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The Regioselectivity of the 1,3-Dipolar Cycloaddition of α-Carbonylformonitrile N-arylimides To Benzylideneacetone and β-Diketones

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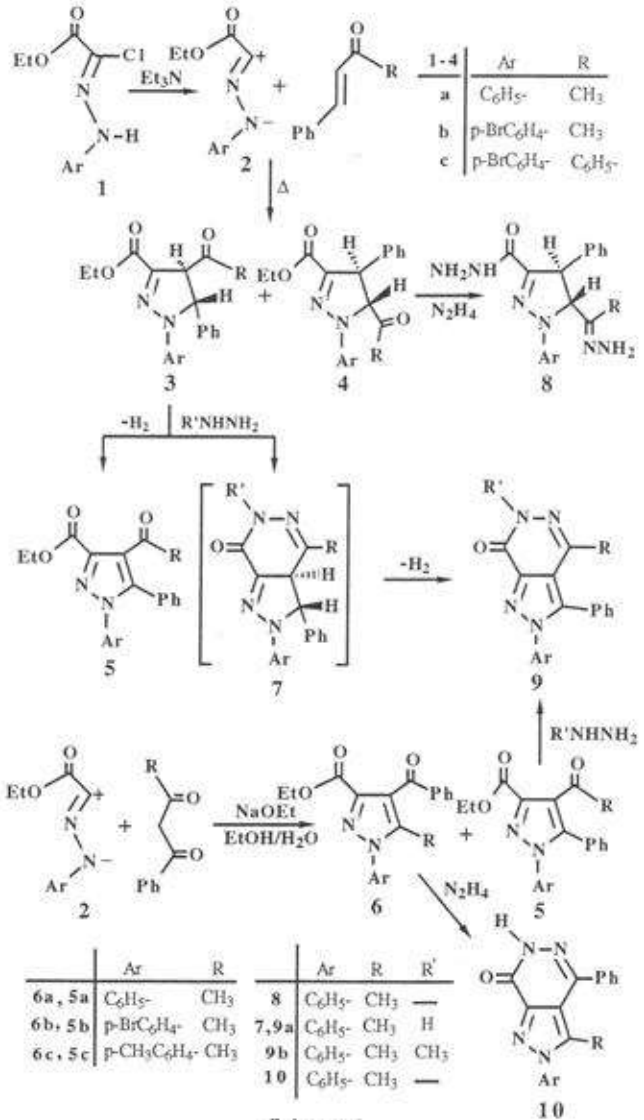
The cycloaddition of the ethoxycarbonylformonitrile N-arylimides **2** to benzylideneacetone afforded two regioisomers, 5-acetyl- and 4-acetyl-dihydropyrazole but the cycloaddition of **2** to benzoylacetone afforded two regioisomers, 4-acetyl- and 4-benzoylpyrazole. Also, some pyrazolopyridazin-7-one and pyrazolopyridazin derivatives were synthesized

The cycloaddition of the nitrile imide **2** to α,β-unsaturated ketones is regioselective and yields 5-acyl (or 5-aroyl)-4-aryl-4,5-dihydro-1H-pyrazole derivatives[1]. Tewari and Parihar[2] have claimed that the cycloaddition of the nitrile imide **2c** to chalcone (1,3-diphenylprop-2-en-1-one) affords exclusively the corresponding 4-benzoyl-1-(p-bromophenyl)-3-ethoxycarbonyl-5-phenyl-4,5-dihydro-1H-pyrazole **3c**. Shawali[3] has found that the above reaction gives a mixture of two regioisomers, namely **3c** and **4c**. Also they claimed that the cycloaddition of benzylideneacetone (4-phenylbut-3-en-2-one) to nitrile imide **2b** gave one of the two possible regioisomers **4b**. These different results[1-3] prompted us to reinvestigate the reactions of the cycloaddition of the nitrile imides **2** with benzylideneacetone and chalcone. Accordingly, we now report the cycloaddition of the nitrile imides **2a-c** and **13** (Scheme 2) to conjugate bases of active methylene compounds [acetyl- and benzoyl-acetone (pentane-1,3-dione and 1-phenylbutane-1,3-dione, respectively)] as means of ascertaining the regiostructures of the dihydropyrazoles **3** and **4** and the pyrazoles **5**, **6**, **11**, **14**,and **15** through the synthesis of some new derivatives of pyrazolopyridazinones and pyrazolopyridazines.

