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Reactions of Pyrazoles and Pyrazolium Salts with Complex Metal Hydrides and Organometallic Reagents. Synthesis of Pyrazolines and Pyrazolidines.

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Abstract : 2-Pyrazolin-4-oximes have been synthesized by reaction of 4-nitroso- and 4-nitropyrazoles with complex metal hydrides and organometallic reagents. Furthermore, 4-nitropyrazolium tetrafluoroborates are reactive substrates towards organolithium and Grignard compounds leading to new and highly substituted 4-nitro-3-pyrazolines and 4-nitropyrazolidines. The formation of 3-pyrazolines is regioselective and, when diastereoisomer pyrazolidines are possible, only the most stable 3,4-trans and/or 4,5-trans isomers were obtained. © 1997 Elsevier Science Ltd.

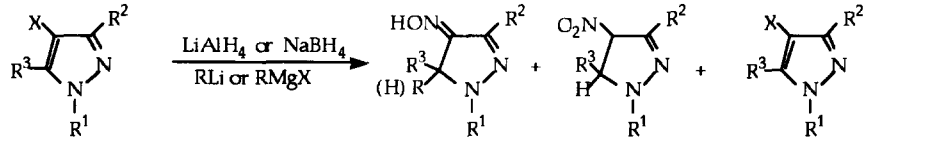
It has previously been established that the pyrazole nucleus is inert toward complex metal hydrides[1,2] and organometallic compounds[3-6]. The quaternization of the ring increases its reactivity toward nucleophilic addition. Thus, pyrazolium salts are reduced with complex metal hydrides leading to 3-pyrazolines[7]. Nevertheless, pyrazolium salts do not react with organometallic reagents. Elguero *et al.*[7] studied the reaction of methyl magnesium iodide with 1-phenyl-2,3,5-trimethyl- and 1-phenyl-2,3-dimethylpyrazolium iodide in ether and they obtained unsuccessful results even after refluxing for 20 hours.

We have recently reported[8] that 2-alkylpyrazolium tetrafluoroborates, bearing electron-withdrawing groups at C-4, react easily with complex metal hydrides leading to total reduction of the ring and giving stereoselectively functionalized pyrazolidines, in which the functional group remains, in general, unchanged. According to these results, we thought that a strong electron-withdrawing group attached at C-4 could sufficiently activate the heterocyclic ring toward the attack of hydrides and organometallic reagents and consequently we might be able to obtain 4-functionalized and highly substituted pyrazolines and pyrazolidines.

The present paper describes the synthesis of 2-pyrazolines by reaction of 4-nitroso and 4-nitropyrazoles with complex metal hydrides ($LiAlH_4$, $NaBH_4$), organolithium or organomagnesium compounds and the synthesis of 3-pyrazolines and pyrazolidines by reaction of 4-nitropyrazolium tetrafluoroborates with the same organometallic reagents.

RESULTS and DISCUSSION

4-Nitroso- and 4-nitropyrazoles **1-11** react with complex metal hydrides (CMH) and organolithium and Grignard reagents (RM) giving 4-hydroxyimino-2-pyrazolines **12** and only one 4-nitro-2-pyrazoline **13.** In some reactions with CMH the pyrazole ring did not experiment attack of hydrides and pyrazoles **14** were obtained resulting from reduction of the functional group (Scheme 1).



1-11, X=NO or NO_2 **12** **13** **14**, X=NH_2 or NHOH

Scheme 1

The results obtained are summarized in Table 1.

The pyrazole nucleus is reduced by complex metal hydrides or alkylated by organometallic reagents only when the group at C-4 is nitro or nitroso. Other functional groups such as carbonyl, cyano, alkoxycarbonyl and bromo do not efficiently activate the pyrazole ring. Thus, 4-acetyl-, 4-benzoyl-, 4-formyl-, 4-cyano-, 4-ethoxycarbonyl- and 4-bromo-3,5-dimethyl-1-phenylpyrazole result unchanged or suffer only reduction or alkylation of the functional group when they react with the cited reagents.

Although the nitro group is a stronger electron-withdrawing group than nitroso, 4-nitropyrazoles were shown less reactive toward complex metal hydrides and organometallic reagents. This may be due to steric hindrance to resonance between the bulky nitro group and the ring. The larger resonance effect of 4-nitroso *versus* 4-nitro group is also shown in their ^{1}H-NMR spectra. The 5-Me of 4-nitroso-3,5-dimethylpyrazoles resonates approximately 0.3 ppm downfield from the 5-Me of 4-nitro-3,5-dimethylpyrazoles. In previous papers we have reported similar steric effects for a 4-nitro group of the isoxazole nucleus[9].

The reactivity of 4-nitroso and 4-nitropyrazoles toward CMH is very limited. The pyrazole nucleus is only reduced when the group attached at N-1 is aryl. 4-Nitroso-1-phenylpyrazoles **3** and **4** are easily reduced with $LiAlH_4$ or $NaBH_4$ to 4-hydroxyimino-2-pyrazolines **12c** and **12e**, respectively, in short times (30 minutes are required) in good yields. Nevertheless, the reduction of the pyrazole nucleus from 4-nitro derivatives is more difficult. They require longer reaction times (2 or 3 hours) and the yields of 2-pyrazolines are lower because they appear contaminated by reduction products of the nitro group. Thus, 4-nitro-3,5-dimethyl-1-phenylpyrazole **5** reacts with $LiAlH_4$ (not with $NaBH_4$) affording a mixture 2.5:1 of *cis* - and *trans* -4-nitro-3,5-dimethyl-1-phenyl-2-pyrazoline **13**, together with 4-amino-3,5-dimethyl-1-phenylpyrazole **14c**. The reduction of 4-nitro-3,5-dimethyl-1-*p*-nitrophenylpyrazole **7** with $LiAlH_4$ gives the 2-pyrazoline **12h**, in which the nitro group has also been reduced to oxime, along with a mixture of aminopyrazoles resulting from the reduction of each or both nitro groups.

The presence in C-3 or C-5 of larger groups than methyl in 4-nitropyrazoles increases the steric hindrance and prevents the conjugate addition of hydride at C-5. Thus, 4-nitro-1,5-diphenylpyrazole **8** resulted unchanged towards $LiAlH_4$ and 3-ethoxycarbonyl-5-methyl-4-nitro-1-phenylpyrazole **11** underwent reduction exclusively in the ethoxycarbonyl group, giving alcohol **14d.**

In contrast to what is observed with CMH, all 4-nitro- and 4-nitrosopyrazoles tested are shown active towards organolithium and Grignard reagents. This may be due to enhancement of

Table 1 Reactions of 4-nitroso- and 4-nitropyrazoles **1-11** with complex metal hydrides[a] and organometallic reagents[b].

