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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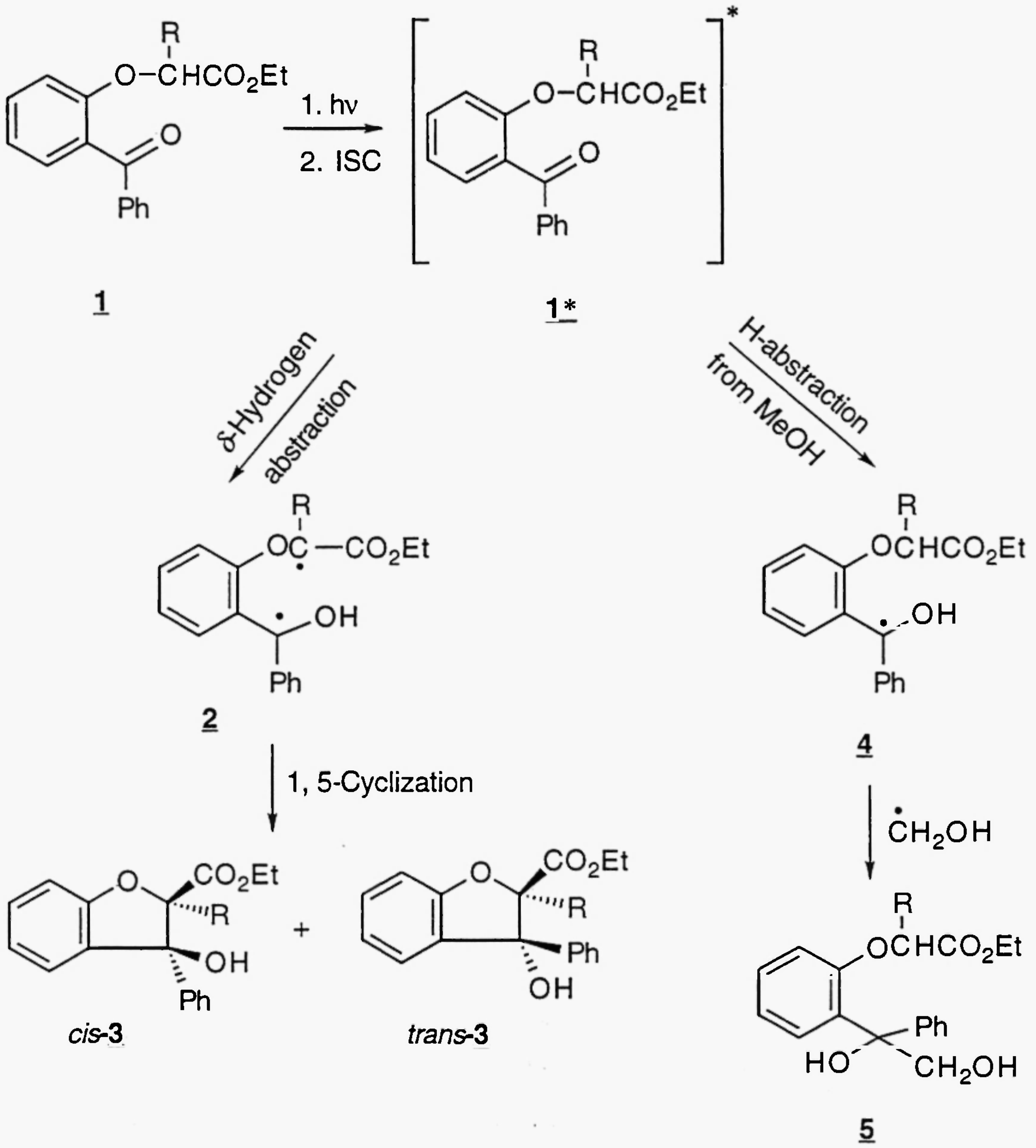
Abstract: Photocyclization reactions were carried out on ethyl 2-(8-oxo-5, 6, 7, 8-tetrahydro-1-naphthyloxy)acetate and 8-oxo-5, 6, 7, 8-tetrahydro-1-naphthyloxyacetonitrile (six-membered ring ketones) 7a-b in Methanol. Irradiation of 7a-b gave *cis-* and *trans*-naphtho[1, 8-*bc*]furanol derivatives **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 benzaldehydes [1-3], acetophenones [2-6], benzophenones [4, 6-16], α-dicarbonyl compounds [17-20], benzoquinones [21-29] or cyclic ketones [1-2, 30-32]. Among the compounds cyclic ketones have been studied from a view-point of reaction mechanisms and synthetic applications [30-31]. 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 phtochemistry 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.

