PREPARATION OF 6-HYDROXY-2H-PYRAN-3(6H)-ONE FROM 2-FURYLCARBINOL BY PHOTOOXIDATION. SYNTHESIS OF A PHEROMONE OF VESPA ORIENTALIS

Yueh-Hsiung Kuo*[a,b] and Kae-Shyang Shih[a]

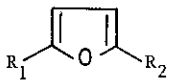
Department of Chemistry, National Taiwan University[a], Taipei, Taiwan, ROC.

National Research Institute of Chinese Medicine[b], Taipei Hsien, Taiwan, ROC

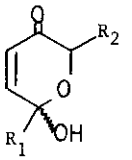
Abstract —— Photooxidation of 2-furylcarbinols followed by reduction with triphenylphosphine afforded 6-hydroxy-2H-pyran-3(6H)-ones in excellent yield. The method was applied to synthesis of 6-undecyltetrahydro-2-pyrone, a pheromone of Vespa orientalis.

Alkylfurans, by action of pyridinium chlorochromate (PCC) in CH_2Cl_2 solution, undergo an oxidative ring fission to trans-enediones in good yields (60-90%).[1] LeGoff demonstrated the efficacy of furan oxidation using m-chloroperbenzoic acid (m-CPBA) to synthesize a number of enedione-functionalized macrocycles from macrocyclic furan precursors.[2] m-CPBA was also used to oxidize 2-furylcarbinols in CH_2Cl_2 or $CHCl_3$ for preparation of 6-hydroxy-2H-pyran-3(6H)-ones. But the yields of this reaction varied from 20% to 85%.[3] 6-Hydroxy-2H-pyran-3(6H)-ones can be also prepared from 5-methyl-2-furylcarbinols in good yields (> 85%)[4] when it was oxidized with pyridinium chlorochromate (PCC). But in our experiment, 2-furylcarbinol without methyl substitution did not give corresponding ß-pyranones as they reacted with PCC. In our result, the reaction of 2-furylcarbinol (1a) or 2-furylmethyl carbinol (1b) with PCC under the condition as Piancatellis[4] afforded furfural or 2-acetylfuran, respectively. The oxidation of 5-alkylfurylcarbinol with t-butylhydroperoxide[5] and acidic isomerization of 2,5-dimethoxy-2,5-dihydrofurylcarbinol[6] can also prepare 6-hydroxy-2H-pyran-3(6H)-one. In this paper we wish to describe a useful method that is able to convert 2-furylcarbinols (1) into 6-hydroxy-2H-pyran-3(6H)-ones (2) in excellent yield without electron-donating group attached at C-5 position, and a use of this procedure to synthesize a pheromone of Vespa orientalis.

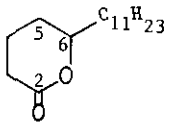
In a typical experiment the furan derivative (1a) and tetraphenylporphine (TPP) were irradiated by tungsten bromine lamp at -70°C for two hours, then excess triphenylphosphine (Ph_3P) dissolved in CH_2Cl_2 was added at the same temperature. After ten minutes the reaction mixture was taken out from dry ice acetone bath. The products were purified by silica gel chromatography and afforded 6-hydroxy-2H-pyran-3(6H)-one (2a) in excellent yield. The results (12 entries) are shown in the Table I. The oxidation of 1e was performed in acetone solution with methylene blue as sensitizer.



