Synthesis of 1-Substituted 3,5-Diaryl-2-pyrazolines by the Reaction of α,β-Unsaturated Ketones with Hydrazines

Albert Lévai [a]* and József Jekő [b]

[a] Department of Organic Chemistry, University of Debrecen, P.O.Box 20, H-4010 Debrecen, Hungary
[b] Department of Chemistry, College of Nyíregyháza, Sóstói u. 31/b, H-4400 Nyíregyháza, Hungary

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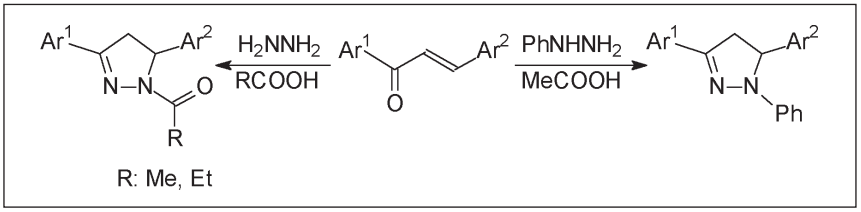

1-Acetyl-, 1-propionyl- and 1-phenyl-3,5-diaryl-2-pyrazolines have been synthesized by the reaction of the appropriate α,β-unsaturated ketones with hydrazine or phenylhydrazine in hot acetic acid or propionic acid. Structures of all new 2-pyrazolines **16**-**40** have been elucidated by microanalyses, ^{1}H and ^{13}C nmr spectroscopies.

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Introduction.

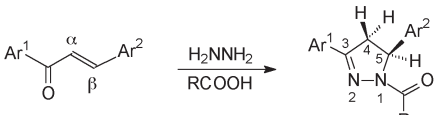
Pyrazolines are important and useful five-membered heterocyclic compounds and various procedures have been worked out for their synthesis [1-5]. Several pyrazoline derivatives were found to possess important bioactivities, *viz*. antibacterial [6,7], antiviral [8], antifungal [9], immunosuppressive [10], central nervous system [11], molluscicidal [12,13], *etc*. activities. 1-Acetyl-3,5-diaryl-2-pyrazolines have been found to inhibit the monoamine oxidases [14]. On the other hand, 1,3,5-triaryl-2-pyrazolines were utilized as scintillation solutes [15]. Recently, 3-(2-pyridyl)-2-pyrazoline derivatives have been used as novel fluorescent probes [16]. All these mentioned bioactivities and other utilities stimulated the research in this field. 2-Pyrazolines proved to be the most useful pyrazoline type compounds and various methods have been developed for their synthesis [4,5,12-38]. A generally used simple and convenient procedure is based on the reaction of α,β-unsaturated aldehydes and ketones with hydrazines. As a continuation of our studies on the synthesis of 2-pyrazolines [32,33,35,36,38] by this method, herein we describe the synthesis of new 1-substituted 3,5-diaryl-2-pyrazolines bearing polycyclic aryl and/or heteroaryl moieties by the reaction of α,β-unsaturated ketones with hydrazines.

Results and Discussion.

Most of the α,β-unsaturated ketones used as starting materials for the synthesis of 2-pyrazolines belong to the substituted chalcones or exocyclic α,β-unsaturated ketones. There are only sporadic literature data on the utilization of α,β-unsaturated ketones bearing polycyclic aromatic rings [23,37], 2-furyl or 2-thienyl moieties [22,27,29]. For this reason, the aim of our present study was to investigate the influence of the space demand of the aromatic rings of the α,β-unsturated ketones, used as starting materials, on the formation of 2-pyrazolines on their reaction with hydrazines. Electronic structures of the aromatic rings of starting materials **1-15** can also influence the electron density of the α,β-unsaturated ketone units of the molecules. Compounds **1-15** seem to be adequate examples to investigate this effect, too.

Compounds **1-15** were allowed to react with hydrazine hydrate in hot acetic acid or propionic acid to afford 1-acetyl-3,5-diaryl-2-pyrazolines **16-28** or 3,5-diaryl-1-