Substrate	R^1	R^2	R^3	X	CMH or RM	Solvent	Temp. (°C)	Time (h)	Products and Yields (%)[c]
1	Me	Me	Me	NO	$LiAlH_4$	Et_2O	25	3	**14a**(76), X=NH_2
					$NaBH_4$	EtOH	25	3	**14b**(79), X=NHOH
					MeLi	Et_2O	0	1	**12a**(81)
					MeMgI	Et_2O	0	1.5	**12a**(68)
					PhMgBr	Et_2O	0	2	**12b**(65)
2	Me	Me	Ph	NO	$NaBH_4$	EtOH	25	3	—[d]
					MeLi	Et_2O	0	1	**12b**(63)
					MeMgI	Et_2O	0	1.5	**12b**(51)
3	Ph	Me	Me	NO	$LiAlH_4$	Et_2O	25	0.5	**12c**(85)
					$NaBH_4$	EtOH	25	0.5	**12c**(79)
					MeLi	Et_2O	0	0.5	**12d**(78)
					MeMgI	Et_2O	0	1	**12d**(66)
4	Ph	Me	Ph	NO	$NaBH_4$	EtOH	25	0.5	**12e**(58)
					MeLi	Et_2O	0	0.5	**12f**(62)
5	Me	Me	Me	NO_2	$LiAlH_4$	Et_2O	25	5	—[d]
					$NaBH_4$	EtOH	25	5	—[d]
					MeLi	Et_2O	0	1	**12a**(68)
					MeMgI	Et_2O	0	1.5	**12a**(55)
					PhLi	Et_2O	0	1.5	**12b**(58)
					PhMgBr	Et_2O	0	2	**12b**(46)
6	Ph	Me	Me	NO_2	$LiAlH_4$	Et_2O	25	2	**13**(58)[e]+**14c**(32),X=NH_2
					$NaBH_4$	EtOH	25	4	—[d]
					MeLi	Et_2O	0	1	**12d**(67)
					MeMgI	Et_2O	0	1.5	**12d**(58)
					BuLi	Et_2O	0	1	**12g**(72)
					PhMgBr	Et_2O	0	2	**12f**(45)
7	pNO_2Ph	Me	Me	NO_2	$LiAlH_4$	Et_2O	25	3	**12h**(51)[f]
8	Ph	H	Ph	NO_2	$LiAlH_4$	Et_2O	25	3	—[d]
					MeMgI	Et_2O	0	1.5	**12i**(40)
9	Me	Me	H	NO_2	$LiAlH_4$	Et_2O	25	5	—[d]
					MeLi	Et_2O	0	1	**5**(31)+**12a**(45)
					MeMgI	Et_2O	0	1.5	**5**(28)+**12a**(41)
10	Ph	Me	H	NO_2	MeMgI	Et_2O	0	1.5	**6**(31)+**12c**(29)
11	Ph	CO_2Et	Me	NO_2	$LiAlH_4$	Et_2O	25	3	**14d**(74), R^2=CH_2OH
					MeLi[g]	Et_2O	-78	2	**12j**(69),R^2=Me_2COH
					MeMgI[g]	Et_2O	-78	3	**12k**(34),R^2=CO_2Et
									+**12l**(28)[h],R^2=COMe

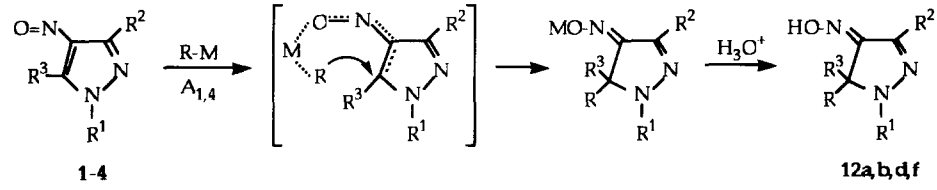
[a] Reactions were carried out using a molar ratio pyrazole/hydride=1:2. [b] Molar ratio 4-nitrosopyrazole/RM=1:1 and 4-nitropyrazole/RM=1:2. [c] Yields refer to isolated pure products. [d] Unchanged pyrazole. [e] Mixture of diastereoisomers cis/trans=2.5:1. [f] Contaminated with a mixture of pyrazoles resulting from reduction of each or both nitro groups. [g] Molar ratio pyrazole/RM=1:4. [h] Starting material (24%) was also obtained.

the C-5 electrophilicity and organometallic nucleophilicity by initial coordination of the metal to the oxygen atom of the nitro or nitroso group.

Both 4-functionalized pyrazoles react readily with organolithium and organomagnesium reagents at 0°C or lower temperatures giving 4-hydroxyimino-2-pyrazolines as only products in very acceptable yields. Starting from 4-nitropyrazoles, it was impossible to isolate 4-nitro-2-pyrazolines, even using a 1:1 pyrazole/RM molar ratio. In these conditions, we have observed that some unreacted material is left even if prolonged reaction times are employed. In our experiments, we have used a 1:2 pyrazole/RM molar ratio in order to ensure completeness of the reaction.

The 3-ethoxycarbonyl-5-methyl-4-nitro-1-phenylpyrazole **11** showed a high reactivity toward methyllithium. Even at -78°C and 1:1 molar ratio, we obtained the 4-hydroxyimino-2-pyrazoline **12j**, in which the ester group had also been alkylated to alcohol. In order to increase the yield a 1:4 pyrazole/RM molar ratio was used. The methylmagnesium iodide was showed less reactive. In the same conditions we isolated some unchanged pyrazole **11** and a mixture of the 2-pyrazolines **12k** and **12l**, in which the ester group remained unaffected and alkylated to ketone, respectively.

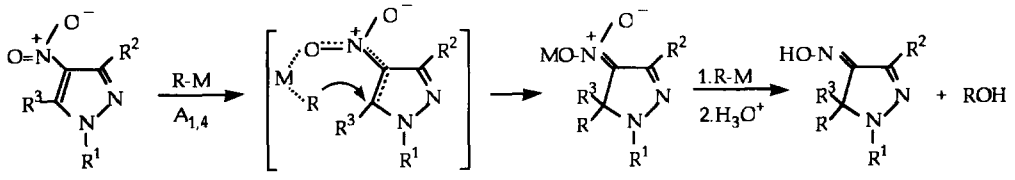
The formation of 5-alkylated 4-hydroxyimino-2-pyrazolines starting from 4-nitroso-pyrazoles could be interpreted by initial coordination of the metal at nitroso group and addition of alkyl group at C-5 in conjugate fashion, through a polar mechanism or through a single-electron-transfer pathway (Scheme 2).



1-4 **12a,b,d,f**

Scheme 2

On the other hand, the isolation of the same 5-alkylated 2-pyrazoline-4-oximes starting from 4-nitropyrazoles, together with the separation of phenol in their reactions with phenyllithium or phenylmagnesium bromide may be due to instability of nitronate intermediate, which immediately is reduced to oxime by reaction with the organometallic excess (Scheme 3).

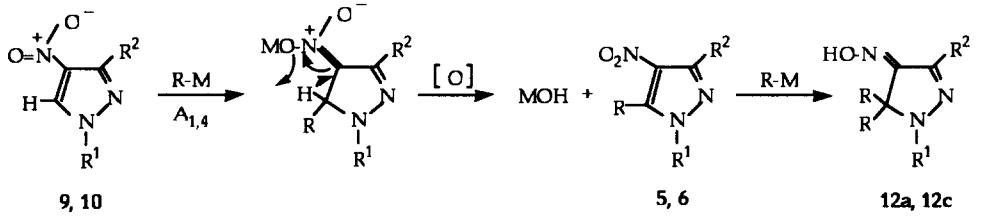


5-8,11 **12a-d, 12f-l**

Scheme 3

When the 5-position of pyrazole is unsubstituted (like **9** and **10**) the alkylation at C-5 is followed by aromatization and formation of 5-alkylated 4-nitropyrazoles **5** and **6**. According to

other studies relative to the reaction between mononitroarenes and Grignard reagents[10], the products should be the corresponding 5-alkyl-4-nitrosopyrazoles. Nevertheless, these authors[11] obtained 7-alkyl-4-nitrobenzothiazoles by reaction of 4-nitrobenzothiazol with the same reagents. They explained this behaviour, which they considered anomalous, by oxidation either of the nitronate intermediate or of the corresponding nitroso derivative during the hydrolysis. The resulting 5-alkylated 4-nitropyrazoles **5** and **6** undergo, in part, ulterior alkylation leading to 5,5-dialkyl-4-hydroxyimino-2-pyrazolines **12a** and **12c**, respectively (Scheme 4).

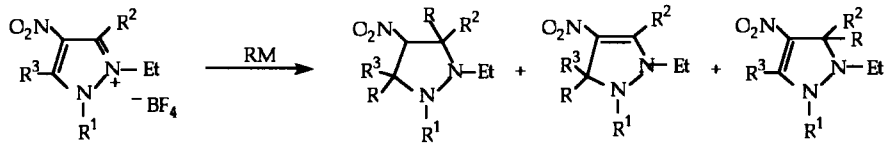


9, 10 **5, 6** **12a, 12c**

Scheme 4

The presence of a nitro group at C-4 in pyrazolium salts satisfactorily activates the ring towards organometallic reagents. Although the nitroso group could have the same behaviour we were unable to prepare 4-nitrosopyrazolium salts, because the 4-nitrosopyrazoles were decomposed in the quaternization conditions (reactions with methyl iodide, dimethyl sulfate and triethyloxonium tetrafluoroborate). Pyrazolium rings bearing electron-withdrawing groups at C-4, other than nitro, do not react with organometallic compounds.

