1,2-DIOXIMES IN THE TROFIMOV REACTION

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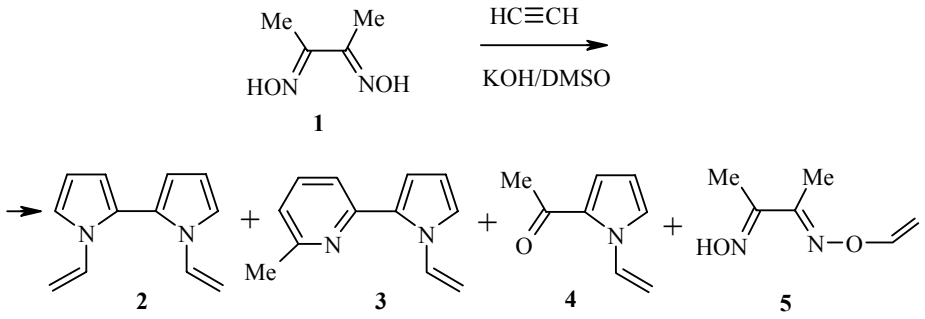
3,3'-Dimethyl-1,1'-divinyl-2,2'-dipyrrole was obtained during the reaction of 3,4-hexanedione dioximes with acetylene under pressure in the potassium hydroxide–DMSO system. In the case of 1,2-cyclohexanedione dioxime 2,2'-dipyrrole and 2-pyridyl- and 2-acylpyrroles were isolated. α-Benzil and α-furil dioximes give 3,4-diphenyl- and 3,4-di(2-furyl)-1,2,5-oxadiazoles respectively in addition to their mono- and divinyl derivatives.

Keywords: acetylene, O-vinyloxime, dioxime, dipyrrole, 1,2,5-oxadiazole, pyridylpyrrole, Trofimov reaction, superbasic system.

The derivatives of 2,2'-dipyrrole widely found in nature exhibit antitumor [1], antimicrobial [1], and immunodepressant [2] activity. Some 2,2'-dipyrroles can be used for the synthesis of extended porphyrins [3] and luminescent materials [4]. Existing methods for the synthesis of 2,2'-dipyrrole and its derivatives are largely based either on the coupling of already prepared pyrrole rings [1, 5-9] or on the addition of a second pyrrole ring using the α substituents of the first [10-12]. In this connection methods based on the single-stage construction of two pyrrole rings from readily available reagents are of special interest.

Earlier it was briefly reported [13] that in the reaction of dimethylglyoxime (**1**) with acetylene in the potassium hydroxide–DMSO system (the Trofimov reaction [14-18]) 2-(6'-methyl-2'-pyridyl)-1-vinylpyrrole (**3**), 2-acetyl-1-vinylpyrrole (**4**), and O-vinyldimethylglyoxime (**5**) (the latter is formed selectively in a shorter reaction time) are formed in addition to 1,1'-divinyl-2,2'-dipyrrole (**2**).



1 **2** **3** **4** **5**

In the present work we extended the Trofimov reaction to other 1,2-dioximes and studied its possible optimization with a view to developing a single-stage synthesis for novel dipyrrole, 2-pyridyl- and 2-acylpyrrole derivatives, and functionally substituted O-vinyloximes, which are of pharmacological interest and are prospective monomers, cross-linking agents, and ligands for the design of metal-complex catalysts.