Scheme 1



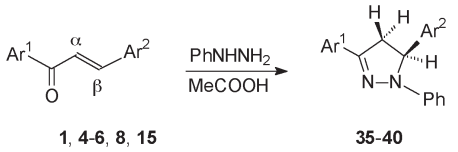
1-15 **16-34**

1, **16:** Ar^1 = phenyl, Ar^2 = 2-naphthyl, R = Me
2, **17:** Ar^1 = 4-bromophenyl, Ar^2 = 9-anthryl, R = Me
3, **18:** Ar^1 = 1-naphthyl, Ar^2 = 9-anthryl, R = Me
4, **19:** Ar^1 = 2-naphthyl, Ar^2 = 4-methoxyphenyl, R = Me
5, **20:** Ar^1 = 2-naphthyl, Ar^2 = 3,4-methylenedioxyphenyl, R = Me
6, **21:** Ar^1 = 2-naphthyl, Ar^2 = 4-chlorophenyl, R = Me
7, **22:** Ar^1 = 2-naphthyl, Ar^2 = 2,4-dichlorophenyl, R = Me
8, **23:** Ar^1 = Ar^2 = 2-naphthyl, R = Me
9, **24:** Ar^1 = 2-naphthyl, Ar^2 = 9-anthryl, R = Me
10, **25:** Ar^1 = 2-phenanthryl, Ar^2 = phenyl, R = Me
11, **26:** Ar^1 = 9-phenanthryl, Ar^2 = phenyl, R = Me
12, **27:** Ar^1 = 2-furyl, Ar^2 = 4-bromophenyl, R = Me
13, **28:** Ar^1 = 2-furyl, Ar^2 = 9-anthryl, R = Me
14, **29:** Ar^1 = phenyl, Ar^2 = 1-naphthyl, R = Et
1, **30:** Ar^1 = phenyl, Ar^2 = 2-naphthyl, R = Et
15, **31:** Ar^1 = 2-naphthyl, Ar^2 = phenyl, R = Et
5, **32:** Ar^1 = 2-naphthyl, Ar^2 = 3,4-methylenedioxyphenyl, R = Et
6, **33:** Ar^1 = 2-naphthyl, Ar^2 = 4-chlorophenyl, R = Et
7, **34:** Ar^1 = 2-naphthyl, Ar^2 = 2,4-dichlorophenyl, R = Et

propionyl-2-pyrazolines **29-34** in good yields (70-89%) (Scheme 1). It should be mentioned that only 1-acylated-2-pyrazolines could be detected in the crude reaction mixtures.

α,β-Unsaturated ketones **1,4-6,8** and **15** have also been reacted with phenylhydrazine in hot acetic acid and 3,5-diaryl-1-phenyl-2-pyrazolines were obtained in high yields (74-90%) (Scheme 2). In the crude reaction mixtures no by-produtcs were detected by chromatography.

Scheme 2



1, **4-6**, **8**, **15** **35-40**

1, **35:** Ar^1 = phenyl, Ar^2 = 2-naphthyl
15, **36:** Ar^1 = 2-naphthyl, Ar^2 = phenyl
4, **37:** Ar^1 = 2-naphthyl, Ar^2 = 4-methoxyphenyl
5, **38:** Ar^1 = 2-naphthyl, Ar^2 = 3,4-methylenedioxyphenyl
6, **39:** Ar^1 = 2-naphthyl, Ar^2 = 4-chlorophenyl
8, **40:** Ar^1 = Ar^2 = 2-naphthyl

Our experimental results prove that this simple procedure is extremely convenient for the preparation of such kind of 1-substituted 3,5-diaryl-2-pyrazolines. Both the space demand and the electronic structure of the aryl groups are almost without influence on the formation of the 2-pyrazoline ring. Even such bulky groups as 1- or 2-naphthyl, 9-anthryl and 9-phenanthryl can easily be accomodated at the C-3 and C-5 atoms of a 2-pyrazoline molecule. This is corroborated by the fact that these 2-pyrazolines are very stable compounds which can be stored at room temperature for a long time without the risk of decomposition.

Structures of the synthesized 2-pyrazolines **16-40** have been elucidated by microanalyses, ^{1}H and ^{13}C nmr spectroscopies. In the ^{1}H nmr spectra of compounds **16-40**, the three hydrogen atoms attached to the C-4 and C-5 carbon atoms of the 2-pyrazoline skeleton gave an ABX spin system. The 2-pyrazoline structure are unequivocally proved both by the chemical shift data and by the coupling constant values (*cf.* Experimental). Characteristic singlet signal of the N-acetyl group of the 1-acetyl-2-pyrazolines **16-28** were detected in each ^{1}H nmr spectrum. Triplet and quartet signals of the ethyl part of the N-propionyl group of compounds **29-34** were observed in each case. Owing to the steric interaction between the N-1 phenyl group and the two 4-H atoms, the *trans*-4-H is shielded and the *cis*-4-H is deshielded. Signals of the aromatic protons are highly overlapped. In the ^{13}C nmr spectra of compounds **16-40**, chemical shift data of carbon atoms C-3 (151-154 or 146-148 ppm), C-4 (41-44 ppm) and C-5 (56-65 ppm) confirm the 2-pyrazoline structure deduced from the ^{1}H nmr measurements. ^{13}C nmr chemical shifts of the N-acetyl and N-propionyl groups have also been detected in the ^{13}C nmr spectra of compounds **16-28** and **29-34** (*cf.* Experimental).

