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Dedicated to Full Member of the Russian Academy of Sciences I.P. Beletskaya on Her Jubilee

N-Isopropenylazoles: I. Direct N-Isopropenylation of Azoles with Propyne and Allene

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Abstract—A number of previously unknown *N*-isopropenyl-substituted pyrroles, indoles, and di- and -triazoles were synthesized in 20–86% yield by reaction of the corresponding azole with an equilibrium mixture of propyne with allene or pure propyne and allene in the system KOH–DMSO (105–145°C, 5–15 h, atmospheric or elevated pressure). The reaction is regioselective. The electronic and steric structure and the degree of conjugation between the exocyclic double bond and the azole ring are discussed on the basis of the ^{1}H and ^{13}C NMR spectra. Almost complete absence of p–π conjugation in α,α'-disubstituted *N*-isopropenylazoles have been found.

Direct vinylation of biologically important NH-heterocycles, such as pyrroles, indoles, and di- and triazoles, with acetylene has been studied in sufficient detail. Pyrrole [1] and substituted NH-pyrroles [2–4] are known to readily react with acetylene in the system KOH–DMSO at 100–120°C (3 h) under atmospheric or elevated pressure to give the corresponding *N*-vinyl derivatives in quantitative yield. Vinylation with acetylene under pressure in aqueous dioxane in the presence of 30% KOH was reported for imidazole, benzimidazole (160–180°C, 1 h) [5], pyrazole (160–165°C, 3 h, with no water added) [6], indole, and 1,2,4-triazole (220°C, 30 min and 3–4 h, respectively) [7, 8]. In the reaction with pyrazole, 3–5% CuCl can be used as catalyst instead of KOH [6]. Vinylation with acetylene under atmospheric pressure was performed for imidazole (5% CuCl as catalyst), benzimidazole [8% $Cd(OAc)_2$, *N*-methylpyrrolidinone, 180°C, 16–28 h) [9], and 1,2,4-triazole (40% KOH, sulfolane or triethylene glycol, 205°C, 12 h) [10]. The yields of the corresponding *N*-vinylazoles ranged from 67 to 91%.

Up to now, only a few *N*-isopropenyl azoles have been reported. *N*-Isopropenyl derivatives of indole, 3-phenylindole, and aza- and diazaindoles were synthesized in 50–56% yield by reaction of the corresponding *N*-acyl derivatives with Tebbe's reagent ($Cp_2TiCH_2ClAlMe_2$) [11]. *N*-Isopropenylbenzotriazole was obtained in two ways: (1) from *N*-vinylbenzotriazole, by reaction with BuLi and subsequent treatment of the lithium derivative with MeI (yield 44%) [12]; and (2) by transvinylation of benzotriazole with isopropenyl acetate in the presence of $HgSO_4$ (yield 81%; *N*-acetylbenzotriazole was formed as by-product) [13]. *N*-Isopropenylimidazole was synthesized in 4% yield by reaction of *N*,*N*′-carbonyldiimidazole with acetone [14]. Physical constants were given only for *N*-isopropenylbenzotriazole [12].

Propyne–allene mixture is a by-product of high-temperature pyrolysis of petroleum derivatives [15]. It is now the most accessible acetylene raw material ranking next after acetylene; moreover, it needs to be utilized. Therefore, development of synthetic procedures on the basis of propyne–allene mixture is justified from the viewpoints of both economy and ecology.

We recently demonstrated for the first time the possibility for direct *N*-isopropenylation of pyrrole with propyne–allene mixture in the system KOH–DMSO under atmospheric pressure [16]. *N*-Isopropenylpyrrole was thus obtained in ~60% yield. This compound may be regarded as a new pyrrole building block and a monomer.