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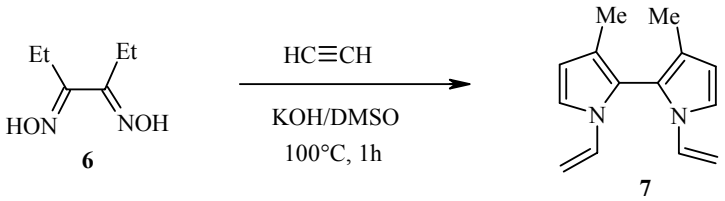
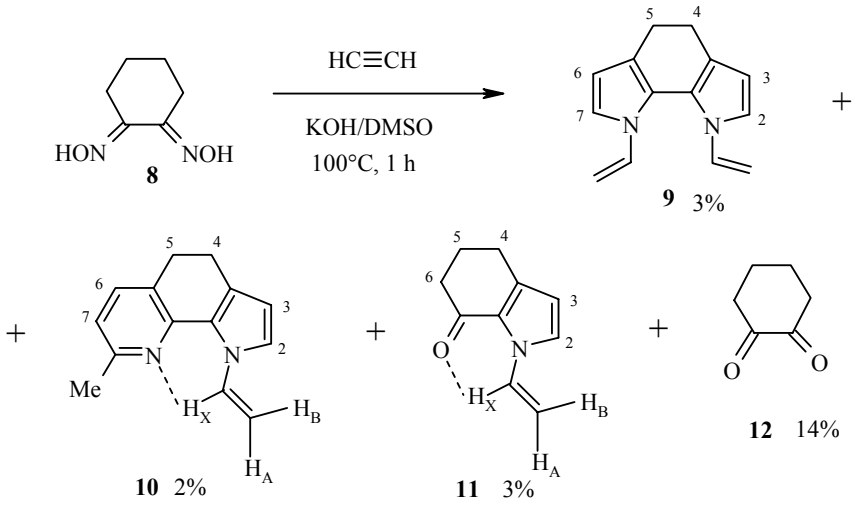
If 3,4-hexanedione dioxime (**6**) is brought into reaction with acetylene (potassium hydroxide-DMSO, 100°C, 1 h, initial acetylene pressure 14 atm), of the expected products only 3,3'-dimethyl-1,1'-divinyl-2,2'-dipyrrole (**7**) is formed with a yield of ~3%.



6 **7**

This is probably the result of the higher susceptibility of the α-methylene groups (compared with methyl groups) in the oximes to pyrrolization.

At the same time 1,2-cyclohexanedione dioxime (**8**) under these conditions gives the pyrroloquinoline **10**, the tetrahydroindolone **11**, and the product from total deoximation of the initial cyclohexanedione (**12**) in addition to the 2,2'-dipyrrole compound **9**.

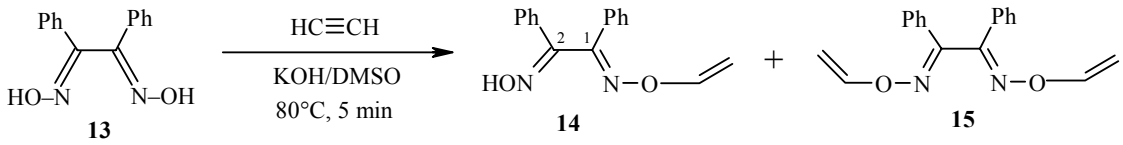


8 **9** 3% **10** 2% **11** 3% **12** 14%

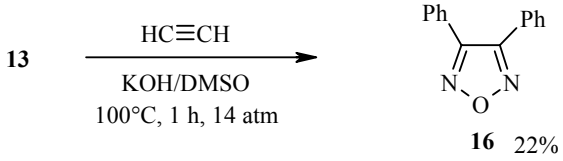
In spite of the known [18] higher reactivity of cyclohexanone oxime in the Trofimov reaction compared with acyclic ketoximes, the six-membered cyclic system containing two conjugated oxime functions is susceptible to a greater degree to the side processes leading to the formation of a pyridine ring and deoximation.

The anomalous downfield shift of the H_X signals of compounds **10** (8.62 ppm) and **11** (7.99 ppm) in the ^1H NMR spectrum is due to the realization of hydrogen bonding with the nitrogen and oxygen atoms of the pyridyl and acyl substituents respectively. The stronger effect due to this bonding in the case of **10** compared with that observed in 2-pyridylpyrrole **3** (7.84 ppm) should be noted. This results from the rigidity of the cyclic system **10**, which promotes closer steric approach of the H_X atoms of the vinyl group and the nitrogen of the pyridine ring.

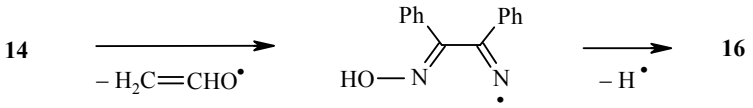
α-Benzil dioxime (**13**), the structure of which excludes the possibility of pyrrolization, reacts with acetylene giving the mono and divinyl derivatives **14** and **15** respectively.



