# Photocyclization Reactions. Part 4 [1]. Synthesis of Naphtho[1,8-*bc*]-furans and Cyclohepta[*cd*]benzofurans Using Photocyclization of Ethyl 2-(8-Oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetates and Ethyl 2-(5-Oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acetates



Essam Mohamed Sharshira, Haruki Iwanami, Mutsuo Okamura, Eietsu Hasegawa and Takaaki Horaguchi*

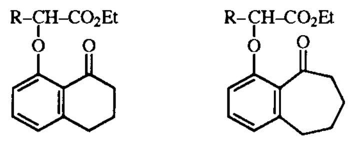
Department of Chemistry, Faculty of Science, Niigata Univeristy, Ikarashi, Niigata 950-21, Japan
Received July 31, 1995

Photocyclization reactions were carried out on ethyl 2-(8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetates **1a-e** and ethyl 2-(5-oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acetates **2a-e** in acetonitrile. Irradiation of **1a-e** gave naphtho[1,8-*bc*]furanols **3a-e** and naphtho[1,8-*bc*]furans **4a-e** in 33-83% yields and ethyl acrylates **5b-d** were produced in 3-25% yields during irradiation of **1b-d**. On the other hand, **2a-e** afforded cyclohepta[*cd*]benzofuranols **6a-e** and cyclohepta[*cd*]benzofurans **7a-e** in 44-87% yields. Ethyl acrylates **8b-d** were also produced in 7-43% yields from irradiation of **2b-d**. Substituent effects on photocyclization and reaction pathways are discussed.

*J. Heterocyclic Chem.*, **33**, 137 (1996).

## Introduction.

It has been shown that irradiation of aromatic carbonyl compounds possessing δ-hydrogen atoms gives benzofuranols. The photoreaction (Norrish type II) is useful for synthesis of benzofuran derivatives [2,3]. For example, irradiation of 2-benzyloxybenzaldehyde affords *cis* and *trans* isomers of 2-phenyl-2,3-dihydro-3-benzofuranol [2a]. The reaction proceeds through intramolecular cyclization of 1,5-biradical formed from δ-hydrogen abstraction by the carbonyl group [3]. In the previous paper [1c], we applied Norrish type II reaction for ether compounds of cyclic ketones such as 8-alkoxy-1,2,3,4-tetrahydro-1-naphthalenone (six-membered ring ketone) and 4-alkoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (seven-membered ring ketone) and discussed conformational effects of six- and seven-membered rings on cyclization step of 1,5-biradicals. In this paper, we report



1    2

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

Figure 1

photochemical synthesis of naphtho[1,8-*bc*]furanols and cyclohepta[*cd*]benzofuranols from ethyl 2-(8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetates **1a-e** (ester compounds of six-membered ring ketone) and ethyl 2-(5-oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)-acetates **2a-e** (ester compounds of seven-membered ring ketone) and discuss substituent effects of alkyl (R) and ethoxycarbonyl groups in the cyclization step of 1,5-biradicals.

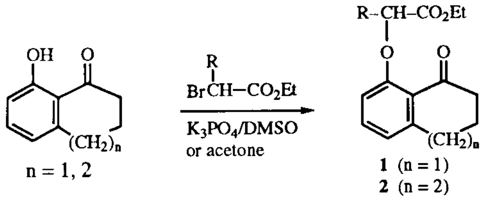
Table 1

Synthesis of Ethyl 2-(8-Oxo-5,6,7,8-tetrahydro-1-naphyloxy)acetates **1a-e** and Ethyl 2-(5-Oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acetates **2a-e**

| Starting material [a] | Reagent | Base | solvent | Temperature (°C) | Time (minutes) | R | Product | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| N | $CH_2BrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 120 | H | **1a** | 78 |
| N | $MeCHBrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 20 | Me | **1b** | 92 |
| N | $EtCHBrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 20 | Et | **1c** | 88 |
| N | *i*-$PrCHBrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 180 | *i*-Pr | **1d** | 46 |
| N | $PhCHBrCO_2Et$ | $K_3PO_4$ | Acetone | 0 | 240 | Ph | **1e** | 7 [b] |
| B | $CH_2BrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 10 | H | **2a** | 100 |
| B | $MeCHBrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 15 | Me | **2b** | 99 |
| B | $EtCHBrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 15 | Et | **2c** | 96 |
| B | *i*-$PrCHBrCO_2Et$ | $K_3PO_4$ | DMSO | 60 | 100 | *i*-Pr | **2d** | 72 |
| B | $PhCHBrCO_2Et$ | $K_3PO_4$ | DMSO | 20 | 120 | Ph | **2e** | 86 |

[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] 90% of starting material was recovered.

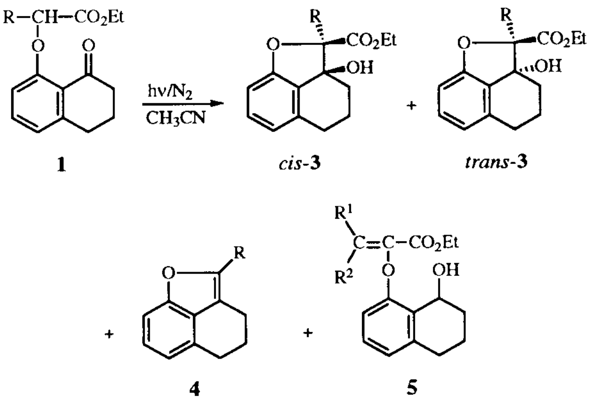
Scheme 1



Results and Discussion.

Ethyl 2-(8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)-acetates **1a-e** were prepared by the reactions of 8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone with ethyl bromoacetate, ethyl 2-bromopropionate, ethyl 2-bromobutyrate, ethyl 2-bromo-3-methylbutyrate or ethyl 2-bromo-2-phenylacetate respectively.

Scheme 2



Similarly, ethyl 2-(5-oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acetates **2a-e** were synthesized from the reaction of 4-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one and the corresponding bromoesters. The results are summarized in Scheme 1 and Table 1.

Table 2
Photocyclization Reactions of Ethyl 2-(8-Oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetates **1a-e** [a]

| Starting material | R | Irradiation time (minutes) | Product Yields (%) 3 (*cis*:*trans*) [b] | 4 | 5 [c] |
|---|---|---|---|---|---|
| **1a** | H | 35 | 50 (1:2) | 11 | – |
| **1b** | Me | 10 | 43 [d] | 8 | 25 |
| **1c** | Et | 15 | 52 [d] | 14 | 19 [e] |
| **1d** | *i*-Pr | 10 | 60 [d] | 23 | 3 |
| **1e** | Ph | 80 | 22 [d] | 11 | – |

[a] An acetonitrile solution (500 ml) of **1a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] *Cis* and *trans* isomers with regard to the ethoxycarbonyl and hydroxyl groups. [c] **5b**, $R^1 = R^2 = H$; **5c**, $R^1 = H$, $R^2 = CH_3$ or $R^1 = CH_3$, $R^2 = H$; **5d**, $R^1 = R^2 = CH_3$. [d] Only one stereoisomer was obtained and the stereochemistry was not determined. [e] *E* and *Z* isomer ratio = 1:4.

