REGIOSELECTIVE ADDITION OF HYDRAZINES TO ALLENYLACETYLENES — CONVENIENT ROUTE TO 3(5)-METHYL-5(3)-SUBSTITUTED PYRAZOLES*

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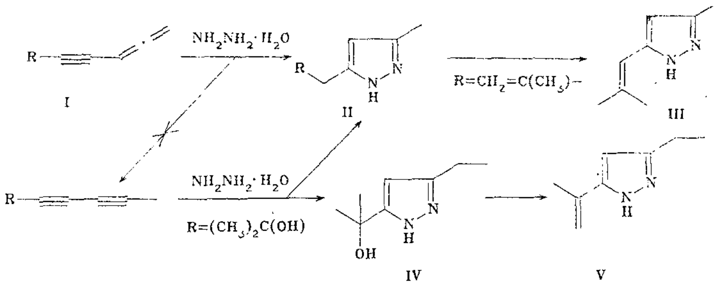
It is shown that hydrazine hydrate, methylhydrazine, and phenylhydrazine add smoothly and regioselectively to allenylacetylenes to give 3(5)-methyl-5(3)-substituted pyrazoles. In addition to the principal process, isomerization of allenylacetylenes to methyldiacetylenes, and the degree of which depends on the structure of the substrate, is observed in the reaction of methylhydrazine in an aqueous alcohol medium.

We have previously demonstrated the possibility of the synthesis of substituted pyrazoles by the addition of hydrazine to allenylacetylenes [2]. A report that this reaction occurs in the case of 2-methyl-5,6-heptadien-3-yn-2-ol did not contain data on the yield of the reaction product [3]. In order to develop methods for the synthesis of substituted methylpyrazoles we studied the reaction of various allenylacetylenes and hydrazines. We showed that the reaction of I with hydrazine hydrate is exothermic and leads to 3(5)-methyl-5(3)-substituted pyrazoles II in good yields.



I, II a $R=(CH_3)_2C(OH)$; b $R=(CH_3)(C_2H_5)C(OH)$; c $R=(CH_3)(C_4H_9)C(OH)$; d $R==C_3H_7CH(OH)$; e $R=CH_2CH_2OH$; f $R=CH_2=C(CH_3)-$; g $R=C_6H_5$

No intermediates or reaction products that provide evidence that the addition proceeds via a different pathway were detected by gas-liquid chromatography (GLC) and thin-layer chromatography (TLC). However, in addition to the principal reaction, a second process, viz., prototropic isomerization of pyrazole IIf to 3(5)-methyl-5(3)-(2-methylpropenyl)-pyrazole (III), occurs in the case of 6-methyl-1,2,6-heptatrien-4-yne (If). The ratio of pyrazoles IIf and III depends on the reaction temperature and varies from 3:1 to 1:1.25 (according to GLC and PMR spectroscopy) when the temperature is raised from 50°C to 100°C. Complete isomerization of pyrazole IIf to III occurs upon prolonged refluxing of the mixture with a methanol solution of sodium hydroxide. The IR spectra of a mixture of pyrazoles IIf and III contain absorption bands at 1360-1380, 1460-1480, and 1580-1585 cm^{-1}, which are characteristic for the aromatic ring of pyrazole [4]. It is noteworthy that the stretching vibrations of the C=C bond in the spectrum of IIf appear at 1640 cm^{-1}, which indicates the absence of conjugation of the double bond with the aromatic ring. At the same time, the signal of the 4-H proton in the PMR spectra of pyrazole III (5.89 ppm) is observed at weaker field as compared with the corresponding signal of IIa-g (5.65-5.75 ppm); this is probably due to the existence of conjugation of the double bond with the aromatic ring.

