http://dx.doi.org/10.5012/bkcs.2012.33.1.90

Reactions of Some Furan-3-ones with 2,3-Diaminopyridine and its Derivatives

Mustafa Saçmacı,* Hilal Bölükbaşı, and Ertan Şahin†

*Department of Chemistry, Faculty of Arts and Sciences, Bozok University, Yozgat, Turkey. *E-mail: msacmaci@hotmail.com*
†Department of Chemistry, Faculty of Science, Atatürk University, Erzurum, Turkey
Received October 1, 2011, Accepted November 3, 2011

The furan-2-ylidene acetates (**3a-d**), obtained from the furan-2,3-diones (**1a-b**) and methyl/ethyl (triphenylphosphoranylidene)-acetates (**2a-b**), were converted via the Michael type reactions with 2,3-diaminopyridine and its derivatives (**4a-c**) into the corresponding pyrrol-2-ylidene-acetates (**5a-j**) in moderate yields (45-94%). Structures of these compounds were determined by the IR, NMR, elemental analysis, and X-ray diffraction method.

Key Words : Pyrrol-3-on, Furan-3-on, 2,3-Diaminopyridine, Wittig Reaction, X-ray structure

Introduction

Pyrrole is one of the most important heterocyclic compounds, having become increasingly important in medicinal chemistry and organic synthesis.[1,2] Pyrrole and its derivatives have shown to possess biological activities such as antibacterial,[3] antitumor,[4] analgesics,[5] antitubercular,[6,7] *anti*-inflammatory, and antiallergic.[8] There are various methods to prepare the synthetic and non-synthetic pyrrole derivatives.[9-11] Recently, a convenient method for pyrrole synthesis, the mechanism of reactions on the interaction of some 2,3-dihydro-furan-3-ones with various nucleophiles, as several primary amines, hydrazines, α/β amino acids, esters and amides, have been reported by our laboratory working group.[12-14]

In this last study, we attempted both to prove reproducibility of the reaction of furan-3-ones (**3a-d**) with 2,3-diaminopyridine and its derivatives (**4a-c**) and to extend our investigations related to preparing new series of substituted pyrroles (**5a-j**). These compounds seem to be suitable candidates for further chemical modification and may show pharmacologically active.

Experimental

Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. Elemental analysis (C, H, N) were carried out using LECO-932 CHNS-O analyzer. IR spectra were recorded on a Perkin Elmer Spectrum 400 FT-IR Spectrometer by using KBr method. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR were obtained Bruker Ultrashield spectrometer using $Si(CH_3)_4$ as the reference. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried by refluxing with appropriate drying agents and distilled before use. All experiments were followed by tlc using DC Alufolien Kieselgel 60 F 254 Merck and Camag TLC lamb (254/366 nm).

General Procedures for Furan-3-one Derivatives (3a-d). Previosly, methyl/ethyl (*Z*)-[2,3-dihydro-4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-3-oxo-furan-2-ylidene]-acetates (**3a-b**) were prepared according to the published method.[12,13] Compounds (**3c-d**) were synthesized as the following procedure: 1.0 mmol 4-ethoxycarbonyl-5-methoxyphenyl-2,3-dihydro-2,3-furandione[15] (**1b**) and methyl/ethyl (triphenylphosphoranylidene)-acetates (**2a-b**) were refluxed in benzene for 3 hours. The solvent was evaporated under reduced pressure to give an oily residue which was triturated with anhydrous ether and finally recrystallized from indicated solvents or mixture for each compound: **3c**: *i*-propanol, **3d**: dichloromethane-cyclohexane.

Methyl-(*Z*)-[2,3-dihydro-4-ethoxycarbonyl)-5-(4-methoxyphenyl)-3-oxofuran-2-ylid-ene]-acetate (3c). Yield 86%; mp 103 °C; IR (KBr, cm^{-1}): ν 3065 (arom. C-H), 3000-2933 (alif. C-H), 1720, 1703, 1675 (C=O), 1602, 1584 (C=C), 1231 (C-O-C). ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.30-7.02 (m, 4H, Ar-H), 6.20 (s, 1H, =C-H), 4.43, 4.41, 4.39, 4.36 (q, 2H, J = 7.14 Hz, -CH_2), 3.94, 3.87 (s, 3H, -OCH_3), 1.42, 1.39, 1.37 (t, 3H, J = 7.14 Hz, 7.14 Hz, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 183.06 (C=O, ring), 180.51 (MeO-C=O), 165.07 (EtO-C=O), 163.91, 162.35, 150.99, 132.87, 119.00, 114.36, 107.90, 100.25 (C=C, arom. and alif.), 61.47 (Me-CH_2), 55.47, 52.32 (OCH_3), 14.19 (CH_3). Anal. Calcd. for $C_{17}H_{16}O_7$: C, 61.44; H, 4.85. Found: C, 61.20; H, 4.60.

