Oxidation of 3-Furfurylcarbinols with Bromine in Acetone-Water

Piin-Jye Harn[a,d] (韓品杰), Chu-Chung Lin[a,c] (林助強) and Hsien-Jen Wu[a,b,*] (吳獻仁)
[a]*Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.*
[b]*Department of Food Science, Yuanpei University, Hsinchu, Taiwan, R.O.C.*
[c]*Department of Medicinal Chemistry, TaiGen Biotechnology Co., Ltd., Taipei, Taiwan, R.O.C.*
[d]*SinoPharm Taiwan Ltd., Tainan County, Taiwan, R.O.C.*

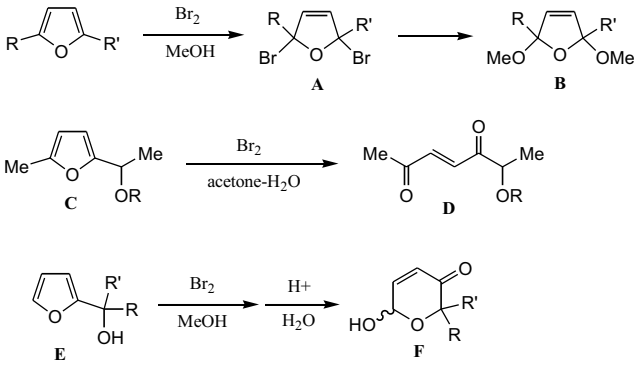
Oxidation of 3-furfurylcarbinols **3a-e** and **7** with bromine in acetone-water solution gave the 2-substituted-3-furfurals **4a-e** and **8** in good yields, respectively. Reaction of 2-alkyl-3-furfurylcarbinols **9a** and **9b** with bromine in acetone-water gave the bromoalkyl 3-furfuryl ketones **10a** and **10b** as the major products. A reaction mechanism *via* the *cis-trans* isomerization of the 2-ene-1,4-diones **13** and **14** was proposed to account for the transposition of the alkyl group of the 3-furfurylcarbinols **3**, **7** and **9** to the 2-position on the furan ring of the products **4**, **8** and **10**.

Keywords: 3-Furfurylcarbinols; Oxidation with bromine.

INTRODUCTION

Furan derivatives and their oxidation products are important intermediates in organic synthesis.[1,2] The oxidation of a furan ring has oftentimes been used to express the latent functionality present within this heterocyclic framework.[3] Oxidation of 2-trimethylsilylfurans with peracetic acid gave Δ^3-butenolides.[4] This transformation was applied for the synthesis of natural products.[5] Oxidation of 2,5-dialkylfurans with peroxy acids afforded the *Z*-isomers of 2-ene-1,4-diones,[6] whereas the *E*-isomers were obtained with pyridinium chlorochromate (PCC) as the oxidation reagent.[7] Treatment of 2-alkylthiofurans with PCC initially gave the *Z*-isomers of *S*-alkyl 4-oxo-2-alkenoates, which were converted to the *E*-isomers when longer reaction times proceeded.[8] The oxidation reaction of furan derivatives with bromine in absolute methanol is known as Clauson-Kaas reaction to give the 2,5-dimethoxy-2,5-dihydrofuran derivatives **B**,[9] presumably *via* the dibromo intermediates **A** (Scheme I). About two decades ago, a direct transformation of **C** to **D** by modified reaction conditions of the bromine oxidation with furan **C** was reported.[10] Reaction of 2-furfuryl alcohols **E** with bromine in methanol followed by mild acid hydrolysis gave 6-hydroxyl-2*H*-pyran-3(6*H*)-ones **F**,[11] a route to monosaccharides from furan compounds. This transformation from **E** to **F** was also accomplished with peroxy acids[12] and PCC.[13] 6-Hydroxy-2*H*-pyran-3(6*H*)-ones are useful intermediates for the synthesis of natural products.[3,11] In this paper, we report the oxidation reaction of 3-furfuryl alcohols with bromine in aqueous acetone solution.