The cycloaddition of the ethoxycarbonylformonitrile N-arylimides **2**, generated in situ by treatment of the corresponding C-ethoxycarbonyl-N-arylformohydrazonoyl chloride **1** with triethylamine, with each of chalcone and benzylideneacetone were carried out in refluxing benzene or chloroform. The results show that the reactions studied are regioselective yielding two possible regioisomers, namely the 4-benzoyl-5-phenyldihydropyrazole **3c** and its 5-benzoyl-4-phenyl isomer **4c**, and the 1-aryl-4-acetyl-5-phenyldihydropyrazole **3a,b** and its 1-aryl-5-acetyl-4-phenyl isomer **4a,b**, respectively (Scheme 1). In each case, the two cycloadducts were separated by column chromatography. The assigned structures of the isolated cycloadducts **3a-c**

and **4a-c** are consistent with the following data. The ^{1}H NMR spectra of **4a-c** were characterized, in each case, by the presence of two doublets (J=6Hz) near δ 4.20-4.45 and 5.60 - 5.78 ppm due to H-4 and H-5 respectively[4,5]. Furthermore, the cycloadducts **3a-c** each showed signals at δ 4.45-4.72(d, 1H, J=6Hz, H-4) and δ 4.68-4.88 (d,1H, J=6Hz, H-5) ppm (Table 1).



Scheme 1

References: see frame 1764

The ^{13}C NMR spectra of the cycloadducts **4a,b** each revealed three signals assignable to C-3 (s, δ 140.7), C-4 (d, δ 67.1) and C-5 (d, δ 69.8 ppm), and the ^{13}C NMR spectra of the cycloadducts **3a,b** each revealed three lines assignable to C-3 (s,δ 140.9), C-4 (d,δ 78.1) and C-5 (d,δ 54.8 ppm) (Table 1)[6].

On the other hand, cycloaddition of the nitrile imides **2a-c** with the sodium salt of benzoylacetone afforded in each case a mixture of the two pyrazoles **5a-c** and **6a-c** which were separated by preparative chromatography. The pyrazole **5a** was also obtained from the dehydrogenation of **3a** by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as dehydrogenation agent. The structure of the cycloadduct **3** was substantiated further by the fact that treatment of **3a** with hydrazine hydrate in refluxing ethanol afforded the pyrazolino[3,4-d] pyridazin-7-one derivative **7**. However, similar treatment of **4a** gave the hydrazide **8**. Oxidation of **7** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the pyrazolino[3,4-d]pyridazin-7-one derivative **9a**, which was also obtained from the reaction of the pyrazole **5a** with hydrazine hydrate. Similarly, reaction of the pyrazole **6** with hydrazine hydrate afforded the pyrazolo[3,4-d]pyridazin-7-one derivative **10** (Scheme 1). It is known[7,8] that the cycloaddition of 1,3-dipolar nitrile imides to the enol form leads to regiospecific 4-aroyl- (or 4-acetyl-) pyrazoles. However, in our case the formation of the two regioisomers **5** and **6** formed from the reaction of nitrile imide **2** with benzoylacetone can be explained on the basis that two different enols are formed during the reaction. These results may supporting the possible mechanism reported in the literature[7]. Both of the regioisomers **5** and **6** obtained above suggest that the carbanion, acting as a base, reacts with **1** to form a nitrile imide dipole **2**. The latter then adds to the two possible enols of the benzoylacetone to give the two regioisomers **5** and **6** after subsequent loss of water.

