

PHOTOCYCLIZATION REACTIONS OF ETHYL 2-(8-OXO-5, 6, 7, 8-TETRAHYDRO-1-NAPHTHYLOXY)ACETATE and 8-OXO-5, 6, 7, 8-TETRAHYDRO-1-NAPHTHYLOXYACETONITRILE IN METHANOL

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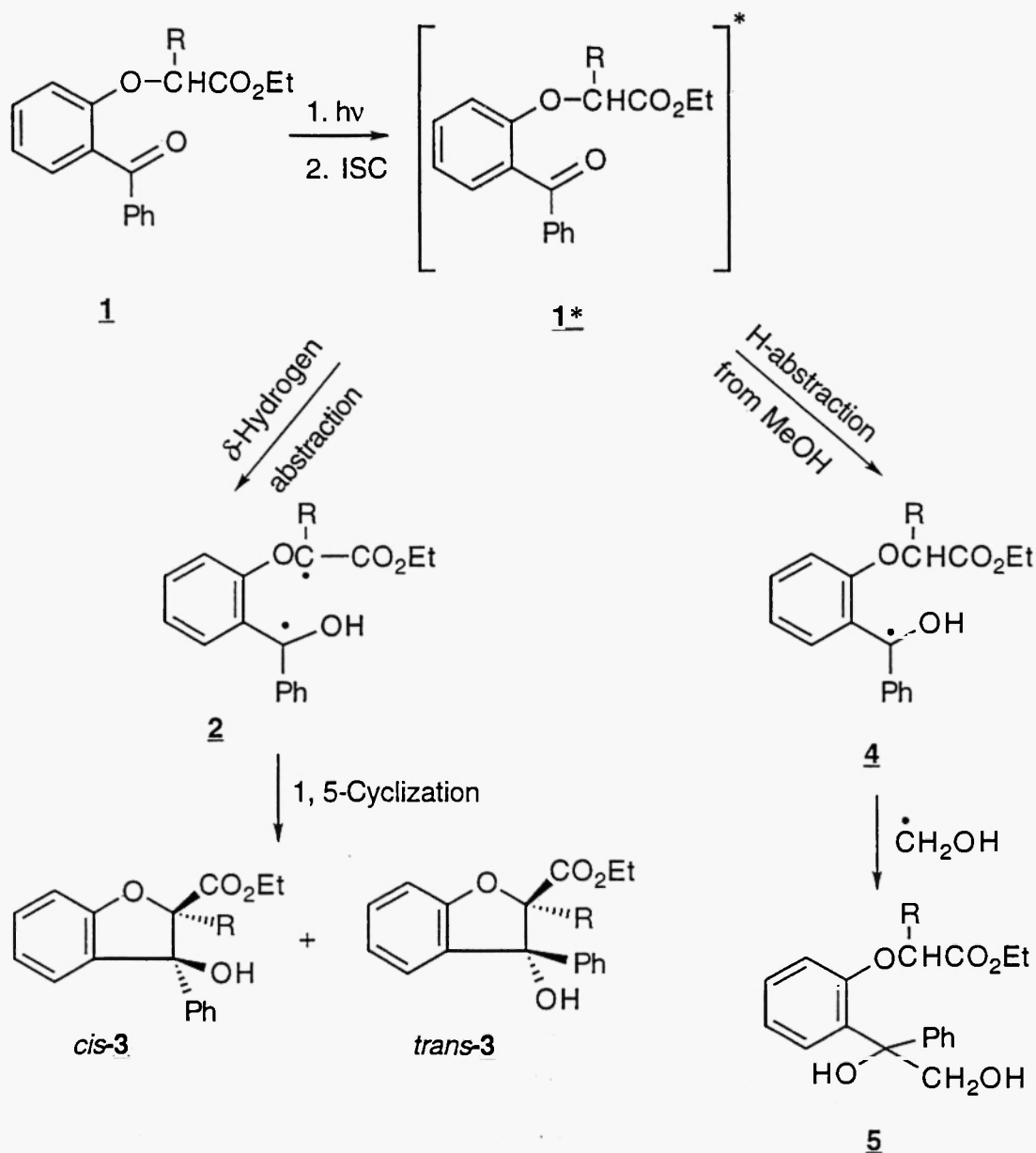
Abstract: Photocyclization reactions were carried out on ethyl 2-(8-oxo-5, 6, 7, 8-tetrahydro-1-naphthyloxy)acetate and 8-oxo-5, 6, 7, 8-tetrahydro-1-naphthyloxyacetonitrile (six-membered ring ketones) **7a-b** in Methanol. Irradiation of **7a-b** gave *cis*- and *trans*-naphtho[1, 8-*bc*]furanol derivatives **8a-b**, *cis*- and *trans*-isomer of methanol incorporated naphtho[1, 8-*bc*]furan **12b** and dehydrated naphtho[1, 8-*bc*]furan **11b**. During irradiation of **7a**, a methanol incorporated product (dihydroxy products) **9a** and a diastereomeric derivative of *meso*- and *dl*-succinate (dimerization product) **10a** were also isolated. The effect of polar protic solvent (methanol) on changing product distribution and reaction pathways of 6-membered cyclic ketones **7a-b** are also discussed.

