Recyclization of 5-hydroxy-2-pyrazolines in the reaction with N-nucleophiles

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Dedicated to Prof. Oleg Kulinkovich on the occasion of his 60th birthday

Abstract

The reactions of 5-hydroxy-1-tosyl-2-pyrazolines with amines or with hydrazine have been investigated. We have shown that these compounds are convenient substrates for the synthesis of 5-aminosubstituted pyrazolines and NH-pyrazoles.

Keywords: Pyrazolines, pyrazoles, a ring-chain tautomerism

Introduction

Tautomeric transformations provide a valuable opportunity for the targeted synthesis of certain classes of compounds.[1,2] The ring-chain transformations in the series of nitrogen-containing heterocycles allow rearranging the five-membered rings to the six-membered rings or reverse. In addition, various heteroatoms may be incorporated into the heterocyclic ring.[2]

It is known, that 5-hydroxy-2-pyrazolines in the solutions can exist in equilibrium with acyclic tautomers (Figure 1). A ratio of both forms is determined by the following factors: solvent, the structure of 1,3-dicarbonyl component and the nature of the substituted hydrazine moiety.[3-7] Electron-withdrawing substituents in the β-dicarbonyl fragment favor the ring and the enhydrazine form, while electron-accepting groups at the nitrogen atom promote hydrazones and cyclic forms. In basic dipolar solvents the tautomeric equilibrium shifts towards the open forms, in non-polar solvents 5-hydroxy-2-pyrazoline structure is preferred.

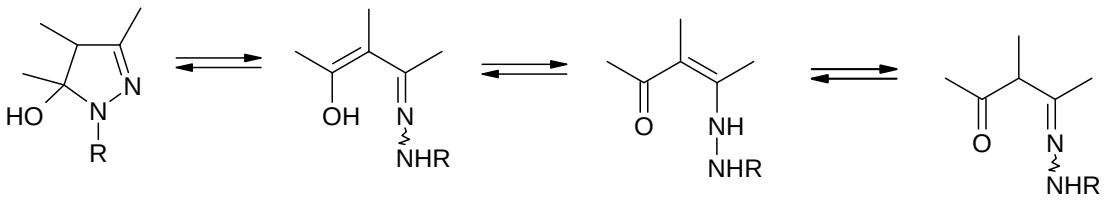
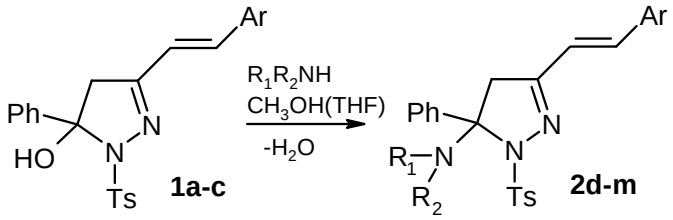


Figure 1

Previously, we synthesized several 5-hydroxy-1-tosyl-2-pyrazolines starting from unsaturated oxiranylketones. The mechanism of this reaction includes intra-molecular cyclization of the 1,3-diketone tosylhydrazone intermediates.[8] The presence of the reactive semi-aminal hydroxyl group[9,10] in 5-hydroxy-1-tosyl-2-pyrazolines allows their conversion to corresponding 5-aminosubstituted pyrazoline derivatives upon the reaction with primary or secondary amines.

Results and Discussion

The series of 5-hydroxy-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazoles **1a-c** reacted with a variety of primary and secondary amines in molar ratio 1:1 – 1:2 in methanol or THF for 6–24 h yielding 5-alkylamino(or dialkylamino)-3-(2-arylvinyl)-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazoles **2d-m** in 36–75% (Scheme 1, Table 1).