1



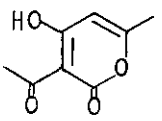
2



4

a R_1 = H, R_2 = CH_2OH
b R_1 = H, R_2 = CHOHMe
c R_1 = Me, R_2 = CH_2OH
d R_1 = Me, R_2 = CHOHMe
e R_1 = R_2 = CH_2OH
f R_1 = CH_2OAc, R_2 = CH_2OH
g R_1 = CH_2OCOPh, R_2 = CH_2OH
h R_1 = H, R_2 = CHOHPh
i R_1 = H, R_2 = CHOHEt
j R_1 = H, R_2 = $CHOHC_{11}H_{23}$
k R_1 = Et, R_2 = CH_2OH
ℓ R_1 = Et, R_2 = CHOHMe
m R_1 = H, R_2 = COMe
n R_1 = Me, R_2 = COMe
o R_1 = H, R_2 = CHO
p R_1 = Et, R_2 = CHO

a R_1 = R_2 = H
b R_1 = H R_2 = Me
c R_1 = Me R_2 = H
d R_1 = R_2 = Me
e R_1 = CH_2OH, R_2 = H
f R_1 = CH_2OAc, R_2 = H
g R_1 = CH_2OCOPh, R_2 = H
h R_1 = H, R_2 = Ph
i R_1 = H, R_2 = Et
j R_1 = H, R_2 = $C_{11}H_{23}$
k R_1 = Et, R_2 = H
ℓ R_1 = Et, R_2 = Me

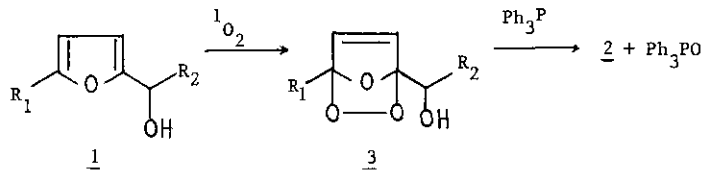


5

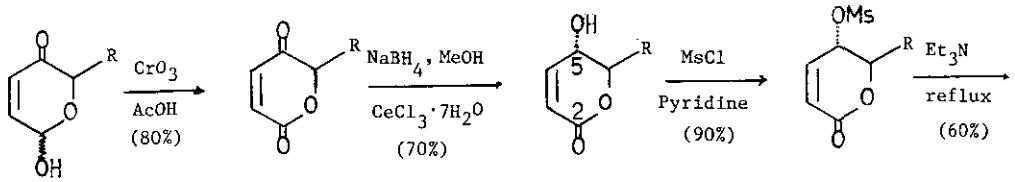
Table I. The yields of photooxidation of furans

Entry	Furan	Product	Yield (%)
1	1a	2a	95
2	1b	2b (2:1)[a]	90
3	1c	2c	93
4	1d	2d (3:2)	89
5	1e	2e	85
6	1f	2f	90
7	1g	2g	90
8	1h	2h (2:1)	65
9	1i	2i (2:1)	90
10	1j	2j (3:2)	80
11	1k	2k	80
12	1ℓ	2ℓ (3:2)	70

a. The radio of mixture



Scheme I



Scheme II

The nmr data of (2b), (2d), (2h), (2i), (2j), and (2ℓ) revealed that they contained cis and trans isomers.

The formation of the products may be rationalized in terms of the mechanism proposed in Scheme I. Addition of $^1O_2$ to 1 would give an ozonize 3 which subsequently reduced with Ph_3P to afford 6-hydroxy-2H-pyran-3(6H)-one and triphenylphosphine oxide.

Compounds (1a), (1c), and (1e) are commercially available. The other raw materials were prepared as follows. Compounds (1b) and (1d) were obtained from sodium borohydride reduction of (1m) and (1n), respectively. Partial acetylation and benzoylation of (1e) afforded (1f) and (1g), respectively. Compounds (1h), (1i), and (1j) were prepared from furfural (1o) by reaction with phenylmagnesium bromide, ethylmagnesium bromide, and undecylmagnesium bromide, respectively. 2-Ethylfuran, dissolved in dimethylforamide, was reacted with phosphorus oxychloride to yield 5-ethylfurfural (1p) which was converted to (1k) and (1ℓ) upon treatment with sodium borohydride and methylmagnesium bromide, respectively. Among twelve products, only six products, (2a), (2c), (2e), (2f), (2g) and (2k), were isolated as only one isomer. The other six products showed two epimeric mixtures which are revealed from their ^1H nmr spectra. 6-Undecyltetrahydro-2-pyrone (4)[7] is a pheromone of the oriental hornet (Vespa orientalis). Bacardit[8] has reported that the synthesis of (4) from the industrially available dehydroacetic acid (5). The synthesis of optically active (4) has been performed by Pirkle[9] and Coke.[10] Now in this report we depicted a new procedure for