Ethyl-(*Z*)-[2,3-dihydro-4-ethoxycarbonyl)-5-(4-methoxyphenyl)-3-oxofuran-2-ylid-ene]-acetate (3d). Yield 91%; mp 143 °C; IR (KBr, cm^{-1}): ν 3056 (arom. C-H), 2987-2844 (alif. C-H), 1710, 1693 (C=O), 1603, 1574 (C=C), 1173 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.28-6.99 (m, 4H, Ar-H), 6.12 (s, 1H, =C-H), 4.41, 4.39, 4.36, 4.34, (q, 2H, J = 7.12 Hz, -OCH_2-furan ring), 4.32, 4.30, 4.27, 4.26 (q, 2H, J = 7.12 Hz, -OCH_2), 3.90 (s, 3H, -OCH_3), 1.39, 1.38, 1.37 (t, 3H, J = 7.12 Hz, -CH_3-furan ring), 1.36, 1.34, 1.33 (t, 3H, J = 7.12, Hz, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 183.06 (C=O-ring), 180.39 (MeO-C=O), 165.04 (EtO-C=O), 163.45, 162.34, 150.83, 133.17, 132.01, 128.57, 114.34, 107.89, 100.74 (C=C, arom. and alif.), 61.41, 61.19

(Me-CH_2), 55.71 (OCH_3), 14.18, 13.95 (CH_3). Anal. Calcd. for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found: C, 62.60; H, 5.45.

General Procedures for Pyrrol-3-one Derivatives (5a-j). 1.0 mmol furan-3-ones (**3a-d**) and 2,3-diaminopyridine and its derivatives (**4a-c**) were refluxed in methanol for 3 hours. After the solvent was removed by evaporation to give an oily residue which was triturated with anhydrous ether and finally recrystallized from indicated solvent or solvent mixtures for each compound: **5a**, **5b** and **5d**: benzen-petrol ether; **5c**: ethyl acetate; **5e** and **5f**: aceton-petrol ether; **5g**, **5h**, **5i** and **5j**: *i*-propanol.

Methyl-(2*RS*)-[1-(2-amino-5-bromopyridin-3-yl)-4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-3-oxo-1,3-dihydro-2*H*-pyrrol-2-ylidene]-acetate (5a). Yield 63%; mp 135 ºC; IR (KBr, cm^{-1}): ν 3465 (OH), 3345 (NH_2), 3050 (arom. C-H), 2952-2839 (alif. C-H), 1700-1693 (C=O), 1600-1574 (arom. C=C, C=N), 1252, 1229, 1171 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.95-6.59 (m, 10H, Ar-H), 5.88 (s, 1H, OH), 3.85, 3.74, 3.67 (s, 3H, -OCH_3), 3.29, 3.23, 2.83, 2.77 (dd, J_{gem} = 16.35, 2H, -CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 195.15, 189.52, 179.27 (C=O), 169.67, 163.68, 162.23, 156.43, 148.41, 140.69, 132.51, 131.14, 130.94, 120.49, 119.19, 114.07, 113.51, 113.18, 105.41 (C=C and C=N, arom.- alif.), 90.25 (C-OH), 55.47, 55.32, 52.27 (OCH_3), 39.21 (-CH_2). Anal. Calcd. for $C_{27}H_{24}BrN_3O_7$: C, 55.68; H, 4.15; N, 7.21. Found: C, 55.45; H, 4.30, N, 7.10.

Methyl-(2*RS*)-[1-(2-amino-5-chloropyridin-3-yl)-4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-3-oxo-1,3-dihydro-2*H*-pyrrol-2-ylidene]-acetate (5b). Yield 52%; mp 109 ºC; IR (KBr, cm^{-1}): ν 3460 (OH), 3344 (NH_2), 3199 (arom. C-H), 2953-2839 (alif. C-H), 1702-1691 (C=O), 1599-1574 (arom. C=C, C=N), 1251, 1228, 1171 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.95-6.28 (m, 10H, Ar-H), 5.78 (s, 1H, OH), 3.83, 3.72, 3.60 (s, 3H, -OCH_3), 3.14, 3.09, 2.77, 2.74 (dd, J_{gem} = 16.41, 2H, -CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 194.51, 188.39, 177.93 (C=O), 169.49, 163.38, 161.73, 157.42, 132.17, 132.02, 131.74, 130.65, 130.35, 116.69, 114.36, 114.20, 113.84, 113.75, 117.17 (C=C and C=N, arom.- alif.), 90.40 (C-OH), 55.97, 55.76, 52.44 (OCH_3), 39.97 (CH_2). Anal. Calcd. for $C_{27}H_{24}ClN_3O_7$: C, 60.28; H, 4.50; N, 7.81. Found: C, 60.40; H, 4.20, N, 7.57.