Scheme I



RESULTS AND DISCUSSION

The required 3-furfuryl alcohols were prepared by Paterno-Büchi photocycloaddition[14] of aldehydes with furan[15] followed by ring opening of the oxetane ring with a catalytic amount of *p*-toluenesulfonic acid (PTSA) in anhydrous ether or CCl_4.[16] The other way to prepare 3-furfuryl alcohols is by nucleophilic addition of organometallic compounds to 3-furfuryl aldehyde. Both methods were adopted in this paper. Photocycloaddition of aldehydes **1a-d** with excess furan in Quartz tubes with wavelength 300 nm light produced by Rayonet photometry for 40 h gave the photocycloadducts **2a-d** in 70-85% yields (based

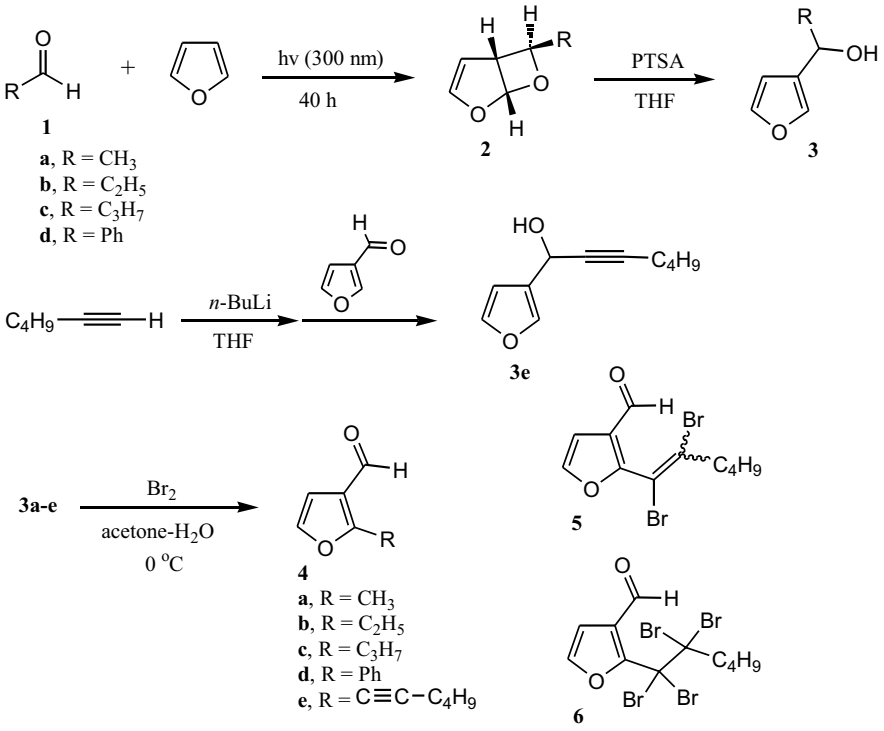
on consumed aldehydes). Treatment of **2a-d** with a catalytic amount of PTSA in dry tetrahydrofuran (THF) at room temperature for 2 h gave the 3-furfuryl alcohols **3a-d** in 65-75% yields. Reaction of 1-hexyne with *n*-butyllithium in dry THF followed by addition of 3-furfural at 0 °C gave the furfuryl alcohol **3e** in 80% yield (Scheme II). Oxidation of the 3-furfuryl alcohols **3a-e** with two equivalents of bromine in acetone-water (volume ratio 85:15) at 0 °C for 2 h gave 2-substituted 3-furfural **4a-e** in 65-75% yields, respectively.

The structure of compounds **4a-e** was identified by their spectral data. The infrared (IR) spectra of **4a-e** revealed strong absorptions at 1685 cm^{-1} for the carbonyl group. The ^1H NMR spectrum of **4a** showed a singlet at δ 9.94 for the aldehyde proton, a doublet (J = 1.5 Hz) at δ 7.31 for the C_5 proton on the furan ring, a doublet (J = 1.5 Hz) at δ 6.69 for the furan ring C_4 proton, and a singlet at δ 2.60 for the methyl protons. The ^{13}C NMR spectrum of **4a** displayed one peak (CH) at δ 184.8 for the aldehyde carbonyl carbon, four peaks at δ 161.9 (C), 141.9 (CH), 122.5 (C) and 108.0 (CH) for the furan ring carbons, and one peak (CH_3) at δ 12.6 for the methyl carbon. The mass spectrum of **4a** showed its molecular parent peak at 110 with 25% relative intensity. In the case of the oxidation of **3e** with two equivalents of bromine in aqueous acetone, the 3-furfural **4e** was obtained in good yield (65%) even in the presence of a carbon-carbon triple bond. The amount of the other products **5** or **6**, which might be obtained by addition of bromine to the triple bond, was too small to be isolated. This result may imply that the reaction rate of the oxidation of bromine on the furan ring of **3e** is much faster than that of the addition of bromine to the triple bond.