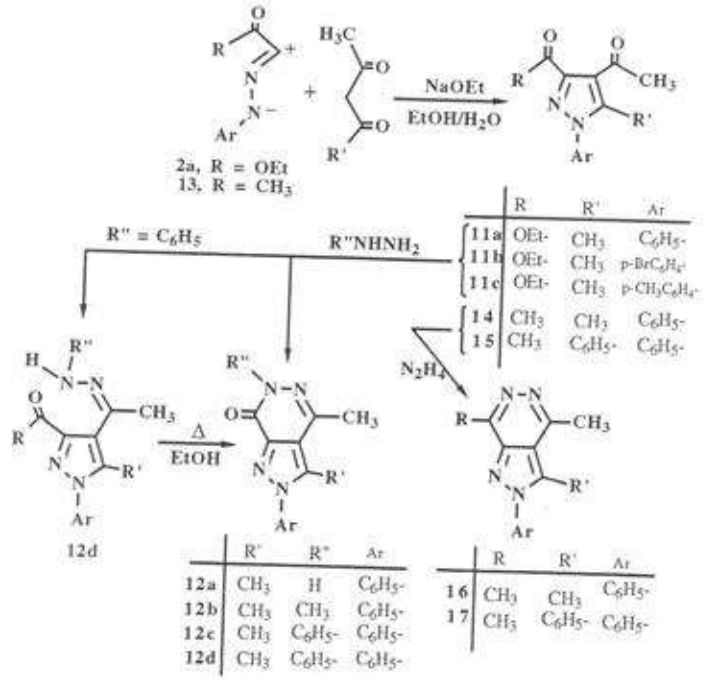
Nevertheless, the cycloaddition of the nitrile imides **2a-c** to the sodium salt of acetylacetone produced in each case only one isomer, 4-acetyl-3-ethoxycarbonyl-5-methyl-1-phenylpyrazole **11a-c**, because in this case, there is no possible formation of different enols. Further evidence for the structure of the regioisomer **11a** was obtained by its reaction with hydrazine derivatives which led to the pyrazolopyridazin-7-one derivatives **12a-c** (Scheme 2).

The above method was used to synthesise some new pyrazolopyridazine derivatives **16** and **17**, as follows. The cycloaddition of the C-acetyl-N-phenyl nitrile imide **13** to the sodium salts of acetylacetone and benzoylacetone yielded, in each case, one regioisomer namely, the 4-acetyl-5-methyl- **14** and 4-acetyl-5-phenylpyrazole **15**, respectively. Treatment of the pyrazoles **14** and **15** with hydrazine hydrate in refluxing ethanol yielded the pyrazolopyridazines **16** and **17**, respectively (Scheme 2).

EXPERIMENTAL

Mps are uncorrected. Infrared spectra were recorded on a Nicolet Magna 520 FT-IR spectrometer, ^{1}H NMR spectra were recorded on a Varian DPX-400 FT-NMR spectrometer, MS

data were obtained with a Shimadzu QP-5000 mass spectrometer and microanalyses were performed on a 2400 Perkin Elmer Series 2 CHNS analyser. The C-ethoxycarbonyl-N-arylformohydrazonoyl chlorides **1a-c** and their C-acetyl analogues were prepared by a known procedure[9,10]. 1,3-Diketones were obtained from Aldrich Chemical Co.,and the benzylidene-acetone and chalcone were prepared by condensation of the appropriate aromatic aldehyde with acetophenone following a known procedure[11].



	R	R'	Ar
11a	OEt-	CH_3	C_6H_5-
11b	OEt-	CH_3	p-BrC_6H_4-
11c	OEt-	CH_3	p-$CH_3C_6H_4$-
14	CH_3	CH_3	C_6H_5-
15	CH_3	C_6H_5-	C_6H_5-

	R"	R'	Ar
12a	CH_3	H	C_6H_5-
12b	CH_3	CH_3	C_6H_5-
12c	CH_3	C_6H_5-	C_6H_5-
12d	CH_3	C_6H_5-	C_6H_5-

	R	R'	Ar
16	CH_3	CH_3	C_6H_5-
17	CH_3	C_6H_5-	C_6H_5-

Scheme 2

Syntheses of 4,5-dihydro-1H-pyrazoles 3 and 4 .