Photocyclization reactions of **1a-e** were carried out with 400-W high-pressure mercury lamp in acetonitrile. The results are shown in Scheme 2 and Table 2.

When **1a** (R = H) was irradiated in acetonitrile naphtho[1,8-*bc*]furanol **3a** (50%) was obtained along with naphtho[1,8-*bc*]furan **4a** (11%). The naphtho[1,8-*bc*]furanol **3a** was a mixture (1:2 ratio) of *cis* and *trans* isomers with regard to the ethoxycarbonyl and hydroxyl groups. The stereochemistry of the two isomers was determined by considering an anisotropic effect of the methylene group at $C_3$ for $C_2$-H in $^1$H nmr spectra. Generally, in dihydrobenzofuranols alkyl group at $C_3$ shield $C_2$-H at the *cis* position and deshield $C_2$-H at the *trans* position [4], that is, in the *cis*-isomer the chemical shift of $C_2$-H appears at a higher magnetic field than *trans* isomer. In photoreactions of **1b-d** (R = Me, Et, *i*-Pr) naphtho[1,8-*bc*]furanols **3b-d** (43-60%), naphtho[1,8-*bc*]furans **4b-d** (8-23%) and ethyl acrylates **5b-d** (3-25%) were isolated. Formation of ethyl acrylates reduced yields of **3b-d** and **4b-d**. Though *cis* and *trans* isomers with regard to the ethoxy carbonyl and hydroxyl groups were possible for naphtho[1,8-*bc*]-furanols **3b-d**, only one isomer was produced in each reaction, showing stereoselectivity in the cyclization step. However, stereochemistry of **3b-d** is not clear. Ester **5c** was a mixture of *E* and *Z* isomers and it was difficult to isolate each component. The *E*:*Z* ratio is 1:4 judging from $^1$H nmr spectrum in which ethoxycarbonyl group in **5c** deshield hydrogen at the *cis* position. Furthermore, when **1e** (R = Ph) was irradiated in acetonitrile, naphtho[1,8-*bc*]furanol **3e** (22%) and naphtho[1,8-*bc*]furan **4e** (11%) were isolated. In the reaction of **1e**, the total yield was not good (33%) due to decomposition of starting material **1e** during irradiation.

Thus, naphtho[1,8-*bc*]furans **3a-e**, **4a-e** were prepared in moderate yields by photocyclization reactions of ethyl 2-(8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetates **1a-e**. However, rearranged products *via* spirocyclization [1a,c,2g] of 1,5-biradicals were not isolated.

Scheme 3

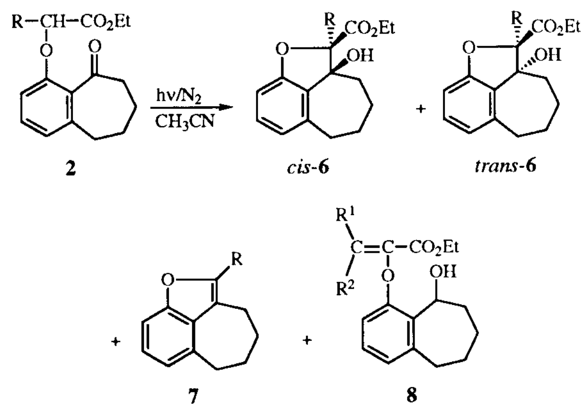


Table 3

Photocyclization Reactions of Ethyl 2-(5-Oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acetates **2a-e** [a]

| Starting material | R | Irradiation time (minutes) | Product 6 (*cis:trans*) [b] | Yields (%) 7 | 8 [c] |
|---|---|---|---|---|---|
| **2a** | H | 40 | 81 (3:1) | 6 | — |
| **2b** | Me | 25 | 36 [d] | 8 | 43 |
| **2c** | Et | 20 | 49 [d] | 11 | 24 [e] |
| **2d** | *i*-Pr | 20 | 63 [d] | 18 | 7 |
| **2e** | Ph | 90 | 56 (1:0) | 4 | — |

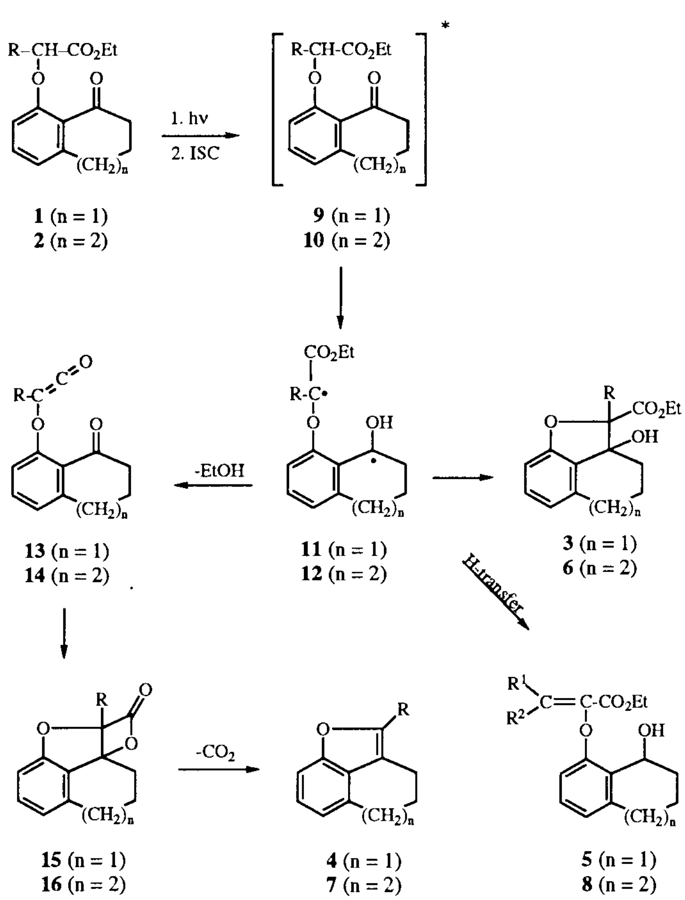
[a] An acetonitrile solution (500 ml) of **2a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] *Cis* and *trans* isomers with regard to the ethoxycarbonyl and hydroxyl groups. [c] **8b**, $R^1 = R^2 = H$; **8c**, $R^1 = H$, $R^2 = CH_3$ or $R^1 = CH_3$, $R^2 = H$; **8d**, $R^1 = R^2 = CH_3$. [d] Only one stereoisomer was obtained and the stereochemistry was not determined. [e] *E* and *Z* isomer ratio = 1:3.

Next, photocyclization reactions of ethyl 2-(5-oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acetates **2a-e** were examined. The results are summarized in Scheme 3 and Table 3.