Scheme 1

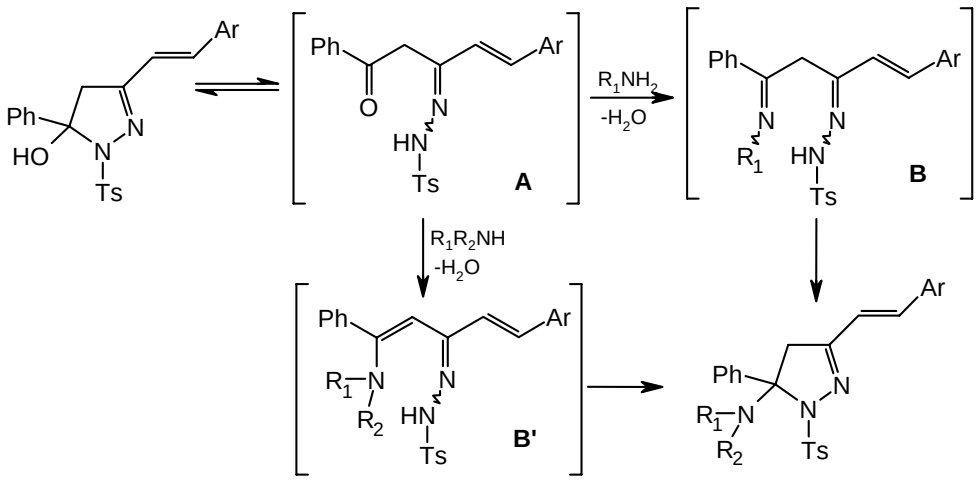
Table 1. Synthesis of 5-R-amino-3-(2-arylvinyl)-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazoles **2d-m**

Entry	R_1	R_2	Ar	Solvent	Compound **2** (Yield)
1	Me	H	Ph	MeOH	**2d** (70%)
2	Pr	H	Ph	THF	**2e** (65%)
3	Ch	H	Ph	MeOH	**2f** (69%)
4	CH_2OCH_2		Ph	THF	**2g** (50%)
5	Pr	H	3-Cl-C_6H_4	MeOH	**2h** (62%)
6	Me	Me	3-Cl-C_6H_4	MeOH	**2i** (64%)
7	Me	H	4-NO_2-C_6H_4	MeOH	**2j** (75%)
8	Ch	H	4-NO_2-C_6H_4	MeOH	**2k** (71%)
9	$PhCH_2$	H	4-NO_2-C_6H_4	MeOH	**2l** (36%)
10	$HO(CH_2)_3$	H	4-NO_2-C_6H_4	THF	**2m** (46%)

The structures of products **2d-m** were confirmed by ^{1}H-NMR and IR spectral data (the presence of N-alkyl proton signals and the absorption at 3375-3385 cm^{-1}, corresponding to NH-bond vibrations, respectively[11]). The absorption band of the hydroxyl group in starting materials, 5-hydroxy-2-pyrazolines at 3505 cm^{-1} are not present in the products, 5-amino-2-pyrazolines.

The formation of 5-amino-5-phenyl-1-tosyl-2-pyrazolines **2d-m** proceeds via acyclic intermediate **A,** which further transforms to the imino-hydrazone intermediate **B** and enamino-

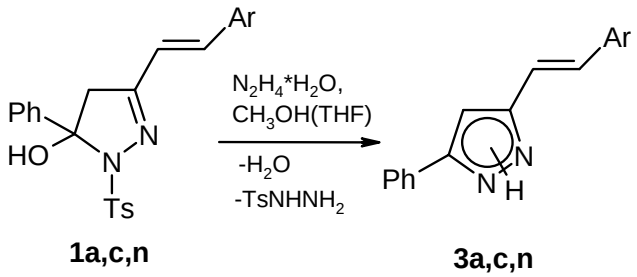
hydrazone **B'** as a result of the intermolecular nucleophilic addition of the amine to the carbonyl group (Scheme 2). Finally, upon preferential 5-exo-trig-attack of the imines group the intermediates **B** or **B'** undergo cyclization to the 5-amino-2-pyrazolines **2d-m**, according to the Baldwin's rule.[12]



Scheme 2

Interestingly, substitution of the hydroxyl group by the amine in a case of 5-hydroxy-1-tosyl-2-pyrazolines **1a-c** proceeds in much milder conditions than in the case of 1-acyl-5-hydroxy-2-pyrazolines,[13,14] which react only in solid phase synthesis conditions, usually at high temperature.