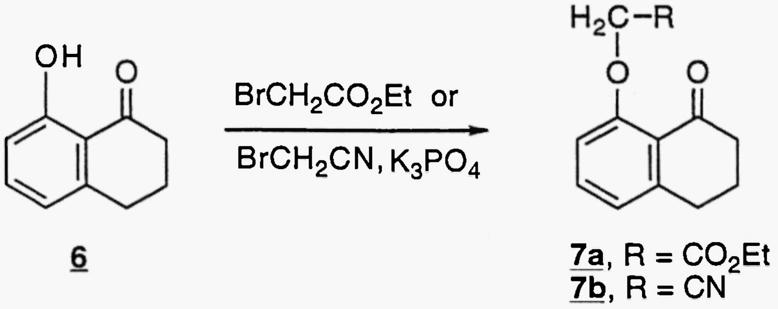
Scheme 1



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 sequnce of the reactions are outlined in Scheme 2.

Scheme 2



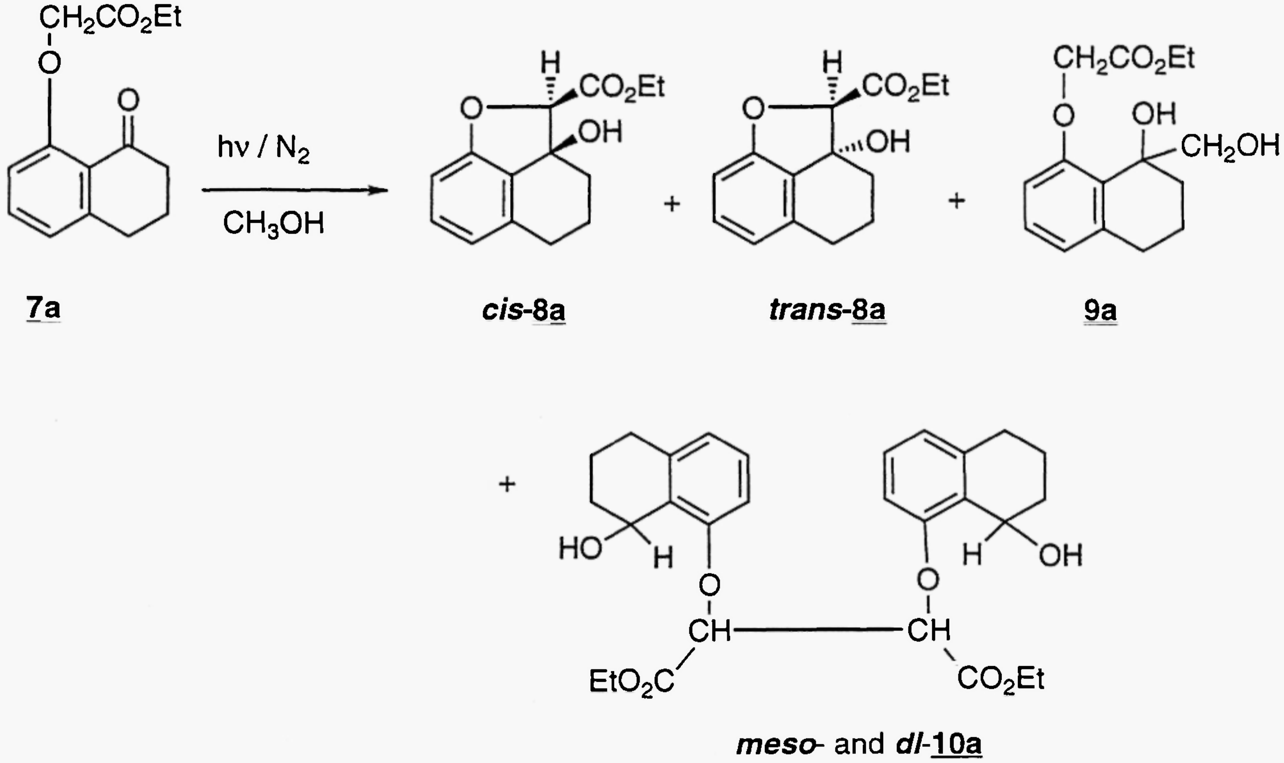
Irradiation of 6-membered ring ketone 7a with high-pressure mercury lamp in methanol afforded *cis-* and *trans-* naphtho[1, 8-*bc*]furanol 8a (40% *cis*: *trans* ratio is 2.5:1)), a diastereomeric products of *meso-* and *dl*-diethyl 2, 3-bis-(5, 6, 7, 8-tetrahydro-8-hydroxy-1-naphthyloxy)succinate 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 C_3 for C_2-H in the ^{1}H nmr spectra. Generally, in dihydrobenzofuranol alkyl group at C_3 shield C_2-H at the *cis* position and deshield C_2-H at the *trans* position [26, 31, 33-36], that is, in the *cis*-isomer the chemical shift of C_2-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 naptho[1, 8-*bc*]furan 12b (38%, *cis*:*trans* ratio = 1:1.1) and dehydrated 4, 5-dihydro-3*H*-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 method [31] using anisotropic effect.

