# Synthesis of some heterocyclic systems of anticipated biological activities via 6-aryl-4-pyrazol-1-yl-pyridazin-3-one

**A.S.A. Youssef, M.I. Marzouk, H.M.F. Madkour, A.M.A. El-Soll, and M.A. El-Hashash**

**Abstract:** 6-Aryl-4-pyrazol-1-yl-pyridazin-3-one (**1**) reacted with a $PCl_5$–$POCl_3$ mixture to give the 3-chloropyridazine derivative **3**. Reaction of **3** with 2-hydroxybenzoylhydrazide and semicarbazide hydrochloride afforded **4** and **5**. Reaction of **1** with ethyl chloroacetate gave **8**. Reaction of **8** with hydrazine hydrate yielded the hydrazide **9**. The hydrazide **9** condensed with the acetylenic ketones and esters **10a**–**10d** and acetylacetone to give the adducts **11a**, **11b**, **12**, **13**, and **14**. Reacting **1** with formaldehyde and piperidine, morpholine, or piperazine, 3-bromopropanoic acid, acetic anhydride, *p*-toluenesulphonyl chloride, succinyl chloride, oxalyl chloride, ethanolamine, or ethyl chloroacetate gave the adducts **15**–**22**. The structures of all newly synthesized compounds were evidenced from their spectral and microanalytical data.

*Key words:* 6-aryl-4-pyrazol-1-yl-pyridazinone derivative, 6-aryl-3-chloropyridazine derivative, 3,6-diaryl-1,2,4-triazino[4,3-*b*]pyridazine derivative, 6-aryl-3-ethoxycarbonylmethoxypyridazine derivative, 6-aryl-3-(ω-benzoylacetophenone)hydrazinocarbonylmethoxypyridazine.

**Résumé :** La 6-aryl-4-pyrazol-1-yl-pyridazin-3-one (**1**) réagit avec un mélange de $PCl_5$–$POCl_3$ pour conduire à la formation du dérivé 3-chloropyridazine **3**. La réaction de **3** avec le 2-hydroxybenzoylhydrazide et le chlorhydrate de semicarbazide conduit aux dérivés **4** et **5**. La réaction de **1** avec le chloroacétate d'éthyle conduit à **8**. La réaction de **8** avec l'hydrate d'hydrazine permet d'obtenir l'hydrazide **9**. L'hydrazide **9** se condense avec les cétones acétyléniques, les esters **10a**–**10d** et l'acétylacétone pour fournir les produits **11a**, **11b**, **12**, **13** et **14**. La réaction de **1** avec le formaldéhyde et la pipéridine, la morpholine ou la pipérazine, l'acide 3-bromopropanoïque, l'anhydride acétique, le chlorure de *p*-toluènesulfonyle, le chlorure de succinyle, le chlorure d'oxalyle, éthanolamine ou le chloroacétate d'éthyle conduit aux adduits **15**–**22**. Les structures de tous les composés nouvellement synthétisés ont été caractérisés par leurs données microanalytiques et spectroscopiques.

*Mots clés :* dérivé de la 6-aryl-4-pyrazol-1-yl-pyridazinone, dérivé de la 6-aryl-3-chloropyridazine, dérivé de la 3,6-diaryl-1,2,4-triazino[4,3-*b*]pyridazine, dérivé de la 6-aryl-3-éthoxycarbonylméthoxypyridazine, 6-aryl-3-(ω-benzoylacétophénone)hydrazinocarbonylméthoxypyridazine.

[Traduit par la Rédaction]

## Introduction

In a recent previous publication (1) we reported the reaction of β-aroylacrylic acid with some nitrogen nucleophiles and active methylene reagents and the utility of some of the reaction products in heterocyclic synthesis. A large number of pyridazin-3-ones were reported to exhibit insecticidal (2–6), allergenic (7), antihypertensive (8–12), analgesic (13, 14), anti-inflammatory, and bactericidal (15, 16) activities. This prompted us to study the behaviour of 6-(4-chloro-3-methyl) phenyl-4-(3,5-dimethyl-pyrazol-1-yl)-4,5-dihydropyridazin-3-one toward various reagents, hoping to get new compounds of anticipated biological activities.

## Results and discussion

It has been reported (17, 18) that the reaction of 6-(4-chloro-3-methyl)phenyl-4-(3,5-dimethylpyrazol-1-yl)-**1a** or 6-(4-chloro-3-methyl) phenyl-4-(5-isopropyl-2-methyl)phenyl-**1b**-2,3,4,5-tetrahydropyridazin-3-one with a phosphorous pentachloride – phosphorous oxychloride mixture yielded 4,6-diaryl-3-chloro-4,5-dihydropyridazine derivatives **2a** and **2b**, respectively. In the present investigation, similar treatment of **1a** with the same reagent afforded 6-aryl-3-chloropyridazine derivative **3**. The previous reports suggested structure **2** for the products where there was a lack of spectroscopic data.

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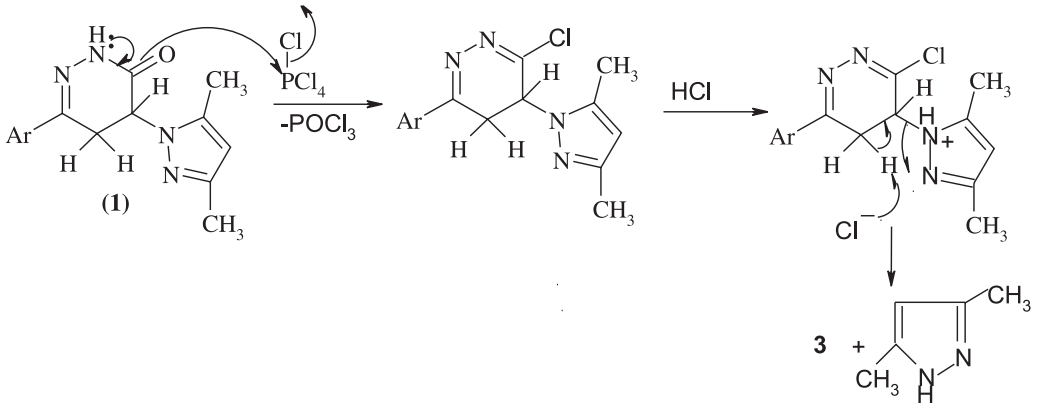
**Scheme 1.**