The highest yields of compounds **14** and **15** (50 and 12% respectively) were obtained at a reaction temperature of 80°C (initial acetylene pressure 14 atm) and reaction time ~5 min. If the reaction time is increased to 1 h (80°C) under these conditions or the temperature is raised to 100°C (~5 min) 3,4-diphenyl-1,2,5-oxadiazole (**16**) is formed, while the vinyl derivatives **14** and **5** cannot be isolated.



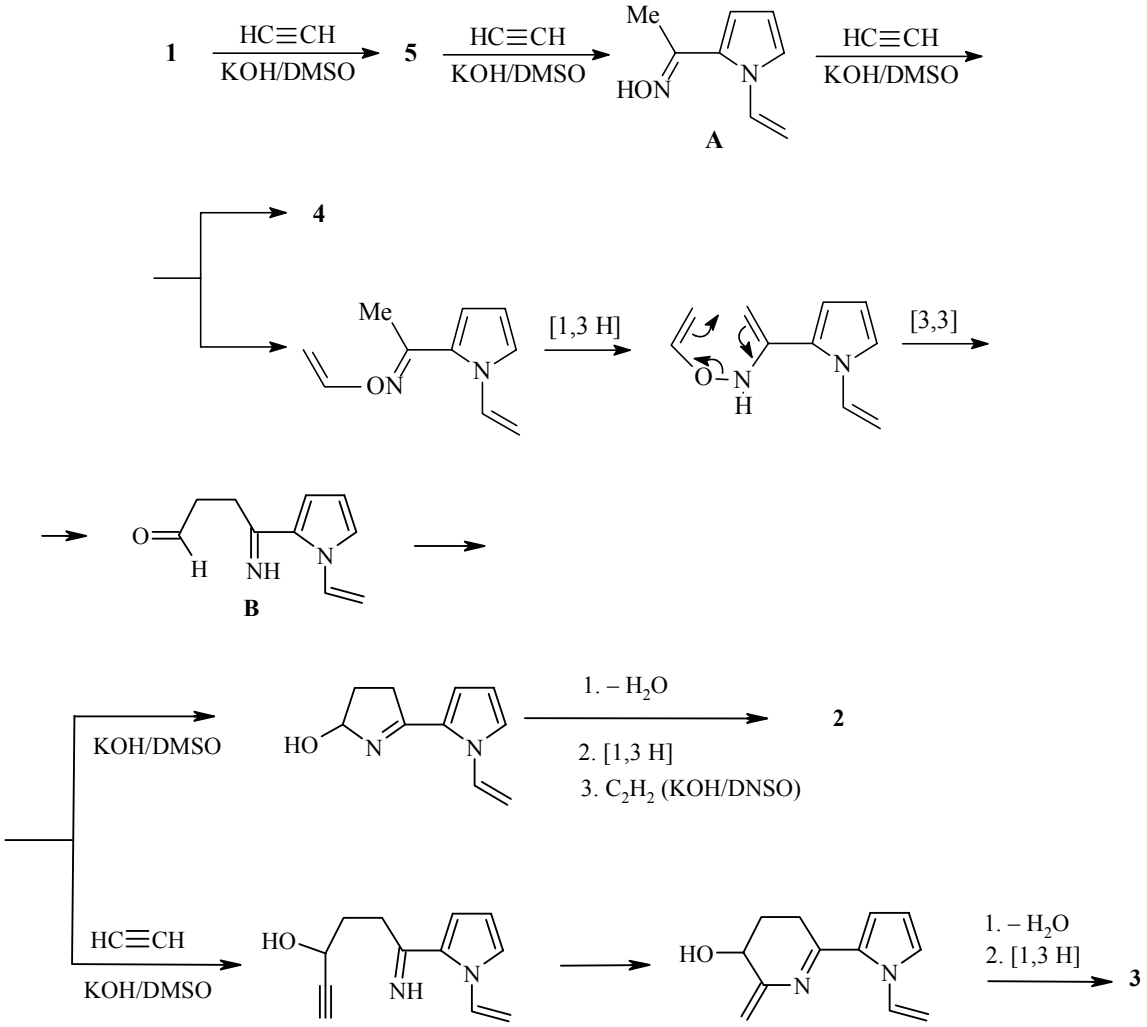
Under the same conditions in the absence of acetylene α-benzil dioxime **13** is inert and does not form the oxadiazole **16**. Radicals generated during the dissociation of the obtained O-vinyloxime derivatives are probably involved in the cyclization.