To a solution of the appropriate hydrazonoyl chloride **1** (0.005 mole) in dried benzene or chloroform (25 mL) was added the appropriate α,β-unsaturated ketone (0.005 mole). The reaction mixture was stirred while triethylamine (0.006 mole) was added dropwise and the mixture was refluxed for 10 h. Then the reaction mixture was allowed to cool, washed with water three times and the organic layer was collected, dried and evaporated under reduced pressure. The crude gum was collected and its ^{1}H-NMR spectrum in $CDCl_3$ showed the presence of two isomers, namely, the (4-benzoyl) 4-acetyl-3-ethoxycarbonyl-1-aroyl-5-phenyl-4,5-dihydro-1H-pyrazoles **3a-c** and (5-benzoyl)5-acetyl-3-ethoxycarbonyl-1-aroyl-4-phenyl-4,5-dihydro-1H-pyrazoles **4a-c** in the ratio 6 : 4 respectively. The components of each mixture

Table 1. IR and ^1H [^{13}C]-NMR data for 4,5-dihydropyrazoles and pyrazoles

Compd. No.	IR υ_{CO} (KBr), cm^{-1}	^1H and [^{13}C] NMR δ ($CDCl_3$), ppm
3a	1715,1705	4.78 (d, 1H-5, CH), 4.45 (d, 1H-4, CH), 4.20 (q, 2H, OCH_2), 2.18 (s, 3H, CH_3), 1.22 (t,3H, CH_3). [204.4 (s, $COCH_3$), 161.4 (s, $COOC_2H_5$), 142.0 (s, C-3), 78.1 (d,C_5), 54.9 (d, C_4),61.3 (t, $COOC_2H_5$), 25.5 (q, $COCH_3$), 14.1 (q, $COOC_2H_5$)].
4a	1710,1703	5.68 (d, 1H-5, CH), 4.22 (d, 1H-4, CH), 4.36 (q, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.39 (t, 3H, CH_3). [202.8 (s, $COCH_3$), 161.2 (s, $COOC_2H_5$), 141.7 (s, C-3), 69.8(d, C-5), 67.1 (d, C-4), 61.2 (t, $COOC_2H_5$), 25.5 (q, $COCH_3$), 14.3 (q, $OCH_2\underline{CH_3}$)].
3b	1712,1703	4.77 (d, 1H-5, CH), 4.45 (d,1H-4, CH), 4.28 (q,2H, OCH_2), 2.15 (s, 3H, CH_3), 1.20 (t, 3H, CH_3). [203.6 (s, $COCH_3$), 161.8 (s, $COOC_2H_5$), 142.0 (s, C-3), 76.2 (d, C-5), 55.8 (d, C-4), 61.9 (t, $COOC_2H_5$), 26.1 (q, $COCH_3$), 14.7 (q, $OCH_2\underline{CH_3}$)].
4b	1716,1710	5.66 (d, 1H-5, CH), 4.40 (d, 1H-4, CH), 4.31 (q, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.41 (t, 3H, CH_3). [202.4 (s, $COCH_3$), 161.1 (s, $COOC_2H_5$),141.8 (s, C-3),70.1 (d, C-5), 67.3 (d, C-4), 61.3 (t, $COOC_2H_5$), 25.5 (q, $COCH_3$), 14.3 (q,OCH_2CH_3)].
3c	1707	4.86 (d, 1H-5), 4.31 (d, 1H-4), 4.20 (q, 2H, OCH_2), 1.20 (s, 3H, CH_3)
4c	1712	5.72 (d, 1H-5, CH), 4.44 (d, 1H-4, CH), 4.20 (q, 2H, OCH_2), 1.27 (s, 3H, CH_3)
5a	1717,1682	4.45(q,2H, OCH_2), 2.37(s,3H, CH_3), 1.42(t,3H, CH_3)
6a	1720,1691	4.08 (q,2H,OCH_2), 2.44 (s, 3H, CH_3), 0.97 (t, 3H, CH_3)
5b	1718,1687	4.49 (q, 2H, OCH_2), 2.33 (s, 3H, CH_3), 1.38(t, 3H, CH_3)
6b	1720,1691	4.01 (q, 2H, OCH_2), 2.38 (s, 3H, CH_3), 0.93 (t, 3H, CH_3)
5c	1718,1687	4.47 (q, 2H, OCH_2), 2.39 (s, 3H, CH_3), 2.13(s,3H,CH_3),1.40 (t, 3H, CH_3),
11a	1716,1703	4.48 (q, 2H, OCH_2), 2.32 (s, 3H, CH_3), 2.63 (s,3H, CH_3), 1.46 (t, 3H,CH_3)
11b	1718,1702	4.46 (q, 2H, OCH_2), 2.34 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 1.43 (t, 3H, CH_3), 7.31 (d, 2H, J=9Hz, Ar-H), 7.68 (d, J=9Hz, 2H, Ar-H)
11c	1716,1702	4.44 (q, 2H, OCH_2), 2.36 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 2.16 (s,3H,CH3), 1.40 (t, 3H, CH_3), 7.01 (d, 2H, J=9Hz, Ar-H), 7.48 (d, J=9Hz, 2H, Ar-H)
14	1701,1685	2.54 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 2.63 (s, 3H, CH_3).
15	1703,1683	2.51 (s, 3H, CH_3), 2.78 (s, 3H, CH_3).