Introduction :

It is well-known that *o*-substituted aromatic carbonyl compounds which possess δ -hydrogen atoms undergo a very facile hydrogen abstraction under irradiation, called Norrish type II reaction. This reaction is useful in the synthesis of furan derivatives. Carbonyl compounds consist of benzaldehydes¹⁻³, acetophenones²⁻⁶, benzophenones^{4, 6-16}, α -dicarbonyl compounds¹⁷⁻²⁰, benzoquinones²¹⁻²⁹ or cyclic ketones^{1-2, 30-32}. Among the compounds cyclic ketones have been studied from a view-point of reaction mechanisms and synthetic applications³⁰⁻³¹. In general, photocyclization reactions of carbonyl compounds **1** proceed via **1**, 5-biradical intermediates **2** formed through δ -hydrogen abstraction by the excited carbonyl group as shown in Scheme 1^{4, 6, 8-10, 12}. Intramolecular cyclization of **2** gives *cis*- and *trans*-dihydrobenzofuranols **3**. On the other hand if the irradiation was carried out in polar solvent like methanol the carbonyl group of **1*** abstracts hydrogen from methanol to give a radical **4** which can give methanol incorporated product **5**¹⁶.

In this paper, we study the photochemistry of 6-membered cyclic ketones **7a-b** in methanol (polar protic solvent) and we demonstrate the effect of substituent and solvent on changing product distribution and reaction pathways.

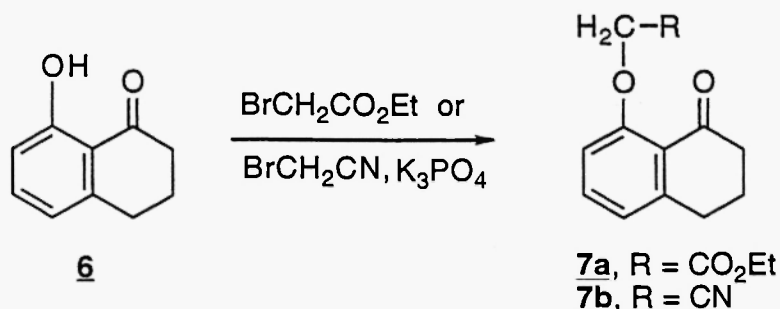
Scheme 1



Results and Discussion :

Ethyl 2-(8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetate and 8-oxo-5,6,7,8-tetrahydro-1-naphthyloxyacetonitrile **7a-b**³⁰⁻³¹ for photocyclization reactions were prepared by the reaction of 8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone **6** with ethyl bromoacetate and bromoacetonitrile in presence of a base the sequence of the reactions are outlined in Scheme 2.