(1)

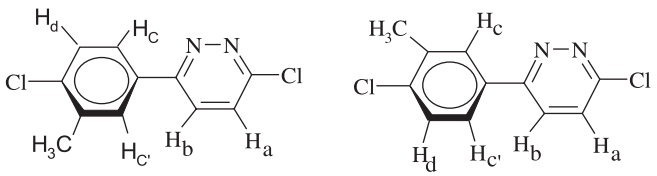
a, Ar = 3,5-dimethylpyrazolyl
b, Ar = 5-*i*-Pr-2-$CH_3C_6H_3$
c, Ar = 2,5-$(CH_3)_2C_6H_3$

(2)

a, Ar = 3,5-dimethylpyrazolyl
b, Ar = 5-*i*-Pr-2-$CH_3C_6H_3$

(3)

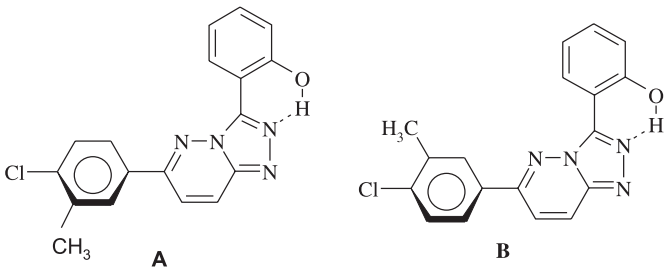
The $^1$H NMR spectrum of compound **3** shows the aromatic proton resonances and doesn't exhibit the signals of the ABX pattern of the $CH_2$-CH- group as well as the signals of the methyl protons of the dimethylpyrazole ring. This infers the absence of these moieties. It discloses AB quartet signals owing to the two protons $H_a$ and $H_b$ of the pyridazine ring. The appearance of extra signals correlated with methyl and the aromatic protons is good evidence for the existence of **3** in the two conformations **A** and **B**, as a result of the limited rotation of the aryl group around the pyridazine ring as shown. The same phenomenon was observed for strucrures **4**, **5**, **8**, **9**, **14**, and **22**. The structure of **3** gets further support from mass spectroscopy. Thus, its EI-MS exhibits a molecular ion peak.



A (3) B

The formation of **3** has been rationalized in terms of the route mentioned in Scheme 1.

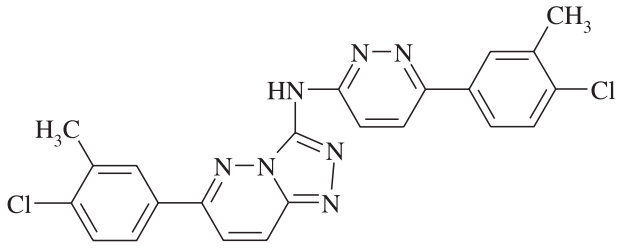
Treating an equimolar amount of 6-aryl-3-chloropyridazine derivative **3** with 2-hydroxybenzoylhydrazide in pyridine gave 3-(2-hydroxy) phenyl-6-aryl-1,2,4-triazolo[4,3-*b*]pyridazine derivative **4**. The structure of compound **4** is substantiated from its microanalytical and spectral data. The $^1$H NMR spectrum of **4** is in accord with the proposed structure. The higher δ value of the OH proton is in accord with the existence of **4** as its chelated form as shown. Further support for the assigned structure of **4** was gained from EI-MS that revealed the molecular ion peak.



A B

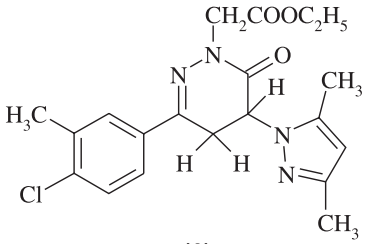
(4)

Reacting **3** with semicarbazide hydrochloride in the presence of triethylamine as a base afforded 3-[6-(4-chloro-3-methyl)phenylpyridazin-3-yl]amino-6-(4-chloro-3-methyl)-phenyl-1,2,4-triazolo[4,3-*b*]pyridazine (**5**).

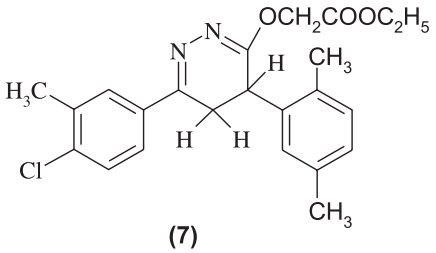


(5)

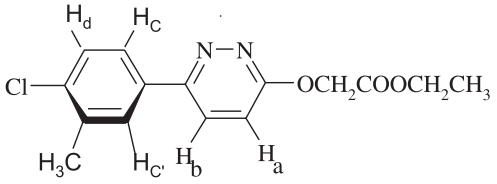
The structure of compound **5** is evidenced from its microanalytical and spectral data. The $^1$H NMR spectrum exhibits exchangeable NH as well as two well-separated singlets consistent with protons of two methyl groups. The



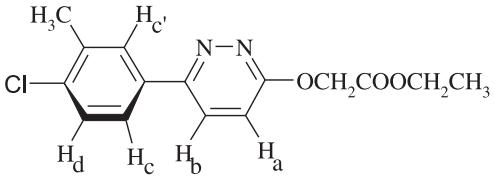
(6)



(7)