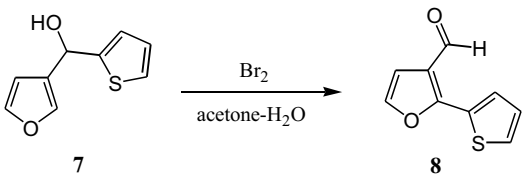
Treatment of thiophene with *n*-BuLi in dry THF at room temperature followed by addition of 3-furfural gave 3-furfuryl-2-thienyl carbinol (**7**) in 70% yield. Reaction of **7** with bromine in the same reaction conditions as the previous oxidations gave compound **8** in 65% yield (Scheme III). The amount of the other products, which might be obtained by reaction on the thiophene ring, was too small to be isolated. Thus, the oxidation selectively took place on the furan ring of **7**.

In order to understand the feasibility of the application of this oxidation reaction to the interexchange of the substituents on the furan ring, the following experiments were performed. Addition of the Grignard reagent, CH_3MgCl, to compound **4b** in dry THF at 0 °C gave the additional product **9a** in 80% yield. Reaction of **4a** with *n*-BuLi in dry THF at 0 °C gave compound **9b** in 85% yield.

Scheme II



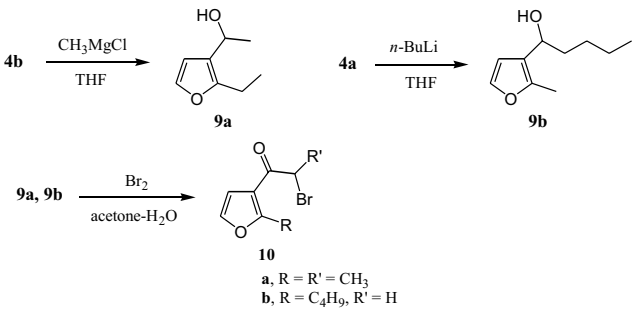
Scheme III



7 **8**

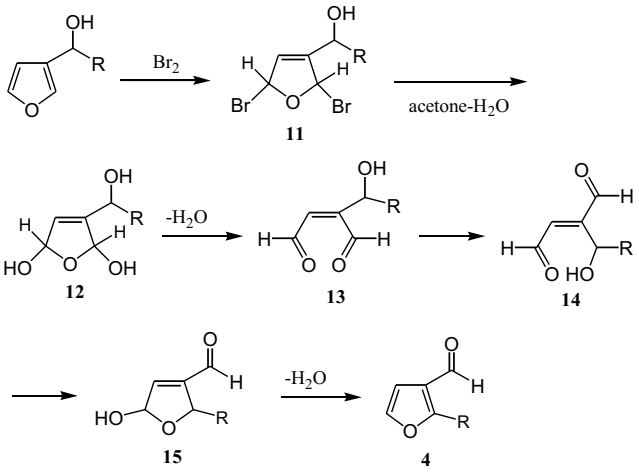
Oxidation of **9a** and **9b** with two equivalents of bromine in acetone-H_2O (85:15) at 0 °C gave compounds **10a** and **10b** as the major products in 50-55% yields, respectively, with a small amount of other unidentified products (Scheme IV). When one equivalent of bromine was used in the oxidation of **9a** and **9b**, compounds **10a** and **10b** were obtained as the major products with unreacted starting compounds **9a** and **9b**, respectively. This result may imply that the reaction rate of the bromination of the α carbon of the carbonyl group of **10** is faster than that of the oxidation of the furan ring of the 3-furfuryl alcohols. The bromine atom of **10a** and **10b** can be eliminated by reduction reaction, for example, with Zn/HOAc. Thus, the substituents at C_2 and C_3 on the furan ring of the 3-furfurylcarbinols can be interchanged by this oxidation reaction.

Scheme IV



A reaction mechanism was proposed for the transformation from the 3-furfuryl alcohols **3a-e** and **7** to the 3-furfurals **4a-e** and **8** (Scheme V). The initial step of this oxidation is similar to the Clauson-Kaas reaction as shown in the first line of Scheme I. The oxidation reaction of **3** with bromine in acetone-water solution gives the 2,5-dihydroxy-2,5-dihydrofuran **12**, presumably *via* the dibromo intermediate **11**. Dehydration of **12** followed by ring opening gives the *Z*-isomer of 2-ene-1,4-dione **13**. *Cis-trans* isomerization of **13** gives the *E*-isomer **14**. Acetal formation by the intramolecular cyclization of **14** gives the hemiacetal **15**, which was followed by dehydration to yield the product **4**.

