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Synthesis of 1-Substituted 5-Alkyl(aryl)-1,3-dihydro-2*H*-pyrrol-2-ones. Azocoupling with Diazonium Salts

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Abstract—Reactions of 5-alkyl- and 5-aryl-3*H*-furan-2-ones with 1,3- and 1,4-binucleophiles of aromatic series were carried out for the first time under various conditions. In the presence of a base the reaction resulted in 1-R-1,3-dihydro-2*H*-pyrrol-2-ones, under milder conditions intermediates were isolated, 4-aryl-4-oxobutanamides. The structure of the latter was proved by spectral methods. By an example of 1-R-1,3-dihydro-2*H*-pyrrol-2-ones the possibility was demonstrated of their functionalization via introducing an aryldiazenyl fragment.

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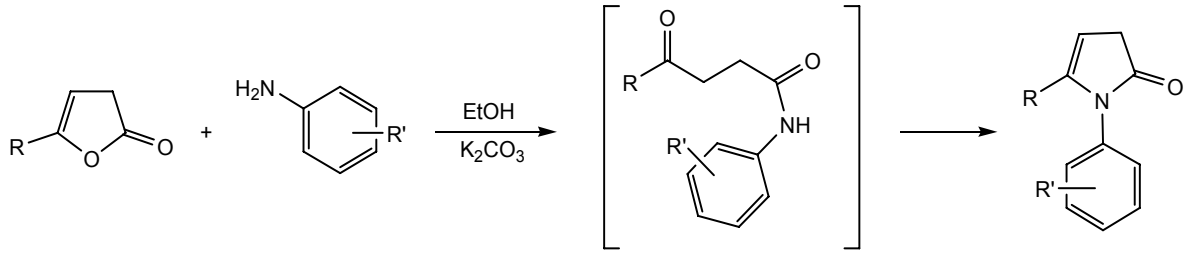
The refinement of pyrrole preparation procedures is very important for organic chemistry since the pyrrole ring is present in the structure of many substances both of biologic origin (vitamin B_{12}, prodigiosin pigment) and purposefully synthesized in a laboratory (for instance, fluorescent dyes of BODIPY class) [1].

The reaction of levulinic acid with methylamine in the presence of Pd/C as catalyst [2, 3] first leads to the formation of 4-(methylamino)pentanoic acid which further undergoes cyclization into pyrrolidone. Pyrrolidones of more complex structure [1] were obtained in over 80% yield in reactions of heterocyclic ketene aminals containing a perimidine fragment with oxalyl chloride in acetonitrile. Compounds of this series significantly differing by electron absorption spectra can exist in three tautomeric forms (enol-imine, keto-amine, and keto-imine). Pyrrolo[1,2-*a*]perimidin-10-ylidenes were obtained from aryl-substituted oxofuran-2(3*H*)-ylidene acetates and 1,8-diaminonaphthalene by heating in methanol in high yield and of a high purity. The today state of the chemistry of fused pyrrol-2,3-diones and reactions with binucleophiles of diverse nature are presented in a review [4].

Cyclization products of 5-R-3*H*-furan-2-ones **1a**–**1d** with 1,3- and 1,4-binucleophiles of aromatic series (1,3-phenylenediamine and benzidine) have not been described before. 5-R-3*H*-Furan-2-ones [5] are convenient initial compounds for the synthesis of functionalized heterocyclic systems.

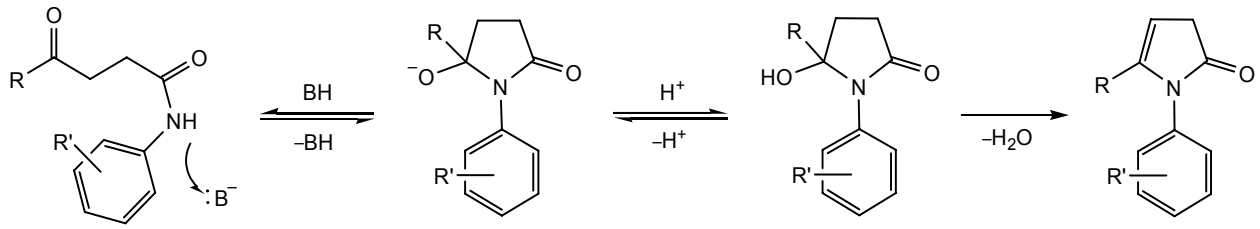
Scheme 1.