a: The value of J for the doublet (d) signal is 6Hz, whereas for the triplet (t) and quartet (q) signals are 7Hz.
b: All compounds exhibit a proton multiplet in the region 7.2-7.6 ppm, except for pyrazoles **11b** and **11c**.

column chromatography in the usual way and were fully characterized by spectral and elemental analysis. The physical constants are listed in Table 1 and 2. **3a**: MS, m/z (%) 336 (M+, 20), 293(100), 246(05), 249(83), 221(94), 220(43), 219(30), 194(52), 117(18).

Syntheses of pyrazoles 5 and 6 .

To an ethanolic solution of NaOEt (prepared from Na metal (1.1 gm, 0.05 g.atom and 30mL of absolute EtOH) was added 0.05 mole of the appropriate 1,3-Diketone. After stirring for 15 min at < 50°C, the appropriate hydrazonoyl chloride **1** (0.05 mole) was added and stirring continued for 4h. during which time the hydrazonoyl chloride dissolved and a pale yellow solid precipitated. The latter was filtered off and washed several times with water. The ^{1}H NMR spectrum of the crude solid in $CDCl_3$ showed the presence of two isomers **5** and **6** in the ratio 6 : 4 respectively. The regioisomer **5a-c** was separated by recrystallisation of the crude product from ethanol and the other isomer **6a,b** was separated by preparative thin layer chromatography . The physical constants for both isomers **5a-c**, **6a** and **6b** are listed in Tables 1 and 2.

Alternative Synthesis of 5a (Dehydrogenation of dihydropyrazole 3a) .

A stirred solution of the dihydropyrazole derivative **3a** (5 mmole) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (5.2 mmole) in xylene was refluxed until the complete disappearance of **3a** was shown by tlc. The solution was extracted with aqueous sodium hydroxide solution (5%). The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo. The solid left was collected and crystallised from ethanol to give the corresponding pyrazole **5a** . The mp was identical with that of the regioisomer **5a** prepared earlier and the mixed mp showed no depression.

Synthesis of 4-methyl-2,3-diphenyl-2,6-dihydropyrazolo[3,4-d]pyridazin-7-one 9a .

A mixture of the dihydropyrazole **3a** (5 mmole) and hydrazine hydrate (2mL) was heated at 100°C for 30 min and then allowed to cool. The solid product was washed with water and dried (yield 78%) . The ^{1}H-NMR spectrum of the latter solid product **7** was showed a pair of doublets at δ 4.53 (d, 1H, J=6Hz, CH) and 4.86 (d, 1H, J=6Hz, CH), indicating this solid to be 4-methyl-2,3-diphenyl-2,3,3a,6-tetrahydropyrazolino[3,4-d]pyridazin-7-one **7**. The dehydrogenation of **7** by the above method yielded the corresponding pyrazolopyridazin-7-one **9a** in 84% yield; mp 244/246°C (ethanol); IR (KBr) υ 3213 (NH) 1670 (CONH) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO) δ 2.56 (s, 3H, CH_3), 7.16-7.52 (m, 10H, Ar-H), 10.2 (bs,1H, NH) ppm. (Calcd. for $C_{18}H_{14}N_4O$: C, 71.50; H, 4.67; N, 18.52. Found : C, 71.17; H; 4.56; N, 18.13). Also, the pyrazolopyridazin-7-one **9a** was obtained in 89% yield when a mixture of the pyrazole **5a** (5mmole) and hydrazine hydrate (2mL) was heated at 100°C for 2h. The product isolated was identical in all respects with **9a** prepared above. Moreover, when the pyrazole **5a** (5 mmole) and