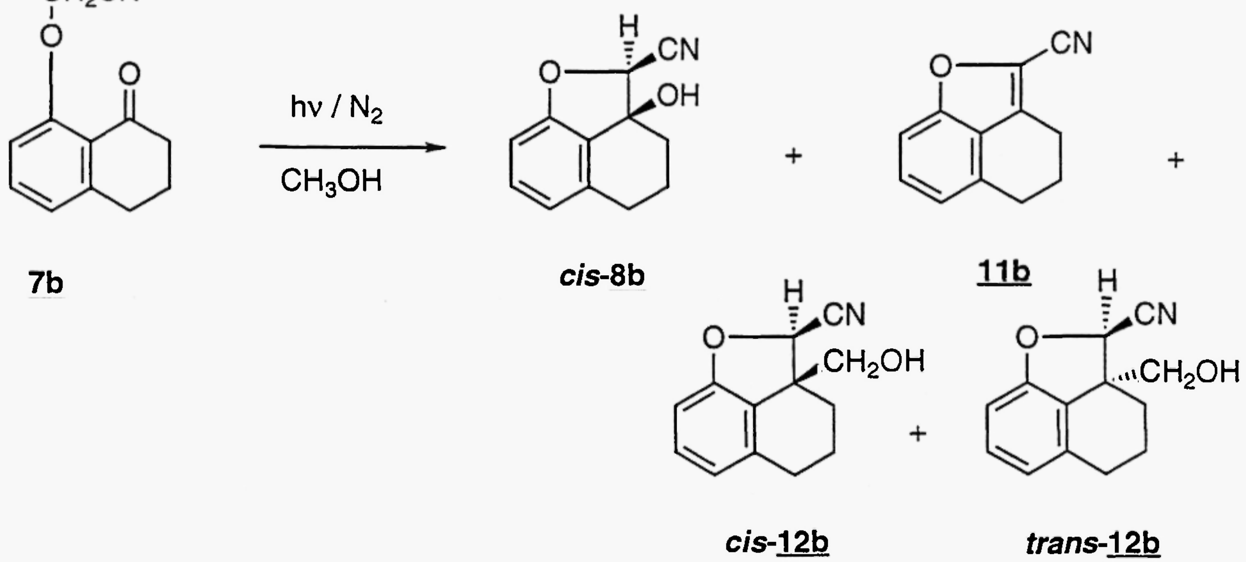
Production of methanol incorporated naptho[1, 8-*bc*]furan 12b was confirmed to be *via* the dehydrated naphtho[1, 8-*bc*]furan-2-carbonitrile 11b. Irradiation of 11b in methanol, afforded the methanol incorporated product 12b. The ^{1}H nmr spectrum of the product in deuteriochloroform shows the protons 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 naptho[1, 8-*bc*]furan 12b.

Scheme 3



Scheme 4



It is noteworthy to report that, when 7a-b was irradiated in acetonitrile [30-31], 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 resonance [37-39] between the electron withdrawing group (CO_2Et or CN group in 7a or 7b, respectively) and the naphthyloxy oxygen atom.

From the results mentioned above, the plausible reaction pathways of photorection 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 naptho[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 ($^{\bullet}CH_2OH$). 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 supress 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 choromatography 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 ^{13}C 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 ^{1}H nmr and ir spectra of this compound is identical with authentic sample obtained by irradiation of 7a in acetonitrile [31].

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 ^{1}H nmr and ir spectra of this compound is identical with authentic sample obtained by irradiation of 7a in acetonitrile [31].