Irradiation of **2a** (R = H) in acetonitrile gave cyclohepta[*cd*]benzofuranol **6a** (81%) and cyclohepta[*cd*]benzofuran **7a** (6%) in good yields. The cyclohepta[*cd*]benzofuranol **6a** was a mixture of *cis* and *trans* isomers (3:1) with regard to ethoxycarbonyl and hydroxyl groups. The stereochemistry of the two stereoisomers was assigned on the basis of $^1$H nmr spectra as mentioned above. In the case of **2b** (R = Me), cyclohepta[*cd*]benzofuranol **6b** and cyclohepta[*cd*]benzofuran **7b** were produced in 36% and 8% yield respectively, however, formation of ethyl acrylate **8b** (43%) lowered the yield of furan derivatives. Though *cis* and *trans* isomers were possible for **6b**, only one isomer was obtained. The stereochemistry of **6b** is not clear. Photocyclization of **2c** (R = Et) afforded one stereoisomer of cyclohepta[*cd*]benzofuranol **6c** (49%), cyclohepta[*cd*]benzofuran **7c** (11%) and ethyl acrylate **8c** (24%). Compound **8c** was a mixture of *E* and *Z* isomers (1:3 ratio) judging from the $^1$H nmr spectrum in which ethoxycarbonyl group in **8c** deshielded hydrogen at the *cis* position. In the case of **2d** (R = *i*-Pr) cyclohepta[*cd*]benzofuranol **6d** (63%), cyclohepta[*cd*]benzofuran **7d** (18%) and ethyl butyrate **8d** (7%) were isolated. We expected high yield of cyclohepta[*cd*]benzofuranol **6e** in the photocyclization reaction of **2e** since formation of ethyl acrylate was not possible. However, the yield of cyclohepta[*cd*]benzofuranol **6e** and cyclohepta[*cd*]benzofuran **7e** was only 60% owing to decomposition of the starting material during irradiation. Though *cis* and *trans* isomers were possible for **6e**, only one isomer was obtained. The stereochemistry of cyclohepta[*cd*]benzofuranol **6e** was assigned to be *cis* by comparison with *trans* isomer prepared from another reaction (see Experimental), showing attractive interaction between the hydroxyl and ethoxycarbonyl groups in the cyclization step.

Finally, we discuss reaction pathways in the photocyclization reactions of **1** and **2**. The mechanism on this type of photoreactions have been well studied [3]. The mechanistic pathways of products formation are summarized in Scheme 4. Irradiation of esters **1**, **2** produces (n, π*) excited triplet states **9**, **10** after intersystem crossing process (ISC). The carbonyl group abstract δ-hydrogen to give 1,5-biradicals **11**, **12** which afford a variety of products. For example, intramolecular cyclization of **11** or **12** affords naphtho[1,8-*bc*]furanols **3** or cyclohepta[*cd*]benzofuranols **6**. On the other hand, if the ketyl radical of **11** or **12** abstracts hydrogen of the alkyl groups (R = Me, Et, or *i*-Pr) ethyl acrylates **5**, **8** would be obtained. The yields of acrylates decreased as alkyl group R changed from methyl to ethyl or propyl groups. The results are attributed to decreasing ability of the ketyl radical to abstract hydrogen from alkyl group R because of steric hindrance. Production of **4** and **7** is not so clear, however, **11** or **12** probably give ketenes **13**, **14** by elimination of ethanol, which is converted to naphtho[1,8-*bc*]furans **4** or cyclohepta[*cd*]benzofurans **7** through formation of β-lactone

Scheme 4



**15**, **16** and following decarboxylation [5]. However, 1,5-biradicals **11**, **12** do not give rearranged products through spirocyclization [2g], beacuse the biradicals are stabilized with ethoxycarbonyl group by resonance and not reactive enough to make epoxide with benzene ring.

From the above results photocyclization reactions are useful to synthesize naphtho[1,8-*bc*]furanols and cyclohepta[*cd*]benzofuranols. The ethoxycarbonyl group suppresses spirocyclization reactions of the 1,5-biradical intermediates.

## EXPERIMENTAL

The melting points are uncorrected. Column choromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulphate 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 equipped 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.

Ethyl 2-(8-Oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate **1a**.

A mixture of 8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone [6] (3.0 g, 18.5 mmoles), ethyl bromoacetate (6.0 g, 35.9 mmoles), tripotassium phosphate (9.0 g, 42.4 mmoles) and dimethyl sulfoxide (20 ml) was stirred at 60° for one hour. 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 **1a** (3.60 g, 78%) as a colorless oil, bp 152° at 0.80 Torr; ir (neat): 1760 ($CO_2CH_2CH_3$), 1680 cm$^{-1}$ (Ar-CO); $^1H$ nmr (deuteriochloroform): δ 1.28 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 2.05 (tt, J = 6 and 6 Hz, 2H, 6-$H_2$), 2.64 (t, J = 6 Hz, 2H, 5-$H_2$ or 7-$H_2$), 2.93 (t, J = 6 Hz, 2H, 5-$H_2$ or 7-$H_2$), 4.25 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.70 (s, 2H, $OCH_2$), 6.73 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.88 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.34 (dd, J = 8 and 8 Hz, 1H, 3-H); $^{13}C$ nmr (deuteriochloroform): δ 14.2 (q), 22.9 (t), 30.7 (t), 40.9 (t), 61.2 (t), 66.8 (t), 113.0 (d), 122.4 (d), 123.3 (s), 133.7 (d), 147.2 (s), 158.6 (s), 168.7 (s), 196.8 (s).

*Anal.* Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.48; H, 6.80.

Ethyl 2-(8-Oxo-5,6,7,8-tetrahydro-1-naphthyloxy)propionate **1b**.

Compound **1b** (92%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 141° at 0.5 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1680 cm$^{-1}$ (Ar-CO); $^1H$ nmr (deuteriochloroform): δ 1.23 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.68 (d, J = 7 Hz, 3H, $CH_3CHCO_2CH_2CH_3$), 2.03 (tt, J = 6 and 6 Hz, 2H, 6-$H_2$), 2.61 (t, J = 6 Hz, 2H, 5-$H_2$ or 7-$H_2$), 2.90 (t, J = 6 Hz, 2H, 5-$H_2$ or 7-$H_2$), 4.20 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.71 (q, J = 7 Hz, 1H, $CH_3CHCO_2CH_2CH_3$), 6.74 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.83 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.31 (dd, J = 8 and 8 Hz, 1H, 3-H); $^{13}C$ nmr (deuteriochloroform): δ 14.1 (q), 18.5 (q), 22.9 (t), 30.7 (t), 40.9 (t), 61.0 (t), 74.8 (d), 114.7 (d), 122.4 (d), 123.7 (s), 133.4 (d), 147.0 (s), 158.3 (s), 171.9 (s), 196.4 (s).

*Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.92; H, 6.64.

Ethyl 2-(8-Oxo-5,6,7,8-tetrahydro-1-naphthyloxy)butyrate **1c**.

Compound **1c** (88%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 150° at 0.6 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1685 cm$^{-1}$ (Ar-CO); $^1H$ nmr (deuteriochloroform): δ 1.15 (t, J = 7 Hz, 3H, $CH_3CH_2$), 1.23 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$ ), 1.88-2.23 (m, 4H, $CH_3CH_2CHO$ and 6-$H_2$), 2.61 (t, J = 7 Hz, 2H, 5-$H_2$ or 7-$H_2$), 2.90 (t, J = 6 Hz, 2H, 5-$H_2$ or 7-$H_2$), 4.20 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.58 (t, J = 6 Hz, 1H, $OCHCH_2CH_3$), 6.64 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.82 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.29 (dd, J = 8 and 8 Hz, 1H, 3-H); $^{13}C$ nmr (deuteriochloroform): δ 9.4 (q), 14.2 (q), 22.9 (t), 26.2 (t), 30.8 (t), 41.0 (t), 60.9 (t), 78.8 (d), 112.9 (d), 121.7 (d), 123.2 (s), 133.4 (d), 147.0 (s), 158.6 (s), 171.2 (s), 196.1 (s).

