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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on his 70th anniversary

4-Dimethylaminoacetophenone *O*-Vinyloxime: Synthesis and Steric Structure

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Abstract—4-Dimethylaminoacetophenone oxime was synthesized from 4-dimethylaminoacetophenone and hydroxylamine hydrochloride. Its reaction with acetylene in the system KOH–DMSO gave previously unknown 4-dimethylaminoacetophenone *O*-vinyloxime as the major product. According to the experimental data and quantum-chemical calculations, 4-dimethylaminoacetophenone *O*-vinyloxime is formed as the only *E* isomer with preferential *s-trans* conformation of the vinyloxy group, which is characterized by essentially nonplanar structure.

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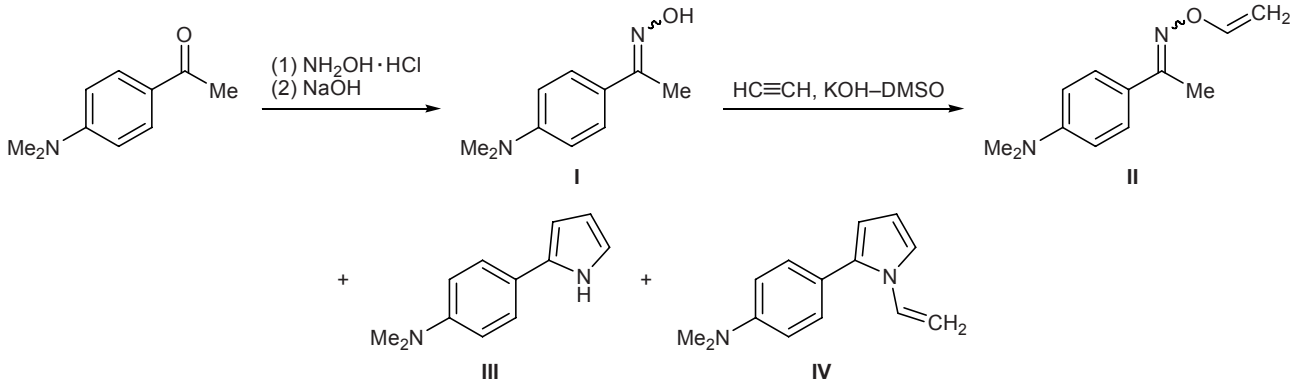
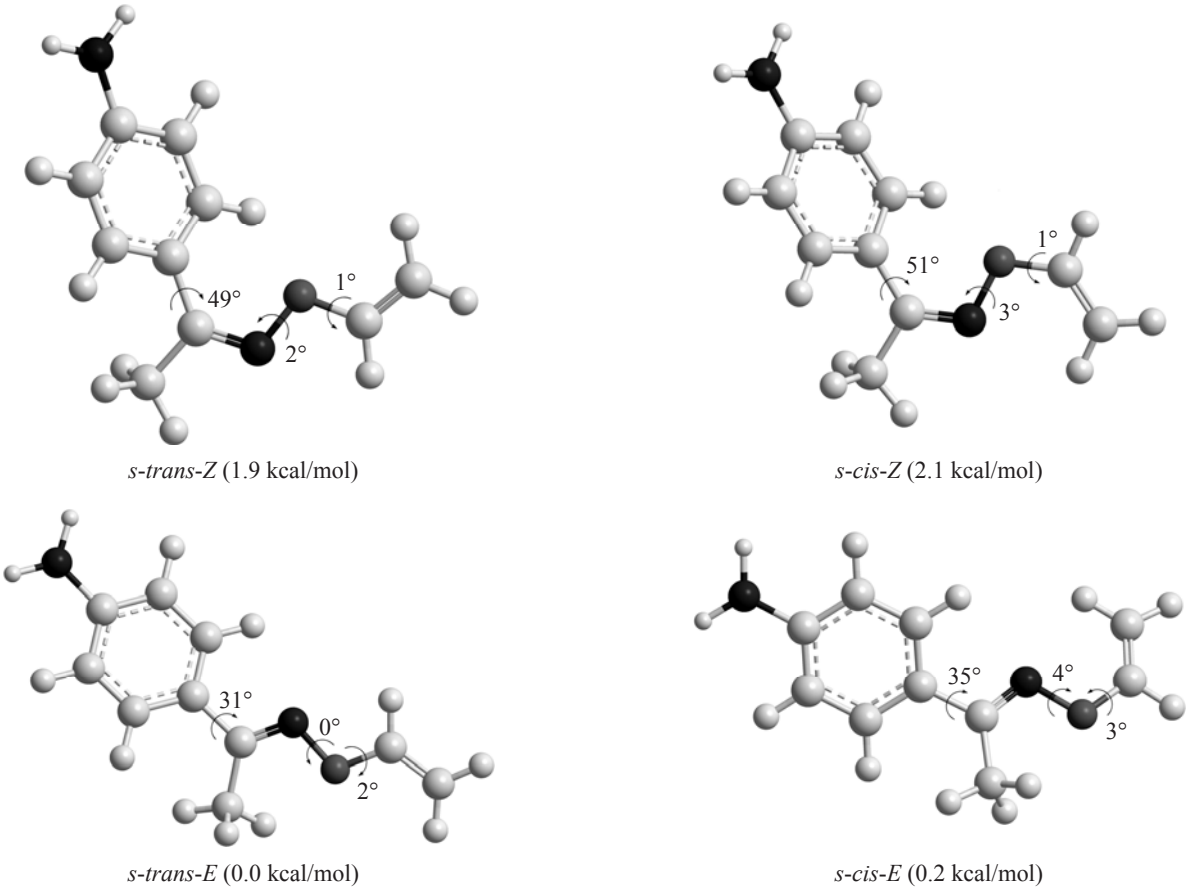
O-Vinyloximes attract persistent interest as promising monomers and intermediate products, especially since the development of a procedure for their synthesis via vinylation of oximes with acetylene [1–5]. The presence in *O*-vinyloxime molecules of a double bond contiguous to two heteroatoms (CH_2=CH–O–N=) endows them with some specific properties which make such compounds interesting models for theoretical and spectral studies [6–8]. However, a serious obstacle hampering studies on O-vinyl oximes is their chemical and thermal instability. It is known that ketone *O*-vinyloximes having a methylene group in the α-position with respect to the oxime moiety are key intermediates in the synthesis of pyrroles from oximes and acetylene (Trofimov reaction) [1, 2]. Alkyl aryl ketone *O*-vinyloximes, especially those containing electron-withdrawing substituents in the aromatic ring are more prone to undergo cyclization to pyrroles, as compared to their aliphatic analogs [4]. It might be expected that acetophenone *O*-vinyloximes having electron-donating groups in the benzene ring should be more stable than unsubstituted acetophenone *O*-vinyloxime and that such derivatives could be isolated as individual substances.