In summary, we have synthesized a series of new 1-substituted 3,5-diaryl-2-pyrazolines by the reaction of α,β-unsaturated ketones with hydrazines in hot acetic acid or propionic acid solution. This simple and convenient procedure made available the preparation of 3,5-diaryl-2-pyrazolines even with bulky aryl groups at positions 3 and 5. All these new 2-pyrazolines are stable compounds which property makes them useful substances in the drug research.

EXPERIMENTAL

Melting points were determined with a Koffler hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C nmr spectra were measured on a Varian Gemini 200 spectrometer at 200/50 MHz in $CDCl_3$ (internal standard TMS, δ = 0.0 ppm) at room temperature. Elemental analyses were measured in-house with a Carlo Erba 1106 EA instrument. The tlc was performed on Kieselgel 60 F_{254} (Merck) layer using hexane:acetone (7:3 v/v) or toluene:ethyl acetate (4:1 v/v) as eluents. Starting materials **1-15** were synthesized according to known methods [37,39-43].

General Procedure for the Preparation of 2-Pyrazolines **16-40**

A mixture of α,β-unsaturated ketone (**1-15**, 10.0 mmoles), hydrazine hydrate or phenylhydrazine (30.0 mmoles), acetic acid (50 ml) (in the case of 2-pyrazolines **16-28** and **35-40**) or propionic acid (50 ml) (in the case of 2-pyrazolines **29-34**) was refluxed for 3 hours, then poured onto crushed ice. The precipitate was separated by filtration, washed with water and crystallized from methanol to afford 2-pyrazolines (Scheme 1).

1-Acetyl-5-(2-naphthyl)-3-phenyl-2-pyrazoline (**16**).

This compound was obtained as white needles in 70% yield, mp 144-145°; ^{1}H nmr ($CDCl_3$): δ 2.46 (3H, s, Me), 3.24 (1H, dd, J = 4.7, 17.7 Hz, 4-H_{trans}), 3.81 (1H, dd, J = 11.8, 17.7 Hz, 4-H_{cis}), 5.76 (1H, dd, J = 4.7, 11.8 Hz, 5-H), 7.25-7.81 (m, 12 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.8, 42.3, 60.1, 123.6, 124.7, 126.0, 126.4, 126.7, 127.8, 128.1, 128.9, 129.2, 130.5, 131.6, 133.5, 139.3, 154.0, 168.1.

Anal. Calcd. for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.39; H, 5.81; N, 8.78.

1-Acetyl-5-(9-anthryl)-3-(4-bromophenyl)-2-pyrazoline (**17**).

This substance was prepared as white needles in 84% yield, mp 272-273°; ^{1}H nmr ($CDCl_3$): δ 2.36 (3H, s, Me), 3.46 (1H, dd, J = 9.8, 18.0 Hz, 4-H_{trans}), 3.87 (1H, dd, J = 13.0, 18.0 Hz, 4-H_{cis}), 6.82 (1H, dd, J = 9.8, 13.0 Hz, 5-H), 7.24-8.48 (m, 13 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.7, 41.5, 56.2, 122.8, 123.2, 124.7, 124.9, 125.0, 126.3, 126.8, 128.2, 128.4, 128.8, 129.6, 130.3, 130.6, 131.4, 131.6, 132.1, 132.2, 153.0, 169.9.

Anal. Calcd. for $C_{25}H_{19}BrN_2O$: C, 67.73; H, 4.32; N, 6.32. Found: C, 67.61; H, 4.37; N, 6.20.

1-Acetyl-5-(9-anthryl)-3-(1-naphthyl)-2-pyrazoline (**18**).

This compound was obtained as white plates in 79% yield, mp 251-252°; ^{1}H nmr ($CDCl_3$): δ 2.39 (3H, s, Me), 3.76 (1H, dd, J = 8.6, 17.8 Hz, 4-H_{trans}), 4.12 (1H, dd, J = 12.7, 17.8 Hz, 4-H_{cis}),

6.92 (1H, dd, J = 8.6, 12.7 Hz, 5-H), 7.12-8.37 (m, 16 arom. H); ^{13}C nmr ($CDCl_3$): δ 20.3, 44.4, 56.8, 123.0, 123.3, 124.7, 125.0, 125.5, 125.9, 126.0, 126.6, 126.8, 127.2, 127.9, 128.0, 128.4, 128.7, 128.9, 129.1, 129.6, 130.3, 130.7, 131.4, 134.6, 137.2, 151.4, 172.9.

