A Novel Facile Synthesis of 2,5-Di- and 2,3,5-Trisubstituted Pyrroles

Boris A. Trofimov,*[a] Ol'ga A. Tarasova,[a] Al'bina I. Mikhaleva,[a] Nina A. Kalinina,[a] Lidiya M. Sinegovskaya,[a] Jochem Henkelmann[b]

[a] A.E. Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1, Favorsky Street, Irkutsk 664033, Russia
Fax +(73952)396046; E-mail: bat@irioch.irk.ru

[b] BASF Aktiengesellschaft, Ammoniaklaboratorium ZAR/C-M 311, 67056 Ludwigshafen, Germany

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Abstract: Heterocyclization of ketoximes with propyne or allene in superbase systems MOR/DMSO (M = K, Cs; R = H, *t*-Bu), which leads to 2-alkyl(aryl, hetaryl)-5-methyl- and 2,3-dialkyl-5-methylpyrroles or 2-methyl-4,5,6,7-tetrahydroindole in yields of up to 63%, has been accomplished for the first time. The reaction is mostly regioselective affording mainly or exclusively 2,5-di- and 2,3,5-trisubstituted pyrroles. The minor isomers in most cases are the corresponding 2,4-di- and 2,3,4-trisubstituted pyrroles, only in the case of acetoxime the isomer ratio is ca 1:1. For oximes of methyl isopropyl ketone and pinacolone, the 4-methyl-isomers become predominant (78, 83%, respectively).

Key words: pyrroles, ketoximes, superbase systems, propyne, allene, heterocycles, regioselectivity

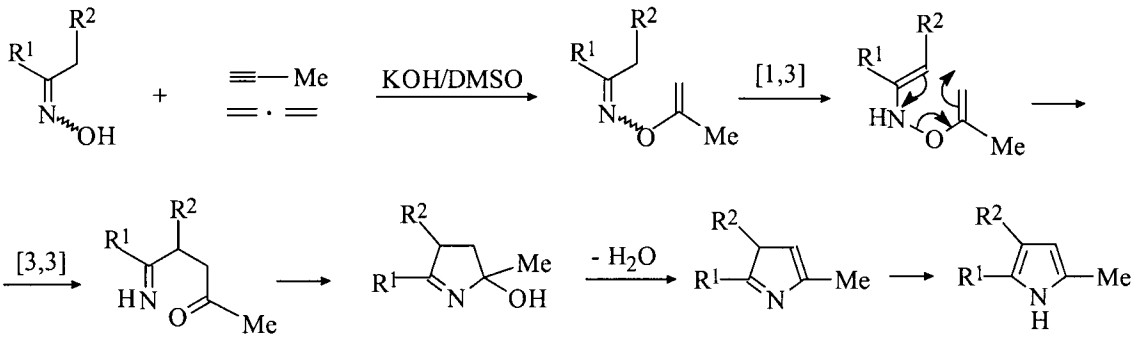
The heterocyclization of ketoximes with acetylene in the system KOH/DMSO[1–3] with the formation of *O*-vinylacetoxime as the first step, provides one of the simplest and most effective methods of pyrrole ring construction (Scheme 1). The reaction has comprehensively been examined with acetylene and only in some cases[4] the study was carried out with phenylacetylene. In the present communication the results on the reaction of ketoximes with the simplest acetylene homolog propyne and its isomer allene are presented.

Since for propyne and allene, the largest positive charge is located on the central carbon atom,[5] the attack of the oximate anion at both the compounds should result in the same adducts, i.e., *O*-2-propenylketoximes. Therefore, one could expect here the formation of 5-methyl substituted pyrroles according to the mechanism shown in Scheme 1, which has been proved in the case of acetylene.[1,2]

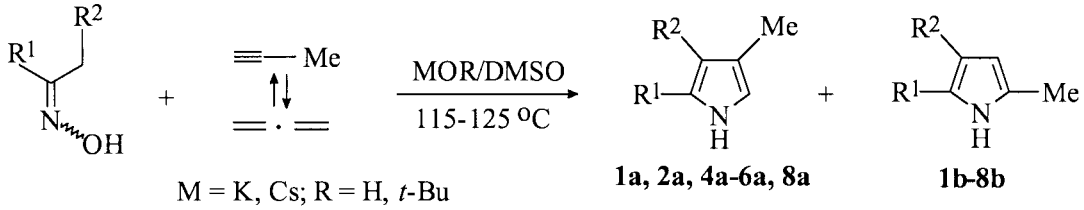
However, the reaction with acetoxime (Scheme 2, R^1 = Me, R^2 = H) performed in systems MOH/DMSO (M = K, Cs) or KOBu-*t*/DMSO, both under atmospheric or elevated pressure, gave a mixture of 2,4- and 2,5-dimethylpyrroles (**1a** and **1b**) in a nearly equal ratio.

