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The Reduction of Functionalized Pyrazolium Salts as a Stereoselective Route to Functionalized Pyrazolidines.

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Abstract: Functionalized pyrazolium salts **1** react with metal complex hydrides ($LiAlH_4$ and $NaBH_4$) to give pyrazolidines **2** with good-to-excellent levels of diastereoselectivity. The stereochemical course of the reduction is essentially *anti*, leading to trans,trans-pyrazolidines. The relative configuration of the crystalline pyrazolidine **2c** has been determined by X-ray crystallographic analysis. Copyright © 1996 Elsevier Science Ltd

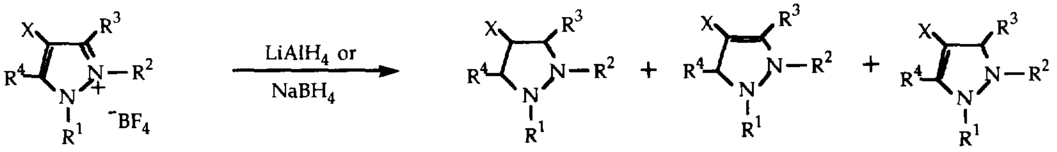
In the course of our investigations on the reactivity of activated azoles toward complex metal hydrides, organometallic compounds and other nucleophiles, two main processes were observed: a) addition of the nucleophilic reagents to the ring giving azoline derivatives and b) reductive ring cleavage leading to open chain products. Thus, 4-functionalized-3,5-dialkylisoxazoles and isoxazolium salts react with complex metal hydrides[1], organolithium, organomagnesium and organoaluminium compounds[2] to give regioselectively 2-, 3- and 4-isoxazolines. On the other hand, N-alkylisoxazolium salts and N-alkylisothiazolium salts undergo ring cleavage when treated with lithium dialkylcuprates and complex metal hydrides leading to β-enaminoketones[3,4] and β-enaminothioketones[5]. Ring cleavage-closure reactions are also observed when 3-unsubstituted isoxazoles and isoxazolium salts react with dinucleophiles[6,7].

The preparation of 3-pyrazolines by reaction of N-methylpyrazolium salts with complex metal hydrides has also been reported[8,9]. Nevertheless, we have found that the reduction of 1,3,5-trisubstituted 2-alkylpyrazolium salts with complex metal hydrides gives 3-pyrazolines[10], whereas the reduction of 3- and/or 5-unsubstituted 2-ethylpyrazolium salts with the same hydrides leads to pyrazolidines[11] as major products.

RESULTS and DISCUSSION

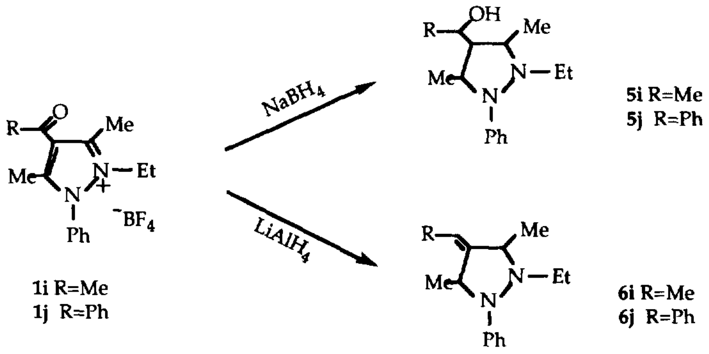
We now report that 2-alkylpyrazolium tetrafluoroborates **1** bearing electron-withdrawing group at C-4, and occasionally at C-5, react easily with complex metal hydrides giving stereoselectively functionalized pyrazolidines **2**, **5** and **6**. Some of these processes also afforded functionalized 3-pyrazolines **3** and **4**.

The functional group attached at C-4 markedly increases the reactivity of nucleus towards attack of hydride, leading to their total reduction and formation of pyrazolidines **2a-h** (Scheme 1), in which the functional group remains unchanged in all cases, except when this is a carbonyl group. The reduction of 4-acetyl- **1i** and 4-benzoylpyrazolium salt **1j** with $NaBH_4$ gave the corresponding tertiary alcohols **5i** and **5j**, whereas they react with $LiAlH_4$ to give the 4-alkylidenpyrazolidines **6i** and **6j** resulting from spontaneous dehydration in the reaction conditions (Scheme 2).



1a X=NO_2, R^1=Ph, R^2=Et, R^3=Me, R^4=H	**2a**[2]	**3a**	
1b X=NO_2, R^1=Ph, R^2=Et, R^3=R^4=Me	**2b**		
1c X=NO_2, R^1=Ph, R^2=Et, R^3=CO_2Et, R^4=Me	**2c**		**4c**
1d X=Br, R^1=Ph, R^2=Et, R^3=Me, R^4=H	**2d**		
1e X=Br, R^1=Ph, R^2=Et, R^3= R^4=Me	**2e**		
1f X=Br, R^1=Ph, R^2=Et, R^3=Me, R^4=Ph	**2f**		
1g X=CO_2Et, R^1= R^2=R^3=R^4=Me	**2g**	**3g**	
1h X=CO_2Et, R^1=Ph, R^2=Et, R^3= R^4=Me	**2h**	**3h**	**4h**

Scheme 1



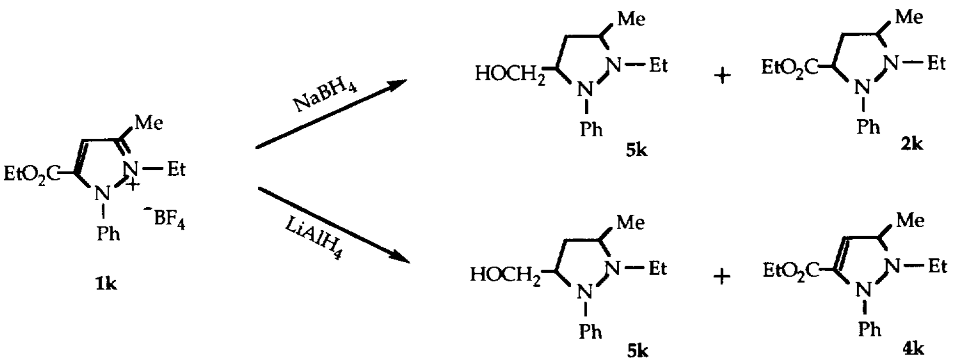
1i R=Me
1j R=Ph

5i R=Me
5j R=Ph

6i R=Me
6j R=Ph

Scheme 2

The only 5-functionalized pyrazolium salt tested was the 2-ethyl-5-ethoxycarbonyl-3-methyl-1-phenylpyrazolium tetrafluoroborate **1k**, which react with $NaBH_4$ at room temperature to give the pyrazolidine **5k** in which the ester group has been reduced to alcohol. Using $LiAlH_4$ at room temperature, together with **5k**, we obtained **4k**, the more stable of the two posible 3-pyrazolines (double bond conjugated with ester group). The reduction of **1k** with $NaBH_4$ at -20ºC led only to 8% of pyrazolidine **2k** in which the functional group remains unaffected. Probably the activation of the nucleus by the ethoxycarbonyl group in C-5 is less, consequently the reactivity of the ring and the ester group towards hydrides is similar, even with $NaBH_4$, leading in all conditions to the 5-hydroxymethylpyrazolidine **5k** as major product (Scheme 3).



Scheme 3

In general, the reactivity with both hydrides ($LiAlH_4$ and $NaBH_4$) is similar. However, the 4-bromopyrazolium salts afforded higher yields of pyrazolidines in their reaction with $NaBH_4$ than $LiAlH_4$, because with this hydride, even at 0ºC, the hydrogenolysis of the C-Br bond probably competes with the reduction of the nucleus.

The results obtained are summarized in Table 1.

Although the reduction with $LiAlH_4$ or $NaBH_4$ is not stereoselective and consequently a mixture of diastereoisomer pyrazolidines may be formed, we have obtained one diastereoisomer, as a sole or majority product. The 4-functionalized 3,5-disubstituted pyrazolium salts afforded 3,4-*trans*,4,5-*trans*-pyrazolidines, except when the functional group in C-4 is a bromine atom. In this case, the pyrazolidine formed had 3,4-*cis*,4,5-*trans* configuration.

This stereochemical outcome is consistent with initial attack of hydride at more electron-deficient C-5, followed by coordination of electrophilic reducing agent (AlH_3 or BH_3) at C-4 in the intermediate **7** from the opposite side to give the less hindered iminium salt **8** with the larger substituents at C-4 and C-5 in an *anti*-orientation. This is then reduced by metal hydride by either an intramolecular hydride delivery to provide 3,4-cis,4,5-*trans*-pyrazolidines or an intermolecular hydride transfer to originate the more stable 3,4-*trans*,4,5-*trans*-pyrazolidine (Scheme 4).

The special behaviour of the 4-bromo derivatives is difficult to explain. Probably, an intramolecular hydride delivery from a Br-coordinated aluminium or borohydride could be involved.

