A New Method for Preparation of 3-Hydroxypyridines from Furfurylamines by Photooxygenation

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Low-temperature photooxygenation (−70 °C) of furfurylamine derivatives followed by treatment with triphenylphosphine provided 3-hydroxypyridines in high yield.

Keywords furfurylamine; photooxygenation; 3-hydroxypyridine

There are many methods available for the preparation of 3-hydroxypyridines. The methods of formation of 3-hydroxypyridines by heating 2-acetylfurans[1] or 2-furoic acid derivatives[2] with ammonia give low yields. The reaction of the naturally occurring maltol glucoside with a wide variety of primary amines gives pyridiones which upon hydrolysis, yield the corresponding 3-hydroxypyridines.[3] Transformation of carbohydrates to 3-hydroxypyridines has also been reported.[4] As to the formation of 3-hydroxypyridines from aminofurans, drastic conditions are required.[5]

Photooxygenation of furans has been studied extensively from mechanistic and synthetic viewpoints.[6] Oxidative ring opening of furans leading to enediones is an important synthetic operation, since furans can be used as a masked 1,4-dicarbonyl unit.[7] Recently, Saito *et al.*[8] reported that low-temperature photooxygenation of furans followed by reduction with dimethyl sulfide stereospecifically provided *cis*-enediones, which, on subsequent treatment with trimethylsilyl cyanide, afforded 2-cyano-5-hydroxy-2,5-dihydrofurans, the latter compounds being important precursors of 4-cyanobutenolides. In the case of 2-furfuryl alcohols, the oxidation with singlet oxygen then reduction with triphenylphosphine (Ph_3P) gave the corresponding *cis*-enediones which spontaneously cyclized to afford 6-hydroxy-2*H*-pyran-3-(6*H*)-ones.[9] In this paper we wish to describe a novel and useful method to convert furfurylamines (**1**) into 3-hydroxypyridines (**2**) in high yieldes. Furfurylamine (**1**) reacted with singlet oxygen at low temperature, and the intermediate ozonides were reduced with Ph_3P to give the corresponding enediones, which underwent spontaneous condensation of the amino and carbonyl groups to yield the α-amino alcohols, which in turn afforded 3-hydroxypyridines (**2**) after dehydration and tautomerization (Chart 1).

A typical experimental procedure was as follows. A furfurylamine (**1**) and tetraphenylporphine (TPP) were dissolved in dry CH_2Cl_2. The solution was irradiated externally with a tungsten bromine lamp at −70 °C under oxygen bubbling. After 2 h, excess Ph_3P in dry CH_2Cl_2 was added to the reaction mixture, which was allowed to warm to ambient temperature after 20 min. The products were purified by neutral alumina column chromatography to afforded 3-hydroxyridines (**2**) in high yields (Table I).

TABLE I. Transformation of Furfurylamines to 3-Hydroxypyridines[a]

Entry	Furfurylamine	3-Hydroxypyridine	Yield (%)[b]
1	**1a**	**2a**	86[c]
2	**1b**	**2b**	80
3	**1c**	**2c**	83
4	**1d**	**2d**	82[c]
5	**1e**	**2e**	83
6	**1f**	**2f**	82
7	**1g**	**2g**	85
8	**1h**	**2h**	84
9	**1i**	**2i**	87

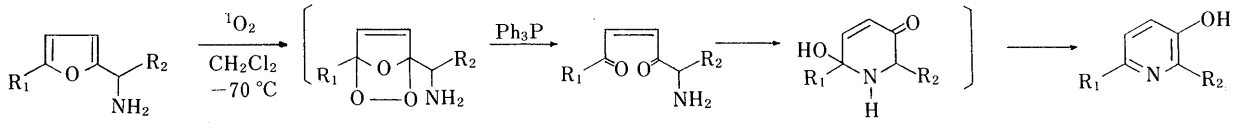
a) Experimental procedures are described in the text. *b*) Yields given are for isolated products. *c*) The product was identical with a commercial product.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were run neat or as a KBr disc on a Perkin-Elmer 983G instrument. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were run on a Varian EM-390 (90 MHz) and Bruker AM-300 (300 MHz) spectrometers in the indicated solvents. Chemical shifts and coupling constants (*J*) were measured in ppm (δ) and hertz (Hz) with respect to tetramethylsilane (TMS). The electron impact mass spectra (EI MS) were obtained on a JEOL model JMS-DX 300 double focusing mass spectrometer.

