N,N'-LINKED BIAZOLES. PART 5. SYNTHESIS OF PYRAZOLYL DIMERS BY THE REACTION OF 3-METHOXYCARBONYL-2-PYRAZOLINE WITH LEAD TETRAACETATE

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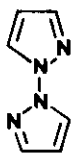
Abstract- Contrary to a previous report by Akhrem *et al.* (*Tetrahedron Lett.* **1973**, 2655), the reaction of 3-methoxycarbonyl-2-pyrazoline with lead tetraacetate affords not only 3-methoxycarbonyl-1-(3-methoxycarbonyl-2-pyrazolin-1-yl)pyrazole (**8**) and 3-methoxycarbonyl-1-(1-methoxycarbonyl-1-cyclopropyl) pyrazole (**9**), but a complex mixture of pyrazoles and pyrazolines depending on the reaction conditions (LTA/pyrazoline ratio and temperature). The structures of all compounds have been established, and a new mechanism is proposed for the reaction. The oxidation of **8** with *N*-bromosuccinimide gave the symmetrical 3,3'-dimethoxycarbonyl-1,1'-bipyrazole (**17**).

Following our interest in *N,N'*-linked biazoles,[1-4] we focussed our attention into the 1,1'-bipyrazole system, **1**. For the synthesis of **1**, the creation of the central N-N bond by oxidation of a suitable *N*-unsubstituted pyrazole precursor seemed attractive, since the usual methods for pyrazole construction (*i.e.*, hydrazine derivatives)[5] cannot be applied in this case, due to the unavailability of 1-hydrazinopyrazole as the necessary starting material.

From the scarce literature data concerning the oxidative dimerization of pyrazoles, some of the early *N,N'*-bipyrazoles described proved to be false. Thus, the von Auwers 'dimer' 2,2'-bi-7,7'-dimethyltetrahydroindazole (**2**)[6] was found to be a cyclic trimer,[7] and the iodine oxidation of tetrahydroindazolones failed to give *N,N'*-linked dimers like **3**,[8] contrary to a previous report by Skarik *et al.*[9]

In fact, only two recent references deal with 'true' *N,N'*-linked bipyrazoles. In one case, 3(5)-amino-4-ethoxycarbonyl-5(3)-phenylaminopyrazole was oxidized either by dibenzoyl or di-*t*-butyl peroxides to give the corresponding dimer, **4**, whose structure has been unequivocally elucidated.[10,11] However, no examples of less substituted pyrazoles have been reported to dimerize similarly, and **4** was quite unsatisfactory as a starting compound for the synthesis of **1**, due to its multi-substituted structure.

In the other example, Akhrem *et al.*,[12,13] described the formation of a mixture of the pyrazoline-pyrazole (**8**) (14% yield) and the cyclopropylpyrazole (**9**) (70% yield) by reacting 3-methoxycarbonyl-2-pyrazoline (**5**) with lead tetraacetate (LTA).



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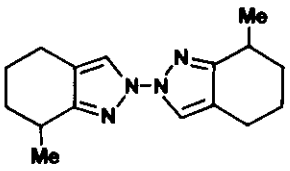

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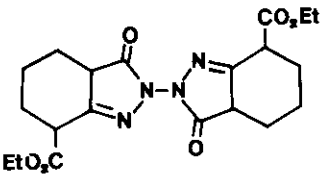

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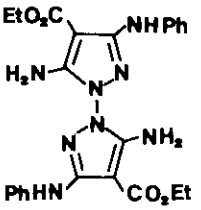