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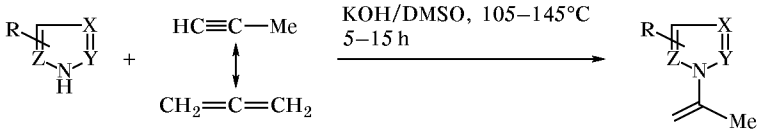
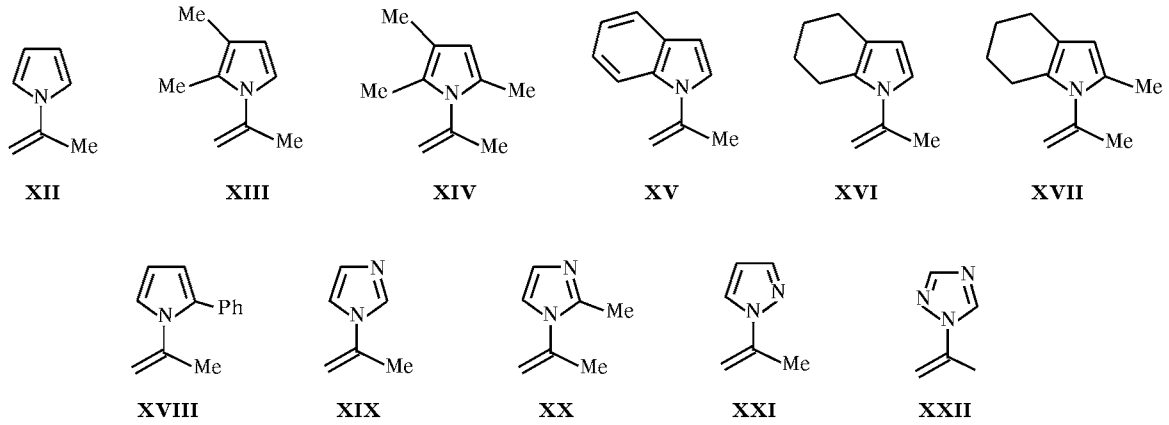
Scheme 1.



I–XI **XII–XXII**



XII **XIII** **XIV** **XV** **XVI** **XVII**

XVIII **XIX** **XX** **XXI** **XXII**

The present communication gives first results of our systematic study of direct isopropenylation of various azoles, namely pyrrole (**I**), 2,3-dimethylpyrrole (**II**), 2,3,5-trimethylpyrrole (**III**), indole (**IV**), 4,5,6,7-tetrahydroindole (**V**), 2-methyl-4,5,6,7-tetrahydroindole (**VI**), 2-phenylpyrrole (**VII**), imidazole (**VIII**), 2-methylimidazole (**IX**), pyrazole (**X**), and 1,2,4-triazole (**XI**). As isopropenylating agent we used both propyne–allene mixture (4 : 1) and its individual components. Experiments were carried out under atmospheric and elevated pressure, the temperature was 105–145°C. The progress of the reactions was monitored by GLC and TLC, following disappearance of the initial azole.

Table 1 contains the reaction conditions and the yields of the products (Scheme 1). It is seen that the reaction direction does not depend on the alkenylating agent. The reaction is regioselective: it gives only the corresponding *N*-isopropenyl derivatives. Only in the reaction with pyrrole (**I**) under pressure, we isolated and identified (by GLC using an authentic sample [17] and by ^{1}H NMR spectroscopy) *N*-(1-*E*-propenyl)-pyrrole. Its yield was 0.7% (1% in the mixture).

With pyrrole (**I**) as an example, we examined the effect of the amount of catalyst and temperature on the yield of *N*-isopropenylpyrrole (**XII**). The reactions were carried out under elevated pressure. Almost no reaction occurred in the presence of 30 wt % of KOH (relative to the initial azole); such concentration of the catalyst is usual for the vinylation of pyrroles [3, 4]. An equimolar or larger amount of alkali was found to be necessary. The presence of a small amount of water is also required to ensure successful and safe process; for this purpose, DMSO containing 0.4% of H_2O may be used. Anhydrous DMSO promotes spontaneous exothermic polymerization of propyne and allene. Addition of a larger amount of water (to a concentration of more than 0.4%) reduces the basicity of the system, and the reaction is suppressed. The relatively high temperature (125–145°C), as compared to vinylation in KOH–DMSO, favors formation of by-products via reaction of DMSO with propyne and allene; presumably, isopropenyl methyl sulfide and diisopropenyl sulfide are thus obtained, by analogy with the formation of methyl vinyl sulfide and divinyl sulfide in the system acetylene–KOH–DMSO [18]. In fact, 1–2% of volatile components was detected by GLC analysis of the reaction mixtures (these components were not examined).