Scheme 1.





s-trans-Z (1.9 kcal/mol) *s-cis-Z* (2.1 kcal/mol)

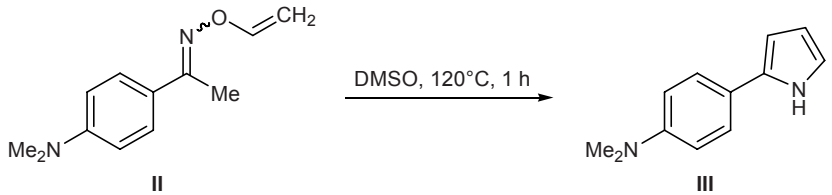
s-trans-E (0.0 kcal/mol) *s-cis-E* (0.2 kcal/mol)

Fig. 1. Equilibrium conformations of the *E* and *Z* isomers of model 4-aminoacetophenone *O*-vinyloxime, optimized by the MP2/6-311G** method. The relative total energies are given in parentheses, and arrows show angular deviations of the phenyl and vinyl group from the plane of the oxime fragment.

In fact, 4-dimethylaminoacetophenone oxime (**I**) prepared in 90% yield from 4-dimethylaminoacetophenone and hydroxylamine hydrochloride reacted with acetylene in the system KOH–DMSO (80°C, 1 h, acetylene pressure 15 atm) to give mainly 4-dimethylaminoacetophenone *O*-vinyloxime (**II**) in 70% yield. Apart from compound **II**, the reaction mixture contained 2-(4-dimethylaminophenyl)pyrrole (**III**, 6%) and its *N*-vinyl derivative **IV** (12%) (Scheme 1). It should be noted for comparison that vinylation of acetophenone oxime under analogous conditions leads to a mixture of acetophenone *O*-vinyloxime (4.5%), 2-phenyl-1*H*-pyrrole (53.4%), and 2-phenyl-1-vinyl-1*H*-pyrrole (0.8%) [4]. We succeeded in raising the yield of vinyl oxime **II** to 85% by carrying out the reaction of 4-dimethylaminoacetophenone oxime with acetylene in pentane which favored removal of the product from the reaction zone. In this case, the only by-product was pyrrole (**III**, yield 5%).

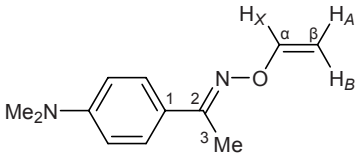
Heating of *O*-vinyloxime **II** in DMSO at 120°C promoted its rearrangement into pyrrole **III** (89%); the latter was synthesized previously in 48% yield by palladium-catalyzed cross coupling of pyrrolyl anion with 4-bromo-*N*,*N*-dimethylaniline [9] or by photolysis of 4-chloro-*N*,*N*-dimethylaniline in the presence of pyrrole (yield 64%) [10]. The rearrangement of **II** into

Scheme 2.



II **III**

Calculated[a] (SOPPA CCSD) and experimental $^{13}C–^{13}C$ and $^{13}C–^{1}H$ coupling constants (Hz) of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**)



Coupling constant	Isomer	Conformation	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	J_{exp}
$^{1}J(C^{1},C^{2})$	*Z*	*s-trans*	0.36	–1.47	0.67	54.34	53.90	60.9
		s-cis	0.35	–1.45	0.66	53.94	53.50	
	E	*s-trans*	0.34	–1.67	0.79	62.68	62.14	
		s-cis	0.35	–1.68	0.76	62.53	61.96	
$^{1}J(C^{2},C^{3})$	*Z*	*s-trans*	0.26	–1.04	0.71	51.46	51.39	41.8
		s-cis	0.26	–1.07	0.71	51.39	51.29	
	E	*s-trans*	0.27	–1.12	0.69	43.33	43.17	
		s-cis	0.27	–1.14	0.69	43.30	43.12	
$^{1}J(C_{\alpha},H_{\beta})$	*Z*	*s-trans*	0.18	–8.06	3.24	85.75	81.11	80.7
		s-cis	0.18	7.96	3.08	84.29	79.59	
	E	*s-trans*	0.18	–8.07	3.25	85.71	81.07	
		s-cis	0.18	–7.98	3.11	84.48	70.79	
$^{1}J(C_{\alpha},H_{X})$	*Z*	*s-trans*	1.00	–0.22	0.26	182.36	183.40	185.0
		s-cis	0.96	–0.10	0.18	179.56	180.60	
	E	*s-trans*	0.99	–0.22	0.26	183.10	184.13	
		s-cis	0.94	–0.09	0.19	179.82	180.86	
$^{1}J(C_{\beta},H_{A})$	*Z*	*s-trans*	0.57	0.76	0.37	160.64	162.34	162.0
		s-cis	0.59	0.76	0.36	159.03	160.74	
	E	*s-trans*	0.56	0.75	0.37	160.98	162.66	
		s-cis	0.59	0.74	0.36	159.13	160.82	
$^{1}J(C_{\beta},H_{B})$	*Z*	*s-trans*	0.61	0.66	0.35	157.03	158.65	158.5
		s-cis	0.66	0.52	0.41	162.38	163.97	
	E	*s-trans*	0.60	0.67	0.35	156.78	158.40	
		s-cis	0.66	0.51	0.40	162.63	164.20	

[a] The calculations were performed for 4-aminoacetophenone *O*-vinyloxime to reduce computational expenses.