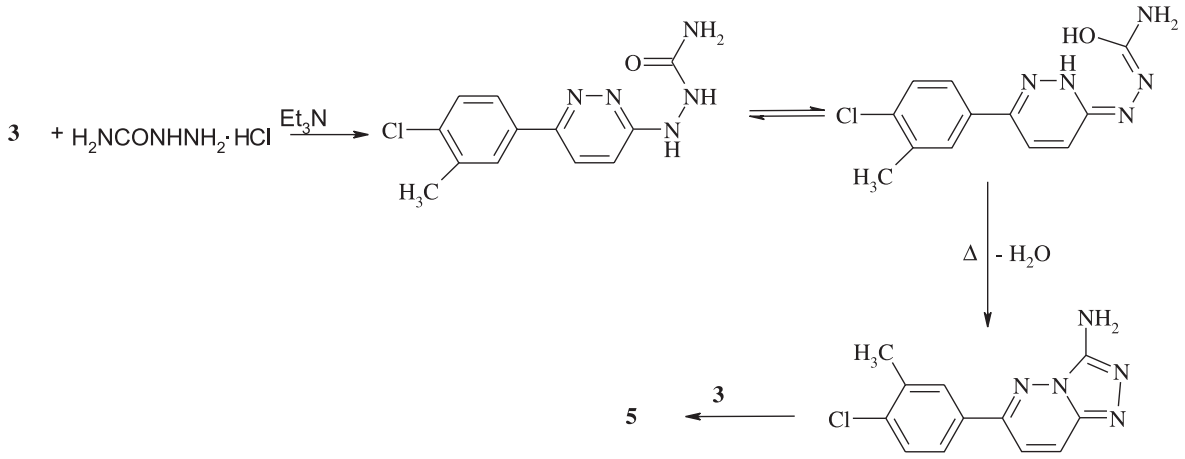
(A)



(B)

(8)

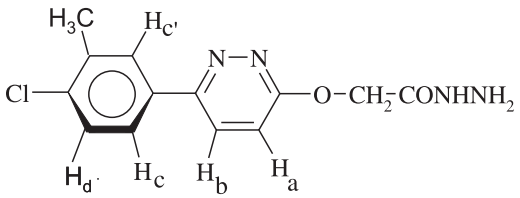
**Scheme 2.**



complexity of signals in the aromatic region suggests the existence of more than two diastereomers. The EI-MS spectrum of **5** doesn't show the molecular ion peak, but instead shows the ($M^{+\cdot}$ – Cl) peak. The formation of **5** is outlined in Scheme 2.

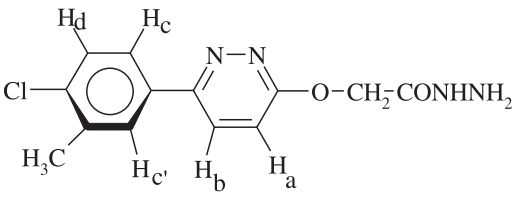
It has been reported (17, 19) that 4,6-diaryl pyridazinone derivatives **1a** and **1c** reacted with ethyl chloroacetate in the presence of potassium carbonate in dry acetone to give the adducts **6** (17) and **7** (19), respectively. In the present work, treatment of **1a** with ethyl chloroacetate in dioxane instead of dry acetone yielded the adduct **8** as a mixture of two conformers **8A** and **8B**. Although compounds **6–8** have the same melting point, the conflict in structure is probably due to the lack in the spectroscopic evidence used by previous authors (17, 19) in the assignment of structures.

The structure of compound **8** is evidenced from its microanalytical and spectral data. Thus, its IR spectrum shows absorptions correlated with the $\nu_{C=O}$ (ester). The $^1$H NMR spectrum shows absorption signals correlated with the $OCH_2$ and $COOCH_2CH_3$ protons. Moreover, the structure of **8** gets further support from its EI-MS as it shows the molecular ion peak and some of the abundant peaks. On the other hand, the treatment of **8** with hydrazine hydrate afforded the hydrazides **9**.



A

(9)



B

The structure of compound **9** is established from its microanalytical and spectral data. Thus, its IR spectrum shows absorptions characteristic for $\nu_{NH}$ and $\nu_{C=O}$ (amide). The $^1$H NMR spectrum supports the proposed structure as it is devoid of any signals corresponding to the protons of the ethyl group, but instead to signals correlated with the hydrazino group. The suggested structure gets further support from the EI-MS as it shows the correct molecular ion peak beside some of the abundant peaks.

The reaction of hydrazide **9** with acetylenic ketones and ester **10a**–**10d** in refluxing dioxane afforded the adducts **11a**, **11b**, **12**, and **13**, respectively. The structures of compounds **11a**, **11b**, **12**, and **13** are deduced from their microanalytical and spectral data. Thus, their IR spectra reveal characteristic bands for $\nu_{NH}$ and $\nu_{C=O}$. The lower absorption values for the C=O and NH groups in **11** and **13** are in good agreement with the existence of compounds **11** and **13** in their chelated forms as shown. Further support for the suggested structure of compounds **11a** and **11b** was gained from their $^1$H NMR spectra, which revealed two ABqs representing AB systems, one owing to the methylene protons of the $CH_2COR$ group and the other owing to the $OCH_2CO$ protons (20–22). The fact that these methylene protons behave as AB systems can be attributed either to the large anisotropic effect of the C=N or C=O groups and the nitrogen lone pair or to the restriction of rotation at the aroyl group by the weak hydrogen bonding between the NH and carbonyl group. The $^1$H NMR spectra of **12** and **13** are in good agreement with the proposed structures.

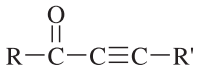
Furthermore, the electron impact mass spectra of compounds **11a** and **11b** don't show the molecular ion peaks, instead they show the ($M^{+\cdot}$ – $ArCOCH_2C(Ar')$=N·NH) peak beside some of the abundant peaks. On the other hand, the EI-MS spectra of compounds **12** and **13** show molecular ion peaks beside some of the abundant peaks.

