Pergamon

Tetrahedron, Vol. 53, No. 52, pp. 17735-17750, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10239-3

Synthesis of New Chiral N-Substituted Fused Pyrazoles and Pyrazolinols.

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Abstract: Treatment of β-diketones and the corresponding β-enaminoketones, having modified carane (2-ethyl-6,6-dimethylbicyclo[3.1.0]hexane) and p-menthane (3-ethyl-1-isopropylcyclopentane) skeletons, with aryl- and alkylhydrazines results in regioselective formation of N-substituted pyrazoles or stable pyrazolinols depending on the nature of the substituent at the hydrazine nitrogen.
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N-Substituted pyrazoles are of interest as chiral auxiliary for stereoselective synthesis[1] and for the resolution of certain racemic compounds.[2] The monoterpene hydrocarbons 3-carene and limonene are among the most available and low cost natural sources of chirality, and β-enaminones and β-diketones with modified carane and *p*-menthane skeletons are readily accessible compounds.[3] β-Enaminones and β-diketones are the most convenient starting compounds for the synthesis of pyrazoles.[4,5] In order to obtain new chiral N-substituted pyrazoles, we have studied the reaction of compounds **1-4** with a number of alkyl- and arylhydrazines.

Reaction of compounds **1-4** with alkylhydrazines lacks regioselectivity and usually proceeds with the formation of both N-positional isomers **5** and **6**, or **8** and **9**. Enaminones **2** and **4** react with methylhydrazine or hydrazinoethanol to afford mixtures of positional isomers. Reaction of diketone **3** with methylhydrazine or hydrazinoethanol also gives mixtures of positional isomers, with predominance of the N^a-substituted **9**. In the case of diketone **1**, only the reaction with methylhydrazine proceeds non-regioselectively giving a 1:2 mixture of isomers **5a** and **6a**. By contrast, when diketone **1** is treated with hydrazinoethanol or hydrazinoacetic acid ethyl ester, regioselective formation of compounds **5b** and **5c** occurs.

Reaction of diketones **1** and **3** with arylhydrazines proceeds regioselectively to give a single isomer of N-substituted pyrazoles. The relative reactivity of the carbonyl groups of diketone **1** differs greatly due to structural peculiarities of cyclopropane-fused derivatives[6] and the formation of a single positional isomer of pyrazole **5** with the aryl substituent at N^b is observed. Surprisingly, reaction of arylhydrazines with diketone **3**, which is known to be a complex mixture of isomeric forms[2], also results in the selective formation of the N^b-isomer. Reaction of acyclic enaminones with arylhydrazine is known to proceed regioselectively with the attack of the terminal amino group of substituted hydrazine to the β-carbon of enaminone.[4] The reaction of

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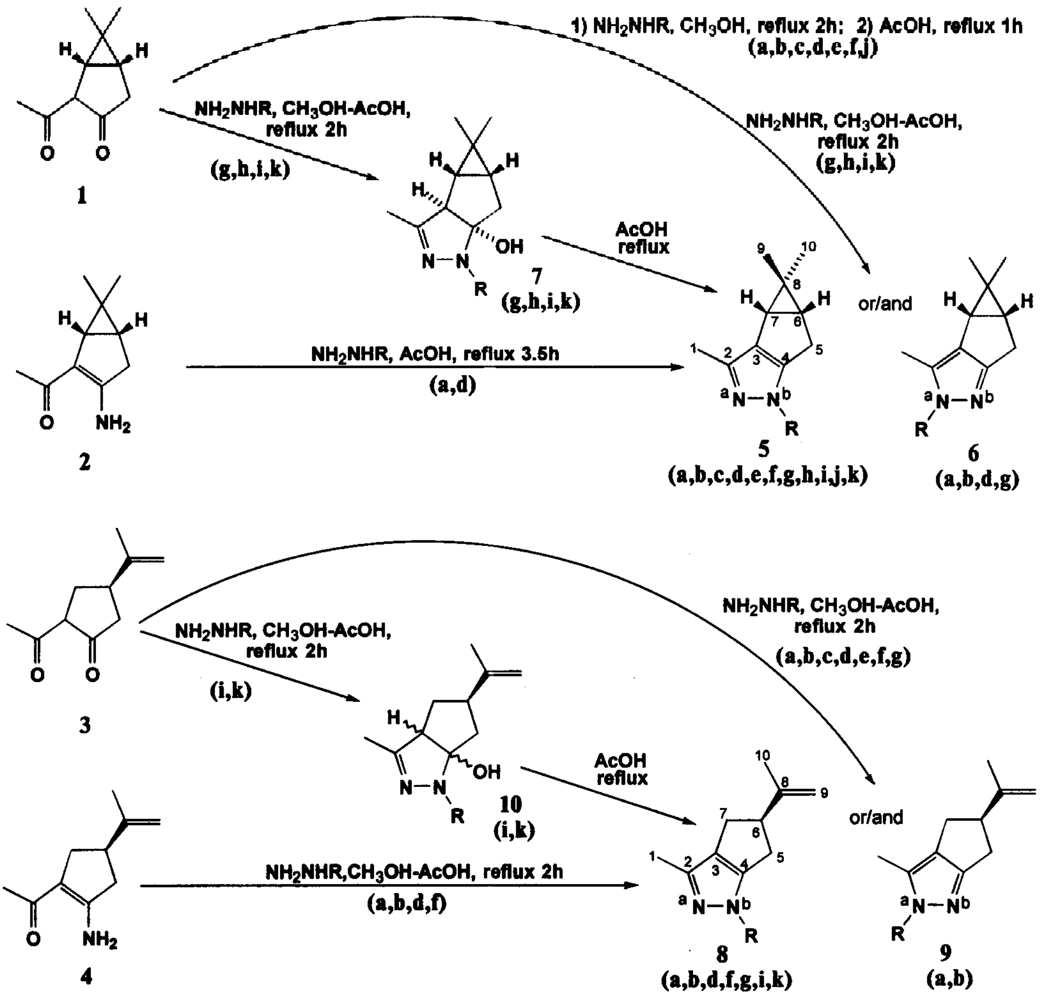
Scheme 1.

Yields and structure of the substituent R are listed in the Table on the next page.

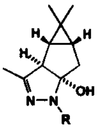
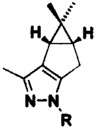
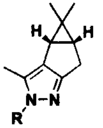
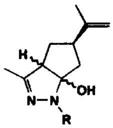
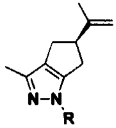
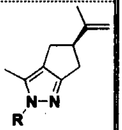
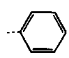
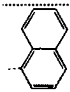
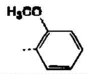
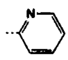
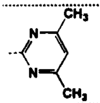
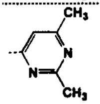
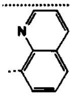
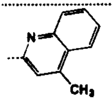
The numbering scheme for the molecules does not coincide with the numbering of the system according to IUPAC and is given for NMR interpretation only.



enaminone **2** with arylhydrazines was found to require quite rigid conditions (refluxing in acetic acid) and proceeds with the formation of both positional isomers **5** and **6**. At the same time, enaminone **4** with the modified *p*-menthane carbon frame reacts with arylhydrazines to afford selectively the positional isomer **8** corresponding to the attack of the terminal amino group of the arylhydrazine at the carbonyl carbon of the enaminone.

The assignment of the structure of the positional isomers was carried out on the basis of detailed NMR investigations. Neither ^{1}H NMR nor ^{14}N NMR spectra are sufficient to make an assignment. Isomers **5** and **6** (as well as **8** and **9**) have different ^{13}C NMR spectra (in the region 120-165 ppm), but it was impossible to determine the position of a substituent without additional data.

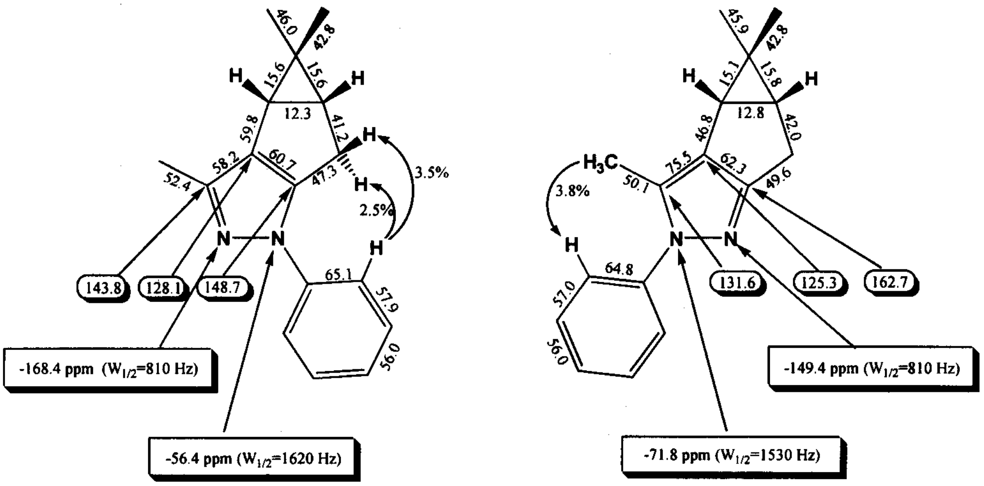
Table. Yields of the Substituted Pyrazoles and Pyrazolinols Prepared According to the ***Scheme 1***.

Structure of the substituent R	Method	Compounds type					
		 **7**	 **5**	 **6**	 **10**	 **8**	 **9**
		Yields					
a $-CH_3$	C	-	24%	49%	-	22%[a] 37%[b]	56%[a] 38%[b]
b $-CH_2CH_2OH$	C	-	66%	-	-	21%[a] 35%[b]	54%[a] 36%[b]
c $-CH_2CO_2CH_2CH_3$	C	-	49%	-			
d 	C D	 -	 23%	 11%	- 	74%[a] 65%[b] 	-
e 	C	-	52%	-			
f 	C	-	68%	-	-	62%[a] 45%[b]	-
g 	A B	34% -	56% 52%	 -	 -	 69%	 -
h 	A B	55% -	- 68%	- -			
i 	A B	54% -	- 55%	- -	93% (7:1)[c] .	- 74%	- -
j 	C	-	58%	-			
k 	A B	46% -	- 59%	- -	75% (2:1)[c] .	19% 71%	. -

[a] Starting from diketone **3**. [b] Starting from enaminone **4**. [c] Mixture of diastereomers.