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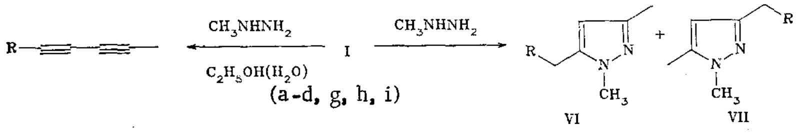
In searching for a probable scheme for the investigated reaction one might have assumed that prototropic isomerization of alkenylacetylenes I to conjugated methyldiacetylenes [5, 6] with subsequent addition of hydrazine precedes addition [7]. However, all of the known reactions involving the addition of hydrazine to unsymmetrical disubstituted diacetylenes lead to mixtures of pyrazoles [3, 8]. A report regarding the exclusive regioselective addition of hydrazine hydrate to 2-methyl-3,5-heptadiyn-2-ol to give pyrazole IIa [3] was not confirmed. Under the conditions described by the authors we obtained a mixture of pyrazoles IIa and IV [3, 8] in a ratio of 2:1. The dehydration of carbinol IV to isopropenylpyrazole V, which is reliable evidence for the formation of carbinol IV [8], was realized by heating the mixture at 200°C.

We recorded the only case of regioselective addition of hydrazine hydrate to unsymmetrical disubstituted diacetylenes in the case of 1-phenyl-1,3-pentadiyne. The reaction leads to 3(5)-methyl-5(3)-benzylpyrazole — the adduct of hydrazine and 5-phenyl-1,2-pentadien-4-yne (Ig) — in high yield. However, whereas heating of the reagents in ethanol at 75-78°C for 8.5 h is required in the first case, in the second case the reaction proceeds exothermally and is complete after 30 min at 40-50°C in the absence of a solvent. Thus allenylacetylenes I differ favorably from the isomeric methyldiacetylenes both with respect to the character of the addition products and the reactivities; this makes it possible to exclude isomerization as a step that precedes the addition of hydrazine and to use the reaction as a preparative method.

The high regioselectivity of the addition of hydrazine to allenylacetylenes I is due to attack by hydrazine on the sp-hybridized carbon atom of the allene grouping with the subsequent formation of a pyrazole ring. The literature data from a study of the regiochemistry of nucleophilic addition to allenic nitriles [9], esters [10], and phosphonates [11], as well as the data that we obtained in a study of the reaction of allenylacetylenes with amines [12, 13], constitute evidence in favor of this.

The addition of methylhydrazine to allenylacetylenes occurs when the reagents are heated in aqueous alcohol or THF at 45-50°C. The reaction proceeds regioselectively with respect to the substrate and nonregioselectively with respect to the reagent, i.e., the central carbon atom of the allene system is attacked by both the primary and secondary nitrogen atoms.



I, VI, VII h $R=C_2H_5OCH_2$—; i $R=CH_2OH$

The 1,3-dimethyl derivative generally predominates in the mixtures of pyrazoles VI and VII. Carrying out the reaction in THF and in an aqueous alcohol medium did not reveal a substantial effect of the solvent on the direction of addition, as one might have expected on the basis of the literature data on the effect of the solvent on the direction of the addition of alkylhydrazines to diacetylenes [14]. Isomeric pyrazoles VI and VII are not separated by TLC on aluminum oxide and silica gel. The ratios of the VI and VII isomers were determined by GLC and PMR spectroscopy. The difference in the isomers is displayed in the PMR spectra primarily in the weak-field shift of the signals of the protons of the 3-CH_3 group of VI as compared with the 5-CH_3 group in the VII isomer [15].

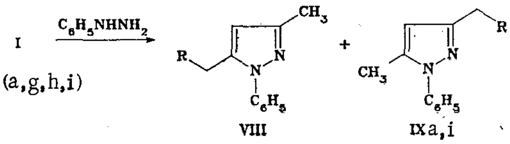
In addition to the principal process, isomerization of allenylacetylenes to methyldiacetylenes, the degree of which depends on the solvent and the nature of the substrate, occurs in the reaction of I with methylhydrazine. Thus only Ig underwent a side reaction when the reaction was carried otu in anhydrous THF. Judging from the PMR spectrum and the GLC data, the crude mixture contained 18-20% 1-phenyl-1,3-pentadiyne. Prototropic isomerization becomes appreciable in an aqueous alcohol medium, in which the amount of diacetylene reaches 80% and 41%, respectively, in the case of Id, g. The results obtained seem unexpected in view of the lower basicity of methylhydrazine as compared with hydrazine [16], for which isomerization is not observed. The existence of a competitive process in the case of methylhydrazine is evidently due to the relatively longer time during which addition is realized.

