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1,3-Dipolar cycloaddition of *N*-[4-nitrophenyl]-*C*-[2-furyl] nitrilimine with some dipolarophiles: A combined experimental and theoretical study

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ABSTRACT

Reaction of vinyl acetate (**3**), 2-propyne-1-ol (**4**) and styrene (**5**) as dipolarphiles with *N*-[4-nitrophenyl]-*C*-[2-furyl] nitrilimine which was generated in situ has been shown to afford 3-(furan-2-yl)-1-(4-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-5-yl acetate (**6**), (3-(furan-2-yl)-1-(4-nitrophenyl)-1*H*-pyrazol-5-yl)methanol (**8**) and 3-(furan-2-yl)-1-(4-nitrophenyl)-5-phenyl-4,5-dihydro-1*H*-pyrazole (**10**). Reactivity and regiochemistry of these reactions were investigated using DFT-based reactivity indexes.

1. Introduction

The cycloaddition of 1,3-dipolar species to an alkene for the synthesis of five-membered rings is a classic and important reaction in organic chemistry [1]. These 1,3-dipolar cycloaddition (1,3-DC) reactions are used for both academia and industrial purposes [2]. These reactions are one of the most important processes with both synthetic and mechanistic interest in organic chemistry. Current understanding of the underlying principles in the Diels–Alder (DA) reactions and the 1,3-dipolar cycloadditions (1,3-DC) has grown from a fruitful interplay between theory and experiment [2–4]. The development of the 1,3-DC reactions has in recent years entered a new stage as control of the stereochemistry in the addition step is now the major challenge. The stereochemistry of these reactions may be controlled either by choosing the appropriate substrates or by controlling the reaction using a metal complex acting as catalyst [5]. Two major factors i.e. the steric and electronic effects can influence the regioselectivity of these reactions [2]. Although transition state theory remains the most widely used and the most rigorous approach for the study of the mechanism and the regiochemistry of these reactions, the localization of transition states is not always easier.

Furthermore, transition-state calculations are often very time consuming when bulky substituents are present in reactive systems.

Recently, reactivity descriptors based on the density functional theory (DFT), such as Fukui indexes, local softnesses and local electrophilicity, have been extensively used for the prediction of the regioselectivity. For instance, several treatments of 1,3-DC reactions of nitrilimines with various dipolarophiles can be found in the literature [6–8]. 1,3-Dipolar cycloadditions of nitrilimines to olefins have been utilized extensively to synthesize pyrazoles and pyrazolidines [9]. Furyl-substituted nitrilimines as useful 1,3-dipoles have received much less attention than their aryl analogues or furyl-substituted nitrile oxides or nitrones. In fact, only a few papers that deal specifically with 2-furannitrilimines have been published [10–12]. This situation most likely reflects the instability of available precursors and presents a relatively unexplored area suitable for further studies. In this context, we became interested in the reactivity of *N*-[4-nitrophenyl]-*C*-[2-furyl] nitrilimine (**2**) as an electron-poor dipole towards several electron-rich dipolarophiles such as vinyl acetate (**3**), 2-propyne-1-ol (**4**) and styrene (**5**) as dipolarphiles in order to synthesize the new 3-(furan-2-yl)-1-(4-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-5-yl acetate (**6**), (3-(furan-2-yl)-1-(4-nitrophenyl)-1*H*-pyrazol-5-yl)methanol (**8**) and 3-(furan-2-yl)-1-(4-nitrophenyl)-5-phenyl-4,5-dihydro-1*H*-pyrazole (**10**) (Scheme 1). In addition, we found it worthwhile to analyze the regioselectivity of these 1,3-DC reactions by DFT-based reactivity indexes. Finally, the gauge-invariant atomic orbi-

