 (s).

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.45; H, 5.59; N, 7.20.

Trans-2-cyano-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2a-ol *trans*-**6g**.

Compound *trans*-**6g** (6%, method A) contains small amount of **4g** and is difficult to isolate in a pure state; ir (potassium bromide): 3380 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 2.15 (tt, J = 6 and 6 Hz, 2H, 4-H_2), 2.70-2.92 (m, 2H, 3-H_2 or 5-H_2), 3.04 (t, J = 6 Hz, 2H, 3-H_2 or 5-H_2), 5.68 (broad s, 2H, OH and 2-H), 7.28-7.62 (m, 3H, 6-H, 7-H and 8-H).

2,2a,3,4,5,6-Hexahydrocyclohepta[*cd*]benzofuran-2a-ol **9a**.

Compound **9a** (79%, method A) was obtained as colorless crystals from benzene, mp 100-101°; ir (potassium bromide): 3320 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 1.18-3.16 (m, 9H, OH, 3-H_2, 4-H_2, 5-H_2 and 6-H_2), 4.13 (d, J = 10 Hz, 1H, 2-H), 4.37 (d, J = 10 Hz, 1H, 2-H), 6.63 (d, J = 8 Hz, 1H, 7-H), 6.63 (d, J = 8 Hz, 1H, 9-H), 7.07 (dd, J = 8 and 8 Hz, 1H, 8-H); ^{13}C nmr (deuterioacetone): δ 26.5 (t), 29.7 (t), 35.6 (t), 38.9 (t), 80.7 (s), 85.2 (t), 108.7 (d), 121.5 (d), 130.2 (d), 131.1 (s), 142.8 (s), 161.3 (s).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.60; H, 7.56.

2-Methyl-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2a-ol **9b**.

Compound **9b** (93%, method A) was obtained as colorless crystals from benzene, mp 91°; ir (potassium bromide): 3525 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 1.37 (d, J = 7 Hz, 3H, CH_3), 1.44-3.16 (m, 9H, OH, 3-H_2, 4-H_2, 5-H_2 and 6-H_2), 4.20 (q, J = 7 Hz, 1H, 2-H), 6.53 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.56 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.00 (dd, J = 8 and 8 Hz, 1H, 8-H); ^{13}C nmr (deuterioacetone): δ 13.4 (q), 26.3 (t), 29.6 (t), 35.7 (t), 38.7 (t), 80.2 (s), 88.3 (d), 108.3 (d), 121.4 (d), 129.9 (d), 131.7 (s), 142.7 (s), 160.3 (s).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.31; H, 7.74.

2-Ethyl-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2a-ol **9c**.

Compound **9c** (73%, method A) was obtained as colorless crystals from benzene, mp 83°; ^1H nmr (deuteriochloroform): δ 1.16 (t, J = 7 Hz, 3H, CH_2CH_3), 1.28-3.12 (m, 11H, OH, CH_2CH_3, 3-H_2, 4-H_2, 5-H_2 and 6-H_2), 4.00 (dd, J = 6 and 7 Hz, 1H, 2-H), 6.61 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.64 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.06 (dd, J = 8 and 8 Hz, 1H, 8-H); ^{13}C nmr (deuteriochloroform): δ 11.1 (q), 21.6 (t), 25.7 (t), 28.8 (t), 35.3 (t), 37.8 (t), 80.3 (s), 93.0 (d), 108.1 (d), 121.0 (d), 129.8 (d), 130.4 (s), 142.0 (s), 159.2 (s).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.25; H, 8.18.

2-Isopropyl-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2a-ol **9d**.

Compound **9d** (72%, method A) was obtained as colorless crystals from benzene, mp 106°; ir (potassium bromide): 3530 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 1.09 (d, J = 7 Hz, 3H, CH_3), 1.14 (d, J = 7 Hz, 3H, CH_3), 1.20-3.18 (m, 10H, OH, $CH(CH_3)_2$, 3-H_2, 4-H_2, 5-H_2 and 6-H_2), 3.72 (d, J = 9 Hz, 1H, 2-H), 6.52 (d, J = 8 Hz, 1H, 7-H), 6.52 (d, J = 8 Hz, 1H, 9-H), 6.99 (dd, J = 8 and 8 Hz, 1H, 8-H); ^{13}C nmr (deuterioacetone): δ 19.8 (q), 20.8 (q), 26.3 (t), 29.1 (d), 29.6 (t), 35.5 (t), 40.4 (t), 80.8 (s), 96.7 (d), 108.3 (d), 121.2 (d), 129.9 (d), 132.0 (s), 142.5 (s), 159.6 (s).

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.68; H, 8.80.

2-Phenyl-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2a-ol **9e**.