Materials Alkylfurans (R = H, Me or Et) acylated at C-5 were obtained by Vilsmeier method[10] or by reaction with acetic or propionic anhydride, with ferric chloride as a catalyst (Chart 2). The acylfurans (**3**) thus obtained reacted with hydroxyamine to give the oximes (**4**), whose reduction with Raney Ni alloy in ethanolic NaOH solution (Chart 2) afforded the furfurylamines (**1**). Details of these reactions are given below. Compounds **3b**, **3d**, **3f**, and **1a** are commercially available.

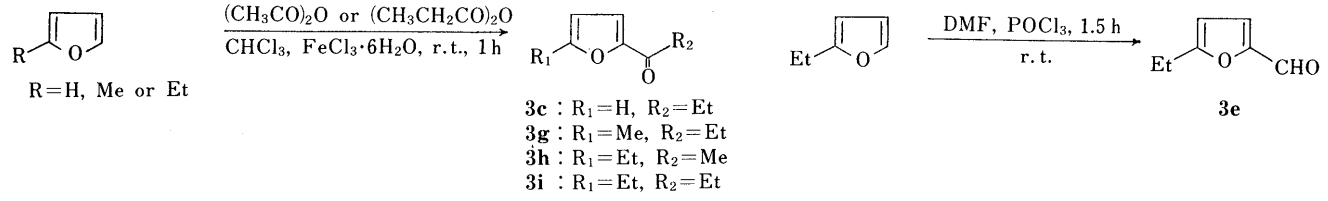
General Procedure for Photooxidation of Furfurylamine A furfurylamine (**1**) (200 mg) and TPP (3 mg) were dissolved in CH_2Cl_2 (15 ml). The solution was irradiated with a 650 W tungsten bromine lamp at −70 °C for 2 h while oxygen was passed through the solution. Then 700 mg of triphenylphosphine in 2 ml of CH_2Cl_2 was added at the same temperature. After 10 min, the reaction mixture was taken out of the dry ice–acetone

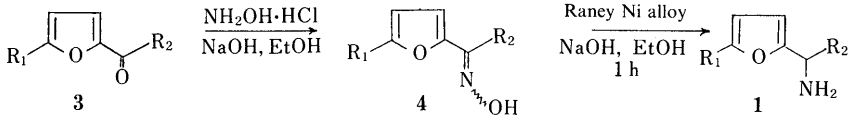


1 2

a : R_1=R_2=H **d** : R_1=Me, R_2=H **g** : R_1=Me, R_2=Et
b : R_1=H, R_2=Me **e** : R_1=Et, R_2=H **h** : R_1=Et, R_2=Me
c : R_1=H, R_2=Et **f** : R_1=R_2=Me **i** : R_1=R_2=Et

Chart 1





a : $R_1=R_2=H$
b : $R_1=H$, $R_2=Me$
c : $R_1=H$, $R_2=Et$
d : $R_1=Me$, $R_2=H$
e : $R_1=Et$, $R_2=H$
f : $R_1=R_2=Me$
g : $R_1=Me$, $R_2=Et$
h : $R_1=Et$, $R_2=Me$
i : $R_1=R_2=Et$

Chart 2

solution bath. The product was purified by neutral alumina chromatography to afford the corresponding 3-hydroxypyridine (**2**) in excellent yield (Table I). Physical data of products **2a**—**2i** are give below.

2a: mp 124—126 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1606, 1568, 1278, 1241, 1020, 842, 702, 639. MS *m/z* (%): 96 ($M^+ + 1$, 5), 95 (M^+, 100), 68 (12), 67 (14), 66 (6), 55 (5), 41 (22). ^{1}H-NMR (CD_3COCD_3) δ: 7.22 (2H, m), 8.08 (1H, t, $J=3.0$ Hz), 8.23 (1H, t, $J=1.5$ Hz).

2b: mp 128—130 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1600, 1574, 1285, 1182, 1130, 797, 761. MS *m/z* (%): 110 ($M^+ + 1$, 5), 109 (M^+, 100), 81 (33), 80 (77), 54 (9), 53 (16), 42 (11). ^{1}H-NMR (CD_3COCD_3) δ: 2.36 (3H, s), 6.98 (1H, dd, $J=7.5$, 4.5 Hz), 7.13 (1H, dd, $J=7.5$, 2.0 Hz), 7.95 (1H, dd, $J=4.5$, 2.0 Hz).