The formation of **11** and **13** seems to proceed by Michael addition of the hydrazide **9** at the β-carbon of the acetylenic compounds **10**. Similarly, compound **12** is formed, followed by ring closure.

On the other hand, the reaction of the hydrazide **9** with acetylacetone in boiling methanol yielded the adduct **14**. The structure of **14** is evidenced by microanalytical, $^1$H NMR, and mass spectral data. Thus, its IR spectrum shows bands characteristic for $\nu_{C=O}$, $\nu_{C=N}$, and (or) $\nu_{C=C}$. Moreover, the assigned structure of compound **14** gets further support from the $^1$H NMR spectrum.

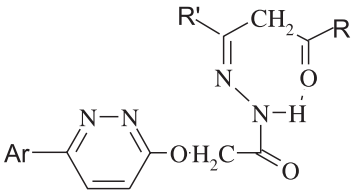
Inspection of the $^1$H NMR spectrum revealed the existence of two closely spaced singlets for the methyl protons attached at position 5 in the pyrazole ring, probably because the rate of rotation of the pyrazole ring around the hindered "partial double bond" is slow (23). This allows the existence of this methyl group in two different conformations (**A** and **B**) under different magnetic environments as shown in the following. Furthermore, the mass spectrum of **14** shows the molecular ion peak in addition to some abundant peaks. Compound **14** is formed through condensation of the hydrazide **9** with one of the two carbonyl groups of acetylacetone followed by ring closure.

Treatment of pyridazinone derivative **1a** with piperidine or morpholine and an excess of 40% formaldehyde solution in refluxing dioxane afforded 6-aryl-2-piperidin-1-yl-methyl-



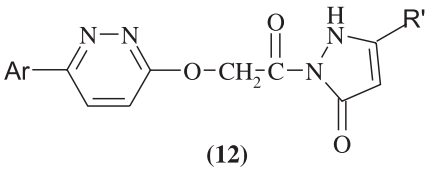
**(10)**

a, R = 4-Cl-$C_6H_4$, R' = $C_6H_5$
b, R = R' = $C_6H_5$
c, R = $OC_2H_5$, R' = 4-Cl$C_6H_4$
d, R = $OC_2H_5$ , R' = $CO_2C_2H_5$



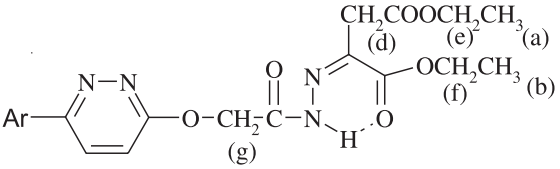
**(11)**

a, Ar = 4-Cl-3-$CH_3C_6H_3$, R = 4-Cl$C_6H_4$ , R' = $C_6H_5$
b, Ar = 4-Cl-3-$CH_3C_6H_3$, R = R' = $C_6H_5$



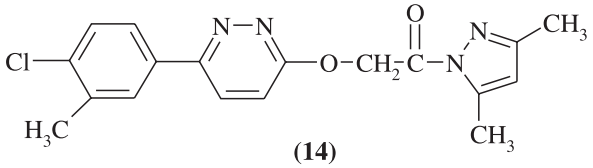
**(12)**

Ar = 4-Cl-3-$CH_3C_6H_3$ , R' = 4-Cl-$C_6H_4$-

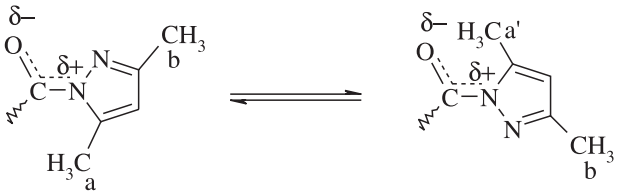


**(13)**

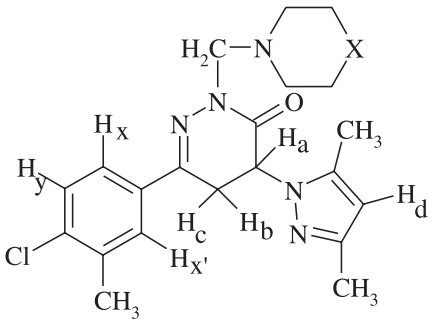
Ar = 4-Cl-3-$CH_3C_6H_3$



**(14)**



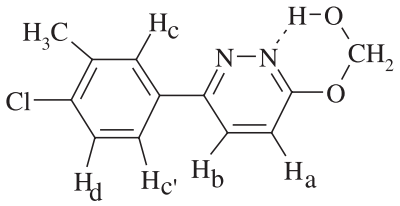
**A** **(14)** **B**



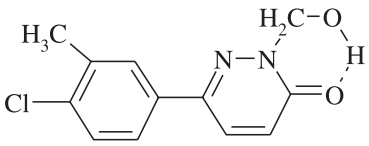
**(15)**

a, X = $CH_2$

b, X = O



**(16)**

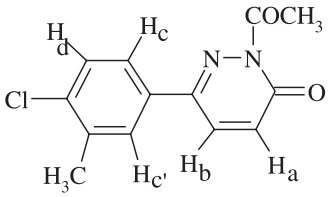


**(17)**

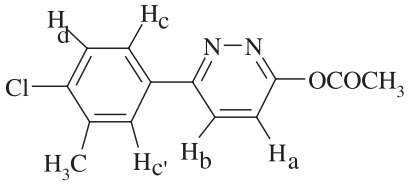
**15a** or 6-aryl-2-morpholin-4-yl-methyl-**15b**-4-(3,5-dimethyl pyrazol-1-yl)-2,3,4,5-tetrahydropyridazin-3-one. However, similar treatment of **1a** with piperazine yielded a mixture of the two isomeric compounds (**3**-hydroxymethoxy-6-arylpyridazine derivative **16** and 2-hydroxymethyl-6-aryl-2,3-dihydropyridazin-3-one derivative **17**, respectively).

