CONDENSATION OF 1-ACYLPYRAZOLINES

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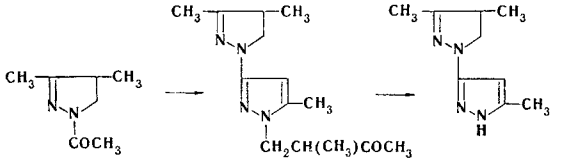
Under the influence of phosphorus oxychloride, 1-acylpyrazolines condense to give 3-pyrazolinylpyrazoles; cleavage of the pyrazoline molecule occurs at the C_3-N_2 bond.

Under the influence of phosphorus oxychloride, 1-acetyl-3,5,5-trimethylpyrazoline condenses to give 3-(3,5,5-trimethyl-1-pyrazolinyl)-5-methylpyrazole (Ia) with splitting out of a mesityl oxide molecule [1]. The course of this condensation has not been ascertained, and there are no data regarding the possibility of the occurrence of this reaction in the case of its homologs.

Our experiments showed that various other 1-acylpyrazolines are completely resinified under the described conditions [1] (no reaction products could be detected chromatographically). However, under milder conditions, the action of $POCl_3$ on 1-acetyl-3,4-dimethylpyrazoline gives IIb, which has the hydrocarbon residue of the starting pyrazoline molecule as a substituent in the 1-position.

When pyrazole IIb is heated (180°C) for a long time in vacuo this substituent is eliminated as methyl isopropenyl ketone [identified by gas–liquid chromatography (GLC)] with the formation of N_1-unsubstituted Ib – an analog of Ia.



The condensation of other alkyl-1-acetylpyrazolines also leads to pyrazolinylpyrazoles II (see Table 1). The molecular weights of these compounds determined by mass spectrometry correspond to the calculated values. The UV spectra are similar to the spectrum of Ia, and, according to the IR spectra, II contain a carbonyl group (1705-1720 cm^{-1}) but do not have an NH group. The PMR spectra in all cases contain signals of the protons of the starting pyrazoline ring and 4-H (5.8-6.0 ppm) and 5-CH_3 (2.4-2.5 ppm) signals of pyrazole, but superimposition of the signals occurs in the aliphatic portion of the spectra.

Condensation of 1-acetyl-3-methyl-5-phenylpyrazoline gives pyrazolinylpyrazole IIc along with a small amount of nitrogen-unsubstituted Ic. When IIc was refluxed in xylene in the presence of catalytic amounts of acid, Ic and benzalacetone were isolated.

The decomposition of IIb,c, makes it possible to assume that substances of the II type are intermediates in the formation of pyrazolinylpyrazoles I, i.e., the initial disintegration of the molecule of starting pyrazoline proceeds at the C_3-N_2 bond. In this case prior isomerization with shifting of the double bond to the 3,4- or 1,5-position does not occur; this is confirmed by examples with gem-substituted 1-acetyl-3,5,5-trimethyl- and 1-acetyl-4,4-dimethyl-5-isopropylpyrazolines.

The loss of a substituent attached to N_1, i.e., cleavage of the C_5-N_1 bond of the starting pyrazoline, is apparently realized via the mechanism of cleavage of β-aminoketones [2], inasmuch as this sort of cleavage is not observed in the case of IId,e, which do not have a labile β proton, while, on the other hand,

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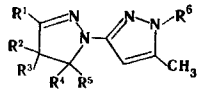
TABLE 1. 

