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## Azo Coupling of 5-Substituted Furan-2(3*H*)-ones and 1*H*-Pyrrol-2(3*H*)-ones with Arene(hetarene)diazonium Salts

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Abstract—5-Substituted furan-2(3H)-ones and 1-phenyl-1*H*-pyrrol-2(3H)-ones reacted with diazonium salts derived from substituted anilines and 1*H*-1,2,4-triazol-5-amine to give azo coupling products at the methylene group in the heteroring. The products were found to exist as hydrazone tautomers.

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Compounds having both imino and carbonyl groups in a single molecule are important for fine organic synthesis. Hydrazones derived from furancarbaldehydes and their nitrogen-containing analogs were used to synthesize various acyclic and heterocyclic compounds. N-Substituted furanimines were prepared via introduction of an imino group into furan ring and intramolecular cyclization of N-substituted 2-amino-4oxobut-2-enoic acids. Furan-2-imines can be obtained from 2,3-dihydrofuran-2,3-diones [1], as well as by intramolecular cyclization of imino derivatives of o-hydroxyphenylglyoxalic acid [2, 3] or 4-R-2,4-dioxobutanoic acids [4]. 4-R-2-Imino-4-oxobutanoic acids undergo spontaneous intramolecular cyclization on heating or by the action of dehydrating agents [5, 6]. Syntheses of hydrazones are generally based on cyclization of acyclic diazocarbonyl compounds [7–9]. In the present article we report on the reactions of

5-substituted furan-2(3H)-ones and 1-phenyl-1*H*-pyrrol-2(3H)-ones with diazonium salts. It is known that azo coupling reactions involve not only arenes activated by strong electron-donor groups but also aliphatic compounds possessing an activated methylene group [10].

4-Nitrobenzenediazonium chloride readily reacted with furan-2(3*H*)-ones in alcohol at -5 to 0°C (Scheme 1). The products were the corresponding arylhydrazones **Ia–Ic** which were isolated in up to 96% yield as orange–red crystals whose color is intrinsic to azo dyes. The reactions of furan-2(3*H*)-ones witt 1*H*-1,2,4-triazole-5-diazonium chloride were characterized by lower yield (~75%), and hetarylhydrazones **IIa** and **IIb** were colored deep red.

The azo coupling products I and II can exist as several tautomers (Scheme 2). Their IR spectra lacked absorption bands assignable to free or H-bonded hy-





 $I, R = Ph (a), C_5H_{11} (b), Bu (c); II, R = Ph (a), 4-MeC_6H_4 (b).$ 



 $R = Ph(a), C_5H_{11}(b), Bu(c), 4-MeC_6H_4(d).$ 

droxy group, but a broad band was observed in the region 3320–3200 cm<sup>-1</sup>. The latter was attributed to stretching vibrations of NH group involved in intramolecular hydrogen bond. The carbonyl absorption band was displaced toward lower frequencies (1760– 1750 cm<sup>-1</sup>), and a band at 1690–1675 cm<sup>-1</sup> (C=N) was present. The <sup>1</sup>H NMR spectra of these compounds contained no signal from methylene protons on C<sup>3</sup> in the furan ring, while signals from vinylic proton ( $\delta$  6.90–6.93 ppm, s) and aromatic protons ( $\delta$  7.30– 7.75 ppm, m) and a broadened signal at  $\delta$  8.2– 8.25 ppm (NH) were observed. These data indicated that compounds I and II exist as hydrazone tautomer **B** stabilized by intramolecular hydrogen bond.

Likewise, 5-substituted 1-phenyl-1*H*-pyrrol-2(3*H*)ones readily reacted with benzenediazonium chloride. However, the substrate molecule, apart from the  $C^{3}H_{2}$ methylene group, possesses one more center capable of reacting with diazonium salt, namely the benzene ring on the nitrogen atom. Therefore, the azo coupling with the above pyrrole derivatives could take different pathways.

Judging by the IR and <sup>1</sup>H NMR spectra of the products, the azo coupling in ethanol at -5 to 0°C occurred at the endocyclic methylene group in 5-substituted 1-phenyl-1*H*-pyrrol-2(3*H*)-ones with formation of compounds **IIIa–IIId**, while no structures like **D** were detected (Scheme 3). The IR spectra of **IIIa–IIId** retained carbonyl absorption band at 1765–1770 cm<sup>-1</sup> typical of unsaturated lactams; also, absorption bands belonging to C=N (1650–1640 cm<sup>-1</sup>) and NH stretching vibrations (3380–3200 cm<sup>-1</sup>, broadened) were present.