Ethyl-(2*RS*)-[1-(2-aminopyridin-3-yl)-4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-3-oxo-1,3-dihydro-2*H*-pyrrol-2-ylidene]-acetate (5c). Yield 87%; mp 145 ºC; IR (KBr, cm^{-1}): ν 3419 (OH), 3291 (NH_2), 3159 (arom. C-H), 2977-2838 (alif. C-H), 1735, 1719, 1663 (C=O), 1635, 1598, 1574 (arom. C=C, C=N) 1248, 1223, 1176 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.90-6.30 (m, 11H, Ar-H), 6.04 (s, 1H, OH), 4.16, 4.12, 4.06, 4.03 (q, 2H, -OCH_2), 3.84, 3.71 (s, 3H, -OCH_3), 3.28, 3.22, 2.86, 2.80 (dd, J_{gem} = 17.23, 2H, -CH_2), 1.29, 1.27, 1.24 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 195.27, 188.99, 179.57 (C=O), 169.14, 163.48, 161.96, 157.58, 147.36, 139.00, 132.43, 131.21, 131.18, 121.01, 118.77, 113.85, 113.35, 113.02, 112.85 (C=C and C=N, arom.- alif.), 90.14 (C-OH), 61.05 (OCH_2), 55.41, 55.24 (OCH_3), 39.28 (CH_2), 14.06 (CH_3). Anal. Calcd. for $C_{28}H_{27}N_3O_7$: C, 63.46; H, 5.82; N, 6.94. Found: C, 63.10; H, 5.50, N, 6.82.

Ethyl-(2*RS*)-[1-(2-amino-5-bromopyridin-3-yl)-4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-3-oxo-1,3-dihydro-2*H*-pyrrol-2-ylidene]-acetate (5d). Yield 59%; mp 102 ºC; IR (KBr, cm^{-1}): ν 3400 (OH), 3347 (NH_2) 3000 (arom. C-H), 2978-2975 (alif. C-H), 1700-1690 (C=O), 1601, 1575, 1500 (arom. C=C, C=N) 1254, 1229, 1172 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.96-6.60 (m, 10H, Ar-H), 6.02 (s, 1H, OH), 4.14, 4.12, 4.10, 4.08 (q, 2H, -OCH_2), 3.85, 3.75 (s, 3H, -OCH_3), 3.26, 3.20, 2.80, 2.79 (dd, J_{gem} = 16.65, 2H, -CH_2), 1.25, 1.23, 1.20 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 195.02, 189.45, 179.14 (C=O), 169.30, 163.66, 162.24, 156.16, 141.16, 132.49, 132.08, 131.10, 130.73, 120.45, 119.56, 114.11, 113.49, 113.29, 105.27 (C=C and C=N, arom.-alif.), 90.21 (C-OH), 61.49 (OCH_2), 55.47, 55.33 (OCH_3), 39.36 (CH_2), 14.12 (CH_3). Anal. Calcd. for $C_{28}H_{26}N_3BrN_3O_7$: C, 56.39; H, 4.39; N, 7.05. Found: C, 56.10; H, 4.20, N, 6.90.

Ethyl-(5*RS*)-1-(2-aminopyridin-3-yl)-5-(2-methoxy-2-oxoethylidene)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5e). Yield 94%; mp 121 ºC; IR (KBr, cm^{-1}): ν 3443 (OH), 3338 (NH_2), 3200 (arom. C-H), 3000-2987 (alif. C-H), 1715-1689 (C=O), 1606, 1577, 1537 (arom. C=C, C=N), 1253, 1213, 1176 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.93-6.36 (m, 7H, Ar-H), 5.88 (s, 1H, OH), 4.15, 4.12, 4.10, 4.08 (q, 2H, -OCH_2), 3.78, 3.61 (s, 3H, -OCH_3), 3.12, 3.06, 2.84, 2.79 (dd, J_{gem} = 16.75, 2H, -CH_2), 1.16, 1.14, 1.12 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 195.26, 181.31, 169.73 (C=O), 162.29, 161.81, 158.03, 147.95, 139.34, 130.63, 121.24, 117.75, 113.30, 113.11, 102.42 (C=C and C=N, arom.- alif.), 89.74 (C-OH), 59.95 (OCH_2), 55.27, 52.20 (OCH_3), 38.52 (CH_2), 14.16 (CH_3). Anal. Calcd. for $C_{22}H_{23}N_3O_7$: C, 59.86; H, 5.25; N, 9.52. Found: C, 59.60; H, 5.10, N, 9.30.