methylhydrazine (6 mmole) were refluxed in ethanol for 8h, and then the reaction mixture cooled, a precipitate was formed. Crystallisation from ethanol afforded the 6-methylpyrazolopyridazin-7-one **9b** in 82% yield; mp 212°C; IR (KBr) υ 1675 (C=O), 1595 (C=N); ^{1}H-NMR ($CDCl_3$) δ 2.28 (s, 3H, CH_3), 3.86 (s,3H, N- CH_3), 7.53 (m, 10H, Ar-H) ppm.

Hydrazinolysis of 4a .

A mixture of the pyrazole **4a** (5 mmole) and hydrazine hydrate (3mL) was heated at 100°C for 3h. The isolated product **8** was obtained in 52% yield; mp 216°C (EtOH); IR(KBr) υ 3380-3280 (-NH and -NH_2) and 1682 (CO) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.73 (s, 3H, CH_3), 4.46 (d, 1H, J=6Hz, CH), 5.76 (d, 1H, J=6Hz,CH),and 7.13-7.48 (m, 10H, Ar-H) ppm.

Hydrazinolysis of pyrazole 6 (Synthesis of 3-methyl-2,4-diphenyl-2,6-dihydropyrazolo[3,4-d]pyridazin-7-one 10).

A mixture of the pyrazole **6** (5 mmole) and hydrazine hydrate (2mL) was heated at 100°C for 3h.. The isolated product **10** was obtained in 82% yield; mp 220/223°C (EtOH); IR (KBr) υ 3216 (NH), 1670(CONH) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO) δ 2.62 (s,3H, CH_3), 7.26-7.72 (m, 10H, Ar-H), 10.2 (bs, 1H, NH) ppm. (Calcd. for $C_{18}H_{14}N_4O$: C, 71.50; H, 4.67; N, 18.52. Found : C, 71.23; H; 4.82; N, 18.32) .

Syntheses of 1-aryl-4-acetyl-3-ethoxycarbonyl-5-methylpyrazoles 11a-c and 5-substituted-3,4-diacetyl-1-phenylpyrazoles 14 and 15 .

To an ethanolic solution of NaOEt (0.05 mole) was added 0.05 mole of the appropriate 1,3-diketone. After the mixture had been stirred for 10 min at 5°C, the appropriate hydrazonoyl chloride (0.05 mole) was added and stirring continued for 2h at 20°C. Then the white precipitate was filtered off, and washed several times with water. The ^{1}H NMR spectrum of the crude solid in $CDCl_3$ showed the presence of only one regioisomer. The crude products **11a-c**, **14** and **15** were recrystallised from ethanol. The physical constants and elemental analyses are listed in Tables 1 and 2.

Hydrazinolysis of 11a.

A mixture of the pyrazole **11** (5 mmole), the appropriate hydrazine derivative (6 mmole) and ethanol (20mL) was refluxed for 3h. The isolated 3,4-dimethyl-2-phenyl-2,6-dihydro-pyrazolo[3,4-d]pyridazin-7-ones **12a-c** were characterised. Their physical constants are given below :

12a : Yield (77%); mp 276/278°C (ethanol); IR (KBr) υ 1658 (CO), 1595 (C=N) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO) δ 2.54 (s, 3H, CH_3), 2.62 (s, 3H, CH_3),and 7.45(m, 5H, Ar-H) ppm. (Calcd. for $C_{13}H_{12}N_4O$: C, 65.00; H, 5.04; N, 23.32. Found : C, 65.32; H, 5.16; N, 22.97).