The thermally initiated (~150°C) spontaneous and in some cases explosive decomposition of compounds containing an O-vinyloxime group was observed earlier in the case of O-vinylketoximes [19] and O-vinylamidoximes [20]. The total yield of the O-vinylation products **14** and **15** and the relative content of the divinyl derivative **15** are doubled if the reaction temperature in the potassium hydroxide–DMSO system is increased from 60 to 80°C. A similar effect can be obtained with increase in the alkali content of the system. It should be noted that the oxime functions in the dioxime **13** retain the *E*,*E*-configuration in the vinylation process.

The behavior of the α-furyldioxime in reaction with acetylene in the potassium hydroxide–DMSO system is reminiscent of the behavior of α-benzil dioxime. However, the formation of significant amounts of 3,4-di(2-furyl)-1,2,5-oxadiazole is observed even under comparatively mild conditions (80°C, ~5 min, initial acetylene pressure 14 atm), and it is not possible to achieve selective formation of the O-vinyl derivatives.

The effect of the conditions for the reaction of dimethylglyoxime **1** with acetylene in superbasic media on the yield and ratio of the formed products was studied. The combination of main processes occurring in such a system is presented below.

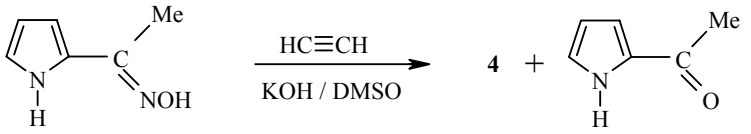


In this case we were unable to obtain the corresponding O,O'-divinyl derivative. The lower reactivity of dimethylglyoxime **1** compared with α-benzil dioxime **13** in nucleophilic addition to acetylene is probably due to the absence of the stabilizing effect of the phenyl rings on the transition state of the given reaction (increase in the nucleophilicity of the oximate ion on account of conjugation with the benzene ring).

If DMSO is replaced by N-methylpyrrolidone in the reaction of dimethylglyoxime **1** with acetylene at 110°C 2-acetyl-1-vinylpyrrole **4** is only formed after 5 h (yield ~3%, ^{1}H NMR), while the products **2**, **3**, and **5** are hardly formed at all. The use of sodium hydroxide as base (120°C, 1 h) leads to the formation of polymeric products. The probable reason is the lower basicity of the sodium hydroxide and its more clearly defined ability, compared with potassium hydroxide, to assist in the deoximation processes, leading to dicarbonyl compounds susceptible to self-condensation in alkaline media.

In the potassium hydroxide–DMSO system with increase in temperature there is an increase in the relative amount of 2-acetyl-1-vinylpyrrole **4** (see Scheme above), while the ratio of the dipyrrole **2** and methylpyridylpyrrole **3** remains practically constant. Increase in the potassium hydroxide content of the system leads to an increase in the relative amounts of 2-acetyl-1-vinylpyrrole **4** and methylpyridylpyrrole **3**. This is the result of the intensification of the deoximation process, leading to the acetylpyrrole **4**, and subsequent ethynylation (in the Favorskii reaction) of the iminoaldehyde **B** formed as a result of [3,3] sigmatropic rearrangement.

Earlier the selective synthesis of 1'-methyl-1-vinyl-2,2'-dipyrrole from 2-acetyl-1-methylpyrrole oxime was realized by the Favorsky reaction [21]. An attempt to use this approach for the selective synthesis of 2,2'-dipyrrole **2** from 2-acetylpyrrole oxime **17**, which has a structure similar to the supposed intermediate **A** (p. 37), was unsuccessful. However, 2-acetyl-1-vinylpyrrole **4** (28%) and the product from deoximation of the oxime **17**, i.e., 2-acetylpyrrole **18** (30%), are formed relatively selectively in the reaction of the oxime **17** with acetylene in the potassium hydroxide–DMSO system (100°C, 1 h).



17 **18**

The direct vinylation of the ketone **18** with acetylene in the potassium hydroxide–DMSO system is accompanied by the formation of resinous products probably as a result of condensation of the initial compound. Thus, the oxime group in the oxime **17** fulfills a protective function with respect to the acetyl fragment and is removed during the vinylation of the pyrrole ring.