Scheme V



A similar reaction mechanism can be applied to account for the transformation from **9a** and **9b** to **10a** and **10b**, except that further bromination on the α-carbon of the carbonyl group of **10** proceeded.

CONCLUSION

In summary, we have demonstrated the oxidation of the 3-furfurylcarbinols **3a-e**, **7**, **9a** and **9b** with brimine in acetone-water solution gave the 2-substituted-3-furfuryl aldehydes **4a-e** and ketones **8**, **10a** and **10b**. A reaction mechanism *via* the *cis-trans* isomerization from the *Z*-isomer **13** of the 2-ene-1,4-dione to the *E*-isomer **14** was proposed to account for the transformation of the alkyl group from the 3-position on the furan ring of the reactants to the 2-position on the furan ring of the products.

EXPERIMENTAL SECTION

Infrared spectra were recorded in $CHCl_3$ solutions or on neat thin films between NaCl disks. ^{1}H NMR spectra were determined at 300 MHz, and ^{13}C NMR spectra were determined at 75 MHz on Fourier transform spectrometers. Chemical shifts are reported in ppm relative to TMS in the solvents specified. The multiplicities of ^{13}C signals were determined by DEPT techniques. High-resolution mass values were obtained with a high-resolution mass spectrometer at the Department of Chemistry, National Tsing Hua University. For thin-layer chromatography (TLC) analysis, precoated TLC plates (Kieselgel 60 F_{254}) were used, and column chromatography was done by using

Kieselgel 60 (70-230 mesh) as the stationary phase. THF was distilled immediately prior to use from sodium benzophenone ketyl under nitrogen.

Preparation of the 3-Furfuryl Alcohols 3a-e

Photoaddition of aldehydes **1a-d** with excess furan in quartz tubes with wavelength 300 nm radiation produced by Rayonet photometry for 40 hours gave the photoadducts **2a-d** in 70-85% yields (based on consumed aldehydes). Treatment of **2a-d** with a catalytic amount of PTSA in dry THF at room temperature for 2 h gave the 3-furfuryl alcohols **3a-d** in 65-75% yields, which are known compounds.[16]

To a solution of 1-hexyne (0.82 g, 10.0 mmol) in dry THF (30 mL) was added *n*-butyllithium (2.5 M in *n*-hexane, 4.0 mL) at 0 °C. The solution was stirred at room temperature for one hour. To this solution was added 3-furfural (0.96 g, 10.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for two hours. The solvent was evaporated, and saturated NH_4Cl (30 mL) was added. After extraction with ether (5 × 30 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **3e** (1.42 g, 80%).

Spectral data for **3e**: pale yellow liquid; IR ($CHCl_3$) 3500-3300, 2220, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.38 (d, J = 3.0 Hz, 1H), 6.49 (d, J = 3.0 Hz, 1H), 5.36 (brs, 1H), 2.40 (brs, 1H), 2.25 (t, J = 6.6 Hz, 2H), 1.38-1.57 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 143.40 (CH), 139.99 (CH), 127.06 (C), 109.17 (CH), 85.92 (C), 79.48 (C), 57.33 (CH), 30.53 (CH_2), 21.87 (CH_2), 18.29 (CH_2), 13.48 (CH_3); LRMS *m/z* (rel int) 178 (M^+, 100), 121 (50); HRMS (EI) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0986.

General Procedure for the Oxidation of 3-Furfurylcarbinols 3a-e with Bromine in Acetone-Water

To a solution of 3-furfurylcarbinol **3a** (0.56 g, 5.0 mmol) in acetone (17 mL) and water (3 mL) was dropwise added bromine (0.80 g, 10.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. This solution was neutralized with saturated $NaHCO_3$ (20 mL) at 0 °C, and the mixture was stirred at room temperature for 20 min. After extraction with ether (5 × 30 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **4a** (0.36 g, 66%).

2-Methyl-3-furfural (4a)

Pale yellow liquid; IR ($CHCl_3$) 1685, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.31 (d, J = 2.1 Hz, 1H), 6.69 (d, J = 2.1 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 184.81 (CH), 161.93 (C), 141.95 (CH), 122.54 (C), 108.03 (CH), 12.58 (CH_3); LRMS *m/z* (rel int) 110 (M^+, 25), 95 (100); HRMS (EI) calcd for $C_6H_6O_2$ 110.0368, found 110.0374.