1a–1d **2a–2d, 3c** **4a–4d, 5c**

R = C_8H_{17} (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**); R' = 3-NH_2 (**2**, **4**), 4-(4-$NH_2C_6H_4$) (**3**, **5**).

Scheme 2.



The reaction of compounds **1a–1d** with 1,3-phenylenediamine and benzidine we investigated under different conditions. At boiling with excess amine in a water-ethanol solution in the presence of K_2CO_3 the reaction proceeds to 39–56% yield (TLC monitoring) (Scheme 1).

IR spectra of the products contain the absorption band amide I in the region 1700–1690 cm^{-1} and narrow bands of the stretching vibrations of a free amino group in the region 3400–3380 cm^{-1}. The absence of the absorption bands amide II confirms the cyclic structure of obtained compounds **4a–4d** and **5c**.

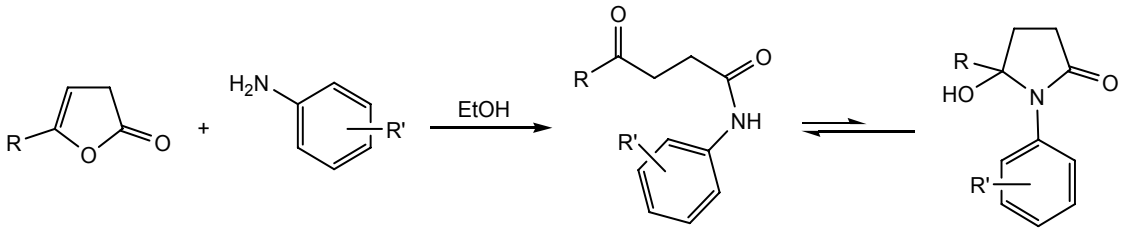
In the ^1H NMR spectra of compounds **4a–4d** and **5c** a characteristic triplet of vinyl proton appears at 5.80–5.88 ppm (1H), the doublet of doublets of the protons of the methylene unit of the heterocycle is observed at 2.80–2.89 ppm (2H), the singlet of primary amino group protons is present at 3.65–3.81 (2H) (**4a–4d**) and 5.56 ppm (2H) (**5c**). The spectrum of compound **4a** contains proton signals of the aliphatic substituent at 0.96–1.94 ppm (17H), spectra of compounds **4c** and **5c**, a singlet of the methyl group protons of the *p*-tolyl substituent at 2.38–2.41 ppm (3H); in the spectrum of compound **4d** the methoxy group protons resonate at 3.81 ppm (3H). The groups of signals of the aromatic protons in the spectra of compounds **4a–4d** and **5c** are observed at 6.44–7.75 ppm (4H, 8H, 8H, 8H, and 12H respectively). The ^{13}C NMR spectra contain characteristic signals of carbonyl groups carbon atoms at 172.3–178.2 ppm, of tertiary carbon atoms at 94.7–96.3 ppm, of carbon atoms of methylene groups at 34.2–36.5 ppm. The signals of carbon atoms of the aliphatic substituent of compound **4a** appear at 14.1–33.4 ppm, of carbon atoms of the methyl groups of the *p*-tolyl substituent, at 21.2–21.3 ppm (**4c** and **5c**), of the carbon atom of methoxy group of compound **4d**, at 55.8 ppm. The signals of aromatic carbon atoms of compounds **4a–4d** and **5c** are observed in the range 107.4–158.8 ppm.