Scheme 2



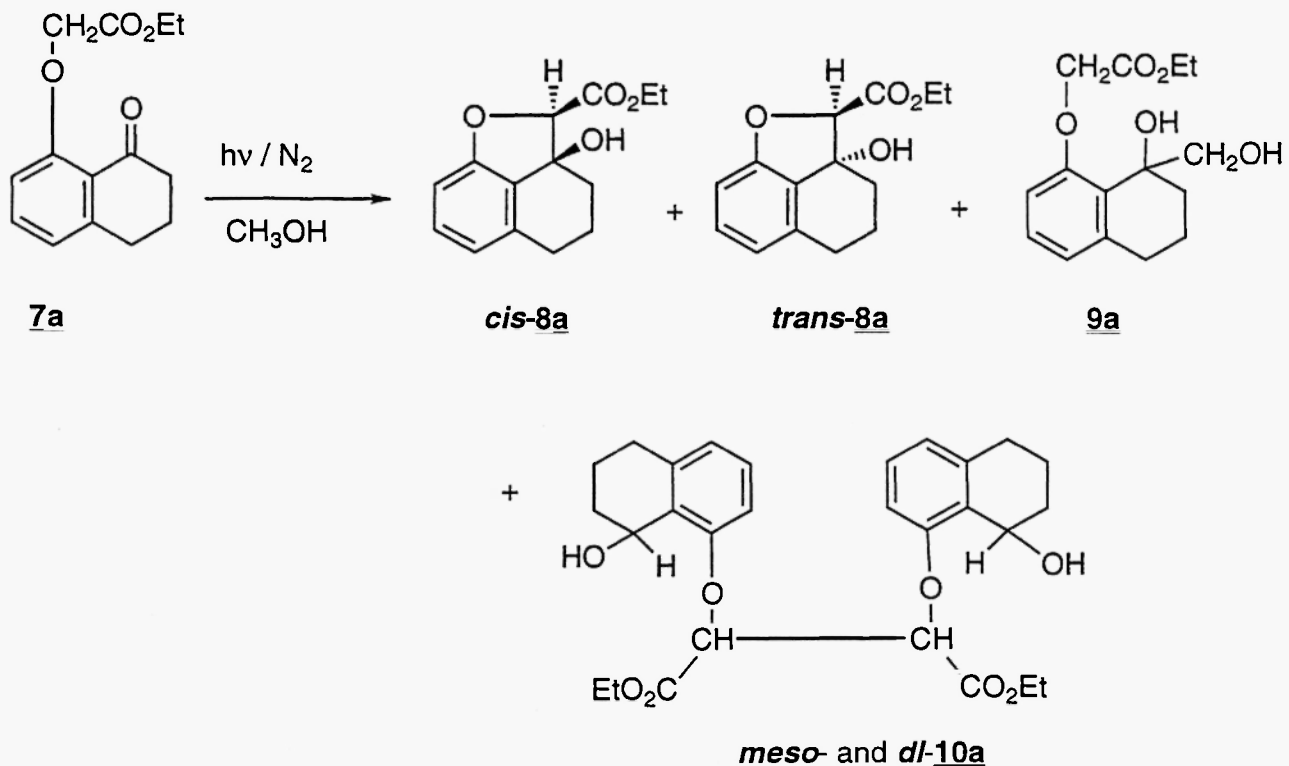
Irradiation of 6-membered ring ketone **7a** with high-pressure mercury lamp in methanol afforded *cis*- and *trans*-naphtho[1, 8-*bc*]furanol **8a** (40% *cis:trans* ratio is 2.5:1), a diastereomeric products of *meso*- and *dl*-diethyl 2, 3-bis-(5, 6, 7, 8-tetrahydro-8-hydroxy-1-naphthyloxy)succinate **10a** in 8% yield (Scheme 3, Table 1). The ratio between the two diastereoisomers was 1.2: 1. During irradiation a methanol incorporated product (dihydroxy product) **9a** was also obtained in 8% yield. The stereochemistry of the two isomers of naphtho[1, 8-*bc*]furanol **8a** was assigned by considering an anisotropic effect of the methylene group at C₃ for C₂-H in the ¹H nmr spectra. Generally, in dihydrobenzofuranol alkyl group at C₃ shield C₂-H at the *cis* position and deshield C₂-H at the *trans* position^{26, 31, 33-36}, that is, in the *cis*-isomer the chemical shift of C₂-H appears at a higher magnetic field than *trans*-isomer.