When hydrazine hydrate is used as a nucleophile in the reaction with 5-hydroxy-2-pyrazolines **1a,c,n,** the 3(5)-(2-arylvinyl)-5(3)-phenyl-1*H*-pyrazoles **3a,c,n** are obtained with 84-89% (Scheme 3, Table 2). Compounds **3a,c,n** are positional isomers of the pyrazoles that we synthesized earlier in our laboratory.[15] They are the products of the reaction of hydrazine hydrate with cynnamoyloxiranes and the following dehydration. Asymmetric β,β'-diaryl-dioxiranylketones upon reaction with hydrazine give β-hydroxyalkylpyrazoles. Their subsequent dehydration yield a mixture of isomeric 3(5)-aryl-5(3)-(2-phenylvinyl)-1*H*-pyrazoles and 5(3)-(2-arylvinyl)-3(5)-phenyl-1*H*-pyrazoles. The reaction of 5-hydroxy-2-pyrazolines **1a,c** with phenylhydrazine instead of hydrazine hydrate displays deeply colored reaction mixture from which it was not possible to isolate individual compounds.



1a,c,n **3a,c,n**

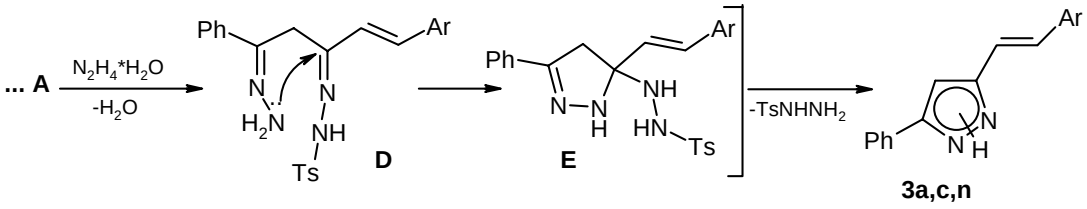
Scheme 3

Table 2. Synthesis of 3(5)-(2-arylvinyl)-5(3)-phenyl-1*H*-pyrazoles **3a,c,n**

Entry	Ar	Compound **3** (Yield)
1	Ph	**3a** (84%)
2	4-NO_2-C_6H_4	**3c** (89%)
3	4-Br-C_6H_4	**3n** (88%)

The IR spectra confirms the structure of pyrazoles **3a,c,n** by the presence the N-H vibrations bands at 3264-3232 cm^{-1}. In the ^1H NMR spectra there is a singlet at 6.75-6.81 ppm of the hydrogen atom at the 4-position of the azole ring;[16] the signals of tosyl moiety protons are absent.

The reaction mechanism of 3-(2-arylvinyl)-5-hydroxy-5-phenyl-1-tosyl-2-pyrazolines **1a,c,n** with hydrazine includes the nucleophilic attack of the substrate acyclic form, however, diketone *bis*-hydrazone **D** cyclization occurs with participation of the more nucleophilic NH_2 group, rather than the NH group of the hydrazone moieties, thus leading to the 5-tosylhydrazine-2-pyrazoline **E** intermediate (Scheme 4). The following elimination of tosylhydrazine affords the final products, 3(5)-(2-arylvinyl)-5(3)-phenyl-1*H*-pyrazoles **3a,c,n**. We were not able to isolate or detect the pyrazolines **E** intermediate by the ^1H NMR method. It is important to note that the color of the solution of 5-hydroxy-2-pyrazolines become yellow or brightly orange immediately after addition even a drop of hydrazine then the reaction mixture gradually becomes colorless. The observed discoloration indicates breaking the conjugation in the intermediate *bis*-hydrazones which is present in the tautomeric equilibrium with enhydrazine form.



Scheme 4

We conclude, that the 5-hydroxy-5-phenyl-1-tosyl-2-pyrazolines can be employed as convenient substrates in the reactions with amines and hydrazine for the synthesis of 5-amine-3-(2-arylvinyl)-5-phenyl-1-tosyl-4,5-dihidro-1*H*-pyrazoles and 3(5)-(2-arylvinyl)-5(3)-phenyl-1*H*-pyrazoles.

Experimental Section

General Procedures. Synthesis of 3-(2-arylvinyl)-5-methyl- or 5-dimethylamino-1-tosyl-5-phenyl-4,5-dihydro-1*H*-pyrazoles (2d,i,j). Double molar excess of methylamine or dimethylamine in methanol was added to the colorless solution of 5-hydroxy-2-pyrazoline **1a-c** in 15 ml of methanol. After the addition of the first drop of the amine the reaction mixture color

instantaneously becomes orange. The mixture was kept at r.t. for 16-24 hours. Then the solvent and an excess of the amine were removed in vacuum and the residue was crystallized from the mixture of chloroform-methanol (1:10). Precipitated solids of 5-aminopyrazolines **2d,i,j** were separated by filtration.