2-Ethyl-3-furfural (4b)

Pale yellow liquid; IR ($CHCl_3$) 1685, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.32 (d, J = 2.1 Hz, 1H), 6.69 (d, J = 2.1 Hz, 1H), 2.99 (q, J = 7.5 Hz, 2H), 1.33 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 184.63 (CH), 166.83 (C), 141.92 (CH), 121.61 (C), 107.86 (CH), 20.33 (CH_2), 12.58 (CH_3); LRMS *m/z* (rel int) 124 (M^+, 20), 123 (40), 57 (100); HRMS (EI) calcd for $C_7H_8O_2$ 124.0524, found 124.0534.

2-*n*-Propyl-3-furfural (4c)

Pale yellow liquid; IR ($CHCl_3$) 1685, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.32 (d, J = 2.1 Hz, 1H), 6.69 (d, J = 2.1 Hz, 1H), 2.93 (t, J = 7.5 Hz, 2H), 1.80-1.73 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 184.72 (CH), 165.93 (C), 141.98 (CH), 122.51 (C), 107.68 (CH), 28.52 (CH_2), 21.58 (CH_2), 13.45 (CH_3); LRMS *m/z* (rel int) 138 (M^+, 24), 95 (100); HRMS (EI) calcd for $C_8H_{10}O_2$ 138.0681, found 138.0688.

2-Phenyl-3-furfural (4d)

Pale yellow oil; IR (neat) 1685, 1600, 1500, 760, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.75-7.71 (m, 2H), 7.53-7.43 (m, 4H), 6.91 (d, J = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 185.65 (CH), 161.53 (C), 142.70 (CH), 130.15 (CH), 128.98 (2CH), 128.86 (C), 128.02 (2CH), 122.92 (C), 109.40 (CH); LRMS *m/z* (rel int) 172 (M^+, 86), 171 (100), 95 (60); HRMS (EI) calcd for $C_{11}H_8O_2$ 172.0524, found 172.0514.

2-(1-Hexynyl)-3-furfural (4e)

Pale yellow oil; IR (neat) 2250, 1695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.33 (d, J = 2.1 Hz, 1H), 6.73 (d, J = 2.1 Hz, 1H), 2.53 (t, J = 6.9 Hz, 2H), 1.68-1.60 (m, 2H), 1.53-1.45 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 184.75 (CH), 143.64 (CH), 128.54 (C), 107.42 (CH), 101.24 (C), 94.42 (C),

68.58 (C), 29.94 (CH_2), 21.87 (CH_2), 19.22 (CH_2), 13.39 (CH_3); LRMS *m/z* (rel int) 176 (M^+, 95), 147 (100); HRMS (EI) calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0848.

Preparation of 2-Thienyl-3-furfurylcarbinol (7)

To a solution of thiophene (0.42 g, 5.0 mmol) in dry THF (30 mL) was added *n*-butyllithium (2.5 M in *n*-hexane, 2.0 mL) at 0 °C. The solution was stirred at room temperature for 4 h. To this solution was added 3-furfural (0.48 g, 5.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for one hour. Then, to this solution was added saturated NH_4Cl (20 mL). After extraction with ether (5 × 30 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **7** (0.63 g, 70%); pale yellow oil; IR ($CHCl_3$) 3600-3200, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.1 Hz, 1H), 7.32 (s, 1H), 7.22 (d, *J* = 2.1 Hz, 1H), 6.92 (d, *J* = 1.8 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 1H), 6.36 (d, *J* = 2.1 Hz, 1H), 5.89 (d, *J* = 4.5 Hz, 1H), 3.10 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 147.07 (C), 143.26 (CH), 139.64 (CH), 128.22 (C), 126.50 (CH), 125.13 (CH), 124.67 (CH), 109.02 (CH), 65.14 (CH); LRMS *m/z* (rel int) 180 (M^+, 78), 85 (100).