In the ^{1}H NMR spectra of the reaction mixtures obtained under harsher conditions (120°C, 3 h) it was possible to identify the signals of the divinylpyrrole **2**, methylpyridylpyrrole **3**, and 2-acetyl-1-vinylpyrrole **4**.

Thus, the fundamental possibility of single-stage synthesis of 2,2'-dipyrrole and 2-pyridyl- and 2-acylpyrroles from readily obtainable 1,2-dioximes and acetylene by the Trofimov reaction was demonstrated. The corresponding mono and divinyl derivatives can be obtained from the 1,2-dioximes, the structure of which rules out the possibility of pyrrolization. In spite of the low product yields the prospects of the method compared with alternative multistage processes are obvious, since it makes it possible to produce potential biologically active compounds, valuable monomers, ligands, and intermediates for fine organic synthesis from available reagents.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400DPX spectrometer (400 and 101 MHz respectively) with HMDS as internal standard (δ, 0.05 ppm). The IR spectra were recorded in potassium bromide on a Bruker ISF-25 instrument. The initial dioximes with the exception of 3,4-hexanedione dioxime **6** were commercial products from Aldrich.

3,4-Hexanedione Dioxime (6). To a mixture of 3,4-hexanedione (7 g, 61 mmol) and $NH_2OH{\cdot}HCl$ in ethanol (35 ml) and water (4 ml) with stirring we added in small portions finely ground sodium hydroxide (6.13 g, 153 mmol). The obtained mass was stirred at room temperature for 1 h and poured into cold water (300 ml). The precipitate was filtered off and washed thoroughly with water. After drying under vacuum we obtained 7.89 g of a white powder. Yield 89%; mp 192-196°C (ethanol). IR spectrum, ν, cm^{-1}: 3282 (s), 3223 (s), 3127 (w), 3085 (w), 3059 (w), 2986 (m), 2945 (m), 2921 (w) 2885 (w), 1655 (w), 1632 (w), 1467 (m), 1435 (m), 1375 (w), 1266 (w), 1247 (m), 1068 (m), 1028 (m), 964 (s), 883 (s), 804 (w), 755 (m), 689 (w), 583 (w). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 11.27 (2H, s, OH); 2.51 (4H, q, $^3J_{MeCH_2}$ = 8.0, CH_2); 0.96 (6H, t, $^3J_{MeCH_2}$ = 8.0, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm; 159.69 (C=N); 16.49 (CH_2); 10.89 (CH_3). Found, %: C 49.90; H 8.26; N 19.33. $C_6H_{12}N_2O_2$. Calculated %: C 49.99; H 8.39; N 19.43.

3,3'-Dimethyl-1,1'-divinyl-2,2'-dipyrrole (7). A mixture of compound **6** (2 g, 14 mmol) and $KOH{\cdot}H_2O$ (3.2 g, 49 mmol) in DMSO (50 ml) was saturated with acetylene at room temperature (initial pressure 14 atm) in a 0.5-liter revolving autoclave, heated to 100°C, and kept at this temperature for 1 h (residual pressure 4 atm). To the reaction mixture unloaded from the autoclave we added 150 ml of water. The product was extracted with

ether (4 × 50 ml), and the extracts were washed with water (3 × 50 ml) and dried over potassium carbonate. After evaporating the ether we obtained 1.6 g of a black-red resinous mass, from which by column chromatography (basic Al_2O_3, eluant diethyl ether) we isolated 0.31 g of a fraction containing compound **7** as the main component (purity ~30%, ^{1}H NMR). Yield ~3%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz); 7.06 (2H, d, $^3J_{4,5}$ = 2.9, H-5); 6.42 (2H, dd, $^3J_{B,X}$ = 15.8, $^3J_{A,X}$ = 9.08, H_X); 6.16 (2H, d, $^3J_{4,5}$ = 2.9, H-4); 4.91 (2H, d, $^3J_{B,X}$ = 15.8, H_B); 4.44 (2H, d, $^3J_{AX}$ = 9.08, H_A); 1.89 (6H, s, CH_3).