As expected, the reactions under pressure were more effective. This follows from the results of isopropenylation of azoles **I**, **VIII**, and **IX**. 2-Phenylpyrrole (**VII**) and 1,2,4-triazole (**XI**) failed to react under atmospheric pressure. The yield of the final *N*-isopropenylazole strongly depends on the substrate-to-reagent ratio (under pressure). The yield increases as the concentration of isopropenylating agent rises (Table 1).

In the vinylation of pyrroles with acetylene in the system KOH–DMSO [1–4], pyrrolate ion readily attacks acetylene molecule at 100–120°C, and substitution of the azole ring weakly affects the yield of

Table 1. Isopropenylation of azoles **I**–**XI** with propyne–allene mixture and pure propyne and alene; molar ratio azole–isopropenylating agent–KOH–DMSO (0.4% H_2O) 1 : 1.5 : 1.1 : 7.7

Initial azole	Isopropenylating agent	Method[a]	Temperature, °C	Reaction time, h	Product	Yield, %
I	Propyne–allene	*a* [16]	125–135	5	**XII**	59
	Allene	*b*	105–115	6		34
		b[b]	125–135	6		Traces
		b[c]	125–135	3.5		Black polymer
			135→300			
		b	125–135	6		73 (86)[d]
II	Propyne–allene	*a*	135–145	10	**XIII**	40
III	Propyne–allene	*a*	130–135	7	**XIV**	39
IV	Propyne–allene	*a*	135–145	15	**XV**	40
V	Propyne	*a*	125–135	9	**XVI**	66
VI	Allene	*b*	125–135	5	**XVII**	34
VII	Allene	*b*	125–135	6	**XVIII**	9
		b	130–140	6		28[e]
VIII	Propyne–allene	*a*	125–135	7	**XIX**	23
	Allene	*b*	135–145	6		60 (70)[f]
IX	Allene	*b*	135–145	5	**XX**	34
X	Propyne–allene	*a*	130–135	8	**XXI**	38
	Allene	*b*	130–140	6		46
XI	Allene	*b*	130–140	6	**XXII**	20

[a] Method *a*: under atmospheric pressure; method *b*: under pressure.
[b] Molar ratio pyrrole–KOH 1 : 0.3; 63% of the initial pyrrole was recovered.
[c] In anhydrous DMSO.
[d] Molar ratio azole–allene 1 : 2.3.
[e] Molar ratio azole–allene 1 : 7.
[f] Molar ratio azole–allene 1 : 3.

Table 2. Boiling points, refractive indices, elemental analyses, and molecular weights (GC–MS data) of *N*-isopropenylazoles **XII**–**XXII**

Comp. no.	bp, °C (*p*, mm)	n_D^{20}	Found, %			Formula	Calculated, %			M^+ (I_{rel}, %)	M_{calc}
			C	H	N		C	H	N		
XII	147[a]	1.5186[a]	78.79	8.48	12.86	C_7H_9N	78.46	8.47	13.17	107 (100)	107.16
XIII	73 (18)	1.5070	79.80	9.63	10.35	$C_9H_{13}N$	79.95	9.69	10.36	135 (100)	135.21
XIV	77 (11)	1.4984	80.50	9.97	9.23	$C_{10}H_{15}N$	80.48	10.13	9.39	149 (100)	149.24
XV	109 (8)	1.6066	84.00	7.03	8.69	$C_{11}H_{11}N$	84.04	7.05	8.91	157 (100)	157.22
XVI	78 (3)	1.5442	81.79	9.30	8.63	$C_{11}H_{15}N$	81.94	9.38	8.69	161 (95)	161.25
XVII	105 (5)	1.5252	81.94	9.70	7.88	$C_{12}H_{17}N$	82.23	9.78	7.99	175 (70)	175.27
XVIII	110 (5)	1.5988	84.92	7.09	7.60	$C_{13}H_{13}N$	85.21	7.15	7.64	183 (100)	183.25
XIX	98 (25)	1.5224	66.39	7.46	25.84	$C_6H_8N_2$	66.64	7.46	25.90	108 (100)	108.14
XX	60 (3)	1.5574	68.67	8.13	22.78	$C_7H_{10}N_2$	68.82	8.25	22.93	122 (100)	122.17
XXI	64 (30)	1.5126	66.43	7.34	25.72	$C_6H_8N_2$	66.64	7.46	25.90	108 (100)	108.14
XXII	75 (14)	1.5040	54.83	6.40	38.30	$C_5H_7N_3$	55.03	6.47	38.50	109 (91)	109.13

