UNUSUAL TRANSFORMATION OF 3-CARBOMETHOXY-Δ^2-PYRAZOLINE UNDER THE INFLUENCE OF LEAD TETRAACETATE

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3-Carbomethoxy-1-(1'-carbomethoxy-1'-cyclopropyl)pyrazole and 3-carbomethoxy-1-(3'-carbomethoxy-1'-pyrazolyl)-Δ^2-pyrazoline were obtained by the action of lead tetraacetate on 3-carbomethoxy-Δ^2-pyrazoline.

It is known that, depending on the structures, Δ^2-pyrazolines are converted by the action of lead tetraacetate (LTA) to 3-acetoxy-Δ^1-pyrazolines, cyclopropane derivatives, or pyrazoles [1-3]. We have observed an unusual reaction of methyl pyrazoline-3-carboxylate (I) with LTA [4], which gives 3-carbomethoxy-1-(1'-carbomethoxy-1'-cyclopropyl)pyrazole (V) and 3-carbomethoxy-1-(3'-carbomethoxy-1'-pyrazolyl)-Δ^2-pyrazoline (VI).

A symmetrical AA'BB' multiplet centered at 1.73 ppm (gem-1,1-disubstituted cyclopropane ring [5, 6]), doublets of the protons attached to C_4 and C_5 of the pyrazole ring at 6.76 and 7.51 ppm [10], and signals of two CH_3 groups (CO_2CH_3 groupings) are observed in the PMR spectrum of pyrazole V (Table 1*). The UV spectrum of V contains an absorption maximum characteristic for pyrazoles [11], and the IR spectrum contains two C=O bands of carbomethoxy groups; the weak band at 1515 cm^{-1} of NH vibrations previously observed in the spectra of N-substituted pyrazoles [12] is absent.

The presence of a 1-substituted Δ^2-pyrazoline fragment in the VI molecule is confirmed by the presence of an intense absorption band of a C=N bond at 1600 cm^{-1} in its IR spectrum [13, 14], characteristic multiplets of protons attached to C_4 and C_5 in the PMR spectrum, and an absorption maximum at 252 nm in its UV spectrum. The protons attached to C_4 and C_5 of the pyrazoline fragment are shifted to weak field by 25 and 43 Hz, respectively, as in the case of 1-acetyl derivative VIII.

The pyrazole fragment of V and VI most likely has a structure corresponding to a 1-substituted 3-carbomethoxy pyrazole derivative. This follows from the presence of a weak absorption band at 1515 cm^{-1} in the IR spectrum and also from the change in the chemical shift of the protons attached to the C_4 and C_5 atoms in the PMR spectra on passing from pyrazole VII to V and VI. In these cases the chemical shift of the proton adjacent to the 1-substituted atom undergoes greater changes, as seen from a comparison of the I-VIII and VII-IX pairs and also from the data in [9, 15]. It is interesting to note that distinct absorption bands at 1500-1680 cm^{-1} are not observed in the IR spectrum of pyrazole VII, whereas pyrazoline I displays an intense bands of a C=N bond at 1560 cm^{-1}, which, as in the case of pyrazoline VIII (1590 cm^{-1}), is shifted to 1600 cm^{-1} in the spectrum of VI.

The mass spectrum of V contains a molecular-ion peak with m/e 224 and a number of peaks with m/e 193, 133, 105, 54, and 79, according to which one of the possible pathways of fragmentation of the pyrazole V molecule can be represented by the scheme on the next page:

*For comparison, the spectral data for specially synthesized 3(5)-carbomethoxypyrazole (VII) [7], 1-acetyl-3-carbomethoxy-Δ^2-pyrazoline (VIII), and 1-acetyl-3-carbomethoxypyrazole (IX), obtained by the methods in [8, 9], are presented in Table 1.

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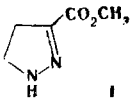
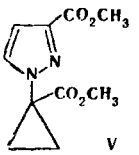
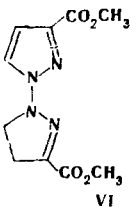
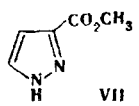
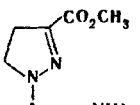
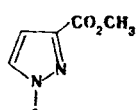
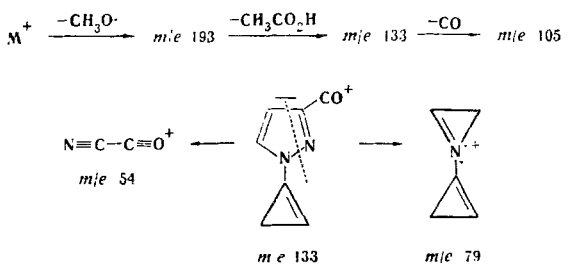
TABLE 1. Data from Spectral Studies of Pyrazoles I and IX