The data of elemental analyses, IR, ^1H and ^{13}C NMR spectra confirm that in the basic medium 1-(3-aminophenyl)-5-R-3*H*-pyrrol-2-ones **4a–4d** and 1-[4'-amino(1,1'-biphenyl)-4-yl]-5-(4-methylphenyl)-1,3-dihydro-2*H*-pyrrol-2-one **5c** were formed.

In reaction proceeding in the basic medium apparently first the ring of furan-2-one opens with the formation of 4-oxoalkanoic acid amide; after that the reaction of intramolecular heterocyclization occurs providing *N*-substituted 5-R-1,3-dihydro-3*H*-pyrrol-2-ones **4a–d** and **5c** (Scheme 2).

Aiming at isolation of the probable intermediate of the reaction, 4-oxo-4-arylbutanamide, we modified the reaction conditions. At a prolonged boiling in ethanol (5–6 h) without a base the reaction of 5-(4-methylphenyl)-3*H*-furan-2-one **1c** with 1,3-phenylenediamine and benzidine expectedly occurred with the ring

Scheme 3.



1c **2c, 3c** **A**

R = 4-MeC_6H_4; R' = 3-NH_2 (**2**), 4-($4NH_2C_6H_4$) (**3**).

opening of furan-2-one and the formation of compounds of acyclic structure, 4-oxobutanoic acid arylamides **2c** and **3c** in 60 and 58% yields respectively (Scheme 3).

Physicochemical characteristics of compounds **2c** and **3c** differ from the properties of the previously obtained compounds **4a–4d** and **5c**. By the data of elemental analyses, IR, ^{1}H and ^{13}C NMR spectra these compounds were identified as *N*-(3-aminophenyl)-4-oxo-4-(4-methyl-phenyl)butanamide **2c** and *N*-[4'-amino(1,1'-biphenyl)-4-yl]-4-oxo-4-(4-methylphenyl)-butanamide **3c**.

Amides of 4-oxobutanoic acid are known to be able to exist in a tautomeric equilibrium with a cyclic isomer, 5-R-5-hydroxypyrrol-2-one **A**. IR spectroscopy permits a sufficiently reliable establishing of the open or cyclic structure of the 4-oxobutanoic acid amides. The main proof of the open structure of the *N*-monosubstituted amides of oxoacids is the presence in the IR spectra of the amide II band (bending vibrations of the amino group δ_{NH}) at 1570–1520 cm^{-1}. Since this band in the spectra of hydroxylactams is present in the region free of other vibration bands, it may be used as characteristic band for isomer identification.

In the IR spectra of compounds **2c** and **3c** the bands of amide II are present at 1518 (**2c**) and 1544 (**3c**) cm^{-1}. The stretching vibrations band of the bound amino group NH is observed at 3364–3440 cm^{-1}, the broadened stretching vibrations band of bound hydroxy groups OH that appear commonly in the same region in the IR spectra of cyclic isomers are absent from the spectra of compounds **2c** and **3c**.

^{1}H NMR spectra of compounds **2c** and **3c** contain broadened singlets from the protons of the amide amino group at 7.70–7.71 ppm (1H) and from protons of the primary amino groups at 3.95 (2H, **2c**) and 5.52 (2H, **3c**) ppm, the values close to those of signals of unsubstituted amino groups of isomeric phenylenediamines and benzidine respectively. Consequently, the effect of the fragments of 4-aryl-4-oxocarboxylic acids on shielding the protons of primary amino groups is insignificant.

In the ^{1}H NMR spectra of compounds **2c** and **3c** multiplets appear of the protons of methylene units at 2.73–2.78 (2H) and 3.43–3.46 (2H) ppm, and also the signal of the protons of the methyl group of the *p*-tolyl substituent in the strong field at 2.40–2.41 ppm (3H). The groups of signals of the aromatic protons are observed at 6.48–7.41 ppm (8H and 12H respectively). In the ^{13}C NMR spectra characteristic signals of carbonyl groups carbon atoms are present at 198.0–198.3 ppm, of the carbonyl groups of amide fragments, at 174.0–177.4 ppm, of aliphatic carbon atoms, in the strong field in the region 21.3–36.3 ppm, the signals of aromatic carbon atoms appear in the downfield region at 116.0–144.4 ppm.