III was accompanied by side formation of 4-dimethylaminoacetophenone, presumably as a result of decomposition of initial *O*-vinyloxime **II** (Scheme 2) [4]. This rearrangement required more prolonged heating (1 h) than did analogous transformation of ethyl mesityl ketone *O*-vinyloxime into the corresponding pyrrole [11], which was complete in 5 min. These findings provide an additional support to thermal stability of *O*-vinyloxime **II**.

Taking into account stereoselectivity of intramolecular cyclization of *O*-vinyloximes [1, 2], it seemed very important to determine the steric structure of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**), in particular configuration of the C=N bond and predominant conformation related to internal rotation of the vinyloxy group.

The results of quantum-chemical calculations performed at the MP2/6-311G** level of theory showed that the *E* isomer of model 4-aminoacetophenone *O*-vinyloxime in the gas phase is more stable than the *Z* isomer by ~2 kcal/mol and that each isomer gives rise to two conformers due to internal rotation of the vinyloxy group, *s-cis* and *s-trans*, with as small energy difference as 0.2 kcal/mol (Fig. 1). Presumably, the *Z*

isomer is less stable owing to strong steric interaction between protons in the *ortho* positions of the benzene ring and the azomethine fragment. This follows from considerable deviation of the phenyl ring from the CH=N plane: the corresponding dihedral angle reaches 35–50° (Fig. 1). The results of calculations allowed us to presume that the only formed isomer of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**) has *E* configuration at the C=N bond; however, preferential conformation of that conformer cannot be determined on the basis of the above data.

It is known that $^{13}C–^{13}C$ coupling constants display pronounced dependence on the orientation of lone electron pair (LEP) on the nitrogen atom in oximes and their derivatives [12]. The lone electron pair on the imino nitrogen atom provides a positive through-space contribution to the $^{13}C–^{13}C$ coupling constant for the neighboring carbon–carbon bond in the *cis* position (J_{cis}) with respect to the LEP; on the other hand, unpaired electron density transfer from the C=N nitrogen atom to the antibonding orbital of the neighboring carbon–carbon bond in the *trans* position reduces the corresponding $^{13}C–^{13}C$ coupling constant (J_{trans}), i.e., the contribution of the nitrogen LEP to that constant is negative. The nature of this effect was studied in detail in [13]. Thus the effect of LEP strongly differentiates the $^{13}C–^{13}C$ coupling constants J_{cis} and J_{trans}, so that they can be used to unambiguously assign configuration of not only oximes and their derivatives but also various Schiff bases (see [14] and references therein).

If $^{13}C–^{13}C$ coupling constants could be determined experimentally for both isomers (J_{cis} and J_{trans}), their assignment is obvious; if only one value (J_{cis} or J_{trans}) could be measured, it is necessary to calculate $^{13}C–^{13}C$ coupling constants for both isomers by quantum-chemical method and compare the calculated value with the experimental one. According to the GLC and ^{13}C NMR data, compounds **I** and **II** exist as a single isomer. First of all, we measured the corresponding $^{13}C–^{13}C$ coupling constants from the position of ^{13}C satellites of the C=N carbon (C^2) signal in the ^{13}C NMR spectrum of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**) (Fig. 2), and the $^{13}C–^{13}C$ and $^{13}C–^{1}H$ coupling constants for both isomers were calculated with account taken of their conformation (see table).