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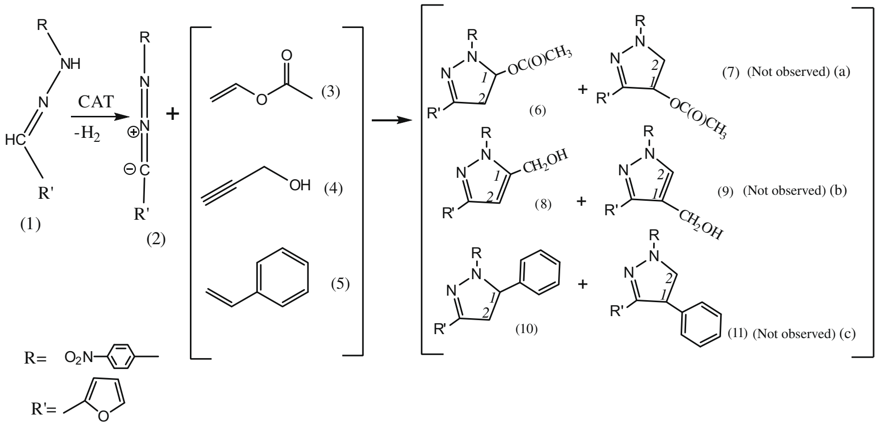


Scheme 1. The regioisomeric pathways for 1,3-DC of nitrilimine (**2**) and dipolarophiles (**3**), (**4**) and (**5**).

tal (GIAO) method [13] was used to calculate NMR chemical shift, to help the experimental cycloadduct determination, because it has shown to yield data comparable to those of the experiment [14].

In the present work, the two following possible mechanisms are considered:

(i) The mechanism corresponding to a four-center reaction. This is the case of asynchronous or a very low asynchronous cycloaddition.
(ii) The mechanism corresponding to a two-center reaction followed by a ring closure. This is the case of a stepwise or a high asynchronous cycloaddition. We note that the prediction of the formation of the first favored bond is sufficient for predicting the regioisomeric pathways.

2. Regioselectivity criteria for four-center reactions

In order to explain the regiochemistry of four-center reactions, Gazquez and Mendez proposed a local version of HSAB (Hard and Soft Acid–Base) principle, which generally states that "*the interaction between any two chemical species will occur through the centers with nearly equal condensed Fukui function*" [15,16]. This can determine the behavior of different reactive sites with respect to the hard and soft reagents. Chandra and Nguyen have correlated the idea of the local HSAB concept and regioselectivity defining a quantity, said 'delta' (Δ_{ij}^{kl}), that suggests a measure of predominance of one reaction over the other on the base of local softnesses [17,18].

This quantity is so defined as Eq. (1):

$$\Delta_{ij}^{kl} = (s_i - s_k)^2 + (s_j - s_l)^2 \tag{1}$$

where i and j are the atoms of a molecule A involved in the formation of a cycloadduct with atoms k and l of a molecule B, and s_i 's are the appropriate type of atomic softnesses (if s_i and s_j are electrophilic then s_k and s_l are obviously nucleophilic). The idea is based on the simultaneous fulfillment of the local HSAB concept at both termini. This is because, in the case of a multicenter addition reaction, it is not the similarities of softness at one-center that are important. (Δ_{ij}^{kl}) can be considered as a measure of how extensively the HSAB principle is satisfied. The reaction associated with a lower (Δ_{ij}^{kl}) value will be the preferred one.

3. Regioselectivity criteria for two-center reactions

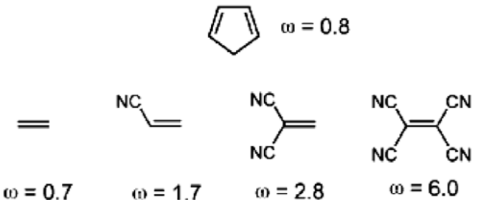
A useful simplification for the study of the regioselectivity in reactions may be obtained by looking at those processes having a markedly polar character, where the transition structure associated with the rate-determining step mostly involves the formation of one single bond between the most electrophilic and other nucleophilic sites. According to the model recently proposed by Chattaraj [19,20], during an electrophile–nucleophile interaction process, when two reactants approach each other from a large distance, they feel only the effect of the global electrophilicity of each other and not its local counterpart. The molecule with the larger ω value will act as an electrophile, and the other will be have as the nucleophile. The preferred interaction will be through the most electrophilic site of the former and the most nucleophilic site of the latter. Local electrophilicity index defined in Eq. (11), is therefore expected to be useful descriptor of regional electrophilicity/nucleophilicity patterns that may account for the observed regioselectivity in two-center reactions with a significant polar character.