the efficient synthesis of (4) from appropriate starting materials (2j). The transformation into (4) from (2j) was described in Scheme II. Tow epimeric mixture of (2j) was oxidized with chromium oxide in acetic acid and afforded enone ester (6) (mp 62-64°C; 1704 and 1680 cm^{-1}). Reduction of (6) with sodium borohydride ($NaBH_4$) in the presence of cerium trichloride ($CeCl_3$)[7] gave hydroxyl-actone (7) (3390 cm^{-1}) exclusively. H-5 in compound (7) shows coupling with H-4 and H-6 with coupling constant 5.9 Hz and 2.6 Hz, respectively. The evidence suggested that C-5 and C-6 disubstitutents in (7) is in trans-diquasi axial orientation. The alcohol (7) was converted to the corresponding methanesulfonate (8) with mesyl chloride in pyridine, which was heated under reflux in triethylamine to afford subsequently 6-undecyl-2-pyrone (9). Hydrogenation of compound (9) with 10% Pd-C in methanol gave a product was identical with 6-undecyltetrahydro-2-pyrone (4),[7] a pheromone of Vespa orientalis.

EXPERIMENTAL

Melting points were uncorrected. Nmr spectra were determined on a Varian EM-390 (90 MHz) and Bruker AM-300 (300 MHz) in the indicated solvents with tetramethylsilane (TMS) as internal standard. Chemical shifts and coupling constants were measured in ppm (δ) and J (Hz), respectively. Ir spectra were run as a neat or KBr disc on a Perkin-Elmer 982G. The EI mass spectra were obtained on JEOL model JMS-DX 300 double focusing mass spectrometer.

General Procedure for Photooxidation of 2-Furylcarbinols.

2-Furylcarbinol (300 mg in 15 ml of CH_2Cl_2) and tetraphenylporphine (TPP) (3 mg) were irradiated by a 650 Watt tungsten bromine lamp at -70°C for 2 h while oxygen passed through the solution. Then 700 mg of triphenylphosphin in 2 ml of CH_2Cl_2 were added at same temperature. After 10 min, the reaction mixture was taken out of dry ice acetone solution bath. The products were purified on silica gel chromatography (ethyl acetate: hexane = 2:8 as eluent) and afforded the pure 6-hydroxy-2H-pyran-3(6)-one in excellent yield.

Physical Data of Products (2a)-(2ℓ).

(2a) (oil): ms m/z (%) 114 (M^+, 4), 97 (7), 84 (100), 69 (5), 68 (4), 56 (27), 55 (51), and 42 (9); ir (neat)(νcm^{-1}) 3353, 3070, 1700, 1678, 1624, 1267, 1150, and 915; ^1H nmr ($CDCl_3$) δ 4.19 and 4.53 (each 1H, d, J = 16.9 Hz), 5.59 (1H, d, J = 3.0 Hz), 6.12 (1H, d, J = 10.4 Hz), and 6.93 (1H, dd, J = 10.4, 3.0 Hz); Anal. Calcd for $C_5H_6O_3$: C, 52.63; H, 5.30. Found C, 52.81; H, 5.25.