The $^{13}C–^{13}C$ coupling constants for compound **II** were calculated in terms of the second-order polarization propagator approximation (SOPPA) with coupled cluster singles and doubles amplitudes (CCSD), which was proposed for the first time in [15]. We used special Dunning's correlation-consistent basis sets [16] extended by correlating functions and optimized for the calculation of $^{13}C–^{13}C$ and $^{13}C–^{1}H$ coupling constants as described in [17]. The total $^{13}C–^{13}C$ and $^{13}C–^{1}H$ cou-

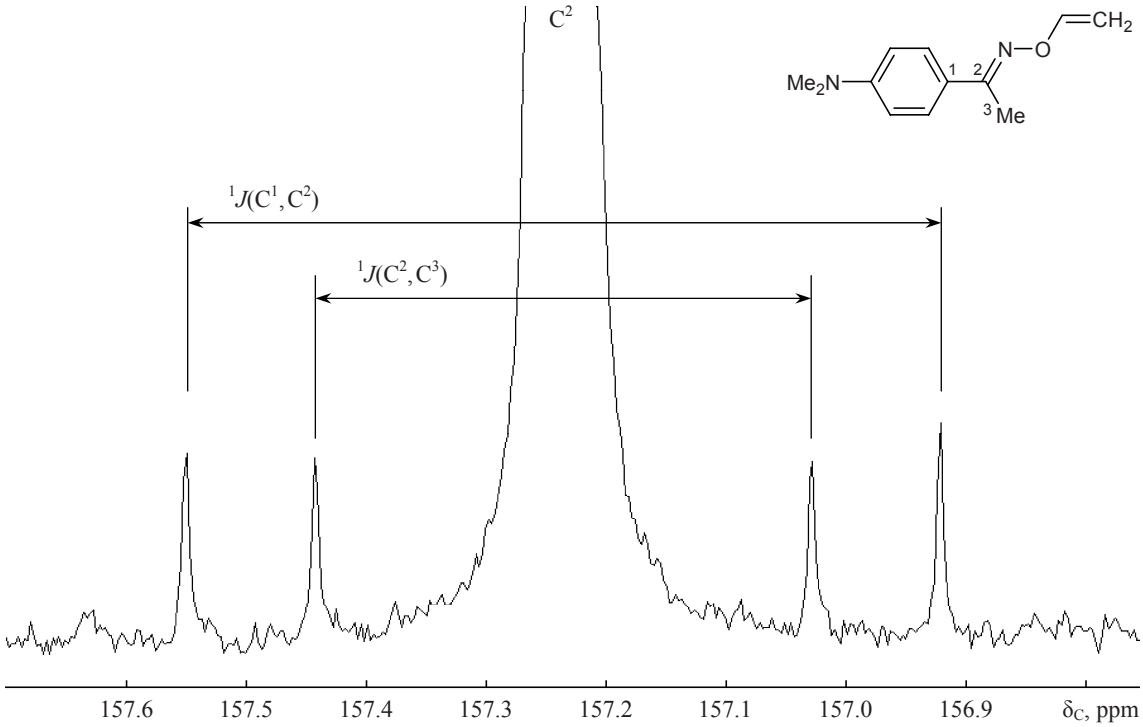


Fig. 2. Satellites of the ^{13}C signal from the azomethine carbon atom in the downfield region of the ^{13}C NMR spectrum (101.61 MHz) of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**) in $CDCl_3$.