4. Computational details

All calculations were performed with the Gaussian98 program suite [21]. For DFT calculations, the B3LYP/6-31G(d) level of theory was employed. The optimizations of equilibrium geometries of reactants were performed using the Berny analytical gradient optimization method [22]. The atomic electronic populations were evaluated according to Merz–Kollman scheme (MK option) [23,24]. This scheme, which already proved to be reliable [25], has been used in most DFT calculation of regiochemistry of 1,3-DCs, and it has also been recently considered as an appropriate local descriptor of charge. Chandra and Nguyen studied the 1,3-dipolar cycloaddition reactions of diazoalkanes with alkyl-substituted phosphaalkynes. They recommended that the atomic charges were calculated by using the technique of electrostatic potential (ESP)-driven charges are reliable. It is well known that Mulliken charges are highly basis set dependent, whereas ESP-driven charges show less basis set dependence and are better descriptors of the molecular density distribution [26]. Therefore, the atomic charges were calculated using the MK option. Parr et al. [27] proposed that the "electrophilicity index" ω, has been used as a measure for reactivity for a variety of reactions including 1,3-dipolar and Diels–Alder cycloadditions. ω is the chemical potential squared divided by two times the hardness value (Eq. (2)):

$$\omega = \frac{\mu^2}{2\eta} \tag{2}$$

In Eq. (2) μ and η are the electronic chemical potential and the chemical hardness of the ground state (GS) of atoms and molecules, respectively.



Scheme 2. Electrophilicity index values for ethylenes for reactions of cyclopentadiene with ethylene, mono-, di-, and tetracyanoethylenes [27].

A representative application of the electrophilicity index was reported by Domingo and co-workers [27] who investigated the polarity of Diels–Alder cycloaddition between cyclopentadiene and mono-, di-, tri-, and tetracyanoethylenes. Scheme 2 shows the ω values for cyclopentadiene and cyanoethylenes. Cyclopentadiene has a lower value of ω and shows that the direction of charge transfer is from diene to cyanoethylenes.

Reactivity indexes [28] were computed in the usual finite difference approximation within the framework of DFT. The global indexes are the molecular hardness

$$\eta = (\mathrm{IP} - \mathrm{EA}) \tag{3}$$

and the electron chemical potential

$$\mu = -(\mathrm{IP} + \mathrm{EA})/2 \tag{4}$$

where IP and EA are the ionization potential and electron affinity, respectively. The latter are computed as vertical differences in molecular energy between the neutral system and the mono-cation and -anion, respectively, i.e.

$$\mathrm{IP} = E(\mathrm{cation}) - E(\mathrm{neutral}) \tag{5}$$

$$\mathrm{EA} = E(\mathrm{neutral}) - E(\mathrm{anion}) \tag{6}$$

As usual, local indexes are computed in atomic condensed form [29]. The well-known Fukui function [30,31] for electrophilic (f_k^-) and nucleophilic attack (f_k^+) can be written as

$$f_k^- = [\rho_k(N) - \rho_k(N-1)] \tag{7}$$

$$f_k^+ = [\rho_k(N+1) - \rho_k(N)] \tag{8}$$

where $\rho_k(N)$, $\rho_k(N-1)$ and $\rho_k(N+1)$ are the gross electronic populations of the site k in neutral, cationic, and anionic systems, respectively.

The atomic softness is computed as

$$s_k^{\pm} = f_k^{\pm} S \tag{9}$$

where S is the global softness and computed as [28]

$$S = \frac{1}{\eta} \tag{10}$$

The local electrophilicity index, ω_k, condensed to atom k is easily obtained by projecting the global quantity onto any atomic center k in the molecule by using the electrophilic Fukui function (i.e. the Fukui function for nucleophilic attack, f_k^+ [32])

$$\omega_k = \omega f_k^+ \tag{11}$$

The ^{1}H and ^{13}C and NMR chemical shifts were calculated by means of the GIAO method [13], using the tetramethylsilane (TMS) as ^{1}H and ^{13}C reference, at the B3LYP/6-31G(d) level of theory (reference values of ^{13}C = 1845307 ppm and ^{1}H = 322892 ppm).

5. Result and discussion

Firstly, the 1,3-DC reaction between nitrilimine 2 and dipolarophiles 3, 4 and 5 (Scheme 1) will be analyzed. Then, a DFT analysis based on the reactivity indexes of the reactants involved in these reactions will be performed.