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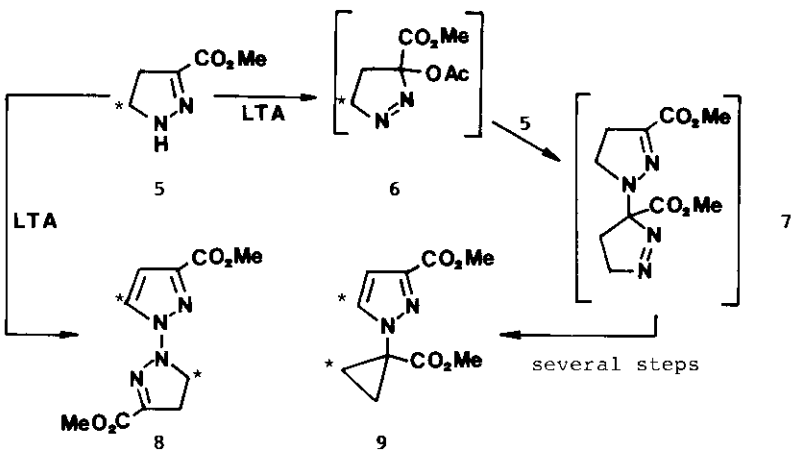
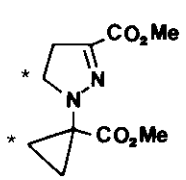
The mechanism proposed by Akhrem for the formation of **9** is outlined in Scheme 1. The conversion of 2-pyrazoline **5** to 1-pyrazoline **6**, followed by the rapid attack of **5** to **6** could explain the formation of **9** , through the intermediacy of the bipyrazoline (**7**). No mechanism accounting for **8** was proposed, however.



Scheme 1

In the hope that the yield of compound **8**, a useful intermediate for a convenient synthesis of 1,1'-bipyrazole (**1**), could be improved by modification of the reaction conditions, we decided to study the influence of the LTA/pyrazoline ratio, as well as of the temperature, on the Akhrem reaction.

In our hands, the reaction of 3-methoxycarbonyl-2-pyrazoline (**5**) with LTA in benzene following the Akhrem procedure,[12,13] yielded not only **8**+**9**, but a complex mixture from which eleven compounds **5** - **16** were isolated by column chromatography and characterized. The product composition was dependent on the reaction conditions (Table I).



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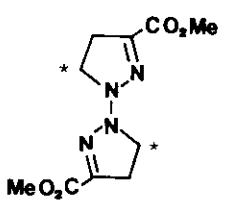

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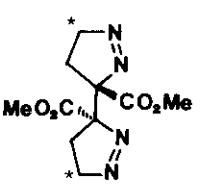

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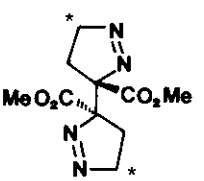

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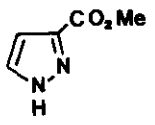

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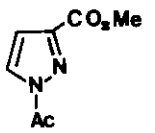

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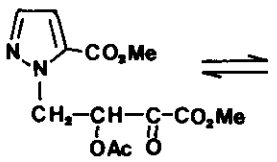
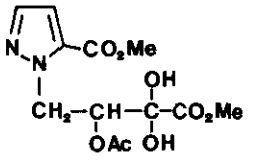


16a



16b

Table I. Effect of the reaction conditions in the relative proportion of isolated compounds.

Run	Temp.°C	[LTA/5]	6	7	8	9	10	11	12	13	14	15	16
1	60	0.6:1	-	-	9.2	36.7	51.7	-	2.4	-	-	-	-
2	0	1:1	5.1	58.6	-	7.3	-	14.9	4.3	9.8	-	-	-
3	60	1:1	2.3	-	12.2	62.8	-	-	7.5	6.7	-	2.2	6.3
4	80[a]	1:1	-	-	11.8	66.8	-	-	-	1.2	18.7	1.5	-
5	60	1.1:1	4.1	-	16.6	53.8	-	-	5.9	11.6	-	1.9	6.1
6	60	2:1	48.9	-	9.7	41.4	-	-	-	-	-	-	-
7	25	3:1	39.5	-	14.5	38.5	-	-	-	-	-	-	7.5

[a]Without neutralization of the crude mixture.

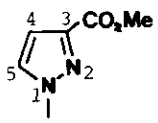
IDENTIFICATION OF THE COMPOUNDS

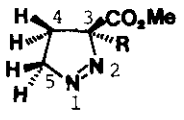
The physical characteristics (mp, ir and ^{1}H nmr) of compounds **8**, **9**, **14** and **15** were identical to those described by Akhrem (although not appearing in Scheme 1, compounds **14** and **15** were prepared by this author as models for his study). Due to their unstability, compounds **6**[14] and **7** were only characterized by spectroscopy.

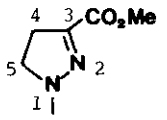
In order to facilitate the interpretation of spectra, the Akhrem reaction was also performed starting from a 5,5-dideuteriated analogue of pyrazoline **5** (obtained with CD_2N_2 and methyl acrylate). By this way we were able to isolate the corresponding labelled analogues of compounds **6** and **8-13** (the position of the deuterium atom is directly indicated by an asterisk in the respective formulae).