TABLE 1. 3(5)-Methyl-5(3)-Substituted Methylpyrazoles (II)

Compound	bp, °C (mm) (mp, °C)	n_D^{20}	R_f	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calc., %			Yield, %
						C	H	N		C	H	N	
II a	135—138 (1) (81)		A 0,67[a]	1360, 1380, 1460, 1480, 1585 (pyrazole ring), 3130, 3160, 3230 (OH and NH)[b]	(CD_3OD): 1,11 [$(CH_3)_2$, s]; 2,10 [3(5)-CH_3]; 2,60 [3(5)-CH_2]; 5,67 (4-H)[c]	62,2	9,1	18,1	$C_8H_{14}N_2O$	62,3	9,1	18,2	71
II b	143—144 (1)	1,5118	A 0,61[a]	1380, 1470, 1580 (pyrazole ring), 3150, 3230 (OH and NH)	(CCl_4): 0,87 ($C\mathbf{H}_3CH_2$, t distorted); 1,05 [$C\mathbf{H}_3C(OH)$, s]; 1,32 (CH_3CH_2, q, distorted); 2,1 [3(5)-CH_3]; 2,62 [3(5)-CH_2]; 5,68 (4-H); 8,40 (OH and NH)	64,2	9,6	16,5	$C_9H_{16}N_2O$	64,3	9,6	16,6	65
II c	149—151 (1)	1,5020	B 0,35[d]	1380, 1460, 1580 (pyrazole ring), 3150, 3210, 3250 (OH and NH)	(CCl_4): 1,85 ($C\mathbf{H}_3CH_2$, t, distorted); 1,07 [$C\mathbf{H}_3C(OH)$, s]; 1,15—1,55 [$(CH_2)_3$]; 2,13 [3(5)-CH_3]; 2,65 [3(5)-CH_2]; 5,68 (4-H); 8,1 (OH and NH)	67,2	10,1	14,2	$C_{11}H_{20}N_2O$	67,3	10,3	14,3	71
II d	142—144 (1)	1,5020	B 0,32[d]	1380, 1460, 1580 (pyrazole ring), 3150 3230 (OH and NH)	(CCl_4): 0,80 (CH_3CH_2, t, distorted); 1,12—1,53 [$(CH_2)_2$, m]; 2,09 [3(5)-CH_3]; 2,62 [3(5)-CH_2, d]; 3,75 (CHOH, m); 5,72 (4-H); 9,02 (OH and NH); $J_{CH_2-CH}=6{,}5$ Hz	64,2	9,7	16,6	$C_9H_{16}N_2O$	64,3	9,6	16,6	71
II e	166—168 (1)	1,5200	B 0,30[d]	1480, 1585 (pyrazole ring), 3160, 3230 (OH and NH)[b]	[$(CD_3)_2SO$]: 1,7 ($CH_2C\mathbf{H}_2CH_2$, m); 2,10 [3(5)-CH_3]; 2,43 [3(5)-$C\mathbf{H}_2$]; 3,4 ($C\mathbf{H}_2OH$, t); 5,72 (4-H)[c]; $J_{CH_2-CH_2}=7$ Hz	59,6	8,5	19,9	$C_7H_{12}N_2O$	60,0	8,6	20,0	71
IIf+IIIe,f	107—109 (2)	1,5185	B 0,40[d]	1640 ($CH_2{=}C-$), 1660 ($-\overset{\vert}{C}{=}CH$), 1450, 1470, 1580 (pyrazole ring), 3130, 3150, 3210 (NH)	(CCl_4): 1,64 ($CH_2{=}CC\mathbf{H}_3$, m); 1,85 [$(CH_3)_2C{=}$, m]; 2,20 [3(5)-CH_3; IIf]; 2,22 [3(5)-CH_3, III]; 3,22 [3(5)-CH_2, IIf]; 4,70 ($C\mathbf{H}_2{=}C$, m); 5,70 (4-H, IIf); 5,89 (4-H, III); 6,10 ($C{=}CH$, m); 11,0 (NH)	70,4	8,5	20,4	$C_8H_{12}N_2$	70,6	8,9	20,6	81
II g	143—145 (1) (76—77)		A 0,60[g]	—	(CCl_4): 2,1 [3(5)-CH_3]; 3,8 [3(5)-CH_2]; 5,48 (4-H); 7,05 (C_6H_5); 12,7 (NH)								

[a] Benzene—methanol (1:1). [b] The IR spectra of suspensions in mineral oil. [c] The NH and OH signals were not visible. [d] Ether. [e] The retention times were 2.70 for pyrazole IIf and 6.1 for III (150°C). The IIf:III ratio was 3:1. [g] Benzene—methanol (3:1).