Ethyl-(5*RS*)-1-(2-amino-5-bromopyridin-3yl)-5-(2-methoxy-2-oxoethylidene)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5f). Yield 70%; mp 171 ºC; IR (KBr, cm^{-1}): ν 3392 (OH), 3345 (NH_2), 3050 (arom. C-H), 3000-2952 (alif. C-H), 1737, 1703, 1661 (C=O), 1602, 1575, 1531 (arom. C=C, C=N), 1254, 1203, 1179 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.95-6.76 (m, 6H, Ar-H), 5.88 (s, 1H, OH), 4.14, 4.11, 4.09, 4.07 (q, 2H, -OCH_2), 3.80, 3.63 (s, 3H, -OCH_3), 3.16, 3.10, 2.84, 2.83 (dd, J_{gem} = 16.60, 2H, -CH_2), 1.15, 1.13, 1.10 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 195.02, 181.06, 169.55 (C=O), 163.22, 162.03, 156.88, 148.79, 141.18, 130.62, 120.90, 118.54, 113.48, 105.51, 102.95 (C=C and C=N, arom.- alif.), 89.89 (C-OH), 60.10 (OCH_2), 55.33, 52.31 (OCH_3), 38.78 (CH_2), 14.13 (CH_3). Anal. Calcd. for $C_{22}H_{22}BrN_3O_7$: C, 50.78; H, 4.26; N, 8.08. Found: C, 50.60; H, 3.97, N, 8.20.

Ethyl-(5*RS*)-1-(2-amino-5-chloropyridin-3yl)-5-(2-methoxy-2-oxoethylidene)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5g). Yield 58%; mp 176 ºC; IR (KBr, cm^{-1}): ν 3406 (OH), 3345 (NH_2), 3160 (arom. C-H), 3000-2986 (alif. C-H), 1736, 1705, 1659 (C=O), 1602, 1575, 1531 (arom. C=C, C=N), 1251, 1204, 1177 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.86-6.79 (m, 6H, Ar-

H), 5.92 (s, 1H, OH), 4.10, 4.09, 4.06, 4.05 (q, 2H, -OCH_2), 3.79, 3.62 (s, 3H, -OCH_3), 3.18, 3.12, 2.81, 2.77 (dd, J_{gem} = 16.64, 2H, -CH_2), 1.14, 1.11, 1.09 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 195.13, 181.09, 169.35 (C=O), 163.19, 162.00, 156.67, 146.54, 138.69, 130.60, 120.98, 118.83, 118.16, 113.47, 103.01 (C=C and C=N, arom.- alif.), 89.92 (C-OH), 60.03 (OCH_2), 55.29, 52.20 (OCH_3), 38.88 (CH_2), 14.11 (CH_3). Anal. Calcd. for $C_{22}H_{22}ClN_3O_7$: C, 55.53; H, 4.66; N, 8.83. Found: C, 55.30; H, 4.40, N, 8.70.

Ethyl-(5*RS*)-1-(2-aminopyridin-3-yl)-5-(2-ethoxy-2-oxo-ethylidene)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5h). Yield 73%; mp 169 ºC; IR (KBr, cm^{-1}): ν 3400 (OH), 3306 (NH_2), 3196 (arom. C-H), 3069-2976 (alif. C-H), 1720-1665 (C=O), 1608, 1596, 1578 (arom. C=C, C=N), 1247, 1214, 1177 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.86-6.40 (m, 7H, Ar-H), 6.07 (s, 1H, OH), 3.99, 3.98, 3.97, 3.95, 3.94, 3.93, 3.92, 3.91 (q, 2H, -OCH_2), 3.73 (s, 3H, -OCH_3), 3.00, 2.95, 2.52, 2.51 (dd, J_{gem} = 16.31, 2H, -CH_2), 1.14, 1.11, 1.09, 1.04, 1.03, 1.02 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 193.85, 179.78, 168.41 (C=O), 162.80, 161.25, 158.61, 148.64, 140.93, 130.45, 122.37, 116.69, 113.50, 113.47, 102.33 (C=C and C=N, arom.- alif.), 89.80 (C-OH), 61.24, 61.00 (OCH_2), 55.65 (OCH_3), 39.43 (CH_2), 14.54, 14.24 (CH_3). Anal. Calcd. for $C_{23}H_{25}N_3O_7$: C, 60.65; H, 5.53; N, 9.23. Found: C, 60.40; H, 5.25, N, 9.10.