2c: IR ν_{max}^{neat} cm^{-1}: 3000—2400, 1574, 1449, 1285, 1167, 1119, 723, 694. MS *m/z* (%): 124 ($M^+ + 1$, 3), 123 (M^+, 59), 122 (100), 104 (8), 95 (10), 80 (12), 73 (11), 71 (14), 67 (20), 57 (19), 58 (25), 55 (32), 43 (28). ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, t, $J=7.0$ Hz), 2.95 (2H, q, $J=7.0$ Hz), 4.50 (1H, br s, –OH), 6.96 (1H, dd, $J=7.5$, 4.5 Hz), 7.15 (1H, dd, $J=7.5$, 1.5 Hz), 8.02 (1H, dd, $J=4.5$, 1.5 Hz).

2d: mp 169—170 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1613, 1569, 1497, 1275, 1221, 827, 655. MS *m/z* (%): 110 ($M^+ + 1$, 8), 109 (M^+, 100), 108 (17), 82 (4), 81 (17), 80 (63), 54 (17), 53 (23), 51 (12), 42 (7). ^{1}H-NMR (CD_3COCD_3) δ: 2.42 (3H, br s), 7.15, 7.28 (each 1H, d, $J=8.0$ Hz), 8.22 (1H, br s), 9.05 (1H, br s, –OH).

2e: mp 102—104 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1566, 1494, 1350, 1275, 1031, 919, 827, 653. MS *m/z* (%): 124 ($M^+ + 1$, 5), 123 (M^+, 58), 122 (100), 108 (8), 95 (14), 80 (3), 67 (7), 53 (9). ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, t, $J=7.0$ Hz), 2.78 (2H, q, $J=7.0$ Hz), 7.10 (1H, d, $J=8.0$ Hz), 7.30 (1H, dd, $J=8.0$, 2.5 Hz), 8.27 (1H, d, $J=2.5$ Hz), 9.00 (1H, br s, –OH).

2f: mp 122—124 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1575, 1494, 1380, 1282, 1126, 829, 793, 711. MS *m/z* (%): 124 ($M^+ + 1$, 35), 123 (M^+, 100), 122 (22), 108 (4), 93 (19), 94 (72), 82 (98), 81 (14), 80 (13), 53 (19), 42 (17). ^{1}H-NMR (CD_3COCD_3) δ: 2.31, 2.35 (each 3H, s), 6.83, 7.03 (each 1H, d, $J=8.0$ Hz).

2g: mp 136—138 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1574, 1492, 1369, 1268, 1162, 1129, 825, 810, 769, 705. MS *m/z* (%): 138 ($M^+ + 1$, 11), 137 (M^+, 67), 136 (100), 122 (6), 94 (5), 81 (7), 80 (8), 53 (13). ^{1}H-NMR (CD_3COCD_3) δ: 1.20 (3H, t, $J=7.0$ Hz), 2.32 (3H, s), 2.77 (2H, q, $J=7.0$ Hz), 6.86, 7.08 (each 1H, d, $J=8.0$ Hz).

2h: mp 115—117 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1573, 1499, 1338, 1279, 832, 699. MS *m/z* (%): 138 ($M^+ + 1$, 21), 137 (M^+, 78), 136 (100), 122 (14), 118 (7), 94 (6), 81 (9), 80 (10), 53 (20). ^{1}H-NMR (CD_3COCD_3) δ: 1.20 (3H, t, $J=7.0$ Hz), 2.40 (3H, s), 2.63 (2H, q, $J=7.0$ Hz), 6.84, 7.07 (each 1H, d, $J=7.0$ Hz).

2i: mp 131—133 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2400, 1600, 1568, 1491, 1430, 1352, 1283, 1128, 833, 760. MS *m/z* (%): 152 (4), 151 (M^+, 50), 150 (100), 136 (6), 135 (12), 123 (8), 108 (6), 80 (5), 67 (4), 65 (4), 55 (4), 52 (5). ^{1}H-NMR (CD_3COCD_3) δ: 1.20 (6H, t, $J=7.0$ Hz), 2.67, 2.80 (each 2H, q, $J=7.0$ Hz), 6.91, 7.15 (each 1H, d, $J=8.0$ Hz).