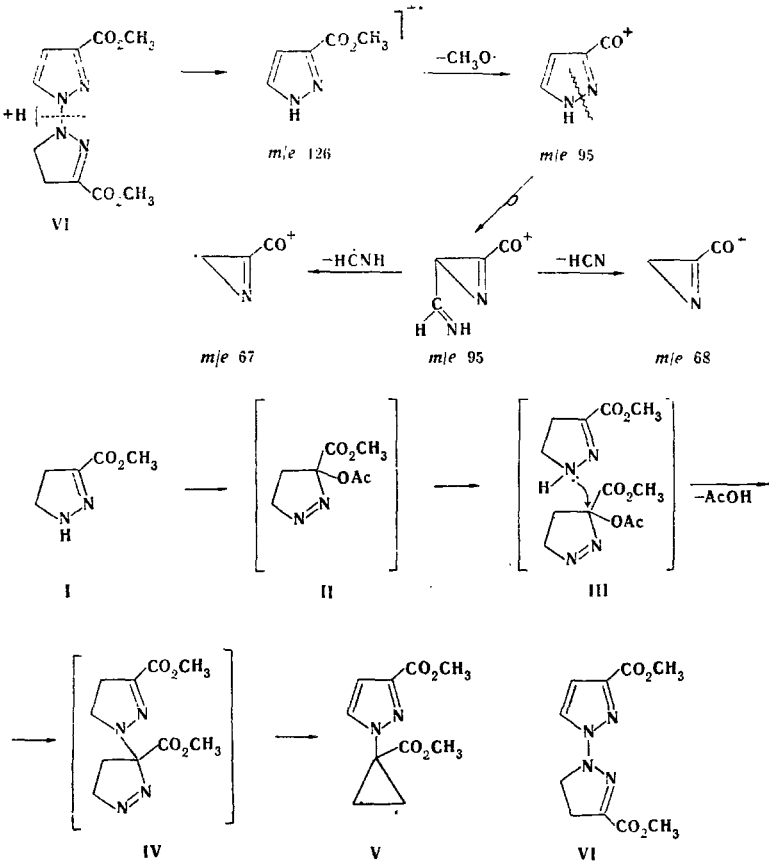
Compound	PMR,* ppm	IR, cm^{-1} (a indicates $CHCl_3$ solutions, and b indicates KBr pellets)				UV (in MeOH)	
		C=O	C=N	NH	others	λ_{max}	$\varepsilon \cdot 10^{-3}$
 I	2,83 m (2H, C_4-H) 3.60 m (2H, C_5-H) 3,78 s (3H, $COOCH_3$) 5.90 s (1H, NH)	a 1710, 1740† b 1715, 1745	1567 1535	3450 3325	—	291	10.4
 V	1.73 m (4H, Cyclo-propane 3,60 s (3H, $COOCH_3$) 3,84 s (3H, $COOCH_3$) 6,76 s (1H, C_4-H, $J_{4,5}$ 2,5 Hz) 7,51 d (1H, C_5-H, $J_{5,4}$ 2.5Hz)	a 1725, 1735 b 1720, 1738 1690†, 1670†	— —	None None	1515 1512	221	12.9
 VI	3,08 m (2H, C_4-H) 3.80 s (3H, $COOCH_3$) 3,85 s (3H, $COOCH_3$) 4,03 m (2H, $C_{4'}$-H) 6,73d (1H, $C_{4'}$-H, $J_{4',5'}$ 2.5Hz) 7.60 d (1H, $C_{5'}$-H, $J_{5',4}$ 2,5Hz)	a 1725, 1735† b 1715 in dioxane 1730, 1750	1600 1592 1600	None None None 3460	1515 1512 1515	213 253	12.5 11.6
 VII	3,95 s (3H, $COOCH_3$) 6,85 d (1H, C_4-H, $J_{4,5}$ 2.5 Hz) 7,90 d (1H, C_5-H, $J_{5,4}$ 2.5 Hz) 16.00 s (1H, NH)	a 1725, 1710‡ b 1740, 1730‡ 1720†	—	3460 3170 3140	—	217	12.0
 VIII	2,35 s (3H, Ac) 3,10 m (2H, C_4-H) 3,87 s (3H, $COOCH_3$) 4,05 m (2H, C_5-H)	a 1730, 1680	1590	None	—	280	19.7
 IX	2,76 s (3H, Ac) 3,94 s (3H, $COOCH_3$) 6.88 d (1H, C_4-H, $J_{4,5}$ 2,5 Hz) 8,22 d (1H, C_5-H. $J_{5,4}$ 2,5 Hz)	—	—	—	—	217	10,1

*The spectra of 10% solutions in $CDCl_3$ were recorded with tetramethylsilane as the internal standard.
†Shoulder.