Ethyl-(5*RS*)-1-(2-amino-5-bromopyridin-3-yl)-5-(2-ethoxy-2-oxoethylidene)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5i). Yield 45%; mp 161 ºC; IR (KBr, cm^{-1}): ν 3418 (OH), 3297 (NH_2), 3159 (arom. C-H), 3000-2984 (alif. C-H), 1730, 1705, 1657 (C=O), 1601, 1574, 1532 (arom. C=C, C=N), 1251, 1197, 1175 (C-O-C). ^{1}H NMR (DMSO): δ (ppm) = 7.96-6.90 (m, 6H, Ar-H), 6.34 (s, 1H, OH), 4.07, 4.04, 4.02, 4.00, 3.98, 3.97, 3.95, 3.93 (q, 2H, -OCH_2), 3.75 (s, 3H, -OCH_3), 3.02, 2.97, 2.71, 2.66 (dd, J_{gem} = 16.68, 2H, -CH_2), 1.14, 1.12, 1.09, 1.05, 1.03, 1.00 (t, 3H, -CH_3). ^{13}C NMR (DMSO): δ (ppm) = 193.92, 180.35, 169.92 (C=O), 168.61, 162.65, 161.15, 157.67, 148.90, 140.78, 130.44, 122.05, 117.88, 113.69, 103.76 (C=C and C=N, arom.- alif.), 90.03 (C-OH), 61.13, 59.13 (OCH_2), 55.73 (OCH_3), 39.13 (CH_2), 14.28, 14.02 (CH_3). Anal. Calcd. for $C_{23}H_{24}BrN_3O_7$: C, 51.70; H, 4.53; N, 7.86. Found: C, 51.50; H, 4.20, N, 7.65.

Ethyl-(5*RS*)-1-(2-amino-5-chloropyridin-3-yl)-5-(2-ethoxy-2-oxoethylidene)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5j). Yield 52%; mp 182 ºC; IR (KBr, cm^{-1}): ν 3481 (OH), 3370 (NH_2), 3217 (arom. C-H), 2983-2947 (alif. C-H), 1723, 1695, 1674 (C=O), 1606, 1575, 1532 (arom. C=C, C=N), 1255, 1199, 1178 (C-O-C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.85-6.79 (m, 7H, Ar-H), 5.95 (s, 1H, OH), 4.16, 4.11, 4.10, 4.09, 4.07, 4.06, 4.05, 4.01 (q, 2H, -OCH_2), 3.79 (s, 3H, -OCH_3), 3.17, 3.12, 2.81, 2.76 (dd, J_{gem} = 16.68, 2H, -CH_2), 1.21, 1.19, 1.16, 1.13, 1.11, 1.09 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 195.21, 180.99, 168.89 (C=O), 163.20, 161.89, 156.66, 146.45, 138.76, 130.61, 121.00, 118.79, 118.23, 113.46, 103.06 (C=C and C=N, arom.- alif.), 89.99 (C-OH), 61.40, 60.00 (OCH_2), 55.29 (OCH_3), 39.22 (CH_2), 14.12, 13.98 (CH_3). Anal. Calcd. for $C_{23}H_{24}ClN_3O_7$: C, 64.98; H, 5.26; N, 8.12. Found: C, 64.70; H, 5.10, N, 7.95.

X-Ray Crystallography. For the crystal structure determination, the single-crystal of compound **5c** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å) and oscillation scans technique with Δω = 5º for one image were used for data collection. The lattice parameters were determined by the least-squares method on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using Crystal Clear (Rigaku/MSC Inc., 2005) software.[16] The structures were solved by direct methods using SHELXS-97[17] and refined by a full-matrix least-squares procedure using the program SHELXL-97.[17] H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance.

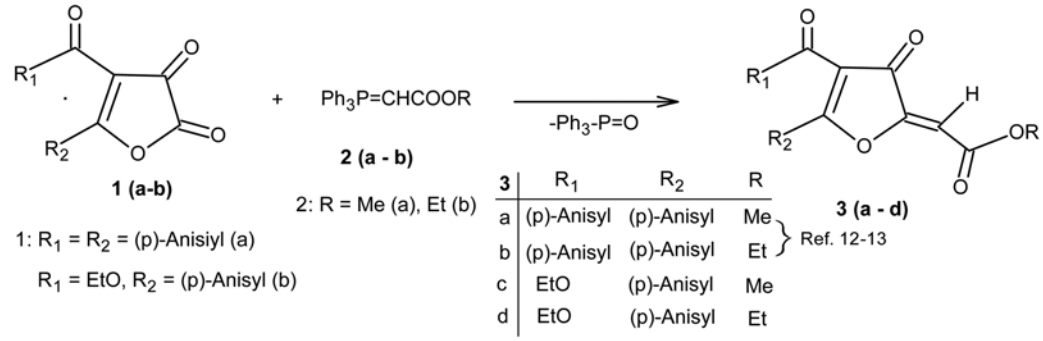
Crystal Data for 5c: Compound **5c** ($C_{28}H_{27}N_3O_7$), which consists of two enantiomers, is a racemic mixture of 2,3-dihydro-1*H*-pyrrol-3-ones. Crystal system, space group: triclinic, *P*-1; (no: 2); unit cell dimensions: a = 9.6257(5), b = 10.5194(8), c = 14.8406(10) Å, α = 104.86(4), β = 97.67(3), γ = 93.73(3)º; volume: 1431.7(2) $Å^3$; Z = 2; calculated density: 1.29 g/cm^3; absorption coefficient: 0.095 mm^{-1}; F(000): 584; θ range for data collection 2.2-26.5º; refinement method: full-matrix least-square on F^2; data/parameters: 2767/387; goodness-of-fit on F^2: 1.037; final R indices [$I > 2\sigma(I)$]: R_1 = 0.082, wR_2 = 0.202; R indices (all data): R_1 = 0.164, wR_2 = 0.256; largest diff. peak and hole: 0.398 and −0.240 $eÅ^3$. Crystallographic data were deposit with CSD under CCDC registration number 834923.