When 8-oxo-5, 6, 7, 8-tetrahydro-1-naphthyloxyacetonitrile **7b** was irradiated in methanol, *cis*-2-cyano-2a-hydroxy-2, 2a, 4, 5-tetrahydro-3-H-naphtho[1, 8-*bc*]furan **8b** was obtained in 25% yield, *cis*- and *trans*-isomer of methanol incorporated naphtho[1, 8-*bc*]furan **12b** (38%, *cis:trans* ratio = 1:1.1) and dehydrated 4, 5-dihydro-3H-naphtho[1, 8-*bc*]furan-2-carbonitrile **11b** in 3% yield (Scheme 4, Table 1). The stereochemistry of **8b** was confirmed to be *cis* by direct comparison with the *trans*-isomer obtained by independent method³¹ using anisotropic effect.

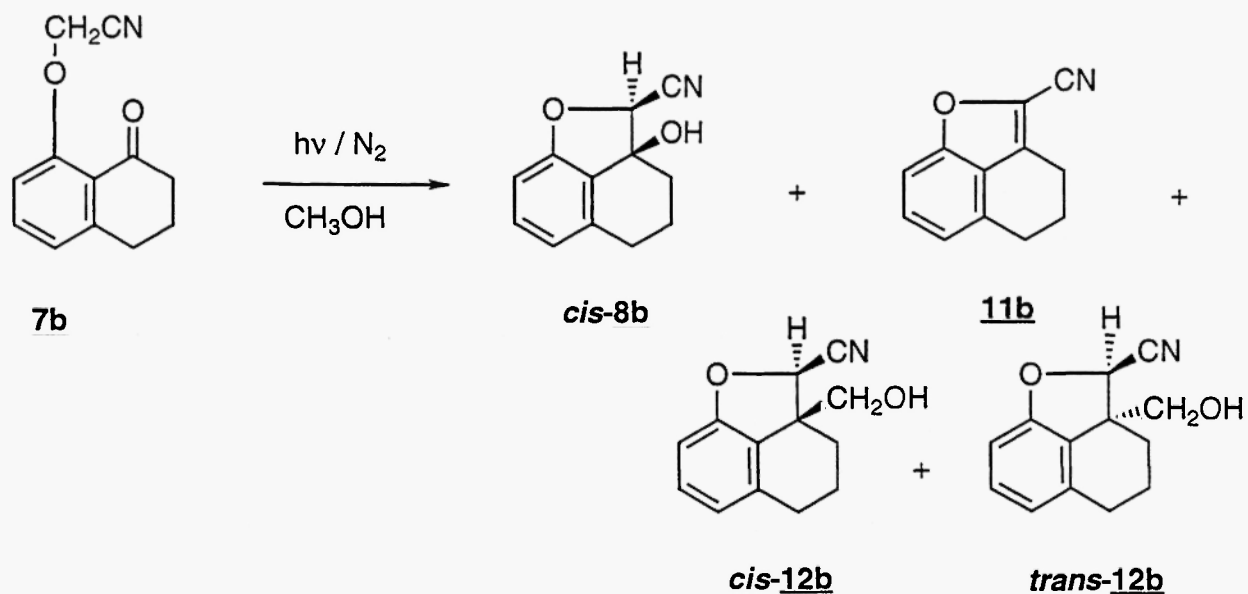
Production of methanol incorporated naphtho[1, 8-*bc*]furan **12b** was confirmed to be *via* the dehydrated naphtho[1, 8-*bc*]furan-2-carbonitrile **11b**. Irradiation of **11b** in methanol, afforded the methanol incorporated product **12b**. The ¹H nmr spectrum of the product in deuteriochloroform shows the protons signals of the methanol incorporated product of **12b** along with other small signal of unidentified compound which is difficult to be separated.