The experimental conditions, yields and product ratios (GC, ^{1}H NMR) are presented in Table 1. When excess of pure propyne or allene was passed through the reaction mixture, the unreacted portion was a propyne-allene mixture (from 80:20 to 69:31, correspondingly). Thus, due to a fast propyne ⇆ allene prototropic isomerization under the reaction conditions, the product is the same irrespective of whether we start from propyne or allene. This is supported by the data in Table 1: the reaction temperature and time do not affect the ratio of pyrroles **1a** and **1b**. There is just a slight dependence of the isomer ratio on the catalyst and pressure of propyne used. Anhydrous CsOH increases the content of 2,4-dimethylpyrrole in the mixture (Table 1). The total yield of pyrroles **1a** and **1b** of 45% is achieved in the presence of a catalytic pair CsF/NaOH. The corresponding *N*-2-propenylpyrroles **1c** and **1d**, the products of further addition of the pyrroles to propyne or allene, are found as byproducts (Scheme 3).

Apparently, the results show that the acetoximate anion attacks not only the C-2 atom of propyne or allene, as it is the case with alkoxide anions,[6] but the C-1 atom of propyne as well to form *O*-2-propenyl- and *O*-1-propenylacetoximes, respectively. As a result of the same rearrangements (Scheme 1), *O*-1-propenylacetoxime affords the pyrrole **1a** (Scheme 4).

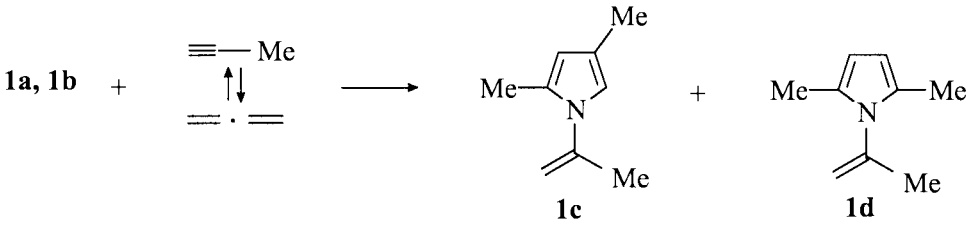


Scheme 1



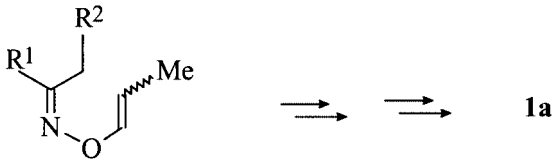
For R^1, R^2, see Table 2.

Scheme 2



Scheme 3

The attack of acetoximate anion on the allene C-1 atom could most likely lead to *O*-3-propenylacetoxime, which, as known,[7] fails to give pyrrole under the same conditions. At the same time, prototropic rearrangement of the intermediate anion, which leads to *O*-1-propenylacetoxime, is also possible. *O*-Propenyloximes have not been isolated in any one of the runs, probably due to their ability to quickly rearrange to pyrroles, in contrast to *O*-vinylacetoxime, which can be obtained in good yield from acetoxime and acetylene in the system KOH/DMSO.[8]



Scheme 4

Unlike acetoxime, the oximes of methyl ethyl ketone, cyclohexanone, methyl isopropyl ketone, pinacolone, acetophenone, 2-acetylfuran and 2-acetylthiophene with propyne or allene in the KOH/DMSO system reacted regioselectively (Table 2). The result of the reaction depends on the ketoxime structure and it is determined by not only electronic, but by steric factors as well. With branching of the alkyl group at the oxime function, the content of the 4-methyl isomer increases. In the case of pinacolone-oxime the ratio becomes 17:83 in favor of 4-methylpyrrole **(5a)**. Seemingly, due to steric factors, the more bulky oximate anion preferably attacks the propyne C-1 atom. At the same time, the oximes of cyclohexanone and 2-acetylfuran form 5-methylpyrroles **3b** and **7b** only.