2-Ethyl-4-nitropyrazolium tetrafluoroborates **15-18** react with organolithium and Grignard reagents at 0°C or lower temperatures giving mainly 4-nitropyrazolidines **19**, together with 4-nitro-3-pyrazolines **20** and **21** (Scheme 5).



15-18 **19** **20** **21**

Scheme 5

The results are summarized in Table 2.

The double activation of the pyrazole ring by 4-nitro group and quaternization of N-2, makes the attack of the reagent possible at both reactive positions C-3 and C-5, affording functionalized 3,5-dialkylated pyrazolidines **19**, together with the 3-pyrazoline **20** or **21**, resulting from monoalkylation in C-5 or C-3, respectively. It should be noted that, in general, the nitro group remains unchanged.

Table 2. Reactions of 2-ethyl-4-nitropyrazolium tetrafluoroborates **15-18** with organometallic reagents.

Substrate	R^1	R^2	R^3	RM	Solvent	Temp. (°C)	Time (h)	Products and Yields[b] (%)
15	Ph	Me	H	MeLi	Et_2O	0	0.5	**19a**(57)+**22**(21)[c]
				MeMgI	Et_2O	0	1	**19a**(51)+**22**(15)[c]
16	Ph	H	Me	MeLi	Et_2O	0	1	___[d]
				EtMgBr	Et_2O	0	1	___[d]
17	Ph	Me	Me	MeLi	Et_2O	0	0.5	**19b**(58)+**20b**(23)
				MeMgI	Et_2O	0	1	**19b**(51)+**20b**(18)
				PhLi	Et_2O	0	0.5	**19c**(56)+**20c**(25)
18	Ph	CO_2Et	Me	MeLi	Et_2O	-78	1	**19d**(66)+**21d**(17)
				MeMgI	Et_2O	-78	2	**19d**(53)+**21d**(25)

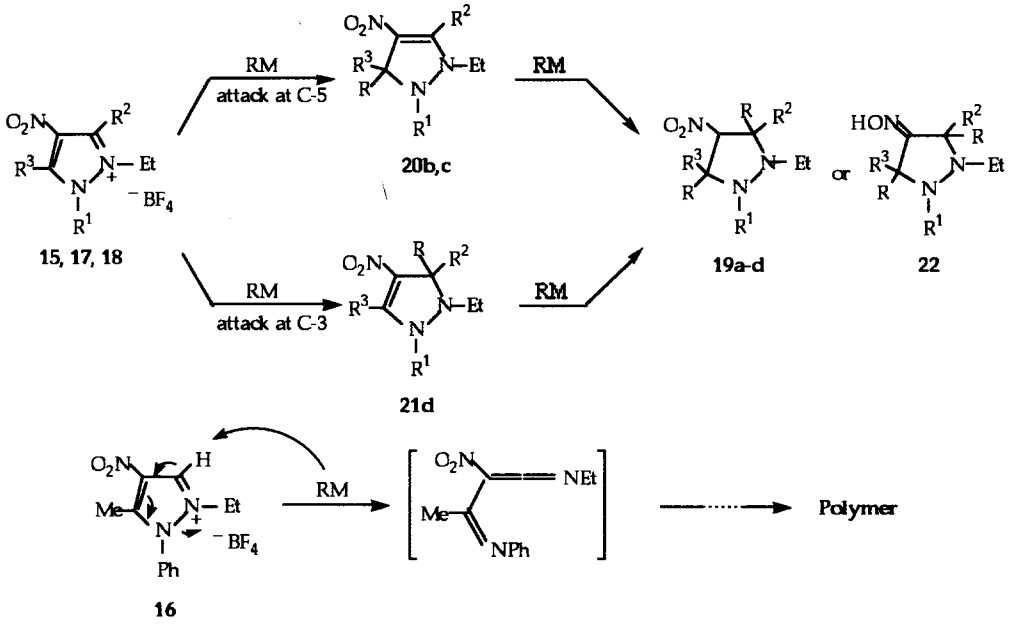
[a]Reactions were carried out using a molar ratio pyrazolium/RM=1:2. [b]Yields refer to isolated pure products. [c]2-Ethyl-4-hydroxyimino-3,3,5-trimethyl-1-phenylpyrazolidine **22**. [d]Pyrazolium salt unchanged and polymeric material.

Although the main products are always pyrazolidines, the extension in which 3-pyrazolines are formed probably depends on steric hindrance of the pyrazolium salt. When we used a 5-unsubstituted pyrazolium salt **15** we obtained only pyrazolidines **19a** and **22**, whereas 3,5-disubstituted 4-nitropyrazolium salts **17** and **18** led to corresponding 3,5-dialkylated pyrazolidines **19b** or **19c** and **19d**, along with minor amounts of 4-nitro-3-pyrazolines **20b** or **20c** and **21d**, respectively. The selective formation of either of the 3-pyrazolines depends on the nature of 3- and 5-substituents. Thus, the 3,5-dimethylpyrazolium salt **17** undergoes initial attack of the organometallic at more electron-deficient C-5, giving the 3-pyrazoline **20b** or **20c**. On the other hand, the 3-ethoxycarbonyl group in the pyrazolium salt **18** enhances the electrophilicity of 3-position affording the 3-pyrazoline **21d**. Both 3-pyrazolines are further alkylated by another molecule of organometallic reagent to originate the corresponding dialkylated pyrazolidine (Scheme 6). In this context, it is interesting to note that in the conditions required in the reaction of **18** with organolithium and Grignard reagents (-78°C), the ethoxycarbonyl group remains unaffected.

If the 3-position is unsubstituted, such as **16**, the ring does not experiment addition of the organometallic compound. Only polymeric material was formed, perhaps through the unstable intermediate β-iminoketenimine resulting from deprotonation at C-3 and concomitant ring opening (Scheme 6). A similar mechanism has been established to explain the ring cleavage of 3-unsubstituted isoxazolium salts by nucleophiles.[12,13]

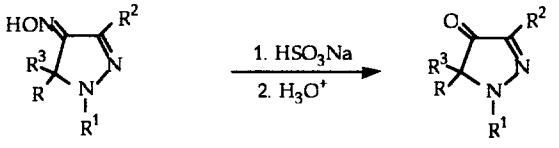
When the alkyl group of organometallic is different from the substitutent at C-3 or C-5, the resulting pyrazolidines may be a mixture of diastereoisomers. Nevertheless, the stereoisomer 4,5-trans of pyrazolidine **19a**, the 3,4-trans of **19d** and 3,4-trans,4,5-trans of **19c** were only obtained. This stereochemical outcome is the same as the one observed in reactions of these substrates with complex metal hydrides[8]. Stereochemistries of these pyrazolines were established by ^{1}H-NOE difference spectroscopy. The pyrazolidine **19a** showed an enhancement in the 5-Me doublet resonance when the 4-H signal was irradiated. From this result, a 4,5-trans-configuration was assigned for **19a**. Moreover, the J=7.8 Hz was in accordance with those described by us for other 4,5-trans-4-nitropyrazolidines[8]. On the other hand, the 3,4-trans relationship of 4-H and 3-Me in the ring of pyrazolidine **19d** was evident since no NOE was observed between them. Finally, the pyrazolidine **19c** did not show an enhancement in the 3-Me and 5-Me signals when the 4-H was

irradiated, but the H_S orto of 5-Ph at δ 7.96 and of 3-Ph at δ 7.64 showed a strong NOE effect with 4-H. Alternatively, irradiation of the aromatic protons at δ 7.96 and δ 7.64 gave an increase in the area of 4-H resonance. Consequently, a *trans,trans* -configuration was assigned for **19c.**



Scheme 6

An additional feature of this methodology should be pointed out: 2-pyrazolin-4-oximes **12** was easily hydrolyzed by aqueous sodium bisulfite to 2-pyrazolin-4-ones **23** (Scheme 7). In the reaction conditions, the tertiary alcohol at C-3 of the 4-hydroxyimino-2-pyrazoline **12j**, was dehydrated leading to the corresponding 3-alkenyl-2-pyrazolin-4-one **23j** in which the double bonds C=C and C=N are conjugated.