1,8-Divinyl-4,5-dihydropyrrolo[3,2-*g*]indole (9), 8-Methyl-1-vinyl-4,5-dihydro-1H-pyrrolo[3,2-*h*]-quinoline (10), and 1-Vinyl-1,4,5,6-tetrahydro-7H-indol-7-one (11). From the dioxime **8** (2 g, 14 mmol) in the presence of KOH·0.5H_2O (0.91 g, 14 mmol) by analogy with compound **7** we obtained 2.26 g of a black resinous mass, from which by column chromatography (basic aluminum oxide, eluant diethyl ether) we isolated 0.2, 0.17, 0.19, and 0.37 g of fractions containing the dipyrrole **9** (purity ~40%, yield ~3%), 2-pyridylpyrrole **10** (purity ~30%, yield ~2%), and 2-acylpyrrole **11** (purity ~40%, yield ~3%) derivatives of pyrrole and the cyclohexanedione **12** (purity ~60%, yield ~14%) respectively as the main components.

1,8-Divinyl-4,5-dihydropyrrolo[3,2-*g*]indole (9). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.96 (2H, dd, $^3J_{B,X}$ = 15.6, $^3J_{A,X}$ = 8.8, H_X); 5.12 (2H, dd, $^2J_{B,X}$ = 15.6, $^2J_{A,B}$ = 1.1, HB); 6.83 (2H, d, $^3J_{2,3}$ = $^3J_{6,7}$ = 2.9, H-2,7); 6.19 (2H, d, $^3J_{2,3}$ = $^3J_{6,7}$ = 2.9, H-3,6); 4.71 (2H, d, $^3J_{A,X}$ = 8.8, H_A); 2.58 (4H, s, CH_2).

8-Methyl-1-vinyl-4,5-dihydropyrrolo[3,2-*h*]quinoline (10). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.62 (1H, dd, $^3J_{B,X}$ = 16.4, $^3J_{A,X}$ = 8.8, H_X); 7.29 (1H, d, $^3J_{6,7}$ = 7.6, H-6); 7.13 (1H, d, $^3J_{2,3}$ = 2.7, H-2); 6.76 (1H, d, $^3J_{6,7}$ = 7.6, H-7); 6.10 (1H, d, $^3J_{2,3}$ = 2.7, H-3); 5.11 (1H, d, $^3J_{B,X}$ = 16,4. H_B); 4.68 (1H, d, $^3J_{A,X}$ = 8.8, H_A); 2.84 (2H, t, $^3J_{4,5}$ = 7.3, H-5); 2.69 (2H, t, $^3J_{4,5}$ = 7.3, H-4); 2.48 (3H, s, $^3J_{2,3}$ = 2.7, CH_3).

1-Vinyl-1,4,5,6-tetrahydro-7H-indol-7-one (11). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.99 (1H, dd, $^3J_{B,X}$ = 16.0, $^3J_{A,X}$ = 8.8, H_X); 7.23 (1H, d, $^3J_{2,3}$ = 2.8, H-2); 6.07 (1H, d, $^3J_{2,3}$ = 2.8, H-3); 5.11 (1H, d, $^3J_{B,X}$ = 16.0, H_B); 4.73 (1H, d, $^3J_{A,X}$ = 8.8, H_A); 2.71 (2H, t, $^3J_{4,5}$ = 6.1, H-4), 2.46 (2H, t, $^3J_{B,X}$ = 6.1, H-6); 2.03 (2H, m, H-5).

O-Vinyl-α-benzil Dioxime (14) and O,O'-Divinyl-α-benzil Dioxime (15). A. A mixture of lithium hydroxide (0.8 g, 33 mmol), cesium fluoride (5.06 g, 33 mmol), and methanol (10 ml) was stirred for 10 min, α-benzil dioxime **13** (4 g, 17 mmol) was added, the mixture was stirred for a further 10 min, and DMSO (10 ml) was added. The methanol was distilled from the obtained mixture under vacuum (~30 mm Hg) with gentle heat (~50°C) until the DMSO began to distil. To the residue, which contained cesium benzildioximate, we added 90 ml of DMSO. The whole mass was transferred to a half-liter autoclave, saturated with acetylene at room temperature (initial pressure 14 atm), heated to 80°C over 30 min, and kept at this temperature for 5 min (residual pressure 6 atm). After the addition of water (150 ml) the reaction mixture unloaded from the autoclave was neutralized with solid CO_2 and extracted with ether (4 × 50 ml). The extracts were washed with water (3 × 50 ml) and dried over potassium carbonate. From the viscous liquid (3.71 g) obtained after removal of the succinic ester we isolated by column chromatography (basic aluminum oxide, eluant diethyl ether, methanol) 2.39. g of the monovinyl oxime **14** and 0.85 g of the divinyl benzil dioxime **15**. The yields were 54 and 18% respectively.