The reduction of 4-acylpyrazolium salts with $NaBH_4$ increased the number of possible diastereoisomers. The carbonyl group was also reduced, leading to a mixture of two epimeric alcohols (*syn* and *anti*) of the corresponding trans,trans-pyrazolidine. The main product can be predicted on the basis of Cram's rule. On the other hand, E- and Z-4-alkyliden-3,5-*cis*-pyrazolidine obtained, when $LiAlH_4$ was used, could arise by subsequent *anti*-elimination in the *syn*- and *anti*-alkoxyaluminium intermediate, respectively.

The 5-functionalized 4-unsubstituted pyrazolium salt **1k** showed a less diastereoselectivity leading to mixtures of two posible *cis*- and *trans*-pyrazolidines. At room temperature, with both hydrides, an approximate 1:1 ratio of two isomers was obtained. However, at lower temperatures better selectivity was achieved. At -20ºC, with both hydrides, a *trans* : *cis* = 4 : 1 mixture was isolated.

Table 1 Reduction of functionalised pyrazolium tetrafluoborates **1** with complex metal hydrides[a].

Substrate	Hydride	Solvent	Products and Yields (%)[b]	Stereoisomer distribution (%)
$\mathbf{1}_a$	LiAlH$_4$	Et$_2$O	$\mathbf{2}_a$ (77)	3,4-*trans* (100)
$\mathbf{1}_a$	NaBH$_4$	EtOH	$\mathbf{2}_a$ (36) + $\mathbf{3}_a$ (37)	3,4-*trans* (100)
$\mathbf{1}_b$	LiAlH$_4$	Et$_2$O	$\mathbf{2}_b$ (83)	3,4-*trans*,4,5-*trans* (85) + 3,4-*cis*,4,5-*trans* (15)
$\mathbf{1}_b$	LiAlH$_4$	THF	$\mathbf{2}_b$ (91)	3,4-*trans*,4,5-*trans* (88) + 3,4-*cis*,4,5-*trans* (12)
$\mathbf{1}_b$	NaBH$_4$	EtOH	$\mathbf{2}_b$ (79)	3,4-*trans*,4,5-*trans* (80) + 3,4-*cis*,4,5-*trans* (20)
$\mathbf{1}_c$	LiAlH$_4$	THF	$\mathbf{2}_c$ (52) + $\mathbf{4}_c$ (26)	3,4-*trans*,4,5-*trans* (100)
$\mathbf{1}_c$	NaBH$_4$	EtOH	$\mathbf{2}_c$ (81)	3,4-*trans*,4,5-*trans* (100)
$\mathbf{1}_d$	LiAlH$_4$[c]	Et$_2$O	$\mathbf{2}_d$ (45)	3,4-*cis* (100)
$\mathbf{1}_d$	NaBH$_4$	EtOH	$\mathbf{2}_d$ (74)	3,4-*cis* (100)
$\mathbf{1}_e$	LiAlH$_4$[c]	Et$_2$O	$\mathbf{2}_e$ (32)	3,4-*cis*,4,5-*trans* (100)
$\mathbf{1}_e$	NaBH$_4$	EtOH	$\mathbf{2}_e$ (61)	3,4-*cis*,4,5-*trans* (100)
$\mathbf{1}_f$	LiAlH$_4$[c]	Et$_2$O	$\mathbf{2}_f$ (26)	3,4-*cis*,4,5-*trans* (85) + 3,4-*trans*,4,5-*trans* (15)
$\mathbf{1}_f$	NaBH$_4$	EtOH	$\mathbf{2}_f$ (80)	3,4-*cis*,4,5-*trans* (78) + 3,4-*trans*,4,5-*trans* (22)
$\mathbf{1}_g$	LiAlH$_4$	Et$_2$O	$\mathbf{2}_g$ (62)	3,4-*trans*,4,5-*trans* (100)
$\mathbf{1}_g$	NaBH$_4$	EtOH	$\mathbf{2}_g$ (43) + $\mathbf{3}_g$ (25)	3,4-*trans*,4,5-*trans* (100)
$\mathbf{1}_h$	LiAlH$_4$	Et$_2$O	$\mathbf{2}_h$ (35) + $\mathbf{3}_h$ (21) + $\mathbf{4}_h$ (14)	3,4-*trans*,4,5-*trans* (100)
$\mathbf{1}_h$	LiAlH$_4$[d]	THF	$\mathbf{6}_h$ (38) + $\mathbf{3}_h$ (35) + $\mathbf{4}_h$ (9)	3,5-*cis* (71) + 3,5-*trans* (29)
$\mathbf{1}_h$	LiAlH$_4$[d,e]	THF	$\mathbf{3}_h$ (55) + $\mathbf{4}_h$ (22)	
$\mathbf{1}_h$	NaBH$_4$	EtOH	$\mathbf{3}_h$ (73) + $\mathbf{4}_h$ (18)	
$\mathbf{1}_i$	LiAlH$_4$	Et$_2$O	$\mathbf{6}_i$ (60)	*Z*,3,5-*cis* (45) + *E*,3,5-*cis* (55)
$\mathbf{1}_i$	NaBH$_4$	EtOH	$\mathbf{5}_i$ (75)	3,4-*trans*,4,5-*trans*[f] (100)
$\mathbf{1}_j$	LiAlH$_4$	Et$_2$O	$\mathbf{6}_j$ (71)	*Z*,3,5-*cis* (35) + *E*,3,5-*cis* (65)
$\mathbf{1}_j$	NaBH$_4$	EtOH	$\mathbf{5}_j$ (68)	*syn*,3,4-*trans*,4,5-*trans* (70) + *anti*,3,4-*trans*,4,5-*trans* (30)
$\mathbf{1}_k$	LiAlH$_4$	Et$_2$O	$\mathbf{5}_k$ (52) + $\mathbf{4}_k$ (34)	3,5-*cis* (53) + 3,5-*trans* (47)
$\mathbf{1}_k$	LiAlH$_4$[e]	Et$_2$O	$\mathbf{5}_k$ (83)	3,5-*cis* (20) + 3,5-*trans* (80)
$\mathbf{1}_k$	NaBH$_4$	EtOH	$\mathbf{5}_k$ (85)	3,5-*cis* (55) + 3,5-*trans* (45)
$\mathbf{1}_k$	NaBH$_4$[e]	EtOH	$\mathbf{2}_k$ (8) + $\mathbf{5}_k$ (72)	3,5-*trans* (100) 3,5-*cis* (20) + 3,5-*trans* (80)

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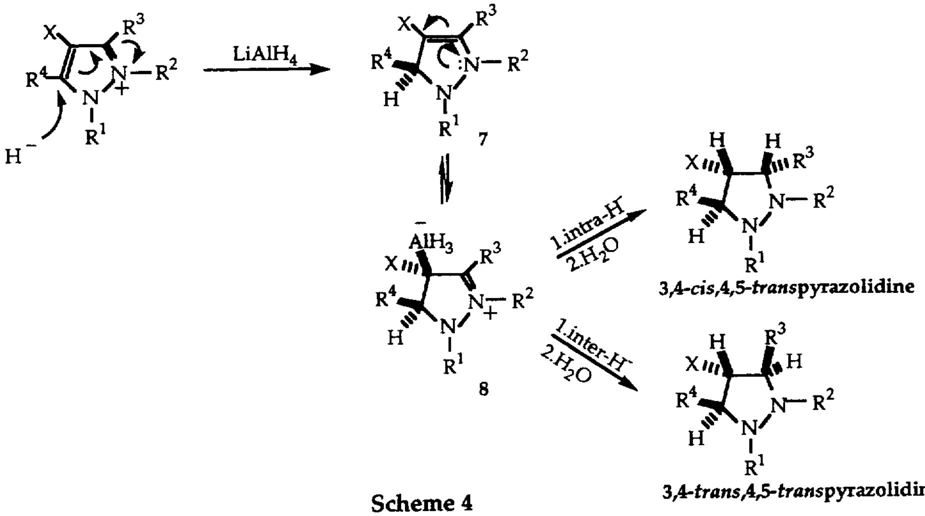
[a] Reactions were carried out at r.t. using a molar ratio 1:hydride=1:1. [b] Yields refer to isolated pure products. [c] Carried out at 0°C. [d] Molar ratio 1:hydride=1:2. [e] Carried out at -20°C. [f] Mixture of epimers in the hydroxyethyl group.



Scheme 4

So far as we know, functionalized pyrazolidines with electron-withdrawing groups have not been previously described. As a result of this, there is no data available on coupling constants that we could use for stereochemical elucidation. Stereochemistries of all pyrazolidines were asigned by ^{1}H-NOESY and ^{1}H-NOE difference spectroscopy, and relative configurations confirmed by X-ray diffraction analysis of one of them (**2c**).