Thus the structure of reaction products of 5-R-3*H*-furan-2-ones with aromatic 1,3- and 1,4-binucleophiles depends on the conditions of the process. In the absence of the basic catalysts open amides of 4-oxobutanoic acid are formed, yet in the basic medium they undergo subsequent heterocyclization affording 1-substituted 1,3-dihydro-2*H*-pyrrol-2-ones that was confirmed by spectral analysis methods.

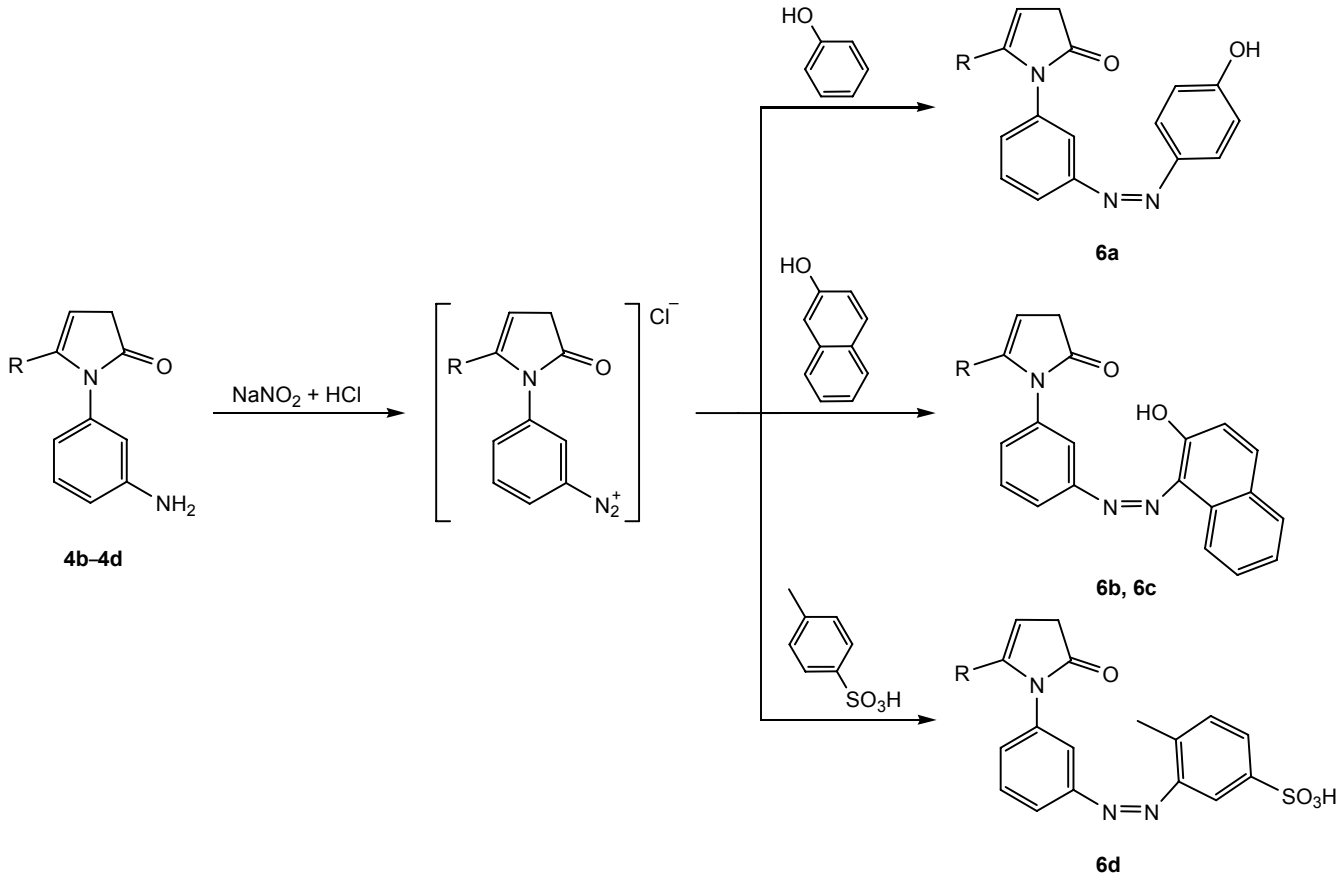
Since 1-(3-aminophenyl)-5-R-1,3-dihydro-2*H*-pyrrol-2-ones **4a–4d** retain a free primary amino group linked to the aromatic ring, it may be involved in a diazotization reaction and a subsequent azocoupling. The azocoupling products may be promising dyes and also in case of favorably located substituent may serve as efficient reagents for cations of multivalent metals [6–8]. We used 1-(3-aminophenyl)-5-R-3*H*-pyrrol-2-ones **4b–4d** for preparation of diazo components which further *in situ* were brought into the reaction with azo components, such as phenol, β-naphthol, and *p*-toluenesulfonic acid. All reactions were carried out under mild conditions, at 0–5°C in water-alcohol solution of sodium acetate (Scheme 4).