(2b) (oil) (major): ms m/z (%) 128 (M^+, 6), 113 (20), 98 (62), 97 (44), 87 (30), 86 (100), 74 (51), 61 (73), 58 (87), 43 (38), 42 (89), and 41 (40); ir (neat)(νcm^{-1}) 3401, 1692, 1628, 1302,

941, 904, and 863; ^{1}H nmr ($CDCl_3$) δ 1.35 (3H, d, J = 7.0 Hz), 4.70 (1H, q, J = 7.0 Hz), 5.61 (1H, d, J = 2.9 Hz), 6.07 (1H, d, J = 10.2 Hz), and 6.90 (1H, dd, J = 10.2, 2.9 Hz). Epi. (2b) (oil) (minor): ^{1}H nmr ($CDCl_3$) δ 1.44 (1H, d, J = 7.0 Hz), 4.21 (1H, dq, J = 2.0, 7.0 Hz), 5.65 (1H, m), 6.10 (1H, dd, J = 10.2, 1.8 Hz), and 6.92 (1H, dd, J = 10.2, 1.7 Hz); Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found C, 56.12, H, 6.31.

(2c) (oil): ms m/z (%) 128 (M^+, 4), 98 (100), 70 (34), 55 (95), 33 (15), 43 (23), 42 (38), and 41 (20); ir (neat)(νcm^{-1}) 3383, 3060, 1683, 1630, 1132, 1096, 998, and 784; ^{1}H nmr ($CDCl_3$) δ 1.59 (3H, s), 4.07 and 4.52 (each 1H, d, J = 16.9 Hz), and 6.02 and 6.84 (each 1H, d, J = 10.3 Hz); Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found C, 56.41; H, 6.20.

(2d) (oil) (major): ms m/z (%) 142 (M^+, 3), 125 (19), 99 (81), 98 (29), 97 (33), 71 (22), 70 (44), 69 (21), 55 (100), 45 (62), and 43 (88); ir (neat)(νcm^{-1}) 3419, 1699, 1244, 1089, 1038, 929 and 849; ^{1}H nmr ($CDCl_3$) δ 1.33 (3H, d, J = 6.8 Hz), 1.60 (3H, s), 4.62 (1H, q, J = 6.8 Hz), and 5.97 and 6.78 (each 1H, d, J = 10.2 Hz). Epi. (2d) (oil): ^{1}H nmr ($CDCl_3$) δ 1.40 (3H, d, J = 6.9 Hz), 1.63 (3H, s), 4.51 (1H, q, J = 6.9 Hz), and 6.00 and 6.84 (each 1H, d, J = 10.3 Hz); Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found C, 59.01; H, 7.15.

(2e) (oil): ms m/z (%) 144 (M^+, 5), 127 (67), 114 (30), 113 (70), 96 (47), 85 (33), 71 (38), 69 (46), 67 (90), 59 (42), 58 (67), 57 (73), 55 (100), 54 (40), 45 (61), and 41 (85); ir (neat)(νcm^{-1}) 3414, 1690, 1630, 1090, 1060, 991, 917, and 868; ^{1}H nmr ($CDCl_3$) δ 3.61 and 3.79 (each 1H, d, J = 11.5 Hz), 4.14 and 4.59 (each 1H, J = 16.8 Hz), and 6.17 and 6.80 (each 1H, d, J = 10.5 Hz); Anal. Calcd for $C_6H_8O_4$: C, 50.00; H, 5.60. Found C, 49.89; H, 5.50.

(2f) (oil): ms m/z (%) 186 (M^+, 2), 114 (28), 113 (38), 101 (18), 97 (20), 95 (18), 68 (39), 57 (22), and 43 (100); ir (neat)(νcm^{-1}) 3426, 1741, 1695, 1630, 1235, and 995; ^{1}H nmr ($CDCl_3$) δ 2.14 (3H, s), 4.08 and 4.42 (each 1H, d, J = 11.7 Hz), 4.19 and 4.58 (each 1H, d, J = 16.9 Hz), and 6.16 and 6.88 (each 1H, d, J = 10.3 Hz); Anal. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41. Found C, 51.48; H, 5.31.

