

Cyanoacetylene and Its Derivatives: XXXII.* Addition of Ammonia and Methylamine to 4-Hydroxy-4,4-diphenyl-2-butyne nitrile

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Abstract—Nucleophilic addition of ammonia (25% aqueous solution) and methylamine to 4-hydroxy-4,4-diphenyl-2-butyne nitrile occurs under mild conditions to afford 4-amino(or methylamino)-2,5-dihydro-5,5-diphenyl-2-iminofurans. 4-Hydroxy-4,4-diphenyl-2-butyne nitrile in anhydrous liquid ammonia gives rise to 3-amino-4-hydroxy-4,4-diphenyl-2-butyne nitrile which is quantitatively converted into the corresponding iminodihydrofuran or iminodihydrofuran hydrochloride in the presence of 10 wt % of KOH or gaseous hydrogen chloride. 4-Amino- and 4-methylamino-2-iminofurans react with 4-hydroxy-4-methyl-2-pentyne nitrile to give 3-(4-amino- and 4-methylamino-5,5-diphenyl-2,5-dihydrofuran-2-ylideneamino)-4-hydroxy-4-methyl-2-pentyne nitriles.

The reactivity of α,β -acetylenic γ -hydroxy carbonitriles [$R^1R^2C(OH)C\equiv C-CN$, $R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Et$; $R^1R^2 = (CH_2)_5$] toward N-centered nucleophiles has been the subject of review articles [2, 3] and original papers [4–7]. These studies have shown that acetylenic hydroxy nitriles in anhydrous liquid ammonia give rise to (*Z*)-3-amino-4-hydroxy-2-alkenenitriles which undergo intramolecular cyclization in the presence of water with formation of 4-amino-5,5-dialkyl-2,5-dihydro-2-iminofurans [4]. Primary amines (aqueous solutions) and amino alcohols react with acetylenic hydroxy nitriles under mild conditions, following the addition–cyclization pattern; as a result, the corresponding 4-amino-2,5-dihydro-2-iminofurans are formed [5, 6]. We previously developed a general synthetic approach to polyconjugated heterocyclic systems consisting of 2,5-dihydro-2-iminofuran units on the basis of the reaction of methylamine and 4-hydroxy-4-methyl-2-pentyne nitrile [7]. The addition of secondary amines occurs in a regio- and stereoselective fashion, yielding (*Z*)-3-dialkylamino-2-alkenenitriles which undergo quantitative cyclization to the corresponding 2,5-dihydro-2-iminofuran hydrochlorides by the action of hydrogen chloride [8]. On the other hand, there are no published data on reactions of amines with acetylenic hydroxy nitriles containing aromatic substituents, though the

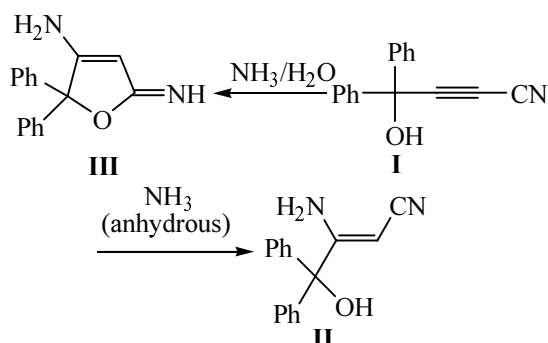
synthesis of new iminodihydrofuran derivatives is an important problem: The 2-imino-2,5-dihydrofuran system is related to the 2,5-dihydrofuran-2-one fragment which constitutes a part of a number of natural compounds, e.g., ascorbic, penicillic, and tetronic acids. Moreover, the presence of aromatic substituents in the iminodihydrofuran molecule could make it possible to use the resulting compounds as materials for optoelectronics.

Taking the above stated into account, the goal of the present work was to elucidate specific features and general relations holding in the addition of amines to acetylenic hydroxy nitriles and to obtain new unsaturated compounds of the 2,5-dihydro-2-iminofuran series. For this purpose, we extended the series of acetylenic hydroxy nitriles by inclusion of 4-hydroxy-4,4-diphenyl-2-butyne nitrile (**I**) and examined its reactions with ammonia and methylamine.