Anal. Calcd. for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.75. Found: C, 84.17; H, 5.30; N, 6.84.

1-Acetyl-5-(4-methoxyphenyl)-3-(2-naphthyl)-2-pyrazoline (**19**).

This material was prepared as white needles in 81% yield, mp 151-152°; ^{1}H nmr ($CDCl_3$): δ 2.48 (3H, s, Me), 3.29 (1H, dd, J = 4.6, 17.6 Hz, 4-H_{trans}), 3.79 (3H, s, MeO), 3.81 (1H, dd, J = 11.7, 17.6 Hz, 4-H_{cis}), 5.60 (1H, dd, J = 4.6, 11.7 Hz, 5-H), 6.85-8.11 (m, 11 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.9, 42.1, 55.2, 59.5, 114.2, 123.2, 126.7, 126.9, 127.1, 127.8, 128.3, 128.4, 129.0, 132.9, 134.1, 153.8, 158.9, 168.7.

Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.84; H, 5.79; N, 8.21.

1-Acetyl-5-(3,4-methylenedioxyphenyl)-3-(2-naphthyl)-2-pyrazoline (**20**).

This compound was prepared as white needles in 83% yield, mp 198-199°; ^{1}H nmr ($CDCl_3$): δ 2.49 (3H, s, Me), 3.28 (1H, dd, J = 4.6, 17.7 Hz, 4-H_{trans}), 3.83 (1H, dd, J = 11.7, 17.7 Hz, 4-H_{cis}), 5.57 (1H, dd, J = 4.6, 11.7 Hz, 5-H), 6.72-8.10 (m, 10 arom. H); ^{13}C nmr ($CDCl_3$): δ 22.0, 42.3, 59.8, 101.1, 106.0, 108.5, 119.1, 123.2, 126.7, 127.1, 127.8, 128.3, 128.5, 128.9, 132.9, 134.1, 135.9, 147.0, 148.1, 153.8, 168.8.

Anal. Calcd. for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.81. Found: 73.62; H, 5.09; N, 7.92.

1-Acetyl-5-(4-chlorophenyl)-3-(2-naphthyl)-2-pyrazoline (**21**).

This substance was obtained as white needles in 89% yield, mp 152-153°; ^{1}H nmr ($CDCl_3$): δ 2.48 (3H, s, Me), 3.27 (1H, dd, J = 4.7, 17.6 Hz, 4-H_{trans}), 3.88 (1H, dd, J = 11.2, 17.6 Hz, 4-H_{cis}), 5.61 (1H, dd, J = 4.7, 11.2 Hz, 5-H), 7.19-8.09 (m, 11 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.9, 42.1, 59.4, 123.2, 126.8, 127.1, 127.3, 128.3, 128.5, 129.0, 132.9, 133.4, 134.1, 140.3, 153.7, 168.8.

Anal. Calcd. for $C_{21}H_{17}ClN_2O$: C, 72.31; H, 4.91; N, 8.03. Found: C, 72.22; H, 4.95; N, 7.92.

1-Acetyl-5-(2,4-dichlorophenyl)-3-(2-naphthyl)-2-pyrazoline (**22**).

This compound was prepared as white plates in 79% yield, mp 183-184°; ^{1}H nmr ($CDCl_3$): δ 2.52 (3H, s, Me), 3.18 (1H, dd, J = 5.1, 17.3 Hz, 4-H_{trans}), 3.96 (1H, dd, J = 11.9, 17.3 Hz, 4-H_{cis}), 5.91 (1H, dd, J = 5.1, 11.9 Hz, 5-H), 7.03-8.08 (m, 10 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.9, 41.2, 57.5, 123.1, 126.8, 127.0, 127.2, 127.4, 127.6, 127.9, 128.4, 128.6, 129.8, 132.5, 132.9, 133.9, 134.2, 137.3, 154.1, 168.9.

Anal. Calcd. for $C_{21}H_{16}Cl_2N_2O$: C, 65.81; H, 4.21; N, 7.30. Found: C, 65.72; H, 4.26; N, 7.21.

1-Acetyl-3,5-di(2-naphthyl)-2-pyrazoline (**23**).

This material was obtained as white plates in 88% yield, mp 238-239°; ^{1}H nmr ($CDCl_3$): δ 2.49 (3H, s, Me), 3.39 (1H, dd, J = 4.8, 17.6 Hz, 4-H_{trans}), 3.83 (1H, dd, J = 11.7, 17.6 Hz, 4-H_{cis}), 5.81 (1H, dd, J = 4.8, 11.7 Hz, 5-H), 7.26-8.12 (m, 14 arom. H); ^{13}H nmr ($CDCl_3$): δ 22.0, 42.3, 60.2, 123.3, 123.4, 124.5, 125.9, 126.2, 126.7, 127.1, 127.2, 127.6, 127.8, 127.9, 128.4, 129.0, 132.9, 133.3, 134.1, 139.1, 153.9, 168.9.