The structures of compounds **15**–**17** are evidenced from their microanalytical and spectral data. Thus, their IR spectra show absorptions characteristic for $\nu_{C=O}$, $\nu_{C=N}$, and (or) $\nu_{C=C}$ in addition to $\nu_{OH}$ for structures **16** and **17**. The lower absorption values for the OH and C=O groups for compounds **16** and **17** are in good agreement with their existence in the chelated forms shown. The $^1$H NMR spectra of compounds **15a** and **15b** disclosed ABX patterns consistent with -$CH_X$-$CH_AH_B$-CO moieties in which each of these coupled protons appears as a doublet of doublet with a geminal coupling constant $J \approx 16.8$ Hz and a vicinal coupling constant of ≈13 or 7 Hz. In addition, they show two central peaks of ABq corresponding to the -$CH_2$-N group. Analysis of the observed $^1$H NMR spectrum of the mixture containing **16** and **17** inferred that they exist in deuterated dimethylsulphoxide in a ratio of 2:1, respectively. Moreover, the structures of compounds **15a** and **15b** and the mixture containing **16** and **17** get further support from the EI-MS spectra, where the spectra of compounds **15b** and the mixture of **16** and **17** show molecular ion peaks, whereas that of compound **15a** doesn't show the molecular ion peak, but does show a peak corresponding to [$M^{+\cdot}$ – dimethylpyrazole].

The reaction of equimolar amounts of **1a** and 3-bromopropanoic acid in refluxing dioxane and in the presence of potassium carbonate as a base gave a mixture of the two isomeric products 6-aryl-2-(2-carboxy) ethylpyridazinone derivative **18** and 6-aryl-3-(2-carboxyl)ethoxy pyridazine derivative **19**.



**(20)**



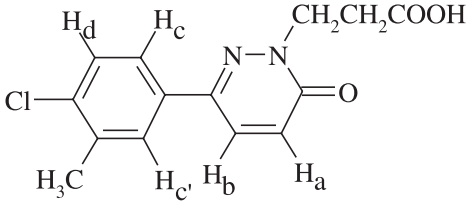
**(21)**

The structures of compounds **18** and **19** are substantiated from microanalytical and spectral data. Thus, the IR spectrum shows absorptions characteristic for $\nu_{OH(br.)}$, $\nu_{C=O}$ (acid), and $\nu_{C=O}$ (amide). Analysis of the $^1$H NMR spectrum inferred that compounds **18** and **19** exist in deuterated dimethylsulphoxide as a mixture in a ratio of 1:1.2. Existence of compounds **18** and **19** as a mixture has been evidenced from the location of two triplet signals consistent with the protons of the $NCH_2$ and $OCH_2$ groups for structures **18** and **19**, respectively. The EI-MS spectrum of compounds **18** and **19** doesn't show the molecular ion peak, but does show a peak at *m*/*e* 220, which corresponds to the [$M^{+\cdot}$ – $CH_2$=CHCOOH] peak beside some of the abundant peaks.

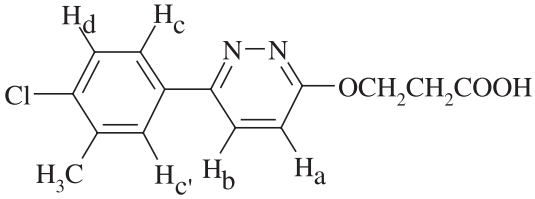
Treatment of **1a** with acetic anhydride yielded a mixture of equimolar amounts of 2-acetyl-6-aryl-2,3-dihydropyridazin-3-one derivative **20** and 3-acetoxy-6-arylpyridazine derivative **21**.

The structures of compounds **20** and **21** are deduced from microanalytical and spectral data. The IR spectrum shows absorptions characteristic for $\nu_{C=O}$, $\nu_{C=N}$, and (or) $\nu_{C=C}$. Moreover, the $^1$H NMR spectrum supports the structures of **20** and **21** as it shows two closely spaced singlets at δ 2.75 and 2.78 correlated with the methyl protons of the $NCOCH_3$ and $OCOCH_3$ groups, respectively. The EI-MS spectrum of the mixture doesn't show the molecular ion peak, but instead the [$M^{+\cdot}$ – $CH_2$=C=O] peak as a base peak.

It has been reported (17) that 6-aryl-4-pyrazolylpyridazinone derivative **1a** reacted with benzenesulphonyl chloride in refluxing acetone and in the presence of potassium carbonate as a base to give the *N*-benzenesulphonyl derivative **23**. However, in the present work, treatment of equimolar amounts of **1** with *p*-toluenesulphonyl chloride, succinyl

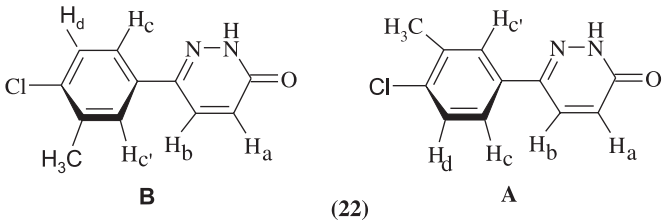



**(18)**

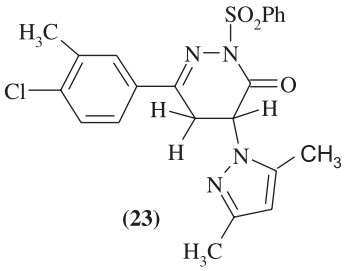



**(19)**

chloride, oxalyl chloride, or ethanolamine in refluxing pyridine or with ethyl chloroacetate in boiling dimethylformamide afforded 6-aryl-2,3-dihydro pyridazin-3-one (**22**) as a mixture of two conformations **22A** and **22B**. Compounds **22** and **23** have identical melting points although they have different structures, as there is a lack in the spectroscopic evidence used by previous authors (17) in their assignment of structure **23**.