The uv, ir, and mass spectra are collected in Table II. They are in agreement to literature data for ir,[14,15,16] uv,[12,15,17,18] and mass[19] spectra of pyrazolines.

All compounds were studied by ^{1}H nmr (Table III), and the unstable intermediate **7** was characterized only by this technique. The numbering of atoms in Table III is as follows:







The assignment of the signals was made according to published data for pyrazoles[20] and 2-pyrazolines.[21] From data for 1-pyrazolines[22] it was easy to assign the upper field signals of the ABCD patterns of compounds **6**, **7**, **12**, and **13** to the position 4, but we were unable to determine which protons were *cis* and which were *trans* to the ester group. Coupling constants of these systems are collected in Table IV. The deuteriated derivatives of **6**, **12**, and **13** showed broad AB systems for each couple of H_4 and H_4, protons (H_A and H_B).

Table II. Uv, ir, and mass spectra.

Comp.	Uv (EtOH) λ_{max} (logϵ)	Ir (KBr) ν_{max} (cm^{-1})	Ms (EI, 70 eV) m/z (relat. abund.%)
5	291(4.02)	3350(N-H);1710(C=O);1555(C=N)	128(M^+,75);97(87);95(100);68(35)
6	326(2.43)	1755(C=O);1560(N=N)[a]	127(9);99(53);56(9);43(100)
8	213(4.10);253(4.07)	1720(C=O);1595(C=N);1510	(see ref. 13)
9	221(4.11)	1740 and 1725(C=O);1510	(see ref. 13)
10	299(4.08)	1720 and 1695(C=O);1555(C=N)	226(M^+,43);195(17);167(100);114(14)
11	291(4.05)	1720(C=O);1580(C=N)	254(M^+,5);226(13);167(48);54(100)
12	327(2.71)	1750(C=O);1560(N=N)	198(15);167(19);139(12);79(100);59(53)[c]
13	323(2.69)	1750(C=O);1570 and 1555(N=N)	198(4);167(14);139(27);79(100);59(70)[c]
14	217(4.08)	3170(N-H);1740(C=O)[b]	126(M^+,56);95(100);67(3);66(7)
15	217(4.00)	1750,1730 and 1720(C=O);1545	168(M^+,10);126(13);95(100);68(5)
16	228(3.93)	3340(O-H);1760 and 1735(C=O); 1525	298(M^+,2);267(2);256(14);159(23); 139(100)

[a]Film; [b]Nujol; [c]At 10 eV: 255(M^++1); by CI(NH_3): 272(M^++18).

Table III. Proton chemical shifts (ppm) and coupling constants (Hz) in $CDCl_3$

Comp.	Pyrazoles			1-Pyrazolines			2-Pyrazolines			Other signals
	Pos.3	Pos.4	Pos.5	Pos.3	Pos.4	Pos.5	Pos.3	Pos.4	Pos.5	
5							3.75[a]	2.85	3.60[b]	6.4[c](NH)
6				2.26(OAc) 3.72[a]	1.66	2.55 4.51 4.87[b]				
7				3.69[a]	2.02	2.32 4.60 4.80	3.69[a]	2.92	3.92	
8	3.85[a]	6.76 (J_{45}=2.5)	7.63[b]				3.89[a]	3.12	4.08[b]	
9	3.86[a]	6.78 (J_{45}=2.5)	7.54[b]							1.77(4H)[d];3.61[a]
10							3.78[a]	2.94	3.64[b]	1.45(4H)[d];3.61[a]
11							3.83[a]	2.92	3.83[b]	
12				3.70[a]	2.50	2.86 4.64 4.85[b]				
13				3.72[a]	1.65	2.03 4.45 4.79[b]				
14	3.95[a]	6.84 (J_{45}=2.4)	7.84							12.7[c](NH)
15	3.90[a]	6.86 (J_{45}=2.4)	8.27							2.74(Ac)
16	7.46	6.83 (J_{34}=2.0)	3.89[a]							2.08(OAc);3.91[a];ABX[e]

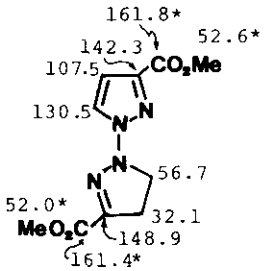
[a]CO_2Me signal; [b]Disappears in the deuteriated analogue; [c]Broad signal; [d]Only two H remain in the deuteriated analogue; [e]ABX-System: δ_A=5.30; δ_B=5.18; δ_X=6.06; J_{AB}=14.4; J_{AX}=5.8; J_{BX}=6.0

Table IV. Proton-proton coupling constants (Hz) of 1-pyrazolines.