*Anal.* Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.72; H, 7.29.

Ethyl 3-Methyl-2-(8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)-butyrate **1d**.

Compound **1d** (46%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 147° at 0.3 Torr; ir (neat): 1760, 1735 ($CO_2CH_2CH_3$), 1685 cm$^{-1}$ (Ar-CO); $^1H$ nmr (deuteriochloroform): δ 1.14 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.19 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.23 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.90-2.20 (m, 2H, 6-$H_2$), 2.24-2.72 (m, 3H, $CH(CH_3)_2$ and 5-$H_2$ or 7-$H_2$), 2.90 (t, J = 7 Hz, 2H, 5-$H_2$ or 7-$H_2$), 4.21 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.43 (d, J = 5 Hz, 1H, $OCHCH(CH_3)_2$), 6.59 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.80 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.29 (dd, J = 8 and 8 Hz, 1H, 3-H); $^{13}C$ nmr (deuteriochloroform): δ 14.2 (q), 17.6 (q), 18.7 (q), 22.9 (t), 30.8 (t), 31.9 (d), 41.0 (t), 60.9 (t), 82.1 (d), 111.5 (d), 121.5 (d), 122.8 (s), 133.4 (d), 147.1 (s), 158.8 (s), 170.8 (s), 196.2 (s).

*Anal.* Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.09; H, 7.75.

Ethyl 2-(8-Oxo-5,6,7,8-tetrahydro-1-naphthyloxy)-2-phenylacetate **1e**.

Compound **1e** (46%) was obtained as colorless crystals in a manner similar to the synthesis of **1a**, mp 103-104° from methanol; ir (potassium bromide): 1750 ($CO_2CH_2CH_3$), 1680 cm$^{-1}$ (Ar-CO); $^1H$ nmr (deuteriochloroform): δ 1.17 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 2.02 (tt, J = 7 and 7 Hz, 2H, 6-$H_2$), 2.67 (t, J = 7 Hz, 2H, 5-$H_2$ or 7-$H_2$), 2.93 (t, J = 7 Hz, 2H, 5-$H_2$ or 7-$CH_2$), 4.17 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.68 (s, 1H, OCHPh), 6.69 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.84 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.18-7.48 (m, 4H, 3-H and Ph-$H_3$), 7.69-7.81 (m, 2H, Ph-$H_2$ ); $^{13}C$ nmr (deuteriochloroform): δ 14.0 (q), 22.8 (t), 30.8 (t), 41.0 (t), 61.4 (t), 79.7 (d), 113.3 (d), 122.3 (d), 123.4 (s), 127.1 (d), 128.3 (d), 128.6 (d), 133.5 (d), 135.4 (s), 147.3 (s), 157.7 (s), 169.7 (s), 196.5 (s).

*Anal.* Calcd. for $C_{20}H_{20}O_4$. C, 74.05; H, 6.22. Found: C, 73.85; H, 6.25.

Ethyl 2-(5-Oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acetate **2a**.

A mixture of 4-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (1.0 g, 5.6 mmoles) [7], ethyl bromoacetate (2.0 g, 11.9 mmoles), tripotassium phosphate (3.0 g, 14.1 mmoles) and dimethyl sulfoxide (7 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 (80)-ether (20) to give **2a** (1.5 g, 100%). It formed colorless crystals from benzene, mp 46-47°; ir (potassium bromide): 1750 ($CO_2CH_2CH_3$), 1690 cm$^{-1}$ (Ar-CO); $^1$H nmr (deuteriochloroform): δ 1.25 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.64-1.94 (m, 4H, 7-$H_2$ and 8-$H_2$), 2.50-2.84 (m, 4H, 6-$H_2$ and 9-$H_2$), 4.21 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.63 (s, 2H, $OCH_2$), 6.72 (d, J = 8 Hz, 1H, 1-H or 3-H), 6.76 (d, J = 8 Hz, 1H, 1-H or 3-H), 7.23 (dd, J = 8 and 8 Hz, 1H, 2-H); $^{13}$C nmr (deuteriochloroform): δ 13.9 (q), 23.5 (t), 25.8 (t), 32.8 (t), 42.5 (t), 60.8 (t), 67.5 (t), 112.9 (d), 122.5 (d), 130.6 (d), 131.8 (s), 139.5 (s), 154.8 (s), 168.5 (s), 205.8 (s).

*Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.84; H, 6.72.

Ethyl 2-(5-Oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)propionate **2b**.

Compound **2b** (99%) was obtained as a colorless oil in a manner similar to the synthesis of **2a**, bp 142° at 0.5 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1700 cm$^{-1}$ (Ar-CO); $^1$H nmr (deuteriochloroform): δ 1.24 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.58 (d, J = 7 Hz, 3H, $OCHCH_3$), 1.66-1.92 (m, 4H, 7-$H_2$ and 8-$H_2$), 2.48-2.84 (m, 4H, 6-$H_2$ and 9-$H_2$), 4.19 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.72 (q, J = 7 Hz, 1H, $OCHCH_3$), 6.73 (d, J = 8 Hz, 1H, 1-H or 3-H), 6.76 (d, J = 8 Hz, 1H, 1-H or 3-H), 7.21 (dd, J = 8 and 8 Hz, 1H, 2-H); $^{13}$C nmr (deuteriochloroform): δ 14.1 (q), 18.4 (q), 23.6 (t), 25.9 (t), 32.8 (t), 42.6 (t), 61.1 (t), 74.7 (d), 113.2 (d), 122.4 (d), 130.7 (d), 131.1 (s), 139.5 (s), 154.3 (s), 171.7 (s), 206.9 (s) .

*Anal.* Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.31; H, 7.24.

Ethyl 2-(5-Oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)butyrate **2c**.

Compound **2c** (96%) was obtained as a colorless oil in a manner similar to the synthesis of **2a**, bp 148° at 0.75 Torr; ir (neat): 1760 ($CO_2CH_2CH_3$), 1705 cm$^{-1}$ (Ar-CO); $^1$H nmr (deuteriochloroform): δ 1.05 (t, J = 7 Hz, 3H, $OCHCH_2CH_3$), 1.23 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.70-2.16 (m, 6H, 7-$H_2$, 8-$H_2$ and $OCHCH_2CH_3$), 2.48-2.90 (m, 4H, 6-$H_2$ and 9-$H_2$), 4.19 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.54 (t, J = 6 Hz, 1H, $OCHCH_2CH_3$), 6.67 (d, J = 8 Hz, 1H, 1-H or 3-H ), 6.74 (d, J = 8 Hz, 1H, 1-H or 3-H), 7.20 (dd, J = 8 and 8 Hz, 1H, 2-H); $^{13}$C nmr (deuteriochloroform): δ 9.4 (q), 14.2 (q), 23.6 (t), 25.9 (t), 26.1 (t), 32.8 (t), 42.6 (t), 61.0 (t), 78.9 (d), 112.3 (d), 122.0 (d), 130.7 (d), 131.3 (s), 139.5 (s), 154.4 (s), 171.3 (s), 206.8 (s).