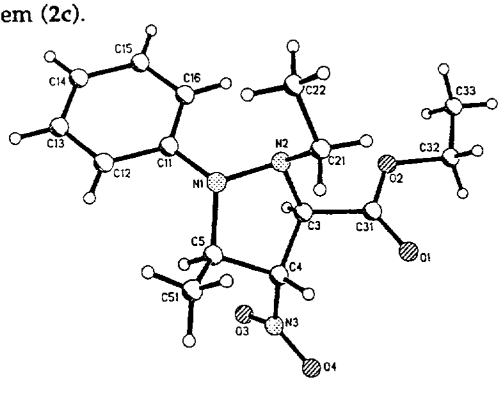


Fig. 1 The molecular structure of the pyrazolidine 2c

The pyrazolidine **2c** showed an enhancement in the 5-methyl doublet resonance when the 4-H signal was irradiated; but led to no observable NOE for the 3-H doublet resonance. Alternatively, irradiation of the 5-methyl doublet gave an increase in the area of the 5-H and 4-H resonances. From these results, a *trans,trans*-configuration was assigned for **2c**. The X-ray crystal structure of **2c** was determined to confirm its geometrical arrangement and the molecular structure is shown in Fig. 1 together with the atomic numbering scheme. The bond distances and angles are in good agreement with the expected values.[12]

The conformation of the pyrazolidine ring is near to half-chair with N-2 (0.15 A) and C-3 (-0.43 A) out of the mean plane defined by atoms N-1, C-4 and C-5. The nitro group is in *trans* position with respect to the ethoxycarbonyl and methyl groups, respectively. The two rings are not coplanar, the angle between them being 43.9°. Bond lengths and angles are listed in Tables 2 and 3, respectively.

A complete assignment of the relative stereochemistries of the remaining pyrazolidines was performed by a detailed investigation of NOEs throughout the molecules. The configuration 3,4-*trans* of **2a**, **2b**, **2g**, **2h**, **5i** and **5j** were assigned on the basis of NOE effect or NOESY interactions between 3-Me and 4-H. Furthermore, the 4,5-*trans* relationship of 4-H and 5-H in the ring of

Table 2. Bond lengths (Å) and angles (°) for 2c.

N(1)-C(11)	1.428(4)	N(1)-N(2)	1.433(3)
N(1)-C(5)	1.484(4)	N(2)-C(3)	1.457(4)
N(2)-C(21)	1.474(4)	N(3)-O(4)	1.165(5)
N(3)-O(3)	1.154(5)	N(3)-C(4)	1.497(5)
O(1)-C(31)	1.191(4)	O(2)-C(31)	1.309(4)
O(2)-C(32)	1.457(4)	C(3)-C(31)	1.511(4)
C(3)-C(4)	1.516(4)	C(4)-C(5)	1.527(5)
C(5)-C(51)	1.519(5)	C(11)-C(16)	1.382(5)
C(11)-C(12)	1.390(5)	C(12)-C(13)	1.406(6)
C(13)-C(14)	1.353(6)	C(14)-C(15)	1.352(6)
C(15)-C(16)	1.381(5)	C(21)-C(22)	1.498(5)
C(32)-C(33)	1.472(5)		
C(11)-N(1)-N(2)	113.7(2)	C(11)-N(1)-C(5)	118.1(3)
N(2)-N(1)-C(5)	110.1(2)	N(1)-N(2)-C(3)	103.4(2)
N(1)-N(2)-C(21)	110.0(2)	C(3)-N(2)-C(21)	114.7(2)
O(4)-N(3)-O(3)	121.9(6)	O(4)-N(3)-C(4)	120.2(4)
O(3)-N(3)-C(4)	117.8(5)	C(31)-O(2)-C(32)	117.1(3)
N(2)-C(3)-C(31)	113.3(3)	N(2)-C(3)-C(4)	104.6(2)
C(31)-C(3)-C(4)	114.6(3)	N(3)-C(4)-C(3)	110.7(3)
N(3)-C(4)-C(5)	112.8(3)	C(3)-C(4)-C(5)	103.2(3)
N(1)-C(5)-C(51)	112.3(3)	N(1)-C(5)-C(4)	103.8(3)
C(51)-C(5)-C(4)	114.2(3)	C(16)-C(11)-C(12)	119.0(3)
C(16)-C(11)-N(1)	121.9(3)	C(12)-C(11)-N(1)	118.9(3)
C(11)-C(12)-C(13)	119.0(4)	C(14)-C(13)-C(12)	120.6(4)
C(15)-C(14)-C(13)	120.2(4)	C(14)-C(15)-C(16)	121.0(4)
C(15)-C(16)-C(11)	120.1(4)	N(2)-C(21)-C(22)	110.3(3)
O(1)-C(31)-O(2)	124.9(3)	O(1)-C(31)-C(3)	123.7(3)
O(2)-C(31)-C(3)	111.4(3)	O(2)-C(32)-C(33)	107.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 2c. U (eq) is defined as one third of the trace of orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	-3676(3)	-1126(3)	8905(1)	70(1)
N(2)	-2495(3)	16(3)	8806(1)	63(1)
N(3)	-374(5)	-3865(5)	9150(2)	120(1)
O(1)	1367(3)	-169(4)	9267(1)	119(1)
O(2)	425(2)	815(3)	8412(1)	73(1)
O(3)	679(8)	-4268(7)	9485(3)	290(4)
O(4)	-778(5)	-4621(5)	8737(2)	154(2)
C(3)	-1147(3)	-1042(4)	8799(1)	64(1)
C(4)	-1212(4)	-2312(4)	9260(1)	81(1)
C(5)	-2955(4)	-2580(4)	9230(1)	80(1)
C(11)	-4840(4)	-1426(4)	8417(2)	72(1)
C(12)	-6023(4)	-2550(5)	8457(2)	96(1)
C(13)	-7207(5)	-2795(6)	7984(3)	110(2)
C(14)	-7210(5)	-1935(7)	7500(2)	113(2)
C(15)	-6069(5)	-828(6)	7465(2)	97(1)
C(16)	-4886(4)	-550(5)	7919(1)	78(1)
C(21)	-2274(4)	1310(4)	9247(1)	80(1)
C(22)	-3696(5)	2378(5)	9197(2)	109(1)
C(31)	365(4)	-91(4)	8860(2)	72(1)
C(32)	1828(4)	1796(5)	8414(2)	88(1)
C(33)	1694(5)	2608(5)	7858(2)	110(1)
C(51)	-3451(6)	-2736(5)	9804(2)	112(2)

pyrazolidines **2b**, **2e**, **2g**, **2h**, **5i** and **5j** was evident since no NOE was observed between these two protons, but the 5-Me group showed a significant NOE effect with the 4-H. On the other hand, the 3,4-*cis* configuration for **2d**, **2e**, and **2f** was also determined in a similar manner. In these cases a strong NOE between 3-H and 4-H was observed. The weaker NOE effect between 3-H and 5-H or 3-Me and 5-Me of 4-alkylidenpyrazolidines **6h**, **6i** and **6j** indicated a 3,5-*cis* configuration, as a result of dehydration of the correponding 3,4-*trans*,4,5-*trans*-4-hydroxyalkylpyrazolidines. Furthermore, the **Z** and E geometry of the double bond of the two **6j** isomers could also be determined from NOE experiments. Irradiation of the olefinic proton at δ 6.32 showed enhancement of the 3-H at δ 3.75 and 3-Me at δ 1.19 of the **Z**-isomer. Meanwhile, a NOE effect was observed between the olefinic proton at δ 6.39 and 5-H signal at δ 4.29 and 5-Me at δ 1.54 of the E-isomers.

Finally, the configuration 3,5-*cis* and 3,5-*trans* of the two **5k** isomers was established by NOESY interactions between the diastereotopic protons 4-H_A and 4-H_B and hydrogen or alkyl groups in C-3 and C-5. Thus, the isomer which was assigned the *cis* configuration showed NOESY interactions of 4-H_B at δ 1.83 with 3-Me and 5-CH_2, and of 4-H_B at δ 2.27 with 3-H and 5-H. The 3,5-*trans* stereochemistry of the other **5k** isomer was confirmed by the NOESY interactions between 4-H_B at δ 1.95 with 3-H and 5-CH_2, and of 4-H_A at δ 2.02 with 3-Me and 5-H.

In summary, the reported method is a highly stereoselective and efficient route for the synthesis of new functionalized pyrazolidines with a wide substitution pattern.

EXPERIMENTAL

Starting materials. The pyrazolium tetrafluoroborates were prepared by reaction of the respective pyrazoles with an approximately equivalent amount of triethyloxonium fluoroborate in dry methylene chloride at 25ºC for several hours (12-20 h). The solvent was removed and the product was recrystallized from acetone-ether. 3-Methyl-4-nitro-1-phenylpyrazole and 3,5-dimethyl-4-nitro-1-phenylpyrazole were obtained by nitration[13] of 3-methyl-1-phenylpyrazole[14] and 3,5-dimethyl-1-phenylpyrazole[15], respectively. 4-Benzoyl-3,5-dimethyl-1-phenyl-pyrazole[16] was prepared by benzoylation of 3,5-dimethyl-1-phenylpyrazole. 4-Ethoxycarbonyl-1,3,5-trimethylpyrazole and 4-ethoxycarbonyl-3,5-dimethyl-1-phenylpyrazole were obtained by reaction of ethyl diacetylacetate[17] in absolute ethanol with methylhydrazine and phenylhydrazine, respectively. 5-Ethoxycarbonyl-3-methyl-1-phenylpyrazole[18] was synthesized by reaction of ethyl 2,4-dioxopentanoate[19] with phenylhydrazine in glacial acetic acid together with 3-ethoxycarbonyl-5-methyl-1-phenylpyrazole, which was converted in 3-ethoxycarbonyl-5-methyl-4-nitro-1-phenylpyrazole[20] by nitration. All 4-bromopyrazoles were obtained by bromination of pyrazoles according to the method of Cannon and Whidden[21]. Finally, 4-acetyl-3,5-dimethyl-1-phenylpyrazole was prepared by reaction of triacetylmethane with phenylhydrazine.