The addition of phenylhydrazine to allenylacetylenes I was carried out by refluxing in THF. Under these conditions allenylethynylcarbinol Ii forms a mixture of pyrazoles VIIIi and IXi in a ratio of 5:1 (according to GLC and PMR spectroscopy). The signals of the protons of the 3-CH_3 group of isomer VIIIi show up in the PMR spectrum at stronger field than the signals of the protons of the 5-CH_3 group of pyrazole IXi [17], i.e., a pattern that is the opposite of that presented above in the spectra of 1-methylpyrazoles VI and VII is observed. This difference should evidently be explained by the anisotropic property of the benzene ring [18], which deshields the 5-CH_3 group of pyrazole IXi. In the case of carbinol Ia pyrazole IXa constitutes no more than 10% of the mixture, whereas the corresponding isomer is not detected at all in the examples with allenylacetylenes Ig, h.



The observed regioselective (with respect to the reagent) addition of phenylhydrazine to allenylacetylenes I correlates with the known fact of the greater activity of the primary nitrogen atom as compared with the secondary nitrogen atom in uncatalyzed nucleophilic addition reactions [19].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Perkin–Elmer R12B spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of thin layers of the compounds were obtained with a UR-20 spectrometer. Gas–liquid chromatography (GLC) was carried out with an LKhM-8MD chromatograph (model 5) with a catharometer and a steel column (2 m by 3 mm) packed with 5% XE-60 on Chromaton N-AW DMCS (0.3-0.4 mm); the carrier gas was helium, and the flow rate was 45 ml/min. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates (A) and on a loose thin layer of activity II aluminum oxide (B).

The starting allenylacetylenes I were synthesized by the reaction of the corresponding acetylenic compounds with propargyl chloride [20].

5,6-Heptadien-3-yn-1-ol (Ie). A 12-ml sample of 25% ammonium hydroxide was added in a nitrogen atmosphere to a mixture of 0.2 g of cuprous chloride, 0.4 g of hydroxylamine hydrochloride, and 15 ml of methanol, after which this mixture was treated successively with a solution of 7.0 g (0.1 mole) of 3-butyn-1-ol in 7 ml of methanol and (in the course of 30 min) a solution of 6 g (0.08 mole) of propargyl chloride in 15 ml of methanol at 25-30°C. The resulting mixture was stirred at the same temperature for 45 min, a solution of 4.2 g of sodium cyanide in 120 ml of water was added to it, and the mixture was extracted with ether. The ether layer was dried with Na_2SO_4 and distilled to give 3.9 g (46.8%), of Ie with bp 76-77°C (1 mm), n_D^{20} 1.4940, and t_{ret} 3.08 (118°C). IR spectrum: 860, 1940 ($CH{=}C{=}CH_2$); 2230 ($-C{\equiv}C-$); 3400 cm^{-1} (OH). PMR spectrum: 2.45 ($CH_2C{\equiv}C$, t, d), 3.62 (CH_2OH, t), 3.60 (OH), and 4.8-5.5 ppm ($CH{=}C{=}CH_2$, m); $J_{CH_2CH_2}$ = 7.0 Hz, $J_{CH_2C{\equiv}CCH}$ = 2.7 Hz. Found: C 77.3; H 7.4%. C_7H_8O. Calculated: C 77.8; H 7.4%.

4,5-Hexadien-2-ynyl Ethyl Ether (Ih). Similarly, from 12.6 g (0.15 mole) of ethyl propargyl ether and 8.2 g (0.11 mole) of propargyl chloride (with DMF instead of methanol) we obtained 6.7 g (50%) of ether Ih with bp 43-44°C (1 mm), n_D^{20} 1.4992, and t_{ret} 5.3 (80°C). IR spectrum: 865. 1950 ($CH{=}C{=}CH_2$); 1100 (C–O–C); 2240 cm^{-1} ($-C{\equiv}C-$). PMR spectrum: 1.12 (CH_3CH_2, t), 3.45 (CH_3CH_2, q), 4.13 ($CH_2C{\equiv}C$, d, t), and 4.9-5.55 ppm ($CH{=}C{=}CH_2$, m); $J_{CH_3CH_2}$ = 7.0, J_{1-6} = 1.0, and J_{1-4} = 2.0 Hz. Found: C 78.4; H 8.0%. $C_8H_{10}O$. Calculated: C 78.7; H 8.2%.