Compound **9e** (79%, method A) was obtained as colorless crystals from benzene, mp 88-89°; ir (potassium bromide): 3450 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 1.20-3.18 (m, 9H, OH, 3-H_2, 4-H_2, 5-H_2 and 6-H_2), 5.22 (s, 1H, 2-H), 6.69 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.79 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.14 (dd, J = 8 and 8 Hz, 1H, 8-H), 7.40 (broad s, 5H, Ph-H_5); ^{13}C nmr (deuterioacetone): δ 26.2 (t), 29.5 (t), 35.8 (t), 38.8 (t), 81.3 (s), 93.9 (d), 108.6 (d), 122.0 (d), 128.4 (d), 128.5 (d), 128.6 (d), 130.0 (d), 131.3 (s), 136.8 (s), 143.0 (s), 160.4 (s).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.32; H, 6.94.

3,4,5,6-Tetrahydrocyclohepta[cd]benzofuran **10a**.

Compound **10a** (80%; method B) was obtained as a colorless oil, bp 112° at 2.0 Torr and identical with an authentic sample [9] in the ir and ^1H nmr spectra.

2-Methyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **10b**.

Compound **10b** (78%, method B) was obtained as a colorless oil, bp 101° at 1.9 Torr; ^1H nmr (deuteriochloroform): δ 1.70-2.10 (m, 4H, 4-H_2 and 5-H_2), 2.33 (s, 3H, CH_3), 2.58-2.82 (m, 2H, 3-H_2 or 6-H_2), 2.92-3.16 (m, 2H, 3-H_2 or 6-H_2), 6.80-7.24 (m, 3H, 7-H, 8-H and 9-H); ^{13}C nmr (deuteriochloroform): δ 11.9 (q), 26.5 (t), 28.3 (t), 28.6 (t), 36.7 (t), 107.5 (d), 114.5 (s), 122.0 (d), 122.4 (d), 128.4 (s), 135.3 (s), 149.0 (s), 154.3 (s).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.65; H, 7.55.

2-Ethyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **10c**.

Compound **10c** (73%, method B) was obtained as a colorless oil, bp 106° at 2.2 Torr; ^1H nmr (deuteriochloroform): δ 1.27 (t, J = 7 Hz, 3H, CH_2CH_3), 1.70-2.10 (m, 4H, 4-H_2 and 5-H_2), 2.58-2.86 (m, 4H, CH_2CH_3, 3-H_2 or 6-H_2), 2.96-3.20 (m, 2H, 3-H_2 or 6-H_2), 6.84-7.24 (m, 3H, 7-H, 8-H and 9-H); ^{13}C nmr (deuteriochloroform): δ 12.5 (q), 19.9 (t), 26.4 (t), 28.4 (t), 28.7 (t), 36.7 (t), 107.8 (d), 113.6 (s), 122.0 (d), 122.6 (d), 128.4 (s), 135.6 (s), 154.0 (s), 154.4 (s).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.86; H, 8.02.

2-Isopropyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **10d**.

Compound **10d** (79%, method B) was obtained as a colorless oil; bp 118°at 1.8 Torr; ^1H nmr (deuteriochloroform): δ 1.29 (d, J = 7 Hz, 6H, $CH(CH_3)_2$), 1.70-2.06 (m, 4H, 4-H_2 and 5-H_2), 2.60-2.82 (m, 2H, 3-H_2 or 6-H_2), 2.88-3.20 (m, 3H, $CH(CH_3)_2$, 3-H_2 or 6-H_2), 6.80-7.28 (m, 3H, 7-H, 8-H and 9-H); ^{13}C nmr (deuteriochloroform): δ 20.9 (q), 26.3 (t), 26.5 (d), 28.4 (t), 28.7 (t), 36.7 (t), 107.8 (d), 112.5 (s), 122.0 (d), 122.4 (d), 128.4 (s), 135.7 (s), 154.2 (s), 157.1 (s).

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.16; H, 8.49.

2-Phenyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **10e**.

Compound **10e** (87%, method B) was obtained as colorless

crystals from benzene-hexane, mp 80°; ^{1}H nmr (deuteriochloroform): δ 1.76-2.18 (m, 4H, 4-H_2 and 5-H_2), 2.88-3.26 (m, 4H, 3-H_2 and 6-H_2), 6.86-7.82 (m, 8H, 7-H, 8-H, 9-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 28.1 (t), 28.3 (t), 28.3 (t), 36.5 (t), 108.0 (d), 116.8 (s), 122.4 (d), 123.8 (d), 126.8 (d), 127.5 (d), 128.3 (d), 128.8 (s), 131.6 (s), 136.5 (s), 149.0 (s), 154.5 (s).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.91; H, 6.49.

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