[a] Data of [16].

the product (75–97% [3, 4, 15]). By contrast, the yield of *N*-isopropenylazoles (Table 1) considerably depends on the initial azole structure, though the reaction is carried out at higher temperature. The presence of a substituent in the α-position of the azole ring is likely to hinder attack on bulkier propyne and allene molecules for steric reasons, so that the yield of *N*-isopropenyl derivatives **XIII**–**XVIII**, and **XX** is lower than the yield of the corresponding products from unsubstituted pyrrole (**I**) and imidazole (**VIII**). Moderate yields of *N*-isopropenylindole (**XV**) and *N*-isopropenyl-2-phenylpyrrole (**XVIII**) are likely to result from the reduced nucleophilicity of the corresponding anions [19] due to electron-acceptor effect of fused benzene ring (indole) and phenyl group (2-phenylpyrrole). The same factor is responsible for the lowest (in the series of unsubstituted azoles) yields of *N*-isopropenyl derivatives from pyrazole and 1,2,4-triazole (40 and 26%, respectively); although their molecules have no bulky substituents, the anions derived therefrom are least nucleophilic.

The structure of products **XII**–**XXII** was confirmed by the NMR, IR, and mass spectra and elemental analyses (Tables 2–4). The mass spectra of all these compounds (Table 2) contain the molecular ion peak which is the base peak or next in intensity.

Analysis of the ^{1}H and ^{13}C NMR spectra (Table 3) revealed some structural features of *N*-isopropenylazoles **XII**–**XXII**. Molecules **XII**, **XIX**, **XXI**, and **XXII** having no other substituents in the heteroring are characterized by coplanar arrangement of the *N*-isopropenyl group and the heteroring. This follows from the upfield shift of the $=CH_2$ carbon signal relative to the corresponding signal of propene (δ_C 115.5 ppm [20]) due to *p*–π conjugation. The presence of a substituent in the α-position with respect to the N^1 atom (compounds **XIII**, **XVIII**, and **XX**), as well as of fused benzene ring (**XV** and **XVI**), hampers coplanar arrangement of the isopropenyl group and the heteroring; therefore, inversion of the H_A and H_B signals is observed due to anisotropic effect of the azole ring and the $=CH_2$ carbon signal shifts downfield by ~10 ppm. In molecules **XIV** and **XV** where both α-positions are occupied, the isopropenyl group is likely to be oriented orthogonally with respect to the heteroring plane: the ^{13}C chemical shift of the $=CH_2$ moiety is the same as in the propene molecule, which means that *p*–π conjugation with the isopropenyl group is absent.

N-Isopropenylazoles **XII**–**XXII** show in the IR spectra (Table 4) a strong absorption band at 1647–1663 cm^{-1}, which corresponds to stretching vibrations of the double C=C bond in the isopropenyl fragment.

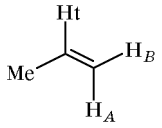
Thus we have developed a new general and simple procedure for introduction of isopropenyl group into azole ring. Previously unknown *N*-isopropenylazoles have been synthesized, which supplement the series of *N*-alkenylazoles, highly reactive building blocks and monomers.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 MHz for ^{1}H and 100.69 MHz for ^{13}C) using chloroform-*d* as solvent and hexamethyldisiloxane as internal reference. The IR spectra were measured on a Bruker IFS-25 spectrometer from samples prepared as thin films. The mass spectra (electron impact, 60 eV) were run on an LKB-2091 GC–MS system (SE-54 capillary column, 38 m; injector temperature 250°C; oven temperature programming from 70 to 200°C at a rate of 10 deg/min; ion source temperature 240°C). The reaction mixtures were analyzed by GLC with an LKhM-8MD chromatograph 3.5-m × 3-mm column packed with 5% of XE-60 on Chromaton N-AW-HMDS; thermal conductivity detector; carrier gas helium; oven temperature 70–180°C, depending on the component volatility; detector temperature 200°C; injector temperature 250°C. Commercial DMSO containing ~0.4% of water and commercial potassium hydroxide containing 15% of water ($2KOH \cdot H_2O$) were used. Allene was prepared by dehalogenation of 2,3-dichloro-1-propene with zinc dust according to the procedure reported in [21]; its purity was >99%. Propyne (98%) was commercial product (Aldrich). Propyne–allene mixture (4 : 1) was prepared from allyl chloride in the system KOH–DMSO.