5.1. Analysis of the 1,3-DC reaction between nitrilimine 2 with dipolarophiles 3, 4 and 5

Nitrilimine **2** was generated in situ from the appropriate aldehyde hydrazone by refluxing a mixture of chloramine-T trihydrate (*N*-chloro-*N*-sodio-4-methylbenzene sulfonamide, CAT) and the dipolarophile in an appropriate solvent. Dipolar cycloaddition of nitrilimine **2** to the dipolarophiles proceeded with complete regioselectivity, thereby affording only **6**, **8** and **10** in very good yields (Scheme 1).

The corresponding regioisomers (compounds **7**, **9** and **11** in Scheme 1) have not been detected in the crude reaction mixture by ^{1}H and ^{13}C NMR spectroscopy. The assignment of the regiochemistry in products **6**, **8** and **10** was confirmed on the basis of ^{1}H and ^{13}C NMR spectral data and comparing with calculated ^{1}H and ^{13}C NMR spectral data of the two possible regioisomers (see Scheme 1 and Table 1).

As it can be seen in Table 1, we obtained the theoretical ^{1}H and ^{13}C NMR chemical shifts values for the products through the GIAO method and compared it with the observed values. The observed values for C1 and C2 in each of the isolated products are in closer proximity to the theoretical values for compounds **6**, 8 and **10**. It seems likely that the isolated regioisomers are structurally similar to **6**, 8 and **10**.

5.2. Prediction of the NED/IED character

The NED (normal electron demand) or IED (inverse electron demand) character of the cycloaddition reactions has been predicted by three approaches, namely, the calculation of HOMO/LUMO gaps (Table 2a), electronic chemical potentials μ and electrophilicity indexes ω (Table 2b). Table 2a turns out that the |LUMO (dipo-

Table 1
The comparison of theoretical ^{1}H and ^{13}C NMR chemical shifts data (δ, ppm) of C-1 and C-2 of each pair of regioisomers with those obtained from the experimental spectroscopy.

Compound	Atom number	Calculated ^{13}C chemical shift	Calculated ^{1}H chemical shift	Experimental ^{13}C chemical shift	Experimental ^{1}H chemical shift
6	C-1	83.1	4.34	83.3	4.26
	C-2	35.7	3.37; 3.12	35.7	3.33; 3.10
7	C-1	77.3	4.81		
	C-2	47.0	3.51; 3.23		
8	C-1	134.9	–	136.1	–
	C-2	108.5	6.23	108.6	6.24
9	C-1	118.4	**–**		
	C-2	121.9	8.24		
10	C-1	58.0	5.19	58.6	5.19
	C-2	38.2	3.90; 3.65	38.7	3.86; 3.60
11	C-1	42.2	3.32		
	C-2	49.5	3.30; 3.12		

Table 2a
Energy difference between the two possible HOMO/LUMO combinations for the dipole and the dipolarophiles (values in eV).

Reaction	$\lvert E^{\mathrm{Dipolarophile}}_{\mathrm{LUMO}} - E^{\mathrm{Dipole}}_{\mathrm{HOMO}} \rvert$ (NED character)	$\lvert E^{\mathrm{Dipole}}_{\mathrm{LUMO}} - E^{\mathrm{Dipolarophile}}_{\mathrm{HOMO}} \rvert$ (IED character)
a	5.799	4.553
b	6.808	4.800
c	5.233	3.804

Table 2b
HOMO, LUMO energies (in a.u.), ionization potential (IP, in a.u.), electron affinity (EA, in a.u.), electronic chemical potential (μ in a.u.), chemical hardness (η, in a.u.), global softness (S, in a.u.) and global electrophilicity (ω, in eV) for dipole and dipolarophile systems.

System	HOMO	LUMO	IP	EA	μ	η	S	ω
Nitrilimine 2	−0.224	−0.082	0.283	0.023	−0.153	0.260	3.846	1.225
Vinyl acetate 3	−0.250	−0.011	0.343	−0.072	−0.136	0.415	2.408	0.606
2-Propyne-1-ol 4	−0.259	0.027	0.356	−0.110	−0.123	0.466	2.146	0.442
Styrene 5	−0.222	−0.031	0.295	−0.033	−0.131	0.328	3.049	0.712

le) − HOMO (dipolarophile)| gaps for the dipole and dipolarophiles are smaller than the |LUMO (dipolarophile) − HOMO (dipole)|.