For methyl ethyl ketoxime, acetophenone and 2-acetylthiophene oximes, the reaction is slightly less selective: the content of corresponding 5-methylpyrroles **2b**, **6b** and **8b** is 90−92%.

Similar to acetylene-based pyrrolization of ketoximes,[1,2] the syntheses include (as minor side reactions) deoximation of ketoximes (to form ~ 1−3% of the starting ketones) and the reaction of NH-pyrroles with propyne or allene, which leads to *N*-2-propenylpyrroles **1c**, **1d** or **3d** (4−15%). In this connection, two points are of interest: (i) analogous to alkoxide anion,[6] the pyrrole anions attack only the C-2 atoms of propyne and allene; and (ii) from the two dimethylpyrroles **1a** and **1b,** 2,4-dimethylpyrrole (**1a**), having the less shielded NH group, is most readily propenylated.

Propyne and allene are less reactive than acetylene, as seen from comparison of the conditions of ketoxime pyrrolization with acetylene (atmospheric pressure, 93−100 °C, 6−10 h, DMSO containing 4−10% of H_2O)[1−3] to those with propyne or allene (115−125 °C, 3−9 h, DMSO containing ~ 0.4% of H_2O, Tables 1 and 2). From ketoximes and acetylene in the KOH/DMSO (~ 0.4% of H_2O), a mixture of pyrroles and *N*-vinylpyrroles forms already at 100 °C,[1] whilst in the reactions with propyne at 115−125 °C *N*-propenylpyrroles form in only negligible amounts. The unsubstituted pyrrole undergoes quantitative vinylation by acetylene in the system KOH/DMSO under atmospheric pressure at 115−120 °C for 2 hours.[9] For comparison, we carried out the reaction of pyrrole with propyne or allene or their mixture in the same system at a temperature of 125−135 °C for 5 hours. As a result, we obtained *N*-2-propenylpyrrole (**9**) (Scheme 5) in a yield of 59% only (unreacted pyrrole remained in the reaction mixture).

Table 1 Reaction of Acetoxime with Propyne or Allene or Their Mixtures (Scheme 2, R^1 = H, R^2 = Me)

Propyne/Allene Ratio	Catalyst, g (mmol)	T (° C)	Time (h)	2,4- + 2,5-Dimethylpyrroles Yield (%)	Ratio (%)	Yield of **1c,d** (%)
80:20[c]	2KOH·H_2O 5 (76)	80−95[a]	2	2	1:1	traces
80:20	2KOH·H_2O 5 (76)	115−126[b]	6	30	1:1	4
80:20[c]	2KOH·H_2O 5 (76)	105−110[a]	4	21	1:1	4
89:11[d]	2KOH·H_2O 5 (76)	100−120[a]	4	35	42:58	11
89:11[d]	2KOH·H_2O 5 (76)	95−113[a]	4	35	43:57	4
100:0	2KOH·H_2O 5 (76)	118−128[b]	6	41	53:47	5
0:100	2KOH·H_2O 5 (76)	118−128[b]	6	42	1:1	5
80:20	CsOH·H_2O 14.9(89)	114−122[b]	7	30	1:1	5
80:20	CsF, NaOH[f] 13.5 (89), 3.56 (89)	112−124[b]	4	32	59:41	4
80:20	*t*-BuOK[f] 9.6 (85.6)	110−119[b]	4	32	46:54	3
84:16 [e]	CsF, NaOH 13.5 (89), 3.56 (89)	95−112[a]	4	45	52:48	8

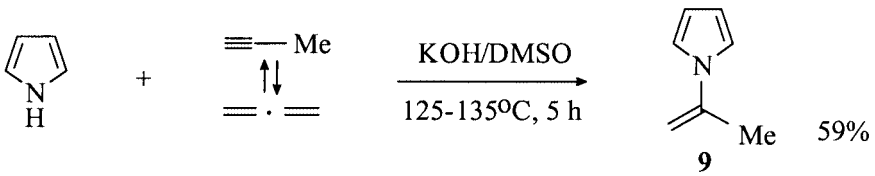
[a] The reaction was carried out in an autoclave.
[b] The reaction was carried out in the flask.
[c] Preliminary reaction mixture was saturated with propyne-allene at r.t. for 7 h.
[d] Initial pressure of propyne-allene was 4.5 atm, preliminary potassium acetoximate was prepared prior to the reaction.
[e] Propyne-allene solution in DMSO prepared at r.t. for 1 h was used.
[f] DMSO <0.2% H_2O.