Brightly colored crystalline compounds **6a–6d** were characterized by the data of elemental analysis, IR, and ^{1}H NMR spectra. The IR spectra of compounds **6a–6d** in the region 1676–1684 cm^{-1} contain the amide I absorption bands; in the region 1598–1600 cm^{-1} a weak absorption band is observed corresponding to the diazo group, and also the bands of aromatic rings vibrations; in the region of 3330–3440 cm^{-1} an absorption band of OH group is present (**6a–6c**).

In the ^{1}H NMR spectra of compounds **6a–6d** a characteristic signal of vinyl proton is observed at 5.50–5.59 ppm, the proton signal of the methylene unit appears at 2.88–2.92 ppm, the group of signals from the protons of the aromatic rings is present at 6.45–8.40 ppm. The downfield singlet of the OH group proton is located at 10.13–10.17 ppm (**6a–6c**).

The obtained azo compounds are sensitive to the pH variation, contrast change occurs in the solu-

Scheme 4.



tion color. Compounds **6a** and **6d** are able to form complexes with the salts of multivalent metals.

Compound **6a** forms complexes with ions Ni^{2+} (pH 3–7), Ca^{2+} (pH 12), Al^{3+} (pH 3–9), Co^{2+} (pH 7–12). The best analytic characteristics (contrasting and sensitivity) were found in compound **6a** with ions Ni^{2+} and Al^{3+} at pH 3. At growing pH the color gets deeper. Complexes with Co^{2+} demonstrate more contrasting variation of the color. Compound **6d** with Co^{2+} and Ni^{2+} forms complex compounds of orange and green color respectively, and with growing pH the color also gradually gets deeper.

EXPERIMENTAL

IR spectra were recorded on an IR Fourier spectrophotometer FSM-1201 from KBr pellets. ^1H NMR spectra were registered on a spectrometer Bruker MSL-400 (400 MHz) in $CDCl_3$, internal reference TMS. The homogeneity of compounds was proved by TLC on Silufol plates, eluent ethyl acetate–hexane–chloroform, 2 : 2 : 1; visualization in iodine vapor.

The investigation of complex formation ability of azo compounds was carried out in the pH range 3–12 (ammonia acetate buffer solutions). The following metal ions were selected: Ca^{2+}, Ba^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}. The metal salts were used in the concentration range 10^{-4}–10^{-2} mol L^{-1}. In a measuring tube was charged 2 mL of buffer solution, 0.2 ml of organic reagent (0.1% water-alcohol solution), and 2–10 drops of metal salt solution. The color of the formed compound was visually compared with the control series prepared in the same conditions but without metal salts.

Compounds **1a–1c** were prepared by procedure [5].