**(22)**




**(23)**

The structure of compound **22** is deduced spectroscopically and chemically. Its IR spectrum shows $\nu_{NH}$ and $\nu_{C=O}$. The $^1$H NMR spectrum is in good agreement with the proposed structure considering the existence of the conformations **22A** and **22B**. Further support for the proposed structure was gained from the EI-MS spectrum as it shows the molecular ion peak beside some of the abundant peaks. A chemical proof for the structure of compound **22** was given by comparison (mp, mixed mp, and TLC) with an authentic sample prepared by treating **1a** with hydrazine hydrate in boiling ethanol. Also, by refluxing compound **1a** with pyridine to give compound **22**. This supports the role of pyridine as a base in the removal of the dimethylpyrazolyl group.

The formation of compounds **16** and **17** (mixture), **18** and **19** (mixture), **20** and **21** (mixture), and **22** upon treating **1** with piperazine–HCHO, 3-bromopropanoic acid – $K_2CO_3$, acetic anhydride, *p*-toluenesulponyl chloride – pyridine, succinyl chloride – pyridine, oxalyl chloride – pyridine, ethanolamine – pyridine, or ethyl chloroacetate – DMF can be explained on the basis of an acid- or base-catalysed removal of the dimethylpyrazolyl moiety, as in case of **22**, followed by nucleophilic attacks of the lactam–lactim tautomer to the reagents used in the other cases.

## Experimental

All melting points are uncorrected. The IR spectra were recorded on FT IR Mattson (infinity series) spectrometers as KBr discs. The $^1$H NMR spectra were measured on a Varian Gemini 200 MHz instrument with chemical shifts (δ) expressed in ppm downfield from TMS. Mass spectra were recorded on a Shimadzu GC-MS-QP 1000 Ex instrument operating at 70 eV. TLC was run using TLC aluminum sheets silica gel $F_{254}$ (Merck). Note: All attempts to separate all of the isomeric mixtures mentioned, including column chromatography, failed possibly because of isomerization taking place during separation.

### Reaction of 1a with the $PCl_5$–$POCl_3$ mixture — Formation of 3

A mixture of **1a** (5 mmol), $PCl_5$ (5 mmol), and $POCl_3$ (10 mL) was gently heated for 3 h, cooled, poured into crushed ice, and the precipitated solid was filtered and recrystallized from benzene to give **3**.

#### *6-(4-Chloro-3-methyl) phenyl-3-chloropyridazine (3)*

Yield: 60%; white crystals, mp 175 to 176 °C, lit. value (17, 18) mp 176 °C. IR ($cm^{-1}$): 3078 ($CH_{aryl}$), 2924, 2854 ($CH_{alkyl}$), 1672, 1600 (C=N and (or) C=C), 821 (C-Cl). $^1$H NMR (200 MHz, $CDCl_3$) δ: 2.439, 2.461 (two singlets, $2CH_3$), 7.37, 7.481 (two doublets, $H_d$, $J_o$ = 8.2 Hz), 7.559 (d, $H_a$, $J_{ab}$ = 9.2 Hz), 7.764 (dd, $H_{c'}$, $J_o$ = 8.2 Hz, $J_m$ = 2.2 Hz), 7.806 (d, $H_b$, $J_{ab}$ = 9.0 Hz), 7.95, 8.041 (two doublets, Hc, $J_m$ = 2.2 Hz). EI-MS *m*/*z*: 238 ($M^{+\cdot}$, 56), 210 ($M^{+\cdot} - N_2$, 23), 150 (4-Cl-3$CH_3C_6H_3C{\equiv}CH$, base), 115 (89), 90 (6), 89 (29), 64 (10), 63 (44). Anal. calcd. for $C_{11}H_8N_2Cl_2$ (%): C 55.26, H 3.37, N 11.72; found: C 55.44, H 3.51, N 11.82.

### Reaction of 3 with 2-hydroxybenzoylhdyrazide — Formation of 4

A mixture of **3** (5 mmol) and 2-hydroxybenzoylhydrazide (5 mmol) in pyridine (10 mL) was refluxed for 6 h. The reaction mixture was left to cool then poured into ice-cold water. The precipitated solid was filtered off, washed, dried, and then recrystallized from methanol to give **4**.

#### *3-(2-Hydroxyphenyl)-6-(4-chloro-3-methyl) phenyl1,2,4-triazolo[4,3-*b*]pyridazine (4)*

Yield: 33%; dark brown crystals, mp 249 to 250 °C. IR ($cm^{-1}$): 3427 (OH), 3062 ($CH_{aryl}$), 2924, 2858 ($CH_{alkyl}$), 1623, 1585 (C=N and (or) C=C). $^1$H NMR (200 MHz, $CDCl_3$) δ: 2.506, 2.528 (two singlets, 2 $CH_3$), 7.049–8.932 (m, 9, ArH), 11.92 (br.s, 1, OH exchangeable). EI-MS *m*/*z* (%): 338 ($M^{+\cdot}$ + 2, 22), 337 ($M^{+\cdot}$ + 1, base), 336 ($M^{+\cdot}$, 60), 184 (49), 183 (58), 157 (16), 156 (16), 127 (34), 126 (15),

125 (20), 102 (14), 101 (15), 89 (50), 77 (35), 76 (18), 65 (18), 64 (34), 63 (52), 52 (22), 51 (59), 50 (28). Anal. calcd. for $C_{18}H_{13}N_4OCl$ (%): C 64.19, H 3.89, N 16.64, Cl 10.53; found: C 64.26, H 3.92, N 16.76, Cl 10.65.