12a; $R^1=R^2=R^3=R=Me$ — **23a**
12d; $R^1=Ph$, $R^2=R^3=R=Me$ — **23d**
12g; $R^1=Ph$, $R^2=R^3=Me$, R=Bu — **23g**
12j; $R^1=Ph$, $R^2=Me_2COH$, $R^3=R=Me$ — **23j**; R= $MeC=CH_2$

Scheme 7

In conclusion, although the reduction of 4-nitroso- and 4-nitropyrazoles with complex metal hydrides is very limited and of little interest, the methodology disclosed above using organometallic reagents seems to be of general applicability. It allows the easy preparation of unusual 2-pyrazoline-4-oximes, which are interesting compounds in themselves and as precursors of corresponding pyrazolinones. This study also shows that 4-nitropyrazolium salts are reactive substrates towards organometallic reagents affording highly substituted 4-nitro-3-pyrazolines and 4-nitropyrazolidines, which are difficult to synthesize by other methods. Formation of 3-pyrazolines is regioselective in the sense that a sole isomer is obtained in each reaction. Furthermore, when diastereoisomer pyrazolidines are possible, only the most stable 3,4-*trans*- and/or 4,5-*trans*-pyrazolidines were isolated.

EXPERIMENTAL

Starting materials. The 4-nitrosopyrazoles[14] were prepared by reaction of isonitroso acetylacetone or isonitrosobenzoylacetone with methyl hydrazine or phenyl hydrazine in absolute ethanol. 1,3,5-trimethyl-4-nitropyrazole[15], 3,5-dimethyl-4-nitro-1-phenylpyrazole[16], 3,5-dimethyl-4-nitro-1-p-nitrophenylpyrazole[17], 4-nitro-1,5-diphenilpyrazole[18], 1,3-dimethyl-4-nitropyrazole[15], 3-methyl-4-nitro-1-phenylpyrazole[16], and 3-ethoxycarbonyl-5-methyl-4-nitro-1-phenylpyrazole[17] were synthesized according to literature procedures. The pyrazolium tetrafluoroborates were prepared by reaction of the respective pyrazoles with an approximately equivalent amount of triethyloxonium fluoroborate in dry methylene chloride at r.t. for several hours (12-20 h). The solvent was removed and the product recrystallized from acetone-ether.

IR spectra were measured on a Pye-Unicam SP-1100 or a FT-Mattson Cygnus 100 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC-300 instrument operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C measurements using $CDCl_3$ as solvent. Chemical shifts being reported as δ(ppm) relative to tetramethylsilane and J values are reported in Hz. Mass spectral data together with GLC data were obtained with a combined Hewlett-Packard GC(5890)-MS(5988A) unit. Reactions were monitored by TLC on a pre-coated plate of silica gel 60 (nano-SIL-20, Macherey-Nagel, Germany). Flash chromatography was performed on silica gel 60 (230-400 mesh, M-N).

General procedure for reduction of 4-nitroso- and 4-nitropyrazoles with lithium aluminium hydride. To a stirred solution of pyrazole(2 mmol) in dry ether (20 cm^3) was added lithium aluminium hydride (0.15 g, 4 mmol) in portions at room temperature. After stirring for the time shown in Table 1, saturated ammonium chloride (10 cm^3) was added dropwise to the mixture which was then extracted with ether (3x10 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The crude residue could be separated by flash chromatography (SiO_2, CH_2Cl_2).

General procedure for reduction of 4-nitroso- and 4-nitropyrazoles using sodium boranuide. To a stirred solution of pyrazole(2 mmol) in absolute ethanol (15 cm^3) was added sodium boranuide (0.15 g, 4 mmol) in portions at room temperature. The mixture was stirred at that temperature for an appropiate time (Table 1) and then hydrolyzed with saturated aqueous ammonium chloride. The ethanol was removed on the rotary evaporator and the residue was extracted with ether (3x10 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated. The crude mixture was chromatographed (SiO_2, CH_2Cl_2).

General procedure for reaction of pyrazoles and pyrazolium salts with organometallic reagents. To a cold solution (0°C) of 4-nitroso pyrazole (3 mmol), 4-nitropyrazole (1.5 mmol) or 4-nitropyrazolium tetrafluoroborate (1.5 mmol) in dry ether (20 cm^3) was added dropwise under nitrogen, the organolithium or Grignard solution (in hexane or ether, 3 mmol). The mixture was stirred at that temperature for the time indicated in Tables 1 and 2 and hydrolyzed by addition of saturated aqueous ammonium chloride. The ethereal layer was separated and the aqueous phase was extracted with ether (2x10cm^3). The combined organic extracts were washed twice with 2N aqueous sodium hydroxide and once with saturated aq NaCl to prevent the hydrolysis of the oximes to ketones during work-up. When the basic treatment was omitted, together with the oxime, the corresponding ketone was isolated. By this washing, the phenol generated in reactions of 4-nitropyrazoles with phenyllithium or phenylmagnesium bromide was easily removed. The organic phase was dried ($MgSO_4$) and then concentrated *in vacuo*. The residue was purified by chromatography on a silica-gel column using CH_2Cl_2 as eluent.

As mentioned in the Discussion, in the reactions of 3-ethoxycarbonyl-5-methyl-4-nitro-1-phenylpyrazole **11** the experiments were carried out with RM/substrate=4:1 molar ratio at -78°C. Reactions of its pyrazolium tetrafluoroborate **18** were also carried out at that temperature. In these cases, the reaction was quenched by addition of MeOH (5cm^3), the temperature was raised to 0°C and the solution was hydrolyzed with sat. aq NH_4Cl.

Spectroscopy and analytical data for the 2-pyrazolines **12** and **13**, pyrazole **14**, pyrazolidines **19** and **22**, 3-pyrazolines **20** and **21** are given below. Results, experimental conditions and yields are displayed in Tables 1 and 2.

4-Hydroxyimino-1,3,5,5-tetramethyl-2-pyrazoline 12a; oil; $R_f(CH_2Cl_2)$ 0.33; υ_{max}(film)/cm^{-1} 3300 br(OH), 1635 and 1570 (C=N); δ_H 9.11 (1H, s br, OH), 2.81 (3H, s, MeN), 1.95 (3H, s, 3-Me) and 1.47 (6H, s, 5-Me_2); δ_C 162.56 (C=NOH), 136.83 (C=N), 67.41 (C-5), 35.46 (MeN), 16.21 (5-Me) and 13.67 (3-Me); m/z 155 (M^+, 22%), 140 (M-Me, 100), 123 (M-Me-OH, 29) and 56 (MeC^+=NMe, 25). (Found: C, 54.37; H 8.31; N 27.22. $C_7H_{13}N_3O$ requires C, 54.17; H, 8.44; N, 27.07%).

4-Hydroxyimino-1,3,5-trimethyl-5-phenyl-2-pyrazoline 12b; oil; R_f (CH_2Cl_2) 0.30; υ_{max}(film) /cm^{-1} 3300 br(OH), 1630 and 1550 (C=N); δ_H 8.8 (1H, s br, OH), 7.29 (5H, s, Ph), 2.65 (3H, s, MeN), 1.98 (3H, s, 3-Me) and 1.83 (3H, s, 5-Me); δ_C 165.22 (C=NOH), 138.88 (C=N), 138.35, 128.13, 127.55 and 126.63 (Ph), 70.88 (C-5), 34.09 (MeN), 15.97 (5-Me) and 11.38 (3-Me); m/z 217 (M^+, 67%), 202 (M-Me, 100), 185 (M-Me-OH, 28), 140 (M-Ph, 73), 118 (PhC^+=NMe, 49) and 77 (Ph^+, 43).