***N*-(3-Aminophenyl)-4-oxo-4-(*p*-tolyl)butanamide (2c).** A mixture of 0.50 g (2.9 mmol) of compound **1c** and 0.93 g (8.6 mmol) of 1,3-phenylenediamine was heated in 25 mL of ethanol for 2.5 h and was left

standing for 12 h. Then the reaction mixture was transferred into a beaker with water (pH 7), dark red crystals were filtered off and washed with toluene Yield 0.49 g (60%), light-yellow crystals, mp 149–150°C. IR spectrum, ν, cm^{-1}: 3340 (NH), 1518 (amide-II), 1320 (C–N). ^1H NMR spectrum, δ, ppm: 2.41 s (3H, Me), 2.78 m (2H, C^2H_2), 3.43 m (2H, C^3H_2), 3.95 s (2H, NH_2), 6.48–7.30 m ($4H_{Ar}$), 6.75–7.41 d.d (4H, 4-$MeC_6\underline{H}_4$), 7.71 s (NH, amide). ^{13}C NMR spectrum, δ, ppm: 21.3 (Me), 30.0 (C^2H_2), 35.1 (C^3H_2), 106.7–147.2 (C_{Ar}), 128.7–142.8 (4-Me$\underline{C}_6H_4$), 177.4 (CONH), 198.3 (C=O). Found, %: C 72.45; H 6.40; N 10.05. $C_{17}H_{18}N_2O_2$. Calculated, %: C 72.32; H 6.43; N 9.92.

***N*-[4'-Amino(1,1'-biphenyl)-4-yl]-4-oxo-4-(*p*-tolyl)butanamide (3c).** A mixture of 2.9 mmol of compound **1c** and 5.8 mmol of benzidine in 25 mL of ethanol was heated for 6 h. Then the reaction mixture was transferred into a beaker with water (pH 7), the separated crystals were filtered off and recrystallized from ethanol. Yield 0.60 g (58%), light-yellow crystals, mp 115–117°C. IR spectrum, ν, cm^{-1}: 3364 (NH), 1544 (amide-II), 1324 (C–N). ^1H NMR spectrum, δ, ppm: 2.40 s (3H, Me), 2.73 m (2H, C^2H_2), 3.46 m (2H, C^3H_2), 5.52 s (2H, NH_2), 6.48–7.30 m ($8H_{Ar}$), 6.70–7.38 d.d (4H, 4-$MeC_6\underline{H}_4$), 7.70 s (NH, amide). ^{13}C NMR spectrum, δ, ppm: 21.3 (Me), 31.1 (C^2H_2), 36.3 (C^3H_2), 116.0–144.4 (C_{Ar}), 174.0 (CONH), 198.0 (C=O). Found, %: C 77.35; H 6.26; N 8.15. $C_{23}H_{22}N_2O_2$. Calculated, %: C 77.07; H 6.19; N 7.82.

1-(3-Aminophenyl)-5-octyl-1,3-dihydro-2*H*-pyrrol-2-one (4a). A mixture of 2.9 mmol of compound **1a**, 8.6 mmol of benzylamine (5.8 mmol of benzidine), and a catalytic quantity of potassium carbonate was heated in 15 mL of ethanol for 4 h. The reaction mixture was acidified with hydrochloric acid till pH 7 and was transferred into a beaker with water, the separated crystals were filtered off and re-crystallized from ethanol. Yield 0.38 g (46%), light-brown crystals, mp 117–119°C. IR spectrum, ν, cm^{-1}: 3380 (NH_2), 1698 (C=O, amide-I). ^1H NMR spectrum, δ, ppm: 0.96 s (3H, Me), 1.26–1.94 m [14H, $(CH_2)_7$], 2.88 d (2H, C^2H_2), 3.65 s (2H, NH_2), 5.81 t (1H, $=C^3H$), 6.46–7.17 m ($4H_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 14.1 (Me), 22.8–33.4 [$(CH_2)_7$], 36.2 (C^2H_2), 95.4 ($=C^3H$), 107.4–147.6 (C_{Ar}), 172.3 (C=O). Found, %: C 75.35; H 9.35; N 10.09. $C_{18}H_{26}N_2O$. Calculated, %: C 75.52; H 9.09; N 9.79.