Furthermore, as it can be seen in Table 2b, the electronic chemical potential of dipolarophiles is greater than that of nitrilimine (dipole), which indicates the charge transfer is taking place from dipolarophile to nitrilimine. On the other hand Table 2b shows that the electrophilicity power of nitrilimine is greater than those of dipolarophiles, and consequently, the nitrilimine can act an electrophile for the 1,3-DC reactions. In conclusion, the 1,3-DC reactions treated in this work have IED character.

5.3. Prediction of regiochemistry

In order to put in evidence the preferential cyclization mode and consequently the major cycloadduct of 1,3-DC reactions under investigation, we will consider two possibilities (two-center/four-center) of the reaction mechanism. Our theoretical predictions of the regioselectivity will be based on the conceptual DFT theories.

5.3.1. Use of DFT-based reactivity indexes

5.3.1.1. Case of a four-centered process. The regioselectivity of four-center reactions is conveniently explained by the Gazquez–Mendez rule [33] which stipulates that “the interaction between two chemical species A and B is favored when it occurs through those atoms whose softnesses are approximately equal”. In our cases, the application of the Gazquez–Mendez rule is reduced to the calculation of the quantities s_3, s_4, s_5, s_6, s_7 and s_8 corresponding to the regioisomeric pathways (Scheme 2). These quantities are expressed by (see the Scheme 2 for atom numbering)

$$s_3 = (s^+_{C3} - s^-_{C4})^2 + (s^+_{N1} - s^-_{C5})^2 \quad (12)$$

$$s_4 = (s^+_{C3} - s^-_{C5})^2 + (s^+_{N1} - s^-_{C4})^2 \quad (13)$$

The s_5, s_6, s_7 and s_8 values are also calculated in similar manner.

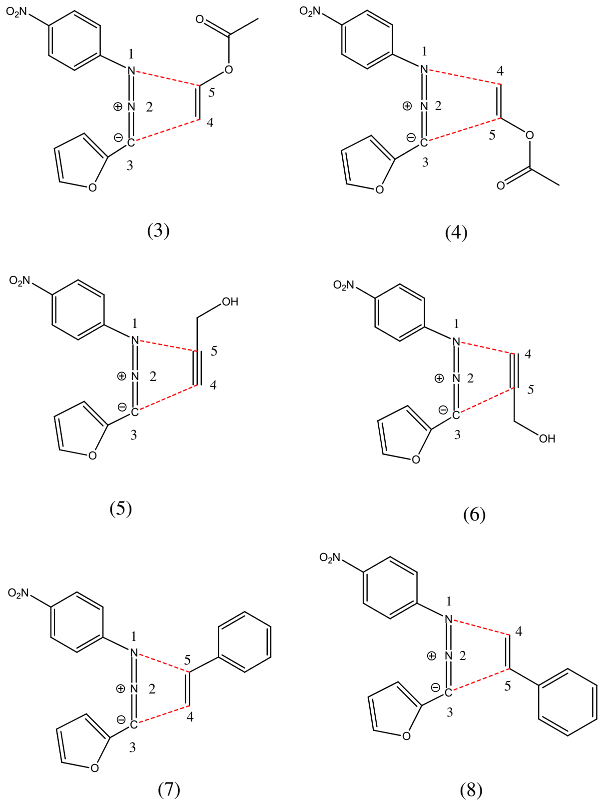
Table 3a
Fukui indexes for the N1 and C3 atoms of the nitrilimine and for atoms C4 and C5 of the dipolarophiles and related local softnesses (s^+_k, s^-_k) values (in a.u.).

	Atom number	f^+_k	f^-_k	s^+_k	s^-_k
Nitrilimine	N1	0.086		0.330	
	C3	0.184		0.707	
Vinyl acetate	C4		0.431		1.037
	C5		−0.240		−0.578
2-Propyn-1-ol	C4		0.328		0.704
	C5		−0.165		−0.353
Styrene	C4		0.314		0.958
	C5		−0.002		−0.006