A pair of N-phenylpyrazoles **5d** and **6d**, which can be separated by column chromatography, was studied by ^{13}C NMR. Measuring of ^{13}C-^{13}C coupling constants in these molecules allowed unambiguous assignments of the carbons C2, C3 and C4, whereas measuring of homonuclear Overhauser effects made it possible to determine the position of the phenyl group. Some NMR parameters of the isomers **5d** and **6d** are shown below on ***Fig. 1***. As can be seen from the carbon chemical shifts (C2, C3 and C4) and carbon-carbon couplings (C2-C3 and C3-C4), the nitrogens give rise to a markedly different delocalization of electron densities in these pyrazole isomers. These data are in agreement with the results of theoretical data obtained by semi-empirical quantum chemical calculations (***Fig.** 2*). The pyrazole ring in isomer **5d** seems "more aromatic" because the bond lengths C2-C3 and C3-C4 are almost equal (as well as the corresponding carbon-carbon couplings). In contrast, isomer **6d** shows poorer delocalization in the pyrazole ring: *l*(C2-C3)=1.381 Å, *J*(C2-C3)=75.5 Hz; *l*(C3-C4)=1.437 Å, *J*(C3-C4)=62.3 Hz. Calculations for pair **8d** and **9d** demonstrated the same effects. Moreover, the calculations for pairs of isomers **5** and **6**, **8** and **9** with a variety of substituents **R** proved that the degree of delocalization in the pyrazole moiety of 3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-c]pyrazole ring system depends very slightly on the nature of the substituent, but strongly depends on the position of the substituent (at N^a or N^b).

Figure 1. Selected carbon-13 chemical shifts (ppm), carbon-carbon coupling constants (Hz, according to INADEQUATE experiments), ^{14}N NMR parameters and Homonuclear (^{1}H) Overhauser Effects for isomeric phenylpyrazoles **5d** and **6d**.



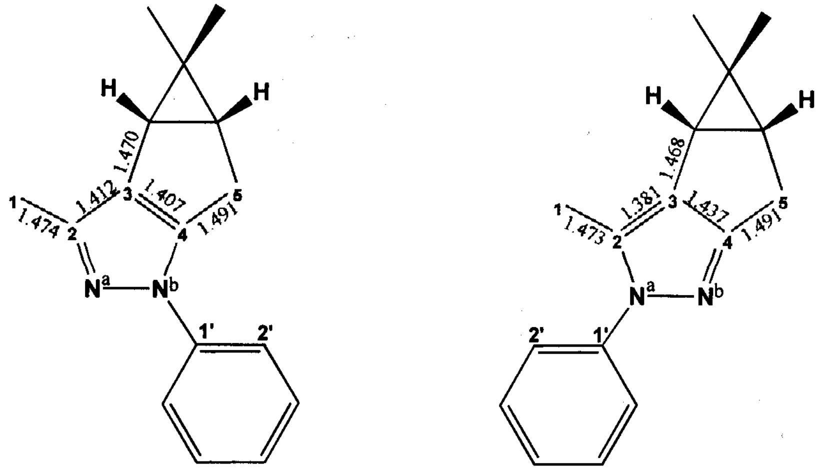
5d **6d**

It is very easy now to determine the position of a substituent by comparison of carbon-13 chemical shifts of atoms C2, C3 and C4 of a molecule studied with those of isomeric pyrazoles **5d** and **6d**. The summarised data for pyrazole derivatives **5** and **6** are shown on ***Fig.** 3*. As mentioned above, the calculation data for pyrazole derivatives **8** and **9** are very close to those for **5** and **6**, so the signal assignment in carbon-13 spectra of isomers **8** and **9** can be made by analogy with **5** and **6**. The validity of this approach was supported by NOE-experiments with N-phenylpyrazole **8d**.

Reaction of diketones **1** and **3** with arylhydrazines such as 2,6-dimethyl-4-pyrimidyl-, 4,6-dimethyl-2-pyrimidyl-, 4-methyl-2-quinolyl- and 2-pyridylhydrazines in methanolic solution either in the presence or in the absence of acetic acid also proceeds regioselectively to form the products corresponding to the primary attack of the terminal amino group of the substituted hydrazine at the carbonyl carbon of acetyl group. Treatment of diketone **1** with 2,6-dimethyl-4-pyrimidyl-, 4,6-dimethyl-2-pyrimidyl-, 4-methyl-2-quinolylhydrazines results in the diastereoselective formation of compounds **7**. Under the same conditions, 2-

pyridylhydrazine forms a 1:1 mixture of corresponding pyrazolinol **7g** and pyrazole **5g**. N-Pyridylpyrazole **8g** is the only product of the reaction of 2-pyridylhydrazine with diketone **3**. Reaction of diketone **3** with 2,6-dimethyl-4-pyrimidylhydrazine results in a 7:1 mixture of diastereomeric pyrazolinols **10i**, while the reaction of 4-methyl-2-quinolylhydrazine under the same conditions gives the mixture of three products (*ca.* 8:4:3) of which the first two are supposed to be a pair of diasteromeric pyrazolinols **10k** (whose structure was confirmed by NMR, MS and IR data) and the last one is found to be the corresponding substituted pyrazole **8k**. N-arylpyrazolinols **7** and **10** are easily transformed to the corresponding N-arylpyrazoles by treatment with boiling acetic acid.

Figure 2. Selected bond lengths (Å), bond and dihedral angles, and torsion barriers according to semi-empirical quantum chemical calculations (PM3-method).



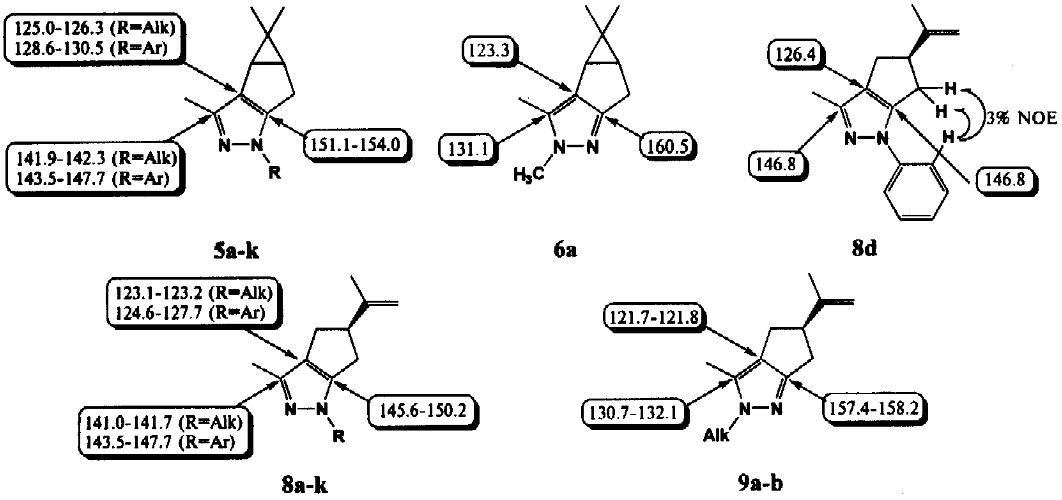
ΔH°_{f}=86.5 kcal/mol, ϕ(C2'-C1'-Nb-C4)=+19° and -19°
Θ(Na-C2-C1)=124°, Θ(Nb-C4-C5)=140°
$\Delta H^{\neq}_{f}$=2.0 kcal/mol, ϕ(C2'-C1'-Nb-C4)=90°
$\Delta H^{\neq}_{f}$=0.2 kcal/mol, ϕ(C2'-C1'-Nb-C4)= 5°

ΔH°_{f}=86.2 kcal/mol, ϕ(C2'-C1'-Na-C1)=+33° and -33°
Θ(Na-C2-C1)=128°, Θ(Nb-C4-C5)=138°
$\Delta H^{\neq}_{f}$=1.2 kcal/mol, ϕ(C2'-C1'-Na-C2)=90°
$\Delta H^{\neq}_{f}$=1.5 kcal/mol, ϕ(C2'-C1'-Na-C2)=0°

Preparation of the N-arylpyrazolinols **7** and **10** was carried out by treatment of diketone **1** with an equimolar amount of substituted hydrazine and 0.5 equivalent of acetic acid in boiling methanol. β-Dicarbonyl compounds react with arylhydrazines to afford arylpyrazoles, and dihydropyrazol-5-ols are believed to be labile intermediates and are not normally isolated. For example, the formation of the corresponding pyrazolinols has not been mentioned in the reaction of acetylacetone and β-keto aldehydes with 2-hydrazino-4,6-dimethylpyrimidine, 4-hydrazino-2,6-dimethylpyrimidine and 4-methyl-2-quinolylhydrazine.[7] A known example of pyrazolin-5-ol - 1-phenyl-4-dialkyl-pyrazolin-5-ol - was obtained by reduction of the corresponding pyrazol-5-one[8]. The carane-type pyrazolin-5-ols **7** are quite stable compounds and are analogues of the corresponding isoxazolin-5-ol whose formation and unusual stability has been already discussed.[6]

The regioselective formation of N^b-substituted pyrazolinols and the corresponding pyrazoles can be explained by the reaction pathway shown on the ***Scheme 2***.

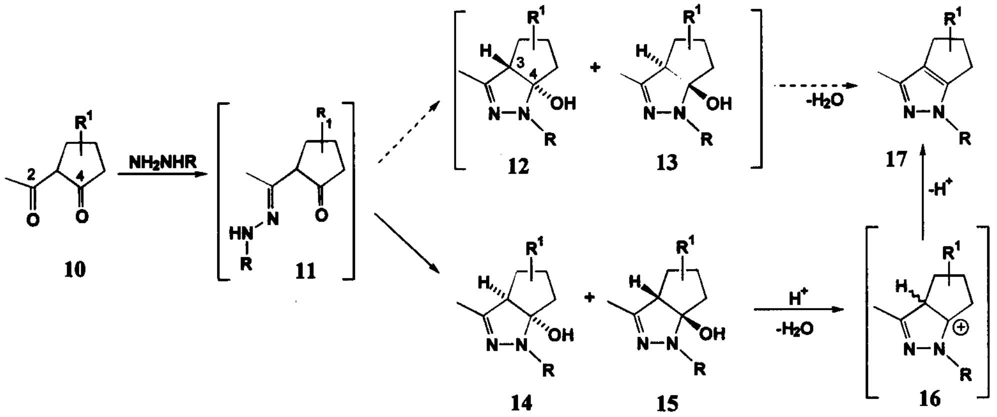
Figure 3. NMR ^{13}C Chemical Shifts and NOE for Isomeric Pyrazoles **5** and **6**, **8** and **9**.