5-Methyl-8,9-decadien-6-yl-5-ol (Ic). This compound was obtained in 27% yield by a procedure similar to that in the preceding experiment and had bp 81-82°C (1 mm) and n_D^{20} 1.5380. IR spectrum: 860, 1955, 1980 ($CH{=}C{=}CH_2$); 2230 ($-C{\equiv}C-$); 3380 cm^{-1} (OH). PMR spectrum: 0.87 (CH_3-CH_2, t, distorted), 1.37 (CH_3, s), 1.3-1.7 [$(CH_2)_3$, m], 2.60 (OH), and 4.8-5.5 ppm ($CH{=}C{=}CH_2$, m). Found: C 80.6; H 9.8%. $C_{11}H_{16}O$. Calculated: C 80.4; H 9.8%.

Reaction of Allenylacetylenes I with Hydrazine Hydrate. A 0.06-mole sample of hydrazine hydrate (dissolved in a twofold volume of THF in the case of Ib, c, d) was added dropwise to 0.02 mole of allenylacetylene I, during which the temperature of the exothermic

TABLE 2. Pyrazoles VI and VII

Compound	bp, °C (mm)	n_D^{20}	t_{ret}, min (C°, column)		R_f (ether)	Ratio, %		IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calculated, %			Yield, %	
			VI	VII		A	B			C	H	N		C	H	N	A	B
VIa+VIIa	104—106 (1)	1,5100	1,9 (152)	1,7 (152)	B 0,47	60:40	55:45	1380, 1460, 1550 (pyrazole ring), 3375 (OH)	1,07 [$(CH_3)_2$, s VI]; 1,13 [$(CH_3)_2$; s VII]; 2,07 (5-CH_3, s VII)[a]; 2,18 (3-CH_3, s VI); 2,53 (5-CH_2, s VI); 2,60 (3-CH_2, s VII); 3,60 (OH); 3,65 (N—CH_3, s); 5,75 (4-H, s, br)	64,3	9,7	16,8	$C_9H_{16}N_2O$	64,3	9,6	16,7	51	87
VIb+VIIb	94—96 (1)	1,5030			B 0,37	75:25		1380, 1460, 1550 (pyrazole ring), 3400 (OH)	0,95 [$C\mathbf{H}_3C(OH)$, s VI]; 1,04 [$C\mathbf{H}_3C(OH)$, s VII]; 0,85—1,50 ($C\mathbf{H}_3C\mathbf{H}_2$, m); 2,07 (5-$CH_3$, s VII); 2,17 (3-$CH_3$, s VI); 2,49 (5-$CH_2$, s VI); 2,58 (3-$CH_2$, VII); 3,17 (OH); 3,66 (N—CH_3, s); 5,70 (4-H)	65,8	9,9	15,4	$C_{13}H_{18}N_2O$	65,9	9,9	15,3	60	
VIc+VIIc	120—122 (1)				0,43	60:40		1375, 1465, 1550 (pyazole ring), 3380 (OH)	0,87 (CH_3CH_2, t, distorted); 0,97 [$C\mathbf{H}_3C(OH)$, s VI]; 1,06 [$C\mathbf{H}_3C(OH)$, s VII]; 1,30 [$(CH_2)_3$, m VI]; 1,36 [$(CH_2)_3$, m VII]; 2,08 (5-CH_3, s VII); 2,19 (3-CH_3, s br, VI); 2,52 (5-CH_2, s, br, VI); 2,60 (3-CH_2, s br, VI); 3,10—3,50 (OH); 3,65 (N—CH_3, s VII); 3,67 (N—CH_3, s, VI); 5,72 (arom. H, s, br)	68,5	10,4	13,3	$C_{12}H_{23}N_2O$	68,5	10,5	13,3	62	