Compounds **4b–4d** and **5c** were similarly prepared.

1-(3-Aminophenyl)-5-phenyl-1,3-dihydro-2*H*-pyrrol-2-one (4b). Yield 0.39 g (54%), light-brown crystals, mp 96–98°C. IR spectrum, ν, cm^{-1}: 3388 (NH_2), 1694 (C=O, amide-I). ^1H NMR spectrum, δ, ppm: 2.89 m (2H, C^2H_2), 3.69 s (2H, NH_2), 5.82 t (1H, $=C^3H$), 6.44–7.73 m ($8H_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 35.7 (C^2H_2), 94.7 ($=C^3H$), 110.4–149.4 (C_{Ar}), 174.9 (C=O). Found, %: C 76.55; H 6.15; N 11.35. $C_{16}H_{14}N_2O$. Calculated, %: C 76.80; H 5.96; N 11.20.

1-(3-Aminophenyl)-5-(*p*-tolyl)-1,3-dihydro-2*H*-pyrrol-2-one (4c). Yield 0.40 g (52%), light-brown crystals, mp 149–150°C. IR spectrum, ν, cm^{-1}: 3384 (NH_2), 1700 (C=O, amide-I). ^1H NMR spectrum, δ, ppm: 2.38 s (3H, Me), 2.86 m (2H, C^2H_2), 3.72 s (2H, NH_2), 5.80 t (1H, $=C^3H$), 6.44–7.75 m ($8H_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 21.2 (Me), 35.2 (C^2H_2), 95.1 ($=C^3H$), 107.6–148.8 (C_{Ar}), 176.8 (C=O). Found, %: C 76.94; H 6.40; N 10.05. $C_{17}H_{16}N_2O$. Calculated, %: C 77.27; H 6.06; N 10.61.

1-(3-Aminophenyl)-5-(4-methoxyphenyl)-1,3-dihydro-2*H*-pyrrol-2-one (4d). Yield 0.32 g (39%), light-brown crystals, mp 95–96°C. IR spectrum, ν, cm^{-1}: 3400 (NH_2), 1695 (C=O, amide-I). ^1H NMR spectrum, δ, ppm: 2.88 d (2H, C^2H_2), 3.76 s (2H, NH_2), 3.81 s (3H, MeO), 5.82 t (1H, $=C^3H$), 6.45–7.56 m ($8H_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 36.5 (C^2H_2), 55.8 (MeO), 94.8 ($=C^3H$), 108.7–158.8 (C_{Ar}), 178.2 (C=O). Found, %: C 72.63; H 6.04; N 10.07. $C_{17}H_{16}N_2O_2$. Calculated, %: C 72.86; H 5.71; N 10.00.

1-[4'-Amino(1,1'-biphenyl)-4-yl]-5-(*p*-tolyl)-1,3-dihydro-2*H*-pyrrol-2-one (5c). Yield 0.55 g (56%), light-brown crystals, mp 79–80°C. IR spectrum, ν, cm^{-1}: 3380 (NH_2), 1698 (C=O, amide-I). ^1H NMR spectrum, δ, ppm: 2.41 s (3H, Me), 2.80 d (2H, C^2H_2), 5.56 s (2H, NH_2), 5.88 t (1H, $=C^3H$), 6.48–7.45 m ($12H_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 21.3 (Me), 34.2 (C^2H_2), 96.3 ($=C^3H$), 116.6–138.8 (C_{Ar}), 176.2 (C=O). Found, %: C 80.98; H 5.69; N 8.46. $C_{23}H_{20}N_2O$. Calculated, %: C 81.18; H 5.88; N 8.24.