Compound	J_{AB} (J_{gem} pos.4)	J_{AC} (J_{cis})	J_{AD} (J_{trans})	J_{BC} (J_{trans})	J_{BD} (J_{cis})	J_{CD} (J_{gem} pos.5)
6	14.0	4.0	8.2	9.2	7.1	18.2
12	13.5	9.0	7.2	6.2	8.3	18.4
13	13.7	4.4	8.8	10.0	8.0	18.0

The differences between the ^{3}J coupling constants and the deshielding (Table III) of the protons at position 4 (H_A and H_B) in compound **12** with respect to compound **13**, correspond to a *threo-erythro* pair. From molecular models examination (proximity of the carbonyl group to the protons at position 4 in **12**), we can tentatively conclude that the *threo*-isomer correspond to **12** and the *erythro*-isomer to **13**.

The ^{13}C chemical shifts of the following compounds were also measured (except **16**, the solvent was $CDCl_3$; 50 MHz). The assignments were based on literature data for pyrazoles,[23] 2-pyrazolines,[24] 1-pyrazolines,[25] and cyclopropanes.[26]



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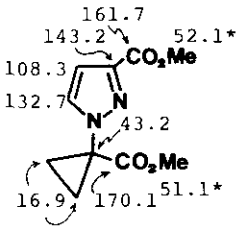

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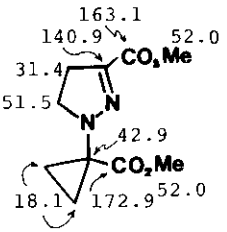

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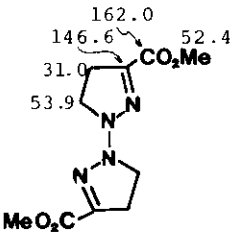

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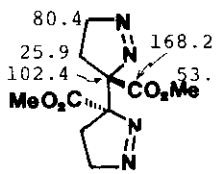

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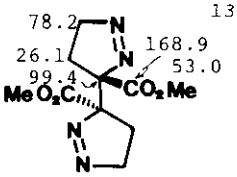

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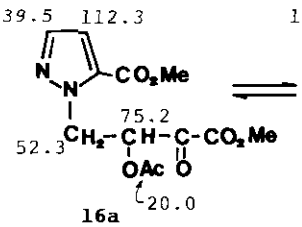
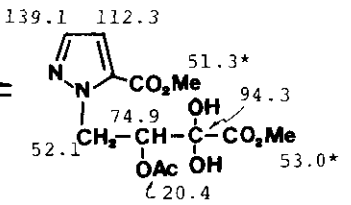
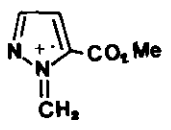


16a

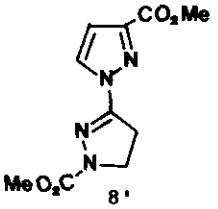


16b

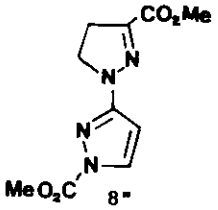
The structure of the rather unexpected open-chain *N*-substituted pyrazole **16** merits some comment. The compound had formula $C_{12}H_{16}N_2O_8$ (elemental analysis), but the highest peak in the mass spectrum was only m/z 298, corresponding to **16a**. Moreover, ir signals were compatible with both the ketoester **16a** (1735 and 1760 cm^{-1}) and the hydrate **16b** (3340 cm^{-1}). In $CDCl_3$ (^{1}H nmr), only **16a** was present (no -OH absorption) but *in acetone* (^{13}C nmr) signals corresponding to both forms were detected. The 1,5-disubstituted pyrazole structure was assigned on the basis of the geminal coupling constant of the ring protons (2.0 Hz), and by the ^{13}C chemical shift of the carbon atom at position **3**. Finally, the pattern ($-CH_2-CHOAc-CO-CO_2Me$) was preferred to the alternative ($-CHOAc-CH_2-CO-CO_2Me$) due to the presence of the intense peak at m/z 139 (100%) in the mass spectra, typical for a *N*-methylene fragment of the pyrazole nucleus.