5-Methylamino-5-phenyl-3-(2-phenylvinyl)-1-tosyl-4,5-dihydro-1*H*-pyrazole (2d). Yield 70%. Mp. 174–175ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (3H, s, C_6H_4-C**H**$_3$), 2.46 (3H, s, C**H**$_3$NH), 3.16 (1H, d, *J* = 18.0, C**H**$_2$), 3.40 (1H, d, *J* = 18.0, C**H**$_2$), 6.63 (1H, d, *J* = 16.4, C**H**=), 7.07 (1H, d, *J* = 16.4, C**H**=), 7.19–7.50 (12H, m, arom), 7.65 (2H, d, *J* = 8.3, C_6**H**$_4$-CH_3). Anal. Calcd for $C_{25}H_{25}N_3O_2S$: C 69.58, H 5.84, N 9.74. Found: C 69.44, H 5.98, N 9.87.

3-[2-(3-Chlorophenyl)vinyl]-5-dimethylamino-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2i). Yield 64%. Mp. 154–156ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (6H, s, (C**H**$_3$)$_2$N), 2.40 (3H, s, C_6H_4-C**H**$_3$), 3.26 (1H, d, *J* = 18.0, C**H**$_2$), 3.47 (1H, d, *J* = 18.0, C**H**$_2$), 6.60 (1H, d, *J* = 16.6, C**H**=), 7.06 (1H, d, *J* = 16.6, C**H**=), 7.21–7.51 (11H, m, arom), 7.64 (2H, d, *J* = 8.3, C_6**H**$_4$-CH_3). Anal. Calcd for $C_{26}H_{26}ClN_3O_2S$: C 65.06, H 5.46, N 8.75. Found: C 64.87, H 5.54, N 8.89.

5-Methylamino-3-[2-(4-nitrophenyl)vinyl]-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2j). Yield 75%. Mp. 169–171ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (3H, s, C_6H_4-C**H**$_3$), 2.46 (3H, s, C**H**$_3$NH), 3.17 (1H, d, *J* = 18.2, C**H**$_2$), 3.42 (1H, d, *J* = 18.2, C**H**$_2$), 6.65 (1H, d, *J* = 16.6, C**H**=), 7.19 (1H, d, *J* = 16.6, C**H**=), 7.21–7.35 (7H, m, arom), 7.53 (2H, d, *J* = 9.0, C_6**H**$_4$-NO_2), 7.57 (2H, d, *J* = 8.4, C_6**H**$_4$-CH_3), 8.20 (2H, d, *J* = 9.0, C_6**H**$_4$-NO_2). Anal. Calcd for $C_{25}H_{24}N_4O_4S$: C 63.01, H 5.08, N 11.76. Found: C 62.84, H 5.31, N 11.82.

General procedure. Synthesis of 3-(2-arylvinyl)-5-R-amino-1-tosyl-5-phenyl-4,5-dihydro-1*H*-pyrazoles (2e,f,g,h,k,l,m)

Procedure has been described elsewhere.[8]

The spectral data of 3-(2-phenylvinyl)-5-cyclohexylamine-1-tosyl-5-phenyl-4,5-dihydro-1*H*-pyrazole **2f** have been reported elsewhere.[8]

5-Phenyl-3-(2-phenylvinyl)-5-propylamino-1-tosyl-4,5-dihydro-1*H*-pyrazole (2e). Yield 65%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (3H, т, *J* = 7.3, C**H**$_3$CH$_2$CH$_2$), 1.60 (2H, m, CH$_3$C**H**$_2$CH$_2$), 2.40 (3H, s, C_6H_4-C**H**$_3$), 2.57 (2H, m, CH$_3$CH$_2$C**H**$_2$), 3.14 (1H, d, *J* = 18.0, C**H**$_2$), 3.37 (1H, d, *J* = 18.0, C**H**$_2$), 6.61 (1H, d, *J* = 16.4, C**H**=), 7.05 (1H, d, *J* = 16.4, C**H**=), 7.19–7.43 (12H, m, arom), 7.59 (2H, d, *J* = 8.3, C_6**H**$_4$-CH_3). IR (KBr, cm^{-1}): ν = 3378 (NH), 2936 (CH), 1368 (S=O), 1168 (S=O) Anal. Calcd for $C_{27}H_{29}N_3O_2S$: C 70.56, H 6.36, N 9.14. Found: C 70.40, H 6.53, N 9.23.