VId+VIId	110—112 (1)	1,5025	6,3 (150)	7,6 (150)	B 0,72	63:37	60:40	1380, 1460, 1550 (pyrazole ring), 3350 (OH)	0,90 ($C\mathbf{H}_3CH_2$, t distorted); m ,15—1,63 ($C\mathbf{H}_2C\mathbf{H}_2$, m); 2,10 (5-$CH_3$, s, br, VII); 2,17 (3-$CH_3$, d VI, J=0,6 Hz); 2,53 (5-CH_2, s, br, VI); 2,61 (3-CH_2, s, br, VII); 3,57 (N—CH_3, s VII); 3,60 (N—CH_3, s, VI); 3,78 (OH); 5,73 (arom. H, s, br)	65,8	9,8	15,1	$C_{10}H_{18}N_2O$	65,9	9,9	15,3	11	77
VIg+VIIg	119—121 (1)	1,5562	13,5 (150)	10,5 (150)	B 0,60	83:17	53:47	1250, 1460, 1550 (pyrazole ring), 730, 770, 790, 1490, 1600, 3040, 3070, 3090 (C_6H_5)	2,02 (5-CH_3, d VI, J=1,0 Hz); 2,06 (3-CH_3, s, br, VII); 3,42 (N—CH_3, VII); 3,50 (N—CH_3, s VI); 3,70 (5-CH_2, c, VI); 3,75 (3-CH_2, s, VII); 5,52 arom. H, s, br VI); 5,58 (arom. H, s, br, VII); 7,1 (C_6H_5, m)	77,4	7,5	15,1	$C_{12}H_{14}N_2$	77,3	7,5	15,0	26	65
VIh+VIIh	70—73 (1)	1,4810	9,9 (120)	7,9 (120)	B 0,57	65:35	72:28	1380, 1460, 1560 (pyrazole ring), 1120 (C—O—C)	1,09 ($C\mathbf{H}_3CH_2$, t =7,0 Hz); 2,06 (5-CH_3, c, or VII); 2,12 (3-CH_3, d VI, J==1,0 Hz); 2,65 (5-CH_2, m VII); 2,72 (3-CH_2, m VI); 3,40 ($CH_3C\mathbf{H}_2$, q J==7,0 Hz); 3,51 ($\mathbf{CH}_2$—CH_2—pyr (m); 3,57 (N—CH_3, s VI); 3,60 (N—CH_3, s VII); 5,72 (arom. H, d, br)	64,2	9,6	16,6	$C_9H_{16}N_2O$	64,2	9,5	16,6	69	72
VIi+VIIi	106—107 (1)	1,5149	4,1 (150)	5,7 (150)	B 0,58	72:28	71:29	1380, 1440, 1555 (pyrazole ring), 3350 (OH)	2,03 (5-CH_3, s, br, VI); 2,10 (3-CH_3, d VI, J=1,0 Hz); 2,60 (5-CH_2, t, VI, J=6,5 Hz); 2,63 (3-CH_2, t VII, J==6,5 Hz); 3,57 (N—CH_3, s); 3,68 ($CH_2C\mathbf{H}_2OH$, t J=6,5 Hz); 4,65 (OH, br); 5,75 (arom. H, br)	59,7	8,6	20,0	$C_7H_{12}N_2O$	59,9	8,6	19,9	61	76

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[a] Signals of the protons of the CH_3 and CH_2 groups bonded to the pyrazole ring (broad).