In addition to the spectroscopic evidence so far presented, some reactions were carried out to verify the structures proposed. In particular, it was of prime importance to establish that compound **8** had a *N,N'*-bonded structure and not a *N,C'*-bonded one. For instance, structures **8'** and **8"**, though improbable from a chemical point of view, if one takes into account the reaction of pyrazoline **5** with LTA, could not be completely discarded on the light of the spectroscopic data alone. However, the main proof for structure **8** was obtained from the oxidation of the compound with *N*-bromosuccinimide. The resulting compound had a molecular ion at m/z=250, a single $\nu_{C=O}$ band at 1760 cm^{-1}, and showed only nmr signals (^{1}H and ^{13}C) for *one* pyrazole ring (see Experimental). From these data, the structure of the *N,N'*-linked bipyrazole **17** was established.



8'



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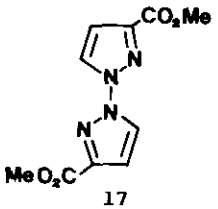

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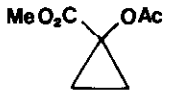
All 1-pyrazolines were found to lose nitrogen to form cyclopropyl- or allyl-derivatives. Thus, the very unstable pyrazoline **7** losed nitrogen spontaneously, giving 1-cyclopropyl-2-pyrazoline (**10**). Similarly, when 1-pyrazoline (**6**) was heated in toluene, cyclopropyl ester (**18**) was formed. However, at lower temperatures (*i.e.*, reflux in dichloromethane), acetic acid eliminated from **6**, yielding the pyrazole **14**. Finally, the 1-pyrazoline dimers **12** and **13**, though more stable, decomposed after several hours of heating in toluene, giving in each case the same mixture of compounds. From this mixture, **19** was isolated and characterized (*Z*-configuration), and traces of the hexadiene **20** and the bi-cyclopropane **21** were detected by ^{1}H nmr but not isolated.



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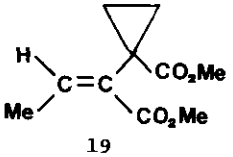

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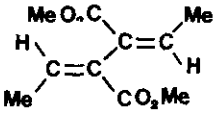

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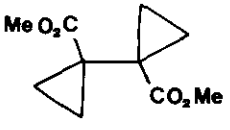

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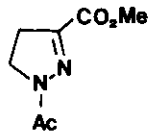
ORIGIN OF THE ISOLATED COMPOUNDS

Having succeeded in isolating the intermediate **7**, we know that it decomposes to the cyclopropylpyrazoline **10**, which could be the precursor of the cyclopropylpyrazole **9**. Therefore, the origin of **9** from **7**, as postulated by Akhrem (Scheme 1) seems likely. We have also isolated the 1-pyrazoline **6**. According to the Akhrem mechanism, **6** reacts with the starting 2-pyrazoline **5** to form the intermediate **7**. However, we checked that a mixture of **5** and **6** failed to react at room temperature, whereas at higher temperatures (reflux in CH_2Cl_2) the isolated products were only unreacted **5**, the pyrazole **14** (see above), and the *N*-acetylpyrazoline **22**. The acetylating agent for the formation of **22** could be either **6** or acetic acid, liberated in the reaction **6**→**14** (we have also checked that **5** is acetylated by acetic acid in CH_2Cl_2 at 4°C). Moreover, attempts to use **6** to create *N,C'*-bonds (with pyrazolyl anion or