(2g) (oil): ir (neat)(νcm^{-1}) 3415, 1720, 1700, 1600, 1490, 1274, 1111, 1071, 1027, and 711; ^{1}H nmr ($CDCl_3$) δ 4.20 and 4.62 (each 1H, d, J = 16.9 Hz), 4.33 and 4.66 (each 1H, d, J = 11.6 Hz), 6.18 and 6.99 (each 1H, d, J = 10.4 Hz), 7.44 (2H, t, J = 7.9 Hz), 7.57 (1H, tt, J = 7.9, 1.0 Hz), and 8.04 (2H, dd, J = 7.9, 1.0 Hz); Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found C, 63.01; H, 4.79.

(2h) (oil) (major): ir (near)(νcm^{-1}) 3419, 3060, 1688, 1626, 1492, 1222, 1027, 945, 742, and 699; ^{1}H nmr ($CDCl_3$) δ 5.53 (1H, s), 5.63 (1H, d, J = 2.5 Hz), 6.13 (1H, d, J = 10.5 Hz), 6.88 (1H, dd, J = 10.5, 2.5 Hz), and 7.20-7.40 (5H, m). Epi. (2h) (oil) (minor): ^{1}H nmr ($CDCl_3$) δ 5.02 (1H, d, J = 1.0 Hz), 5.67 (1H, m), 6.18 (1H, dd, J = 10.5, 1.0 Hz), 6.90 (1H, dd, J = 10.5, 1.5 Hz), and 7.20-7.40 (5H, m); Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found C, 69.32; H, 5.22.

(2i) (oil) (major): ms m/z (%) 142 (M^+, 3), 125 (9), 97 (6), 85 (12), 84 (100), 56 (55), 55 (87), 45 (5), and 41 (11); ir (neat)(νcm^{-1}) 3407, 2971, 1684, 1624, 1433, 1226, 1157, 1082, and 1029; ^1H nmr ($CDCl_3$) δ 0.98 (3H, t, J = 7.5 Hz), 1.72 (2H, m), 4.49 (1H, dd, J = 6.9, 4.5 Hz), 5.64 (1H, br s), 6.07 (1H, d, J = 10.0 Hz), and 6.92 (1H, br d, J = 10.0 Hz). Epi. (2i) (oil) (minor): ^1H nmr ($CDCl_3$) δ 0.99 (3H, t, J = 7.5 Hz), 1.90 (2H, m), 4.00 (1H, dd, J = 7.1, 4.5 Hz), 5.62 (1H, d, J = 3.6 Hz), 6.09 (1H, dd, J = 10.2, 3.6 Hz), and 6.90 (1H, d, J = 10.2 Hz); Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found C, 59.02; H, 7.01.

(2j) (major): mp 75-77°C (from hexane); ms m/z (%) 268 (M^+, 2), 251 (7), 166 (3), 114 (11), 97 (5), 84 (100), 69 (6), and 55 (35); ir (KBr)(νcm^{-1}) 3323, 1672, 1623, 1464, 1098, 1080, 1025, 773, and 717; ^1H nmr ($CDCl_3$) δ 0.88 (3H, t, J = 7.4 Hz), 1.30 (18H, br s), 1.60-1.90 (2H, m), 4.52 (1H, t, J = 6.0 Hz), 5.65 (1H, d, J = 3.0 Hz), 6.10 (1H, d, J = 10.2 Hz), and 6.90 (1H, dd, J = 10.2, 3.0 Hz). Epi. (2j) (oil) (minor): ^1H nmr ($CDCl_3$) δ 0.90 (3H, t, J = 7.4 Hz), 1.30 (18H, br s), 1.60-1.90 (2H, m), 4.06 (1H, dd, J = 6.9, 4.1 Hz), 5.62 (1H, d, J = 2.2 Hz), 6.12 (1H, dd, J = 10.3, 2.2 Hz), and 6.90 (1H, d, J = 10.2 Hz); Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found C, 71.48; H, 10.47.