B. A mixture of α-benzil dioxime **13** (4 g, 17 mmol) and KOH·0.5H_2O (2.16 g, 33 mmol) in DMSO (100 ml) in a half-liter revolving autoclave was saturated with acetylene at room temperature (initial pressure 14 atm, residual pressure 5 atm). See method A for the further treatment. From 3.2 g of amber liquid we isolated 2.27 g of monovinylbenzil dioxime **14** and 0.61 g of divinylbenzil dioxime **15**. The yields were 50 and 12% respectively.

O-Vinyl-α-benzil Dioxime (14). mp 124-126°C (methanol). IR spectrum, ν, cm^{-1}: 3251 (s), 3062 (w), 2924 (w), 2893 (w), 1638 (s), 1603 (w), 1572 (w), 1494 (m), 1446 (m), 1379 (w), 1334 (w), 1309 (w), 1260 (m), 1167 (s), 1142 (s), 1080 (m), 1031 (w), 987 (s), 949 (w), 937 (s), 917 (w), 866 (m), 841 (m), 752 (m), 688 (s), 611 (m), 550 (w). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.10 (1H, br. s, OH); 7.69 (2H, m, *o*-H-2); 7.59

(2H, m, *o*-H-1); 7.38 (1H, m, *p*-H-2); 7.38 (1H, m, *p*-H-1); 7.35 (2H, m, *m*-H-2); 7.35 (2H, m, *m*-H-1); 6.95 (1H, dd, $^3J_{B,X}$ = 14.2, $^3J_{A,X}$ = 6.8, H_X); 4.66 (1H, dd, $^3J_{B,X}$ = 14.2, $^2J_{A,B}$ = 1.8, H_B); 4.18 (1H, dd, $^2J_{A,X}$ = 6.8, $^2J_{A,B}$ = 1.8, H_A). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 153.54 (C(1)); 152.45 (C(2)); 152.33 (C_α); 130.71 (C_p(2)); 130.27 (C_p(1)); 128.92 (C_m(1)); 128.92 (C_p(2)); 126.82 (C_o(2)); 126.38 (C_o(1)); 89.40 (C_β). Found %: C 71.50; H 5.53; N 9.95. $C_{16}H_{14}N_2O_2$. Calculated, %: C 72.17; H 5.30; N 10.52.

O,O'-Divinyl-α-benzil Dioxime (15). n^D_{20} 1.6031. IR spectrum, ν, cm^{-1}: 3065 (s), 3041 (w), 2954 (w), 2926 (s), 2854 (m), 1641 (s), 1610 (m), 1567 (w), 1548 (w), 1535 (w), 1495 (m), 1446 (s), 1381 (m), 1332 (m), 1309 (m), 1292 (w), 1270 (s), 1168 (s), 1143 (s), 1070 (m), 1029 (w), 992 (s), 968 (w), 944 (s), 919 (w), 882 (s), 850 (s), 785 (w), 762 (s), 734 (w), 691 (s), 629 (m), 600 (s), 561 (m), 528 (w). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.64 (4H, m, *o*-H); 7.40 (2H, m, *p*-H); 7.34 (4H, m, *p*-H); 6.92 (2H, dd, $^3J_{B,X}$ = 14.0, $^3J_{A,X}$ = 6.7, H_X); 4.64 (2H, dd, $^2J_{A,B}$ = -1.4, $^3J_{B,X}$ = 14.0, H_B); 4.16 (2H, dd, $^2J_{A,B}$ = -1.4, $^3J_{A,X}$ = 6.7, H_A). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 153.19 (C=N); 152.20 (C_α); 131.00 (C_i); 130.71 (C_p); 128.95 (C_m); 126.77 (C_o); 89.47 (C_β). Found, %: C 73.72; H 5.48; N 9.81. $C_{18}H_{16}N_2O$. Calculated, %: C 73.95; H 5.52; N 9.58.