TABLE 3. Pyrazoles VIII and IX

Compound	bp, °C (mm)	n_D^{20}	t_{ret}, min (°C, column)	R_f (ether)	Time, h	IR spectrum, cm^{-1}	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calculated, %			Yield, %
									C	H	N		C	H	N	
VIIIa+IXa	146—148 (1)	1,5632	3,1 (200)	B 0,45	12	9:1	710, 770, 1560, 1600, 3060 (C_6H_5), 1380, 1460, 1560 (pyrazole ring), 3340 (OH)	0,92 [$(CH_3)_2$, s VIII]; 1,12 [$(CH_3)_2$, s IX]; 2,17 (5-CH_2, VIII); 2,25 (5-CH_2, IX); 2,63 [3(5)-CH_2]; 2,8 (OH); 6,00 (4-H); 7,3 (C_6H_5, m)	72,9	7,8	12,1	$C_{14}H_{18}N_2O$	73,0	7,9	12,2	61
VIIIg	200 (1)[a]		8,5 (200)	B 0,71	16		760, 1500, 1600, 3030, 3060 (C_6H_5), 1380, 1460, 1560 (pyrazole ring)	2,20 (3-CH_3); 3,9 (5-CH_2); 5,78 (4-H); 7,0—7,4 (C_6H_5)	82,0	6,7	11,4	$C_{17}H_{16}N_2$	82,2	6,4	11,3	64
VIIIh	120—122 (1)	1,5547	4,8 (180)	B 0,74	8		760, 1500, 1600, 3060 (C_6H_5), 1380, 1450, 1550 (pyrazole ring)	0,11 (CH_3CH_2, t); 2,15 (3-CH_3, s); 2,73 (5-CH_2, t); 3,28 (CH_2CH_3, q); 3,42 (OCH_2CH_2, m); 5,94 (4-H, s); 7,30 (C_6H_5, m); $J_{CH_2—CH_2}=6,5$ Hz	72,9	8,0	12,4	$C_{14}H_{18}N_2O$	73,0	7,9	12,2	74
VIIIi+IXi	163—165 (1)	1,5865	5,5 (200)	B 0,41	7,5	5:1	710, 760, 1500, 1600, 3060 (C_6H_5), 1380, 1440, 1460, 1550 (pyrazole ring), 3300 (OH)	2,12 (3-CH_3, VIII); 2,18 (5-CH_3, IX); 2,58 (5-CH_2, t, VIII); 2,61 (3-CH_2, t IX); 3,46 (CH_2OH, t VIII); 3,68 (CH_2OH, t IX), 4,2 (OH); 5,91 (4-H); 7,32 (C_6H_5, m); $J_{CH_2—CH_2}=6,5$ Hz.	71,0	7,0	14,0	$C_{12}H_{14}N_2O$	71,3	7,0	13,8	51

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[a] Distilled in a flanged flask at a bath temperature of 200°C.

reaction was maintained at 50-60°C. At the end of the exothermic reaction, the mixture was stirred for another 30 min at 40-50°C, after which the low-boiling components were removed by distillation, and the residue was distilled in vacuo to give pyrazoles II, the physicochemical constants and spectral characteristics of which are presented in Table 1.

3(5)-Methyl-5(3)-(2-methylpropenyl)pyrazole (III). A 1.3-g sample of a mixture of pyrazoles IIf and III in a ratio of 3:1 was refluxed for 34 h with 8 ml of a 10% solution of sodium methoxide in methanol, after which 40 ml of water was added, and the mixture was extracted with ether. The ether extract was dried with $MgSO_4$ and distilled to give 1.1 g (85%) of isomer III with bp 109-110°C (1 mm), n_D^{20} 1.5350, and R_f 0.46 (B, ether). Bands of pyrazole IIf were absent in the IR and PMR spectra (see Table 1); the signal of an NH proton was observed at 12.8 ppm. Found: C 70.3; H 8.8; N 20.5%. $C_8H_{12}N_2$. Calculated: C 70.6; H 8.9; N 20.6%.

Reaction of 2-Methyl-3,5-heptadiyn-2-ol with Hydrazine. A 3-g (0.06 mole) sample of hydrazine hydrate was added to 2.45 g (0.02 mole) of 2-methyl-3,5-heptadiyn-2-ol, and the mixture was heated at 100-110°C. The excess hydrazine hydrate was then removed by distillation, and the residue was distilled in vacuo to give 2.1 g (68%) of a mixture of IIa and IV in a ratio of 2:1 with bp 133-137°C (1 mm). PMR spectrum: 1.12 (CH_3CH_2, t), 1.45 [$(CH_3)_2$, s], 2.51 (CH_2CH_3, q), and 5.75 ppm (4-H, IV); signals of IIa were also present (Table 1). IR spectrum: 1380, 1480, 1580 (pyrazole ring); 3200 cm^{-1} (OH and NH). The same result was obtained when the reaction was carried out at 65-70°C for 6.5 h.