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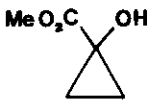
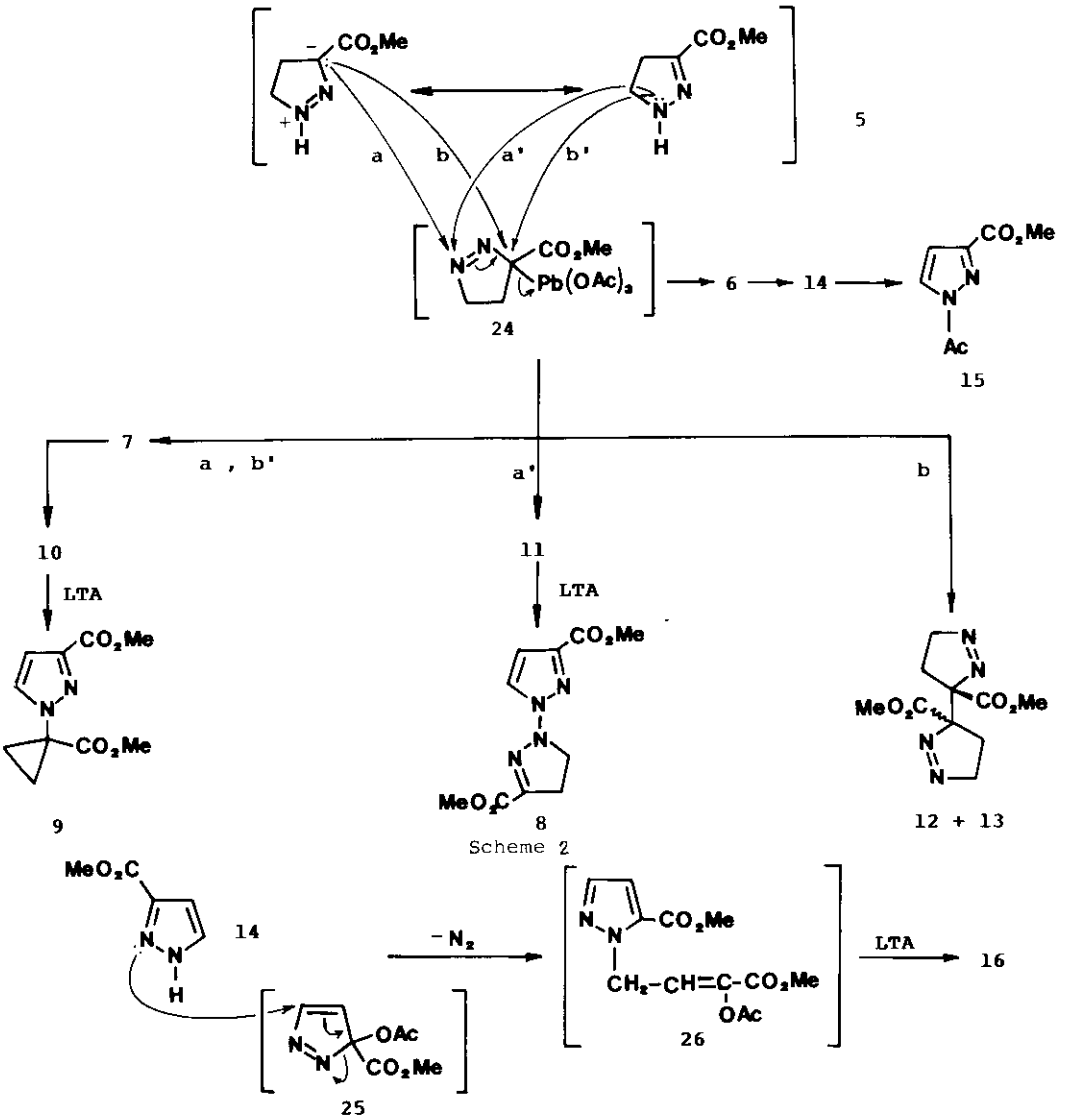


23

pyrrolidine) failed, the only isolated products being pyrazole **14** and the cyclopropanes **18** and **23**.

If we take into account the literature results for the oxidation of 2-pyrazolines by lead tetraacetate,[15] we can assume that the reaction intermediate should have the structure **24**, the 'enamine' reactivity of 2-pyrazolines explaining the different structures obtained (Scheme 2).

The sequence **5**→**24**→**6** is identical to that described in the literature;[15] we have established the ease of the reaction **6**→**14**, and the last compound, **15**, probably arises from the acetylation of **14** by **6**.



Scheme 2

Scheme 3

The origin of the pyrazole **16** remains less clear, however. We tentatively propose an attack of 3-methoxycarbonylpyrazole (**14**) to a *3H*-pyrazole intermediate like **25** or a related species arising from **6**, followed by the LTA oxidation of the resulting intermediate **26** (Scheme 3).