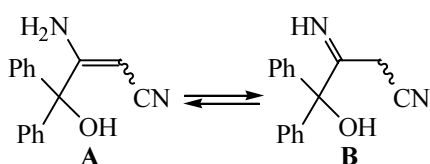
Cyanoacetylene **I** reacted with anhydrous liquid ammonia under mild conditions (-33°C , 3 h) to give (*Z*)-3-amino-4-hydroxy-4,4-diphenyl-2-butyne nitrile (**II**) in 70% yield with high stereoselectivity. The reaction of **I** with 25% aqueous ammonia afforded 4-amino-5,5-diphenyl-2-imino-2,5-dihydrofuran (**III**) (Scheme 1). Substituted aminoacrylonitrile **II** was isolated as a colorless powder which is soluble in chloroform, acetonitrile, ethanol, and dimethyl sulfoxide and insoluble in diethyl ether and hex-

* For communication XXXI, see [1].

Scheme 1.



Scheme 2.

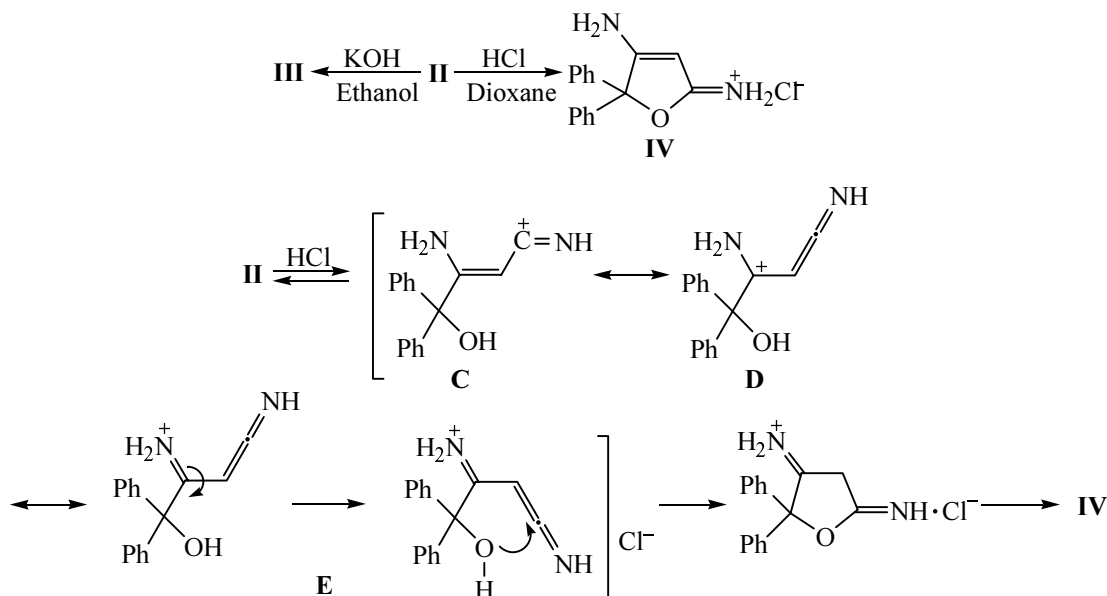


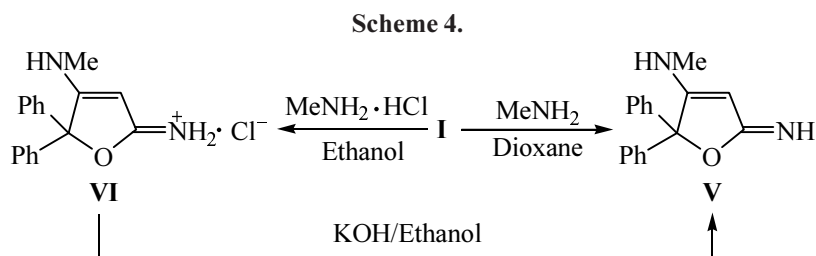
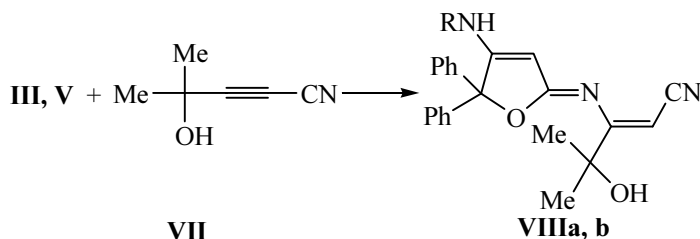
ane. Aminoacrylonitrile **II** can exist as *E* and *Z* isomers and tautomers **A** and **B** (Scheme 2). The tautomeric transformation $\text{A} \rightleftharpoons \text{B}$ should facilitate *Z,E*-isomerization. The 3600–3000- cm^{-1} region of the IR spectrum of a solution of aminoacrylonitrile **II** in carbon tetrachloride ($c \approx 0.01 \text{ M}$; $d = 0.5, 2, \text{ and } 5 \text{ cm}$) contained absorption bands from both associated and unassociated hydroxy and amino groups, ν, cm^{-1} : 3608, 3276 (OH); 3508, 3480, 3400, 3375 (NH_2). The associates decompose in going to more dilute solutions ($c \approx 0.001 \text{ M}$, $d = 5 \text{ cm}$), and absorption bands belonging to only unassociated OH (3608 cm^{-1}) and NH_2 groups (3508 and 3400 cm^{-1}) are observed in