5-Morpholino-5-phenyl-3-(2-phenylvinyl)-1-tosyl-4,5-dihydro-1*H*-pyrazole (2g). Yield 50%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (3H, s, C_6H_4-C**H**$_3$), 2.99 (4H, m, C**H**$_2$NC**H**$_2$), 3.46 (1H, d, *J* = 17.9, C**H**$_2$), 3.64 (1H, d, *J* = 17.9, C**H**$_2$), 3.76 (4H, m, C**H**$_2$OC**H**$_2$), 6.63 (1H, d, *J* = 16.4, C**H**=), 7.02 (1H, d, *J* = 16.4, C**H**=), 7.22–7.71 (14H, m, arom). Anal. Calcd for $C_{28}H_{29}N_3O_3S$: C 68.97, H 5.99, N 8.62. Found: C 68.81, H 6.14, N 8.78.

3-(2-(3-Chlorophenyl)vinyl)-5-phenyl-5-propylamino-1-tosyl-4,5-dihydro-1*H*-pyrazole (2h). Yield 62%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (3H, т, *J* = 7.3,

C**H**$_3$CH$_2$CH$_2$), 1.61 (2H, m, CH$_3$C**H**$_2$CH$_2$), 2.41 (3H, s, C$_6$H$_4$-C**H**$_3$), 2.56 (2H, m, CH$_3$CH$_2$C**H**$_2$), 3.12 (1H, d, *J* = 18.0, C**H**$_2$), 3.35 (1H, d, *J* = 18.0, C**H**$_2$), 6.53 (1H, d, *J* = 16.4, C**H**=), 7.04 (1H, d, *J* = 16.4, C**H**=), 7.21–7.51 (11H, m, arom), 7.59 (2H, d, *J* = 8.3, C$_6$**H**$_4$-CH$_3$). IR (KBr, cm^{-1}): ν = 3375 (NH), 2935 (CH), 1359 (S=O), 1168 (S=O). Anal. Calcd for $C_{27}H_{28}ClN_3O_2S$: C 65.64, H 5.71, N 8.51. Found: C 65.49, H 5.87, N 8.34.

5-Cyclohexylamino-3-[2-(4-nitrophenyl)vinyl]-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2k). Yield 71%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21–2.27 (10H, m, C$_6$**H**$_{11}$), 2.39 (3H, s, C$_6$H$_4$-C**H**$_3$), 2.83 (1H, m, C$_6$**H**$_{11}$), 3.17 (1H, d, *J* = 18.0, C**H**$_2$), 3.55 (1H, d, *J* = 18.0, C**H**$_2$), 6.65 (1H, d, *J* = 16.4, C**H**=), 7.18 (1H, d, *J* = 16.4, C**H**=), 7.21–7.36 (7H, m, arom), 7.53 (2H, d, *J* = 9.0, C$_6$**H**$_4$-NO$_2$), 7.57 (2H, d, *J* = 8.4, C$_6$**H**$_4$-CH$_3$), 8.20 (2H, d, *J* = 9.0, C$_6$**H**$_4$-NO$_2$). Anal. Calcd for $C_{30}H_{32}N_4O_4S$: C 66.16, H 5.92, N 10.29. Found: C 66.03, H 6.00, N 10.45.

5-Benzylamino-3-[(2-(4-nitrophenyl)vinyl]-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2l). Yield 36%. Mp. 230ºC (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (3H, s, C$_6$H$_4$-C**H**$_3$), 3.18 (1H, d, *J* = 18.0, C**H**$_2$), 3.44 (1H, d, *J* = 18.0, C**H**$_2$), 4.82 (2H, d, *J* = 1.1, C**H**$_2$Ph), 6.57 (1H, d, *J* = 16.4, C**H**=), 7.11–7.80 (17H, m, arom, C**H**=), 8.19 (2H, d, *J* = 8.7, C$_6$**H**$_4$-NO$_2$), 8.39 (1H, br.t, N**H**). Anal. Calcd for $C_{31}H_{28}N_4O_4S$: C 67.37, H 5.11, N 10.14. Found: C 67.20, H 5.34, N 10.25.