Oxidation of Compound 7 with Bromine in Acetone-Water

The same reaction conditions for the oxidation of compounds **3a-e** with bromine were applied for the oxidation of **7** with bromine to give compound **8** in 65% yield; pale yellow oil; IR ($CHCl_3$) 1685, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.69 (d, *J* = 4.2 Hz, 1H), 7.50 (d, *J* = 5.1 Hz, 1H), 7.39 (d, *J* = 1.5 Hz, 1H), 7.16 (dd, *J* = 4.2, 5.1 Hz, 1H), 6.68 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 184.63 (CH), 155.32 (C), 142.15 (CH), 130.82 (C), 128.60 (CH), 128.19 (CH), 127.99 (CH), 121.73 (C), 109.87 (CH); LRMS *m/z* (rel int) 178 (M^+, 34), 177 (20), 121 (100).

General Procedure for the Preparation of Compounds 9a and 9b

To a solution of compound **4b** (0.62 g, 5.0 mmol) in dry THF (40 mL) was slowly added methylmagnesium chloride (2.5 M in THF, 2.0 mL) at 0 °C. The reaction mixture was stirred at room temperature for one hour. To this solution was slowly added saturated NH_4Cl (10 mL) at 0 °C. After extraction with ether (5 × 30 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give compound **9a** (0.56 g, 80%).

2-Ethyl-3-furfuryl Methyl Carbinol (9a)

Pale yellow oil; IR ($CHCl_3$) 3600-3200, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2.1 Hz, 1H), 6.36 (d, *J* = 2.1 Hz, 1H), 4.82 (q, *J* = 6.6 Hz, 1H), 2.64 (q, *J* = 7.2 Hz, 2H), 2.19 (brs, 1H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 152.58 (C), 140.31 (CH), 122.54 (C), 108.21 (CH), 62.20 (CH), 23.97 (CH_3), 19.51 (CH_2), 13.13 (CH_3); LRMS *m/z* (rel int) 140 (M^+, 7), 125 (100); HRMS (EI) calcd for $C_8H_{12}O_2$ 140.0837, found 140.0830.

2-Methyl-3-furfuryl *n*-Butyl Carbinol (9b)

Pale yellow oil; IR ($CHCl_3$) 3600-3200 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2.1 Hz, 1H), 6.33 (d, *J* = 2.1 Hz, 1H), 4.57 (t, *J* = 6.6 Hz, 1H), 2.26 (s, 3H), 1.88 (s, 1H), 1.80-1.18 (m, 6H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 148.04 (C), 140.40 (CH), 122.37 (C), 108.53 (CH), 66.66 (CH), 37.46 (CH_2), 27.91 (CH_2), 22.46 (CH_2), 13.95 (CH_3), 11.65 (CH_3); LRMS *m/z* (rel int) 168 (M^+, 8), 43 (100); HRMS (EI) calcd for $C_{10}H_{16}O_2$ 168.1151, found 168.1160.

General Procedure for the Oxidation of Compounds 9a and 9b

The same reaction conditions for the oxidation of compounds **3a-e** were applied for the oxidation of compounds **9a** and **9b** to give the bromoketones **10a** and **10b** as the major products, respectively. When one equivalent of bromine was used in the oxidation of **9a** and **9b**, compounds **10a** and **10b** were obtained as the major products with the unreacted compounds **9a** and **9b**.

2-Methyl-3-furfuryl α-Bromoethyl Ketone (10a)

Pale yellow oil; IR (neat) 1685, 1570 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.1 Hz, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 4.86 (q, *J* = 6.6 Hz, 1H), 2.63 (s, 3H), 1.83 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 189.44 (C), 161.18 (C), 140.37 (CH), 118.05 (C), 110.01 (CH), 44.51 (CH), 19.66 (CH_3), 14.47 (CH_3); LRMS *m/z* (rel int) 219 (M^+, 4), 217 (M^+, 4), 109 (100).

2-*n*-Butyl-3-furfuryl Bromomethyl Ketone (10b)

Pale yellow oil; IR (neat) 1685, 1575 cm^{-1}; ^1H NMR

(300 MHz, $CDCl_3$) δ 7.29 (d, J = 2.1 Hz, 1H), 6.65 (d, J = 2.1 Hz, 1H), 4.19 (s, 2H), 3.02 (t, J = 7.2 Hz, 2H), 1.68-1.63 (m, 2H), 1.40-1.32 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 186.96 (C), 165.02 (C), 140.63 (CH), 117.56 (C), 109.87 (CH), 33.27 (CH_2), 29.60 (CH_2), 27.85 (CH_2), 22.31 (CH_2), 13.72 (CH_3); LRMS *m/z* (rel int) 247 (M^+, 15), 245 (M^+, 16), 165 (100).

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