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; ^{1}H nmr (deuteriochloroform): δ 1.32 (t, J = 7 Hz, 3H, $CO_2CH_2\mathit{CH_3}$), 1.46-2.86 (m, 7H, 5-H_2, 6-H_2, 7-H_2 and OH), 3.62 (d, J = 12 Hz, 1H, $\mathit{CH_2}OH$), 3.97 (d, J = 12 Hz, 1H, $\mathit{CH_2}OH$), 4.30 (q, J = 7 Hz, 2H, $CO_2\mathit{CH_2}CH_3$), 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); ^{13}C 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).

$C_{15}H_{20}O_5$ 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; ^{1}H nmr (deuteriochloroform): δ 1.28 (t, J = 7 Hz, 3H, $CO_2CH_2\mathit{CH_3}$), 1.43-2.28 (m, 4H, 5-H_2 and 6-H_2), 2.62-2.96 (m, 2H, 7-H_2), 3.94-4.44 (m, 4H, $CO_2\mathit{CH_2}CH_3$, 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); ^{13}C 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).

$C_{28}H_{34}O_8$ 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; ^{1}H nmr (deuteriochloroform): δ 1.31 (t, J = 7 Hz, 3H, $CO_2CH_2\mathit{CH_3}$), 1.42-2.22 (m, 4H, 5-H_2 and 6-H_2), 2.24-2.63 (m, 2H, 7-H_2), 4.01-4.40 (m, 4H, $CO_2\mathit{CH_2}CH_3$, 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); ^{13}C 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).

$C_{28}H_{34}O_8$ requires C, 67.47; H, 6.83. Found: C, 67.45; H, 6.84.

Cis-2-Cyano-2a, 3, 4, 5-tetrahydro-2*H*-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 ^{1}H nmr and ir spectra of this compound is identical with authentic sample obtained by irradiation of **7a** in acetonitrile ^{30}.

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

Compound **11b** (3%) was obtained as a colorless oil. The ^{1}H 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-2*H*-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); ^{1}H nmr (deuteriochloroform): δ 1.22-2.67 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$ and OH), 4.45 (d, J = 2 Hz, 2H, C*H2*OH), 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); ^{13}C 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).

$C_{13}H_{13}NO_2$ 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-2*H*-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); ^{1}H nmr (deuteriochloroform): δ 1.24-1.82 (m, 5H, 3-H$_2$, 4-H$_2$ and OH), 2.46-2.84 (m, 2H, 5-H$_2$), 4.80 (d, J = 2 Hz, 2H, C*H2*OH), 5.23 (s, 1H, 2-H), 6.83-6.27 (m, 3H, 6-H, 7H and 8-H); ^{13}C 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).

$C_{13}H_{13}NO_2$ requires C, 72.56; H, 6.04; N, 6.51. Found: C, 72.55; H, 6.06; N, 6.53.

References :

(1) E. M. Sharshira and T. Horaguchi, *J. Heterocyclic Chem.*, 34, 1837 (1997).
(2) T. Horaguchi, C. Tsukada, E. Hasegawa, T. Shimizu, T. Suzuki and K. Tanemura, *J. Heterocyclic Chem.*, **28**, 1261 (1991).
(3) T. Horaguchi, C. Tsukada, E. Hasegawa, T. Shimizu, T. Suzuki and K. Tanemura, *J. Heterocyclic Chem.*, **28**, 1273 (1991).
(4) P. J. Wagner, M. A. Meador and J. C. Scaiano, *J. Am. Chem. Soc.*, **106**, 7988 (1984).
(5) G. A. Kraus, P. J. Thomas and M. D. Schwinden, *Tetrahedron Letters*, **31**, 1819 (1990).
(6) P. J. Wagner, M. A. Meador and B. -S. Park, *J. Am. Chem. Soc.*, **112**, 5199 (1990).
(7) P. J. Wagner and J. S. Jang, *J. Am. Chem. Soc.*, **115**, 7914 (1993).
(8) G. R. Lappin and J. S. Zannucci, *J. Chem. Soc.*, 1113 (1969).
(9) G. R. Lappin and J. S. Zannucci, *J. Org. Chem.*, 36, 1808 (1971).
(10) M. A. Meador and P. J. Wagner, *J. Org. Chem.*, **50**, 419 (1985).
(11) P. J. Wagner, M. A. Meador, B. P. Giri and J. C. Scaiano, *J. Am. Chem. Soc.*, 107, 1087 (1985).
(12) P. J. Wagner, *Acc. Chem. Res.*, **22**, 83 (1989).