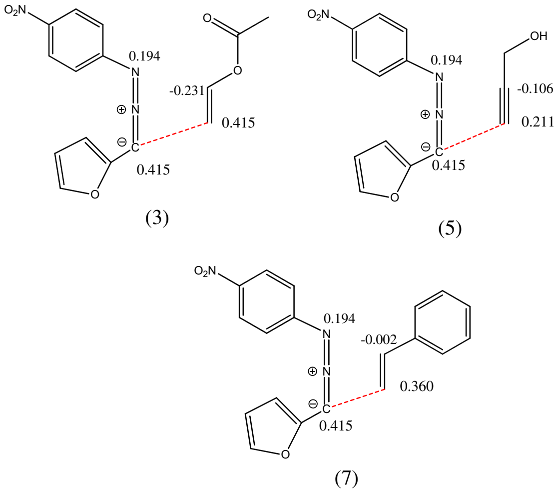
Table 3b
Values of s_3, s_4, s_5, s_6, s_7 and s_8 quantities calculated with MK population analysis.

s_3	s_4	s_5	s_6	s_7	s_8
0.933	2.151	0.466	1.264	0.176	0.902

The Fukui indexes and local softnesses for the atoms N1 and C3 of the dipole (nitrilimine) and for the atoms C4, C5 of the dipolaro-



Scheme 3. The two possible cyclization modes and atom numbering.



Scheme 4. Local nucleophilicities ω^-_k (in eV), for dipolarophile centers, and local electrophilicities, ω^+_k (in eV), for the nitrilimine centers, calculated with MK population analysis.

philes (vinyl acetate, 2-propyne-1-ol and styrene), calculated with MK population analysis are given in Table 3a. The values of the quantities of s_3, s_4, s_5, s_6, s_7 and s_8 are given in Table 3b. The small value of s_3 compared to s_4, for the reaction a, s_5 compared to s_6 for reaction b and s_7 compared to s_8 for reaction c shows that the cycloaddition channel leading to the cycloadduct 3, 5 and 7 (see Scheme 3) is the most favored. Thus, the experimental regioselectivity is correctly predicted using DFT-based indexes.

5.3.1.2. Case of a two-center process. In Scheme 4, we have reported the values of local electrophilicities ω_k^+ for atoms N1 and C3 (nitrilimine) and the local nucleophilicities ω_k^- for atoms C4 and C5 of dipolarophiles. According to the Chattaraj's model [19,20], the local philicity indexes (ω_k^+, ω_k^-) seem to be a reliable tool for the prediction of the most favored interaction in a two-center polar process. The results show that the most favored interaction will take place between C3 center of nitrilimine (possessing the highest value of ω_k^+) and the C4 center of dipolarophiles (possessing the highest value of ω_k^-). Consequently, the experimental regioselectivity is correctly predicted by Chattaraj's model.

6. Conclusion

The regioselectivity for the 1,3-dipolar cycloaddition reactions of nitrilimine (**2**) with vinyl acetate (**3**), 2-propyn-1-ol (**4**) and styrene (**5**) has been investigated using experimental and theoretical ^{1}H and ^{13}C NMR studies together with the DFT-based reactivity indexes at the B3LYP/6-31G(d) level of theory. The results obtained in this work clearly predict the regiochemistry of the isolated cycloadducts.

7. Experimental

The melting points were recorded on an electrothermal type 9100 melting point apparatus. The ^{1}H NMR (500 MHz) spectra were recorded on a Bruker AM-500 spectrometer. ^{13}C NMR spectra were determined using the Bruker AM-500 instrument operating at 125 MHz. IR spectra were determined as KBr pellets on a Shimadzu model 470 spectrophotometer. The mass spectra were scanned on a Varian Mat CH-7 instrument at 70 eV. Column chromatography was performed on silica gel (200–400 mesh; Kieselgel 60, E Merck) using chloroform as eluent. Elemental analyses were carried out on Carlo Erba CHNS-O 1108 apparatus and were in good accord with theoretical data. Hydrazone 1 the precursor of nitrilimine 2 is a known compound were prepared according to generally used methods.

*7.1. General procedure for synthesis 3-(furan-2-yl)-1-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-5-yl acetate (**6**), (3-(furan-2-yl)-1-(4-nitrophenyl)-1H-pyrazol-5-yl)methanol (**8**) and 3-(furan-2-yl)-1-(4-nitrophenyl)-5-phenyl-4,5-dihydro-1H-pyrazole (**10**)*

The mixture of 4 mmol of hydrazone and 4.5–5 mmol of chloramine-T (CAT) in ethanol (40 cm^3) was added at room temperature to the excess of dipolarophile (6–7 mmol) in ethanol (25 cm^3). The reaction mixture was heated to 80 °C and kept under reflux for 4–6 h (TLC). Inorganic salts were filtered off; filtrate was evaporated under vacuum to obtain the crude product. The pure product was separated by column chromatography (chloroform as eluent). Obtained products were crystallized from ethanol or methanol.