With Scheme 2 in mind, the results of Table I can be explained as follows:

i) An excess of lead tetraacetate favors the 1-pyrazoline (**6**)(runs 6 and 7), formed from the intermediate **24**.

ii) An excess of starting pyrazoline (run 1) affords mainly the cyclopropyl-2-pyrazoline (**10**).

iii) At low temperature (run 2), the unstable bipyrazoline **7**, as well as the bipyrazoline **11**, can be isolated. Consequently, the amount of oxidized compounds, like **8** and **9**, diminishes.

Changes in temperature or concentration did not significatively enhance the ratio of *N,N'*- over *N,C'*- or *C,C'*-bonded dimers, showing the importance of paths **a** and **b'** in Scheme 3. Although we were unable of increase the Akhrem yields of *N,N'*-linked dimers, we discovered another precursor of 1,1'-bipyrazole (**1**), namely the bipyrazoline **11**, and reasonable mechanisms have been proposed for all the isolated compounds.

EXPERIMENTAL

Melting points (uncorrected) and analysis of new isolated pyrazoles and pyrazolines are collected in Table V. Perkin-Elmer (R-24A) and Varian (EM-390 or XL-100) instruments were used to register ^{1}H nmr spectra. ^{13}C Nmr data were registered on a Bruker WP 200 SY instrument.

Table V. Mp and elemental analysis of new isolated compounds.

Name	M p (cryst.solv.)	Elemental analysis (%)	C	H	N
3-Methoxycarbonyl-1-(3-methoxycarbonyl-1-cyclopropyl)-2-pyrazoline(**10**)	64-5°C (cyclohexane)	Calc.($C_{10}H_{14}N_2O_4$):	53.09	6.19	12.38
		Found:	52.94	6.27	12.74
3,3'-Dimethoxycarbonyl-1,1'-bi-2-pyrazoline(**11**)	137-9°C (ethanol)	Calc.($C_{10}H_{14}N_4O_4$):	47.24	5.51	22.05
		Found:	47.22	5.85	21.98
Threo-3,3'-Dimethoxycarbonyl-1,1'-bi-2-pyrazoline (**12**)	93-4°C (cyclohexane)	Calc.($C_{10}H_{14}N_4O_4$):	47.24	5.51	22.05
		Found:	47.17	5.54	22.17
Erythro-3,3'-Dimethoxycarbonyl-1,1'-bi-2-pyrazoline (**13**)	97-9°C (cyclohexane)	Calc.($C_{10}H_{14}N_4O_4$):	47.24	5.51	22.05
		Found:	47.51	5.66	21.88
5-Methoxycarbonyl-1-(methyl 3-acetoxy-2,2-dihydroxybutanoyl)pyrazole (**16 b**)	98-100°C (CH_2Cl_2)	Calc.($C_{12}H_{16}N_2O_8$):	45.57	5.10	8.85
		Found:	45.81	5.41	8.79
3,3'-Dimethoxycarbonyl-1,1'-bipyrazole (**17**)	167°C(ethanol and sublim.)	Calc.($C_{10}H_{10}N_4O_4$):	48.00	4.00	22.40
		Found:	47.86	4.13	22.15

*Reaction of 3-methoxycarbonyl-2-pyrazoline (**5**) with lead tetraacetate.* To a solution of **5** in benzene, lead tetraacetate was added in small portions. Stoicheometries, temperatures, reaction times and yields are indicated in Table VI. The reaction mixture was cooled to room temperature and the resulting solid was filtered off and washed with benzene. The combined filtrates were evaporated, and the oily

residue was dissolved in chloroform and washed with saturated sodium carbonated. The chloroform solution was dried over sodium sulfate and evaporated. The mixture of compounds was separated by column chromatography (silica gel, hexane/ethyl ether 1:6). Both normal pressure or rapid 'flash' techniques[27] were employed, the latter affording higher overall yields (runs 2-5). Compounds emerged from the column in the following order: **15, 6, 10, 12, 11, 9, 7, 14, 8, 16** and **13**. In no case was any starting **5** recovered.