4-Hydroxyimino-3,5-dimethyl-1-phenyl-2-pyrazoline 12c; pale yellow crytals, m.p. 130-132° (from hexane); R_f (CH_2Cl_2) 0,32; $\upsilon_{max}(CCl_4)$/cm^{-1} 3350 br (OH), 1630 and 1550 (C=N); δ_H 9.15 (1H, s br, =N-OH), 7.27 (2H, dd, J 7.2 and 8.7, NPh H_S meta), 7.19 (2H, d, J 8.7, NPh H_S orto), 6.94 (1H, t, J 7.2, NPh H para), 4.96 (1H, q, J 6.5, 5-H), 2.11 (3H, s, 3-Me) and 1.53 (3H, d, J 6.5, 5-Me); δ_C 162.48 (C=NOH), 148.78 (=C, NPh), 140.83 (C=N), 128.87 (=CH meta), 120.19 (=CH para), 115.62 (=CH orto), 70.05 (HC-5), 16.29 (5-Me) and 13.52 (3-Me); m/z 203 (M^+, 30%), 188 (M-Me, 100), 185 (M-Me-OH, 11), 118 (MeC^+=NPh, 42) and 77 (Ph^+, 55). (Found: C, 64.83; H, 6.58; N 20.45. $C_{11}H_{13}N_3O$ requires C, 65.01; H, 6.45; N, 20.67%).

4-Hydroxyimino-3,5,5-trimethyl-1-phenyl-2-pyrazoline 12d; oil; $R_f(CH_2Cl_2)$ 0.30; υ_{max}(film) /cm^{-1} 3310 br(OH), 1650 and 1550 (C=N); δ_H 11.0 (1H, s br, OH), 7.30 (2H, dd, J 7.3 and 8.6, NPh H_S meta), 7.21 (2H, d, J 8.6, NPh H_S orto), 6.95 (1H, t, J 7.3, NPh H para), 2.08 (3H, s, 3-Me) and 1.81 (6H, s, 5-Me_2); δ_C 166.11 (C=NOH), 143.04 (=C, NPh), 140.32 (C=N), 128.36 (=CH meta), 122.43 (=CH para), 116.13 (=CH orto), 70.82 (C-5), 20.15 (5-Me_2) and 14.01 (3-Me); m/z 217 (M^+, 36%), 202

(M-Me, 100), 185 (M-Me-OH, 8), 118 (MeC^+=NPh, 49) and 77 (Ph^+, 52). (Found:C, 66,58; H, 7.09; N 19.16. $C_{12}H_{15}N_3O$ requires C, 66.34; H, 6.96; N, 19.34%).

4-Hydroxyimino-3-methyl-1,5-diphenyl-2-pyrazoline 12e; oil; R_f (CH_2Cl_2) 0.28; υ_{max}(film) /cm^{-1} 3400 (OH), 1630 and 1560 (C=N); δ_H 9.0 (1H, s br, OH), 7.29 (5H, s, 5-Ph), 7.35-6.96 (5H, m, NPh), 6.72 (1H, s, 5-H), and 2.01 (3H, s, 3-Me); δ_C 166.31 (C=NOH), 141.82 (C=N), 148.47, 129.02, 121.63 and 116.13 (NPh), 139.95, 128.22, 127.58 and 126.43 (5-Ph), 75.41 (HC-5), and 14.36 (3-Me); m/z 265 (M^+, 60%), 188 (M-Ph, 100), 171 (M-Ph-OH, 25) and 77 (Ph^+, 40).

4-Hydroxyimino-3,5-dimethyl-1,5-diphenyl-2-pyrazoline 12f; oil; R_f(CH_2Cl_2) 0.23; υ_{max} (film)/cm^{-1} 3300 br(OH), 1645 and 1560 (C=N); δ_H 9.30 (1H, s br, OH), 7.30 (5H, s, 5-Ph), 7.24 (2H, dd, J 7.2 and 8.4, N-Ph $H_S$meta), 7.15 (2H, d, J 8.4, NPh H_S orto), 6.93 (1H, t, J 7.2, NPh H para), 2.10 (3H, s, 3-Me) and 1.91 (3H, s, 5-Me); δ_C 166.41 (C=NOH), 143.16 (=C, NPh), 141.41 (C=N), 129.30 (=CH meta, NPh), 122.66 (=CH para, NPh), 116.01 (=CH orto, NPh), 139.15, 128.18, 127.63 and 126.83 (5-Ph), 73.57 (C-5), 20.26 (5-Me) and 13.65 (3-Me); m/z 279 (M^+, 55%), 264 (M-Me, 100), 202 (M-Ph, 68) and 77 (Ph^+, 46). (Found: C, 72.89; H, 6.27; N, 15.28. $C_{17}H_{17}N_3O$ requires C, 73.10; H, 6.13; N, 15.04%).

5-Buthyl-4-hydroxyimino-3,5-dimethyl-1-phenyl-2-pyrazoline 12g; oil; R_f(CH_2Cl_2) 0.36; υ_{max}(film)/cm^{-1} 3300 br(OH), 1650 and 1560 (C=N); δ_H 8.90 (1H, s br, OH), 7.27 (2H, dd, J 7.2 and 8.7, NPh H_S meta), 7.19 (2H, d, J 8.7, NPh H_S orto), 6.94 (1H, t, J 7.2, NPh H para), 2.31-2.02 (2H, m, 5-CH_ACH_B), 2.10 (3H, s, 3-Me), 1.71 (3H, s, 5-Me), 1.25-1.06 (4H, m, CH_2-CH_2) and 0.78 (3H, t, J 7.1, *Me*CH_2); δ_C 163.47 (C=NOH), 142.58 (=C, NPh), 141.03 (C=N), 128.87 (=CH meta), 121.09 (=CH para), 116.80 (=CH orto), 71.42 (C-5), 33.70 (5-CH_2), 26.36 (5-CH_2*C*H_2), 22.49 (5-$(CH_2)_2$*C*H_2), 19.29 (5-Me), 13.82 (3-Me) and 11.41 (5-$(CH_2)_3$*C*H_3)); m/z 259 (M^+, 10%), 244 (M-Me, 1), 202 (M-Bu, 100), 185 (M-Bu-OH, 6), 118 (MeC^+=NPh, 27) and 77 (Ph^+, 34). (Found:C, 69.65; H, 7.89; N, 16.07. $C_{15}H_{21}N_3C$ requires C, 69.47; H, 8.16; N, 16.20%).

4-Hydroxyimino-3,5-dimethyl-1-p-nitrophenyl-2-pyrazoline 12h; yellow crystals; m.p. 139-140°C (from hexane); R_f (CH_2Cl_2) 0.25; υ_{max}(CCl_4)/cm^{-1} 3350 (OH), 1635 and 1570 (C=N), 1530 and 1350 (NO_2); δ_H 8.19 (2H, dd, J 9.4 and 2.0, H_S orto at NO_2), 7.79 (1H, s br, =N-OH), 7.09 (2H, dd, J 9.4 and 2.0, H_S meta at NO_2), 5.07 (1H, q, J 6.6, 5-H), 2.20 (3H, s, 3-Me) and 1.58 (3H, d, J 6.6, 5-Me); δ_C 153.36 (C=NOH), 146.28 (=C-N), 145.51 (C=N), 139.73 (=CNO_2), 126.05 (=CH orto at NO_2), 111.80 (=CH meta at NO_2), 55.62 (HC-5), 13.83 (5-Me) and 11.45 (3-Me); m/z 248 (M^+, 45%), 233 (M-Me, 73), 232 (M-O, 100), 218 (M-NO, 20), 202 (M-NO_2, 20) and 187 (M-Me-NO_2, 45). (Found:C, 53.46; H, 5.01; N, 22.32. $C_{11}H_{12}N_4O_3$ requires C, 53.22; H, 4.87; N, 22.57%).