Compound (**6**) dark red solid: yield: 88%, m.p.: 98 °C, MS *m*/*z* 315 (M$^+$), Anal. Calcd for $C_{15}H_{13}N_3O_5$: C, 57.14; H, 4.16; N, 13.33. Found: C, 57.12; H, 4.15; N, 13.31. IR (KBr) cm^{-1}: 1725 (C=O), 1647 (C=N), 1558 $(NO_2)_{as}$, 1336 $(NO_2)_s$. ^{1}H NMR (DMSO-d$_6$) δ_H: 2.37 (s, 3H, CH_3), 3.10 (dd, 1H, CH_2), 3.33 (dd, 1H, CH_2), 4.26 (t, 1H, CH), 6.62 (t, 1H, CH, 2-furan ring), 6.84 (d, 1H, CH, 2-furan ring), 7.12 (d, 2H, CH, phenyl ring), 7.71 (d, 1H, CH, 2-furan ring), 8.13 (d, 2H, CH, phenyl ring); ^{13}C NMR (DMSO-d$_6$) δ_C: 21.8 (CH_3), 35.7 (CH_2), 83.3 (CH), 109.6, 109.8, 112.1, 126.5, 136.1, 142.3, 142.7, 150.7 (C_{Ph} and C_{Fu}), 156.4 (C=N), 169.3 (C=O).

Compound (**8**) orange solid: yield: 80%, m.p.: 143 °C, MS *m*/*z* 285(M$^+$), Anal. Calcd for $C_{14}H_{11}N_3O_4$: C, 58.95; H, 3.89; N, 14.73. Found: C, 58.92; H, 3.86; N, 14.70., IR (KBr) cm^{-1}: 1558 $(NO_2)_{as}$, 1336 $(NO_2)_s$,1672(C=N), 3650 (OH), ^{1}H NMR (DMSO-d$_6$) δ_H: 3.64 (s, 1H, OH), 4.82 (s, 2H, CH_2), 6.24 (s, 1H, CH), 6.83 (t, 1H, CH, 2-furan ring), 7.71 (d, 1H, CH, 2-furan ring), 7.89 (d, 1H, CH, 2-furan ring), 8.13 (d, 2H, CH, phenyl ring), 8.44 (d, 2H, CH, phenyl ring); ^{13}C NMR (DMSO-d$_6$) δ_C: 55.0 (OCH_2), 107.6, 112.1, 126.5, 142.7, 146.5, 156.4 (C_{Ph} and C_{Fu}), 108.6($\underline{C}$H=C), 136.1($\underline{C}$=CH), 139.1(C=N).

Compound (**10**) light red solid: yield: 85%, m.p.: 114 °C, MS *m*/*z* 333(M$^+$), Anal. Calcd for $C_{19}H_{15}N_3O_3$: C, 68.46; H, 4.54; N, 12.61. Found: C, 68.48; H, 4.58; N, 12.62. IR (KBr) cm^{-1}: 1647 (C=N), 1558 $(NO_2)_{as}$, 1336 $(NO_2)_s$. ^{1}H NMR (DMSO-d$_6$) δ_H: 3.60 (dd, 1H, CH_2), 3.86 (dd, 1H, CH_2), 5.11 (t, 1H, CH), 6.52 (t, 1H, CH, 2-furan ring), 6.81 (d, 1H, 2-furan ring), 7.12 (d, 2H, CH, phenyl ring), 7.21 (m, 1H, CH, phenyl ring), 7.25 (m, 2H, CH, phenyl ring), 7.40 (m, 2H, CH, phenyl ring), 7.72 (d, 1H, CH, 2-furan ring), 8.12 (d, 2H, CH, phenyl ring); ^{13}C NMR (DMSO-d$_6$) δ_C: 38.7 (CH_2), 58.6 (CH), 108.9, 110.1, 111.3, 124.8, 126.6, 126.9, 129.1, 136.8, 140.1, 141.3, 144.2, 149.9 (C_{Ph} and C_{Fu}), 155.9 (C=N).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.01.059.

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