**Reaction of 3 with semicarbazide hydrochloride — Formation of 5**

A solution of **3** (3 mmol) and semicarbazide hydrochloride (3.5 mmol) in dry dioxane (20 mL) was refluxed for 12 h in the presence of potassium carbonate (1.0 g). The reaction mixture was concentrated, cooled, and then poured into ice-cold water. The solid formed was filtered off, washed, dried, and then recrystallized from methanol to give **5**.

***3-[6-(4-Chloro-3-methyl)phenylpyridazin-3-yl]amino-6-(4-chloro-3-methyl)phenyl-1,2,4-triazolo[4,3-b]pyridazine (5)***

Yield: 54%; violet crystals, mp 194–196 °C. IR ($cm^{-1}$): 3447 (NH), 3057 ($CH_{aryl}$), 2983, 2900, 2859 ($CH_{alkyl}$), 1687, 1603, 1573 (C=N and (or) C=C). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 2.423, 2.491 (two singlets, $2CH_3$), 7.146–8.184 (m, 11, ArH + NH). EI-MS *m/z*: 426 ($M^{+\cdot}$ – Cl, 11), 390 (40), 360 (14), 297 (14), 244 (24), 216 (25), 164 (77), 151 (37), 150 (15), 125 (25), 115 (40), 89 (82), 63 (80). Anal. calcd. for $C_{23}H_{17}N_7Cl_2$ (%): C 59.75, H 3.71, N 21.21, Cl 15.34; found: C 60.01, H 3.79, N 21.36, Cl 15.41.

**Reaction of 1a with ethyl chloroacetate — Formation of 8**

A solution of **1a** (5 mmol) in dry dioxane (20 mL) was heated with ethyl chloroacetate (5 mmol) for 24 h in the presence of potassium carbonate (3 g). The reaction mixture was concentrated, cooled then poured into ice-cold water. The precipitated solid was filtered off, dried, and then recrystallized from petroleum ether 80–100 °C.

***6-(4-Chloro-3-methyl)phenyl-3-ethoxycarbonylmethoxypyridazine (8)***

Yield: 70%; pale yellow crystals, mp 100 °C, lit. value (17, 19) mp 96 °C, 89 °C. IR ($cm^{-1}$): 3071 ($CH_{aryl}$), 2987, 2911 ($CH_{alkyl}$), 1749 (C=O), 1672, 1596 (C=N and (or) C=C). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 1.292 (t, 3, $CH_3CH_2O$, $J$ = 7.2 Hz), 2.403, 2.421 (two singlets, $2CH_3$), 4.255 (q, 2, $CH_3CH_2O$, $J$ = 7.2 Hz), 4.956 (s, 2, $OCH_2CO$), 7.041, 7.646 (two doublets, $H_a$, $J_{ab}$ = 9.8 Hz), 7.292, 7.399 (two doublets, $H_d$, $J_o$ = 8.4 Hz), 7.551, 7.501 (two doublet doublets, $H_c$, $J_o$ = 8.6 Hz, $J_m$ = 1.8 Hz), 7.557, 7.771 (two doublets, $H_{c'}$, $J_m$ = 1.8 Hz), 7.676, 7.682 (two doublets, $H_b$, $J_{ba}$ = 9.6 Hz). EI-MS *m/z*: 308 ($M^{+\cdot}$ + 2, 20), 306 ($M^{+\cdot}$, 55), 263 ($M^{+\cdot}$ + 2-$OC_2H_5$, 9), 261 ($M^{+\cdot}$ – $OC_2H_5$, 4), 233 ($M^{+\cdot}$ + 2-$COOC_2H_5$, base), 231 ($M^{+\cdot}$ – $COOC_2H_5$, 41), 205 (19), 198 (13), 170 (17), 163 (51), 128 (23), 115 (15), 89 (17), 63 (73). Anal. calcd. for $C_{15}H_{15}N_2O_3Cl$ (%): C 58.73, H 4.93, N 9.13, Cl 11.56; found: C 58.81, H 5.00, N 9.22, Cl 11.63.

**Reaction of 8 with hydrazine hydrate**

A solution of **8** (3 mmol) in ethanol (20 mL) was refluxed with hydrazine hydrate (5 mmol) for 4 h. The reaction mixture was cooled. The precipitated solid was filtered off and recrystallized from methanol.

***6-(4-Chloro-3-methyl) phenyl-3-hydrazinocarbonylmethoxypyridazine (9)***

Yield: 82%; white crystals, mp 210–212 °C. IR ($cm^{-1}$): 3409, 3306, 3205 (NH), 3055 ($CH_{aryl}$), 2953, 2921, 2853 ($CH_{alkyl}$), 1667 (C=O), 1589, 1533 (C=N and (or) C=C). $^1H$ NMR (200 MHz, DMSO-$d_6$) δ: 2.393, 2.413 (two singlets, $2CH_3$), 4.306 (br.s, 2, $NH_2$ exchangeable), 4.742 (s, 2, $OCH_2$), 7.078, 7.090 (two doublets, $H_a$, $J_{ab}$ = 9.78 Hz), 7.491, 7.541 (two doublets, $H_d$, $J_o$ = 8.4 Hz), 7.732, 7.774 (two doublet doublets, $H_c$, $J_o$ = 8.52 Hz, $J_m$ = 1.86 Hz), 7.885, 7.929 (two doublets, $H_{c'}$, $J_m$ = 1.82 Hz), 8.086, 8.110 (two doublets, $H_b$, $J_{ba}$ = 9.8 Hz), 9.316 (br.s, 1, NH exchangeable). EI-MS *m/z*: 292 ($M^{+\cdot}$, 5), 263 ($M^{+\cdot}$ + 2-$NHNH_2$, 59), 261 ($M^{+\cdot}$ – $NHNH_2$, 17), 235 ($M^{+\cdot}$ + 2-$CONHNH_2$, 29), 231 ($M^{+\cdot}$ – $CONHNH_2$, base), 205 (12), 198 (13), 170 (15), 163 (21), 151 (10), 89 (15), 63 (20). Anal. calcd. for $C_{13}H_{13}N_4O_2Cl$ (%): C 53.34, H 4.48, N 19.14, Cl 12.11; found: C 53.46, H 4.52, N 19.24, Cl 12.35.