IR spectra were measured on a Pye-Unicam SP-1100 or a FT-Mattson Cygnus 100 spectrometer. ^1H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC-300 instrument operating at 300 MHz for ^1H 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 pyrazolium salts using lithium aluminium hydride. To a stirred solution of the pyrazolium salt (1.3 mmol) in dry ether or THF (10 cm^3) was added lithium aluminium hydride (0.1g, 2.6 mmol) in portions at room temperature. After 1 h., saturated ammonium chloride (5 cm^3) was added dropwise to the mixture which was then extracted with ether (3 x 10 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The crude residue was chromatographed (SiO_2, CH_2Cl_2).

General procedure for reduction of pyrazolium salts with sodium boranuide. To a stirred solution of the pyrazolium salt (1.5 mmol) in absolute ethanol (10 cm^3) was added sodium boranuide (0.1g, 3 mmol) in portions at room temperature. After 2 h., saturated aqueous ammonium chloride (10 cm^3) was added slowly to a mixture which was then extracted with ethyl acetate (3 x 10 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated. The crude mixture could be separated by flash chromatography (SiO_2, CH_2Cl_2).

Spectroscopic and analytical data for the pyrazolidines (**2**, **5** and **6**) and 3-pyrazolines (**3** and **4**) are presented below. Results, yields and diastereoisomer distributions are displayed in Table 1.

***trans*-2-Ethyl-3-methyl-4-nitro-1-phenylpyrazolidine 2a**; oil; $R_f(CH_2Cl_2)$ 0.75; $\upsilon_{max}(film)/cm^{-1}$ 1560 and 1370 (NO_2); δ_H 7.15 (2H, dd, J 7.1 and 8.7, NPh H_s meta), 6.96 (2H, d, J 8.7, NPh H_s orto), 6.74 (1H, t, J 7.1, NPh H para), 4.70 (1H, ddd, J 8.5, 7.8 and 5.1, 4-H), 4.35 (1H, dd, J 5.1 and 12.4, 5-H *trans* at NO_2), 3.98 (1H, dq, J 8.5 and 6.5, 3-H), 3.92 (1H, dd, J 7.8 and 12.4, 5-H *cis* at NO_2), 2.74 (2H,m, J 7.1 and 11.7, CH_2N), 1.17 (3H, d, J 6.5, 3-Me) and 1.02 (3H, t, J 7.1, *Me*CH_2N); δ_C 151.88 (=C), 128.78 (=CH meta), 119.23 (=CH para), 113.53 (=CH orto), 91.78 (HC-NO_2), 64.82 (HC-3), 52.87 (H_2C-5), 51.95 (CH_2N), 13.52 (3-Me) and 13.26 (*Me*CH_2N); m/z 235 (M^+, 27%), 206 (M-Et, 5), 187 (M-NO_2-H_2, 4), 173 (M-NO_2-MeH, 23), 159 (M-NO_2-EtH, 75) and 77 (Ph^+, 100). (Found: C, 61.4; H, 7.2; N, 18.0. $C_{12}H_{17}N_3O_2$ requires C, 61.2; H, 7.3; N, 17.8 %).

2-Ethyl-3-methyl-4-nitro-1-phenyl-3-pyrazoline 3a; oil; $R_f(CH_2Cl_2)$ 0.48; $\upsilon_{max}(film)/cm^{-1}$ 1650 (C=C), 1550 and 1360 (NO_2); δ_H 7.20 (2H, dd, J 7.2 and 8.5, NPh H_s meta), 6.99 (2H, d, J 8.5, NPh H_s orto), 6.71 (1H, t, J 7.2, NPh H para), 4.64 (2H, s, 5-H), 3.43 (2H, q, J 7.1 CH_2N), 2.48 (3H, s, 3-Me) and 1.12 (3H, t, J 7.1, *Me* CH_2N); m/z 233 (M^+, 2%), 187 (M-NO_2, 9), 158 (M-NO_2-Et, 78), 157 (M-NO_2-EtH, 69), 130(42) and 77 (Ph^+, 100).

***trans,trans*-2-Ethyl-3,5-dimethyl-4-nitro-1-phenylpyrazolidine *t,t*-2b**; oil; $R_f(CH_2Cl_2)$ 0.78; $\upsilon_{max}(film)/cm^{-1}$ 1550 and 1370 (NO_2); δ_H 7.15 (2H, dd, J 7.2 and 8.6, NPh H_s meta), 6.93 (2H, d, J 8.6, NPh H_s orto), 6.75 (1H, t, J 7.2, NPh H para), 4.73 (1H, dd, J 6.8 and 9.9, 4-H), 4.17 (1H, quintuplet, J 6.8 , 5-H), 3.57 (1H, dq, J 9.9 and 6.7, 3-H), 2.97 and 2.61 (total 2H, dq, J 11.2 and 7.0, CH_AH_BN), 1.57 (3H, d, J 6.8 5-Me), 1.30 (3H, d, J 6.7, 3-Me) and 1.03 (3H, t, J 7.0, *Me* CH_2N); δ_C 151.58 (=C), 128.89 (=CH meta), 119.45 (=CH para), 113.24 (=CH orto), 98.29 (HC-NO_2), 65.84 (HC-5), 63.31 (HC-3), 45.78 (CH_2N), 23.09 (5-Me), 13.77 (3-Me) and 12.56 (*Me* CH_2N); m/z 249 (M^+, 30%), 220 (M-Et, 6), 203 (M-NO_2, 1), 173 (M-NO_2-EtH, 80) and 77 (Ph^+, 100). (Found: C, 62.4; H, 7.8; N, 16.6.$C_{13}H_{19}N_3O_2$ requires C, 62.6; H, 7.7; N, 16.8 %).

***cis,trans*-2-Ethyl-3,5-dimethyl-4-nitro-1-phenylpyrazolidine *c,t*-2b**; oil; $R_f(CH_2Cl_2)$ 0.76; $\upsilon_{max}(film)/cm^{-1}$ 1555 and 1370 (NO_2); δ_H 7.20 (2H, dd, J 7.3 and 8.6, NPh H_s meta), 6.92 (2H, d, J 8.6, NPh H_s orto), 6.74 (1H, t, J 7.3, NPh H para), 5.16 (1H, dd, J 7.4 and 6.8, 4-H), 4.40 (1H, dq, J 7.4

and 6.5 , 5-H), 3.85 (1H, quintuplet, J 6.8, 3-H), 2.80 (2H, m, CH_2N), 1.55 (3H, d, J 6.5, 5-Me), 1.14 (3H, t, J 7.1,*Me*CH_2N) and 0.82 (3H, d, J 6.8, 3-Me); δ_C 151.23 (=C), 128.71 (=CH meta), 118.83 (=CH para), 112.46 (=CH orto), 94.05 (HC-NO_2), 61.83 (HC-5), 59.64 (HC-3), 53.17 (CH_2N), 22.77 (5-Me), 14.68 (*Me*CH_2N) and 13.18 (3-Me); m/z 249 (M^+, 24%), 220 (M-Et, 15), 203 (M-NO_2, 5), 173 (M-NO_2-EtH, 75) and 77 (Ph^+, 100). (Found: C, 62.7; H, 7.9; N, 16.9.$C_{13}H_{19}N_3O_2$ requires C, 62.6; H, 7.7; N, 16.8 %).

***trans,trans*-3-Ethoxycarbonyl-2-ethyl-5-methyl-4-nitro-1-phenylpyrazolidine 2c**; pale yellow crystals, m.p. 60-61ºC (from hexane); R_f(CH_2Cl_2) 0.66; υ_{max}(film)/cm^{-1} 1740 (OC=O), 1560 and 1380 (NO_2); δ_H 7.24 (2H, dd, J 7.1 and 8.6, NPh H_s meta), 7.10 (2H, d, J 8.6, NPh H_s orto), 6.92 (1H, t, J 7.1, NPh H para), 5.42 (1H, dd, J 8.0 and 7.2, 4-H), 4.45 (1H, d, J 8.0 , 3-H), 4.32 (2H, q, J 7.0 CH_2OCO), 4.20 (1H, dq, J 7.2 and 6.5, 5-H), 2.82 (2H, m, J 11.2 and 7.0, CH_2N), 1.62 (3H, d, J 6.5, 5-Me), 1.35 (3H, t, J 7.0, *Me*CH_2OCO) and 1.11 (3H, t, J 7.0, *Me*CH_2N); δ_C 167.57 (OC=O), 149.63 (=C), 128.61 (=CH meta), 121.06 (=CH para), 116.00 (=CH orto), 92.80 (HC-NO_2), 68.22 (HC-CO_2Et), 64.15 (HC-5), 62.26 (*CH_2*OCO), 49.29 (CH_2N), 20.96 (5-Me), 14.00 (*Me* CH_2OCO) and 12.63 (*Me* CH_2N); m/z 307 (M^+, 22%), 278 (M-NO, 1), 188 (M-CO_2Et-NO_2, 22), and 173 (M-PhNNEt, 100). (Found: C, 58.8; H, 6.6; N, 13.9.$C_{15}H_{21}N_3O_4$ requires C, 58.6; H, 6.7; N, 13.7 %).