Preparation of 3c by Propionylation of Furan Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 0.04 g) was added to a solution of furan (1 g) in 15 ml of $CHCl_3$ and propionic anhydride (3.0 g), then the reaction mixture was stirred at room temperature for 2 h. Saturated ethylenediaminetetraacetate (EDTA) was added to the reaction mixture to remove the ferric ion, and the whole was washed with 2 N aqueous NaOH solution. The organic layer was dried with $CaCl_2$ and concentrated. Chromatography of the residue on silica gel gave compound **3c** (0.55 g).

Preparation of 3g, 3h, and 3i by Acetylation or Propionylation of 2-Methyl- or 2-Ethylfuran Acetic anhydride (or propionyl anhydride, 3.5 g) was added to a solution of 2-methyl- or 2-ethylfuran (1 g) in 30 ml of 1,2-dichloroethane. Then $FeCl_3 \cdot 6H_2O$ (0.08 g) was added, and the reaction mixture which was heated under reflux for 1 h. Work up as mentioned above gave **3g**, **3h** or **3i** (35—40% yield).

Preparation of 3e by Vilsmeier's Method $POCl_3$ (1.8 ml) was added dropwise to a mixture of 2-ethylfuran (2 g) and dimethylformamide (DMF 1.8 g) at 0—5 °C, and the reaction mixture was allowed to stand at room temperature for 1.5 h. Then the mixture was poured into ice water, neutralized with NaOAc, and extracted with ether. The extract was purified on silica gel chromatography to give **3e** (0.95 g).

3c: IR ν_{max}^{neat} cm^{-1}: 3130, 1673, 1564, 1465, 1391, 1248, 1163, 1091, 1076, 1032, 882, 762. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, t, $J=7.5$ Hz), 2.86 (2H, q, $J=7.5$ Hz), 6.46 (1H, dd, $J=3.5$, 1.5 Hz), 7.20 (1H, d, $J=3.5$ Hz), 7.58 (1H, d, $J=1.5$ Hz).

3e: IR ν_{max}^{neat} cm^{-1}: 3117, 1674, 1569, 1515, 1396, 1321, 1023, 961, 806, 766. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, t, $J=7.7$ Hz), 2.60 (2H, q, $J=7.7$ Hz), 6.16, 7.10 (1H, d, $J=3.5$ Hz), 9.40 (1H, s).

3g: IR ν_{max}^{neat} cm^{-1}: 3115, 1670, 1584, 1510, 1349, 1204, 1035, 903, 797. ^{1}H-NMR ($CDCl_3$) δ: 1.15 (3H, t, $J=7.5$ Hz), 2.39 (3H, s), 2.77 (2H, q, $J=7.5$ Hz), 6.17, 7.07 (each 1H, d, $J=3.0$ Hz).

3h: IR ν_{max}^{neat} cm^{-1}: 3117, 1670, 1584, 1511, 1355, 1297, 1206, 1109, 1015, 923, 802. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, $J=7.6$ Hz), 2.40 (3H, s), 2.70 (2H, q, $J=7.6$ Hz), 6.12, 7.07 (each 1H, d, $J=3.4$ Hz).

3i: IR ν_{max}^{neat} cm^{-1}: 3115, 1670, 1584, 1510, 1320, 1204, 1013, 903, 797. ^{1}H-NMR ($CDCl_3$) δ: 1.19, 1.30 (each 3H, t, $J=7.5$ Hz), 2.72, 2.82 (each 2H, q, $J=7.5$ Hz), 6.15, 7.10 (each 1H, $J=3.0$ Hz).

The Oximes (4b—4i) from the Acylfurans (3b—3i) An acylfuran (**3**) (1.0 g), $H_2NOH \cdot HCl$ (1.01 g), and NaOH (1.82 g) were dissolved in a mixture of 10 ml of ethanol and 2 ml of H_2O. The reaction mixture was refluxed for 20 min. The reaction mixture was acidified with 2 N HCl, and extracted with ether. The ether extract was purified to give the corresponding oxime (**4**) (75—82%).

4b: mp 41—42 °C. IR ν_{max}^{KBr} cm^{-1}: 3204, 1576, 1489, 1310, 1162, 1003, 947, 896, 826, 740. MS *m/z* (%): 126 ($M^+ + 1$, 10), 125 (M^+, 100), 108 (11), 93 (15), 84 (10), 68 (63), 65 (23), 55 (17), 53 (16). ^{1}H-NMR ($CDCl_3$) δ: 2.19 (3H, s), 6.40 (1H, dd, $J=3.4$, 1.8 Hz), 6.60 (1H, d, $J=3.4$ Hz), 7.40 (1H, d, $J=1.8$ Hz), 9.56 (1H, br s, –OH).