the spectrum. The cyano group gives rise to only one absorption band with its frequency at 2197 cm^{-1} , indicating formation of an acrylonitrile fragment (unconjugated cyano group is characterized by absorption in the region 2260–2240 cm^{-1} [9]). These data suggest that compound **II** exists mainly as acrylonitrile tautomer **A**. In the ^1H NMR spectrum of **II** in CDCl_3 , the olefinic proton signal appeared at δ 3.83 ppm; also, signals at δ 2.77 (OH), 5.14 (NH_2), and 7.39–7.28 ppm (aromatic protons) were present. The ^{13}C NMR data also confirm configurational homogeneity of compound **II**.

Unlike 3-amino-4-hydroxy-2-alkenenitriles obtained previously [4], aminoacrylonitrile **II** undergoes only partial intramolecular cyclization to iminodihydrofuran **III** on storage at room temperature. After storage for a month, the ^1H NMR spectrum contained a signal at δ 3.83 ppm due to *Z* isomer **II** and a signal at δ 5.18 ppm, which belongs to iminodihydrofuran **III**. In the presence of potassium hydroxide (10 wt %), compound **II** in ethanol is quantitatively converted into iminodihydrofuran **III** in 2 h at 20–25°C. Presumably, KOH favors transformation of unsaturated nitrile **II** into the *E* isomer which is capable of undergoing intramolecular cyclization. In addition, the basic medium promotes ionization of the hydroxy group. Analogous intramolecular cyclization involving the hydroxy and cyano groups was effected by passing gaseous hydrogen chloride through a solution of aminoacrylonitrile **II** in dioxane (20–25°C, 3 h). In this case, the product was iminodihydrofuran hydrochloride **IV** (yield 96%, Scheme 3). Obviously, the cyclization begins with proto-

Scheme 3.



**Scheme 5.**

R = H (a), Me (b).

nation of the cyano group to give mesomeric cation **C** \leftrightarrow **D** \leftrightarrow **E** in which rotation about the C²–C³ bond is not restricted and no steric constraint (*Z* configuration of the initial nitrile) on intramolecular addition of the hydroxy group to cyano exists (azaallene system).

Nucleophilic addition of methylamine to cyanoacetylene **I** also occurs under mild conditions (dioxane, 20–25°C, 1 h) to afford 2-imino-4-methylamino-5,5-diphenyl-2,5-dihydrofuran (**V**) in 84% yield. The reaction of **I** with methylamine hydrochloride (ethanol, 50°C, 3 h) gave iminodihydrofuran hydrochloride **VI** which can be converted into free base **V** by treatment with an equimolar amount of potassium hydroxide (ethanol, 20–25°C, 2 h; Scheme 4).

Iminodihydrofurans **III** and **V** are crystalline substances. The IR spectrum of **III** in CHCl₃ (*c* = 0.01–0.02 M; *d* = 0.5, 1, and 2 cm) contained three absorption bands in the region 3000–3600 cm⁻¹: 3306 (=NH); 3405, 3499 cm⁻¹ (NH₂). Iminodihydrofuran **V** displayed two absorption bands in the same region: 3305 (=NH) and 3441 cm⁻¹ (NH). The IR spectra of both compounds lacked absorption bands assignable to cyano and hydroxy groups. In the ¹H NMR spectra of iminodihydrofurans **III** and **V** in CDCl₃ we observed only one olefinic proton signal at δ 5.18 and 4.94 ppm, respectively. The electron absorption spectra of compounds **III** and **V** are characterized by two maxima at λ 266 (log ε = 4.13) and 261 nm (log ε = 4.12) (**III**) and 268 (log ε = 4.36) and 261 nm (log ε = 4.32) (**V**).