5-Ethoxycarbonyl-1-ethyl-3-methyl-4-nitro-2-phenyl-3-pyrazoline 4c; oil; R_f(CH_2Cl_2) 0.38; υ_{max}(film)/cm^{-1} 1735 (OC=O), 1620 (C=C), 1560 and 1380 (NO_2); δ_H 7.50 (5H, m,Ph), 4.98 (1H, s, 5-H), 4.36 (2H, q, J 7.1, CH_2OCO), 2.96 (2H, q, J 7.0, CH_2N), 2.45 (3H, s, 3-Me), 1.25 (3H, t, J 7.1 *Me* CH_2OCO) and 1.17 (3H, t, J 7.0, *Me* CH_2N); m/z 305 (M^+, 1%), 232 (M-CO_2Et, 100), 186 (M-CO_2Et-NO_2, 10) and 77 (Ph^+, 18).

***cis*-4-Bromo-2-ethyl-3-methyl-1-phenylpyrazolidine 2d**; oil; R_f(CH_2Cl_2) 0.80; δ_H 7.20 (2H, dd, J 7.8 and 7.3, NPh H_s meta), 6.98 (2H, d, J 7.8, NPh H_s orto), 6.78 (1H, t, J 7.3, NPh H para), 4.68 (1H, dt, J 5.9 and 7.5, 4-H), 4.19 (1H, dd, J 7.5 and 10.6 , 5-H *trans* at Br), 3.56 (1H, dd, J 7.5 and 10.6, 5-H *cis* at Br), 3.36 (1H, dq, J 5.9 and 6.9, 3-H), 2.79 (2H, m, CH_2N), 1.11 (3H, d, J 6.9, 3-Me) and 1.09 (3H, t, J 7.0, *Me* CH_2N); δ_C 152.78 (=C), 128.43 (=CH meta), 118.42 (=CH orto), 113.15 (=CH para), 61.81 (HC-Br), 57.83 (H_2C-5), 52.06 (CH_2N), 47.37 (HC-3), 16.99 (3-Me) and 13.43 (*Me* CH_2N); m/z 268 (M^+, 28%), 239 (M-Et, 53), 189 (M-Br, 4), 159 (M-Br-EtH, 60) and 77 (Ph^+, 100).(Found: C, 53.3; H, 6.5; N, 10.6.$C_{12}H_{17}BrN_2$ requires C, 55.1; H, 6.8; N, 9.9 %).

***cis,trans*-4-Bromo-2-ethyl-3,5-dimethyl-1-phenylpyrazolidine 2e**; oil; R_f(CH_2Cl_2) 0.82; δ_H 7.22 (2H, dd, J 7.2 and 8.7, NPh H_s meta), 7.00 (2H, d, J 8.7, NPh H_s orto), 6.79 (1H, t, J 7.2, NPh H para), 4.41 (1H, dd, J 5.9 and 8.1, 4-H), 3.77 (1H, dq, J 8.1 and 6.4 , 5-H), 3.44 (1H, dq, J 5.9 and 6.8, 3-H), 2.87 (2H, m,J 7.2 and 11.9, CH_2N), 1.62 (3H, d, J 6.4, 5-Me), 1.14 (3H, t, J 7.2, *Me*CH_2N) and 1.05 (3H, d, J 6.8, 3-Me); δ_C 152.74 (=C), 128.45 (=CH meta), 118.37 (=CH para), 112.51 (=CH orto), 66.16 (HC-Br), 62.03 (HC-5), 55.53 (HC-3), 53.01 (CH_2N), 21.37 (5-Me), 16.98 (3-Me) and 13.47 (*Me* CH_2N); m/z 282 (M^+, 8%), 253 (M-Et, 15), 173 (M-Br-EtH, 12) and 77 (Ph^+, 100).(Found: C, 55.3; H, 6.7; N, 9.7.$C_{13}H_{19}BrN_2$ requires C, 55.1; H,6.8;N, 9.9%).

***cis,trans*-4-Bromo-2-ethyl-3-methyl-1,5-diphenylpyrazolidine *c,t*-2f**; oil; R_f(CH_2Cl_2) 0.83; d_H (7.60.(2H, d, J 6.6) and 7.37 (3H, m), 5-Ph), 7.13 (2H, dd, J 7.2 and 8.8, NPh H_s meta), 6.91 (2H, d, J 8.8, NPh H_s orto), 6.76 (1H, t, J 7.2, NPh H para), 4.66 (1H, d, J 9.0, 5-H), 4.40 (1H, dd, J 9.0 and 5.8, 4-H), 3.54 (1H, dq, J 5.8 and 6.6, 3-H), 3.04 and 2.96 (2H, dq, J 11.6 and 7.2, CH_AH_BN), 1.17 (3H, d, J 6.6, 3-Me), and 1.26 (3H, t, J 7.2, *Me* CH_2N); d_C 152.81 , 128.32 , 118.64 and 112.78 (NPh), 142.28, 132.47, 128.15 and 126.43 (5-Ph), 75.03 (HC-5), 66.06 (HC-Br), 57.36 (HC-3), 52.54 (CH_2N), 17.36 (3-

Me) and 13.46 (*Me* CH$_2$N); m/z 344 (M$^+$, 4%), 315 (M-Et, 2), 265 (M-Br, 2), 131 (M-Br-PhNNEt, 100) and 77 (Ph$^+$, 59).(Found: C, 62.4; H, 6.3; N,8.3.C$_{18}$H$_{21}$BrN$_2$ requires C,62.6; H,6.1 ; N,8.1%).

***trans,trans*-4-Bromo-2-ethyl-3-methyl-1,5-diphenylpyrazolidine *t,t*-2f**; oil; R$_f$(CH$_2$Cl$_2$) 0.83; δ$_H$ (7.54.(2H, d, J 6.7) and 7.37 (3H, m), 5-Ph), 7.16 (2H, dd, J 7.2 and 8.4, NPh H$_s$ meta), 6.97 (2H, d, J 8.4, NPh H$_s$ orto), 6.79 (1H, t, J 7.2, NPh H para), 4.79 (1H, d, J 7.9, 5-H), 4.00 (1H, dd, J 7.9 and 10.8, 4-H), 3.41 (1H, dq, J 10.8 and 6.8, 3-H), 3.00 and 2.95 (2H, dq, J 11.5 and 7.1, CH$_A$H$_B$N), 1.37 (3H, d, J 6.8, 3-Me), and 1.24 (3H, t, J 7.1, *Me* CH$_2$N); m/z 344 (M$^+$, 13%), 315 (M-Et, 20), 265 (M-Br, 5), 131 (M-Br-PhNNEt, 82) and 77 (Ph$^+$, 100).(Found: C,62.8; H,6.2; N,8.0.C$_{18}$H$_{21}$N$_2$Br requires C,62.6; H,6.1; N,8.1%).

***trans,trans*-4-Ethoxycarbonyl-1,2,3,5-tetramethylpyrazolidine 2g**; oil; R$_f$ (CH$_2$Cl$_2$) 0.78; υ_{max}(film)/cm^{-1} 1730 (OC=O); δ$_H$ 4.15 (2H, q, J 7.2 CH$_2$OCO), 3.34 (2H, dq, J 11.6 and 6.6, 3-H and 5-H), 2.66 (6H, s, 2 x MeN), 2.48 (1H, t, J 11.6, 4-H), 1.23 (6H, d, J 6.6, 3-Me and 5-Me), and 1.20 (3H, t, J 7.2, *Me* CH$_2$OCO); δ$_C$ 171.68 (OC=O), 63.25 (HC-CO$_2$Et), 59.83 (*C*H$_2$OCO), 58.33 (*HC* -Me), 43.71 (MeN), 14.16 (*Me* CH$_2$OCO) and 13.64 (*Me* CH); m/z 200 (M$^+$, 44%), 185 (M-Me, 100), 155 (M-OEt, 31), and 111 (M-CO$_2$Et-MeH, 62). (Found: C,60.2; H,10.0; N,14.1.C$_{10}$H$_{20}$N$_2$O$_2$ requires C,60.0; H,10.1; N,14.0%).