Compound	R^1	R^2	R^3	R^4	R^5	R^6	Isolation meth.	mp, °C bp, °C (mm)	Empirical formula	Found, % C	Found, % H	Calc., % C	Calc., % H	UV spectrum λ_{max}, nm	UV spectrum lg ε	R_f	Yield, %
Ia[1]	CH_3	H	H	CH_3	CH_3	H	A	180 (10), 100	$C_{10}H_{16}N_4$					250 388	3,90 2,31	0,35	85
Ib	CH_3	CH_3	H	H	H	H	A, C	185 105	$C_9H_{14}N_4$	60,8	7,9	60,6	7,9	250	3,86	0,33	93 (from IIb)
Ic	CH_3	H	H	C_6H_5	H	H	B,C	185	$C_{14}H_{16}N_4$	69,5	6,8	70,0	6,7	248 379	3,86 1,90	0,30	8
If*	C_2H_5	CH_3	H	H	H	H	A	220 (20)	$C_{10}H_{16}N_4$	62,7	8,7	62,5	8,4	239 267	3,83 3,72	0,35	7
Ig	CH_3	H	H	CH_3	H	H	A	190 (15) 137	$C_9H_{14}N_4$	60,4	7,8	60,6	7,9	244 251	3,91 3,91	0,35	92
IIb	CH_3	CH_3	H	H	H	$-CH_2CH(CH_3)COCH_3$	C	150—152 (1)	$C_{14}H_{22}N_4O$	63.9	8,4	64,2	8,3	256	4,10	0,80	85
IIc	CH_3	H	H	C_6H_5	H	$C_6H_5CHCH_2COCH_3$	C	117	$C_{24}H_{26}N_4O$	74,7	6,7	74,5	6,7	249 365	3,58 1,11	0,70	60
IId	H	CH_3	CH_3	i-C_3H_7	H	i-$C_3H_7CHC(CH_3)_2CHO$	A	195 (10)	$C_{20}H_{34}N_4O$	69,4	9,9	69,5	9,8	245	3,90	0,75	80
IIe	H	CH_3	CH_3	i-C_3H_7	H	i-$C_3H_7CHC(CH_3)_2CHO$	A	199 (10) 71	$C_{22}H_{38}N_4O$	70,2	10,1	70,5	10,2	251	3,82	0,75	39
IIi	H	CH_3	H	C_2H_5	H	$C_2H_5CHCH(CH_3)CHO$	C	195 (9)	$C_{16}H_{26}N_4O$	66,4	9,1	66,2	9,0	238	3,98	0,75	82

* Obtained from the 1-acetyl-4-methyl-3-ethylpyrazoline present in 1-acetyl-4-methyl-5-ethylpyrazoline along with IIi.

when electron-donor alkyl groups are in the 5-position of the staring pyrazoline ring (for example, in 1-acetyl-3,5,5-trimethyl- and 1-acetyl-3,5-dimethylpyrazolines), II cannot be isolated here even when the reaction is carried out in dilute solution at room temperature.

N_1-Unsubstituted I (see Table 1) are analogs of the known Ia with respect to all of their chemical properties, chromatographic mobilities, and spectral characteristics. In contrast to II, which do not have NH groups, the IR spectra of I contain absorption at 3100-3250 cm^{-1}, while the PMR spectra contain a signal at 9.7-10 ppm (and the aliphatic portion of the spectrum is satisfactorily interpreted). Like the spectrum of Ia, the mass spectrum of Ib contains peaks typical for the pyridazinium ion (m/e 95, 96), an intense molecular ion peak (178), and peaks that characterize disintegration of the pyrazoline ring with m/e 163, 137, 109, and 108.

Inasmuch as the α protons of the acyl group participate in this condensation [1], 1-propionyl-4,4-dimethyl-5-isopropylpyrazoline was also introduced into the reaction. As one should have expected, the reaction proceeds with a great deal of resinification and the product is obtained in low yield; the 1-(1-oxo-2,2,4-trimethyl-3-pentyl)-3-(4,4-dimethyl-5-isopropyl-1-pyrazolinyl)-4-methyl-5-ethylpyrazole (IId) obtained is similar in all of its properties to the other II obtained from 1-acetylpyrazolines.

EXPERIMENTAL

The PMR spectra of CCl_4 solutions were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of mineral oil and hexachlorobutadiene suspensions were recorded with IKS-22 and UR-20 spectrometers. The UV spectra of ethanol solutions were recorded with a Cary spectrophotometer. The mass spectra were recorded with an MKh-1303 spectrometer with introduction of the sample into the ion source. Thin-layer chromatography was carried out on aluminum oxide in benzene–methanol (10:1) with development in UV light; the compounds were chromatographed with a column (20 cm by 1.5 cm) filled with Al_2O_3 with elution by benzene.

General Method of Condensation. A mixture of 0.05 mole of 1-acrylpyrazoline and 0.1 mole of $POCl_3$ in 100 ml of absolute ether was refluxed for 10-15 h, after which it was decomposed with ice, and the impurities were extracted with ether. The aqueous layer was made alkaline with potassium carbonate and extracted with ether or chloroform. The extract was dried with magnesium sulfate, and the product was isolated by distillation (A), recrystallization (B), or column chromatography (C) (see Table 1).

LITERATURE CITED

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