These data can be obtained free of charge from The *Cambridge Crystallographic Data Centre* (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

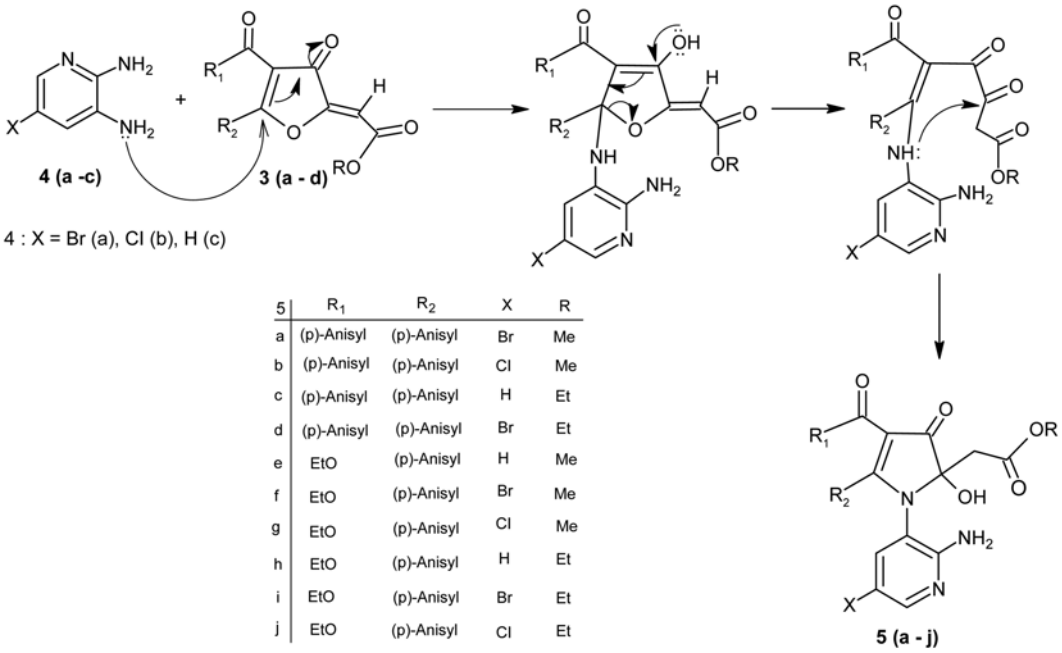
In a first step of this study, the Wittig reactions were carried out by 4-ethoxycarbonyl-5-methoxy phenyl-2,3-dihydro-2,3-furandione (**1b**) with methyl/ethyl (triphenylphosphoranylidene)-acetates (**2a-b**) in refluxing benzene to give (**3c-d**) as shown in Scheme 1. In the next step of the study, the reactions of 2,3-dihydrofuran-3-ones (**3a-d**) with 2,3-diaminopyridine and its derivatives (**4a-c**) were performed in refluxing methanol at 1-4 h. A number of pyrrole derivatives (**5a-j**) were obtained in moderate yields (45-94%) from the reaction of (**3a-d**) and the corresponding (**4a-c**).

In recent years, few Wittig reactions with some furan-2,3-diones have been reported, and the reactions of some 2,3-dihydrofuran-3-ones with non-heterocyclic diamines have been reported by our working group.[12-14] However, the reactions of 2,3-dihydrofuran-3-ones with heterocyclic diamines as 2,3-diaminopyridine have not been reported so far.



3	R_1	R_2	R
a	(p)-Anisyl	(p)-Anisyl	Me
b	(p)-Anisyl	(p)-Anisyl	Et
c	EtO	(p)-Anisyl	Me
d	EtO	(p)-Anisyl	Et

Scheme 1. The Wittig reactions of furan-2,3-diones with phosphorans.