4-Hydroxyimino-5-methyl-1,5-diphenyl-2-pyrazoline 12i; oil; R_f (CH_2Cl_2) 0.26; υ_{max}(film) /cm^{-1} 3330 br(OH), 1650 and 1565 (C=N); δ_H 8.76 (1H, s br, OH), 7.53-6.75 (11H, m, 5-Ph, NPh and 3-H) and 1.87 (3H, s, 5-Me); m/z 265 (M^+, 32%), 254 (M-Me, 100), 188 (M-Ph, 75) and 77 (Ph^+, 37). (Found:C, 72.20; H, 5.83; N, 16.01. $C_{16}H_{15}N_3O$ requires C, 72.43; H, 5.70; N, 15.84%).

4-Hydroxyimino-3-(1-hydroxy-1-methyl)ethyl-5,5-dimethyl-1-phenyl-2-pyrazoline 12j; oil; R_f (CH_2Cl_2) 0.13; υ_{max}(film)/cm^{-1} 3600 and 3350 br (OH), 1650, 1550 (C=N); δ_H 8.40 (1H, s br, =N-OH), 7.38 (2H, dd, J 8.4 and 7.5, NPh H_S meta), 7.13 (2H, d, J 8.4, NPh H_S orto), 7.07(1H, t, J 7.5, NPh H para), 1.78 (6H, s, 5-Me_2), 1.60 (6H, s, HO*C*Me_2) and 0.99 (1H, s br, C-OH); m/z 243 (M-H_2O, 75%), 228 (M-H_2O-Me, 21), 118 (MeC^+=NPh, 81), 77 (Ph^+, 100) and 59 (Me_2C^+OH, 16). (Found:C, 64.16; H, 7.44; N, 16.27. $C_{14}H_{19}N_3O_2$ requires C, 64.35; H, 7.33; N, 16.08%).

3-Ethoxycarbonyl-4-hydroxyimino-5,5-dimethyl-1-phenyl-2-pyrazoline 12k; oil; R_f (CH_2Cl_2) 0.22; υ_{max}(film)/cm^{-1} 1720 (OC=O), 1625 and 1540 (C=N); δ_H 8.8 (1H, s br, OH), 7.41 (2H, dd, J 8.3 and 7.4, NPh H_S meta), 7.21 (2H, d, J 8.3, NPh H_S orto), 7.10 (1H, t, J 7.4, NPh H para), 4.30 (2H, q, J 7.1, CH_2OCO), 1.66 (6H, s, 5-Me_2) and 1.37 (3H, t, J 7.1, *Me*CH_2OCO); m/z 275 (M^+, 15%), 243 (M-Me-OH, 22), 230 (M-OEt, 44), 202 (M-CO_2Et, 100), 187 (M-CO_2Et-Me, 18), 118 (MeC^+=NPh, 65) and 77 (Ph^+, 35).

3-Acetyl-4-hydroxyimino-5,5-dimethyl-1-phenyl-2-pyrazoline 12l; oil; R_f (CH_2Cl_2) 0.20; υ_{max}(film)/cm^{-1} 1680 (C=O), 1625 and 1540 (C=N); δ_H 9.10 (1H, s br, OH), 7.39 (2H, dd, J 8.5 and 7.5, NPh H_S meta), 7.20 (2H, d, J 8.5, NPh H_S orto), 7.07 (1H, t, J 7.5, NPh H para), 2.18 (3H, s, MeCO), and 1.58 (6H, s, 5-Me_2); m/z 245 (M^+, 22%), 213 (M-Me-OH, 15), 202 (M-MeCO, 100), 187 (M-MeCO-Me, 26), 118 (MeC^+=NPh, 45), 77 (Ph^+, 39) and 43 ($MeCO^+$, 52).

4,5-*cis*-3,5-dimethyl-4-nitro-1-phenyl-2-pyrazoline *c*-13; oil; R_f(CH_2Cl_2) 0.41;υ_{max}(film)/cm^{-1} 1545 and 1360 (NO_2); δ_H 7.27 (2H, dd, J 7.2 and 8.4, NPh H_S meta), 7.05 (2H, d, J 8.4, NPh H_S orto), 6.82 (1H, t, J 7.2, NPh H para), 4.17 (1H, d, J 9.2, 4-H), 4.08 (1H, dq, J 9.2 and 6.3, 5-H), 2.09 (3H, s, 3-Me) and 1.17 (3H, d, J 6.3, 5-Me); δ_C 145.19 (=C, NPh), 139.97 (C=N), 128.86 (=CH meta), 119.06 (=CH para), 113.52 (=CH orto), 96.05 (HC-NO_2), 59.02 (HC-5), 13.35 (5-Me) and 10.07 (3-Me); m/z 219 (M^+, 12%), 172 (M-NO_2H, 100), 157 (M-NO_2H-Me, 20), 130 (45) and 77 (Ph^+, 56).

4,5-*trans*-3,5-dimethyl-4-nitro-1-phenyl-2-pyrazoline *t*-13; oil; R_f (CH_2Cl_2) 0.41; υ_{max}(film)/cm^{-1} 1550 and 1360 (NO_2); δ_H 7.27 (2H, dd, J 7.3 and 8.3, NPh H_S meta), 7.04 (2H, d, J 8.3, NPh H_S orto), 6.80 (1H, t, J 7.3, NPh H para), 3.78 (1H, dq, J 5.1 and 6.4, 5-H), 3.61 (1H, d, J 5.1, 4-H), 2.11 (3H, s, 3-Me) and 1.28 (3H, d, J 6.4, 5-Me); δ_C 146.81 (=C, NPh), 140.72 (C=N), 128.94 (=CH meta), 119.47 (=CH para), 114.91 (=CH orto), 99.43 (HC-NO_2), 61.91 (HC-5), 16.99 (5-Me) and 10.18 (3-Me); m/z 219 (M^+, 20%), 172 (M-NO_2H, 100), 157 (M-NO_2H-Me,13) and 77 (Ph^+, 45).

4-Amino-1,3,5-trimethylpyrazole 14a; pale yellow crystals, m.p. 104-105°C (from hexane) (reported[19] m.p. 102-104°C).

4-Hydroxyamino-1,3,5-trimethylpyrazole 14b; pale yellow crystals, m.p. 85-86°C (from hexane); υ_{max}(CCl_4)/cm^{-1} 3500 br (OH and NH), 1570 (ring); δ_H 3.76 (3H, s, NMe), 2.14 and 2.17 (6H, s, 3-Me and 5-Me) and 1.5 (2H, s br, NHOH); (Found: C, 50.82; H, 7.98; N, 29.93. $C_6H_{11}N_3C$ requires C, 51.05; H, 7.85; N, 29.76%).

4-Amino-3,5-dimethyl-1-phenylpyrazole 14c; crystals, m.p.58-60°C (from hexane) (reported[20] m.p. 59°C).

3-Hydroxymethyl-5-methyl-4-nitro-1-phenylpyrazole 14d; oil; υ_{max}(CCl_4)/cm^{-1} 3350 br (OH), 1560 and 1370 (NO_2); δ_H 7.68-7.23 (5H, m, Ph), 4.94 (2H, s, 3-CH_2OH), 2.90 (1H, s br, OH) and 2.62 (3H, s, 5-Me); (Found: C, 56.43; H, 4.89; N, 18.26. $C_{11}H_{11}N_3O_3$ requires C, 56.65; H, 4.75; N, 18.02%).