It is noteworthy that in the reaction of methyl ethyl ketoxime with propyne or allene or their mixture (Table 2), it is only the methylene group that contributes to the pyrrole ring construction in spite of elevated temperature (115−125 °C), no 2-ethyl-5-methylpyrrole being identified (Scheme 6).

With acetylene the regioselectivity is not observed under the same conditions: apart from the methylene group, the methyl group also gets involved in the reaction and as a result 2-ethyl-1-vinylpyrrole appears in the reaction mixture.[1]

This synthesis of pyrroles from ketoximes and the available[6] propyne or allene or their mixture significantly extends the scope of pyrrolization of ketoximes with acetylenes. First of all, it enables 5-methyl substituted pyrroles with various substituents in the 2 and 3 positions to be obtained much more easily than before.

GC analysis of the products of the reaction of ketoximes with propyne or allene or their mixture was performed on an LXM-8MD chromatograph (column 3.5 m × 3 mm, XE-60 on Chromaton N-AW-HMDS, detector katharometer, gas-carrier He, isothermal con-



Scheme 5

Table 2 The Yield and Ratio of Products in the Reaction of Ketoximes with Propyne or Allene (Scheme 2)

R^1	R^2	Yield[a] (%)	Ratio (%)		Propyne/Allene (%)
			4-Me-pyrrole	5-Me-pyrrole	
Me	H	30	50, **1a**	50, **1b**	80:20
Me	Me	60	8, **2a**	92, **2b**	95:5
$(CH_2)_4$		63	traces	~100, **3b**	71:29
i-Pr	H	40	78, **4a**	22, **4b**	93:7
t-Bu	H	46	83, **5a**	17, **5b**	90:10
Ph	H	51	10, **6a**	90, **6b**	80:20
2-furyl	H	23[b]	traces	~100, **7b**	80:20
2-thienyl	H	18[c]	8, **8a**	92, **8b**	69:31

[a] Yield denotes total yield of pyrroles.
[b] Reaction time 3 h.
[c] Reaction time 9 h.

ditions, temperature in the column, katharometer and evaporator: 100−190, 200 and 250 °C). Separation of 2,4- and 2,5-dimethylpyrroles (**1a** and **1b**) and isolation of *N*-2-propenylpyrroles **1c, 1d** and **3d** were carried out on a PAKhV-07 preparative chromatograph (column 5 m × 10 mm, column temperature 85−170 °C, other parameters being the same as described above). IR spectra were recorded on a Bruker IFS 25 instrument (as films for liquids, KBr pellets for solids. For most of the pyrrole the ν NH absorption is recorded in CCl_4). ^{1}H NMR spectra were run on a Bruker DPX-400 (400.13 MHz) in $CDCl_3$ with HMDS as internal standard. In most runs the use was made of commercial DMSO containing ~ 0.4% of H_2O. Commercial KOH containing 15% of H_2O ($2KOH•H_2O$) was employed. The starting propyne (Aldrich Chemical Co.) was of 98% purity. The pure allene was prepared by zinc-assisted dechlorination of 2,3-dichloro-1-propene.[10]

2,4-Dimethyl- and 2,5-Dimethylpyrroles (1a and 1b); Typical Procedures

Method A, using KOH/DMSO: Into a 250 mL glass flask equipped with a stirrer, a cooler, a thermometer, a bubbler for propyne supply and a gas outlet, acetoxime (6.25 g, 85.6 mmol), $2KOH•H_2O$ (5 g, 76 mmol) and DMSO (125 mL) were placed. A propyne-allene mixture containing 20% of allene (evaporation temperature ~ −15 °C) was passed while stirring for 6 h through the reaction mixture heated up to 115−125 °C. After cooling to r.t. H_2O (200 mL) was added to the mixture and extracted with Et_2O (4 × 50 mL). The combined Et_2O extracts were washed with H_2O to remove DMSO and dried ($MgSO_4$). After distilling off Et_2O and evaporation at 50 Torr, the residue was placed in a column of Al_2O_3. At first elution with pentane was performed to isolate 0.56 g (4%) of *N*-(2-propenyl)pyrroles (**1c** and **1d**) (purity 82%), mixed with 0.1 g of pyrroles **1a** and **1b** (separated by preparative GC). The **1c**:**1d** ratio in the isolated product was 89:11 (^{1}H NMR). Then the column content was eluted with a 3:1 pentane/Et_2O mixture to give 2.33 g of a 1:1 mixture of 2,4-and 2,5-dimethylpyrroles (**1a** and **1b**) (total yield 30%) (GC, ^{1}H NMR), which were separated by preparative GC (Table 1).