Synthesis of *N*-isopropenylazoles XII–XXII (*general procedure*). *a. Under atmospheric pressure.* A 250-ml glass flask equipped with a stirrer, reflux condenser, thermometer, and gas-inlet and gas-outlet tubes was charged with 0.2 mol of azole **I**–**XI**, 14 g (0.215 mol) of $2KOH \cdot H_2O$, and 100 ml of DMSO. The mixture was heated to 125–145°C (Table 1), and propyne–allene mixture (4 : 1) or propyne (in the case of 4,5,6,7-tetrahydroindole) was passed through the mixture over a period of 5–15 h (depending on the substrate, see Table 1) under stirring. Unreacted propyne and allene were collected in a trap cooled to –78°C and were returned to the reaction. When the reaction was complete, the mixture was cooled and diluted with 200 ml of water. Pyrroles **XIII** and **XIV** and indoles **XV** and **XVI** were isolated by extraction with ether (4 × 50 ml), the combined extracts were washed with three portions of water to remove

Table 3. ^{1}H and ^{13}C NMR spectra of *N*-isopropenylazoles **XII**–**XXII**



Comp. no.	^{1}H NMR spectrum,[a] δ, ppm				^{13}C NMR spectrum, δ_C, ppm			
	H_A, q	H_B, q	Me, d.d	azole	>C=	$=CH_2$	Me	azole
XII	4.54	4.91	2.19	6.95 t (2H, 2-H, 5-H), 6.21 t (2H, 3-H, 4-H), ^3J = 2.2 Hz	140.69	97.93	20.39	118.24 (C^2, C^5), 109.56 (C^3, C^4)
XIII	4.94	4.82	2.09	5.96 d (4-H), 6.57 d (5-H), ^3J = 2.8 Hz; 2.14 s (2-Me), 2.02 s (3-Me)	142.19	108.37	22.70	124.49 (C^2), 116.17 (C^3), 109.34 (C^4), 118.15 (C^5), 10.88 (2-Me), 11.49 (3-Me)
XIV	5.28	4.92	1.95	5.68 s (4-H), 2.06 s (2-Me), 1.97 s (3-Me), 2.12 s (5-Me)	142.00	115.11	22.97	123.12 (C^2), 113.58 (C^3), 107.40 (C^4), 125.94 (C^5), 10.00 (2-Me), 11.05 (3-Me), 12.14 (5-Me)
XV	5.06	5.16	2.27	7.21 d (2-H), 6.55 d (3-H), ^3J = 3.3 Hz, 7.62 m (4-H), 7.21 m (5-H), 7.11 m (6-H), 7.62 m (7)	140.85	105.73	22.16	126.33 (C^2), 103.11 (C^3), 121.18 (C^4), 122.35 (C^5), 120.36 (C^6), 112.02 (C^7), 135.61 (C^8), 129.58 (C^9)
XVI	4.80	4.78	2.12	6.64 d (2-H), 5.96 d (3-H), ^3J = 2.8 Hz, 2.52 m (2H, 4-H), 1.75 m (4H, 5-H, 6-H), 2.59 m (2H, 7-H)	141.15	105.24	22.37	118.27 (C^2), 107.39 (C^3), 23.35 (C^4), 23.88 (C^5), 23.35 (C^6), 24.22 (C^7), 127.78 (C^8), 119.06 (C^9)
XVII	5.22	4.90	1.98	5.69 s (3-H), 2.46 m (4H, 4-H, 7-H), 1.74 m (4H, 5-H, 6-H), 2.16 s (2-Me)	141.33	114.28	22.88	126.71 (C^2), 15.36 (C^3), 23.02 (C^4), 23.85 (C^5), 23.65 (C^6), 22.55 (C^7), 126.71 (C^8), 116.44 (C^9), 12.25 (2-Me)
XVIII	4.97	4.95	1.90	6.30 d.d (3-H), 6.22 t (4-H), 6.78 d.d (5-H), $^3J_{3,4}$ = 3.8 Hz, $^3J_{4,5}$ = 2.8 Hz, $^4J_{3,5}$ = 3.8 Hz, 7.42 m (2H, *o*-H), 7.32 m (2H, *m*-H), 7.22 m (*p*-H)	143.34	110.14	22.38	133.08 (C^2), 110.50 (C^3), 108.34 (C^4), 123.58 (C^5), 133.82 (C^i), 127.53 (C^o), 128.30 (C^m), 123.58 (C^p)
XIX	4.74	5.05	2.22	7.72 s (2-H), 7.08 d (4-H), 7.15 d (5-H), ^3J = 1.4 Hz	138.14	101.64	20.20	134.72 (C^2), 129.81 (C^3), 116.48 (C^5)
XX	5.13	4.96	2.10	6.92 d (4-H), 6.87 d (5-H), ^3J = 0.8 Hz	140.10	111.24	22.30	143.86 (C^2), 118.51 (C^4), 127.31 (C^5), 14.03 (2-Me)
XXI	4.68	5.33	2.28	7.60 d.d (3-H), 6.34 t (4-H), 7.68 d.d (5-H), $^3J_{3,4}$ = $^3J_{4,5}$ = 2.0 Hz, $^4J_{3,5}$ = 0.8 Hz	140.94	99.61	19.50	140.44 (C^3), 106.78 (C^4), 126.57 (C^5)
XXII	4.84	5.48	2.26	7.94 s (3-H), 8.25 s (5-H)	138.07	103.32	18.99	151.97 (C^3), 140.63 (C^5)