4-Ethoxycarbonyl-1,2,3,5-tetramethylpyrazoline 3g; oil; R$_f$(CH$_2$Cl$_2$) 0.63; υ_{max}(film)/cm^{-1} 1720 (OC=O) and 1640 (C=C); δ$_H$ 4.18 (2H, q, J 7.1 CH$_2$OCO), 3.84 (1H, q, J 6.3, 5-H), 2.92 (3H, s, 2-Me), 2.38 (3H, s, 1-Me), 2.17 (3H, s, 3-Me), 1.35 (3H, t, J 7.1,*Me* CH$_2$OCO) and 1.22 (3H, d, J 6.3, 5-Me); δ$_C$ 163.95 (OC=O), 154.27 (=C Me), 107.43 (=C-CO$_2$Et), 65.24 (HC-5), 56.82 (*C*H$_2$OCO), 46.21 (2-Me), 44.46 (1-Me), 14.35 (*Me* CH$_2$OCO), 14.01 (3-Me) and 13.26 (5-Me); m/z 188 (M$^+$, 6%), 173 (M-Me, 100), 143 (M-OEt, 12), and 115 (M-CO$_2$Et, 8).

***trans,trans*-4-Ethoxycarbonyl-2-ethyl-3,5-dimethyl-1-phenylpyrazolidine 2h**; oil; R$_f$(CH$_2$Cl$_2$) 0.71; υ_{max}(film)/cm^{-1} 1740 (OC=O); δ$_H$ 7.20 (2H, dd, J 8.6 and 7.3, NPh H$_s$ meta), 7.03 (2H, d, J 8.6, NPh H$_s$ orto), 6.76 (1H, t, J 7.3, NPh H para), 4.16 (2H, q, J 7.1 CH$_2$OCO), 3.90 (1H, dq, J 8.4 and 6.5, 5-H), 3.31 (1H, dq, J 11.0 and 6.7, 3-H), 2.93 (1H, dd, J 11.0 and 8.4, 4-H), 2.91 and 2.60 (total 2H, dq, J 11.2 and 7.0, CH$_A$H$_B$N), 1.55 (3H, d, J 6.5, 5-Me), 1.29 (3H, d, J 6.7, 3-Me), 1.25 (3H, t, J 7.1,*Me* CH$_2$OCO) and 1.11 (3H, t, J 7.0, *Me*CH$_2$N); δ$_C$ 172.44 (OC=O), 152.47 (=C), 128.63 (=CH meta), 118.24 (=CH orto), 113.06 (=CH para), 65.13 (HC-CO$_2$Et), 61.75 (HC-5), 60.81 (*C*H$_2$OCO), 59.48 (HC-3), 45.20 (CH$_2$N), 23.98 (5-Me), 14.66 (3-Me), 14.24 (*Me* CH$_2$OCO) and 12.64 (*Me* CH$_2$N); m/z 276 (M$^+$, 78%), 247 (M-Et, 100), 231 (M-OEt, 5), 201 (M-OEt-EtH, 30), 173 (M-CO$_2$Et-EtH, 70) and 77(Ph$^+$, 85). (Found: C,69.3; H,8.6; N,10.3.C$_{16}$H$_{24}$N$_2$O$_2$ requires C,69.5; H,8.7; N,10.1%).

4-Ethoxycarbonyl-2-ethyl-3,5-dimethyl-1-phenyl-3-pyrazoline 3h; oil; R$_f$(CH$_2$Cl$_2$) 0.50; υ_{max}(film)/cm^{-1} 1720 (OC=O) and 1650 (C=C); δ$_H$ 7.23 (2H, dd, J 7.8 and 8.3, NPh H$_s$ meta), 6.95 (2H, d, J 7.8, NPh H$_s$ orto), 6.90 (1H, t, J 8.3, NPh H para), 4.44 (1H, q, J 6.2, 5-H), 4.07 (2H, q, J 7.1, CH$_2$OCO), 3.40 and 3.07 (total 2H, dq, J 14.5 and 7.0, CH$_A$H$_B$N), 2.25 (3H, s, 3-Me), 1.43 (3H, d, J 6.2, 5-Me), 1.20 (3H, t, J 7.1,*Me* CH$_2$OCO) and 1.09 (3H, t, J 7.0, *Me* CH$_2$N); δ$_C$ 165.07 (OC=O), 154.63 (=C Me), 152.34 (=C, Ph), 128.90 (=CH meta), 121.27 (=CH para), 115.18 (=CH orto), 103.50 (=C-CO$_2$Et), 68.18 (HC-5), 58.86 (*C*H$_2$OCO), 43.99 (CH$_2$N), 24.47 (5-Me), 14.37 (*Me* CH$_2$OCO), 14.22 (3-Me) and 12.01 (*Me* CH$_2$N); m/z 274 (M$^+$, 10%), 259 (M-Me, 89), 231 (13), 229 (M-OEt, 8), 201 (M-CO$_2$Et, 1) and 77 (Ph$^+$, 100).

4-Ethoxycarbonyl-1-ethyl-3,5-dimethyl-2-phenyl-3-pyrazoline 4h; oil; R$_f$(CH$_2$Cl$_2$) 0.43; υ_{max}(film)/cm^{-1} 1725 (OC=O) and 1660 (C=C); δ$_H$ 7.30 (2H, dd, J 7.3 and 8.2, NPh H$_s$ meta), 6.97

(2H, d, J 8.2, NPh H_s orto), 6.93 (1H, t, J 7.3, NPh H para), 4.18 (2H, q, J 7.1, CH_2OCO), 3.99 (1H, q, J 6.2, 5-H), 2.75 (2H, q, J 7.2, CH_2N), 2.18 (3H, s, 3-Me), 1.29 (3H, d, J 6.2, 5-Me), 1.23 (3H, t, J 7.1,*Me* CH_2OCO) and 1.01 (3H, t, J 7.2, *Me* CH_2N); δ_C 165.94 (OC=O), 152.56 (=C Me), 142.51 (=C, Ph), 128.56 (=CH meta), 124.15 (=CH para), 116.07 (=CH orto), 103.12 (=C-CO_2Et), 62.45 (HC-5), 50.91 (*C*H_2OCO), 43.74 (CH_2N), 23.53 (3-Me), 14.14 (*Me* CH_2OCO), 13.31 (5-Me) and 11.28 (*Me* CH_2N); m/z 274 (M^+, 8%), 259 (M-Me, 100), 231 (21), 229 (M-OEt, 10)and 77(Ph^+, 31).

***cis*-2-Ethyl-3,5-dimethyl-4-methylen-1-phenylpyrazolidine *c*-6h;** oil; $R_f(CH_2Cl_2)$ 0.82; υ_{max}(film)/cm^{-1} 1660 (C=C) and 890 (=CH_2); δ_H 7.30 (2H, dd, J 7.2 and 8.6, NPh H_s meta), 7.15 (2H, d, J 8.6, NPh H_s orto), 6.84 (1H, t, J 7.2, NPh H para), 5.08 (1H, t, J 2.3, C=CH_A), 5.00 (1H, t, J 2.5, C=CH_B), 4.17 (1H, m, 5-H), 3.62 (1H, m, 3-H), 2.78 and 2.41 (total 2H, dq, J 11.4 and 7.1, CH_AH_BN), 1.59 (3H, d, J 6.6 5-Me), 1.37 (3H, d, J 6.7, 3-Me) and 1.16 (3H, t, J 7.1, *Me* CH_2N); δ_C 157.53 (=C), 152.54, 128.69, 117.82 and 111.94 (Ph), 103.49 (=CH_2), 60.50 (HC-5), 59.12 (HC-3), 45.11 (CH_2N), 22.01 (5-Me), 13.09 (3-Me) and 12.22 (*Me* CH_2N); m/z 216 (M^+, 20%), 201 (M-Me, 12), 187 (M-Et, 25) and 77 (Ph^+, 100). (Found: C, 77.9; H,9.4; N,13.0. $C_{14}H_{20}N_2$ requires C, 77.7; H,9.3; N,12.9%).

***trans*-2-Ethyl-3,5-dimethyl-4-methylen-1-phenylpyrazolidine *t*-6h;** oil; $R_f(CH_2Cl_2)$ 0.82; υ_{max}(film)/cm^{-1} 1660 (C=C) and 890 (=CH_2); δ_H 7.25 (2H, dd, J 7.0 and 8.7, NPh H_s meta), 7.10 (2H, d, J 8.7, NPh H_s orto), 6.80 (1H, t, J 7.0, NPh H para), 5.12 (1H, dd, J 2.6 and J 1.8, C=CH_A), 5.06 (1H, dd, J 2.3 and 1.4, C=CH_B), 4.21 (1H, m, 5-H), 3.62 (1H, m, 3-H), 2.80 and 2.78 (total 2H, dq, J 10.3 and 7.1, CH_AH_BN), 1.59 (3H, d, J 6.6, 5-Me), 1.16 (3H, t, J 7.1, *Me* CH_2N) and 1.06 (3H, d, J 6.8, 3-Me); δ_C 158.21 (=C), 152.84, 128.54, 117.29 and 112.26 (Ph), 104.83 (=CH_2), 65.21 (HC-5), 62.10 (HC-3), 55.55 (CH_2N), 22.68 (5-Me), 15.26 (3-Me) and 12.36 (*Me* CH_2N); m/z 216 (M^+, 80%), 201 (M-Me, 45), 187 (M-Et, 90) and 77 (Ph^+, 100). (Found: C,77.6; H,9.2; N,13.1. $C_{14}H_{20}N_2$ requires C,77.7; H,9.3; N,12.9%).