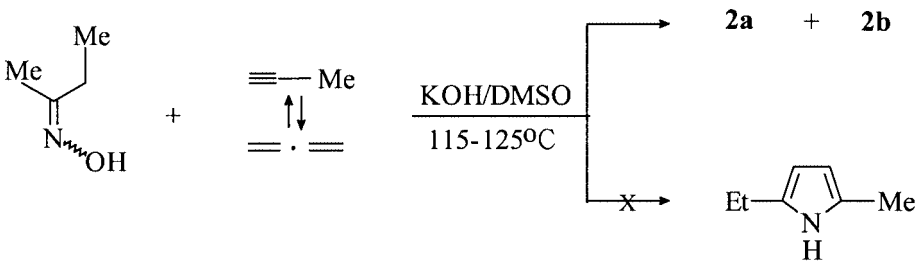
Method B, using CsOH/DMSO: A 1-L steel rotating autoclave was charged with acetoxime (6.25 g, 85.6 mmol), CsF (13.5 g, 89 mmol), NaOH (3.56 g, 89 mmol), and propyne-allene mixture (84:16, 13.6 g) dissolved in DMSO (~ 0.4% of H_2O, 125 mL) at r.t. The autoclave was heated at 95−112 °C for 4 h. Further treatment was performed in the same way as described in Method A. As a result, 0.92 g (8%) of pyrroles **1c** and **1d** and 3.68 g of **1a** and **1b** were prepared (total yield 45%, 52:48 ratio) (Table 1).

2,4-Dimethylpyrrole (1a)

Purity after preparative GC 90%; n_D^{22} 1.5002; brown fluid, did not freeze at −78 °C.

^{1}H NMR: δ = 7.58 (br s, 1 H, NH), 6.35 (s, 1 H, H-5), 5.71 (s, 1 H, H-3), 2.18 (s, 3 H, 2-CH_3), 2.05 (s, 3 H, 4-CH_3).

IR (film): ν = 563, 648, 731, 789, 956w, 985w, 1038w, 1112, 1148w, 1257w, 1290w, 1392, 1418, 1448, 1514w, 1590, 1653, 2870, 2926, 3085, 3119w, 3487 (ν NH, in CCl_4) cm^{-1}.



Scheme 6

Anal. calcd for C_6H_9N: C 75.74, H 9.53, N 14.72. Found C 75.70, H 9.47, N 14.69.

2,5-Dimethylpyrrole (1b)
Purity after preparative GC ca 100%; n_D^{22} 1.5037; light-yellow fluid freezing at −78 °C.

^{1}H NMR: δ = 7.51 (br s, 1 H, NH), 5.72 (s, 2 H, H-3 and H-4), 2.20 (s, 6 H, 2,5-CH_3).

IR (film): ν = 562, 649, 770, 993, 1037, 1186, 1259, 1381, 1395, 1419, 1446, 1516, 1595, 2865, 2903, 2927, 2972, 3083, 3106w, 3477 (ν NH, in CCl_4) cm^{-1}.

Anal. calcd for C_6H_9N: C 75.74, H 9.53, N 14.72. Found C 75.80, H 9.51, N 14.63.

2,4-Dimethyl-*N*-2-propenylpyrrole (1c)
Content: 89% mixed with pyrrole **1d**.

^{1}H NMR: δ = 6.44 (s, 1 H, H-5), 5.75 (s, 1 H, H-3), 4.91 and 4.81 (2 s, 2 H, =CH_2), 2.20 (s, 3 H, 2-CH_3), 2.08 (s, 3 H, 4-CH_3), 2.04 (s, 3 H, CH_3).