12b : Yield (83%); mp > 320°C (ethanol); IR (KBr) υ 1664 (CO), 1595 (C=N) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO) δ 2.58 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 3.82 (s, 3H, CH_3),and 7.46 (m, 5H, Ar-H) ppm .

12c : Yield (72%) IR (KBr) υ 1662 (C=O), 1595 (C=N) cm^{-1}; ^{1}H-NMR ($CDCl_3$+ DMSO) δ 2.56 (s,3H,CH_3), 2.69 (s,3H,CH_3), 7.48 (m,10H,Ar-H).

12d : Yield (65%); mp 108/111°C (ethanol); IR (KBr) υ 1716 (COOEt), 1595 (C=N) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.32 (t, 3H, J=7Hz, CH_3), 2.25 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.42 (q, 2H, J=7Hz, OCH_2),and 7.43 (m, 10H, Ar-H) ppm .

Hydrazinolysis of 14 and 15 .

A mixture of the pyrazoles **14** and **15** and excess hydrazine hydrate was heated at 100°C for 6h. The physical constants of the isolated products **16** and **17** are given below :

16 : Yield (87%); mp 239/40°C (ethanol); IR (KBr) υ 1592 (C=C), 1595 (C=N) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.83 (s, 3H, CH_3), 2.86 (s, 6H, $2CH_3$), 7.56 (m, 5H, Ar-H)ppm .

(Calcd. for $C_{14}H_{14}N_4$: C, 70.57; H, 5.92; N, 23.50. Found : C, 70.96; H, 6.13; N, 23.16.

17 : Yield (87%); mp 227/29°C (ethanol); IR (KBr) υ 1590 (C=C), 1596 (C=N) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO) δ 2.46 (s, 3H, CH_3), 2.96 (s, 6H, $2CH_3$), 7.33 (m, 10H, Ar-H)ppm.

(Calcd. for $C_{19}H_{16}N_4$: C, 76.00; H, 5.37; N, 18.65. Found : C, 75.71; H, 5.49; N, 18.38.

Table 2. Physical properties and elemental analyses for dihydropyrazoles and pyrazoles

Compd. No.	mp °C	yield %[a]	Molecular formula	Anal. Calcd. (Found) C % , H % , N %
3a	110/12	60	$C_{20}H_{20}N_2O_3$	71.41(71.33), 5.99(6.03), 8.32(8.41)
4a	96	40	$C_{20}H_{20}N_2O_3$	71.41(71.51), 5.99(6.14), 8.32(8.22)
3b	174[c]	55	$C_{20}H_{19}BrN_2O_3$	
4b	153	45	$C_{20}H_{19}BrN_2O_3$	57.83(58.11), 4.61(4.39), 6.74(6.93)
3c	138[d]	30	$C_{25}H_{21}BrN_2O_3$	
4c	148[e]	70	$C_{25}H_{21}BrN_2O_3$	
5a	108	60	$C_{20}H_{18}N_2O_3$	71.84(72.08), 5.43(5.39), 8.37(8.43)
6a	84	40	$C_{20}H_{18}N_2O_3$	71.84(72.13), 5.43(5.49), 8.37(8.47)
5b	128	60	$C_{20}H_{17}BrN_2O_3$	58.12(57.88), 4.15(4.01), 6.77(6.83)
6b	107	40	$C_{20}H_{17}BrN_2O_3$	58.12(58.29), 4.15(4.21), 6.77(6.68)
11a	liquid	82[b]	$C_{15}H_{16}N_2O_3$	
11b	97	73[b]	$C_{15}H_{15}BrN_2O_3$	51.29(51.33), 4.30(4.41), 7.97(8.08)
14	130	82[b]	$C_{14}H_{14}N_2O_2$	69.41(69.63),5.83(5.91),11.56(11.61)
15	113	76[b]	$C_{19}H_{16}N_2O_2$	71.24(71.05), 5.04(4.98), 8.74(8.61)

a : the ratio was determined by ^{1}H-NMR analysis . **b** : isolated yield . c : Lit. mp 173°C (Ref. 3).

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