5	R_1	R_2	X	R
a	(p)-Anisyl	(p)-Anisyl	Br	Me
b	(p)-Anisyl	(p)-Anisyl	Cl	Me
c	(p)-Anisyl	(p)-Anisyl	H	Et
d	(p)-Anisyl	(p)-Anisyl	Br	Et
e	EtO	(p)-Anisyl	H	Me
f	EtO	(p)-Anisyl	Br	Me
g	EtO	(p)-Anisyl	Cl	Me
h	EtO	(p)-Anisyl	H	Et
i	EtO	(p)-Anisyl	Br	Et
j	EtO	(p)-Anisyl	Cl	Et

Scheme 2. Reactions of furan-3-ones with 2,3-diaminopyridines.

A reasonable proposal different from that discussed 2,3-diaminopyridine and its derivatives (**4a-c**) for reaction pathway from 2,3-dihydrofuran-3-ones (**3a-d**) to pyrrol derivatives (**5a-j**) is outlined briefly in Scheme 2. It is assumed that the amino group of 2,3-diaminopyridine attacks the C-5 position of the furan-3-one cycle leading to ring opening similar to a Michael type addition. Then, the intermediate formed the ring closure through nucleophilic addition of the N-H to the carbonyl (C=O) lead to the products (**5a-j**) as shown in Scheme 2. Synthesis of pyrrole systems *via* Michael type addition of several primary amines, hydrazines, α/β amino acids, esters and amides are well established.[12-14] The elucidation of the structures of (**5a-j**) was deduced mainly from elemental analysis and X-ray diffraction (in addition to, for compound **5c**), IR, ^{1}H and ^{13}C NMR spectroscopic data. The IR spectrum of **5c** showed characteristic absorption bands at 3419 cm^{-1} for OH group, at 3291 cm^{-1} for NH_2 group, at 1735, 1719 and 1663 cm^{-1} for (C=O) groups. The ^{1}H NMR spectrum of **5c** showed signals at 7.90-6.30 ppm for aromatic protons (Ar-H), at 6.04 ppm singlet signal for OH proton, at 4.16, 4.12, 4.06, 4.03 ppm quartet signals for (OCH_2) protons, at 3.28, 3.22, 2.86, 2.80 ppm signals two AB type doublets for CH_2, at 1.29, 1.27, 1.24 ppm for CH_3

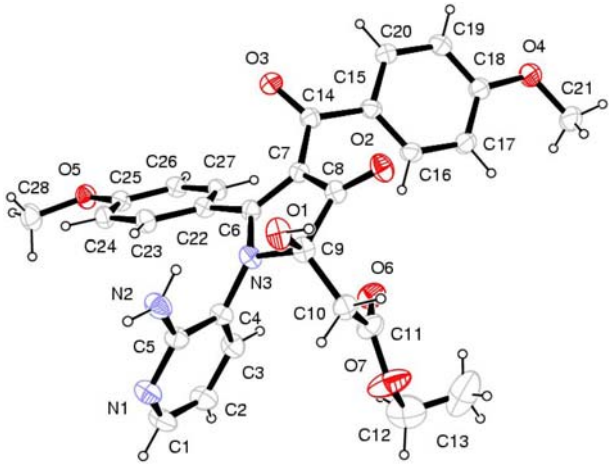


Figure 1. ORTEP drawing of the **5c** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 1

Selected Bond Lengths (Å)		
O(1)	H(10)	0.820(4)
O(1)	C(9)	1.415(6)
O(2)	C(8)	1.234(6)
O(3)	C(14)	1.216(6)
O(4)	C(18)	1.362(6)
O(4)	C(21)	1.429(7)
O(5)	C(25)	1.363(6)
O(5)	C(28)	1.427(7)
O(6)	C(11)	1.195(7)
N(3)	C(6)	1.376(6)
N(3)	C(4)	1.430(6)
N(2)	H(2A)	0.860(5)

Table 2

Selected Bond Angles (°)			
C(18)	O(4)	C(21)	118.1(5)
C(25)	O(5)	C(28)	116.8(4)
C(6)	N(3)	C(4)	124.6(4)
C(5)	N(1)	C(1)	118.1(5)
N(3)	C(6)	C(22)	119.9(4)
N(3)	C(6)	C(7)	112.8(4)

Table 3

Selected Torsion Angles (°)				
C(21)	O(4)	C(18)	C(17)	1.1
C(21)	O(4)	C(18)	C(19)	-178.5
C(4)	N(3)	C(6)	C(22)	25.3
C(4)	N(3)	C(6)	C(7)	-154.5
N(3)	C(4)	C(3)	C(2)	-178.2
C(3)	C(4)	C(5)	N(2)	-175.7
C(3)	C(4)	C(5)	N(1)	2.0