Iminodihydrofurans **III** and **V** reacted with 4-hydroxy-4-methyl-2-pentenenitrile (**VII**) under mild conditions (acetonitrile, 20–50°C, 0.5–3 h) to give 3-(4-amino- and 4-methylamino-5,5-diphenyl-2,5-dihydrofuran-2-ylidene-

amino)-4-hydroxy-4-methyl-2-pentenitriles **VIIIa** and **VIIIb** (Scheme 5). Compounds **VIIIa** and **VIIIb** were isolated as crystalline substances, which showed in the IR spectra C≡N absorption band at 2213 cm⁻¹. Stretching vibrations of the amino group gave rise to two absorption bands at 3405 and 3502 cm⁻¹ (compound **VIIIa** in CHCl₃) or one band at 3435 cm⁻¹ (**VIIIb** in CCl₄). No absorption was present at 3306 cm⁻¹, i.e., at a frequency corresponding to stretching vibrations of the =N–H group in iminodihydrofuran **III**. These data suggest that the addition of iminodihydrofurans **III** and **V** to nitrile **VII** involves the imino group in the former, despite the presence of two nucleophilic centers (=NH and NH₂ or NH) in their molecules. The ¹H NMR spectra of **VIIIa** and **VIIIb** contained two olefinic proton signals at δ, ppm: 5.28 and 5.07 (**VIIIa**); 4.24 and 3.52 (**VIIIb**).

Thus nucleophilic addition of ammonia and methylamine to cyanoacetylene **I** led to formation of polyconjugated heterocyclic systems, iminodihydrofurans having aromatic substituents. These compounds can be used as synthons in fine organic synthesis, biologically active substances, and intermediate products for the preparation of new materials for optoelectronics [10].

EXPERIMENTAL

The IR spectra were recorded on Specord 75-IR and Bruker IFS-25 spectrometers from samples prepared as KBr pellets (or thin films) or solutions in CCl₄ and CHCl₃ (*c* ≈ 0.01 M, *d* = 0.5–5 cm). The ¹H and ¹³C NMR spectra were obtained on a Bruker DPX-400 instrument (400 MHz for ¹H) from solutions in CDCl₃ or DMSO-*d*₆ (compounds **II**, **VIIIa**, and **VIIIb**) using HMDS as internal reference. The electron absorption spectra were

measured on a Specord UV-Vis spectrophotometer from solutions in alcohol. The mass spectra were obtained on an LKB-2091 instrument with direct sample admission into the ion source (ion source temperature 240°C). The progress of reactions was monitored by thin-layer chromatography on Al₂O₃ using chloroform–benzene–ethanol (20 : 4 : 1) as eluent.

Liquid ammonia, 25% aqueous ammonia, methylamine, and methylamine hydrochloride were commercial products. 4-Hydroxy-4-methyl-2-pentynenitrile (**VII**) was synthesized by the procedure described in [11]; its physical constants coincided with published data.

4-Hydroxy-4,4-diphenyl-2-butynenitrile (**I**).

A solution of 37 g (129 mmol) of 3-bromo-1,1-diphenyl-2-propyn-1-ol in 20 ml of DMF was added dropwise at 20°C to a mixture of 64 g (715 mmol) of CuCN and 80 ml of anhydrous DMF. The mixture warmed up to 35°C and was stirred for 5 h at 75°C. The hot dark brown thick material was slowly poured into 500 ml of cold water, and the mixture was stirred until a solid precipitate was formed. The precipitate was filtered off and washed with diethyl ether (5 × 30 ml), and the aqueous filtrate was extracted with diethyl ether (5 × 50 ml). The extracts were combined, washed with cold water, dried over magnesium sulfate, and evaporated to obtain 15 g (50%) of cyanoacetylene **I** as a viscous oily liquid. IR spectrum (film), ν , cm⁻¹: 3450–3350, 3080, 3060, 3030, 2290 (2260 sh), 1960, 1900, 1600, 1580, 1495, 1450, 1390, 1320, 1280, 1170, 1160, 1140, 1070, 1030, 1000, 940, 920, 895, 805, 770, 700, 650. Found, %: C 82.70; H 4.43; N 5.67. C₁₆H₁₁NO. Calculated, %: C 82.38; H 4.75; N 6.00.