(2k) (oil): ms m/z (%) 142 (M^+, 8), 125 (14), 113 (100), 112 (91), 97 (32), 84 (23), 83 (33), 69 (8), 57 (32), 56 (9), 55 (46), and 43 (2); ir (near)(νcm^{-1}) 3399, 1681, 1622, 1418, 1260, 1076, 1024, 969, and 867; ^1H nmr ($CDCl_3$) δ 1.00 (3H, t, J = 7.5 Hz), 2.83 (2H, q, J = 7.5 Hz), 4.07 and 4.75 (each 1H, d, J = 17.4 Hz), and 6.09 and 6.88 (each 1H, d, J = 9.2 Hz); Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found C, 59.02; H, 7.15.

(2l) (oil) (major): ms m/z (%) 156 (M^+, 2), 139 (17), 127 (30), 112 (100), 109 (18), 99 (20), 98 (38), 97 (43), 83 (52), 70 (10), 57 (12), 55 (68), and 43 (47); ir (neat)(νcm^{-1}) 3406, 1686, 1369, 1233, 1117, 1091, 1001, 813, and 754; ^1H nmr ($CDCl_3$) δ 0.98 (3H, t, J = 7.5 Hz), 1.35 (3H, d, J = 7.5 Hz), 1.83 (2H, q, J = 7.5 Hz), 4.63 (1H, q, J = 7.5 Hz), and 6.05 and 6.79 (each 1H, d, J = 10.3 Hz). Epi. (2l)(oil) (minor): ^1H nmr ($CDCl_3$) δ 0.99 (3H, t, J = 7.4 Hz), 1.34 (3H, d, J = 7.5 Hz), 1.82 (2H, q, J = 7.4 Hz), 4.45 (1H, q, J = 7.5 Hz), and 6.02 and 6.81 (each 1H, d, J = 10.4 Hz); Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found C, 61.40; H, 7.83.

Compounds (2b), (2d), (2h), (2i), (2j), and (2l) show two epimeric mixtures, respectively. These two epimeric mixtures can not be separated by silica gel chromatography. But the nmr data of two epimers can be easily recognized from its nmr spectrum.

Preparation of (1j) from Furfural by Reaction with Grignard Reagent

Magnesium power (1.3 g) was set in two neck flask and then 44 mmol of undecyl bromide (9.9 g) (mole reatio of Mg: RBr = 1.2:1) in 30 ml of dry ether was added slowly. After 8 h, the magnesium dissolved completely, the flask was transferred to ice bath and then 20.8 mmol of furfural (2 g) dissolved

in 25 ml of dry ether was added slowly. The reaction mixture was set at room temperature for 5 h, and then saturated aqueous NH_4Cl solution was added to quench the reaction. Then the aqueous layer was extracted with ether for three times. The combined ether extract was purified on silica gel chromatography (ethyl acetate: hexane = 1:9 as eluent) and afforded (1j) (3.96 g) (oil) (75% yield based on furfural); ms m/z (%) 252 (M^+, 11), 235 (3), 123 (3), 110 (13), 97 (100), 95 (18), 81 (8), 69 (18), 55 (28), 43 (39), and 41 (37); ir (neat)(νcm^{-1}) 3354, 1563, 1497, 1183, 1069, 1008, 883, 806, and 733; ^1H nmr ($CDCl_3$) δ 0.84 (3H, t, J = 7.5 Hz), 1.23 (18H, br s), 1.60-1.90 (2H, m), 4.58 (1H, t, J = 7.5 Hz), 6.16 (1H, d, J = 3.0 Hz), 6.28 (1H, dd, J = 3.0, 2.0 Hz), and 7.30 (1H, d, J = 2.0 Hz); Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found C, 76.03; H, 11.09.