5a-k **6a** **8d**

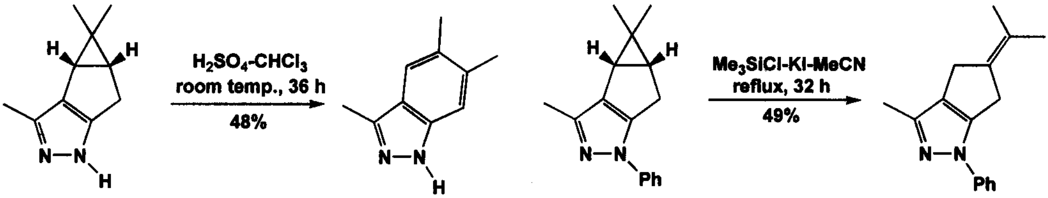
8a-k **9a-b**

Scheme 2.



In the case of N-arylhydrazines, the terminal nitrogen is more reactive in the reaction of nucleophilic addition to carbonyl group. The carbonyl group of the acetyl fragment in compounds **1** and **3** seems to be sterically less hindered and therefore more active, so the primary reaction is the addition of the terminal nitrogen of the arylhydrazine to the C-2 carbonyl moiety with the intermediate formation of hydrazone **11** whose subsequent heterocyclization provides the heterocyclic moiety. The formation of four diasteromeric pyrazolinols **12-15** might be expected. According to MM2 calculations, *trans*-isomers **12** and **13** are significantly less stable as compared to *cis*-isomers **14** and **15** ($\Delta\Delta H°$=16-23 kcal/mol for carane-type derivatives, R_1=fused dimethylcyclopropane; $\Delta\Delta H°$=11-13 kcal/mol for limonene-type compounds, R_1=*iso*-propenyl). Additionally, antiperiplanar alignment of the hydroxyl and H-3 makes bimolecular water elimination very easy and slightly dependent on the nature of the substituent in the hydrazine moiety. Therefore, the participation of *trans*-isomers **12** and **13** seems to be questionable. In the case of carane-type derivatives, only one diastereomer of the *cis*-pyrazolinol is formed. The cyclization of hydrazone **11** is stereoselective in the case of carane-type derivatives and results in a single isomer due to attack of the nitrogen at the C-4 carbonyl from the least hindered side of the molecule (opposite to dimethylcyclopropane unit). Cyclization of limonene-type hydrazone **11** results in both diastereomers **14** and **15**. In compounds **14** and **15**, bimolecular elimination of water is unfavourable because the dihedral angle H3-C3-C4-O is about 4°-8.5° (depending on the structure of the aryl substituent). The only possible way of the formation of pyrazole **17** under the given conditions is monomolecular dehydration via intermediate C4-cation **16**. In this case, electron acceptors at the nitrogen atom must diminish the stability of C4 cation and reduce the rate of dehydration. Experimental data lend support to this scheme. The ratio pyrazolinol/pyrazole in the reaction of diketone **1** with N-substituted hydrazines depends strongly on the nature of the substituents at the hydrazine nitrogen. The presence of strong acceptors (2,6-dimethyl-4-pyrimidyl-, 4,6-dimethyl-2-pyrimidyl- and 4-methyl-2-quinolyl-) leads to the formation of pyrazolinols. Less acceptor (2-pyridyl-) affords roughly a 1:1 mixture of pyrazolinol and pyrazole. In the case of such substituents as phenyl-, 2-methoxyphenyl-, 2-hydroxyethyl-, ethoxycarbonylmethyl- the formation of the corresponding pyrazoles occurs, while no pyrazolinols are detected.

Although pyrazoles are stable compounds, the tricyclic carbon skeleton is quite labile towards acidic reagents. Treatment of unsubstituted pyrazole **18** with sulfuric acid at room temperature resulted in indazole **19**. Reaction of phenyl pyrazole **5d** with Me$_3$SiCl and KI demonstrated another way of cyclopropane cleavage, giving isopropylidene derivative **20**.



18 **19** **5d** **20**

EXPERIMENTAL

All the solvents used were reagent quality. Diethyl ether was freshly distilled. Removal of all solvents was carried out under reduced pressure and all commercial reagents were used without additional purification. Analytical TLC plates were **Silufol®** (Silpearl on aluminum foil, Czechoslovakia). Preparative column chromatography was performed on **SiO$_2$** ("KSK", Russia, 100-200 mesh, air dried and activated at 140°C for 5h). IR spectra in CHCl$_3$ solutions were obtained using a ***Specord M-80*** infrared spectrophotometer. UV spectra were obtained for 1% solutions in **EtOH** using a ***Specord UV VIS*** spectrometer. A ***Polamat A*** polarimeter was used to measure optical rotations at 578 nm for CHCl$_3$ solutions. Melting points were obtained using a ***Kofler*** melting point apparatus. Mass spectra were obtained on a ***Finnigan MAT 8200*** instrument using the Electron Impact Ionization technique (100-220°C, 70eV). ^{1}H and ^{13}C NMR spectra were recorded at 25°C using a ***Bruker AC-200*** instrument (^{1}H 200.13 MHz, ^{13}C 50.32 MHz,). ^{14}N NMR spectra and ^1H and ^{13}C NMR spectra of phenylpyrazoles **5d**, **6d** and **8d** were recorded on a ***Bruker AM-400*** instrument (^1H 400.13 MHz, ^{13}C 100.61 MHz, ^{14}N 28.91 MHz) using the standard Bruker NMR Software System. Carbon and proton chemical shifts were calculated relative to the solvent signal using as the internal standard: $CDCl_3$ (δ_H 7.24 ppm and δ_C 76.90 ppm), C_6D_6 (δ_H 7.15 ppm and δ_C 128.00 ppm), acetone-d_6 (δ_H 2.05 ppm and δ_C 29.80 ppm), pyridine-d_5 (δ_H 7.19 ppm and δ_C 123.50 ppm). Nitrogen chemical shifts were measured relative to 9M HNO_3 as the external standard with δ_N −14.4 ppm (relative to CH_3NO_2).

Enaminones **2** and **4** were prepared as described earlier.[3] Preparation of diketones **1** and **3** were performed according to literature procedures.[2,6] The following substituted hydrazines were prepared by known methods: 2-hydrazino-4,6-dimethylpyrimidine,[9] 4-hydrazino-2,6-dimethylpyrimidine,[10] 2-hydrazino-4-methylquinoline,[11] 8-hydrazinoquinoline,[12] 2-methoxyphenylhydrazine.[13] 2-Hydrazinoethanol, 2-hydrazinopyridine and hydrazinoacetic acid ethyl ester were purchased from *Fluka*.

Preparation of pyrazolinols 7 and 10 from diketones 1 and 3 (Method A).

A solution of a substituted hydrazine (3.5 mmol) and diketone **1** (0.55 g, 3.3 mmol) in a mixture of methanol (15 ml) and glacial acetic acid (0.1 g, 1.6 mmol) was stirred at reflux for 2 h . The solvent was evaporated, the residue was treated with water (100 ml) and extracted with ether (3×20 ml). The combined ethereal extracts were washed with $NaHCO_3$ (0.5 M, 50 ml), dried (Na_2SO_4) and evaporated at reduced pressure to give the crude product which was then chromatographed on a silica gel column (pentane-Et_2O) to give pure pyrazolinol **7**.

Treatment of diketone **3** in the same manner gives the mixture of diastereomers **10,** which were purified on a silica gel column.

(3aR,3bR,4aR,5aR)-3,4,4-Trimethyl-1-(4,6-dimethyl-2-pyrimidyl)-1,3a,3b,4,4a,5-hexahydrocyclopropa-[3,4]cyclopenta[1,2-c]pyrazol-5a-ol (**7h**): 55%, colourless glass with $[\alpha]^{22}$-182 (c 2.06, $CHCl_3$). IR: 3420 (O-H), 1580, 1560, 1490, 1380, 1320, 960. UV: 217 sh (ε 5110), 269 (ε 23720), 305 (ε 3720). MS (*m/z*, %): 286.1799 (M^+, 16%, $C_{16}H_{22}N_4O$ requires 286.1794), 271 (5), 253 (8), 204 (100), 189 (53), 163 (10), 107 (8). ^1H NMR ($CDCl_3$): 0.93 *s* (3H), 1.11 *s* (3H), 2.06 *s* (3H), 2.26 *s* (6H), 1.00 *dd* (***J*** = 7.1, 1.2 Hz), 1.06 *ddd* (***J*** = 7.1, 6.7, 1.3 Hz), 2.06 *dd* (***J*** = 14.9, 1.5 Hz), 2.73 *dd* (***J*** = 14.9, 6.7 Hz), 3.10 *br.s*, 6.33 *br.s* (OH), 7.18 *s*. ^{13}C NMR ($CDCl_3$): 167.60 *s*, 157.32 *s*, 154.88 *s* (C-2), 111.06 *d*, 108.27 *s* (C-4), 61.98 *d* (C-3), 41.53 *t* (C-5), 32.58 *d* (C-7), 30.80 *d* (C-6), 26.62 *q* (C-9), 23.98 *q*, 20.55 *s* (C-8), 14.72 *q* (C-1), 14.22 *q* (C-10).

(3aR,3bR,4aR,5aR)-3,4,4-Trimethyl-1-(2,6-dimethyl-4-pyrimidyl)-1,3a,3b,4,4a,5-hexahydrocyclopropa[3,4]cyclopenta[1,2-c]pyrazol-5a-ol (**7i**): 54%, m.p. 190-191°C (MeCN), $[\alpha]^{20}$-198 (c 1.73, $CHCl_3$). IR: 3450 (O-H), 1590, 1490, 1410, 1320, 1190, 1060, 980. UV: 211 (ε 11000), 228 (ε 24400), ε 13200); MS (*m/z*, %): 286.1802 (M^+, 16%, $C_{16}H_{22}N_4O$ requires 286.1794), 271 (5), 253 (8), 204 (100), 189 (41), 163 (8), 107 (9). ^1H NMR ($CDCl_3$): 0.99 *s* (3H), 1.04 *dd* (***J*** = 7.2, 0.9 Hz), 1.15 *s* (3H), 1.15 (1H), 2.08 *s* (3H), 2.14 *dd* (***J*** = 15.1 and 1.7 Hz), 2.29 *s* (3H), 2.42 *s* (3H), 2.84 *dd* (***J*** = 15.1 and 7.0 Hz), 3.13 *br.s* (1H), 5.41 *br.s* (W=45 Hz), 6.73 *s*. ^{13}C NMR ($CDCl_3$): 165.85 *s*, 165.53 *s*, 158.45 *s*, 155.85 *s* (C-2), 108.36 *s* (C-4), 101.31 *d*, 62.13 *d* (C-3), 41.42 *t* (C-5), 32.57 *d* (C-7), 30.80 *d* (C-6), 26.66 *q* (C-9), 25.82 *q*, 23.94 *q*, 20.73 *s* (C-8), 14.64 *q* (C-1), 14.19 *q* (C-10).