***trans,trans* - 2-Ethyl-4-(1-hydroxyethyl)-3,5-dimethyl-1-phenylpyrazolidine 5i;** oil; mixture of diastereoisomers *syn*/*anti*; $R_f(CH_2Cl_2)$ 0.32; υ_{max}(film)/cm^{-1} 3430 (OH); δ_H 7.22 (2H, dd, J 7.3 and 8.1, NPh H_s meta), 6.96 (2H, d, J 8.1, NPh H_s orto), 6.75 (1H, t, J 7.3, NPh H para), 4.01 (1H, m, *C*HOH), 3.59 (1H, m, 5-H), 3.27 (1H, m, 3-H), 2.83 and 2.59 (2H, dq, J 11.4 and 7.1, CH_AH_BN), 2.35 (1H, m, 4-H), 2.04 (1H, s br, OH), 1.52 and 1.46 (1H, d, J 6.7, 5-Me both isomers), 1.25 and 1.16 (3H, d, J 6.5, *Me*CHOH both isomers), 1.05 (3H, t, J 7.1*Me* CH_2N) and 0.85 and 0.90 (3H, d, J 6.6, 3-Me, both isomers); m/z 248 (M^+, 31%), 233 (M-Me, 6), 219 (M-Et, 61), 199 (M-MeH-H_2O, 100), and 77 (Ph^+, 53). (Found: C,72.7; H,9.8; N,11.5. $C_{15}H_{24}N_2O$ requires C,72.5; H,9.7; N,11.3%).

Z,*cis*-2-Ethyl-4-ethylen-3,5-dimethyl-1-phenylpyrazolidine Z,*c*-6i; oil; $R_f(CH_2Cl_2)$ 0.78; υ_{max}(film)/cm^{-1} 1670 (C=C) and 830 (C=CH); δ_H 7.28 (2H, dd, J 7.3 and 8.4, NPh H_s meta), 7.17 (2H, d, J 8.4, NPh H_s orto), 6.83 (1H, t, J 7.3, NPh H para), 5.22 (1H, qt, J 6.8 and 1.9, =CH), 4.31 (1H, dq, J 1.9 and 6.6, 5-H), 3.66 (1H, dq, J 1.9 and 6.7, 3-H), 2.83 and 2.60 (2H, dq, J 11.3 and 7.1, CH_AH_BN), 1.68 (3H, d, J 6.8, =C*Me*), 1.36 (3H, d, J 6.6, 5-Me), 1.25 (3H, d, J 6.7, 3-Me) and 1.08 (3H, t, J 7.1, *Me* CH_2N); δ_C 153.24, 128.36, 118.43 and 112.33 (Ph), 149.78 (=C), 114.23 (=CH), 60.04 (HC-5), 59.41 (HC-3), 45.21 (CH_2N), 21.46 (5-Me), 18.91 (=C*Me*), 12.72(3-Me) and 12.07 (*Me* CH_2N); m/z 230 (M^+, 12%), 215 (M-Me, 100), 199 (M-EtH-H_2, 36) and 77 (Ph^+, 21). (Found: C,78.0; H,9.7; N,12.4. $C_{15}H_{22}N_2$ requires C,78.2; H,9.6; N,12.2%).

E,*cis*-2-Ethyl-4-ethylen-3,5-dimethyl-1-phenylpyrazolidine E,*c*-6i; oil; $R_f(CH_2Cl_2)$ 0.78; υ_{max}(film)/cm^{-1} 1670 (C=C) and 830 (C=CH); δ_H 7.26 (2H, dd, J 7.3 and 8.1, NPh H_s meta), 7.10 (2H, d, J 8.1, NPh H_s orto), 6.85 (1H, t, J 7.3, NPh H para), 5.29 (1H, qt, J 7.4 and 2.1, =CH), 4.18 (1H, dq, J 2.1 and 6.5, 5-H), 3.43 (1H, dq, J 2.1 and 6.8, 3-H), 2.75 and 2.50 (2H, dq, J 11.4 and 7.1, CH$_A$H$_B$N), 1.65 (3H, d, J 7.4, =C*Me*), 1.47 (3H, d, J 6.5, 5-Me), 1.12 (3H, d, J 6.8, 3-Me) and 1.05 (3H, t, J 7.1, *Me* CH$_2$N); δ_C 155.41, 128.75, 118.27 and 112.62 (Ph), 150.03 (=C), 115.11 (=CH), 62.48 (HC-5), 57.23 (HC-3), 42.69 (CH$_2$N), 25.32 (5-Me), 20.04 (=C*Me*), 12.45 (3-Me) and 12.23 (*Me* CH$_2$N); m/z 230 (M$^+$, 62%), 215 (M-Me, 44), 201 (M-Et, 78) and 77 (Ph$^+$, 100). (Found: C,78.4; H,9.7; N,12.0. C$_{15}$H$_{22}$N$_2$ requires C,78.2; H,9.6; N,12.2%).

***syn,trans,trans*-2-Ethyl-4-(hydroxy(phenyl)methyl)-3,5-dimethyl-1-phenylpyrazolidine *s,t,t*-5j**; oil; R$_f$(CH$_2$Cl$_2$) 0.30; υ_{max}(film)/cm^{-1} 3530 sharp and 3400 broad (OH); δ_H 7.64-7.27 (5H,m, CPh), 7.20 (2H, dd, J 7.2 and 7.7, NPh H$_s$ meta), 7.00 (2H, d, J 7.7, NPh H$_s$ orto), 6.73 (1H, t, J 7.2, NPh H para), 4.70 (1H, d, J 9.1, C*H*OH), 3.78 (1H, dq, J 6.8 and 6.3, 5-H), 2,96 (1H, m, 4-H), 2.92 (1H, m, 3-H), 2.88 and 2.78 (2H, dq, J 11.8 and 7.1, CH$_A$H$_B$N), 2.10 (1H, s br, OH), 1.64 (3H, d, J 6.3, 5-Me), 1.08 (3H, t, J 7.1, *Me* CH$_2$N) and 0.80 (3H, d, J 6.5, 3-Me); δ_C 152.38, 128.50, 117.32 and 112.29 (NPh), 143.08, 128.77, 126.81 and 125.45 (*Ph*COH), 75.29 (CHOH), 62.71 (HC-5), 60.48 (HC-3), 55.95 (HC-4), 51.66 (CH$_2$N), 25.19 (5-Me), 15.71 (3-Me), and 12.23 (*Me* CH$_2$N); m/z 310 (M$^+$, 100%), 281 (M-Et, 57), 263 (M-Et-H$_2$O, 57), and 173 (M-Et-PhCHOH, 21). (Found: C,77.6; H,8.5; N,8.8. C$_{20}$H$_{26}$N$_2$O requires C,77.4; H,8.4; N,9.0%).

***anti,trans,trans*-2-Ethyl-4-(hydroxy(phenyl)methyl)-3,5-dimethyl-1-phenylpyrazolidine *a,t,t*-5j**; oil; R$_f$(CH$_2$Cl$_2$) 0.28; υ_{max}(film)/cm^{-1} 3450 (OH); δ_H 7.44-7.29 (5H,m, CPh), 7.19 (2H, dd, J 7.2 and 8.0, NPh H$_s$ meta), 6.96 (2H, d, J 8.0, NPh H$_s$ orto), 6.73 (1H, t, J 7.2, NPh H para), 4.55 (1H, d, J 8.2, C*H*OH), 3.26 (1H, quintuplet, J 6.7, 5-H), 3.12 (1H, dq, J 9.5 and 6.4, 3-H), 2.93 and 2.64 (total 2H, dq, J 11.3 and 7.1, CH$_A$H$_B$N), 2.35 (1H, ddd, J 6.8, 8.2 and 9.5, 4-H), 1.40 (3H, d, J 6.7, 5-Me), 1.06 (3H, t, J 7.1, *Me* CH$_2$N) and 0.87 (3H, d, J 6.4, 3-Me); δ_C 151.64, 128.15, 115.76 and 112.83 (NPh), 142.79, 129.33, 127.42 and 125.54 (*Ph*CHOH), 75.15 (CHOH), 64.81(HC-5), 61.40 (HC-3), 51.32 (CH$_2$N), 49.63 (HC-4), 23.46 (5-Me), 17.42 (3-Me), and 12.70 (*Me* CH$_2$N); m/z 310 (M$^+$, 56%), 281 (M-Et, 40), 263 (M-Et-H$_2$O, 25), 173 (M-Et-PhCHOH, 18) and 77 (Ph$^+$, 100). (Found: C,77.6; H,8.3; N,9.2. C$_{20}$H$_{26}$N$_2$O requires C,77.4;H,8.4; N,9.0 %).