IR (film): ν = 622, 719, 751, 785, 877, 1142, 1200, 1352, 1407, 1438, 1512, 1653, 2865, 2897, 2924, 2975, 3105w cm^{-1}.

Anal. calcd for $C_9H_{13}N$: C 79.95, H 9.69, N 10.36. Found 79.70, H 9.47, N 10.61.

2,5-Dimethyl-*N*-2-propenylpyrrole (1d)
Content: 11% mixed with pyrrole **1c**.

^{1}H NMR: δ = 5.77 (s, 2 H, H-3 and H-4), 5.28 and 4.94 (2 s, 2 H, =CH_2), 2.15 (s, 6 H, 2,5-CH_3), 1.95 (s, 3 H, CH_3).

Pyrroles 2a, 4a−6a, 8a, 2b−8b and 3d (Table 2)
These were prepared analogously by Method A.

2,3,4-Trimethylpyrrole (2a)
Identified by ^{1}H NMR spectrum in a mixture with pyrrole **2b**; content: 8%.

^{1}H NMR: δ = 7.27 (br s, 1 H, NH), 5.75 (s, 1 H, H-5), 2.18 (s, 3 H, 2-CH_3), 1.97 and 1.98 (2 s, 6 H, 3,4-CH_3).

2,3,5-Trimethylpyrrole (2b)
Purity 92% after column chromatography (Al_2O_3, eluent: hexane) and distillation; bp 82 °C/22 Torr; n_D^{20} 1.5045.

^{1}H NMR: δ = 7.27 (br s, 1 H, NH), 5.60 (s, 1 H, H-4), 2.14 and 2.07 (2 s, 6 H, 2,5-CH_3), 1.93 (d, 3 H, 3-CH_3, $J_{Me,H-4}$ = ~ 2 Hz).

IR (film): ν = 638, 648, 785, 1157w, 1296, 1388, 1402, 1441, 1522w, 1609, 2864, 2921, 2968, 3088w, 3477 (ν NH, in CCl_4) cm^{-1}.

Anal. calcd for $C_7H_{11}N$: C 77.01, H 10.16, N 12.83. Found C 77.12, H 9.95, N 12.70.

2-Methyl-4,5,6,7-tetrahydroindole (3b)
Purity 98.8% after column chromatography (Al_2O_3, eluent: hexane) and distillation; bp 91 °C/3 Torr; n_D^{21} 1.5389.

^{1}H NMR: δ = 7.30 (br s, 1 H, NH), 5.61 (s, 1 H, H-3), 2.50 (m, 2 H-7), 2.40 (m, 2 H-4), 1.77 and 1.71 (2 m, 2 H-5, 2 H-6), 2.50 (s, 3 H, 2-CH_3).

IR (film): ν = 549, 639, 781, 823w, 922w, 1132, 1234w, 1278, 1307w, 1335w, 1363, 1398, 1443, 1465, 1526, 1605, 1654w, 2846, 2889, 2924, 3087w, 3480 (ν NH, in CCl_4) cm^{-1}.

Anal. calcd for $C_9H_{13}N$: C 79.95, H 9.69, N 10.36. Found C 79.78, H 9.60, N 10.40.

2-Methyl-*N*-2-propenyl-4,5,6,7-tetrahydroindole (3d)
Isolated by preparative GC; purity 99%; n_D^{23} 1.5240.

^{1}H NMR: δ = 5.68 (s, 1 H, H-3), 5.21 and 4.89 (2 s, 2 H, =CH_2), 2.46 (m, 4 H, 2 H-4 and 2 H-7), 1.72 (m, 4 H, 2 H-5 and 2 H-66), 2.15 (s, 3 H, 2-CH_3), 1.98 (s, 3 H, CH_3).

IR (film): ν = 772, 812, 897, 1086, 1147, 1236, 1260, 1300, 1316, 1362, 1388, 1428, 1522, 1654, 2841, 2924, 2975, 3084w, 3101w cm^{-1}.

Anal. calcd for $C_{12}H_{17}N$: C 82.23, H 9.78, N 7.99. Found C 82.78, H 9.60, N 7.40.

2-Isopropyl-4-methylpyrrole (4a) and 2-Isopropyl-5-methylpyrrole (4b)
Isolated as a 78:22 mixture (Table 2); bp 73 °C/10 Torr.