Anal. Calcd. for $C_{25}H_{20}N_2O$: C, 82.39; H, 5.53; N, 7.68. Found: C, 82.29; H, 5.59; N, 7.79.

1-Acetyl-5-(9-anthryl)-3-(2-naphthyl)-2-pyrazoline (**24**).

This compound was isolated as white plates in 77% yield, mp 217-218°; ^{1}H nmr ($CDCl_3$): δ 2.43 (3H, s, Me), 3.62 (1H, dd, J = 9.3, 18.0 Hz, 4-H_{trans}), 4.02 (1H, dd, J = 13.1, 18.0 Hz, 4-H_{cis}), 6.92 (1H, dd, J = 9.3, 13.1 Hz, 5-H), 7.24-8.53 (m, 16 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.8, 41.7, 56.1, 123.1, 123.3, 123.6, 124.7, 125.0, 126.3, 126.7, 126.9, 127.3, 128.0, 128.5, 128.7, 129.2, 129.6, 130.3, 131.6, 131.7, 132.1, 133.2, 134.4, 154.2, 169.9.

Anal. Calcd. for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.75. Found: C, 84.14; H, 5.39; N, 6.65.

1-Acetyl-3-(2-phenanthryl)-5-phenyl-2-pyrazoline (**25**).

This substance was prepared as white needles in 83% yield, mp 190-191°; ^{1}H nmr ($CDCl_3$): δ 2.51 (3H, s, Me), 3.30 (1H, dd, J = 4.7, 17.6 Hz, 4-H_{trans}), 3.86 (1H, dd, J = 11.7, 17.6 Hz, 4-H_{cis}), 5.65 (1H, dd, J = 4.7, 11.7 Hz, 5-H), 7.26-8.70 (m, 14 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.9, 42.3, 60.1, 122.8, 123.2, 124.0, 125.5, 126.7, 126.9, 127.2, 127.8, 128.6, 128.8, 129.4, 129.8, 131.3, 131.7, 132.4, 141.8, 153.6, 168.8.

Anal. Calcd. for $C_{25}H_{20}N_2O$: C, 82.39; H, 5.53; N, 7.68. Found C, 82.49; H, 5.48; N, 7.59.

1-Acetyl-3-(9-phenanthryl)-5-phenyl-2-pyrazoline (**26**).

This compound was prepared as white plates in 76% yield, mp 204-205°; ^{1}H nmr ($CDCl_3$): δ 2.54 (3H, s, Me), 3.47 (1H, dd, J = 4.6, 17.4 Hz, 4-H_{trans}), 4.06 (1H, dd, J = 11.8, 17.4 Hz, 4-H_{cis}), 5.62 (1H, dd, J = 4.6, 11.8 Hz, 5-H), 7.27-9.41 (m, 14 arom. H); ^{13}C nmr ($CDCl_3$): δ 22.1, 44.9, 58.8, 122.8, 123.1, 125.8, 126.8, 127.2, 127.6, 127.8, 128.4, 129.1, 129.2, 129.3, 130.5, 130.7, 131.1, 131.3, 142.1, 154.4, 169.1.

Anal. Calcd. for $C_{25}H_{20}N_2O$: C, 82.39; H, 5.53; N, 7.68. Found: C, 82.48; H, 5.58; N, 7.76.

1-Acetyl-5-(4-bromophenyl)-3-(2-furyl)-2-pyrazoline (**27**).

This material was isolated as white needles in 83% yield, mp 162-163°; ^{1}H nmr ($CDCl_3$): δ 2.40 (3H, s, Me), 3.04 (1H, dd, J = 5.6, 17.4 Hz, 4-H_{trans}), 3.70 (1H, dd, J = 11.3, 17.4 Hz, 4-H_{cis}), 5.51 (1H, dd, J = 5.6, 11.3 Hz, 5-H), 6.51-7.57 (m, 7 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.8, 41.8, 58.9, 111.9, 112.6, 121.3, 131.9, 140.5, 144.8, 145.4, 146.6, 168.7.

Anal. Calcd. for $C_{15}H_{13}BrN_2O_2$: C, 54.07; H, 3.93; N, 8.40. Found.: C, 54.15; H, 3.98; N, 8.32.

1-Acetyl-5-(9-anthryl)-3-(2-furyl)-2-pyrazoline (**28**).