pling constants were calculated with account taken of four contributions: Fermi-contact (J_{FC}), spin–dipole (J_{SD}), diamagnetic spin–orbital (J_{DSO}), and paramagnetic spin–orbital (J_{PSO}). It is seen that the calculated total coupling constants $^1J(C^1,C^2)$ and $^1J(C^2,C^3)$ are determined almost completely by the Fermi-contact contribution. As might be expected, their values for the *E* and *Z* isomers of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**) differ by more than 10 Hz (see above). The calculated $^1J(C^1,C^2)$ and $^1J(C^2,C^3)$ values for the *E* isomer of **II** approach those found experimentally (the difference is within the experimental error). The calculated $^1J(C^1,C^2)$ value for the *Z* isomer is lesser than the experimental value by more than 10 Hz, whereas the calculated $^1J(C^2,C^3)$ value exceeds the experimental coupling constant by more than 10 Hz. These data unambiguosuly indicate that both 4-dimethylaminoacetophenone *O*-vinyloxime (**II**) and its precursor, 4-dimethylaminoacetophenone (**I**), are *E* isomers with respect to the C=N bond. It should be specially emphasized that the constants $^1J(C^1,C^2)$ and $^1J(C^2,C^3)$ are not sensitive to conformational behavior related to internal rotation of the vinyloxy group (see table). This means that the described method can be used to determine configuration of conformationally heterogeneous *O*-vinyloximes.

On the other hand, comparison of the experimental and calculated coupling constants $^1J(C_\beta,H_A)$, $^1J(C_\beta,H_B)$, $^1J(C_\alpha,H_X)$, and $^1J(C_\alpha,C_\beta)$, which strongly depend on the orientation of the vinyloxy group (see table), allowed us to unambiguously assign preferential *s-trans* conformation to both isomers of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**).

EXPERIMENTAL

The IR spectra (400–4000 cm^{-1}) were recorded in KBr on a Bruker IFS-25 spectrometer. The ^1H, ^{13}C, and ^{15}N NMR spectra were measured on a Bruker DPX 400 instrument at 400.13, 100.61, and 40.56 MHz, respectively. The chemical shifts were determined relative to tetramethylsilane (^1H, ^{13}C) or nitromethane (^{15}N). The ^{13}C–^{13}C coupling constants were determined from the positions of ^{13}C satellites in the ^{13}C NMR spectrum of 4-dimethylaminoacetophenone *O*-vinyloxime (**II**) with native concentration of ^{13}C isotope; the spectrum was recorded on a Bruker Avance-400 spectrometer (101.61 MHz) from a concentrated solution in $CDCl_3$ (accumulation time 12 h).

Quantum-chemical calculations were performed using GAMESS [18] and DALTON software [19] with either standard basis sets or those modified by the authors (for details, see [20]).

The reaction mixtures and products were analyzed by thin-layer chromatography on Silufol UV-254 plates using hexane–diethyl ether (1 : 1 or 1 : 3) as eluent. 4-Dimethylaminoacetophenone was synthesized by alkylation of 4-aminoacetophenone with paraformaldehyde in the presence of formic acid (Leuckart–Wallach reaction) according to the procedure described in [21].

4-Dimethylaminoacetophenone oxime (I). A mixture of 2.00 g (12.3 mmol) of 4-dimethylaminoacetophenone, 1.45 g (20.8 mmol) of hydroxylamine hydrochloride, 40 ml of ethanol, and 4 ml of water was stirred for 15 min at room temperature. Pelletized sodium hydroxide, 2.73 g (68.2 mmol), was then added over a period of 0.5 h, and the mixture was stirred for 1 h at room temperature and for 1 h at 50°C, cooled, and neutralized with 10% hydrochloric acid. The precipitate was filtered off, washed with water (3×50 ml), dried in air, and recrystallized from chloroform. Yield 2.14 g (98%), light yellow crystals, mp 203°C. IR spectrum, ν, cm^{-1}: 3220, 2904, 2820, 1607, 1552, 1528, 1484, 1447, 1412, 1373, 1363, 1319, 1233, 1201, 1176, 1132, 1086, 1067, 1002, 947, 914, 819, 764, 727, 583, 556, 512, 485, 436. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.08 s (3H, Me), 2.91 s (6H, Me), 6.68 d (2H, H_{arom}, J = 8.9 Hz), 7.47 d (2H, H_{arom}, J = 8.9 Hz), 10.68 br.s (1H, OH). ^{15}N NMR spectrum (DMSO-d_6), δ_N, ppm: –23.5 (NOH), –329.1 (NMe_2). Found, %: C 67.64; H 8.21; N 15.49. $C_{10}H_{14}N_2O$. Calculated, %: C 67.39; H 7.92; N 15.72.