4c: mp 65—68 °C (*cis*+*trans*). IR ν_{max}^{KBr} cm^{-1}: 3255, 3120, 1649, 1411, 1206, 1108, 1068, 988, 952, 988, 952. MS *m/z* (%): 140 ($M^+ + 1$, 23), 139 (M^+, 100), 122 (41), 107 (27), 93 (32), 94 (78), 93 (55), 81 (40), 79 (27), 68 (35), 55 (24). ^{1}H-NMR ($CDCl_3$) δ: 1.27 (3H, t, $J=7.5$ Hz), 2.70 (2H, q, $J=7.5$ Hz), 6.55 (1H, dd, $J=3.0$, 1.5 Hz), 749 (1H, d, $J=1.5$ Hz), 7.52 (1H, d, $J=3.0$ Hz), 8.80 (1H, br s, –OH). One isomer: ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, t, $J=7.5$ Hz), 2.80 (2H, q, $J=7.5$ Hz), 6.67 (1H, d,

J=3.0, 1.5 Hz), 7.18 (1H, d, J=3.0 Hz), 7.57 (1H, d, J=1.5 Hz), 8.80 (1H, br s, –OH).

4d: mp 81—83 °C. IR ν_{max}^{KBr} cm^{-1}: 3174, 3023, 1637, 1586, 1517, 1310, 1208, 1024, 964, 894, 802. MS m/z (%): 126 (M^++1, 7), 125 (M^+, 100), 108 (10), 82 (46), 81 (17), 79 (12), 52 (92), 51 (28), 43 (22), ^{1}H-NMR ($CDCl_3$) δ: 2.32 (3H, s), 6.14, 7.13 (each 1H, d, J=3.0 Hz), 7.44 (1H, s), 9.50 (1H, br s, –OH).

4e: mp 83—85 °C (*cis*+*trans*). IR ν_{max}^{KBr} cm^{-1}: 3201, 1641, 1583, 1521, 1327, 1185, 983, 833. MS m/z (%): 140 (M^++1, 4), 139 (M^+, 71), 124 (100), 79 (13), 69 (9), 67 (13), 65 (15), 50 (12), 51 (18). ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, t, J=7.5 Hz), 2.63 (2H, q, J=7.5 Hz), 6.01, 6.46 (each 1H, d, J=3.0 Hz), 7.90 (1H, s), 9.50 (1H, br s, –OH). One isomer: ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, t, J=7.5 Hz), 2.63 (2H, q, J=7.5 Hz), 6.08, 7.20 (1H, d, J=3.0 Hz), 7.40 (1H, s), 9.50 (2H, br s, –OH).

4f: mp 48—50 °C (*cis*+*trans*). IR ν_{max}^{KBr} cm^{-1}: 3254, 1623, 1592, 1543, 1374, 1221, 1208, 1018, 964, 787, 742. MS m/z (%): 140 (M^++1, 8), 139 (M^+, 88), 122 (14), 107 (8), 82 (36), 81 (13), 53 (100), 52 (21), 43 (19). ^{1}H-NMR ($CDCl_3$) δ: 2.15, 2.30 (each 3H, s), 5.99, 6.47 (each 1H, d, J=3 Hz). One isomer: ^{1}H-NMR ($CDCl_3$) δ: 2.15, 2.30 (each 3H, s), 6.10 and 7.33 (each 1H, d, J=3.3 Hz).

4g: mp 50—52 °C (*cis*+*trans*). IRν_{max}^{KBr} cm^{-1}: 3247, 3140, 1644, 1619, 1587, 1520, 1207, 1112, 1026, 997, 948, 885, 792. MS m/z (%): 154 (M^++1, 9), 153 (M^+, 100), 136 (17), 109 (22), 108 (25), 107 (20), 96 (17), 82 (36), 53 (62), 43 (28). ^{1}H-NMR ($CDCl_3$) δ: 1.28 (3H, t, J=7.5 Hz), 2.30 (3H, s), 2.72 (2H, q, J=7.5 Hz), 6.15, 7.43 (each 1H, d, J=3.0 Hz). One isomer: ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, t, J=7.5 Hz), 2.30 (3H, s), 2.70 (2H, q, J=7.5 Hz), 6.01, 6.55 (each 1H, d, J=3.0 Hz).