The presence in the mass spectrum of peaks with m/e 54 and 79, formed as a result of the cleavage of the heteroring that is characteristic for pyrazoles [16] indicates the site of the addition of the cyclopropane residue to the pyrazole molecule.

The mass spectrum of VI contains a molecular-ion peak with m/e 258 and peaks with m/e 126, 95, 68, and 67; one of the possible pathways of its fragmentation can be represented by the following scheme. (See scheme on following page.) In this case the presence of a peak with m/e 95 with fragmentation characteristic for it [17], which leads to ions with m/e 67 and 68, confirms the structure of VI.



On the basis of data on the mechanism of conversion of pyrazolines under the influence of LTA [2, 3], the formation of V can be presented by a scheme that assumes, as a key step, nucleophilic attack by the most nucleophilic 1-nitrogen atom of pyrazoline I [18] (or pyrazole VII) on the intermediately formed 3-acetoxy derivative II through intermediate IV.

It is interesting to note that the 1-acetyl derivative of Δ^2-pyrazoline VIII does not undergo any changes on treatment with LTA or benzoyl peroxide in refluxing benzene. These negative results are in agreement with the proposed scheme of conversion of pyrazoline I under the influence of LTA. Pyrazole VII was not detected in the products of reaction of I with LTA, although this might have been expected [19], and the attack by the 1-nitrogen atom of pyrazole on II in the key step of the proposed scheme is therefore unlikely.

The formation of small amounts of VI is not surprising if one takes into account that various intermediates are formed in the initial steps of the reaction of LTA with pyrazolines [2, 3].

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer, the UV spectra were recorded with a Specord spectrophotometer, the PMR spectra were recorded with a JNM Ps-100 spectrometer, and the mass spectra were recorded with a Varian MAT-311 spectrometer with direct introduction of the samples into the source at 90° and an ionizing voltage of 70 eV. The melting points were determined in capillaries and were not corrected. Thin-layer chromatography (TLC) was carried out on microplates in a fixed layer of Woelm silica gel with detection of the spots in iodine vapors and in UV light.

Reaction of Pyrazoline I with LTA. A 16.8-g (3.9 mmole) sample of LTA was added in portions in the course of 30 min to a heated (to 70°) solution of 5.0 g (3.9 mmole) of I in 350 ml of absolute benzene in a three-necked flask equipped with a reflux condenser and a stirrer, and the mixture was refluxed on an oil bath for 2 h. It was then cooled to room temperature, and the resulting precipitate was removed by filtration and washed with 50 ml of absolute benzene. The combined filtrates were evaporated, and the residual oil was separated with a column filled with silicic acid [elution with hexane-ether (4:1)] to give 0.7 g (14%) of 3-carbomethoxy-1-(3'-carbomethoxy-1'-pyrazolyl)-Δ^2-pyrazoline (VI) with mp

114-115° (from alcohol). Found: C 47.5; H 4.8; N 22.2%. $C_{10}H_{12}N_4O_4$. Calculated C 47.5; H 4.7; N 22.2%. M^+ 252.

Subsequent elution yielded 3.1 g (71%) of 3-carbomethoxy-1-(1'-carbomethoxy-1'-cyclopropyl)pyrazole (V) with mp 104-106° (from alcohol). Found: C 53.6; H 5.6; N 12.5%. $C_{10}H_{12}N_2O_4$. Calculated: C 53.6; H 5.3; N 12.5%. M^+ 224.

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SYNTHESIS OF ISOMERIC PYRAZOLES BY REACTION OF PROPARGYL ACETATE WITH ALKYL DIAZOACETATES

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A mixture of 3(5)-carbalkoxy-5(3)-acetoxy- and 3(5)carbalkoxy-4-acetoxymethylpyrazoles was obtained by reaction of propargyl acetate with alkyl diazoacetates.

It is known that only 3(5)-carbethoxy-5(3)-hydroxymethylpyrazole is formed in the reaction of propargyl alcohol with ethyl diazoacetate [1]. We have observed [2] that two products — 3(5)-carbethoxy-5(3)-acetoxy- and 3(5)-carbethoxy-4-acetoxymethylpyrazoles (IIIa and IVa) — are formed from propargyl acetate (I) and ethyl diazoacetate (IIa).

The absorption maximum characteristic for the pyrazole heteroring at 221 nm and a shoulder at 238 nm (in the case of isomer IVa), the presence of which has been noted [3] for some pyrazoles with carbonyl-containing substituents, are observed in the UV spectra of IIIa and IVa. The IR spectra of isomeric pyrazoles IIIa and IVa are almost identical. The signal of the C_4 proton in the PMR spectrum of 3,5-disubstituted isomer IIIa is located at

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