(3aR,3bR,4aR,5aR)-3,4,4-Trimethyl-1-(4-methyl-2-quinolyl)-1,3a,3b,4,4a,5-hexahydrocyclopropa[3,4]-cyclopenta[1,2-c]pyrazol-5a-ol (**7k**): 46% pale yellow crystals with m.p. 134-136°C (pentane-toluene), $[\alpha]^{19}$-202 (c 2.0, $CHCl_3$). IR: 3380 (O-H), 1610, 1560, 1480, 1430, 1320, 1190, 1060. UV: 216 (ε 20500), 244 (ε 21000), 267 (ε 31000), 283 (ε 22500), 293 (ε 16500), 344 (ε 8000);MS (*m/z*, %): 321.1846 (M^+, 30%, $C_{20}H_{23}N_3O$ requires 321.1841), 306 (10), 288 (15), 239 (100), 224 (62), 198 (15), 158 (20), 142 (24), 115 (16) ^{1}H NMR ($CDCl_3$): 1.06 *s* (3H), 1.10 *dd* (*J* = 7.3, 1.1 Hz), 1.23 *ddd* (*J* = 7.3, 7.1, 1.6 Hz), 1.26 *s* (3H), 2.16 *d* (*J* = 0.8 Hz, 3H), 2.28 *dd* (*J* = 14.7, 1.8 Hz), 2.61 *d* (*J* = 1.0 Hz, 3H), 3.02 (*J* = 14.7, 7.1 Hz), 3.21 *br.s* (1H), 6.46 *br.s* (W=15 Hz), 7.28 *ddd* (*J* = 8.2, 6.8, 1.4 Hz), 7.38 *q* (*J* = 1.0 Hz), 7.53 *ddd* (*J* = 8.4, 6.8, 1.5 Hz), 7.66 *dd* (*J* = 8.4, 1.4, 0.5 Hz), 7.80 *dd* (*J* = 8.2, 1.5, 0.5 Hz). ^{13}C NMR ($CDCl_3$): 153.89 *s* (C-2), 153.07 *s*, 146.29 *s*, 145.51 *s*, 129.08 *d*, 126.82 *d*, 124.01 *s*, 123.57 *d*, 122.41 *d*, 112.05 *d*, 109.09 *s* (C-4), 61.94 *d* (C-3), 41.15 *t* (C-5), 32.33 *d* (C-7), 30.99 *d* (C-6), 26.67 *q* (C-9), 20.53 *s* (C-8), 18.71 *q*, 14.71 *q* (C-1), 14.32 *q* (C-10).

(±)-1-(2,6-Dimethyl-4-pyrimidyl)-5-isopropenyl-3-methyl-3a,4,5,6-tetrahydro-1H-cyclopentapyrazol-6a-ol (**10i**). Treatment of 0.45 g (2.7 mmol) of diketone **3** with 4-hydrazino-2,6-dimethylpyrimidine yields a 7:1 mixture of two diastereomers (0.72 g, 93%). MS (*m/z*): 286.1796 (M^+, $C_{16}H_{22}N_4O$ requires 286.1794). IR: 3615 (O-H). NMR data (CCl_4-benzene-d_6, 5:1 v/v):

Major component

^{1}H NMR: (1.26 *ddd* (*J* = 12.1, 12.1 and 10.2 Hz, 1H), 1.68 *br.s* (3H), 1.80 *dd* (*J* = 12.4 and 12.4 Hz, 1H), 1.95 *s* (3H), 2.09-2.35 m (2H), 2.26 *s* (3H), 2.39 *s* (3H), 2.54-2.95 m (2H), 3.19 *dd* (*J* = 9.7 and 9.7 Hz, 1H), 4.66 *br.s* (2H), 5.3 br. (1H), 6.66 *s* (1H). ^{13}C NMR: 166.09 *s*, 165.91 *s*, 159.11 *s*, 154.87 *s* (C-2), 145.56 *s* (C-8), 110.33 *t* (C-9), 101.76 *s* (C-4), 61.01 *d* (C-3), 48.06 *t* (C-5), 46.99 *d* (C-6), 35.61 *t* (C-7), 26.18 *q*, 24.37 *q*, 21.59 *q* (C-10), 14.96 *q* (C-1).

Minor component:

^{13}C NMR: 165.89 *s*, 165.86 *s*, 159.37 *s*, 155.23 *s* (C-2), 145.37 *s* (C-8), 110.42 *t* (C-9), 101.70 *s* (C-4), 60.03 *d* (C-3), 45.54 *t* (C-5), 45.38 *d* (C-6), 33.68 *t* (C-7), 26.20 *q*, 24.39 *q*, 21.42 *q* (C-10), 14.80 *q* (C-1).

(±)-5-Isopropenyl-3-methyl-1-(4-methyl-2-quinolyl)-3a,4,5,6-tetrahydro-1H-cyclopentapyrazol-6a-ol (**10k**). Treatment of 0.45 g (2.7 mmol) of diketone **3** with 2-hydrazino-4-methylquinoline yields 0.72 g of a mixture of a pair of diastereomers **10k** and corresponding pyrazole **8k** (8:4:3). MS (*m/z*): 321.1840 (M^+, $C_{20}H_{23}N_3O$ requires 321.1841). IR: 3620 (O-H). NMR data (CCl_4-benzene-d_6, 5:1 v/v):

Major pyrazolinol

^{1}H NMR: 1.64 *br.s* (3H), 1.95 *s* (3H), 2.50 *s* (3H), 4.65 *br.s* (2H), 6.3 br (1H). ^{13}C NMR: 153.84 *s*, 153.41 *s*, 147.49 *s*, 145.73 *s*, 145.07 *s*, 129.28 *d*, 127.49 *d*, 124.36 *s*, 123.72 *d*, 122.59 *d*, 112.52 *d*, 110.18 *t* (C-9), 102.13 *s* (C-4), 59.95 *d* (C-3), 45.64 *t* (C-5), 45.57 *d* (C-6), 33.89 *t* (C-7), 21.49 *q* (C-10), 19.18 *q*, 14.85 *q* (C-1).

Minor pyrazolinol:

^{1}H NMR: 1.67 *br.s* (3H), 1.95 *s* (3H), 2.50 *s* (3H), 4.65 *br.s* (2H), 6.3 br (1H). ^{13}C NMR: 153.52 *s*, 152.80 *s*, 147.26 *s*, 145.87 *s*, 145.14 *s*, 129.31 *d*, 127.46 *d*, 124.43 *s*, 123.75 *d*, 122.47 *d*, 111.78 *d*, 110.14 *t* (C-9), 102.21 *s* (C-4), 61.04 *d* (C-3), 48.34 *t* (C-5), 47.27 *d* (C-6), 35.82 *t* (C-7), 21.65 *q* (C-10), 19.20 *q*, 15.01 *q* (C-1).

Reaction of diketone **1** (0.33 g, 2.0 mmol) with 2-hydrazinopyridine (2.0 mmol) resulted in 0.45 g (90%) of a mixture of pyrazolinol **7g** and pyrazole **8g** (3:5, according to ^{1}H NMR) as dark viscous oil. ^{1}H NMR data

(CCl_4-benzene-d_6, 5:1 v/v) for *(3aR,3bR,4aR,5aR)-3,4,4-trimethyl-1-(2-pyridyl)-1,3a,3b,4,4a,5-hexahydrocyclopropa[3,4]cyclopenta[1,2-c]pyrazol-5a-ol* (**7g**): 0.96 *s* (3H), 1.13 *s* (3H), 2.00 *s* (3H), 3.02 *br.s* (1H), 6.52 *dd* (*J* = 8.2 and 6.8 Hz), 7.34 *ddd* (*J* = 8.2, 6.8 and 1.5 Hz), 7.85 *d* (*J* = 8.2 Hz), 8.08 *dd* (*J* = 6.8 and 1.5 Hz).

*Preparation of pyrazoles **5** and **8** from diketones **1** and **3** (Method B).*

A solution of a substituted hydrazine (6.9 mmol) and diketone **1** or **3** (1.00 g, 6 mmol) in methanol (15 ml) was stirred at reflux for 2 h . The solvent was distilled off, the residue was dissolved in acetic acid (5 ml) and the resulting mixture was refluxed for 1 h. The solvent was distilled off at reduced pressure, and the residue was treated with water (100 ml) and extracted with benzene (50 ml). The organic phase was washed with NaOH (5%, 20 ml), dried (Na_2SO_4) and concentrated at reduced pressure to give the crude product which was percolated on a silica gel column (benzene) to give pure pyrazole.

(3bR,4aR)-1-(2-pyridyl)-3,4,4-trimethyl-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole (**5g**): 52%, m.p. 96-97°C (MeCN), $[\alpha]^{21}$+233 (c 1.07, $CHCl_3$). IR: 1060, 1190, 1290, 1380, 1460, 1480, 1580, 1690. UV: 213 (ε 9300), 237 (ε 9000), 292 (ε 15600); MS (*m/z*, %): 239.1421 (M^+, 33%, $C_{15}H_{17}N_3$ requires 239.1422), 224 (100), 183 (22), 78 (28).). ^{1}H NMR ($CDCl_3$): 0.69 *s* (3H), 1.09 *s* (3H), 1.72-1.84 m (2H), 2.26 *s* (3H), 2.98 *ddd* (*J* = 18.2, 1.5 and 1.5 Hz), 3.18 *dd* (*J* = 18.2 and 6.6 Hz), 7.01 *dd* (*J* = 8.2 and 6.8 Hz), 7.68 *ddd* (*J* = 8.2, 6.8 and 1.5 Hz), 7.78 *d* (*J* = 8.2 Hz), 8.30 *dd* (*J* = 6.8 and 1.5 Hz). ^{13}C NMR ($CDCl_3$): 152.16 *s* (C-4), 151.15 *s*, 147.81 *d*, 145.49 *s* (C-2), 137.96 *d*, 128.76 *s* (C-3), 119.68 *d*, 111.71 *d*, 34.66 *d* (C-6), 27.97 *t* (C-5), 26.33 *q* (C-9), 25.83 *d* (C-7), 21.80 *s* (C-8), 13.71 *q* (C-10), 12.74 *q* (C-1).