5-(3-Hydroxypropyl)amino-3-[2-(4-nitrophenyl)vinyl]-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2m). Yield 46%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (2H, m, HOCH$_2$C**H**$_2$CH$_2$NH), 2.41 (3H, s, C$_6$H$_4$-C**H**$_3$), 2.69 (2H, m, HOCH$_2$CH$_2$C**H**$_2$NH), 3.18 (1H, d, *J* = 18.0, C**H**$_2$), 3.42 (1H, d, *J* = 18.0, C**H**$_2$), 3.86 (2H, m, HOC**H**$_2$CH$_2$CH$_2$NH), 6.45 (1H, d, *J* = 16.4, C**H**=), 7.18 (1H, d, *J* = 16.4, C**H**=), 7.20–7.56 (11H, m, arom), 8.20 (2H, d, *J* = 8.7, C$_6$**H**$_4$-NO$_2$). Anal. Calcd for $C_{27}H_{28}N_4O_5S$: C 62.29, H 5.42, N 10.76. Found: C 62.02, H 5.57, N 10.59.

General procedure. Synthesis of 3(5)-(2-arylvinyl)-5(3)-phenyl-1*H*-pyrazoles (3a,c,n). To the solution of 2.5 mmol 5-hydroxy-2-pyrazolines **1a,c,n** in 20 ml MeOH-THF mixture (5:1) 0.2 ml hydrazine hydrate was added. Reaction mixture was left at 25ºC for 12 hours. Solvent was removed in vacuum and residue was diluted with ether. Solid pyrazoles **3a,c,n** were filtered off as a yellow crystals.

5(3)-Phenyl-3(5)-(2-phenylvinyl)-1*H*-pyrazole (3a). Yield 84%. Mp. 136–138ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75(1H, s, C(4)-**H**), 7.04 (1H, d, *J* = 16.4, C**H**=), 7.11 (1H, d, *J* = 16.4, C**H**=), 7.17–7.73 (10H, m, arom). IR (KBr, cm^{-1}): ν = 3264 (NH), 1596 (arom), 957 (HC=) Anal. Calcd for $C_{17}H_{14}N_2$: C 82.90, H 5.73, N 11.37. Found: C 82.85, H 5.84, N 11.45.

3(5)-[2-(4-Nitrophenyl)vinyl]-5(3)-phenyl-1*H*-pyrazole (3c). Yield 89%. Mp. 187–188ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (1H, s, C(4)-**H**), 7.17 (1H, d, *J* = 16.6, C**H**=), 7.24 (1H, d, *J* = 16.6, C**H**=), 7.35–7.47 (3H, m, C$_6$**H**$_5$), 7.60 (2H, d, *J* = 8.7, C$_6$**H**$_4$), 7.67 (2H, m, C$_6$**H**$_5$), 8.21 (2H, d, *J* = 8.7, C$_6$**H**$_4$). IR (KBr, cm^{-1}): ν = 3232 (NH), 1593 (arom), 1508 (NO$_2$), 1344 (NO$_2$), 960 (HC=). Anal. Calcd for $C_{17}H_{13}N_3O_2$: C 70.09, H 4.50, N 14.42. Found: C 69.91, H 4.67, N 14.38.

3(5)-[2-(4-Bromophenyl)vinyl]-5(3)-phenyl-1*H*-pyrazole (3n). Yield 88%. Mp. 223–225ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75(1H, s, C(4)-**H**), 7.04 (2H, s, C**H**=C**H**), 7.32–7.48 (7H, m,

arom), 7.69 (2H, m, arom). IR (KBr, cm^{-1}): ν = 3263 (NH), 1595 (arom), 958 (HC=). Anal. Calcd for $C_{17}H_{13}BrN_2$: C 62.79, H 4.03, N 8.61. Found: C 62.62, H 4.26, N 8.79.

Acknowledgements

We thank Prof. Oleg Kulinkovich for the assistance in carrying out of spectroscopic analysis.

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