1-{3-[(4-Hydroxyphenyl)diazenyl]phenyl}-5-(*p*-tolyl)-1,3-dihydro-2*H*-pyrrol-2-one (6a). To a freshly prepared solution of 0.1 mmol of 1-(3-aminophenyl)-5-(*p*-tolyl)-1,3-dihydro-2*H*-pyrrol-2-one **4c** and 0.1 mmol of sodium nitrite at cooling and stirring was poured a freshly prepared solution of 0.1 mmol of phenol and 3 mmol of 30% sodium hydroxide in hot water (80°C). The separated precipitate of azodye was filtered off, washed with water, recrystallized from ethanol or 2-propanol. Yield 0.21 g (58%), mp 176–

178°C. IR spectrum, ν, cm^{-1}: 3350 (OH), 1676 (C=O, amide-I), 1600 (N=N, C=C). ^1H NMR spectrum, δ, ppm: 2.41 s (3H, Me), 2.88 d (2H, C^2H_2), 5.56 t (1H, $=C^3H$), 6.94–8.25 m ($12H_{Ar}$), 10.14 br.s (1H, OH). Found, %: C 74.54; H 5.08; N 12.12. $C_{22}H_{17}N_3O_2$. Calculated, %: C 74.35; H 4.82; N 11.82.

Azo compounds **6b** and **6c** were analogously synthesized.

1-{3-[(2-Hydroxynaphthalen-1-yl)diazenyl]-phenyl}-5-phenyl-1,3-dihydro-2*H*-pyrrol-2-one (6b). Yield 0.24 g (60%), mp 195–198°C. IR spectrum, ν, cm^{-1}: 3330 (OH), 1682 (C=O, amide-I), 1598 (N=N, C=C). ^1H NMR spectrum, δ, ppm: 2.90 d (2H, C^2H_2), 5.58 t (1H, $=C^3H$), 7.16–8.20 m ($15H_{Ar}$), 10.17 br.s (1H, OH). Found, %: C 76.86; H 5.12; N 10.28. $C_{26}H_{19}N_3O_2$. Calculated, %: C 77.02; H 4.72; N 10.36.

1-{3-[(2-Hydroxynaphthalen-1-yl)diazenyl]-phenyl}-5-(*p*-tolyl)-1,3-dihydro-2*H*-pyrrol-2-one (6c). Yield 0.23 g (55%), mp 178–180°C (decomp.). IR spectrum, ν, cm^{-1}: 3336 (OH), 1684 (C=O, amide-I), 1600 (N=N, C=C). ^1H NMR spectrum, δ, ppm: 2.41 s (3H, Me), 2.89 d (2H, C^2H_2), 5.59 t (1H, $=C^3H$), 7.20–8.25 m ($14H_{Ar}$), 10.13 br.s (1H, OH). Found, %: C 76.85; H 4.98; N 10.31. $C_{27}H_{21}N_3O_2$. Calculated, %: C 77.31; H 5.05; N 10.02.

3-({3-[5-(4-Methoxyphenyl)-2-oxo-2,3-dihydro-1*H*-pyrrol-1-yl]phenyl}diazenyl)-4-methylbenzenesulfonic acid (6d). To a freshly prepared solution of 0.1 mmol of 1-(3-aminophenyl)-5-(4-methoxyphenyl)-1,3-dihydro-2*H*-pyrrol-2-one **4d** and 0.1 mmol of sodium nitrite at cooling and stirring was poured 0.1 mmol of *p*-toluenesulfonic acid. The separated precipitate of azodye was filtered off, washed with water, recrystallized from ethanol or 2-propanol. Yield 0.24 g (52%), mp 142–145°C (decomp.). IR spectrum, ν, cm^{-1}: 3440 (OH), 1680 (C=O, amide-I), 1598 (N=N, C=C). ^1H NMR spectrum, δ, ppm: 2.43 s (3H, Me), 2.92 d (2H, C^2H_2), 3.81 s (3H, MeO), 5.50 t (1H, $=C^3H$), 6.86–8.40 m ($11H_{Ar}$). Found, %: C 61.75; H 4.85; N 8.86; S 7.24. $C_{24}H_{21}N_3O_5S$. Calculated, %: C 62.19; H 4.57; N 9.07; S 6.91.

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