(3bR,4aR)-1-(4,6-dimethyl-2-pyrimidyl)-3,4,4-trimethyl-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole (**5h**): 68%, m.p. 95-96°C (toluene-pentane), $[\alpha]^{20}$+167 (c 1.26, $CHCl_3$). IR: 1060, 1080, 1190, 1280, 1340, 1430, 1480, 1550, 1590. UV: 207 (ε 8400), 247 (ε 10600), 277 (ε 13200); MS (*m/z*, %): 268.1678 (M^+, 29%, $C_{16}H_{20}N_4$ requires 268.1688), 253 (100), 212 (10), 107 (7). ^{1}H NMR (CCl_4-benzene-d_6): 0.70 *s* (3H), 1.05 *s* (3H), 1.65 *ddd* (*J* = 6.6, 6.6 and 1.5 Hz), 1.73 *dd* (*J* = 6.6 and 1.5 Hz), 2.23 *s* (3H), 2.31 *s* (6H), 2.92 *ddd* (*J* = 18.2, 1.5 and 1.5 Hz), 3.12 *dd* (*J* = 18.2 and 6.6 Hz), 6.50 *s* (1H). ^{13}C NMR (CCl_4-benzene-d_6): 168.09 *s*, 156.35 *s*, 152.14 *s* (C-4), 146.14 *s* (C-2), 129.05 *s* (C-3), 115.84 *d*, 34.88 *d* (C-6), 29.01 *t* (C-5), 26.93 *q* (C-9), 26.65 *d* (C-7), 24.04 *q*, 22.09 *s* (C-8), 14.34 *q* (C-10), 13.30 *q* (C-1).

(3bR,4aR)-1-(2,6-dimethyl-4-pyrimidyl)-3,4,4-trimethyl-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole (**5i**): 55%, m.p. 67-68°C (toluene-pentane), $[\alpha]^{20}$+219 (c 1.55, $CHCl_3$). IR: 1590, 1570, 1480, 1440, 1390, 1370, 1290, 1190, 1070. UV: 213 (ε 9200), 249 (ε 6300), 293 (ε 13200); MS (*m/z*, %): 268.1673 (M^+, 32%, $C_{16}H_{20}N_4$ requires 268.1688), 254 (18), 253 (100), 212 (11), 107 (11). ^{1}H NMR ($CDCl_3$): 0.67 *s* (3H), 1.07 *s* (3H), 1.70-1.80 *m* (2H), 2.23 *s* (3H), 2.43 *s* (3H), 2.56 *s* (3H), 2.98 *ddd* (*J* = 18.5, 1.6, 1.6 Hz), 3.18 (*J* = 18.5, 4.8, 2.4 Hz), 7.37 *s* (1H). ^{13}C NMR ($CDCl_3$): 168.12 *s*, 167.30 *s*, 157.40 *s*, 151.92 *s* (C-4), 147.30 *s* (C-2), 129.79 *s* (C-3), 103.61 *d*, 34.62 *d* (C-6), 28.23 *t* (C-5), 26.24 *q* (C-9), 25.74 *q*, 25.71 *d* (C-7), 24.08 *q*, 21.77 *s* (C-8), 13.61 *q* (C-10), 12.73 *q* (C-1).

(3bR,4aR)-1-(4-methyl-2-quinolyl)-3,4,4-trimethyl-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole (**5k**): 59%, m.p. 162-164°C (MeCN-toluene), $[\alpha]^{21}$+323 (c 2.15, $CHCl_3$). IR: 1600, 1510, 1480, 1450, 1390, 1290, 1190, 1070, 1060. UV: 217 (ε 37000), 244 (ε 21000), 265 (ε 26000), 287 (ε 17200),

326 (ε 12200), 337 (ε 13500). MS (*m/z*, %): 303.1728 (M^+, 30%, $C_{20}H_{21}N_3$ requires 303.1735), 288 (100), 247 (17), 142 (14), 115 (17). ^{1}H NMR ($CDCl_3$): 0.73 *s* (3H), 1.12 *s* (3H), 1.77-1.86 *m* (2H), 2.32 *s* (3H), 2.68 *d* (*J* = 0.8 Hz, 3H), 3.18 *ddd* (*J* = 18.5, 1.6 and 1.6 Hz), 3.38 *ddd* (*J* = 18.5, 5.0 and 2.1 Hz), 7.41 *ddd* (*J* = 8.2, 6.8 and 1.4 Hz), 7.62 *ddd* (*J* = 8.2, 6.8 and 1.4 Hz), 7.85-7.94 *m* (3H). ^{13}C NMR ($CDCl_3$): 151.59 *s* (C-4), 150.38 *s*, 146.62 *s*, 146.60 *s*, 145.60 *s* (C-2), 129.32 *d*, 129.09 *s* (C-3), 128.77 *d*, 126.26 *s*, 124.77 *d*, 123.55 *d*, 112.08 *d*, 34.73 *d* (C-6), 28.27 *t* (C-5), 26.33 *q* (C-9), 25.83 *d* (C-7), 21.78 *s* (C-8), 18.66 *q*, 13.72 *q* (C-10), 12.77 *q* (C-1).

(±)-5-Isopropenyl-3-methyl-1-(2-pyridyl)-1,4,5,6-tetrahydrocyclopentapyrazole (**8g**): 69%, m.p. 61-63°C (MeCN). IR: 1640 ($C=CH_2$), 1590, 1575, 1480, 1440, 1380, 1080, 890 ($=CH_2$). UV: 264 (ε 14400), 285 (ε 16800) MS (*m/z*, %): 239.1419 (M^+, 100%, $C_{15}H_{17}N_3$ requires 239.1422), 238 (29), 224 (29), 198 (35), 197 (36), 183 (21), 157 (9), 143 (5), 105 (5). ^{1}H NMR (CCl_4-benzene-d_6): 1.72 *br.s* (3H), 2.15 *s* (3H), 2.39 *dd* (*J* = 14.0 and 7.0 Hz, 1H), 2.60 *dd* (*J* = 14.0 and 8.0 Hz, 1H), 2.99 *dd* (*J* = 16.0 and 7.5 Hz, 1H), 3.33 *dd* (*J* = 16.0 and 8.0 Hz, 1H), 3.51 *dddd* (*J* = 8.0, 8.0, 7.5 and 7.0 Hz, 1H), 4.66 *br.s* (1H), 4.76 *br.s* (1H), 6.83 *dd* (*J* = 7.3 and 4.8 Hz, 1H), 7.52 *dd* (*J* = 8.0 and 7.3 Hz, 1H), 7.80 *d* (*J* = 8.0 Hz, 1H), 8.17 *d* (*J* = 4.8 Hz, 1H). ^{13}C NMR (CCl_4-benzene-d_6): 153.05 *s*, 148.69 *s* (C-4), 147.87 *d*, 147.47 *s* (C-2), 144.63 *s* (C-8), 137.85 *d*, 126.82 *s* (C-3), 119.52 *d*, 112.29 *d*, 110.13 *t* (C-9), 53.05 *d* (C-6), 33.66 *t* (C-5), 28.09 *t* (C-7), 20.71 *q* (C-10), 13.23 *q* (C-1).

(±)-5-Isopropenyl-3-methyl-1-(2,6-dimethyl-4-pyrimidyl)-1,4,5,6-tetrahydrocyclopentapyrazole (**8i**): 74%, m.p. 77-78°C (toluene-pentane), IR: 1640 ($C=CH_2$), 1590, 1580, 1480, 1450, 1390, 1080, 890, ($=CH_2$). UV: 252 (ε 8800), 284 (ε 22700) MS (*m/z*, %): 268.1692 (M^+, 100%, $C_{16}H_{20}N_4$ requires 268.1688), 267 (24), 253 (25), 227 (24), 212 (17), 200 (5), 145 (6), 120 (6), 107 (9). ^{1}H NMR (CCl_4-benzene-d_6): 1.72 *br.s* (3H), 2.12 *s* (3H), 2.35 *dd* (*J* = 14.5 and 7.0 Hz, 1H), 2.36 *s* (3H), 2.49 *s* (3H), 2.57 *dd* (*J* = 14.5 and 8.0 Hz, 1H), 2.95 *dd* (*J* = 16.5 and 7.5 Hz, 1H), 3.30 *dd* (*J* = 16.5 and 8.0 Hz, 1H), 3.50 *dddd* (*J* = 8.0, 8.0, 7.5 and 7.0 Hz, 1H), 4.68 *br.s* (1H), 4.76 *br.s* (1H), 7.32 *s* (1H). ^{13}C NMR (CCl_4-benzene-d_6): 168.10 *s*, 167.28 *s*, 158.06 *s*, 149.43 *s* (C-4), 147.19 *s* (C-2), 146.22 *s* (C-8), 127.73 *s* (C-3), 110.44 *d* (C-9), 104.17 *d*, 52.95 *d* (C-6), 33.68 *t* (C-5), 28.04 *t* (C-7), 26.07 *q*, 24.48 *q*, 20.57 *q* (C-10), 13.25 *q* (C-1).

(±)-5-Isopropenyl-3-methyl-1-(4-methyl-2-quinolyl)-1,4,5,6-tetrahydrocyclopentapyrazole (**8k**): 71% m.p. 157-159°C (MeCN-$CHCl_3$), IR: 1640 ($C=CH_2$), 1600, 1510, 1480, 1430, 1390, 1250, 1070, 890 ($=CH_2$). UV: 213 (ε 32000), 262 (ε 36000) 235 sh (ε 17000), 320 (ε 11000), 334 (ε 12000); MS (m/z): 303.1728 (M^+, 100%, $C_{20}H_{21}N_3$ requires 303.1735), 288 (26), 262 (30), 261 (25), 247 (24), 143 (12), 142 (13), 116 (11), 115 (17). ^{1}H NMR ($CDCl_3$): 1.72 *br.s* (3H), 2.19 *s* (3H), 2.42 *dd* (*J* = 14.5 and 7.0 Hz, 1H), 2.56 *s* (3H), 2.62 *dd* (*J* = 14.5 and 8.0 Hz, 1H), 3.11 *dd* (*J* = 15.0 and 6.0 Hz, 1H), 3.4-3.8 m (3H), 4.96 *br.s* (1H), 4.78 *br.s* (1H), 7.28 *dd* (*J* = 7.5 and 7.5 Hz, 1H), 7.49 *ddd* (*J* = 7.0, 7.0 and 1.0 Hz, 1H), 7.72-7.82 m (2H), 7.82 *br.s* (1H). ^{13}C NMR ($CDCl_3$): 150.37 *s*, 149.09 *s* (C-4), 147.26 *s* (C-2), 146.47 *s*, 146.46 *s*, 144.98 *s* (C-8), 129.14 *d*, 128.64 *d*, 127.08 *s* (C-3), 126.12 *s*, 124.62 *d*, 123.36 *d*, 112.04 *d*, 109.42 *t* (C-9), 52.44 *d* (C-6), 33.23 *t* (C-5), 27.51 *t* (C-7), 20.00 *q* (C-10), 18.50 *q*, 12.65 *q* (C-1).