*Anal.* Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.08; H, 7.57.

Ethyl 3-Methyl-2-(5-oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)butyrate **2d**.

Compound **2d** (72%) was obtained as a colorless oil in a manner similar to the synthesis of **2a**, bp 144° at 1.6 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1700 cm$^{-1}$ (Ar-CO); $^1$H nmr (deuteriochloroform): δ 1.04 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.05 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.22 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.64-1.98 (m, 4H, 7-$H_2$ and 8-$CH_2$), 2.10-2.44 (m, 1H, $OCHCH(CH_3)_2$), 2.48-2.84 (m, 4H, 6-$H_2$ and 9-$H_2$), 4.18 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.39 (d, J = 5 Hz, 1H, $OCHCH(CH_3)_2$), 6.64 (d, J = 7 Hz, 1H, 1-H or 3-H), 6.72 (d, J = 7 Hz, 1H, 1-H or 3-H), 7.18 (dd, J = 7 and 7 Hz, 1H, 2-H); $^{13}$C nmr (deuteriochloroform): δ 14.2 (q), 17.5 (q), 18.6 (q), 23.7 (t), 25.9 (t), 31.7 (d), 32.7 (t), 42.5 (t), 60.8 (t), 82.1 (d), 111.6 (d), 121.7 (d), 130.6 (d), 131.1 (s), 139.4 (s), 154.4 (s), 170.8 (s), 206.5 (s).

*Anal.* Calcd. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.20; H, 8.04.

Ethyl 2-(5-Oxo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)phenylacetate **2e**.

Compound **2e** (86%) was obtained as a colorless oil in a manner similar to the synthesis of **2a**; ir (neat): 1765 ($CO_2CH_2CH_3$), 1705 cm$^{-1}$ (Ar-CO); $^1$H nmr (deuteriochloroform): δ 1.17 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.64-1.92 (m, 4H, 7-$H_2$ and 8-$H_2$), 2.56-2.84 (m, 4H, 6-$H_2$ and 9-$H_2$), 4.15 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.65 (s, 1H, OCHPh), 6.64-6.80 (m, 2H, 1-H and 3-H), 7.06-7.60 (m, 6H, 2-H and Ph-$H_5$); $^{13}$C nmr (deuteriochloroform): δ 14.0 (q), 23.2 (t), 25.7 (t), 32.6 (t), 42.4 (t), 61.4 (t), 79.9 (d), 113.1 (d), 122.6 (d), 126.9 (d), 128.6 (d), 128.7 (d), 130.8 (d), 131.6 (s), 135.4 (s), 139.7 (s), 153.7 (s), 169.6 (s), 206.5 (s).

*Anal.* Calcd. for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.28; H, 6.30.

General Procedure for Photocyclization Reactions of Esters **1a-e** and **2a-e**.

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 ester 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.

Ethyl *cis*-2a-Hydroxy-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]-furan-2-carboxylate *cis*-**3a**.

Compound *cis*-**3a** (17%) was obtained as colorless crystals from benzene, mp 122-122.5°; ir (potassium bromide): 3470 (OH), 1760 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.35 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.46-3.08 (m, 7H, 3-$H_2$, 4-$H_2$, 5-$H_2$ and OH), 4.34 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.78 (s, 1H, 2-H), 6.73 (d, J = 8 Hz, 1H, 6-H), 6.73 (d, J = 8 Hz, 1H, 8-H), 7.18 (dd, J = 8 and 8 Hz, 1H, 7-H); $^{13}$C nmr (deuteriochloroform): δ 14.3 (q), 18.7 (t), 24.9 (t), 31.5 (t), 61.5 (t), 75.0 (s), 91.3 (d), 107.8 (d), 120.7 (d), 127.9 (s), 130.8 (d), 136.3 (s), 158.0 (s), 167.4 (s).

*Anal.* Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.58; H, 6.32.

Ethyl *trans*-2a-Hydroxy-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2-carboxylate *trans*-**3a**.

Compound *trans*-**3a** (33%) was obtained as colorless crystals from benzene, mp 106.5-107°; ir (potassium bromide): 3520 (OH), 1740 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.25 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.40-3.02 (m, 7H, 3-$H_2$, 4-$H_2$, 5-$H_2$ and OH), 4.17 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.21 (s, 1H, 2-H), 6.72 (d, J = 7 Hz, 1H, 6-H or 8-H), 6.80 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.22 (dd, J = 8 and 8 Hz, 1H, 7-H); $^{13}$C nmr (deuteriochloroform): δ 14.2 (q), 18.6 (t), 24.7 (t), 30.1 (t), 61.3 (t), 77.0 (s), 91.7 (d), 107.3 (d), 120.4 (d), 126.9 (s), 131.2 (d), 136.2 (s), 159.2 (s), 168.3 (s).

*Anal.* Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.82; H, 6.38.

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

Compound **4a** (11%) was obtained as a colorless oil, bp 68° at 1.4 Torr and identical with an authentic sample [8] in the ir and $^1$H nmr spectra.

Ethyl 2a-Hydroxy-2-methyl-2a,3,4,5-tetrahydro-2*H*-naphtho-[1,8-*bc*]furan-2-carboxylate **3b**.

Compound **3b** (43%) was obtained as colorless crystals from benzene, mp 106-107°; ir (potassium bromide): 3450 (OH), 1745 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.36 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.38 (s, 3H, $CH_3$), 1.48-3.06 (m, 7H, 3-$H_2$, 4-$H_2$, 5-$H_2$ and OH), 4.35 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.73 (d, J = 8 Hz, 1H, 6-H), 6.73 (d, J = 8 Hz, 1H, 8-H), 7.18 (dd, J = 8 and 8 Hz, 1H, 7-H); $^{13}$C nmr (deuteriochloroform): δ 14.2 (q), 18.8 (t), 19.8 (q), 25.0 (t), 28.5 (t), 61.4 (t), 77.5 (s), 97.0 (s), 108.1 (d), 120.3 (d), 127.1 (s), 130.8 (d), 136.9 (s), 157.0 (s), 170.4 (s).

*Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.44; H, 6.86.

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

Compound **4b** (8%) was obtained as a colorless oil, bp 76° at 0.4 Torr and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Ethyl 2-(8-Hydroxy-5,6,7,8-tetrahydro-1-naphthyloxy)acrylate **5b**.

Compound **5b** (25%) was obtained as a colorless oil; ir (neat): 3500 (OH), 1720 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.25 (t, J= 7 Hz, 3H, $CO_2CH_2CH_3$), 1.40-3.02 (m, 6H, 5-$H_2$, 6-$H_2$ and 7-$H_2$), 3.50 (br s, 1H, OH), 4.21 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.08 (dd, J = 4 and 4 Hz, 1H, 8-H), 5.28 (d, J = 2 Hz, 1H, CH=C), 5.87 (d, J = 2 Hz, 1H, CH=C), 6.72 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.84 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.11 (dd, J = 8 and 8 Hz, 1H, 3-H); $^{13}$C nmr (deuteriochloroform): δ 14.0 (q), 17.8 (t), 29.7 (t), 30.5 (t), 61.9 (d), 61.9 (t), 108.1 (t), 113.7 (d), 124.9 (d), 127.9 (d), 129.3 (s), 139.8 (s), 149.0 (s), 154.6 (s), 162.9 (s).

*Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.40; H, 7.09.

Ethyl 2-Ethyl-2a-hydroxy-2a,3,4,5-tetrahydro-2*H*-naphtho-[1,8-*bc*]furan-2-carboxylate **3c**.

Compound **3c** (52%) was obtained as colorless crystals from benzene, mp 110.5-111°; ir (potassium bromide): 3450 (OH), 1740 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 0.94 (t, J = 7 Hz, 3H, $CH_3CH_2$), 1.36 (t, J = 7 Hz, 3H $CO_2CH_2CH_3$), 1.48-3.06 (m, 9H, $CH_2$, 3-$H_2$, 4-$H_2$, 5-$H_2$ and OH), 4.35 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.68 (d, J = 8 Hz, 1H, 6-H or 8-H), 6.72 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.17 (dd, J = 8 and 8 Hz, 1H, 7-H); $^{13}$C nmr (deuteriochloroform): δ 8.3 (q), 14.4 (q), 18.9 (t), 25.1 (t), 26.2 (t), 28.3 (t), 61.4 (t), 77.6 (s), 100.8 (s), 108.2 (d), 120.2 (d), 127.7 (s), 130.8 (d), 136.6 (s), 157.2 (s), 169.8 (s).

*Anal.* Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.45; H, 7.26.

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

Compound **4c** (14%) was obtained as a colorless oil, bp 86° at 0.6 Torr and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Ethyl *E*- and *Z*-2-(8-Hydroxy-5,6,7,8-tetrahydro-1-naphthyl-oxy)-2-butenoate *E*-**5c** and *Z*-**5c**.

These compounds were obtained as a mixture (oil) and difficult to isolate each component.

Compound *E*-**5c** had ir (neat): 3500 (OH), 1720 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.16 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.50-2.88 (m, 7H, 5-$H_2$, 6-$H_2$, 7-$H_2$ and OH), 2.12 (d, J = 7 Hz, 3H, $CH_3C$=C), 4.15 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.06-5.18 (m, 1H, 8-H), 6.10 (q, J = 7 Hz, 1H, HC=C), 6.40-7.12 (m, 3H, 2-H, 3-H, 4-H).

Compound *Z*-**5c** had ir (neat): 3500 (OH), 1715 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.18 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.50-2.88 (m, 7H, 5-$H_2$, 6-$H_2$, 7-$H_2$ and OH), 1.82 (d, J = 8 Hz, 3H, $CH_3C$=C), 4.15 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.14-5.28 (m, 1H, 8-H), 6.40-7.14 (m, 3H, 2-H, 3-H and 4-H), 6.68 (q, J = 8 Hz, 1H, CH=C).

Ethyl 2a-Hydroxy-2-isopropyl-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2-carboxylate **3d**.

Compound **3d** (60%) was obtained as colorless crystals from benzene, mp 141-142°; ir (potassium bromide): 3470 (OH), 1750 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 0.42 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.00 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.35 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.50-3.04 (m, 8H, 3-$H_2$, 4-$H_2$, 5-$H_2$, OH and $CH(CH_3)_2$), 4.31 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.64 (d, J = 8 Hz, 1H, 6-H or 8-H), 6.68 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.14 (dd, J = 8 and 8 Hz, 1H, 7-H); $^{13}$C nmr (deuteriochloroform): δ 14.2 (q), 16.9 (q), 18.7 (q), 19.0 (t), 25.2 (t), 28.3 (t), 32.3 (d), 61.1 (t), 77.2 (s), 102.5 (s), 107.1 (d), 120.0 (d), 128.0 (s), 130.8 (d), 135.6 (s), 159.1 (s), 170.1 (s).

*Anal.* Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.59; H, 7.64.

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

Compound **4d** (23%) was obtained as a colorless oil, bp 84° at 0.3 Torr and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Ethyl 2-(8-Hydroxy-5,6,7,8-tetrahydro-1-naphthyloxy)-3-methyl-2-butenoate **5d**.

Compound **5d** (3%) was obtained as colorless crystals from benzene, mp 62-63°, ir (potassium bromide): 3480 (OH), 1695 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.13 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.50-3.00 (m, 7H, 5-$H_2$, 6-$H_2$, 7-$H_2$ and OH), 1.90 (s, 3H, $CH_3$), 2.26 (s, 3H, $CH_3$), 4.12 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.10-5.26 (m, 1H, 8-H), 6.52 (d, J = 8 Hz, 1H, 2-H or 4H), 6.74 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.06 (dd, J = 8 and 8 Hz, 1H, 3-H); $^{13}$C nmr (deuteriochloroform): δ 14.0 (q), 18.0 (t), 19.9 (q), 20.3 (q), 29.9 (t), 30.4 (t), 61.1 (t), 61.9 (d), 109.9 (d), 123.2 (d), 127.8 (d), 127.9 (s), 136.1 (s), 139.5 (s), 140.0 (s), 155.5 (s), 163.5 (s).

*Anal.* Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.10; H, 7.53.

Ethyl 2a-Hydroxy-2-phenyl-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-2-carboxylate **3e**.

Compound **3e** (22%) was obtained as colorless crystals from benzene, mp 155-156°; ir (potassium bromide): 3430 (OH), 1745 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.34 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.50-2.94 (m, 7H, 3-$H_2$, 4-$H_2$, 5-$H_2$ and OH), 4.37 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$) 6.68 (d, J = 8 Hz, 1H, 6-H or 8-H), 6.95 (d, J = 8 Hz, 1H, 6-H or 8-H), 7.04-7.60 (m, 6H, 7-H and Ph-$H_5$); $^{13}$C nmr (deuteriochloroform): δ 14.1 (q), 19.0 (t), 24.8 (t), 31.2 (t), 62.2 (t), 79.7 (s), 99.7 (s), 107.4 (d), 120.9 (d), 126.4 (s), 126.4 (d), 128.1 (d), 128.1 (d), 131.1 (d), 135.2 (s), 137.1 (s), 157.9 (s), 169.5 (s).

*Anal.* Calcd. for $C_{20}H_{20}O_4$: C, 74.06; H, 6.22. Found: C, 74.20; H, 6.15.

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

Compound **4e** (11%) was obtained as colorless crystals from benzene, mp 51.5-52.5° and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Ethyl *cis*-2a-Hydroxy-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]-benzofuran-2-carboxylate *cis*-**6a**.

Compound *cis*-**6a** (61%) was obtained as colorless crystals from benzene, mp 95-97°; ir (potassium bromide): 3470 (OH), 1760 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.34 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.48-3.20 (m, 9H, 3-$H_2$, 4-$H_2$, 5-$H_2$, 6-$H_2$ and OH), 4.32 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.76 (s, 1H, 2-H), 6.68 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.77 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.13 (dd, J = 8 and 8 Hz, 1H, 8-H); $^{13}$C nmr (deuteriochloroform): δ 14.3 (q), 25.7 (t), 28.6 (t), 35.1 (t), 38.1 (t), 61.5 (t), 82.4 (s), 89.1 (d), 108.8 (d), 122.1 (d), 128.2 (s), 130.5 (d), 142.1 (s), 158.9 (s), 168.0 (s).

*Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.82; H, 6.88.

Ethyl *trans*-2a-Hydroxy-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]-benzofuran-2-carboxylate *trans*-**6a**.

This compound (20%) was obtained as a mixture with *cis*-**6a**; $^1$H nmr (deuteriochloroform): δ 1.28 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.42-3.16 (m, 9H, 3-$H_2$, 4-$H_2$, 5-$H_2$, 6-$H_2$ and OH), 4.18 (q, J = 7 Hz , 2H, $CO_2CH_2CH_3$), 4.90 (s, 1H, 2-H), 6.60 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.70 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.08 (dd, J = 8 and 8 Hz, 1H, 8-H).

3,4,5,6-Tetrahydrocyclohepta[*cd*]benzofuran **7a**.

Compound **7a** (6%) was obtained as a colorless oil, bp 112° at 2.0 Torr and identical with an authentic sample [7] in the ir and $^1$H nmr spectra.

Ethyl 2a-Hydroxy-2-methyl-2,2a,3,4,5,6-hexahydrocyclohepta-[*cd*]benzofuran-2-carboxylate **6b**.

Compound **6b** (36%) was obtained as colorless crystals from benzene, mp 115.5-116°; ir (potassium bromide): 3430 (OH), 1755 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.33 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.51 (s, 3H, $CH_3$), 1.56-3.12 (m, 9H, 3-$H_2$, 4-$H_2$, 5-$H_2$, 6-$H_2$ and OH), 4.30 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.66 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.74 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.13 (dd, J = 8 and 8 Hz, 1H, 8-H); $^{13}$C nmr (deuteriochloroform): δ 14.2 (q), 20.8 (q), 25.2 (t), 28.7 (t), 33.8 (t), 35.6 (t), 61.5 (t), 84.2 (s), 94.2 (s), 109.0 (d), 122.1 (d), 128.1 (s), 130.4 (d), 142.1 (s), 158.1 (s), 170.7 (s).

*Anal.* Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.76; H, 7.32.

2-Methyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **7b**.

Compound **7b** (8%) was obtained as a colorless oil, bp 101° at 1.9 Torr and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Ethyl 2-(5-Hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)acrylate **8b**.

Compound **8b** (43%) was obtained as a colorless oil; ir (neat): 3490 (OH), 1730 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.31 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.40-3.50 (m, 9H, 6-$H_2$, 7-$H_2$, 8-$H_2$, 9-$H_2$ and OH), 4.26 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.76 (d, J = 2 Hz, 1H, CH=C), 5.39 (d, J = 7 Hz, 1H, 5-H), 5.61 (d, J = 2 Hz, 1H, CH=C), 6.60-7.20 (m, 3H, 1-H, 2-H and 3-H); $^{13}$C nmr (deuteriochloroform): δ 14.1 (q), 24.4 (t), 28.2 (t), 32.8 (t), 35.5 (t), 61.7 (t), 65.7 (d), 103.2 (t), 117.4 (d), 126.9 (d), 128.4 (d), 134.4 (s), 145.8 (s), 151.4 (s), 152.5 (s), 162.6 (s).

*Anal.* Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.34; H, 7.45.

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

Compound **6c** (49%) was obtained as colorless crystals from benzene, mp 123.5-124°; ir (potassium bromide): 3450 (OH), 1740 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 0.99 (t, J = 7 Hz, 3H, $CH_2CH_3$), 1.34 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.48-3.12 (m, 11H, $CH_2CH_3$, 3-$H_2$, 4-$H_2$, 5-$H_2$, 6-$H_2$ and OH), 4.31 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.65 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.78 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.11 (dd, J = 8 and 8 Hz, 1H, 8-H); $^{13}$C nmr (deuteriochloroform): δ 8.8 (q), 14.4 (q), 25.2 (t), 27.0 (t), 28.8 (t), 33.4 (t), 35.7 (t), 61.4 (t), 84.3 (s), 97.9 (s), 109.0 (d), 122.1 (d), 128.5 (s), 130.4 (d), 141.9 (s), 158.3 (s), 170.0 (s).

*Anal.* Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.46; H, 7.52.

2-Ethyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **7c**.

Compound **7c** (11%) was obtained as a colorless oil, bp 106° at 2.2 Torr and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Ethyl *E*- and *Z*-2-(5-Hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)-2-butenoate *E*-**8c** and *Z*-**8c**.

These compounds (24%) were obtained as a mixture (oil) and difficult to isolate each component.

Compound *E*-**8c** had ir (neat): 3470 (OH), 1720 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.24 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.36-3.48 (m, 9H, 6-$H_2$, 7-$H_2$, 8-$H_2$, 9-$H_2$ and OH), 2.07 (d, J = 8 Hz, 3H, $CH_3C$=C), 4.16 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.48-5.70 (m, 1H, 5-H), 5.90 (q, J = 7 Hz, 1H, CH=C), 6.40-7.10 (m, 3H, 1-H, 2-H and 3-H).

Compound *Z*-**8c** had ir (neat): 3470 (OH), 1720 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.18 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.36-3.48 (m, 9H, 6-$H_2$, 7-$H_2$, 8-$H_2$, 9-$H_2$ and OH), 1.86 (d, J = 7 Hz, 3H, $CH_3C$=C), 4.11 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.68-5.84 (m, 1H, 5-H), 6.60 (q, J = 8 Hz, 1H, CH=C), 6.40-7.10 (m, 3H, 1-H, 2-H and 3-H).

Ethyl 2a-Hydroxy-2-isopropyl-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2-carboxylate **6d**.

Compound **6d** (63%) was obtained as colorless crystals from benzene, mp 155-156°; ir (potassium bromide): 3500 (OH), 1750 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 0.66 (d, J = 7 Hz, 3H, $CH_3$), 1.03 (d, J = 7 Hz, 3H, $CH_3$), 1.33 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.48-2.96 (m, 10H, CH, 3-$H_2$, 4-$H_2$, 5-$H_2$, 6-$H_2$ and OH), 4.29 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.62 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.77 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.09 (dd, J = 8 and 8 Hz, 1H, 8-H); $^{13}$C nmr (deuteriochloroform): δ 14.3 (q), 17.4 (q), 19.0 (q), 25.4 (t), 28.8 (t), 32.6 (d), 32.8 (t), 36.0 (t), 61.1 (t), 83.9 (s), 99.5 (s), 108.0 (d), 121.9 (d), 128.9 (s), 130.5 (d), 140.9 (s), 160.0 (s), 170.3 (s).

*Anal.* Calcd. for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 70.97; H, 7.99.

2-Isopropyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **7d**.

Compound **7d** (18%) was obtained as a colorless oil, bp 118° at 1.8 Torr and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Ethyl 2-(5-Hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-4-yloxy)-3-methyl-2-butenoate **8d**.

Compound **8d** (7%) was obtained as a colorless oil; ir (neat): 3460 (OH), 1720 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.10 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.28-3.40 (m, 9H, 6-$H_2$, 7-$H_2$, 8-$H_2$, 9-$H_2$ and OH), 1.90 (s, 3H, $CH_3$), 2.21 (s, 3H, $CH_3$), 4.09 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.60-5.76 (m, 1H, 5-H), 6.40-7.06 (m, 3H, 1-H, 2-H and 3-H); $^{13}$C nmr (deuteriochloroform): δ 14.0 (q), 19.9 (q), 20.3 (q), 23.7 (t), 27.7 (t), 32.0 (t), 34.9 (t), 60.7 (t), 66.0 (d), 111.4 (d), 124.5 (d), 127.9 (d), 131.7 (s), 137.0 (s), 138.6 (s), 144.8 (s), 155.1 (s), 163.5 (s).