The <sup>1</sup>H NMR spectra were more informative from the viewpoint of determination of tautomer structure. Compounds **IIIa–IIId** displayed in the <sup>1</sup>H NMR spectra a singlet at  $\delta$  5.98–6.00 ppm from vinylic proton, signals from the substituent on C<sup>5</sup> ( $\delta$  0.85–2.02 ppm for 5-alkyl derivatives **IIIb** and **IIIc**). The absence of a doublet of doublets typical of methylene protons on C<sup>3</sup> in the initial pyrroles and the presence of a broadened NH signal at  $\delta$  8.50–8.56 ppm allowed us to conclude that benzenediazonium salt reacted with 5-substituted 1-phenyl-1*H*-pyrrol-2(3*H*)-ones at the endocyclic methylene group with formation of azo coupling products **IIIa–IIId** as hydrazone tautomer.

## EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrometer from samples dispersed in mineral oil. The <sup>1</sup>H NMR spectra were obtained on a Varian FT-80A spectrometer (80 MHz) from solutions in CDCl<sub>3</sub> using tetramethylsilane as internal reference. Initial 5-alkyl-(aryl)dihydrofuran-2(3*H*)-ones [11] and 5-alkyl(aryl)- 1-phenyl-1*H*-pyrrol-2(3*H*)-ones [12] were synthesized according to known procedures.

3-[2-(4-Nitrophenyl)hydrazinylidene]-5-phenylfuran-2(3*H*)-one (Ia). A solution of 1 g (6.25 mmol) of 5-phenylfuran-2(3*H*)-one was added dropwise under stirring to a freshly prepared solution of 0.8 g of (6.25 mmol) of 4-nitrobenzenediazonium chloride, cooled to -5 to 0°C. The precipitate was filtered off and recrystallized from hexane–chloroform. Yield 1.57 g (81%), orange–red crystals, mp 139–140°C. IR spectrum, v, cm<sup>-1</sup>: 3274 (NH), 1738 (C=O), 1648 (C=N), 1339 (NO<sub>2</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 6.90 s (1H, 4-H), 7.30–7.75 m (9H, H<sub>arom</sub>), 8.25 s (1H, NH). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 92.0, 113.2, 124.7, 127.9, 128.3, 130.3, 137.5, 149.1, 152.6, 153.7, 155.0 Found, %: C 62.54; H 3.90; N 13.56. C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>. Calculated, %: C 62.14; H 3.56; N 13.59.

Compounds **Ib**, **Ic**, **IIa**, **IIb**, and **IIIa–IIId** were synthesized in a similar way.

**3-[2-(4-Nitrophenyl)hydrazinylidene]-5-pentylfuran-2(3H)-one (Ib).** Yield 1.83 g (91%), orange–red crystals, mp 139–141°C. IR spectrum, v, cm<sup>-1</sup>: 3330 (NH), 1715 (C=O), 1629 (C=N), 1335 (NO<sub>2</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.85–2.05 m (11H, C<sub>5</sub>H<sub>11</sub>), 6.90 s (1H, 4-H), 7.20–7.40 m (4H, H<sub>arom</sub>), 8.25 s (1H, NH). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 14.1, 22.8, 28.4, 30.6, 31.9, 94.1, 113.8, 124.0, 137.9, 149.6, 152.4, 154.7, 171.5. Found, %: C 59.02; H 5.41; N 13.62. C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>. Calculated, %: C 59.40; H 5.61; N 13.86.

**5-Butyl-3-[2-(4-nitrophenyl)hydrazinylidene]furan-2(3***H***)-one (Ic). Yield 1.76 g (95%), orange–red crystals, mp 140–141°C. IR spectrum, v, cm<sup>-1</sup>: 3281 (NH), 1712 (C=O), 1630 (C=N), 1347 (NO<sub>2</sub>). <sup>1</sup>H NMR spectrum, \delta, ppm: 6.93 s (1H, 4-H), 0.87–2.02 m (9H, C<sub>4</sub>H<sub>9</sub>), 7.20–7.50 m (4H, H<sub>arom</sub>), 8.20 s (1H, NH). <sup>13</sup>C NMR spectrum, \delta\_{\rm C}, ppm: 14.5, 22.3, 29.1, 32.9, 94.8, 113.6, 12.1, 137.2, 148.4, 153.2, 155.4, 171.8. Found, %: C 58.02; H 5.31; N 14.62. C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>. Calculated, %: C 58.13; H 5.19; N 14.53.** 