This compound was prepared as pale yellow needles in 81% yield, mp 242-243°; ^{1}H nmr ($CDCl_3$): δ 2.34 (3H, s, Me), 3.45 (1H, dd, J = 9.4, 18.1 Hz, 4-H_{trans}), 3.86 (1H, dd, J = 13.1, 18.1 Hz, 4-H_{cis}), 6.54 (1H, dd, J = 9.4, 13.1 Hz, 5-H), 6.75-8.50 (m, 12 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.7, 41.3, 55.6, 112.1, 112.8, 122.9, 123.1, 124.7, 124.9, 126.3, 126.7, 128.4, 128.7, 129.5, 130.3, 131.2, 131.5, 132.0, 145.0, 147.1, 153.8, 169.8.

Anal. Calcd. for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12; N, 7.90. Found: C, 77.84; H, 5.16; N, 7.98.

5-(1-Naphthyl)-3-phenyl-1-propionyl-2-pyrazoline (**29**).

This substance was obtained as white needles in 89% yield, mp 164-165°; ^{1}H nmr ($CDCl_3$): δ 1.31 (3H, t, J = 7.6 Hz, $CH_2C\underline{H}_3$), 2.98 (2H, q, J = 7.6 Hz, $C\underline{H}_2CH_3$), 3.16 (1H, dd, J = 8.1, 17.7 Hz, 4-

H_{trans}), 3.93 (1H, dd, J = 11.8, 17.7 Hz, 4-H_{cis}), 6.36 (1H, dd, J = 8.1, 11.8 Hz, 5-H), 7.19-8.06 (m, 12 arom. H); ^{13}C nmr ($CDCl_3$): δ 8.9, 27.5, 41.8, 57.4, 112.4, 121.7, 123.0, 125.7, 125.8, 126.4, 126.7, 128.2, 128.8, 129.3, 130.4, 131.7, 134.5, 136.6, 154.4, 172.7.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.57; H, 6.18; N, 8.61.

5-(2-Naphthyl)-3-phenyl-1-propionyl-2-pyrazoline (**30**).

This material was isolated as white plates in 86% yield, mp 133-134°; ^{1}H nmr ($CDCl_3$): δ 1.21 (3H, t, J = 7.4 Hz, $CH_2C\underline{H}_3$), 2.83 (2H, q, J = 7.4 Hz, $C\underline{H}_2CH_3$), 3.21 (1H, dd, J = 4.8, 17.8 Hz, 4-H_{trans}), 3.80 (1H, dd, J = 11.8, 17.8 Hz, 4-H_{cis}), 5.72 (1H, dd, J = 4.8, 11.8 Hz, 5-H), 7.28-7.84 (m, 12 arom. H); ^{13}C nmr ($CDCl_3$): δ 8.8, 27.5, 42.0, 60.2, 123.6, 124.7, 126.0, 126.3, 126.7, 127.8, 128.1, 129.1, 130.4, 131.7, 133.1, 133.5, 139.5, 153.7, 172.6.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.38; H, 6.09; N, 8.47.

3-(2-Naphthyl)-5-phenyl-1-propionyl-2-pyrazoline (**31**).

This compound was obtained as white plates in 81% yield, mp 144-145°; ^{1}H nmr ($CDCl_3$): δ 1.29 (3H, t, J = 7.5 Hz, $CH_2C\underline{H}_3$), 2.90 (2H, q, J = 7.5 Hz, $C\underline{H}_2CH_3$), 3.30 (1H, dd, J = 4.8, 17.0 Hz, 4-H_{trans}), 3.84 (1H, dd, J = 11.9, 17.0 Hz, 4-H_{cis}), 5.65 (1H, dd, J = 4.8, 11.9 Hz, 5-H), 7.21-8.09 (m, 12 arom. H); ^{13}C nmr ($CDCl_3$): δ 8.8, 27.5, 41.9, 60.2, 123.4, 125.7, 126.9, 127.1, 127.3, 127.7, 128.0, 128.5, 128.6, 129.0, 129.3, 133.2, 134.3, 142.3, 153.8, 172.6.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.53; H, 6.18; N, 8.63.

5-(3,4-Methylenedioxyphenyl)-3-(2-naphthyl)-1-propionyl-2-pyrazoline (**32**).

This substance was prepared as white plates in 74% yield, mp 143-144°; ^{1}H nmr ($CDCl_3$): δ 1.26 (3H, t, J = 7.5 Hz, $CH_2C\underline{H}_3$), 2.89 (2H, q, J = 7.5 Hz, $C\underline{H}_2CH_3$), 3.27 (1H, dd, J = 4.7, 17.6 Hz, 4-H_{trans}), 3.82 (1H, dd, J = 11.8, 17.6 Hz, 4-H_{cis}), 5.53 (1H, dd, J = 4.7, 11.8 Hz, 5-H), 5.91 (2H, s, $C\underline{H}_2$), 6.73-8.11 (m, 10 arom. H); ^{13}C nmr ($CDCl_3$): δ 8.7, 27.5, 41.9, 59.9, 101.1, 106.1, 108.6, 119.2, 123.4, 126.9, 127.1, 127.3, 127.9, 128.5, 128.6, 129.3, 133.1, 134.3, 136.3, 147.2, 148.3, 153.7, 172.6.