Generally, photocyclization reaction of *o*-substituted carbonyl compounds in polar protic solvent such as methanol produces a mixture of *cis*- and *trans*-isomer of furanol derivatives^{1, 16}. In contrast to this result, photocyclization reaction of **7b** in methanol produced one-isomer of *cis*-naphtho[1, 8-*bc*]furanol **8b** selectively. The *trans*-isomer of **8b** would be produced in the medium and undergo dehydration to afford **11b**. The ease of dehydration of the *trans*-isomer of **8b** than the *cis*-isomer of **8b** would be attributed to the spatial direction of the hydroxyl group with regard to the hydrogen atom. In the case of *trans*-**8b**, the hydroxyl group and the hydrogen atom are arranged at the same direction and therefore, it can be easily dehydrated to give **11b** which can undergo further photoreaction with methanol to give *cis*- and *trans*-isomer of methanol incorporated naphtho[1, 8-*bc*]furan **12b**.

Scheme 3



Scheme 4



It is noteworthy to report that, when **7a-b** was irradiated in acetonitrile³⁰⁻³¹, products such as methanol incorporated products **9a**, *cis*- and *trans*-isomers of **12b** and dimerization product **10a** were not isolated at all. The dramatic change on products distribution would be attributed to the effect of methanol (polar protic solvent) on changing reaction pathway^{1, 16}. Moreover, in the photoreaction of ethyl 2-(8-oxo-5, 6, 7, 8-tetrahydro-1-naphthyloxy)acetate **7a** and 8-oxo-5, 6, 7, 8-tetrahydro-1-naphthyloxy-acetonitrile **7b**, rearranged products *via* spirocyclization of 1, 5-biradicals^{2, 4, 30} were not observed because the biradical **13** formed is stable by push-pull resonance³⁷⁻³⁹ between the electron withdrawing group (CO₂Et or CN group in **7a** or **7b**, respectively) and the naphthyloxy oxygen atom.

From the results mentioned above, the plausible reaction pathways of photoreaction of **7** are shown in Scheme 5. Irradiation of **7** produces (n, π^*) excited triplet state **7*** after intersystem crossing process (ISC). The carbonyl group of **7*** abstracts δ -hydrogen to give 1, 5-biradicals **13**^{4, 6, 8-10}. Intramolecular cyclization of **13** affords *cis*- and *trans*-isomers of dihydrobenzofuranols **8a-b**. Production of methanol incorporated naphtho[1, 8-*bc*]furan **12b** would occur *via* the dehydrated naphtho[1, 8-*bc*]furan-2-carbonitrile **11b** and subsequent addition of a methanol molecule on the double bond of the furan ring in a nonstereoselective manner to give a mixture of *cis*- and *trans*-isomer of **12b**. Formation of the dimerization product **10a** is not clear, however, it would be formed through the 1, 5-biradical intermediate **13** followed by dimerization and hydrogen abstraction from methanol. On the other hand, the carbonyl group of **7*** abstracts hydrogen from methanol to give ketyl radicals **14**⁴⁰⁻⁵² and hydroxymethyl radical ($\cdot\text{CH}_2\text{OH}$). Intermolecular coupling of **14** with hydroxymethyl radical gives dihydroxy products **9a**.

From the above results, photocyclization reactions of 6-membered ring ketones **7a-b** are useful to prepare naphtho[1, 8-*bc*]furan derivatives. Electron withdrawing group such as ethoxycarbonyl and cyano groups suppress spirocyclization reactions of the 1, 5-biradical intermediate. Polar protic solvent like methanol can change product distribution and reaction pathways *via* intermolecular hydrogen abstraction.

Experimental :

The melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Ether refers to diethyl ether. Methanol was used after distillation. Photoreactions were carried out with 400-W high-pressure mercury lamp (Riko UVL-400 HA) with Pyrex filter. The IR spectra were determined on a Hitachi Model 270-30 IR spectrometer. The ¹H and ¹³C NMR spectra were determined at 200 MHz and 50 MHz on a Varian Gemini 200 FT NMR spectrometer, using tetramethylsilane as the internal standard.