^{1}H NMR: protons of pyrrole **4a**, δ = 7.27 (br s, 1 H, NH), 6.39 (s, 1 H, H-5), 5.75 (s, 1 H, H-3), 2.85 (m, 1 H, CH), 2.07 (s, 3 H, 4-CH_3), 1.20 (d, 6 H, 2 CH_3); protons of pyrrole **4b**, δ = 7.27 (br s, 1 H, NH), 5.75 (s, 2 H, H-3, H-4), 2.43 (m, 1 H, CH), 2.22 (s, 3 H, 5-CH_3), 1.20 (d, 6 H, 2 CH_3).

IR (film): ν = 734, 768, 791, 962, 1095, 1115, 1333, 1363, 1383, 1462, 1588, 1652, 2870, 2929, 2962, 3080w, 3098w, 3487 (ν NH, in CCl_4) cm^{-1}.

Anal. calcd for $C_8H_{13}N$: C 78.00, H 10.64, N 11.37. Found C 78.11, H 10.46, N 11.44.

2-*tert*-Butyl-4-methylpyrrole (5a) and 2-*tert*-Butyl-5-methylpyrrole (5b)
Isolated as a 83:17 mixture (see Table 2); bp 68 °C/10 Torr.

^{1}H NMR: protons of pyrole **5a**, δ = 7.86 (br s, 1 H, NH), 6.38 (s, 1 H, H-5), 5.76 (s, 1 H, H-3), 2.07 (s, 3 H, 4-CH_3), 1.24 (s, 9 H, *t*-C_4H_9); protons of pyrrole **5b**, δ = 7.86 (br s, 1 H, NH), 5.75 (s, 2 H, H-3, H-4), 2.22 (s, 3 H, 5-CH_3), 1.25 (s, 9 H, *t*-C_4H_9).

IR (film): ν = 734, 768, 792, 958, 1101, 1120, 1203, 1223, 1255, 1302, 1363, 1395, 1416, 1463, 1507, 1587, 1701, 2869, 2903, 2932, 2963, 3099w, 3495 (ν NH, in CCl_4) cm^{-1}.

Anal. calcd for $C_9H_{15}N$: C 78.78, H 11.02, N 10.21. Found C 78.90, H 10.87, N 10.23.

4-Methyl-2-phenylpyrrole (6a)
Identified by ^{1}H NMR spectrum in a mixture with the pyrrole **6b** (10%).

^{1}H NMR: δ = 8.05 (br s, 1 H, NH), 6.57 and 6.32 (2 m, 2 H, H-5, H-3), **,** 2.11 (s, 3 H, 4-CH_3). The protons of C_6H_5 are masked by **6b**.

5-Methyl-2-phenylpyrrole (6b)
Purity 90%; contains 10% of pyrrole **6a**; colorless crystals; mp 95−96 °C (after sublimation).

^{1}H NMR: δ = 8.05 (br s, 1 H, NH), 6.37 (dd, 1 H, H-3), 5.93 (m, 1 H, H-4, $J_{H-3,\ H-4}$ = 2.8 Hz, $J_{Me,\ H-4}$ = 0.8 Hz), 7.38, 7.30, and 7.13 (3 m, 5 H, C_6H_5), 2.30 (s, 3 H, 5-CH_3).

IR (kBr): ν = 553, 689, 753, 775, 900, 1040, 1074, 1217, 1253, 1386, 1452, 1475, 1513, 1588, 1604, 2855w, 2923, 3023w, 3044w, 3060w, 3477 (ν NH, in CCl_4) cm^{-1}.

Anal. calcd for $C_{11}H_{11}N$: C 84.04, H 7.05, N 8.91. Found C 83.96, H 7.07, N 8.85.

2-(2-Furyl)-5-methylpyrrole (7b)
Colorless crystals; mp 39−40 °C (after sublimation).

^{1}H NMR: δ = pyrrole ring protons: 8.16 (br s, 1 H, NH); 6.28 (dd, 1 H, H-3), 5.89 (m, 1 H, H-4, $J_{H-3,\ H-4}$ = 3.0 Hz, $J_{Me,H-4}$ = 0.8 Hz; furan ring protons: 7.28 (dd, 1 H, H-5), 6.37 (dd, 1 H, H-4), 6.24 (dd, 1 H, H-3, $J_{H-3,\ H-4}$ = 3.3 Hz, $J_{H-3,\ H-5}$ = 1.0 Hz), 2.27 (s, 3 H, 5-CH_3).

