

AN UNUSUAL REACTION OF 3-METHOXYCARBONYL- $\Delta^2$ -PYRAZOLINE  
WITH LEAD TETRAACETATE

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
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It is well known that pyrazolines acted on by lead tetraacetate are converted into 3-acetoxy- $\Delta^1$ -pyrazolines, cyclopropane derivatives or pyrazoles, depending on the structure of the initial compounds<sup>2,3</sup>. The interaction of methyl ester  $\Delta^2$ -pyrazoline-3-carboxylic acid<sup>4</sup> (1) with  $\text{Pb}(\text{OAc})_4$  by boiling of the reagents (in 1:1 mol proportion) for 2.5 hours in benzene resulted in the disappearance of initial 1 and thin layer chromatography data<sup>5</sup> revealed only two new products. Separation by column chromatography on silicic acid and elution with a mixture of hexane-ether, yielded 3-methoxycarbonyl-1-(1-methoxycarbonyl-1'-cyclopropyl)pyrazole<sup>6</sup> (2, m.p. 104-106°C from ether, 70% yield) and 3-methoxycarbonyl-1-[3:(5')-methoxycarbonyl-1'-pyrazoly]  $\Delta^2$ -pyrazoline (4, m.p. 114-115°C from ether, 14% yield). The spectral analysis data<sup>7</sup> of 1, 2, 4 and also of 3(5)-methoxycarbonyl pyrazole<sup>8</sup>(5) and  $N_1$ -acetyl-3-methoxycarbonyl- $\Delta^2$ -pyrazoline<sup>9</sup>(6), studied as model compounds, are shown in Table 1.

Consideration of the data permits only the following structure interpretation of 2: (a) the NMR spectrum displays (i) symmetric  $A_2B_2$  multiplet with a centre at 1,73, typical of 1,1-disubstituted cyclopropane derivatives<sup>10,11</sup>; (ii) doublets of protons at  $C_4$  and  $C_5$  of pyrazole ring<sup>12</sup> at 8,6,76 and 7,51; (iii) signals of two  $\text{CH}_3$ -groups, belonging to  $\text{COOCH}_3$  groupings; (b) there is absorption maximum characteristic of pyrazoles<sup>13</sup> in the UV spectrum; (c) the IR spectrum reveals (i) two carbonyl stretching absorptions; (ii) a weak band of  $1515 \text{ cm}^{-1}$  which was previously observed<sup>14</sup> in  $N_1$ -substituted pyrazoles;