Table 4

Hydrogen-bond geometry (Å, º)				
D–H···A	*D*–H	H···A	*D*···A	∠*D*–H···A
O(1)–H(1O)···O(2)	^{i}0.82	1.90	2.706(4)	169
N(2)–H(2A)···N(1)	^{ii}0.86	2.23	3.085(6)	177

Symmetry codes: (i) –x, –y, –z; (ii) 1–x, 1–y, –z.

protons. The ^{13}C NMR spectrum of **5c** showed signals at 195.27, 188.99, 179.57 ppm for carbons of (C=O) groups, at 169.14-112.85 ppm for (C=C), at 90.14 ppm for (C-OH), at 61.05 ppm for (OCH_2), at 55.41, 55.24 ppm for (OCH_3), 39.28 ppm for (CH_2), 14.06 ppm for (CH_3).

The ORTEP drawing of **5c** with the atomic labelling was shown in Figure 1 and selected bond lengths, bond angles and torsion angles were given in Table 1-4. Compound **5c** crystallize in the triclinic space group *P*-1, containing two formula units and the disordered solvent ethyl acetate in the unit cell. The structure consists of hydrogen bonded chains running along the [110] axis referring to Table 4, O(1)-H(1O)···O(2) and N(2)-H(2A)···N(1) are the intramolecular hydrogen bonds detected in the structure. These bonds link the molecules into chain as shown in Figure 2.

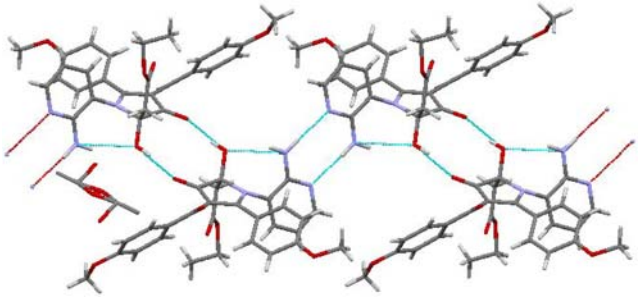


Figure 2. *H*-bonded chains running along the [110] axis of **5c**.

Acknowledgments. This work was financially supported by the Research Center of Bozok University (Project No: I. F. E/2010-27).

References and Notes

1. Robertson, J.; Hatley, R. J. D.; Watkin, D. J. *J. Chem. Soc. Perkin Trans 1* **2000**, *20*, 3389.
2. Robinson, R. S.; Dovey, M. C.; Gravestock, D. *Tetrahedron Lett*. **2004**, *45*, 6787.
3. Demirayak, S.; Karaburun, A. C.; Kiraz, N. *Eur. Journal of Med. Chem*. **1999**, *34*, 275.
4. Halazy, S.; Magnus, P. *Tetrahedron Lett*. **1984**, *25*, 1421.
5. Thiault, G. A.; Guen, Y. Le, Boucherle, Walrant, A. P. *Farmaco Sci*. **1984**, *39*, 524.
6. Bijev, A. *Arzneim.-Fors/Drug Res*. **2006**, *56*, 96.
7. Sbardella, G.; Mai, A.; Artico, M.; Loddo, R.; Setzuc, M. G.; Collac, P. L. *Biorg. Med. Chem. Lett*. **2004**, *14*, 1537.
8. Brikner, C.; Leyck, S.; Christ, B. K. Kesselring, German Patent 3, **1986**, 506.
9. Schmuck, A. C.; Rupprecht, D. *Synthesis* **2007**, 3095.
10. Bellina, F.; Rossi, R. *Tetrahedron* **2006**, *62*, 7213.
11. Balme, G. *Angew. Chem. Int. Ed*. **2004**, *43*, 6238.
12. Üngören, Ş. H.; Saçmacı, M.; Akçamur, Y.; Arıcı, C.; Ülkü, D. *J. Heterocyclic Chem*. **2004**, *41*, 151.
13. Saçmacı, M.; Üngören, Ş. H.; Akçamur, Y. *Amino Acids* **2006**, *31*, 397.
14. Saçmacı, M.; Üngören, Ş. H.; Akçamur, Y.; Arıcı, C.; Ülkü, D. *Heteroatom Chemistry* **2005**, *16*, 235.
15. Saalfrank, R. W.; Lutz, T.; Hörner, B.; Gündel, J.; Peters, K.; von Schnering, H. G. *Chem. Ber*. **1991**, *124*, 2289.
16. Rigaku/MSC, Inc., 9009 New Trails Drive, The Woodlands, TX 77381.
17. Sheldrick, G. H. SHELXS97 and SHELXL97. [Program for Crystal Structure Solution and Refiniment], University of Göttingen, Germany, 1997.