3,3'-Dimethoxycarbonyl-1,1'-bipyrazole (**17**). To a suspension of 3-methoxycarbonyl-1-(3-methoxycarbonyl-2-pyrazolin-1-yl)pyrazole (**8**)(0.500 g, 1.98 mmol) in 8 ml of carbon tetrachloride, *N*-bromosuccinimide (NBS)(0.425 g, 2.38 mmol) and a few drops of dry pyridine were added. The mixture was refluxed for 4 h, and allowed to cool to room temperature. The resulting solid was filtered and recrystallized in ethanol. Sublimation (145-150°C/0.1 torr) was however necessary to remove traces of unreacted NBS. The yield of **17**, after sublimation, was 0.273 g (55%). Ir (KBr): 1700 and 1515 cm^{-1}. ^1H Nmr ($CDCl_3$, 100 MHz): δ 3.96(CO_2Me), 7.01(C_4), and 7.99(C_5) (J_{45}=2.6 Hz). ^{13}C Nmr ($CDCl_3$): δ 52.3(OMe), 109.1(C_4), 129.4(C_5), 142.3(C_3), and 161.3(CO). Mass spectrum: m/z 250(M^+,54%),219(30%),159(16%),95(32%),66(41%),59(100%)

Thermal decomposition of 1-pyrazolines. Samples of 1-pyrazolines were heated to reflux in toluene or dichloromethane for several hours. The reaction mixtures were investigated by ^1H nmr. *Methyl 1-acetoxycyclopropanecarboxylate* (**18**): δ 1.23m and 1.51m (cyclopropane), 2.09(Ac), and 3.72(CO_2Me). *Methyl 2-(1-cyclopropyl-1-methoxycarbonyl)-2-butenoate* (*Z*-configuration)(**19**): δ 0.96m and 1.42m (cyclopropane) 2.02(J=7.3 Hz)(Me), 3.60(CO_2Me), 3.71(CO_2Me), and 6.18(CH).

Reactions of 3-acetoxy-3-methoxycarbonyl-1-pyrazoline (**6**).

i) *With pyrazolyl-Na*. Equimolecular amounts of the pyrazoline **6** and the sodium salt of pyrazole (prepared from a sodium dispersion and pyrazole in xylene) were mixed and allowed to react at room temperature. After 5 min, no starting pyrazoline was detected by t.l.c. The solids of the reaction mixture were separated by centrifugation, and the remaining solution was evaporated and submitted to column chromatography, yielding *pyrazole* (0.21 g), *3(5)-methoxycarbonylpyrazole* (**14**)(0.22 g), and a mixture of cyclopropanes **18** and **23**. The ^1H nmr spectrum of *methyl 1-hydroxycyclopropanecarboxylate* (**23**)($CDCl_3$) showed signals at 1.21m (cyclopropane), 3.69(CO_2Me), and 5.88(broad, OH) ppm.

ii) *With pyrrolidine*. A mixture of **6** and pyrrolidine (molar ratio 1:1.6) was maintained for 3 h in benzene at room temperature. The major component (81%) of the resulting mixture was found to be the pyrazole **14** (chromatography).

iii) *With 3-methoxycarbonyl-2-pyrazoline* (**5**). An equimolecular mixture of pyrazolines **5** and **6** was refluxed for 28 h in dichloromethane (^1H nmr revealed that no reaction took place after 3 days at room temperature). Analysis of the crude reaction mixture (^1H nmr) showed the presence of *3(5)-methoxycarbonylpyrazole* (**14**)(45%), unreacted **5**(23%), and *1-acetyl-3-methoxycarbonyl-2-pyrazoline* (**22**)(13%)[δ 2.34(Ac), 3.06m(C_4), 3.86(CO_2Me), and 3.99m(C_5) ppm].

Table VI. Experimental conditions for the LTA oxidation of pyrazoline **5**.

Run	Weight of **5**	Conc.(mol.l^{-1})	Ratio LTA/**5**	Temp.(°C)	Reaction time(min)	Total yield*
1	6.17	0.68	0.6:1	60	60	46.6
2	5.38	0.60	1:1	0	180	85.7
3	5.73	1.06	1:1	60	30	85.3
4	6.42	0.71	1:1	80	120	81.5
5	6.77	0.75	1.1:1	60	45	69.1
6	2.58	0.33	2:1	60	30	44.1
7	3.09	0.60	3:1	25	30	40.0

*Sum of yields of isolated compounds.

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