Synthesis of Starting Materials **7a-b** :

Starting compounds **7a**³¹ and **7b**³⁰ were prepared according to Published procedures.

General Procedure for Photoreactions of **7a-b** :

A methanol 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 starting compounds almost disappeared. After irradiation the methanol 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*-8a :

Compound *cis*-8a (29%) was obtained as colorless crystals from benzene, mp 122-122.5°. The ¹H nmr and ir spectra of this compound is identical with authentic sample obtained by irradiation of 7a in acetonitrile³¹.

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

Compound *trans*-8a (11%) was obtained as colorless crystals from benzene, mp 106.5-107°. The ¹H nmr and ir spectra of this compound is identical with authentic sample obtained by irradiation of 7a in acetonitrile³¹.

Ethyl 2-[8-Hydroxy-8-hydroxymethyl-5, 6, 7, 8-tetrahydro-1-naphthyloxy]acetates 9a :

Compound 9a (8%) was obtained as colorless crystals from ethyl acetate-hexane, mp 115-116°; ir (potassium bromide): 3460 (OH) and 1750 Cm^{-1} CO_2Et ; ¹H nmr (deuteriochloroform): δ 1.32 (t, J = 7 Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.46-2.86 (m, 7H, 5-H₂, 6-H₂, 7-H₂ and OH), 3.62 (d, J = 12 Hz, 1H, CH_2OH), 3.97 (d, J = 12 Hz, 1H, CH_2OH), 4.30 (q, J = 7 Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.67 (s, 2H, OCH_2), 4.93 (s, 1H, OH), 6.61 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.80 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.24 (dd, J = 8 and 8 Hz, 1H, 3-H); ¹³C nmr (deuteriochloroform): δ 14.1 (q), 20.0 (t), 30.6 (t), 32.5 (t), 61.8 (t), 65.5 (t), 66.9 (t), 74.3 (s), 109.5 (d), 123.5 (d), 127.8 (s), 128.1 (d), 140.8 (s), 156.3 (s), 168.5 (s).

$\text{C}_{15}\text{H}_{20}\text{O}_5$ requires C, 64.29; H, 7.14. Found: C, 64.31; H, 7.14.

Meso- or *dl*-Diethyl 2, 3-bis-(5, 6, 7, 8-tetrahydro-8-hydroxy-1-naphthyloxy)succinate 10a :

These diastereoisomers 10a were obtained as colorless crystals from methanol in 16% yield and the ratio between them was 1.2:1. The first isomer had a mp = 159-160°; ir (potassium bromide): 3510 (OH) and 1750 Cm^{-1} CO_2Et ; ¹H nmr (deuteriochloroform): δ 1.28 (t, J = 7 Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.43-2.28 (m, 4H, 5-H₂ and 6-H₂), 2.62-2.96 (m, 2H, 7-H₂), 3.94-4.44 (m, 4H, $\text{CO}_2\text{CH}_2\text{CH}_3$, 8-H and OH), 5.65 (s, 1H, O-CH), 6.42 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.67 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.23 (dd, J = 8 and 8 Hz, 1H, 3-H); ¹³C nmr (deuteriochloroform): δ 14.2 (q), 20 (t), 31.1 (t), 37.3 (t), 61.3 (t), 66.4 (d), 75.6 (d), 110.2 (d), 123.7 (d), 127.2 (d), 130.3 (s), 143.0 (s), 157.1 (s), 167.9 (s).

$\text{C}_{28}\text{H}_{34}\text{O}_8$ requires C, 67.47; H, 6.83. Found: C, 67.45; H, 6.84.