[a] $^4J(CH_3, H_A)$ = 1.2 Hz, $^4J(CH_3, H_B)$ = 0.6 Hz.

Table 4. IR spectra of *N*-isopropenylazoles **XII**–**XXII**

Comp. no.	IR spectrum, ν, cm^{-1}
XII	602, 726 s, 851, 906 w, 957, 1002, 1048, 1093 s, 1260, 1306, 1345, 1381, 1441, 1484, 1525, 1554, 1647 s (C=CH_2), 2924, 2955, 2990, 3106, 3140
XIII	612 w, 634, 700 s, 826 w, 881, 902 sh, 931 w, 999 w, 1052 w, 1077 w, 1160 w, 1196, 1250 w, 1340 s, 1387, 1434, 1486 s, 1520 w, 1580 w, 1653 s (C=CH_2), 2739 w, 2864, 2920 s, 2980, 3100 w
XIV	626, 679 w, 775 s, 900 s, 974 w, 1003 w, 1149 w, 1169 w, 1261 w, 1331 s, 1359 s, 1387 s, 1416 s, 1439 sh, 1524, 1595 w, 1656 s (C=CH_2), 2732 w, 2959 s, 2919 s, 2973 s, 3024 sh, 3085 w, 3101 w
XV	581, 599 w, 671, 719, 742 s, 766, 882, 931 w, 988 w, 1017, 1081 w, 1121 w, 1153 w, 1178, 1215 s, 1250, 1295, 1332 s, 1351, 1370, 1457 s, 1475, 1519, 1573 w, 1607 w, 1650 s (C=CH_2), 2949 w, 2921 w, 2953 w, 2986 w, 3050, 3080 w, 3107 w, 3130 sh
XVI	609, 637, 699 s, 852, 864, 913, 958 w, 992 w, 1059, 1141, 1158, 1181 s, 1239, 1256 w, 1294, 1311, 1323, 1341 s, 1385 s, 1439 s, 1483 s, 1516 w, 1581 w, 1649 s (C=CH_2), 2845 s, 2928 s, 2982, 3098 w
XVII	600 w, 625 w, 645 w, 701 w, 727 w, 772 s, 812, 897 s, 944 w, 1006 w, 1086, 1147, 1236, 1260, 1300, 1316, 1362, 1388 s, 1428 s, 1522, 1594 w, 1654 s (C=CH_2), 2730 w, 2841 s, 2924 s, 2975, 3084 w, 3101 w
XVIII	611, 661, 699 s, 713 s, 759 s, 795, 884 s, 912, 938 w, 974, 1005, 1028, 1053, 1075 s, 1112 w, 1155, 1192, 1241 w, 1266 w, 1295, 1325 s, 1341, 1377, 1415, 1443, 1463 s, 1496, 1543, 1574 w, 1602, 1653 s (C=CH_2), 2848 w, 2878 w, 2920, 2958, 2982, 3032 sh, 3059, 3079, 3103
XIX	605, 657, 733, 815, 870, 903, 1012, 1080, 1109, 1165, 1252, 1307, 1319, 1362, 1388, 1449, 1490 s, 1511, 1656 s (C=CH_2), 2924 w, 2956 w, 2991 w, 3111
XX	602, 669, 699 w, 729, 898, 985, 1063 w, 1129, 1150, 1206, 1313 s, 1378 w, 1416 s, 1433 sh, 1494, 1524, 1658 s (C=CH_2), 2925 w, 2959 w, 2987 w, 3107
XXI	612 s, 645, 752 s, 870 s, 916, 956 s, 1000, 1048 s, 1085 s, 1169, 1201, 1334 s, 1394 s, 1434 s, 1519 s, 1657 s (C=CH_2), 2921 w, 2968 w, 2993, 3124, 3145