**5-(4-Methylphenyl)-3-[2-(1***H***-1,2,4-triazol-5-yl)hydrazinylidene]furan-2(3***H***)-one (IIa). Yield 1.70 g (92%), yellow–orange crystals, mp 227–229°C. IR spectrum, v, cm<sup>-1</sup>: 3271 (NH), 1766 (C=O), 1596 (C=N). <sup>1</sup>H NMR spectrum, \delta, ppm: 2.25 s (3H, CH<sub>3</sub>), 5.99 s (1H, 4-H), 7.25–7.45 m (4H, H<sub>arom</sub>), 8.23 s (1H, N<sup>1</sup>H), 10.61 s (1H, NH). <sup>13</sup>C NMR spectrum, \delta\_{C}, ppm: 21.3, 92.0, 127.3, 128.9, 130.4, 137.6, 146.5, 147.3, 152.4, 154.0, 155.7. Found, %: C 58.21; H 3.88; N 26.18. C<sub>13</sub>H<sub>11</sub>N<sub>5</sub>O<sub>2</sub>. Calculated, %: C 57.99; H 4.12; N 26.01.**  **5-Phenyl-3-[2-(1***H***-1,2,4-triazol-5-yl)hydrazinylidene]furan-2(3***H***)-one (IIb). Yield 1.72 g (93%), yellow–orange crystals, mp 199–201°C. IR spectrum, v, cm<sup>-1</sup>: 3276 (NH), 1788 (C=O), 1688 (C=N). <sup>1</sup>H NMR spectrum, δ, ppm: 6.91 s (1H, 4-H), 7.20–7.40 m (5H, H<sub>arom</sub>), 8.20 s (1H, N<sup>1</sup>'H), 10.66 s (1H, NH). <sup>13</sup>C NMR spectrum, \delta\_C, ppm: 91.6, 127.9, 128.6, 130.0, 145.0, 147.7, 153.1, 153.8, 155.4. Found, %: C 56.94; H 3.52; N 27.40. C<sub>12</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>. Calculated, %: C 56.47; H 3.55; N 27.44.** 

**1,5-Diphenyl-3-(2-phenylhydrazinylidene)-1***H***-pyrrol-2(3***H***)-one (IIIa).** Yield 1.66 g (90%), orangeyellow crystals, mp 143–145°C. IR spectrum, v, cm<sup>-1</sup>: 3269 (NH), 1716 (C=O), 1634 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 5.98 s (1H, 4-H), 7.20–7.75 m (15H, Ph), 8.56 s (1H, NH). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 88.7, 113.9, 122.4, 127.9, 128.1, 128.3, 128.6, 128.9, 129.5, 132.7, 134.2, 143.0, 153.3, 154.6, 161.1. Found, %: C 77.98; H 5.14; N 12.56. C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>O. Calculated, %: C 77.87; H 5.01; N 12.39.

**5-Pentyl-1-phenyl-3-(2-phenylhydrazinylidene)-1H-pyrrol-2(3H)-one (IIIb).** Yield 1.73 g (94%), orange–yellow crystals, mp 149–151°C. IR spectrum, v, cm<sup>-1</sup>: 3338 (NH), 1723 (C=O), 1625 (C=N). <sup>1</sup>H NMR spectrum, δ, ppm: 0.89–2.02 m (11H, C<sub>5</sub>H<sub>11</sub>), 6.00 s (1H, 4-H), 7.20–7.50 m (10H, Ph), 8.50 s (1H, NH). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 13.8, 22.1, 28.6, 32.5, 33.4, 90.8, 114.2, 122.6, 128.0, 128.3, 129.0, 129.4, 138.2, 142.7, 155.3, 157.8, 161.4. Found, %: C 75.62; H 7.09; N 12.76. C<sub>21</sub>H<sub>23</sub>N<sub>3</sub>O. Calculated, %: C 75.67; H 6.90; N 12.61.

**5-Butyl-1-phenyl-3-(2-phenylhydrazinylidene)-1***H***-pyrrol-2(3***H***)-one (IIIc).** Yield 1.60 g (86%), orange–yellow crystals, mp 151–153°C. IR spectrum, v, cm<sup>-1</sup>: 3321 (NH), 1741 (C=O), 1637 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.85–1.90 m (9H, C<sub>4</sub>H<sub>9</sub>), 6.00 s (1H, 4-H), 7.20–7.48 m (10H, Ph), 8.53 s (1H, NH). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 14.2, 22.8, 29.4, 33.7, 91.3, 114.5, 122.1, 127.8, 128.4, 129.0, 129.1, 138.5, 143.2, 155.4, 158.8, 161.2. Found, %: C 75.46; H 7.00; N 13.36. C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O. Calculated, %: C 75.24; H 6.58; N 13.17.

**5-(4-Methylphenyl)-1-phenyl-3-(phenylhydrazinylidene)-1***H*-**pyrrol-2(3***H***)-one (IIId).** Yield 1.69 g (91%), orange–yellow crystals, mp 151–153°C. IR spectrum, v, cm<sup>-1</sup>: 3294 (NH), 1716 (C=O), 1632 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.23 s (3H, CH<sub>3</sub>), 6.01 s (1H, 4-H), 7.30–7.84 m (14H, H<sub>arom</sub>), 8.60 s (1H, NH). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 21.4, 88.3, 114.2, 122.8, 128.0, 128.3, 128.4, 128.9, 129.3, 129.4, 132.4, 133.9, 137.6, 143.2, 152.7, 154.0, 160.2. Found, %: C 75.46; H 7.00; N 13.36. C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O. Calculated, %: C 75.24; H 6.58; N 13.17.

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