4,5-*trans*-2-Ethyl-3,3,5-trimethyl-4-nitro-1-phenylpyrazolidine 19a; oil; R_f (CH_2Cl_2) 0.72; υ_{max}(film)/cm^{-1} 1555 and 1360 (NO_2); δ_H 7.17(2H, dd, J 7.4 and 8.3, NPh H_S meta), 6.94 (2H, d, J 8.3, NPh H_S orto), 6.75 (1H, t, J 7.4, NPh H para), 4.75 (1H, d, J 7.8, 4-H), 4.48 (1H, dq, J 7.8 and 6.3, 5-H), 2.96 and 2.63 (total 2H, dq, J 11.4 and 7.1, CH_ACH_BN), 1.55 (3H, d, J 6.3, 5-Me), 1.44 (3H, s, 3-Me trans at NO_2), 1.12 (3H, t, J 7.1, *Me*CH_2N) and 0.90 (3H, s, 3-Me *cis* at NO_2); δ_C 151.55 (=C), 128.76 (=CH meta), 119.63 (=CH para), 113.32 (=CH, orto), 98.36 (H-C-NO_2), 65.76 (HC-5), 64.63 (C-3), 46.13 (CH_2N), 23.15 (5-Me), 14.11 (3-Me trans at NO_2), 12.97 (*Me*CH_2N) and 9.71 (3-Me cis at NO_2); m/z 263 (M^+, 32%), 234 (M-Et, 10), 187 (M-NO_2-EtH, 75), and 77 (Ph^+, 80). (Found:C, 64.04; H, 8.16; N, 16.10. $C_{14}H_{21}N_3O_2$ requires C, 63.85; H, 8.04; N, 15.96%).

2-Ethyl-3,3,5,5-tetramethyl-4-nitro-1-phenylpyrazolidine 19b; oil; R_f (CH_2Cl_2)0.69; υ_{max} (film)/cm^{-1} 1560 and 1370 (NO_2); δ_H 7.20 (2H, dd, J 8.4 and 6.9, NPh H_S meta), 7.18 (2H, d, J 8.4, NPh H_S orto), 6.86 (1H, t, J 6.9, NPh H para), 4.96 (1H, s, 4-H), 2.91 (2H, m, J 7.1 and 11.4, CH_2N), 1.70 (3H, s, 5-Me *trans* at NO_2), 1.45 (3H, s, 3-Me *trans* at NO_2), 1.38 (3H, s, 5-Me *cis* at NO_2), 1.17 (3H, t, J 7.1, *Me*CH_2N) and 0.94 (3H, s, 3-Me *cis* at NO_2); δ_C 149.31 (=C), 128.45 (=CH meta), 121.62 (=CH para), 120.15 (=CH orto), 98.81 (HC-NO_2), 65.03 (C-5), 64.27 (C-3), 46.53 (CH_2N), 24.63 (5-Me trans at N_2O), 18.46 (5-Me cis at NO_2), 14.01 (3-Me trans at NO_2), 13.86 (*Me*CH_2N) and 9.58 (3-Me cis at NO_2); m/z 277 (M^+, 39%), 248 (M-Et, 24), 201 (M-EtH-NO_2, 73), 97 (M-NO_2-PhNNEt, 100) and 77 (Ph, 85^+). (Found:C, 65.18; H, 8.21; N, 15.36. $C_{15}H_{23}N_3O_2$ requires C, 64.96; H, 8.36; N, 15.15%).

3,4-*trans*, 4,5-*trans*-2-Ethyl-3,5-dimethyl-4-nitro-1,3,5-triphenylpyrazolidine 19c; oil;R_f (CH_2Cl_2) 0.75; υ_{max}(film)/cm^{-1} 1560 and 1370 (NO_2); δ_H 7.96(2H, d, J 7.3, 5-Ph H_S orto), 7.64(2H, d, J 7.8, 3-Ph H_S orto), 7.48 (2H, dd, J 7.2 and 8.2, NPh H_S meta), 7.39 (2H, d, J 8.2, NPh, H_S orto), 7.28 (6 H, m, 5-Ph and 3-Ph H_S meta and para), 7.03 (1H, t, J 7.2, NPh H para), 5.93 (1H, s, 4-H), 3.18 and 2.95 (total 2H, dq, J 12.4 and 7.2. CH_AH_BN), 1.26 (3H, s, 5-Me *cis* at NO_2), 1.22 (3H, s, 3-Me *cis* at NO_2) and 1.12 (3H, t, J 7.2, *Me*CH_2N); δ_C 150.38, 128.88, 122.69 and 116.03 (NPh), 147.78, 141.18, 128.71, 128.34, 127.20, 127.11, 126.01 and 125.93 (3-Ph and 5-Ph), 108.05 (HC-NO_2), 71.66 (C-5), 69.96 (C-3), 48.12 (CH_2N), 26.82 (5-Me), 25.56 (3-Me) and 15.56 (*Me*CH_2N); m/z 401 (M^+, 28%), 372 (M-Et, 3), 238 (M-PhMeC=$CHNO_2$, 6), 221 (M-PhC^+=NPh, 21), 143 (26), 105 (34), 91 (51) and 77 (Ph^+, 100).

3,4-*trans*-3-Ethoxycarbonyl-2-ethyl-3,5,5-trimethyl-4-nitro-1-phenylpyrazolidine 19d; pale yellow crystals, m.p. 85-87°C (from ethanol); R_f (CH_2Cl_2) 0.63; υ_{max}(CCl_4)/cm^{-1} 1730 (OC=O), 1550 and 1380 (NO_2); δ_H 7.21(2H, dd, J 8.4 and 6.8, NPh H_S meta), 7.17 (2H, d, J 8.4, NPh H_S orto), 6.89 (1H, t, J 6.8, NPh H para), 5.77 (1H, s, 4-H), 4.28 (2H, q, J 7.1, CH_2OCO), 3.01 (2H, m, J 11.9 and 7.1, CH_2N), 1.68 (3H, s, 5-Me *trans* at NO_2), 1.45 (3H, s, 3-Me), 1.43 (3H, s, 5-Me cis at NO_2), 1.34 (3H, t, J 7.1, *Me*CH_2OCO) and 0.98 (3H, t, J 7.1, *Me*CH_2N); δ_C 171.89 (OC=O), 148.86 (=C), 128.20 (=CH meta), 121.32 (=CH para), 120.01 (=CH orto), 99.15 (HC-NO_2), 70.81 (*C*-CO_2Et), 64.97 (C-5), 62.39 (CH_2OCO), 48.37 (CH_2N), 29.64 (3-Me), 24.25 (5-Me trans at NO_2), 18.22 (5-Me cis at NO_2) 14.21 (*Me*CH_2OCO) and 14.05 (*Me*CH_2N); m/z 335 (M^+, 9%), 306 (M-Et, 10), 290 (M-OEt, 1), 289 (M-NO_2, 2), 262 (M-CO_2Et, 4), 216 (M-CO_2Et-NO_2, 12), 201 (M-PhN=NEt, 100), 118 (MeC^+=NPh, 7) and 77 (Ph^+, 16). (Found:C, 61.03; H, 7.42; N, 12.37. $C_{17}H_{25}N_3O_4$ requires C, 60.88; H, 7.51; N, 12.53%).

2-Ethyl-3,5,5-trimethyl-4-nitro-1-phenyl-3-pyrazoline 20b; oil; R_f (CH_2Cl_2) 0.47; υ_{max}(film) /cm^{-1} 1650 (C=C), 1550 and 1360 (NO_2); δ_H 7.35(2H, dd, J 7.4 and 6.8, NPh H_S meta), 7.20 (2H, d, J 7.4, NPh H_S orto), 7.05 (1H, t, J 6.8, NPh H para), 3.35 (2H, q, J 7.1, CH_2N), 2.55 (3H, s, 3-Me), 1.46 and 1.43 (6H, s, 5-Me_2) and 1.22 (3H, t, J 7.1, *Me*CH_2N); δ_C 150.83 (=C-NO_2), 144.66, 129.01, 126.53 and 124.64 (NPh), 112.72 (=*C*-Me), 69.95 (C-5), 42.40 (CH_2N), 39.44 (3-Me), 25.53 and 25.39 (5-Me_2) and 13.62 (*Me*CH_2N); m/z 261 (M^+, 6%), 246 (M-Me, 100), 230 (M-O-Me, 3), 185 (M-2Me-NO_2, 18), 118 (MeC^+=NPh, 30) and 77 (Ph^+, 72). (Found:C, 64.14; H, 7.45; N, 16.22. $C_{14}H_{19}N_3O_2$ requires C, 64.35; H, 7.33; N, 16.08%).