Preparation of pyrazoles 5, 6, 8 and 9 (Method C).

A solution of a substituted hydrazine (6.9 mmol) and diketone **1** or **3** (1.00 g, 6 mmol) or enaminone **4** (1.0 g, 6.1 mmol) in a mixture of methanol (15 ml) and AcOH (5 ml) was stirred at reflux for 2 h. The solvent was distilled off at reduced pressure, and the residue was treated with water (100 ml) and extracted with benzene (50 ml). The organic phase was washed with $NaHCO_3$ (0.5 M, 50 ml), NaOH (5%), dried (Na_2SO_4) and evaporated at reduced pressure to give the crude product which was percolated on a silica gel column (benzene) to give the pure pyrazole.

(3bR,4aR)-1,3,4,4-tetramethyl-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole (**5a**) and *(3bR,4aR)-2,3,4,4-tetramethyl-3b,4,4a,5-tetrahydro-2H-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole* (**6a**), 73% (ca 1:2 mixture of the isomers), yellow oil, IR: 1540, 1490, 1445, 1430, 1370, 1290,1260. UV: 223 (ε 62370), 291 (ε 9630), 400 (ε 350).MS (*m/z*, %): 176.1316 (M^+, 21%, $C_{13}H_{16}N_2$ requires 176.1313), 162 (11), 161 (100), 146 (24), 135 (3), 120 (7). NMR data (CCl_4-benzene-d_6, 5:1 v/v):

(**6a**) ^{1}H NMR: 0.66 *s* (3H), 1.02 *s* (3H), 1.56 *ddd* (***J*** = 6.8, 6.8 and 1.2 Hz, 1H), 1.68 *dd* (***J*** = 6.8 and 1.2 Hz, 1H), 2.00 *s* (3H), 2.43 *ddd* (***J*** = 16.5, 1.2 and 1.2 Hz, 1H), 2.70 *dd* (***J*** = 16.5 and 6.8 Hz, 1H), 3.42 *s* (3H). ^{13}C NMR: 160.47 *s* (C-4), 131.12 *s* (C-2), 123.31 *s* (C-3), 36.11 *q*, 34.22 *d* (C-6), 27.24 *q* (C-9), 26.82 *d* (C-7), 24.72 *t* (C-5), 22.82 *s* (C-8), 14.74 *q* (C-10), 10.45 *q* (C-1).

(**5a**) ^{1}H NMR: 0.63 *s* (3H), 1.00 *s* (3H), 1.56 *ddd* (***J*** = 6.8, 6.8 and 1.5 Hz, 1H), 1.70 *dd* (***J*** = 6.8 and 1.5 Hz, 1H), 2.10 *s* (3H), 2.28 *ddd* (***J*** = 16.5, 1.5 and 1.5 Hz, 1H), 2.52 *dd* (***J*** = 16.5 and 6.8 Hz, 1H), 3.36 *s* (3H). ^{13}C NMR: 151.15 *s* (C-4), 141.59 *s* (C-2), 125.10 *s* (C-3), 36.37 *q*, 34.76 *d* (C-6), 27.27 *q* (C-9), 26.81 *d* (C-7), 23.52 *t* (C-5), 22.41 *s* (C-8), 14.17 *q* (C-10), 12.87 *q* (C-1).

(3bR,4aR)-2-(3,4,4-Trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-c]pyrazol-1-yl)-ethanol (**5b**): 66%, m.p. 84-86 °C (MeCN), $[\alpha]^{16}$+97.8 (c 1.9, $CHCl_3$), IR: 3605 (O-H), 1530, 1490, 1430, 1280, 1190, 1060. UV: 209 (ε 3400), 241 (ε 5200); MS (m/z): 206.1421 (M^+, 30, $C_{12}H_{18}N_2O$ requires 206.1419), 192 (12), 191 (100),173 (22), 163 (4), 159 (4), 147 (20), 133 (5), 132 (5), 118 (3), 117 (5), 106 (6), 105 (4). ^{1}H NMR (CCl_4-benzene-d_6): 0.62 *s* (3H), 1.00 *s* (3H), 1.56 *ddd* (***J*** = 6.9, 6.9 and 1.0 Hz), 1.70 *dd* (***J*** = 6.9 and 1.5 Hz), 2.09 *s* (3H), 2.36 *ddd* (***J*** = 16.5, 1.5 and 1.0 Hz), 2.60 *dd* (***J*** = 16.5 and 6.9 Hz), 3.68 *s* (4H), 4.41 *br.s* (W=18 Hz, 1H). ^{13}C NMR (CCl_4-benzene-d_6, 5:1 v/v): 151.65 *s* (C-4), 142.21 *s* (C-2), 125.05 *s* (C-3), 61.32 *t*, 52.07 *t*, 34.61 *d* (C-6), 26.99 *d* (C-7), 26.78 *q* (C-9), 23.77 *t* (C-5), 22.57 *s* (C-8), 14.16 *q* (C-10), 12.74 *q* (C-1).

(3bR,4aR)-(3,4,4-Trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-c]pyrazol-1-yl)-acetic acid ethyl ester (**5c**): 49%, $[\alpha]^{17}$+58.0 (c 1.6, $CHCl_3$). IR(neat): 1750 (C=O), 1490, 1440, 1370, 1220, 1195, 1090, 1020. UV: 209 (ε 4400), 242 (ε 5400); MS (*m/z*, %): 248.1527 (M^+, 28, $C_{14}H_{20}N_2O_2$ requires 248.1525), 233 (19), 218 (25), 204 (10), 174 (16), 172 (5), 160 (7), 160 (14), 159 (100), 145 (7), 132 (5), 118 (4). ^{1}H NMR (CCl_4-benzene-d_6, 5:1 v/v): 0.66 *s* (3H), 0.97 *s* (3H), 1.03 *t* (***J*** = 7.0 Hz, 3H), 1.54 *ddd* (***J*** = 6.7, 6.5, 1.1 Hz), 1.68 *dd* (***J*** = 6.5, 1.5 Hz), 2.05 *s* (3H), 2.31 *ddd* (***J*** = 16.5, 1.5, 1.1 Hz Hz), 2.52 *dd* (***J*** = 16.5, 6.7 Hz), 3.93 *q* (***J*** = 7.0 Hz, 2H), 4.31 *d* (***J*** = 17.1 Hz), 4.41 *d* (***J*** = 17.1). ^{13}C NMR (CCl_4-benzene-d_6, 5:1 v/v): 167.58 *s*, 151.44 *s* (C-4), 142.51 *s* (C-2), 126.35 *s* (C-3), 61.14 *t*, 51.38 *t*, 34.73 *d* (C-6), 27.11 *d* (C-7), 26.80 *q* (C-9), 23.86 *t* (C-5), 22.56 *s* (C-8), 14.36 *q*, 14.15 *q* (C-10), 12.83 *q* (C-1).

(3bR,4aR)-3,4,4-Trimethyl-1-(1-naphthyl)-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta[1,2-c]-pyrazole (**5e**), 52%, red oil, $[\alpha]^{20}$+ 114 (c 2.0, $CHCl_3$). IR: 3040, 2970, 1610, 1515, 1230. UV: 223 (ε 62370), 291 (ε 9630), 400 (ε 350).MS (*m/z*, %): 288.1632 (M^+, 39%, $C_{20}H_{20}N_2$ requires 288.1626), 273 (100), 217 (13), 127 (14), 115 (5). ^{1}H NMR ($CDCl_3$): 0.81 *s* (3H), 1.12 *s* (3H), 1.72 *ddd* (***J*** = 6.6, 6.6 and 1.3 Hz, 1H),

1.92 *dd* (***J*** = 6.6 and 2.0 Hz, 1H), 2.35 *s* (3H), 2.41 *ddd* (***J*** = 17.0, 2.0 and 1.3 Hz, 1H), 2.72 *dd* (***J*** = 17.0 and 6.6 Hz, 1H), 7.30-7.55 m (4H), 7.75-7.90 m (3H). ^{13}C NMR ($CDCl_3$): 152.35 *s* (C-4), 143.68 *s* (C-2), 136.47 *s*, 134.11 *s*, 129.04 *s* (C-3), 127.95 *d*, 127.69 *d*, 126.50 *d*, 126.49 *s*, 126.07 *d*, 124.71 *d*, 123.63 *d*, 122.53 *d*, 34.10 *d* (C-6), 26.36 *d* (C-7), 26.24 *q* (C-9), 24.42 *t* (C-5), 22.26 *s* (C-8), 13.74 *q* (C-10), 12.52 *q* (C-1)

(3bR,4aR)-1-(2-Methoxyphenyl)-3,4,4-trimethyl-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta-[1,2-c]pyrazole (**5f**): 68%, reddish oil with $[\alpha]^{18}$+123 (c 1.5, $CHCl_3$). IR: 1600, 1500, 1475, 1370, 1275, 1235, 1020. UV: 208 (ε 19000), 252 sh (ε 7460), 283 (ε 6520). MS (m/z): 268.1571 (M^+, 28, $C_{17}H_{20}N_2O$ requires 268.1576), 254 (18), 253 (100), 238 (10), 221 (19), 196 (4), 180 (3). ^{1}H NMR (CCl_4-benzene-d_6, 5:1 v/v): 0.72 *s* (3H), 1.05 *s* (3H), 2.19 *s* (3H), 3.57 *s* (3H), 1.60 *ddd* (***J*** = 6.6, 6.6 and 1.3 Hz), 1.77 *dd* (***J*** = 6.6 and 1.7 Hz), 2.45 *ddd* (***J*** = 17.0, 1.7 and 1.3 Hz), 2.67 *dd* (***J*** = 17.0 and 6.6 Hz), 6.74 *dd* (***J*** = 8.2 and 1.3 Hz), 6.86 *ddd* (***J*** = 7.6, 7.6 and 1.3 Hz), 7.07 *ddd* (***J*** = 8.2, 7.6 and 1.8 Hz), 7.44 *dd* (***J*** = 7.6 and 1.8 Hz). ^{13}C NMR (CCl_4-benzene-d_6, 5:1 v/v): 152.46 *s*, 152.41 *s* (C-4), 143.54 *s* (C-2), 130.48 *s* (C-3), 127.88 *d*, 127.40 *d*, 126.46 *s*, 121.18 *d*, 112.31 *d*, 55.72 *q*, 34.55 *d* (C-6), 26.90 *q* (C-9), 26.85 *d* (C-7), 25.76 *t* (C-5), 22.39 *s* (C-8), 14.26 *q* (C-10), 13.02 *q* (C-1).