Preparation of (6) from (2j) by Chromium Oxide in Acetic Acid

Chromium oxide (0.12 g) dissolved in 1 ml of acetic acid was added dropwise to the solution of (2j) (0.1 g) in 1 ml of acetic acid at room temperature. The reaction mixture was set for 1 h, and then was poured into excess of water (50 mg). The product was extracted with ether three times and the organic layer was washed with aqueous $NaHCO_3$ and saturated NaCl solutions, and evaporated. The residual oil was chromatographed on a silica gel (ethyl acetate: hexane = 1:19 as eluent) and yielded (6) (81 mg) (80%) [mp 62-64°C (from EtOH); $C_{16}H_{26}O_3$; ms m/z (%) 266 (M^+, 2), 163 (4), 112 (40), 97 (8), 82 (100), 69 (8), 54 (27), 43 (23), and 41 (27); ir (KBr)(νcm^{-1}) 3080, 1704, 1680, 1620, 1357, 1295, 1136, 1088, 848, and 722; ^1H nmr ($CDCl_3$) δ 0.88 (3H, t, J = 6.0 Hz), 1.12-1.50 (18H, br s), 2.22-2.50 (2H, m), 4.95 (1H, t, J = 7.5 Hz), and 6.78 and 6.95 (each 1H, d, J = 10.5 Hz)]; Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found C, 72.25; H, 9.75.

Reduction of (6) with Sodium Borohydride and Cerium Trichloride

Compoun (6) (0.1 g) was dissolved in 1.5 ml of 0.4 M methanolic $CeCl_3 \cdot 7H_2O$ and sodium borohydride (25 mg) was slowly added (1-2 min) with stirring. The mixture was allowed to react for 30 min, then treated with 50 ml of water and extracted with ether for three times. The product was purified on silica gel chromatography (ethyl acetate: hexane = 1:4 as eluent) and yielded pure compound (7) (70 mg) (70%): mp 53-55°C; ms m/z (%) 269 ($M^+ + 1$, 20), 268 (M^+, 1), 251 (5), 95 (6), 84 (100), 69 (7), and 55 (23); ir (KBr)(νcm^{-1}) 3390, 3070, 1690, 1623, 1468, 1398, 1284, 1106, 1077, 1003, 966, 869, 838, and 725; ^1H nmr ($CDCl_3$) δ 0.85 (3H, t, J = 6.8 Hz), 1.20-1.58 (18H, br s), 1.65-1.96 (2H, m), 4.03 (1H, dd, J = 5.9, 2.6 Hz, H-5), 4.26 (1H, m, H-6), 6.07 (1H, d, J = 9.6 Hz), and 6.99 (1H, dd, J = 9.6, 5.9 Hz); Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found C, 71.72; H, 10.44.

Mesylation of (7) with Methanesulfonyl Chloride

Compound (7) (0.1 g) was dissolved in dry pyridine (2 ml) at 0-5°C, and methanesulfonyl chloride (0.12 g) was slowly added. After addition of methanesulfonyl chloride, the reaction mixture was set at room temperature under stirring overnight. The reaction mixture was poured into excess ice water, extracted with ether, and then the extract was washed with 1 N HCl and aquoeus $NaHCO_3$, and evaporated. The product was purified on silica gel chromatography (ethyl acetate: hexane = 1:4 as eluent) and afforded mesylate (8) (112 mg, 85%): mp 67-69°C (from EtOH); ms m/z (%) 267 ($M^+-CH_3SO_2$, 4), 251 (12), 162 (44), 123 (11), 109 (12), 97 (20), 95 (24), 83 (100), 68 (15), 57 (20), 55 (42), 43 (35), and 41 (38); ir (KBr)(νcm^{-1}) 3040, 1734, 1630, 1467, 1361, 1259, 1181, 1096, 960, 903, 832, and 725; ^1H nmr ($CDCl_3$) δ 0.85 (3H, t, J = 6.0 Hz), 1.20-1.56 (18H, br s), 1.60-1.90 (2H, m), 3.07 (3H, s), 4.45 (1H, m, H-6), 5.02 (1H, dd, J = 5.8, 2.5 Hz, H-5), 6.23 (1H, d, J = 9.8 Hz), and 6.99 (1H, dd, J = 9.8, 5.9 Hz); Anal. Calcd for $C_{17}H_{30}O_5S$: C, 58.93; H, 8.72. Found C, 58.81; H, 8.65.