4h (*cis*+*trans*): IR ν_{max}^{neat} cm^{-1}: 3225, 3170, 1624, 1588, 1522, 1378, 1322, 1202, 1119, 1013, 982, 963, 901, 797, 742. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, J=7.0 Hz), 2.17 (3H, s), 2.68 (2H, q, J=7.0 Hz), 6.02, 6.50 (each 1H, d, J=3.5 Hz), One isomer: ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, J=7.0 Hz), 2.23 (3H, s), 2.68 (2H, q, J=7.0 Hz), 6.14, 7.37 (each 1H, d, J=3.5 Hz).

4i (*cis*+*trans*): IR ν_{max}^{KBr} cm^{-1}: 3238, 1622, 1587, 1520, 1320, 1201, 1018, 983, 938, 796. MS m/z (%): 168 (M^++1, 22), 167 (M^+, 100), 152 (37), 150 (16), 135 (11), 112 (12), 106 (12), 97 (19), 96 (16), 79 (13), 67 (17), 65 (13). ^{1}H-NMR ($CDCl_3$) δ: 1.20 (6H, m), 2.65 (4H, q, J=7.8 Hz), 6.02, 6.50 (each 1H, d, J=3.0 Hz). One isomer: ^{1}H-NMR ($CDCl_3$) δ: 1.20 (6H, m), 2.65 (4H, q, J=7.8 Hz), 6.13, 7.37 (each 1H, d, J=3.0 Hz).

The Furfurylamines (1b—1i) from the Oximes (4b—4i) by Raney Ni Reduction Excess of Raney Ni alloy was added to a solution of an oxime (0.5 g) in 10 ml of ethanol and 10 ml of 2 N aqueous NaOH. The reaction mixture was stirred at ambient temperature for 1 h, then extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated and the residue was purified on silica gel (saturated with Et_3N) chromatography to give the corresponding (79—85%).

1b: IR ν_{max}^{neat} cm^{-1}: 3300, 3120, 1639, 1520, 1357, 1149, 1012, 799, 734. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (3H, d, J=6.7 Hz), 4.03 (1H, q, J=6.7 Hz), 4.78 (2H, br s, –NH_2), 6.04 (1H, d, J=3.1 Hz), 6.49 (1H, dd, J=3.1, 1.8 Hz), 7.28 (1H, d, J=1.8 Hz).

1c: IR ν_{max}^{neat} cm^{-1}: 3350, 3120, 1639, 1163, 1009, 945, 895, 737. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, d, J=7.0 Hz), 1.71 (2H, quintet, J=7.0 Hz), 3.75 (1H, t, J=7.0 Hz), 6.09 (1H, d, J=3.0 Hz), 6.27 (1H, dd, J=3.0, 1.5 Hz), 7.26 (1H, d, J=1.5 Hz).

1d: IR ν_{max}^{neat} cm^{-1}: 3344, 1574, 1442, 1129, 1021, 944, 824. ^{1}H-NMR ($CDCl_3$) δ: 2.24 (3H, s), 3.74 (2H, s), 5.86, 5.98 (each 1H, d, J=2.9 Hz).

1e: IR ν_{max}^{neat} cm^{-1}: 3350, 3120, 1639, 1163, 1009, 954, 885, 737. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, d, J=7.5 Hz), 1.88 (2H, br s, –NH_2), 2.65 (2H, q, J=7.5 Hz), 3.72 (2H, s), 5.87, 6.00 (each 1H, d, J=1.5 Hz).

1f: IR ν_{max}^{neat} cm^{-1}: 3286, 3130, 1600, 1562, 1310, 1163, 1018, 944, 784, 738. ^{1}H-NMR ($CDCl_3$) δ: 1.35 (3H, d, J=6.7 Hz), 2.23 (3H, s), 4.00 (1H, q, J=6.7 Hz), 5.83, 5.93 (each 1H, d, J=3.0 Hz).

1g: IR ν_{max}^{neat} cm^{-1}: 3234, 3100, 1560, 1375, 1207, 1058, 1013, 781. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=7.5 Hz), 1.60 (2H, quintet, J=7.5 Hz), 2.30 (3H, s), 3.72 (1H, t, J=7.5 Hz), 5.82, 5.93 (each 1H, d, J=3.0 Hz).