Z,*cis*-2-Ethyl-3,5-dimethyl-1-phenyl-4-phenylmethylenpyrazolidine Z,*c*-6j; oil; R$_f$(CH$_2$Cl$_2$) 0.72; υ_{max}(film)/cm^{-1} 1650 (C=C) and 820 (C=CH); δ_H 7.59-7.20 (7H, m, Ph), 7.12 (2H, d, J 7.7 Ph), 6.75 (1H, t, J 7.0, Ph), 6.32 (1H, s, =C*H*Ph), 4.80 (1H, q, J 6.4, 5-H), 3.75 (1H, q, J 6.8, 3-H), 2.84 and 2.64 (2H, dq, J 11.3 and 7.1, CH$_A$H$_B$N), 1.63 (3H, d, J 6.4, 5-Me), 1.19 (3H, d, J 6.8, 3-Me) and 1.09 (3H, t, J 7.1, *Me* CH$_2$N); m/z 292 (M$^+$, 40%), 277 (M-Me, 28), 263 (M-Et, 72) and 77 (Ph$^+$, 100). (Found: C,82.0; H,8.2; N,9.8. C$_{20}$H$_{24}$N$_2$ requires C,82.1;H,8.3; N,9.6 %).

E,*cis*-2-Ethyl-3,5-dimethyl-1-phenyl-4-phenylmethylenpyrazolidine E,*c*-6j; oil; R$_f$(CH$_2$Cl$_2$) 0.72; υ_{max}(film)/cm^{-1} 1645 (C=C) and 820 (C=CH); δ_H 7.56-7.18 (7H, m, Ph), 7.08 (2H, d, J 7.8 Ph), 6.72 (1H, t, J 7.0, Ph), 6.39 (1H, s, =C*H*Ph), 4.29 (1H, q, J 6.5, 5-H), 4.00 (1H, q, J 6.7, 3-H), 3.00 and 2.82 (2H, dq, J 11.2 and 7.1, CH$_A$H$_B$N), 1.54 (3H, d, J 6.5, 5-Me), 1.39 (3H, d, J 6.7, 3-Me) and 1.10 (3H, t, J 7.1, *Me* CH$_2$N); m/z 292 (M$^+$, 74%), 277 (M-Me, 42), 263 (M-Et, 64), 233 (13) and 77 (Ph$^+$, 100). (Found: C,82.3; H,8.3; N,9.4. C$_{20}$H$_{24}$N$_2$ requires C,82.1;H,8.3; N,9.6 %).

***cis*-2-Ethyl-5-hydroxymethyl-3-methyl-1-phenylpyrazolidine *c*-5k**; oil; R$_f$(CH$_2$Cl$_2$) 0.17; υ_{max}(film)/cm^{-1} 3387 br (OH); δ_H 7.26-7.19 (4H, m, Ph), 6.84-6.79 (1H, m, Ph), 3.85 (2H, m, CH$_A$H$_B$O), 3.71 (1H, m, 5-H), 3.19 (1H, ddq, J 5.8, 12,.4 and 6.7, 3-H), 2.89 and 2.60 (total 2H, dq, J 11.5 and 7.1, CH$_A$H$_B$N), 2.27 (1H, ddd, J 12.1, 6.8 and 5.8, 4-H *trans* at Me and CH$_2$OH), 1.96 (1H, s br, OH), 1.83 (1H, ddd, J 12.1, 8.2 and 12.4, 4-H *cis* at Me and CH$_2$OH), 1.29 (3H, d, J 6.7, 3-Me) and 1.13 (3H, t, J 7.1, *Me* CH$_2$N); δ_C 153.54 (=C), 128.32 (=CH meta), 118.59 (=CH para), 113.67 (=CH orto), 65.60 (CH_2OH), 65.60 (HC-5), 57.38 (HC-3), 43.56 (CH_2N), 35.38 (H_2C-4), , 15.27 (3-Me) and 12.89 (*Me* CH_2N); m/z 220 (M^+, 32%), 205 (M-Me, 2), 191 (M-Et, 42), 189 (M-CH_2OH, 38), 159 (M-CH_2OH-EtH, 9) and 77 (Ph^+, 100). (Found: C,71.1; H,9.2; N,12.5. $C_{13}H_{20}N_2O$ requires C,70.9; H,9.1; N,12.7%)

***trans*-2-Ethyl-5-hydroxymethyl-3-methyl--1-phenylpyrazolidine *t*-5k**; oil; $R_f(CH_2Cl_2)$ 0.19; υ_{max}(film)/cm^{-1} 3380 br (OH); δ_H 7.26-7.19 (4H, m, Ph), 6.84-6.79 (1H, m, Ph), 3.92 (1H, m, 5-H), 3.85 (2H, m, CH_AH_BO), 3.30 (1H, dquintuplet, J 9.3 and 6.7, 3-H), 2.79 (2H, m, CH_2N), 2.20 (1H, s br, OH), 2.02 (1H, ddd, J 12.3, 10.3 and 5.9, 4-H trans at CH_2OH and cis at Me), 1.95 (1H, ddd, J 12.3, 7.8 and 6.7, 4-H *trans* at Me and cis at CH_2OH), 1.14 (3H, t, J 7.1*Me*CH_2N) and 0.96(3H, d, J 6.8, 3-Me); δ_C 153.87 (=C), 128.50 (=CH meta), 118.72 (=CH para), 113.67 (=CH orto), 67.67 (CH_2OH), 67.06 (HC-5), 59.06 (HC-3), 52.69 (CH_2N), 37.07 (H_2C-4), , 20.87 (3-Me) and 13.58 (*Me* CH_2N); m/z 220 (M^+, 26%), 205 (M-Me, 3), 191 (M-Et, 20), 189 (M-CH_2OH, 39), 159 (M-CH_2OH-EtH, 2) and 77 (Ph^+, 100). (Found: C,70.8; H,9.0; N,12.8. $C_{13}H_{20}N_2O$ requires C,70.9; H,9.1; N,12.7%).

3-Ethoxycarbonyl-1-ethyl-5-methyl-2-phenyl-3-pyrazoline 4k; oil; $R_f(CH_2Cl_2)$ 0.21; υ_{max}(film)/cm^{-1} 1725 (OC=O), 1660 (C=C); δ_H 7.30 (2H, dd, J 7.4 and 8.3, Ph H_s meta), 7.12 (2H, d, J 8.3, Ph H_s orto), 6.95 (1H, t, J 7.4, Ph H para), 6.40 (1H, d, J 3.1, 4-H), 4.28 (2H, q, J 7.1, CH_2OCO), 3.62 (1H, dq, J 3.1 and 6.7, 5-H), 2.99 (2H, m, CH_2N), 1.26 (3H, t, J 7.1,*Me* CH_2OCO), 1.13 (3H, t, J 7.2, *Me* CH_2N) and 1.07 (3H, d, J 6.7, 5-Me); m/z 260 (M^+, 6%), 245 (M-Me, 45), 231 (M-Et, 5), 215 (M-OEt, 32), 187 (M-CO_2Et, 18) and 77(Ph^+, 100).

***trans*-5-Ethoxycarbonyl-2-ethyl-3-methyl-1-phenylpyrazolidine 2k**; oil; $R_f(CH_2Cl_2)$ 0.65; υ_{max}(film)/cm^{-1} 1738 (OC=O); δ_H 7.28-7.17 (4H, m, Ph), 6.87-6.77 (1H, m, Ph), 4.21 (2H, q, J 7.1 CH_2OCO), 3.98 (1H, dd, J 7.2 and 6.4, 5-H), 3.60 (1H, m, 3-H), 2.57 and 2.87 (2H, dq, J 11.5 and 7.0, CH_AH_BN), 2.33 (1H, ddd, J 9.8, 6.4 and 12.4, 4-H *trans* at CO_2Et and *cis* at Me), 2.23 (1H, ddd, J 7.2, 5.5 and 12.4, 4-H *cis* at CO_2Et and *trans* at Me), 1.21 (3H, t, J 7.1,*Me* CH_2OCO), 1.18 (3H, d, J 6.6, 3-Me) and 1.11 (3H, t, J 7.0, *Me* CH_2N); m/z 262 (M^+, 44%), 233 (M-Et, 42), 189 (M-CO_2Et, 73) and 77(Ph^+, 100). (Found: C,68.5; H,8.5; N,10.5.$C_{15}H_{22}N_2O_2$ requires C,68.7; H,8.4; N,10.7%).

X-Ray-crystal structure determination of the pyrazolidine 2c. Suitable yellow crystals of **2c** were grown from hexane.

Crystal data. $C_{15}H_{21}N_3O_4$, M=307.35, monoclinic, $P2_1/c$, a=8.733(2), b=8.058(2), c=23.985(5) A, β=100.20(3)^o, Z=4, F(000)=656, D_c=1.229 g.cm^{-3}, λ(CuKα)= 1.54178 A, μ(CuKα)=0.746 mm^{-1}.

Structure, analysis and refinement. 1758 reflections (1705 unique) were collected on a Rigaku AFC7 four-circle diffractometer coupled to a copper target rotating anode X-ray source, using $\omega/2\theta$ method ($5^o<2\theta<45^o$). Three standard reflections were measured every 100 reflections as orientation and intensity control, and no significant intensity decay was observed. The structure was solved by direct methods, and subsequent Fourier difference techniques[22]. The structure was refined by a full-matrix least-squares based on F^2 to R=0.056 with all non-H atoms anisotropic[23]; H-atoms were placed in idealized positions and allowed to ride on the relevant C atom. Largest peak and hole in the final differences map 0.18 and 0.228 eA^{-3}, respectively. The atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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