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Benzo[*b*]furan in the Povarov reaction

Gulnaz F. Krainova, Yulia O. Chudinova, Alexey A. Gorbunov, Olga A. Mayorova and Vladimir A. Glushkov*

General methods

All the chemicals used were reagent grade as supplied from Alfa Aesar. Melting points were determined on automated melted point system OptiMelt (Stanford Research Systems, USA). Analytical thin-layer chromatography was performed using silica gel plates *Sorbfil* in hexanes−AcOEt mixture (1:1, v/v); compound spots were visualized by UV light (254 nm) and/or by staining with 5% H_2SO_4 and heating (120-150 °C). Flash chromatography was performed on silica gel 60 (220-440 Mesh, Alfa Aesar). IR spectra were recorded on a Bruker IFS 66ps spectrometer in thin film performed after evaporation of solution of compounds in $CHCl_3$ just on the glass. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury+300 instrument at 300 and 75 MHz respectively, in $CDCl_3$ or DMSO-d_6 and were referenced to HMDS (^{1}H NMR δ=0.055 ppm) and residual $CHCl_3$ (^{13}C NMR δ=77.0 ppm). Mass spectra were recorded on GC-MS system Agilent 6890N series with mass-selective detector MSD 5975B (EI, 70 eV). Elemental analyses (C,H,N) were obtained using Leco CHNS 9321P elemental analyzer at the Institute of Technical Chemistry, Perm.

General procedure for imines **1-3**.

Substituted aniline (1 mmol) was dissolved in 20 ml toluene (for **1**,**2**) or ethanol (for **3**); and ethyl glyoxylate (2 mmol, 50% in toluene), corresponding aryl glyoxal (1 mmol) or aromatic aldehyde (1 mmol) was added (it was profitable to use molecular sieves (4A) in some cases). After 1 h of reflux, solvent was evaporated, residue was recrystallized from ethanol (**1**,**3**) or AcOEt/hexanes (**2**).

Ethyl 4-bromophenyliminoacetate **1a** was synthesized earlier [Z.-B. Zhu, L.-X. Shao and M. Shi, *Eur. J. Org. Chem.*, 2009, no. 15, 2576]. Yield 88%. Colorless crystals. R_f 0.65, mp 138.4 °C. IR (ν, cm^{-1}): 1726 (C=O), 1592 (CH=N), 1373, 1293, 1233, 1147, 1020, 814. ^{1}H NMR, δ: 0.91 t

(3H, *J* = 7.2 Hz, $\underline{CH_3}CH_2$), 3.06 q (2H, *J* = 7.2 Hz, $O\underline{CH_2}CH_3$), 6.24 d (2H, *J* = 7.2 Hz, 3,5-H), 7.18 m (2H, *J* = 7.2 Hz, 2,6-H), 7.88 s (1H, CH=N); GC-MS *m/z* 256 ($M^{+\cdot}$).

Ethyl 4-methylphenyliminoacetate **1b**. Yield 41%. Colorless crystals. R_f 0.68. mp 96.3 °C. IR (*v*, cm^{-1}): 1730 (C=O), 1615 (CH=N), 1517, 1376, 1297, 1228 1147, 1026, 810. ^1H NMR, *δ*: 1.39 t (3H, *J* = 6.9 Hz, $\underline{CH_3}CH_2$), 2.36 s (3H, CH_3), 4.40 q (2H, *J* = 6.9 Hz, $O\underline{CH_2}CH_3$), 6.60 d (2H, *J* = 8.1 Hz, 3,5-H), 6.96 d (2H, *J* = 8.1 Hz, 2,6-H), 7.91 s (1H, CH=N). GC-MS *m/z* 191 ($M^{+\cdot}$).

Ethyl 4-ethoxycarbonylphenyliminoacetate **1c**. Yield 95%. Yellow crystals. R_f 0.60, mp 107.7 °C. IR (*v*, cm^{-1}): 1754 (C=O), 1605 (CH=N), 1525, 1319, 1232, 1155, 1073, 1020, 940, 849. ЯМР ^1H NMR, *δ*: 1.23 t (3H, CH_3), 1.33 t (3H, CH_3), 4.27 m (4H, $2OCH_2$), 5.40 s (1H, CH=N), 6.67 d (2H, H_{arom}), 7.86 d (2H, H_{arom}). GC-MS *m/z* 249 ($M^{+\cdot}$).

Compounds **2a-c** were isolated from hexanes/ethyl acetate mixture as solvates with ethyl acetate; moreover, **2a-c** were detected as a mixture of *anti/syn* isomers.

1-(4-Methoxyphenyl)-2-(phenylimino)ethanone **2a**. Yield 86%. Bright yellow crystals. R_f 0.60, mp 73.9 °C. IR (*v*, cm^{-1}): 1677 (C=O), 1598 (CH=N), 1515, 1376, 1306, 1260, 1177, 1149, 1024, 927, 820. ^1H NMR, *δ*: 3.89 s (3H, OCH_3), 6.98 d (2H, *J* = 9.3 Hz, 3',5'-H), 7.13 t (2H, *J* = 9.3 Hz, 2',6'-H), 8.07 d (2H, *J* = 9.3 Hz, 2,6-H), 8.26 s (1H, N=CH), 8.33 d (2H, *J* = 9.3 Hz, 3,5-H). GC-MS *m/z* 257 ($M^{+\cdot}$).