Demesylation of (8) with Triethylamine

Compound (8) (80 mg) was heated in triethylamine (5 ml) under reflux for 12 h. After evaporation of triethylamine under vancuo, the reaction mixture was extracted with ether. The ether layer was washed with 1 N HCl and aqueous $NaHCO_3$ solution. After purification on silica gel chromatography (ethyl acetate: hexane = 1:9 as eluent), the reaction mixture gave elimination product (9) (35 mg, 60%); mp 67-69°C (from EtOH); ms m/z (%) 250 (M^+, 18), 165 (18), 128 (48), 123 (44), 115 (100), 95 (92), 81 (32), 68 (26), 58 (59), 67 (37), 56 (45), 43 (55), and 41 (57); ir (KBr)(νcm^{-1}) 2926, 2855, 1741, 1639, 1558, 1462, 1379, 1091, and 804; ^1H nmr ($CDCl_3$) δ 0.82 (3H, t, J = 7.5 Hz), 1.10-1.40 (16H, m), 1.60 (2H, quintet, J = 7.5 Hz), 2.40 (2H, t, J = 7.5 Hz), 5.90 (1H, d, J = 6.4 Hz, H-5), 6.10 (1H, d, J = 9.5 Hz, H-3), and 7.21 (1H, dd, J = 9.5, 6.4 Hz, H-4); Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found C, 76.88; H, 10.36.

Hydrogenation of (9) with Pd-C as Catalyst

Compound (9) (50 mg) was hydrogenated in methanol (10 ml) with 10% Pd-C (30 mg) at room temperature for 5 h. The product was purified by chromatography on silica gel (ethyl acetate: hexane = 1:9 as eluent) to afford (4) (oil) (47 mg, 93%); $C_{16}H_{30}O_2$; ms m/z (%) 254 (M^+, 4), 236 (8), 192 (9), 183 (5), 143 (9), 128 (53), 115 (100), 99 (97), 83 (32), 71 (58), 55 (80), and 43 (9); ir (neat) (νcm^{-1}) 1734, 1463, 1262, 1041, and 805; ^1H nmr ($CDCl_3$) δ 0.85 (3H, t, J = 6.5 Hz), 1.10-1.40 (20H, m), 1.42-1.98 (4H, m), 2.40-2.61 (2H, m), and 4.25 (1H, m).

ACKNOWLEDGEMENT

This research was supported by the National Science Council of the ROC.

REFERENCES

1. G. Piancatelli, A. Scettri, and M. D'Auria, Tetrahedron, 1980, 36, 661.
2. P. D. Williams and E. LeGoff, J. Org. Chem., 1981, 46, 4143.
3. R. Laliberté, G. Médawar, and Y. Lefebvre, J. Med. Chem., 1973, 16, 1084.
4. P. Piancatelli, A. Scettri, and M. D'Auria, Tetrahedron Lett., 1977, 2199.
5. T. Ohta, H. Tsuchiyama, and S. Nozoe, Heterocycles, 1986, 24, 1137.
6. T. Shono and Y. Matsumura, Tetrahedron Lett., 1976, 1363.
7. a) R. Ikan, R. Gottlieb, E. D. Bergmann, and J. Ishay, J. Insect. Physiol., 1969, 15, 1709.
   b) J. L. Coke and A. B. Richon, J. Org. Chem., 1976, 41, 3516.
8. R. Bacardit and M. Moreno-Manas, Chemistry Lett., 1982, 5.
9. W. H. Pirkle and P. E. Adams, J. Org. Chem., 1979, 44,, 2169.
10. J. L. Coke and A. B. Richon, J. Org. Chem., 1976, 41, 3516.
11. J.L. Luche, L. Rodriguez-Hahn, and P. Crabbe, J. Chem. Soc., Chem. Commun., 1978, 601.

Received, 7th May, 1990