4-Dimethylaminoacetophenone *O*-vinyloxime (II). *a*. A 250-ml steel rotating high-pressure reactor was charged with 1.00 g (5.61 mmol) of oxime **I**, 0.314 g (5.61 mmol) of KOH, and 40 ml of DMSO. The mixture was saturated with acetylene to a pressure of 15 atm and heated for 1 h at 80°C. After cooling, the mixture was diluted with 150 ml of water and extracted with diethyl ether (5×50 ml). The combined extracts were washed with water (2×50 ml), dried over $MgSO_4$, and evaporated, and the residue was subjected to column chromatography on Al_2O_3 using diethyl ether–hexane (1 : 1) as eluent. Yield 0.80 g (70%), light gray crystals, mp 51°C.

b. The reaction was performed in a similar way using 1.00 g (5.61 mmol) of oxime **I**, 0.314 g (5.61 mmol) of KOH, 40 ml of DMSO, and 40 ml of pentane. After cooling, the pentane layer was separat-

ed, washed with water, and dried over magnesium sulfate. Removal of the solvent gave 0.54 g (47%) of oxime **II**. The dimethyl sulfoxide solution was treated as described above in *a* to isolate 0.44 g (38%) of oxime **II** and 0.05 g (5%) of pyrrole **III**. IR spectrum of **II**, ν, cm^{-1}: 2922, 2862, 2820, 1639, 1609, 1546, 1524, 1481, 1443, 1369, 1319, 1283, 1231, 1202, 1183, 1076, 1003, 969, 947, 881, 845, 821, 787, 724, 689, 583, 558, 506, 483. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 s (3H, Me), 2.96 s (6H, Me), 4.11 d (1H, H_B, J_{BX} = 15.0 Hz), 4.64 d (1H, H_A, J_{AX} = 7.4 Hz), 6.65 d (2H, H_{arom}, J = 8.9 Hz), 6.99 d.d (1H, H_X, J_{AX} = 7.4 Hz, J_{BX} = 15.0 Hz), 7.57 d (2H, H_{arom}, J = 8.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.5, 40.2, 87.8, 111.5, 122.5, 128.2, 151.1, 152.8, 156.8. ^{15}N NMR spectrum ($CDCl_3$), δ_N, ppm: –15.0 (NO), –328.4 (NMe_2). Found, %: C 70.74; H 8.00; N 13.55. $C_{12}H_{16}N_2O$. Calculated, %: C 70.56; H 7.89; N 13.71.

2-(4-Dimethylaminophenyl)-1*H*-pyrrole (III). A solution of 0.52 g (2.55 mmol) of *O*-vinyloxime **II** in 30 ml of DMSO was heated for 1 h at 120°C. The mixture was cooled to room temperature and diluted with 150 ml of water, and the precipitate was filtered off, dried in air, and purified by sublimation. Yield 0.42 g (89%), light yellow crystals, mp 180°C. IR spectrum, ν, cm^{-1}: 3420, 2921, 2887, 2801, 1614, 1597, 1517, 1481, 1441, 1323, 1227, 1193, 1168, 1125, 1062, 1033, 947, 881, 818, 789, 711, 589, 546. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.93 s (6H, Me), 6.24 d.d (1H, 4-H, J = 2.4, 6.0 Hz), 6.33 m (1H, 3-H), 6.71 d (2H, H_{arom}, J = 8.9 Hz), 6.75 m (1H, 5-H), 7.33 d (2H, H_{arom}, J = 8.9 Hz), 8.33 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.6, 103.8, 109.6, 112,8, 117.4, 121.8, 125.0, 132.7, 149.0. Found, %: C 77.14; H 7.36; N 14.97. $C_{12}H_{14}N_2$. Calculated, %: C 77.38; H 7.58; N 15.04.

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