The second isomer had a mp = 115-116°; ir (potassium bromide): 3510 (OH) and 1750 Cm^{-1} CO_2Et ; ¹H nmr (deuteriochloroform): δ 1.31 (t, J = 7 Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.42-2.22 (m, 4H, 5-H₂ and 6-H₂), 2.24-2.63 (m, 2H, 7-H₂), 4.01-4.40 (m, 4H, $\text{CO}_2\text{CH}_2\text{CH}_3$, 8-H and OH), 5.79 (s, 1H, O-CH), 6.36 (d, J = 8 Hz, 1H, 2-H or 4-H), 6.69 (d, J = 8 Hz, 1H, 2-H or 4-H), 7.03 (dd, J = 8 and 8 Hz, 1H, 3-H); ¹³C nmr (deuteriochloroform): δ 14.2 (q), 21.0 (t), 31.6 (t), 36.3 (t), 61.3 (t), 65.3 (d), 82.5 (d), 109.6 (d), 122.4 (d), 127.1 (d), 128.6 (s), 143.3 (s), 157.7 (s), 168.3 (s).

$\text{C}_{28}\text{H}_{34}\text{O}_8$ requires C, 67.47; H, 6.83. Found: C, 67.45; H, 6.84.

Cis-2-Cyano-2a, 3, 4, 5-tetrahydro-2H-naphtho[1, 8-bc]furan-2a-ol cis-8b :

Compound cis-8b (29%) was obtained as colorless crystals from benzene-hexane, mp 113-114°. The ¹H nmr and ir spectra of this compound is identical with authentic sample obtained by irradiation of 7a in acetonitrile ³⁰.

4, 5-Dihydro-3H-naphtho[1, 8-bc]furan-2-carbonitrile 11b :

Compound 11b (3%) was obtained as a colorless oil. The ¹H nmr and ir spectra of this compound is identical with authentic sample obtained by irradiation of 7b in acetonitrile ³⁰.

Cis-2a-hydroxymethyl-2a, 3, 4, 5-tetrahydro-2H-naphtho[1, 8-bc]furan-2-carbonitrile cis-12b :

Compound cis-12b (18%) was obtained as colorless crystals from ethyl acetate-hexane, mp 169-170°; ir (potassium bromide): 3540 Cm⁻¹ (OH); ¹H nmr (deuteriochloroform): δ 1.22-2.67 (m, 7H, 3-H₂, 4-H₂, 5-H₂ and OH), 4.45 (d, J = 2 Hz, 2H, CH₂OH), 4.80 (s, 1H, 2-H), 6.64 (d, J = 8 Hz, 1H, 6-H), 6.82 (d, J = 8 Hz, 1H, 8-H), 7.10 (dd, J = 8 and 8 Hz, 1H, 7-H); ¹³C nmr (deuteriodimethylsulfoxide): δ 20.1 (t), 30.4 (t), 35.9 (t), 53.4 (s), 81.2 (t), 81.2 (s), 110.5 (d), 116.3 (s), 123.1 (d), 127.3 (d), 128.5 (d), 142.0 (s), 156.0 (s).

C₁₃ H₁₃ NO₂ requires C, 72.56; H, 6.04; N, 6.51. Found: C, 72.53; H, 6.01; N, 6.49.

Trans-2a-hydroxymethyl-2a, 3, 4, 5-tetrahydro-2H-naphtho[1, 8-bc]furan-2-carbonitrile trans-12b :

Compound trans-12b (20%) was obtained as colorless crystals from ethyl acetate-hexane, mp 196-197°; ir (potassium bromide): 3530 Cm⁻¹ (OH); ¹H nmr (deuteriochloroform): δ 1.24-1.82 (m, 5H, 3-H₂, 4-H₂ and OH), 2.46-2.84 (m, 2H, 5-H₂), 4.80 (d, J = 2 Hz, 2H, CH₂OH), 5.23 (s, 1H, 2-H), 6.83-6.27 (m, 3H, 6-H, 7H and 8-H); ¹³C nmr (deuteriodimethylsulfoxide): δ 19.2 (t), 30.6 (t), 37.6 (t), 54.7 (s), 78.8 (t), 78.9 (s), 112.2 (d), 116.3 (s), 124.3 (d), 127.4 (d), 130.3 (d), 141.0 (s), 155.7 (s).

C₁₃ H₁₃ NO₂ requires C, 72.56; H, 6.04; N, 6.51. Found: C, 72.55; H, 6.06; N, 6.53.

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Received on September 12, 2001