1h: IR ν_{max}^{neat} cm^{-1}: 3280, 3100, 1562, 1379, 1217, 1020, 785. ^{1}H-NMR ($CDCl_3$) δ: 1.19 (3H, t, J=7.5 Hz), 1.36 (3H, t, J=6.9 Hz), 2.60 (2H, q, J=7.5 Hz), 4.00 (1H, q, J=6.9 Hz), 5.84, 5.95 (each 1H, d, J=3.0 Hz).

1i: IR ν_{max}^{neat} cm^{-1}: 3290, 3101, 1556, 1374, 1323, 1057, 1011, 779. ^{1}H-NMR ($CDCl_3$) δ: 0.92 (6H, m), 1.72 (2H, m), 2.62 (2H, q, J=7.5 Hz), 3.76 (1H, t, J=7.5 Hz), 5.84, 5.96 (each 1H, d, J=3.0 Hz).

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References

1) L. A. Walter, C. K. Springer, J. Kenney, S. K. Galen and N. Sperber, *J. Med. Chem.*, **11**, 792 (1968).
2) H. Greuter and D. Bellus, *J. Heterocycl. Chem.*, **14**, 203 (1977).
3) M. Yasue, N. Kawamura and J. Sakakibara, *Yakugaku Zasshi*, **90**, 1222 (1970).
4) *a*) H. Tsuchida, M. Komoto, H. Kato and M. Fujimaki, *Agric. Biol. Chem.*, **39**, 1143 (1975); *b*) K. Olsson, P. A. Pernemaim and O. Theander, *Acta Chem. Scand., Ser. B*, **32**, 249 (1978); *c*) H. Tsuchida, M. Komoto, H. Kato, T. Kurata and M. Fujimaki, *Agric. Biol. Chem.*, **40**, 2051 (1976).
5) *a*) J. V. S. Peterson, K. Norris, N. Clauson-Kaas and K. Svanaholt, *Acta Chem. Scand.*, **23**, 1785 (1969); *b*) J. V. B. Peterson, US. Patent 3658826 (1972) [*Chem. Abstr.*, **77**, 883341 (1972)]; *c*) I. F. Belśkii, F. I. Belśkii and V. M. Shostakovskii, *Izv. Akad. Nauk SSSR, Ser. Kim*, **1977** 1364 [*Chem. Abstr.*, **87**, 152127 (1977)].
6) *a*) I. Saito and S. S. Nittala, "The Chemistry of Peroxides," ed. by S. Patai, Wiley-Interscience, New York, 1983, p. 311; *b*) H. H. Wasserman and B. H. Lipshutz, "Singlet Oxygen," ed. by H. H. Wasserman and R. W. Murray, Academic Press, New York, 1979, p. 430; *c*) K. Gollnick and A. Griesheck, *Tetrahedron*, **41**, 2057 (1985) and references cited therein; *d*) E. L. Clennan and M. E. Mehrsheikn-Mohammadi, *J. Am. Chem. Soc.*, **106**, 7112 (1984); *e*) Y.-H. Kuo and K.-S. Shih, *J. Photochem. Photobiol. A: Chem.*, **41**, 79 (1987); *f*) Y.-H. Kuo, K.-S. Shih and S. M. Lee, *J. Photochem. Photobiol., A: Chem.*, **45**, 97 (1988); *g*) Y.-H. Kuo, K.-S. Shih, G.-H. Lee and Y. Wang, *Heterocycles*, **27**, 599 (1988).
7) *a*) G. Piancatelli, A. Scettri and M. D'Auria, *Tetrahedron*, **36**, 661 (1980); *b*) P. D. Williams and E. LeGoff, *J. Org. Chem.*, **46**, 4113 (1981); *c*) *Idem*, *Tetrahedron Lett.*, **26**, 1367 (1985); *d*) M. Petrini, R. Ballini, G. Rosini and E. Marotta, *Tetrahedron*, **42**, 151 (1986).
8) I. Saito, Y.-H. Kuo and T. Matsuura, *Tetrahedron Lett.*, **27**, 2757 (1986).
9) Y.-H. Kuo and K.-S. Shih, *Heterocycles*, in press (1990).
10) O. Achmatowicz and M. H. Burzynska, *Tetrahedron*, **38**, 3507 (1982).