Anal. Calcd. for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52. Found: C, 74.28; H, 5.46; N, 7.60.

5-(4-Chlorophenyl)-3-(2-naphthyl)-1-propionyl-2-pyrazoline (**33**).

This compound was prepared as white needles in 82% yield, mp 192-193°; ^{1}H nmr ($CDCl_3$): δ 1.23 (3H, t, J = 7.5 Hz, $CH_2C\underline{H}_3$), 2.89 (2H, q, J = 7.5 Hz, $C\underline{H}_2CH_3$), 3.39 (1H, dd, J = 4.9, 17.7 Hz, 4-H_{trans}), 3.90 (1H, dd, J = 11.9, 17.7 Hz, 4-H_{cis}), 5.60 (1H, dd, J = 4.9, 11.9 Hz, 5-H), 7.19-8.10 (m, 11 arom. H); ^{13}C nmr ($CDCl_3$): δ 8.7, 27.4, 41.8, 59.6, 123.4, 126.9, 127.2, 127.3, 128.0, 128.5, 128.7, 129.1, 129.2, 133.1, 133.6, 134.6, 134.3, 140.8, 153.7, 172.6.

Anal. Calcd. for $C_{22}H_{19}ClN_2O$: C, 72.82; H, 5.28; N, 7.72. Found: C, 72.91, H, 5.33; N, 7.81.

5-(2,4-Dichlorophenyl)-3-(2-naphthyl)-1-propionyl-2-pyrazoline (**34**).

This substance was isolated as white needles in 71% yield, mp 195-196°; ^{1}H nmr ($CDCl_3$): δ 1.29 (3H, t, J = 7.5 Hz, $CH_2C\underline{H}_3$), 2.94 (2H, q, J = 7.5 Hz, $C\underline{H}_2CH_3$), 3.18 (1H, dd, J = 5.2, 17.8 Hz, 4-H_{trans}), 3.95 (1H, dd, J = 11.9, 17.8 Hz, 4-H_{cis}), 5.92 (1H, dd, J = 5.2, 11.9 Hz, 5-H), 7.04-8.09 (m, 10 arom. H); ^{13}C nmr ($CDCl_3$): δ 8.8, 27.4, 40.8, 57.4, 123.3, 126.9, 127.2, 127.3, 127.8, 128.0, 128.5, 128.7, 128.9, 129.0, 129.9, 133.1, 134.3, 137.7, 154.1, 172.7.

Anal. Calcd. for $C_{22}H_{18}Cl_2N_2O$: C, 66.51; H, 4.57; N, 7.05. Found: C, 66.60; H, 5.52; N, 7.12.

1,3-Diphenyl-5-(2-naphthyl)-2-pyrazoline (**35**).

This compound was prepared as pale yellow needles in 83% yield, mp 145-146°; ^{1}H nmr ($CDCl_3$): δ 3.22 (1H, dd, J = 7.4, 17.2 Hz, 4-H_{trans}), 3.95 (1H, dd, J = 12.6, 17.2 Hz, 4-H_{cis}), 5.42 (1H, dd, J = 7.4, 12.6 Hz, 5-H), 6.79-7.86 (m, 17 arom. H); ^{13}C nmr ($CDCl_3$): δ 43.5, 64.8, 112.4, 113.6, 119.3, 123.9, 124.8, 125.9, 126.1, 126.5, 127.9, 128.0, 128.7, 128.8, 129.0, 129.5, 132.9, 133.1, 133.7, 140.2, 145.2, 147.0.

Anal. Calcd. for $C_{25}H_{20}N_2$: C, 86.18; H, 5.78; N, 8.04. Found: C, 86.29; H, 5.84; N, 8.13.

1,5-Diphenyl-3-(2-naphthyl)-2-pyrazoline (**36**).

This substance was obtained as yellow plates in 90% yield, mp 225-226°; ^{1}H nmr ($CDCl_3$): δ 3.23 (1H, dd, J = 7.2, 17.1 Hz, 4-H_{trans}), 3.92 (1H, dd, J = 12.6, 17.1 Hz, 4-H_{cis}), 5.31 (1H, dd, J = 7.2, 12.6 Hz, 5-H), 6.75-8.18 (m, 17 arom. H); ^{13}C nmr ($CDCl_3$): δ 43.5, 64.6, 113.4, 119.2, 123.5, 125.0, 126.3, 126.4, 127.6, 127.8, 128.1, 128.9, 129.2, 130.4, 133.3, 133.4, 142.6, 144.7, 146.8.