(Z)-3-Amino-4-hydroxy-4,4-diphenyl-2-butenenitrile (II**).** Compound **I**, 1 g (4.3 mmol), was added to 30 ml of anhydrous liquid ammonia, the mixture was kept for 3 h at –33°C, and removal of ammonia left 0.75 g (70%) of compound **II** with mp 130–132°C (decomp.). IR spectrum (KBr), ν , cm⁻¹: 3471 s, 3376 s, 3282 s, br, 3107 w, 3088 w, 3055 w, 3030 w, 2197 s, 1950 w, 1890 w, 1805 w, 1635 s, 1613 s, 1574 s, 1489 m, 1445 m, 1376 m, 1311 w, 1280 w, 1208 w, 1184 v.w, 1159 v.w, 1091 w, 1050 m, 1031 w, 1000 w, 970 w, 923 w, 847 w, 770 m, 744 m, 698 s, 675 m, 659 m, 615 v.w, 584 w, 503 w, 473 w. ¹H NMR spectrum, δ , ppm: 3.83 s (1H, =CH), 2.77 s (1H, OH), 5.14 s (2H, NH₂), 7.39–7.28 m (10H, H_{arom}). ¹³C NMR spectrum, δ _C, ppm: 92.67 (Ph₂C), 119.28 (CN), 127.03 (C^p), 127.18 (C^o), 127.22 (C^m), 139.09 (Cⁱ), 79.71 (=CH), 168.25 (C=CH). Mass spectrum, m/z (I_{rel} , %): 250 (100.0), 182 (14.8), 173 (10.9), 105 (82.0), 77 (64.5), 32 (12.5). Found, %: C 76.61;

H 5.77; N 10.79. C₁₆H₁₄N₂O. Calculated, %: C 76.78; H 5.64; N 11.19.

4-Amino-2-imino-5,5-diphenyl-2,5-dihydrofuran (**III**).

a. Cyanoacetylene **I**, 0.23 g (1 mmol), was added to 30 ml of 25% aqueous ammonia, and the mixture was kept for 6 h at room temperature. The precipitate was filtered off and washed with diethyl ether. Yield 0.20 g (80%), mp 162–164°C (decomp.). IR spectrum (KBr), ν , cm⁻¹: 3297 s, 3058 s, 1633 s, 1616 s, 1492 m, 1447 m, 1403 m, 1338 s, 1230 m, 1187 m, 1111 s, 1081 m, 1035 w, 1010 w, 973 s, 940 s, 911 m, 849 v.w, 799 m, 773 s, 732 m, 697 s, 672 s, 637 w, 596 w, 571 w, 513 v.w, 486 w. ¹H NMR spectrum, δ , ppm: 5.18 s (1H, =CH), 4.89 br.s (3H, NH₂, =NH), 7.34–7.35 m (10H, H_{arom}). ¹³C NMR spectrum, δ _C, ppm: 92.23 (Ph₂C), 127.54 and 128.66 (C^o, C^m), 128.84 (C^p), 139.65 (Cⁱ), 89.44 (=CH), 163.90 (C=CH), 171.64 (C=NH). Mass spectrum, m/z (I_{rel} , %): 250 (42.2), 221 (14.1), 206 (7.0), 183 (7.0), 105 (100.0), 77 (74.2), 51 (23.4), 41 (7.8). Found, %: C 76.49; H 5.89; N 10.95. C₁₆H₁₄N₂O. Calculated, %: C 76.78; H 5.64; N 11.19.

b. A mixture of 0.08 g (0.3 mmol) of aminoacrylonitrile **II** and 0.008 g of potassium hydroxide in 4 ml of ethanol was stirred for 2 h at 20–25°C. The mixture was then passed through a 3–4-cm layer of Al₂O₃, the sorbent was washed with ethanol, the solvent was removed under reduced pressure, and the solid residue was washed with anhydrous diethyl ether. Yield of iminodihydrofuran **III** 0.08 g (100%).

4-Amino-2-imino-5,5-diphenyl-2,5-dihydrofuran hydrochloride (**IV**).