*Anal.* Calcd. for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 71.14; H, 7.92.

Ethyl *cis*-2a-Hydroxy-2-phenyl-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2-carboxylate *cis*-**6e**.

Compound *cis*-**6e** (56%) was obtained as colorless crystals from benzene, mp 100-101°; ir (potassium bromide): 3490 (OH), 1715 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.33 (t, 3H, J = 7 Hz, $CO_2CH_2CH_3$), 0.80-3.12 (m, 8H, 3-$H_2$, 4-$H_2$, 5-$H_2$ and 6-$H_2$), 2.78 (s, 1H, OH), 4.36 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.70 (d, J = 8 Hz, 1H, 7-H or 9-H), 6.94 (d, J = 8 Hz, 1H, 7-H or 9-H), 7.04-7.62 (m, 6H, 8-H and Ph-$H_5$); $^{13}$C nmr (deuteriochloroform): δ 14.1 (q), 25.2 (t), 28.2 (t), 35.4 (t), 37.3 (t), 62.0 (t), 86.4 (s), 96.9 (s), 108.0 (d), 122.6 (d), 126.4 (d), 127.7 (s), 128.1 (d), 128.2 (d), 130.5 (d), 136.3 (s), 142.4 (s), 159.1 (s), 169.6 (s).

*Anal.* Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.66; H, 6.62.

Ethyl *trans*-2a-Hydroxy-2-phenyl-2,2a,3,4,5,6-hexahydrocyclohepta[*cd*]benzofuran-2-carboxylate *trans*-**6e**.

Compound *trans*-**6e** (25%) was obtained along with *cis*-**6e** (43%) as colorless crystals by heating a mixture of **2e**, ethyl 2-bromo-2-phenylacetate and tripotassium phosphate in DMSO at 60° for 1 hour, mp 128-129° from benzene; ir (potassium bromide): 3520 (OH), 1730 cm$^{-1}$ ($CO_2CH_2CH_3$); $^1$H nmr (deuteriochloroform): δ 1.16 (t, 3H, J = 7 Hz, $CO_2CH_2CH_3$), 1.42 (1H, s, OH), 1.50-3.14 (m, 8H, 3-$H_2$, 4-$H_2$, 5-$H_2$ and 6-$H_2$), 4.11 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.67 (d, J = 7 Hz, 1H, 7-H or 9-H), 6.89 (d, J = 7 Hz, 1H, 7-H or 9-H), 7.16 (dd, J = 7 and 7 Hz, 1H, 8-H), 7.18-7.84 (m, 5H, Ph-$H_5$); $^{13}$C nmr (deuteriochloroform): δ 13.9 (q), 25.5 (t), 28.6 (t), 35.0 (t), 36.6 (t), 61.8 (t), 85.0 (s), 95.6 (s), 108.2 (d), 122.1 (d), 127.3 (d), 127.7 (d), 128.1 (d), 128.8 (s), 130.2 (d), 134.9 (s), 141.8 (s), 158.7 (s), 170.1 (s).

*Anal.* Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.82; H, 6.55.

2-Phenyl-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **7e**.

Compound **7e** (4%) was obtained as colorless crystals from benzene-hexane, mp 80° and identical with an authentic sample [1c] in the ir and $^1$H nmr spectra.

Acknowledgement.

We thank Mr. Yoshiaki Matsuda for the elemental analyses.

REFERENCES AND NOTES

[1a] Part 1, T. Horaguchi, C. Tsukada, E. Hasegawa, T. Shimizu, T. Suzuki and K. Tanemura, *J. Heterocyclic Chem.*, **28**, 1261 (1991); [b] Part 2, T. Horaguchi, C. Tsukada, E. Hasegawa, T. Shimizu, T. Suzuki and K. Tanemura, *J. Heterocyclic Chem.*, **28**, 1273 (1991); [c] Part 3, E. M. Sharshira, H. Iwanami, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, **33**, 17 (1996).

[2a] S. P. Pappas and J. E. Blackwell, Jr., *Tetrahedron Letters*, 1171 (1966); [b] S. P. Pappas, B. C. Pappas and J. E. Blackwell, Jr., *J. Org. Chem.*, **32**, 3066 (1967); [c] G. R. Lappin and J. S. Zannucci, *J. Chem. Soc., Chem. Commun.*, 1113 (1969); [d] S. P. Pappas, J. E. Alexander and R. D. Zehr, *J. Am. Chem. Soc.*, **92**, 6927 (1970); [e] G. R. Lappin and J. S. Zannucci, *J. Org. Chem.*, **36**, 1808 (1971); [f] S. P. Pappas and R. D. Zehr, *J. Am. Chem. Soc.*, **93**, 7112 (1971); [g] P. J. Wagner, M. A. Meador and J. C. Scaiano, *ibid.*, **106**, 7988 (1984); [h] M. A. Meador and P. J. Wagner, *J. Org. Chem.*, **50**, 419 (1985); [i] P. J. Wagner, M. A. Meador, B. P. Giri and J. C. Scaiano, *J. Am. Chem. Soc.*, **107**, 1087 (1985); [j] G. A. Kraus, P. J. Thomas and M. D. Schwinden, *Tetrahedron Letters*, **31**, 1819 (1990); [k] M. A. -Aziz, J. V. Auping and M. A. Meador, *J. Org. Chem.*, **60**, 1303 (1995).

[3a] P. J. Wagner, *Acc. Chem. Res.*, **22**, 83 (1989); [b] P. J. Wagner, M. A. Meador and B. S. Park, *J. Am. Chem. Soc.*, **112**, 5199 (1990).

[4a] E. C. Hayward, D. S. Tarbell and L. D. Calebrook, *J. Org. Chem.*, **33**, 399 (1968); [b] M. P. Mertes and L. J. Powers, *ibid.*, **36**, 1805 (1971); [c] T. Kozuka, *Bull. Chem. Soc. Japan*, **55**, 2415 (1982); [d] W. D. Crow, U. E. -Low and Y. T. Pang, *Aust. J. Chem.*, **37**, 1915 (1984); [e] T. Suzuki, *Bull. Chem. Soc. Japan*, **58**, 2821(1985).

[5a] W. T. Brady and Y.-Q. Gu, *J. Heterocyclic Chem.*, **25**, 969 (1988); [b] W. T. Brady and Y.-Q. Gu, *J. Org Chem.*, **53**, 1353 (1988).

[6] I. A. Kaye, R. S. Matthews and A. A. Scala, *J. Chem. Soc.*, 2816 (1964).

[7] T. Horaguchi, E. Hasegawa, T. Shimizu, K. Tanemura and T. Suzuki, *J. Heterocyclic Chem.*, **26**, 365 (1989).

[8] T. Horaguchi, T. Shimizu and T. Suzuki, *Bull. Chem. Soc. Japan*, **48**, 1249 (1975).