Anal. Calcd. for $C_{25}H_{20}N_2$: C, 86.18; H, 5.78; N, 8.04. Found: C, 86.08; H, 5.71, N, 7.93.

5-(4-Methoxyphenyl)-3-(2-naphthyl)-1-phenyl-2-pyrazoline (**37**).

This compound was prepared as yellow plates in 77% yield, mp 176-177°; ^{1}H nmr ($CDCl_3$): δ 3.11 (1H, dd, J = 6.9, 17.1 Hz, 4-H_{trans}), 3.69 (3H, s, MeO), 3.74 (1H, dd, J = 12.3, 17.1 Hz, 4-H_{cis}), 5.15 (1H, dd, J = 6.9, 12.3 Hz, 5-H), 6.70-8.10 (m, 16 arom. H); ^{13}C nmr ($CDCl_3$): δ 43.4, 55.2, 64.0, 113.6, 114.6, 123.6, 124.8, 125.1, 126.1, 126.5, 127.2, 127.8, 128.2, 128.4, 129.0, 129.1, 130.2, 133.6, 134.8, 144.9, 146.9, 159.2.

Anal. Calcd. for $C_{26}H_{22}N_2O$: C, 82.51; H, 5.86; N, 7.39. Found: C, 82.62; H, 5.91; N, 7.28.

5-(3,4-Methylenedioxyphenyl)-3-(2-naphthyl)-1-phenyl-2-pyrazoline (**38**).

This material was prepared as yellow needles in 82% yield, mp 192-193°; ^{1}H nmr ($CDCl_3$): δ 3.24 (1H, dd, J = 7.1, 17.1 Hz, 4-H_{trans}), 3.92 (1H, dd, J = 12.7, 17.1 Hz, 4-H_{cis}), 5.25 (1H, dd, J = 7.1, 12.7 Hz, 5-H), 5.92 (2H, s, CH_2), 6.81-8.20 (m, 15 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.3, 44.2, 63.7, 116.4, 116.7, 120.5, 121.5, 123.8, 123.9, 124.4, 128.7, 134.4, 134.5, 138.7, 139.4, 140.3, 140.7, 141.7, 143.6, 144.3, 145.1, 145.7, 148.6.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.13. Found: C, 79.44; H, 5.18; N, 7.22.

5-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-2-pyrazoline (**39**).

This substance was obtained as pale yellow needles in 74% yield, mp 160-161°; ^{1}H nmr ($CDCl_3$): δ 3.23 (1H, dd, J = 7.1, 17.0 Hz, 4-H_{trans}), 3.97 (1H, dd, J = 12.3, 17.0 Hz, 4-H_{cis}), 5.80 (1H, dd, J = 7.1, 12.3 Hz, 5-H), 6.79-8.20 (m, 16 arom. H); ^{13}C nmr ($CDCl_3$): δ 43.4, 63.9, 113.5, 119.4, 123.4, 125.1, 125.4,

126.5, 127.3, 127.8, 128.1, 128.2, 128.8, 129.0, 129.4, 129.9, 130.2, 133.3, 133.5, 141.0, 144.5, 146.8.

Anal. Calcd. for $C_{25}H_{19}ClN_2$: C, 78.42; H, 5.01; N, 7.31. Found: C, 78.53; H, 5.06; N, 7.42.

3,5-Di(2-naphthyl)-1-phenyl-2-pyrazoline (**40**).

This compound was prepared as yellow plates in 81% yield, mp 205-206°; ^{1}H nmr ($CDCl_3$): δ 3.34 (1H, dd, J = 7.4, 17.1 Hz, 4-H_{trans}), 4.04 (1H, dd, J = 11.3, 17.1, 4-H_{cis}), 5.50 (1H, dd, J = 7.4, 11.3 Hz, 5-H), 6.81-8.20 (m, 19 arom. H); ^{13}C nmr ($CDCl_3$): δ 43.5, 64.9, 113.5, 119.3, 122.2, 123.5, 123.8, 124.7, 125.1, 125.9, 126.4, 126.8, 127.8, 128.1, 128.2, 128.9, 129.4, 130.4, 132.9, 133.3, 133.4, 133.5, 140.0, 144.8, 146.9.

Anal. Calcd. for $C_{29}H_{22}N_2$: C, 87.41; H, 5.56; N, 7.03. Found: C, 87.52; H, 5.61; N, 7.12.

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