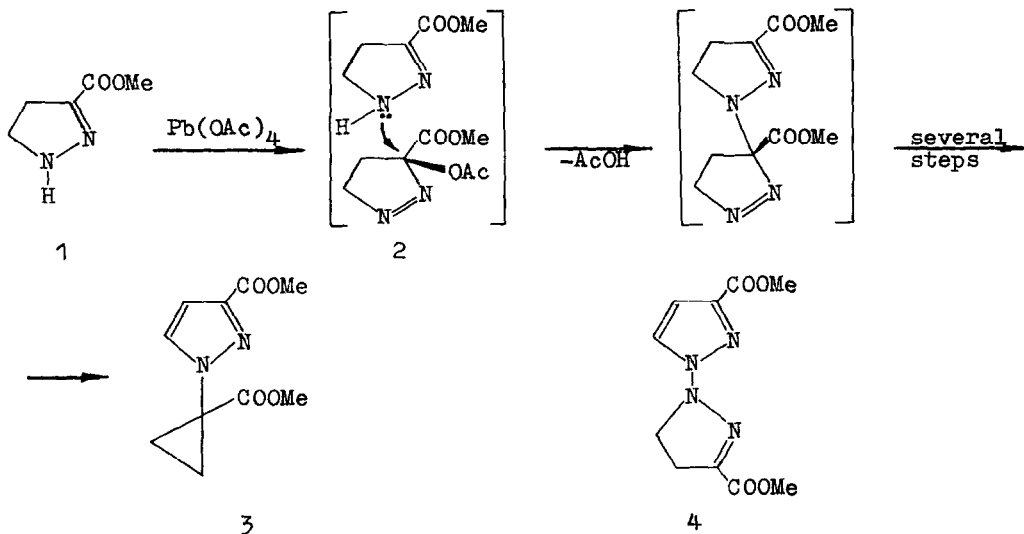
TABLE 1

## Spectral analysis data

Compound	NMR <sup>7</sup> ( $\delta$ ppm from TMS)	IR <sup>7</sup> ( $\text{cm}^{-1}$ ; <u>a</u> - in $\text{CHCl}_3$ ; <u>b</u> - in KBr)	C=N	N-H	others	$\lambda_{\text{max}}$	UV <sup>7</sup> (nm)
			C=O			$\epsilon$	
1	2,83 m centre, C <sub>4</sub> -2H	<u>a</u> 1710 (shs. at 1700 and 1740)	1567	3450		291	10420
	3,60 m centre, C <sub>5</sub> -2H						
	3,78 s, COOCH <sub>3</sub>	<u>b</u> 1715; 1745	1555	3325	1615		
	5,90, N-H						
	1,73 centre of symm. m, 					221	12950
3	3,60 s, cyclopropane-COOCH <sub>3</sub>	<u>a</u> 1725; 1735		absence	1515		
	3,84 s, pyrazole-COOCH <sub>3</sub>	<u>b</u> 1720; 1738 (shs. at 1690 and 1670)		"	1512		
4	6,76 d, J <sub>4,5</sub> =2,5 Hz, C <sub>4</sub> -1H	<u>a</u> 1725 (sh. at 1735)	1600	absence	1515	213	12530
	7,51 d, J <sub>4,5</sub> =2,5 Hz, C <sub>5</sub> -1H					253	11640
	3,08 m centre, C <sub>4</sub> -2H	<u>b</u> 1715 in dioxane:	1592	"	1512		
	3,80 s, pyrazoline-COOCH <sub>3</sub>						
5 <sup>8</sup>	3,85 s, pyrazole-COOCH <sub>3</sub>	1730; 1750	1600	"	1515		
	4,03 m centre, C <sub>5</sub> -2H						
	6,73 d, J <sub>4,5</sub> =2,5 Hz, C <sub>4</sub> -1H	<u>a</u> 1725 (sh. at 1710)	3170; 3460			217	12020
	7,60 d, J <sub>4,5</sub> =2,5 Hz, C <sub>5</sub> -1H						
6 <sup>9</sup>	3,95 s, COOCH <sub>3</sub>	<u>b</u> 1740 (shs. at 1730, 1720 and 1690)	1590	absence		280	19700
	2,35 s, CH <sub>3</sub> CO						
	3,10 m centre, C <sub>4</sub> -2H	1680 (amide)					
	3,87 s, COOCH <sub>3</sub>						
	4,05 m centre, C <sub>5</sub> -2H						

(iii) the band of  $\nu$  N-H is absent.

On the basis of the data the following scheme may be proposed as a key step in the mechanism of converting pyrazolines by the action of  $\text{Pb}(\text{OAc})_4$  which is discussed in literature<sup>2,3</sup> - namely a nucleophilic attack of the most nucleophilic  $\text{N}_1$ -nitrogen atom of 1<sup>15</sup> (or of 5<sup>16</sup>) on the interia 3-acetoxy derivative 2 :



In the NMR, IR and UV spectra of 4 there are features typical of both 3(5)-methoxycarbonyl pyrazole and of 3-methoxycarbonyl  $\Delta^2$ -pyrazoline. The presence of a  $\text{N}_1$ -substituted  $\Delta^2$ -pyrazoline fragment in the molecule of 4 is borne out by (i) an intensive absorption band  $\nu$  C=N at  $1600\text{ cm}^{-1}$  which is typical of such structures<sup>17</sup>; (ii) peculiar multiplets of protons at  $\text{C}_4$  and  $\text{C}_5$  in the NMR spectrum; (iii) an absorption maximum at 252 nm in the UV spectrum. The  $\text{C}_4$  and  $\text{C}_5$  protons of the pyrazoline fragment are shifted over to a weaker field of 25 and 43Hz respectively, which is similar in the case of the  $\text{N}_1$ -acetyl derivative 6. According to the IR spectra (weaker absorption band at  $1515\text{ cm}^{-1}$ ), the most probable structure of the pyrazole fragment must be the  $\text{N}_1$ -derivative of 3-methoxycarbonyl pyrazole. It is of interest to note that the IR spectrum of 2 does not show clear absorption bands within the wavelength values of  $1500\text{--}1680\text{ cm}^{-1}$ , whereas 1 displays an intensive band of  $\nu$  C=N at  $1560\text{ cm}^{-1}$  which in 4 is shifted to  $1600\text{ cm}^{-1}$  which is similar to the  $\nu$  C=N band of 6 reaching  $1590\text{ cm}^{-1}$ .

The small quantities of 4 produced are in keeping with the fact that in the initial reaction of  $\text{Pb}(\text{OAc})_4$  with pyrazolines various intermediates are formed<sup>2,3</sup>.

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4. J.A. Moore, J. Org. Chem., 20, 1607(1955).
5. Thin layer chromatography was performed on a silica gel (Woelm) plates, ether being used as eluent, spots being detected by uv light and iodine vapours (Rf: 1 - 0.30; 3 - 0.40; 4 - 0.35; 5 - 0.32; 6 - 0.25).
6. A satisfactory C, H and N elementary analysis has been obtained for all the substances studied in the present paper.
7. The nmr spectra were obtained on a Varian HA 100 spectrometer using ca. 15% solutions in  $CDCl_3$ . The ir spectra were taken on a Carl Zeiss (DDR) Model UR-20 spectrophotometer. The uv spectra were determined on a Carl Zeiss (DDR) Model "Specord" recording spectrophotometer in abs. MeOH.
8. Obtained according to J. Elguero, G. Guiraud, R. Jacquier, Bull. soc. chim. France, 1966, 619; m.p. 139-140°C from benzene.
9. Obtained from 1 acted on by  $Ac_2O$  in AcOH, m.p. 101-103°C from  $C_2H_5OH$ .
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16. The attack of  $N_1$ -pyrazole 5 appears unlikely as it has not been detected in the reaction products, although this might have been expected, e.g. see: J.P. Freeman, J. Org. Chem., 28, 885(1963).
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