(13) T. Sumathi and Balasubramanian, *Tetrahedron Letters*, **31**, 3775 (1990).
(14) P. J. Wagner and G. Laidig, *Tetrahedron Letters*, **32**, 895 (1991).
(15) M. A. Aziz, J. V. Auping and M. A. Meador, *J. Org. Chem.*, 60, 1303 (1995).
(16) E. M. Sharshira, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, 34, 861, (1997).
(17) S. P. Pappas, B. C. pappas and J. E. Blackwell, Jr., *J. Org. Chem.*, **32**, 3066 (1997).
(18) S. P. Pappas, J. E. Alexander and R. D. Zehr, *J. Am. Chem. Soc.*, **92**, 6927 (1970).
(19) S. P. Pappas and R. D. Zehr, *J. Am. Chem. Soc.*, 93, 7112 (1971).
(20) P. J. Wagner, P. Kelso, A. E. kemppainen and R. G. Zepp, *J. Am. Chem. Soc.*, 94, 7500 (1972).
(21) C. M. Orlando and Jr., H. Mark, *Tetrahedron Letters*, 3003, (1966).
(22) C. M. Orlando, Jr., H. Mark, A. k. Bose and M. S. Manhas, *J. Am. Chem. Soc.*, 89, 6527, (1967).
(23) C. M. Orlando, Jr., H. Mark, A. k. Bose and M. S. Manhas, *J. Org. Chem.*, **33**, 2512 (1968).
(24) J. M. Bruce and D. Creed, *J. Chem. Soc., C*, 649 (1970).
(25) J. M. Bruce, D. Creed and K. dawes, *J. Chem., Soc., C*, 2244 (1971).
(26) T. Kozuka, *Bull. Chem. Soc. Japan*, **25**, 2415 (1982).
(27) K. Maruyama, H. Iwamoto, O. Soga and A. Takuwa, *Chem. Letters*, 1343 (1984).
(28) K. Maruyama, H. Iwamoto, O. Soga and A. Takuwa, *Chem. Letters*, 1675 (1985).
(29) H. Iwamoto, *J. Org. Chem.*, **53**, 1507 (1988).
(30) E. M. Sharshira, H. Iwanami, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, **33**, 17 (1996).
(31) E. M. Sharshira, H. Iwanami, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, **33**, 137 (1996).
(32) M. Yoshioka, H. Arai, K. Ichikawa and T. Hessegawa, *J. Chem. Soc. Chem. Commun.*, 848 (1988).
(33) E. C. Hayward, D. S. Tarbell and L. D. Calebrook, *J. Org. Chem.*, **33**, 399 (1968).
(34) M. P. Mertes and L. J. Powers, *J. Org. Chem.*, 36, 1805 (1971).
(35) W. D. Crow, U. E. -Low and Y. T. Pang, *Aust. J. Chem.*, **37**, 1915 (1984).
(36) T. Suzuki, *Bull. Chem. Soc. Japan*, **58**, 2821 (1985).
(37) L. Stella, Z. Janousek, R. Merenyi, H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, 17, 691 (1978).
(38) H. G. Viehe, R. Merenyi, L. Stella and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, **18**, 917 (1979).
(39) R. W. Baldock, P. Hudson, A. R. Katritzky and F. Soti, *J. Chem. Soc. Perkin Trans. 1*, 1422 (1974).
(40) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).
(41) J. N. Pitts, Jr., H. W. Johnson, Jr. and T. Kuwana, *J. Phys. Chem.*, 66, 2456 (1962).
(42) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959).
(43) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961).
(44) W. M. Moore, G. S. Hammond And R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).
(45) G. S. Hammond, W. P. Baker and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).
(46) A. Beckett and G. Porter, *Trans. Farady Soc.*, **59**, 2051 (1963).
(47) A. Padwa, Tetrahedron Letters, 3465 (1964).
(48) S. G. Cohen and M. N. Siddigui, *J. Am. Chem. Soc.*, 86, 5047 (1964).
(49) C. Walling and M. j. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).
(50) J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966).
(51) P. J. Wagner, R, J. Truman and J. C. Scaiano, *J. Am. Chem. Soc.*, **107**, 7093 (1985).
(52) P. J. Wagner, R, J. Truman, A. E. Puchalski and R. Wake, *J. Am. Chem. Soc.*, **108**, 7727 (1986).

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