Gaseous hydrogen chloride was passed over a period of 3 h through a solution of 0.10 g (0.4 mmol) of compound **II** in 2 ml of anhydrous dioxane. The solvent was removed under reduced pressure to obtain 0.11 g (96%) of hydrochloride **IV**, mp 177–178°C (decomp.). IR spectrum (KBr), ν , cm⁻¹: 3414–2861 s, br, 1646 s, 1562 s, 1493 w, 1448 m, 1288 v.w, 1254 v.w, 1230 v.w, 1191 v.w, 1118 w, 1071 w, 1036 v.w, 1012 m, 985 m, 934 w, 913 v.w, 889 v.w, 870 w, 805 w, 764 m, 735 w, 698 m, 615 v.w, 589 v.w, 477 w. ¹H NMR spectrum, δ , ppm: 5.35 s (1H, =CH), 3.34 s (3H, NH₂, =NH), 7.49–7.47 m (5H, H_{arom}), 7.39–7.36 m (5H, H_{arom}). ¹³C NMR spectrum, δ _C, ppm: 98.56 (Ph₂C), 128.82 and 130.34 (C^o, C^m), 138.17 (Cⁱ), 81.03 (=CH), 178.79 (NC=CH), 178.56 (C=NH). Found, %: C 66.72; H 5.61; Cl 12.77; N 9.36. C₁₆H₁₅ClN₂O. Calculated, %: C 67.02; H 5.27; Cl 12.36; N 9.77.

2-Imino-4-methylamino-5,5-diphenyl-2,5-dihydrofuran (V**).** Cyanoacetylene **I**, 0.23 g (1 mmol), was

slowly added to a solution of 0.6 g (19.4 mmol) of methylamine in 5 ml of dioxane, cooled to 0°C. The mixture was kept for 1 h at that temperature, allowed to warm up to room temperature, and stirred for 1 h. The solvent was removed under reduced pressure to obtain 0.22 g (83%) of compound **V** with mp 193–195°C. IR spectrum (KBr), ν , cm^{-1} : 3426 w, br, 3302 m, 3209 w, 3182 w, 3114 w, 3059 w, 2993 m, 2936 w, 2882 w, 2814 v.w, 1669 s, 1615 s, 1529 m, 1493 m, 1448 m, 1418 m, 1345 s, 1257 w, 1230 w, 1195 w, 1143 m, 1105 m, 1069 w, 1035 w, 1002 s, 973 m, 933 s, 911 w, 848 w, 806 w, 774 m, 742 m, 699 m, 681 w, 595 v.w, 583 v.w, 512 v.w, 483 w. ^1H NMR spectrum, δ , ppm: 4.94 s (1H, =CH), 2.82 s (3H, NMe), 4.06–3.98 (NH), 7.31–7.34 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 31.99 (NMe), 127.51–128.51 (C^o , C^m), 128.53 (C^p), 145.44 (C^i), 85.85 (=CH), 165.63 (C=CH), 177.21 (C=NH). Mass spectrum: m/z 264. Found, %: C 77.09; H 6.10; N 10.64. $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}$. Calculated, %: C 77.25; H 6.10; N 10.60.

2-Imino-4-methylamino-5,5-diphenyl-2,5-dihydrofuran hydrochloride (VI). Cyanoacetylene **I**, 0.21 g (0.9 mmol), was added at 20–25°C to a solution of 0.25 g (3.7 mmol) of methylamine hydrochloride in 20 ml of ethanol. The mixture was stirred for 1 h, 0.22 g of potassium hydroxide was added, and the mixture was stirred for 3 h at 50°C. The precipitate (KCl) was filtered off, the filtrate was diluted with an equal volume of diethyl ether, and the precipitate was filtered off and washed with diethyl ether. Yield 0.20 g (74%), mp 258–260°C (decomp.). IR spectrum (KBr), ν , cm^{-1} : 3364 s, br, 3230–2855 s, br, 1690 s, 1624 s, 1557 w, 1527 w, 1493 w, 1447 w, 1417 s, 1373 s, 1301 v.w, 1249 m, 1193 m, 1143 m, 1085 v.w, 1072 v.w, 1057 m, 1035 v.w, 993 m, 960 m, 944 v.w, 933 v.w, 914 v.w, 785 w, 772 w, 747 w, 709 m, 697 m, 664 w, 589 w, 569 w, 470 w. ^1H NMR spectrum, δ , ppm: 5.44 s (1H, =CH), 2.81 s (3H, NMe), 7.30 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 31.96 (NMe), 127.26–128.64 (C^o , C^m), 129.53 (C^p), 136.63 (C^i), 78.62 (=CH), 172.03 (C=CH), 173.87 (C=NH), 96.68 (Ph_2C). Found, %: C 67.44; H 5.51; Cl 10.98; N 9.71. $\text{C}_{17}\text{H}_{17}\text{ClN}_2\text{O}$. Calculated, %: C 67.88; H 5.70; Cl 11.79; N 9.31.