The mixture of IIa and IV was heated to 200°C, after which it was distilled in vacuo at 160-180°C (1 mm). The PMR spectrum of the resulting mixture contained signals of IIa and signals at 1.11 (CH_3CH_2, t), 1.98 ($CH_5C{=}CH_2$, m), 2.52 (CH_3CH_2, q), 4.90 ($CH{=}CCH_3$, q), 5.34 ($CH{=}CCH_3$, m), 5.98 ppm (4-H, V); $J_{CH_3-CH_3}$ = 7.0 Hz, J_{CH_3-H} = 1.4 Hz. The ratio of IIa and V was 1:1.4. IR spectrum: 1380, 1470, 1580 (pyrazole ring); 1630, 890 ($-C{=}CH_2$); 3103, 3200 cm^{-1} (OH and NH).

3(5)-Methyl-5(3)-benzylpyrazole (IIg). A solution of 2 g (14.2 mmole) of methylphenyldiacetylene and 3 g of hydrazine hydrate in 12 ml of ethanol was heated at 75-78°C for 8.5 h, after which the solvent was removed, and the residue was distilled to give 2 g (82%) of pyrazole IIg with bp 150-151°C (1 mm) [21].

Reaction of Allenylacetylenes I with Methylhydrazine. A) A solution of 0.02 mole of sodium hydroxide in 10 ml of water was added at 5-10°C to 0.01 mole of methylhydrazine sulfate, after which a solution of 0.005 mole of allenylacetylene I in 10 ml of ethanol was added, and the mixture was heated at 45-50°C for 4-5 h. The solvent was removed, and the residue was distilled to give a mixture of pyrazoles VI and VII (Table 2).

The following results were obtained by investigation of the crude mixtures by means of PMR spectroscopy and GLC: 15% 2-methyl-3,5-heptadiyn-2-ol in the case of Ia, 18% 2,4-hexadiyn-1-ol in the case of Ii, 10% 3-methyl-4,5-octadiyn-3-ol and 5-methyl-6,8-decadiyn-5-ol in the case of Ib and Ic, respectively, 41% 1-phenyl-1,3-pentadiyne in the case of Ig, and 80% 5,7-nonadiyn-4-ol in the case of Id [22-24].

B) A solution of 0.01 mole of methylhydrazine and 0.005 mole of allenylacetylene I in 15 ml of THF was heated at 45-50°C for 5 h, after which the solvent was removed by distillation, and the residue was distilled in vacuo to give a mixture of VI and VII (Table 2). In the case of Ig 18-20% 1-phenyl-1,3-pentadiyne was detected in the crude mixture.

Reaction of Allenylacetylenes I with Phenylhydrazine. A solution of 0.01 mole of allenylacetylene I and 0.01 mole of phenylhydrazine in 30 ml of dry THF was refluxed for 7.5-12 h (see Table 3), after which the THF was removed by distillation, and the residue was distilled. The constants and spectral characteristics of pyrazoles VIII and IX are presented in Table 3.

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FIRST REPRESENTATIVE OF MACROHETEROCYCLIC LIGANDS OF THE DIBENZO[c,m]DIPYRAZOLO[3,4-f:4',3'-j][1,2,5,8,9,12]HEXAAZACYCLOTETRADECENE CLASS

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The first representative of macroheterocyclic ligands of the dibenzo[c,m]dipyrazolo[3,4-f:4',3'-j][1,2,5,8,9,12]hexaazacyclotetradecene class was obtained by nontemplate cyclization of 4,4'-azobis(5-chloro-2,3-dimethyl-1-phenyl-1H-pyrazolium) bis(methylsulfate) with 2,2'-diaminoazobenzene in an aprotic solvent in the presence of potassium carbonate or magnesium oxide.

Macroheterocyclic compounds of the 1,2,5,8,9,12-hexaazacyclotetradecene class have been obtained by the template method exclusively in the form of metal complexes [1] and are of practical interest [1-8]. The corresponding metal-free ligands have not been isolated despite the diversity of demetallization methods that have been used [1].

In the present research we were able to realize the nontemplate synthesis of a free ligand of the type under consideration by using a component with increased reactivity. Instead of 4,4'-azobis(5-chloro-3-methyl-1-phenyl-1H-pyrazole) (I, $R^1 = R^2 = Cl$) [9] we used the corresponding bispyrazolium salt, viz., 4,4'-azobis(5-chloro-2,3-dimethyl-1-phenyl-1H-pyrazolium) bis(methylsulfate) (II), in nucleophilic substitution with 2,2'-diaminoazobenzene (IV).

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