3,4-Diphenyl-1,2,5-oxadiazole (16). A mixture of α-benzil dioxime **13** (4 g, 17 mmol) and KOH·0.5H_2O (2.16 g, 33 mmol) in 100 ml of DMSO was saturated with acetylene at room temperature (initial pressure 14 atm) in a half-liter revolving autoclave was heated to 80°C and kept at this temperature for 1 h. After the addition of water (150 ml) the reaction mixture unloaded from the autoclave was extracted with ether (4 × 50 ml). The extracts were washed with water (3 × 50 ml) and dried over potassium carbonate. From the dark-brown resinous mass (4.11 g) obtained after removal of the ether we isolated by column chromatography (basic aluminum oxide, eluant hexane) 0.83 g of compound **16** in the form of white crystals. Yield 22%; mp 86-88°C. IR spectrum, ν, cm^{-1}: 3056 (w), 3034 (w), 2924 (w), 2850 (w), 1607 (w), 1577 (w), 1548 (w), 1493 (m), 1443 (s), 1368 (m), 1339 (w), 1313 (m), 1294 (m), 1279 (m), 1179 (w), 1158 (w), 1075 (m), 1026 (m), 1002 (w), 989 (s), 927 (w), 892 (s), 852 (w), 787 (s), 765 (s), 733 (s), 698 (s), 673 (w), 624 (m), 608 (m), 560 (m), 515 (m). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.52 (4H, m, *o*-H); 7.46 (2H, m, *p*-H); 7.41 (4H, m, *m*-H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 153.16 (C(3,4)); 130.52 (C_p); 129.00 (C_o); 128.93 (C_m); 125.92 (C_i). Found, %: C 75.25; H 4.51; N 12.59. $C_{14}H_{10}N_2O$. Calculated, %: C 75.66; H 4.54; N 12.60.

3,4-Di(2-furyl)-1,2,5-oxadiazole. This compound was obtained similarly to compound **16**. By column chromatography (basic aluminum oxide) we isolated 0.52 g of a fraction containing ~65% (^{1}H NMR) of 3,4-di(2-furyl)-1,2,5-oxadiazole. Yield 8%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.64 (2H, d, $^3J_{4',5'}$ = 1-7, H-5'); 7.11 (2H, d, $^3J_{3',4'}$ = 3.5, H-3'); 6.57 (2H, dd, $^3J_{3',4'}$ = 3.5, $^3J_{4',5'}$ =1.7, H-4').

2-Acetyl 1-Vinylpyrrole (4). From 2-acetylpyrrole oxime **17** (1.94 g, 15.6 mmol) in the presence of KOH·0.5H_2O (1.02 g, 15.6 mmol) by analogy with the synthesis of **7** we obtained 1.4 g of a black liquid (residual pressure 7 atm), from which by column chromatography (basic aluminum oxide, eluant diethyl ether) we isolated 0.51 g (30%) of 2-acetylpyrrole **18** and 0.59 g (28%) of compound **4** (characteristics of **4** in [13]).

2-Acetylpyrrole (18). IR spectrum, ν, cm^{-1}: 3266 (bs), 3113 (w), 3085 (w), 2969 (w), 2927 (w), 2687 (w), 2558 (w), 1776 (w), 1736 (w), 1641 (s), 1547 (m), 1506 (w), 1429 (m), 1400 (s), 1363 (m), 1323 (m), 1262 (w), 1220 (w), 1141 (m), 1129 (m), 1074 (m), 1044 (m), 1019 (m), 972 (m), 926 (m), 887 (w), 842 (m), 773 (s), 749 (s), 669 (w), 631 (m), 608 (m), 553 (m), 511 (m). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.95 (1H, br. s, NH); 7.04 (1H, s, H-5); 6.91 (1H, s, H-3); 6.26 (1H, s, H-4); 2.43 (3H, s, CH_3).

^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 188.40 (C=O); 132.25 (C(2)); 125.37 (C(5)); 117.35 (C(3)); 110.57 (C(4)); 25.50 (CH_3).

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