PREPARATION OF THE SIMPLEST Δ^1-PYRAZOLINES BY ISOMERIZATION OF Δ^2-PYRAZOLINES

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Δ^2-Pyrazolines that do not have substituents in the 1- and 3-positions are not capable of isomerization to 3-substituted pyrazolines and can be converted to Δ^1-pyrazolines by slow distillation in the presence of bases. This method, which is completely analogous to the synthesis of azo compounds from alkylhydrazones, gives good results when applied to 4-alkyl- and 5,5-dialkyl-Δ^2-pyrazolines and makes it possible to obtain the corresponding Δ^1-pyrazolines in yields of 40-70%. 4-Ethyl-, 5-methyl-5-ethyl-, and 5,5-diethyl-Δ^1-pyrazolines are described for the first time.

In 1963 in our laboratory we observed that 5,5-dimethyl-Δ^2-pyrazoline is converted to the Δ^1-isomer during distillation with a rectification column at atmospheric pressure [1]. It was subsequently shown [2-4] that acyclic analogs of Δ^2-pyrazolines – monosubstituted hydrazones of aldehydes and ketones that are isomerized to the corresponding azo compounds on distillation over alkalis – undergo a similar transformation. This sort of isomerization may serve as a convenient method for the synthesis of various aliphatic and aliphatic-aromatic azo compounds [3, 4]. In this connection, it seemed of considerable interest to ascertain the possibilities of using the migration of the azomethine bond for the synthesis of cyclic azo compounds, particularly Δ^1-pyrazolines. Cases of reverse isomerization, viz., the facile, and, from time to time, spontaneous conversion of Δ^1-pyrazolines to the Δ^2-isomers (see [5], for example), are well known. The conversion of Δ^2-pyrazolines to the Δ^1-isomers was proposed as an intermediate step in the thermal decomposition of Δ^2-pyrazolines [6] and in the isomeric transformations of 5-substituted Δ^2-pyrazolines to the 3-substituted isomers [7, 8], but there was no direct experimental confirmation of the $\Delta^2 \rightarrow \Delta^1$ transition before the appearance of [1].

We have set up experiments involving the isomerization of Δ^2-pyrazolines with different numbers and positions of the alkyl substituent under the catalytic influence of potassium tert-butoxide (1%) during slow vacuum distillation with a column (15 theoretical plates) at 70-90°. It turned out that 5,5-dialkyl substituted Δ^1-pyrazolines, for the simplest representatives of which this transformation was first noted [1], are formed most readily and smoothly under these conditions. Good yields of the corresponding Δ^1-pyrazolines were also obtained from 4-alkyl-Δ^2-pyrazolines (see Table 1). The isomerization of 3-alkyl-substituted Δ^2-pyrazolines, however, did not occur under these conditions because of the much higher thermodynamic stability of these isomers and their lower rate of isomerization.

A fraction containing 78% of the Δ^1-isomer was isolated by distillation of 5-methyl-Δ^2-pyrazoline over potassium tert-butoxide, but it could not be freed of the starting 5-methyl-isomer and the 3-methyl-Δ^2-isomer formed in the process.

Thus, according to our data, the preparative possibilities of the use of the isomerization of Δ^2-pyrazolines to obtain Δ^1-pyrazolines is restricted to the cases of 4-substituted and 5,5-disubstituted Δ^2-pyrazolines, i.e., Δ^2-pyrazolines whose structure excludes the formation of the most stable 3-substituted Δ^2-pyrazolines under the reaction conditions.

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TABLE 1. Δ^1-Pyrazolines Obtained by the Isomerization of Δ^2-Pyrazolines

Name	bp (mm)	d_4^{20}	n_D^{20}	n_C^{20}	Δ_{FC}^{20}	ω_{FCD}	$\nu_{N=N}$, cm^{-1}	λ max, nm (ε)[b]	MR_D		Empirical formula	N, %		Purity, %[c]	Yield, %
									found	calc.[a]		found	calc.		
4-Methyl-Δ^1-pyrazoline[d]	42,0—44,5 (25)	0,9280	1,4374	1,4348	90,4	20,6	1580	319 (416)	23,76	24,56	$C_4H_8N_2$	33,0; 32,9	33,3	95	42
4-Ethyl-Δ^1-pyrazoline	72—74 (40)	0,9089	1,4459	1,4428	90,0	20,1	1560	320 (170)	28,78	29,20	$C_5H_{10}N_2$	28,2; 28,1	28,5	99,5	70
5-Methyl-5-ethyl-Δ^1-pyrazoline	76,5—78,5 (40)	0,9017	1,4440	1,4415	87,7	19,8	1560	324 (250)	33,05	33,85	$C_6H_{12}N_2$	25,2; 25,3	25,0	98	46
5,5-Diethyl-Δ^1-pyrazoline	48,5—49,5 (5)	0,9102	1,4552	1,4527	91,5	20,1	1561	324 (60)	37,63	38,50	$C_7H_{14}N_2$	22,4; 22,3	22,2	94	52

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[a] From the Vogel bond refractions.

[b] In alcohol solutions (data of O. V. Sverdlova).

[c] From gas-liquid chromatographic data [9].

[d] This pyrazoline was obtained in [12] by the oxidation of pyrazolidine but was not characterized.

EXPERIMENTAL

For this work, we used Δ^2-pyrazolines, prepared by slow addition of the appropriate carbonyl compound to an equimolar amount of hydrazine hydrate, previously described in [9]. The 5,5-dialkyl-Δ^2-pyrazolines were obtained by the condensation of tertiary acetylenic chlorides with anhydrous hydrazine [10].

Isomerization of Δ^2-Pyrazolines. This was carried out, after the addition of 1% potassium tert-butoxide, by means of slow distillation of the volatile fractions under nitrogen at reduced pressure at 70-90° with a Vigreaux column with a metric dephlegmator. The distillate, which was enriched in the Δ^1-isomer, was then distilled with the same column in vacuo without a catalyst. The pure Δ^1-pyrazolines (Table 1) obtained in this way were yellowish, mobile liquids with boiling points lower than those of the corresponding Δ^2-isomers. The IR spectra contained a band of the valence vibrations of the N=N group at ~1560 cm^{-1}, and the band of the valence vibrations of the NH group at 3270-3305 cm^{-1} was absent [11].

The long-wave absorption bands in the UV with λ_{max} 319-324 nm are characteristic for the azo group and are an additional proof of the Δ^1-structure. The molecular refractions were less than those calculated for the Δ^1-pyrazolines by 0.42-0.87 ml/mole, which attests to considerably lower refraction of the N=N bond in the syn configuration as compared with the anti-azo compounds, on the basis of which the additive constants available in the literature were calculated.

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