IR (KBr): ν = 591, 651, 681, 712, 728, 776, 877, 950, 1009, 1037, 1081, 1158, 1212, 1253, 1292, 1317, 1397, 1442, 1515, 1562, 1619, 2905w, 2921w, 2948w, 3110w, 3130w, 3475 (ν NH, in CCl_4) cm^{-1}.

Anal. calcd for C_9H_9NO: C 73.45, H 6.16, N 9.52. Found C 73.39, H 6.63, N 9.62.

4-Methyl-2-(2-thienyl)pyrrole (8a)
Identified in a mixture with pyrrole **8b**; content: 8%.

^{1}H NMR: δ = pyrrole ring protons: 7.94 (br s, 1 H, NH), 6.52 (m, 1 H, H-5), 6.23 (m, 1 H, H-3); thiophene ring protons: 7.09 (dd, 1 H, H-5), H-3, H-4 protons are masked by signals of **8b**, 2.10 (s, 3 H, 4-CH_3).

5-Methyl-2-(2-thienyl)pyrrole (8b)
Purity 92%; contains 8% of pyrrole **8a**; colorless crystals, mp 34−36 °C (after sublimation).

^{1}H NMR: δ = pyrrole ring protons: 7.94 (br s, 1 H, NH), 6.26 (dd, 1 H, H-3), 5.89 (m, 1 H, H-4, $J_{H\text{-}3,\ H\text{-}4}$ = 3.0 Hz, $J_{Me,H\text{-}4}$ = 0.8; thiophene ring protons: 7.07 (dd, 1 H, H-5), 6.96 (dd, 1 H, H-4), 6.93 (dd, 1 H, H-3, $J_{H\text{-}3,\ H\text{-}4}$ = 3.6 Hz, $J_{H\text{-}4,\ H\text{-}5}$ = 5.0 Hz, $J_{H\text{-}3,H\text{-}5}$ = 1.1 Hz), 2.28 (s, 3 H, 5-CH_3).

IR (KBr): ν = 559, 582, 630, 678, 692, 770, 818, 842, 1037, 1081, 1193, 1253, 1340 w, 1394, 1430, 1534, 1594, 2852w, 2901w, 2923, 2966w, 3068w, 3100w, 3464 and 3474 cm^{-1} (ν NH, in CCl_4).

Anal. calcd for C_9H_9NS: C 66.22, H 5.56, N 8.58, S 19.64. Found C 66.29, H 5.68, N 8.56, S 20.42.

***N*-2-Propenylpyrrole (9)**
Into a glass flask equipped with a stirrer, a cooler, a thermometer, a bubbler for propyne supply and a gas outlet, pyrrole (6.7 g, 0.1 mol), 2KOH•H_2O (6 g, 92 mmol) and DMSO (60 mL) were placed. A propyne-allene mixture containing 19% of allene was passed while stirring for 5 h through the reaction mixture heated up to 125−135 °C. Then the formed pyrrole **9** was distilled off together with DMSO at 4−5/Torr (the unreacted pyrrole remained in the solid residue as potassium pyrrolate). The resultant solution was diluted with H_2O, extracted with Et_2O (4 × 50 mL), the combined Et_2O extracts were washed with H_2O to remove DMSO and dried ($MgSO_4$). After evaporating the Et_2O, the residue was distilled to afford **9**; yield: 6.33 g (59%); bp 147 °C/760 Torr; n_D^{23} 1.5174; 99% purity.

^{1}H NMR: δ = 6.92 (t, 2 H, H-2 and H-5), 6.20 (t, 2 H, H-3 and H-4, $J_{H\text{-}2,H\text{-}3}$ = 2.2 Hz), 4.89 and 4.51 (2 s, 2 H, =CH_2), 2.16 [dd, 3 H, CH_3, $J_{Me,}$ = CH_2 = 1.2 (*trans*), 0.5 Hz (*cis*)].

IR (film): ν = 603, 724, 851, 906, 957, 1002, 1048, 1093, 1260, 1306, 1344, 1381, 1438, 1483, 1523, 1553, 1647, 2924, 2955, 2990, 3106, 3140 cm^{-1}.

Anal. calcd C_7H_9N: C 78.46, H 8.47, N 13.07. Found C 78.79, H 8.48, N 12.86.

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