1-(4-Methoxyphenyl)-2-(4'-flourophenylimino)ethanone **2b**.Yield 86%. Bright yellow crystals. R_f 0.60, mp 73.9 °C. IR (*v*, cm^{-1}): 1677 (C=O), 1598 (CH=N), 1515, 1376, 1306, 1260, 1177, 1149, 1024, 927, 820. ^1H NMR, *δ*: 3.89 s (3H, OCH_3), 6.98 d (2H, *J* = 9.3 Hz, 3',5'-H), 7.13 t (2H, *J* = 9.3 Hz, 2',6'-H), 8.07 d (2H, *J* = 9.3 Hz, 2,6-H), 8.26 s (1H, N=CH), 8.33 d (2H, *J* = 9.3 Hz, 3,5-H). GC-MS *m/z* 257 ($M^{+\cdot}$).

1-(4-Chlorophenyl)-2-(4'-flourophenylimino)ethanone **2c**. Yield 80%. Bright yellow crystals. R_f 0.65, mp 52.7 °C. IR (*v*, cm^{-1}): 1686 (C=O), 1589 (CH=N), 1306, 1256, 1209, 1158, 1094, 1047, 1006, 908, 816. ^1H NMR, *δ*: (major isomer) 7.14 m (2H, H_{aarom}), 7.36 m (2H, H_{arom}), 7.47 m (2H, 3,5-H), 8.14 s (1H, CH=N), 8.28 m (2H, 2,6-H). GC-MS *m/z* 261 ($M^{+\cdot}$).

Benzylideneaniline **3a** [lit., L. A. Bigelow and H. Eatough, *Organic Syntheses*, 1941, coll. vol. 1, p. 80]; benzylidene-4-flouroaniline **3b** [lit., A. Roe and J. A. Montgomery, *J. Am. Chem. Soc.*, 1953, **75**, 910].

*Diethyl (6*R*S**, 6a*R**, 11b*R**)-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline-2,6-dicarboxylate* **4c**. Yield 87%. Colorless needles, mp 140.5 °C, R_f 0.45. IR (thin film) (ν/cm^{-1}): 3376 (NH), 2983, 1740 (O-C=O), 1701 (O-C=O), 1609 (C=C), 1513, 1475, 1371, 1281, 1219, 1140, 1102, 961, 756; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (t, 3H, J = 7.2, Me), 1.40 (t, 3H, J = 7.2, Me), 4.07 (d, 1H, H-6, J = 2.4), 4.32 (q, 2H, J = 7.2, OCH_2), 4.42 (q, 2H, J = 7.2, OCH_2), 4.74 (d, 1H, J = 9.0, H-11b), 5.65 (dd, 1H, H-6a, ^3J = 9.0, 2.4), 6.63 (d, 1H, H-4, ^3J = 8.4), 6.73 (m, 1H, H_{arom}), 6.80 (m, 1H, H_{arom}), 7.07 (m, 1H, H_{arom}), 7.23 (m, 1H, H_{arom}), 7.71 (dd, 1H, H-3, ^3J = 8.4, ^4J = 2.1), 8.01 (d, 1H, H-1, ^4J = 2.1); NH group is not observed in the ^{1}H NMR spectrum due to proton exchange; ^{13}C NMR, δ: 14.18, 14.43, 42.99, 57.48, 60.51, 62.12, 83.39, 109.79, 115.28, 121.12, 121.77, 121.81, 123.69, 124.82, 128.74, 129.27, 129.58, 129.86, 148.00, 158.94, 166.47 (C=O), 168.87 (C=O), 168.89 (C=O). GC-MS *m/z* = 367 [$M^{+\cdot}$]. Found (%): C, 68.45; H, 5.15; N, 3.74. Calc. for $C_{21}H_{21}NO_5$ (%): C, 68.65; H, 5.76; N, 3.81.

*6-(4-Chlorobenzoyl)-2-fluoro-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline* **5c**. Yield 96%. Colorless needles, mp 186.0 °C, R_f 0.66. IR (thin film) (ν/cm^{-1}): 3423 (NH), 2921, 2842, 1687 (C=O), 1589 (C=C), 1493 (C=C), 1471, 1233, 1140, 1090, 1002, 804, 739; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (d, 1H, J = 9.3, H-11b), 4.13 (d, 1H, J = 2.1, H-6), 5.63 (dd, 1H, H-6a, ^3J = 9.3, 2.1), 6.65 (m, 2H, H_{arom}), 6.78 (m, 2H, H_{arom}), 7.00-7.07 (m, 2H, H_{arom}), 7.12 (d, 1H, J = 6.9, H_{arom}), 7.49 (d, 2H, H-3',5', ^3J = 8.4), 7.92 (d, 2H, H-2',6', ^3J = 8.4); NH group is not observed in the ^{1}H NMR spectrum due to proton exchange; ^{13}C NMR ($CDCl_3$), δ: 44.18, 62.40, 84.34, 109.77, 113.93, 114.23, 114.52, 117.78, 117.88, 121.09, 124.57, 126.23, 128.83, 129.27, 129.67, 133.71, 139.98, 159.40, 194.79(C=O). GC-MS *m/z* = 377 [$M^{+\cdot}$-2]. Found (%): C, 69.16; H, 3.65; N, 3.99. Calc. for $C_{22}H_{15}ClFNO_2$ (%): C, 69.57; H, 3.98; N, 3.69.