(3bR,4aR)-3,4,4-Trimethyl-1-(8-quinolyl)-3b,4,4a,5-tetrahydro-1H-cyclopropa[3,4]cyclopenta[1,2-c]-pyrazole (**5j**), 58%, red oil, $[\alpha]^{20}$+ 210 (c 1.3, $CHCl_3$). IR: 1610, 1590, 1550, 1500, 1480, 1390, 1370, 1240, 1080. UV: 229 (ε 21290), 305 sh (ε 6190), 315 (ε 6420).MS (*m/z*, %): 289 (M^+, 3%), 274.1342 (M^+ -CH_3 $C_{18}H_{13}N_3$ requires 274.1344, 100), 247(4), 233 (10), 218 (6), 128 (5), 116 (6). ^{1}H NMR ($CDCl_3$): 0.80 *s* (3H), 1.07 *s* (3H), 1.69 *ddd* (***J*** = 6.6, 6.6 and 1.3 Hz, 1H), 1.88 *dd* (***J*** = 6.6 and 2.0 Hz, 1H), 2.30 *s* (3H), 2.48 *ddd* (***J*** = 17.0, 2.0 and 1.3 Hz, 1H), 2.88 *dd* (***J*** = 17.0 and 6.6 Hz, 1H), 7.33 *dd* (***J*** = 8.2 and 4.2 Hz, 1H), 7.52 *dd* (***J*** = 8.2 and 7.5 Hz, 1H), 7.71 *dd* (***J*** = 8.2 and 1.5 Hz, 1H), 7.85 *dd* (***J*** = 7.3 and 1.5 Hz, 1H), 8.10 *dd* (***J*** = 8.4 and 1.8 Hz, 1H), 8.85 *dd* (***J*** = 4.2 and 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): 153.99 *s* (C-4), 149.98 *d*, 144.47 *s* (C-2), 141.81 *s*, 137.45 *s*, 135.65 *d*, 128.63 *s* (C-3), 126.98 *s*, 126.74 *d*, 126.01 *d*, 125.60 *d*, 121.17 *d*, 34.13 *d* (C-6), 26.17 *q* (C-9), 26.15 *d* (C-7), 26.05 *t* (C-5), 22.14 *s* (C-8), 13.74 *q* (C-10), 12.45 *q* (C-1).

(±)-5-Isopropenyl-1,3-dimethyl-1,4,5,6-tetrahydro-cyclopentapyrazole (**8a**) and *(±)-5-Isopropenyl-2,3-dimethyl-2,4,5,6-tetrahydro-cyclopentapyrazole* (**9a**), 78% (from diketone **3**, a 1:2.5 mixture of the isomers), 75% (from enaminone **4**, a 1:1 mixture of the isomers), yellow oil IR: 1640 (C=CH_2), 1600, 1575, 1490, 1440, 1375, 890 (=CH_2). UV: 233 (ε 6260), 250 sh (ε 1080) MS (*m/z*, %): 176.1316 (M^+, 90%, $C_{13}H_{16}N_2$ requires 176.1313), 175 (65), 162 (12), 161 (100), 160 (9), 159 (8), 147 (17), 146 (30), 145 (13), 135 (8), 134 (5), 133 (8), 132 (7).). NMR data (CCl_4-benzene-d_6, 5:1 v/v):

(**9a**) ^{1}H NMR: 1.69 *br.s* (3H), 2.03 *s* (3H), 2.30-2.85 m (4H), 3.27 *tt* (***J*** = 8.0 and 8.0 Hz, 1H), 3.52 *s* (3H), 4.65 *br.s* (1H), 4.73 *br.s* (1H). ^{13}C NMR: 157.40 *s* (C-4), 147.85 *s* (C-8), 130.69 *s* (C-2), 121.71 (C-3), 109.93 *t* (C-9), 52.26 *d* (C-6), 36.07 *q*, 30.43 *t* (C-5), 28.66 *t* (C-7), 20.90 *q* (C-10), 10.56 *q* (C-1).

(**8a**) ^{1}H NMR: 1.69 *br.s* (3H), 2.03 *s* (3H), 2.30-2.85 m (4H), 3.47 *tt* (***J*** = 8.0 and 8.0 Hz, 1H), 3.49 *s* (3H), 4.65 *br.s* (1H), 4.73 *br.s* (1H). ^{13}C NMR: 147.94 *s* and 147.32 *s* (C-4 and C-8), 141.04 *s* (C-2), 123.16 *s* (C-3), 110.18 *t* (C-9), 53.78 *d* (C-6), 36.50 *q*, 29.03 t and 28.97 *t* (C-5 and C-7), 20.70 *q* (C-10), 12.87 *q* (C-1).

(±)-2-(5-Isopropenyl-3-methyl-5,6-dihydro-4H-cyclopentapyrazol-1-yl)-ethanol (**8b**) *and* *(±)-2-(5-Isopropenyl-3-methyl-5,6-dihydro-4H-cyclopentapyrazol-2-yl)-ethanol* (**9b**), 75% (from diketone **3**, *ca* 1:2.5 mixture of the isomers), 71% (from enaminone **4**, a 1:1 mixture of the isomers), yellow oil, IR: 3390, 1640

($C{=}CH_2$), 1490, 1440, 1375, 1070,890 ($=CH_2$). UV: 232 (ε 8860), MS (*m/z*, %): 206.1419 (M^+, 79%, $C_{12}H_{18}N_2O$ requires 206.1419), 191 (29), 176 (22), 175 (100), 163 (17), 162 (29), 161 (25), 147 (32), 133 (13), 107(11). NMR data (CCl_4-benzene-d_6, 5:1 v/v):

(**9b**) ^{1}H NMR: 1.66 *br.s* (3H), 1.99 *s* (3H), 2.25-2.80 m (4H), 3.28 *tt* (*J* = 8.0 and 8.0 Hz, 1H), 3.65-3.90 m (4H), 4.5 br (OH), 4.66 *br.s* (1H), 4.73 *br.s* (1H). ^{13}C NMR: 158.18 *s* (C-4), 147.66 *s* (C-8), 132.06 *s* (C-2), 121.77 (C-3), 109.96 *t* (C-9), 61.54 *t*, 52.31 *d* (C-6), 50.96 *t*, 30.39 *t* (C-5), 28.56 *t* (C-7), 20.87 *q* (C-10), 10.45 *q* (C-1).

(**8b**) ^{1}H NMR: 1.64 *br.s* (3H), 2.03 *s* (3H), 2.25-2.80 m (4H), 3.40 *tt* (*J* = 8.0 and 8.0 Hz, 1H), 3.65-3.90 m (4H), 4.5 br (OH), 4.66 *br.s* (1H), 4.71 *br.s* (1H). ^{13}C NMR: 149.12 *s* and 147.31 *s* (C-4 and C-8), 141.68 *s* (C-2), 123.08 *s* (C-3), 110.09 *t* (C-9), 61.37 *t*, 53.48 *d* (C-6), 52.27 *t*, 29.25 t and 28.75 *t* (C-5 and C-7), 20.64 *q* (C-10), 12.71 *q* (C-1).

(±)-5-Isopropenyl-3-methyl-1-phenyl-1,4,5,6-tetrahydrocyclopentapyrazole (**8d**): 74% (from diketone **3**), 65% (from enaminone 4), reddish oil, IR: 1640 ($C{=}CH_2$), 1595, 1500, 1490, 1480, 1370, 1180, 1060, 890 ($=CH_2$). UV: 210 (ε 12200), 264 (ε 15400); MS (m/z): 238.1467 (M^+, 100%, $C_{16}H_{18}N_2$ requires 238.1470), 237 (59), 223 (88), 209 (15), 196 (12), 182 (9) 167 (12), 154 (6), 128 (10), 115 (5). ^{1}H NMR (acetone-d_6): 1.79 *ddd* (*J* = 1.5, 0.8, 0.4 Hz, 3H), 2.17 *s* (3H), 2.49 *ddddd* (*J* = 14.3, 7.8, 1.4, 1.4, 0.4 Hz, 1H), 2.74 *ddd* (*J* = 14.3, 8.4, 1.2 Hz, 1H), 2.98 *dddd* (*J* = 15.5, 8.0, 1.2, 1.2 Hz, 1H), 3.19 *ddd* (*J* = 15.5, 8.5, 1.3 Hz, 1H), 3.68 *ddddm* (*J* = 8.5, 8.4, 8.0, 7.8 Hz, $W_{1/2}$=2.7 Hz, 1H), 4.77 *ddq* (*J* = 2.0, 0.6, 1.5 Hz, 1H), 4.86 *ddq* (*J* = 2.0, 1.2, 0.8 Hz, 1H), 7.19 *m* (1H), 7.42 *m* (2H), 7.66 *m* (2H). ^{13}C NMR ($CDCl_3$): 146.78 *s* (C-4), 146.87 *s* (C-2), 143.71 *s* (C-8), 140.22 *s*, 128.94 *d* (2C), 126.42 *s* (C-3), 124.84 *d*, 118.43 *d* (2C), 109.70 *t* (C-9), 52.88 *d* (C-6), 31.78 *t* (C-5), 27.64 *t* (C-7), 20.07 *q* (C-10), 12.43 *q* (C-1).