XXII	612 s, 637, 672 s, 741, 882 s, 956 s, 998 s, 1058 w, 1128 s, 1159, 1217 s, 1249 w, 1282 s, 1303 s, 1349, 1381 sh, 1424 s, 1449, 1508 s, 1663 s (C=CH_2), 2857 w, 2926, 2962, 2994, 3119 s

DMSO, dried over $MgSO_4$, and evaporated under reduced pressure (50 mm). Further purification from unreacted pyrrole was performed by column chromatography on aluminum oxide using hexane or petroleum ether (bp 40–70°C) as eluent; the subsequent vacuum distillation gave pure products. *N*-Isopropenylimidazole (**XIX**) and *N*-isopropenylpyrazole (**XXI**) were isolated from the reaction mixture (after dilution with water) by extraction into chloroform (6 × 40 ml); the combined extracts were washed with six portions of water to remove DMSO, dried over $CaCl_2$, and evaporated, and the residue was distilled under reduced pressure.

b. Under pressure. A steel rotating high-pressure reactor was charged with 0.2 mol of the corresponding azole, 14 g (0.215 mol) of 2KOH·H2O, 100 ml of DMSO, and 12 g (0.3 mol) of allene which was placed in a glass tube cooled to –78°C. The reactor was closed and heated at 125–145°C for 5–6 h (see Table 1). When the reaction was complete, the reactor was cooled and opened (in none of the cases pressure release was observed), and the products, *N*-isopropenylazoles **XII** and **XV**–**XXII** were isolated and purified as described above in *a*. The yields, physical constants, and spectral parameters of compounds **XII**–**XXII** are given in Tables 1–4.

***N*-[(*E*)-1-Propenyl)pyrrole** was isolated as a 1:1 mixture with *N*-isopropenylpyrrole (**XII**) (0.3 g) by distillation of the ether extract of the reaction mixture obtained according to method *b*. Yield 0.7%, bp 83–86°C (80 mm). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.77 t (2H, α-H, pyrrole), 6.16 t (2H, β-H, pyrrole), $J_{\alpha,\beta}$ = 2.2; 6.58 d.q (1H, NCH=), 5.60 m (1H, =C**H**CH_3), J_{trans} = 13.7; 1.73 d.d (3H, CH_3), $^3J_{CH,Me}$ = 6.8, $^4J_{=CH,Me}$ = 1.7. The GLC and ^{1}H NMR data coincided with those reported in [17].

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