2-Ethyl-3,5-dimethyl-4-nitro-1,5-diphenyl-3-pyrazoline 20c; oil; R_f (CH_2Cl_2) 0.50; υ_{max}(film) /cm^{-1} 1640 (C=C), 1545 and 1360 (NO_2); δ_H 7.68-6.82 (total 10H, m, NPh and 5-Ph), 3.50 and 3.31(total 2H, dq, J 14.8 and 7.0, CH_AH_BN), 2.68 (3H, s, 3-Me), 1.62 (3H, s, 5-Me) and 1.20 (3H, t, J 7.0, *Me*CH_2N); m/z 323 (M^+, 12%), 308 (M-Me, 54), 263 (M-NO_2+H, 10), 246 (M-Ph, 55), 217 (M-Ph-Et, 12), 180 (PhC^+=NPh, 49), 105 (36), 91 (30) and 77 (Ph^+, 100).

5-Ethoxycarbonyl-1-ethyl-3,5-dimethyl-4-nitro-2-phenyl-3-pyrazoline 21d; oil; R_f (CH_2Cl_2) 0.37; υ_{max}(film)/cm^{-1} 1740 (OC=O), 1630 (C=C), 1560 and 1380 (NO_2); δ_H 7.53(2H, dd, J 7.5 and 6.9, NPh H_S meta), 7.44(2H, d, J 7.5, NPh H_S orto), 7.18 (1H, t, J 6.9, NPh H para), 4.26 (2H, q, J 7.1,CH_2OCO), 2.94 (2H, q, J 7.0, CH_2N), 2.30 (3H, s, 3-Me), 1.84 (3H, s, 5-Me), 1.34 (3H, t, J 7.1, *Me*CH_2OCO) and 0.98 (3H, t, J 7.0, *Me*CH_2N); m/z 319 (M^+, 8%), 246 (M-CO_2Et, 86), 231 (M-CO_2Et-Me, 14), 214 (37), 202 (M-CO_2Et-Me-Et, 44), 118 (MeC^+=NPh, 100) and 77(Ph^+, 58). (Found: C, 60.26; H, 6.71; N, 12.98. $C_{16}H_{21}N_3O_4$ requires C, 60.18; H, 6.63; N, 13.16%).

4-Hydroxyimino-2-ethyl-3,3,5-trimethyl-1-phenylpyrazolidine 22; oil; R_f (CH_2Cl_2) 0.32; υ_{max} (film)/cm^{-1} 3300 br (OH), 1630 (C=N); δ_H 8.24 (1H, s br, =NOH), 7.19 (2H, dd, J 8.7 and 7.4, NPh H_S meta), 7.00 (2H, d, J 8.7, NPh H_S orto), 6.72 (1H, t, J 7.4, NPh H para), 4.57 (1H, q, J 7.0, 5-H), 2.98 and 2.65 (total 2H, dq, J 11.5 and 7.1, CH_AH_BN), 1.74 (3H, d, J 7.0, 5-Me), 1.38 (3H, s, 3-Me trans at 5-Me), 1.10 (3H, t, J 7.1, *Me*CH_2N)and 1.05 (3H, s, 3-Me cis at 5-Me); δ_C 170.51 (C=NOH), 151.66 (=C, Ph), 128.69 (=CH meta), 117.58 (=CH para), 11.62 (=CH orto), 66.38 (C-3), 57.69 (HC-5), 48.73 (CH_2N), 22.67 (5-Me), 20.85 (3-Me trans at 5-Me), 20.14 (3-Me cis at 5-Me) and 12.61 (*Me*CH_2N); m/z

247 (M^+, 79%), 232 (M-Me, 100), 218 (M-Et, 88), 203 (M-Et-Me, 31), 188 (M-Et-2Me, 21), 118 (MeC^+=NPh, 27) and 77 (Ph^+, 91). (Found:C, 67.73; H, 8.65; N, 17.21. $C_{14}H_{21}N_3O$ requires C, 67.98; H, 8.56; N, 16.99%).

Cleavage of oximes to ketones[21]. The oxime (1mmol), dissolved in 50% aqueous ethanol (10 cm^3) was refluxed with sodium bisulfite (3.5 mmol) until thin layer chromatography indicated complete reaction. After removal of the ethanol by distillation, the residue was dissolved in chloroform, and an excess of dilute hydrochloric acid was added. The ketone was extracted into the organic layer. The extract was washed with sat. aq NaCl and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue quickly purified by flash chromatography (SiO_2, CH_2Cl_2). The following 2-pyrazolin-4-ones **23** were obtained:

1,3,5,5-Tetramethyl-2-pyrazolin-4-one 23a from 12a; yield 86%; oil; R_f (CH_2Cl_2) 0.52; υ_{max}(film)/cm^{-1} 1705 (C=O) and 1570 (C=N); δ_H 2.93 (3H, s, NMe), 2.32 (3H, s, 3-Me) and 1.31 (6H, s, 5-Me_2); m/z 140 (M^+, 2%), 125 (M-Me, 100) and 56 (MeC^+=NMe, 28).

3,5,5-Trimethyl-1-phenyl-2-pyrazolin-4-one 23d from 12d; yield 87%; colorless crystals; m.p. 83-84°C (from hexane) lit.[22] m.p. 84-85°C (from petroleum light); R_f (CH_2Cl_2) 0.48; υ_{max} (CCl_4)/cm^{-1} 1705 (C=O) and 1560 (C=N); δ_H 7.30 (4H, m, NPh H_S meta and orto), 7.00 (1H, m, NPh H para), 2.19 (3H, s, 3-Me) and 1.45 (6H, s, 5-Me_2); m/z 202 (M^+, 22%), 133 (MeC^+=N-NHPh, 20), 118 (MeC^+=NPh, 100) and 77 (Ph^+, 35).

5-Buthyl-3,5-dimethyl-1-phenyl-2-pyrazolin-4-one 23g from 12g; yield 83%; oil; R_f (CH_2Cl_2) 0.60; υ_{max}(film)/cm^{-1} 1700 (C=O) and 1565 (C=N); δ_H 7.32 (4H, m, NPh H_S meta and orto), 7.06 (1H, m, NPh H para), 2.16 (3H, s, 3-Me), 2.10 and 1.98 (2H, dt, J 11.4 and 5.1, 5-CH_ACH_B), 1.39 (3H, s, 5-Me), 1.13 (2H, m, 5-CH_2CH_2), 0.81 (2H, m, 5-$(CH_2)_2CH_2$) and 0.74 (3H, t, J 7.3, 5-$(CH_2)_3CH_3$); δ_C 203.41 (C=O), 141.69 (C=N), 141.41 (=C), 129.30 (=CH meta), 122.66 (=CH para), 116.01 (=CH orto), 70.34 (C-5), 38.00 (5-CH_2), 25.47 (5-CH_2CH_2), 22.88 (5-Me), 22.44 (5-$(CH_2)_2CH_2$), 13.65 (3-Me) and 9.55 (5-$(CH_2)_3CH_3$); m/z 240 (M^+, 12%), 187 (M-Bu, 12), 133 (MeC^+=N-NHPh, 30), 118 (MeC^+=NPh, 100) and 77 (Ph^+, 79).

5,5-Dimethyl-1-phenyl-3-(2-propenyl)-2-pyrazoline-4-one 23j from 12j; yield 78%; oil; R_f (CH_2Cl_2) 0.70; υ_{max}(film)/cm^{-1} 1705 (C=O), 1630 (C=C), 1550 (C=N) and 890 (=CH_2); δ_H 7.38 (2H, dd, J 8.4 and 7.5, NPh H_S meta), 7.13 (2H, d, J 8.4, NPh H_S orto), 7.07 (1H, t, J 7.5, NPh H para), 6.20 (1H, d, J 1.6, C=CH_A), 5.33 (1H, d, J 1.6, C=CH_B), 2.18 (3H, s, *Me*C=CH_2) and 1.50 (6H, s, 5-Me_2); m/z 228 (M^+, 21%), 213 (M-Me, 12), 185 (M-Me-CO, 100), 118 (MeC^+=NPh, 33) and 77 (Ph^+, 67).

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