(±)-5-Isopropenyl-3-methyl-1-(2-methoxyphenyl)-1,4,5,6-tetrahydrocyclopentapyrazole (**8f**): 62% (from diketone **3**), 45% (from enaminone **4**), m.p. 60-61°C (pentane-CH_2Cl_2). IR: 1640 ($C{=}CH_2$), 1600, 1520, 1505, 1480, 1430, 1370, 1280, 1020, 890 ($=CH_2$). UV: 283 (ε 6200), 248 (ε 9820), 219 (ε 16400). MS (*m/z*, %): 268.1579 (M^+, 100%, $C_{17}H_{20}N_2O$ requires 268.1576), 253 (44), 239 (12), 237 (19), 223 (7), 209 (8), 200 (18), 199 (19), 197 (9),183 (5),181 (5), 147 (6), 92 (13), 91 (12), 77 (30). ^{1}H NMR (CCl_4-benzene-d_6, 5:1 v/v): 1.65 *br.s* (3H), 2.15 *s* (3H), 2.34-2.79 *m* (4H), 3.42 *dddd* (*J* = 7.9, 7.9, 7.9, 7.9 Hz), 3.49 *s* (3H), 4.63 *br.s* (1H), 4.71 *br.s* (1H), 6.69 *dd* (*J* = 8.2, 1.2 Hz), 6.82 *ddd* (*J* = 7.8, 7.6, 1.2 Hz), 7.01 *ddd* (*J* = 8.2, 7.8, 1.8 Hz), 7.48 *dd* (*J* = 7.6, 1.8 Hz). ^{13}C NMR (CCl_4-benzene-d_6, 5:1 v/v): 152.40 *s*, 150.22 *s* (C-4), 147.76 *s* (C-2), 143.25 *s* (C-8), 130.64 *s*, 127.80 *d*, 127.36 *d*, 124.63 *s* (C-3), 121.19 *d*, 112.41 *d*, 109.91 *t* (C-9), 55.64 *q*, 53.34 *d* (C-6), 31.45 *t* (C-5 or C-7), 28.74 *t* (C-7 or C-5), 20.63 *q* (C-10), 13.01 *q* (C-1).

*Preparation of a mixtures of positional isomers **5a,d** and **6a,d** from enaminone **2** (Method D).*

A solution of enaminone **1** (1.0 g, 6.1 mmol) and methylhydrazine (15 mmol) in AcOH (10 ml) was refluxed for 3.5 h. The resulting reaction mixture was concentrated at reduced pressure, washed with an excess of concentrated aqueous ammonia and extracted with ether (2×20 ml). The combined ethereal extracts were washed with 1M HCl, 0.5 M Na_2CO_3, dried (Na_2SO_4) and concentrated at reduced pressure. The crude product was percolated on a silica gel column (benzene) to give *ca* 1:1 mixture of **5a** and **6a** in 73% yield. NMR data of the compounds are identical to those given above.

A solution of enaminone **1** (4.5 g, 27 mmol) and phenylhydrazine (1 g, 65 mmol) in AcOH (50 ml) was refluxed for 3.5 h. The resulted mixture was concentrated at reduced pressure, washed with an excess of concentrated aqueous ammonia, extracted with ether (2×20 ml). The combined ethereal extracts were washed with 1M HCl, 0.5 M Na_2CO_3, dried (Na_2SO_4) and concentrated at reduced pressure to give the crude mixture of isomers as a brown viscous oil (5.0 g). This oil was chromatographed on a silica gel column (pentane:benzene 10:1, v/v) to give 1.5 g (23%) of phenyl pyrazole **5d**, 1.7 g of a mixture of isomers **5d** and **6d**, and 0.7 g (11%) of phenyl pyrazole **6d**. Phenylpyrazole **5d** was identical to the sample described before,[6] ^1H NMR ($CDCl_3$): 0.69 *s* (3H), 1.09 *s* (3H), 1.78 *ddd* (*J* = 7.1, 6.5 and 1.2 Hz, 1H), 1.85 *dd* (*J* = 6.5 and 1.7 Hz, 1H), 2.27 *s* (3H), 2.77 *ddd* (*J* = 16.8, 1.7 and 1.2 Hz, 1H), 3.05 *dd* (*J* = 16.8 and 7.1 Hz, 1H), 7.14 (1H), 7.35*m* (2H), 7.55*m* (2H). ^{13}C NMR ($CDCl_3$): 148.68 (J_{C-H} = 5.7, 3.7, 3.7 and 3.7 Hz, C-4), 143.80 (J_{C-H} = 4.3, 4.3, 4.3, 1.0 and 1.0 Hz, C-2), 139.83 *s*, 128.73 *d* (2C), 128.12 *s* (C-3), 124.43 *d* (1C), 117.66 *d* (2C), 34.27 (J_{C-H} = 165.8 Hz, C-6), 26.35 (J_{C-H} = 133.0, 133.0, 4.1 and 1.3 Hz, C-5), 25.88 (J_{C-H} = 125.3, 125.3, 125.3, 4.6, 4.6, 4.6, 4.6 and 4.6 Hz, C-9), 25.54 ($J_{C-H} \approx$ 170 Hz, C-7), 21.67 *s* (C-8), 13.28 *qq* (J_{C-H} = 125.5, 125.5, 125.5, 4.0, 4.0 and 4.0 Hz, C-10), 12.27 (J_{C-H} = 127.1, 127.1 and 127.1 Hz, C-1). Carbon-carbon coupling constants $^1J_{C-C}$ are given on ***Fig. 1.***

(3bR,4aR)-3,4,4-Trimethyl-2-phenyl-3b,4,4a,5-tetrahydro-2H-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole (**6d**): m.p. 74-75°C (pentane-toluene), $[\alpha]^{12}$+8.1 (c 5.4, $CHCl_3$). IR: 1070, 1190, 1370, 1480, 1505, 1600. UV: 209 (ε 9400), 266 (ε 12000); MS (*m/z*, %): 238.1469 (M^+, 44%, $C_{16}H_{18}N_2$ requires 238.1470), 223 (100), 208 (7), 207 (5), 180 (3), 167 (8), 104 (3), 77 (34). ^1H NMR ($CDCl_3$): 0.70 *s* (3H), 1.05 *s* (3H), 1.68 *ddd* (*J* = 7.0, 6.6 and 1.1 Hz, 1H), 1.78 *dd* (*J* = 6.6 and 1.1 Hz, 1H), 2.20 *s* (3H), 2.56 *ddd* (*J* = 17.0, 1.1 and 1.1 Hz, 1H), 2.83 *dd* (*J* = 17.0 and 7.0 Hz, 1H), 7.17 *m* (1H), 7.25-7.40 *m* (4H). ^{13}C NMR ($CDCl_3$): 162.71 *s* (C-4), 140.15 *s*, 131.80 *s* (C-2), 128.36 *d* (2C), 126.04 *d* (1C), 125.27 *s* (C-3), 123 .73 *d* (2C), 33.63 *d* (C-6), 26.29 *q* (C-9), 25.80 *d* (C-7), 24.04 *t* (C-5), 22.43 *s* (C-8), 13.93 *q* (C-10), 11.38 *q* (C-1). Carbon-carbon coupling constants $^1J_{C-C}$ are given on ***Fig. 1.***

*Preparation of rearranged pyrazoles **19** and **20**.*

Concentrated H_2SO_4 (5 g, 51 mmol) was added to a solution of unsubstituted pyrazole (**5**, R=H) (0.5 g , 3.1 mmol) in $CHCl_3$ (5 ml). The resulted mixture was kept at room temperature for 36 h, then carefully poured in the ice-cold water (50 ml). The resulting mixture was neutralised with NH_4OH and extracted with $CHCl_3$ (2×20 ml). The combined extracts were dried over Na_2SO_4 and concentrated at reduced pressure to give 0.24 g (48 %) of *3,5,6-trimethyl-1H-indazole* (**19**) as white crystals with m.p. 152-154°C (CH_3CN) ,IR: 3480 (N-H), 1625, 1500, 1440, 1430, 1285, 1240, 1190, 1100, 1060, 970, 840. UV: 217 (ε 17600), 259 (ε 4100), 293 (ε 4500), 307 (ε 4100); MS (*m/z*, %): 160.1005 (M^+, 100%,$C_{10}H_{12}N_2$ requires 160.1000), 159 (60), 145 (57), 119 (6), 118 (6), 116 (6), 115 (7), 91 (11) ^1H NMR (pyridine-d_5): 2.25 *s* (3H), 2.29 *s* (3H), 2.65 *s* (3H), 7.43 *s* (1H), 7.48 *s* (1H), 8.6 *br*. ^{13}C NMR (pyridine-d_5): 141.64 *s*, 141.26 *s*, 135.71 *s*, 128.64 *s*, 122.05 *s*, 119.77 *d*, 110.45 *d*, 20.56 *q*, 20.03 *q*, 12.19 *q*.

Me_3SiCl (10 ml) and KI (6 g, 36 mmol) were added to a solution of phenyl pyrazole **5d** (6.5 g, 27.3 mmol) in acetonitrile (50 ml). The resulting mixture was stirred at reflux for 32 h. The solvent was removed at reduced pressure, the residue was treated with water (30 ml) and extracted with ether (2×50 ml). The combined ethereal extracts were washed with water (20 ml), 0.5 M $NaHCO_3$ (50 ml), 1M HCl (50 ml), dried over Na_2SO_4 and concentrated at reduced pressure to give 5.5 g of a brown oil which solidified on staying. The resulting product was percolated on a silica gel column (benzene-pentane, 1:1 v/v) and crystallised from a mixture of benzene-pentane to give pale yellow crystals (3.2 g, 49 %) of *5-isopropylidene-3-methyl-1-phenyl-1,4,5,6-tetrahydrocyclopentapyrazole* (**20**). M.p.78-79°C (pentane-toluene). IR: 1590, 1500, 1440, 1360, 1190, 1060, 1040. UV: 210 (ε 17600), 229 (ε 11400), 265 (ε 13000); MS (*m/z*, %): 238.1463 (M^+, 46%,$C_{16}H_{18}N_2$ requires 238.1470), 223 (100), 208 (4), 207 (3), 180 (4), 167 (8), 118 (4), 104 (3) 77(22). ^1H NMR (CCl_4-benzene-d_6, 5:1 v/v): 1.61 *br.s* (6H), 2.17 *s* (3H), 3.08 *s* (2H), 3.47 *s* (2H), 7.00 *t* (*J* = 7.4 Hz, 1H), 7.24 *dd* (*J* = 8.0, 7.4 Hz, 2H), 7.55 *d* (*J* = 8.0 Hz, 2H). ^{13}C NMR (CCl_4-benzene-d_6, 5:1 v/v): 145.64 *s* (C-4), 143.53 *s* (C-2), 141.13 *s*, 136.66 *s* (C-8), 129.21 *d* (2C), 125.98 *s* (C-3), 125.89 *s* (C-6), 124.65 *d*(1C), 118.29*d* (2C), 32.77 *t* (C-5), 28.18 *t* (C-7), 21.17 *q* and 20.92 *q* (C-9 and C-10), 13.09 *q* (C-1).

Acknowledgments: *The authors thank Mr. Andrey V. Chernobrivets for the experimental assistance and Dr. Aleksey V. Rukavishnikov for the literature search. The research described in this publication was made possible in part by Grant No. INTAS-93-1588-EXT. The authors thank Russian Foundation for Basic Research (Grant 96-03-33222) for the financial support of this work.*

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(*Received in UK* 9 *July* 1997; *revised* 20 *October* 1997; *accepted* 23 *October* 1997)