A mixture of 0.04 g (0.13 mmol) of hydrochloride **VI** and 0.004 g of potassium hydroxide in 3 ml of ethanol was stirred for 2 h at 20–25°C. The mixture was passed through a 3–4-cm layer of Al_2O_3 , the sorbent was washed with ethanol, the solvent was removed under reduced pressure, and the solid residue was washed with anhydrous diethyl ether. Yield of iminodihydrofuran **V** 0.03 g (86%).

3-(4-Amino-5,5-diphenyl-2,5-dihydrofuran-2-ylideneamino)-4-hydroxy-4-methyl-2-pentenenitrile (VIIIa). A solution of 0.18 g (1.65 mmol) of cyanoacetylene **VII** in 0.5 ml of acetonitrile was added to a solution of 0.40 g (1.6 mmol) of iminodihydrofuran **III** in 4 ml of acetonitrile. The mixture was stirred for 0.5 h at 40°C and evaporated under reduced pressure to obtain 0.57 g (100%) of compound **VIIIa** with mp 168–170°C. IR spectrum (KBr), ν , cm^{-1} : 3431 s, 3310–3212 br.m, 3074 w, 2990 w, 2978 w, 2935 v.w, 2209 m, 1635 s, 1588 s, 1490 w, 1449 m, 1405 m, 1337 w, 1278 m, 1217 m, 1186 m, 1140 w, 1095 m, 1036 w, 983 m, 956 w, 936 m, 886 w, 819 m, 785 w, 764 w, 754 w, 706 w, 695 m, 668 w, 604 w, 581 w, 529 w, 501 w, 458 w, 432 w. ^1H NMR spectrum, δ , ppm: 1.15 (6H, CH_3), 4.85 s (1H, =CH), 5.08 s (1H, =CH), 5.12 (1H, OH), 7.02 (2H, NH_2), 7.36–7.48 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 28.79 (CH_3), 81.85 and 75.66 (=CH), 91.25 (Ph_2C), 119.48 (CN), 127.83–128.67 (C^o , C^m), 128.89 (C^p), 136.98 (C^i), 165.15 (=N–C=), 168.00 ($\text{H}_2\text{N–C=}$), 178.62 (C=N). Found, %: C 73.26; H 6.32; N 11.79. $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2$. Calculated, %: C 73.52; H 5.89; N 11.69.

4-Hydroxy-4-methyl-3-(4-methylamino-5,5-diphenyl-2,5-dihydrofuran-2-ylideneamino)-2-pentenenitrile (VIIIb). A solution of 0.06 g (0.55 mmol) of cyanoacetylene **VII** in 0.5 ml of acetonitrile and 1.5 ml of triethylamine were added to a solution of 0.14 g (0.5 mmol) of iminodihydrofuran **V** in 2 ml of acetonitrile. The mixture was stirred for 1 h at 20°C and for 2 h at 50°C and evaporated under reduced pressure to obtain 0.11 g (58%) of compound **VIIIb**, mp 115–117°C. IR spectrum (KBr), ν , cm^{-1} : 3433–3349 br.s, 3115 v.w, 3085 v.w, 3058 w, 3027 v.w, 2985 w, 2932 w, 2870 w, 2806 w, 2189 s, 1662 m, 1623 s, 1494 w, 1445 m, 1411 m, 1384 v.w, 1666 v.w, 1344 m, 1264 m, 1237 v.w, 1195 w, 1170 m, 1068 w, 1037 m, 1009 s, 975 s, 933 w, 917 w, 869 w, 817 w, 767 m, 704 m, 660 m, 531 w. ^1H NMR spectrum, δ , ppm: 4.32 s (1H, =CH), 3.59 s (1H, =CH), 2.82 s (3H, NMe), 1.84 and 1.76 (6H, CH_3), 7.32 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 27.21 and 26.54 (CH_3), 32.16 (NMe), 83.40 and 86.37 (=CH), 91.04 (Ph_2C), 120.64 (CN), 127.21–128.22 (C^o , C^m), 128.36 (C^p), 142.38 (C^i), 146.00 (=C–N=), 156.97 (=N–C=), 167.56 (C=N). Found, %: C 73.54; H 6.98; N 11.74. $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_2$. Calculated, %: C 73.99; H 6.17; N 11.26.

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