**Reactions of 9 with acetylenic ketones, esters 10a–10d, and with acetylacetone**

***General procedure***

A mixture of **9** (3 mmol) and **10a**–**10d** (3 mmol) in dioxane (15 mL) or acetylacetone (3 mmol) in methanol (20 mL) was refluxed for 10 h. The reaction mixture was concentrated, left to stand at room temperature. The solid formed was recrystallized from a suitable solvent to give **11a**, **11b**, **12**, **13**, and **14**.

***6-(4-Chloro-3-methyl)phenyl-3-[ω-(4-chlorobenzoyl)acetophenone]hydrazonocarbonylmethoxypyridazine (11a)***

Yield: 62%; white crystals, mp 198–200 °C (from methanol). IR ($cm^{-1}$): 3391 (NH), 3039 ($CH_{aryl}$), 2954, 2906, 2843 ($CH_{alkyl}$), 1662 (C=O). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 2.421 (s, 3, $CH_3$), 3.371, 3.752 (ABq, 2, $CH_2CO$, $J$ = 18.5 Hz), 4.848 (br.s, 1, NH), 5.355, 5.688 (ABq, 2, $OCH_2CO$, $J$ = 16.4 Hz), 7.005–7.756 (m, 14, Ar-H). EI-MS *m/z*: 533 ($M^{+\cdot}$, missed), 272 (3.5), 263 (8.4), 261 (24.5), 256 (38.5), 254 (base), 235 (5.3), 233 (15), 170 (56.4), 153 (10.1), 151 (27), 115 (12.9), 113 (6.1), 111 (9.1), 103 (3.8), 89 (27.7), 82 (4.2), 63 (24.1). Anal. calcd. for $C_{28}H_{22}N_4O_3Cl_2$ (%): C 63.30, H 4.16, N 10.50; found: C 63.54, H 4.23, N 10.67.

***6-(4-Chloro-3-methyl)phenyl-3-(ω-benzoylacetophenone)hydrazonocarbonylmethoxypyridazine (11b)***

Yield: 21%; pale yellow crystals, mp 118–120 °C (from benzene). IR ($cm^{-1}$): 3435 (NH), 3063, 3032 ($CH_{aryl}$), 2960, 2920, 2859 ($CH_{alkyl}$), 1668 (C=O). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 2.418 (s, 3, $CH_3$), 3.409, 3.756 (ABq, 2, $CH_2CO$, $J$ = 18.3 Hz), 4.905 (br.s, 1, NH exchangeable), 5.410, 5.590 (ABq, 2, $OCH_2CO$, $J$ = 16.6 Hz), 6.988–7.755 (m, 15, Ar-H). EI-MS *m/z*: 498 ($M^{+\cdot}$, missed), 240 (8.2), 238 (24.2), 263 (41.2), 261 (base), 235 (23.5), 233 (79.1), 220 (40.9), 170 (27.8), 153 (5.1), 151 (14.5), 118 (2), 115 (12.4), 77 (61.2), 103 (9.3), 89 (17.9), 87 (3.1), 63 (22.3). Anal. calcd. for $C_{28}H_{23}N_4O_3Cl$ (%): C 67.40, H 4.65, N 11.23; found: C 67.65, H 4.81, N 11.44.

***6-[4-Chloro-3-methyl)phenyl-3-[3-(4-chlorophenyl-5-oxo-2,5-dihydro-pyrazol-1-yl)carbonylmethoxypyridazine (12)***

Yield: 19%; white crystals, mp > 300 °C (from methanol).

IR ($cm^{-1}$): 3154 (NH), 3032 ($CH_{aryl}$), 2958, 2920, 2850 ($CH_{alkyl}$), 1673 (C=O), 1628, 1586 (C=N and (or) C=C). $^1H$ NMR (200 MHz, DMSO-$d_6$) δ: 2.478 (s, 3, $CH_3$), 4.855 (s, 2, $OCH_2$), 7.090–8.135 (m, 10, ArH + CH=), 10.469 (br.s, 1, NH exchangeable). EI-MS *m*/*z*: 454 ($M^{+\cdot}$, 6), 234 (18), 208 (10), 163 (base), 64 (10). Anal. calcd. for $C_{22}H_{16}N_4O_3Cl_2$ (%): C 58.04, H 3.54, N 12.31, Cl 15.57; found: C 58.22, H 3.62, N 12.44, Cl 15.68.

***6-(4-Chloro-3-methyl) phenyl-3-(1,2-diethoxycarbonyl acetaldehyde hydrazonocarbonyl)methoxypyridazine (13)***

Yield: 36%; white crystals, mp 179 to 180 °C (from methanol). IR ($cm^{-1}$): 3233, 3150 (NH), 3090 ($CH_{aryl}$), 2920, 2851 ($CH_{alkyl}$), 1736, 1711 (C=O ester), 1661 (C=O amide), 1626, 1592 (C=N and (or) C=C). $^1H$ NMR (200 MHz, $DCl_3$) δ: 1.287 (t, 3, $CH_{3(a)}$, $J$ = 7.02 Hz), 1.346 (t, 3, $CH_{3(b)}$, $J$ = 7.05 Hz), 2.409, 2.426 (two singlets, $CH_3$(Ar)), 3.662 (s, 2, $CH_{2(d)}$), 4.129 (q, 2, $CH_{2(e)}$, $J$ = 7.08 Hz), 4.311 (q, 2, $CH_{2(f)}$, $J$ = 7.08 Hz), 5.468 (s, 2, $CH_{2(g)}$), 7.051–7.731 (m, 5, ArH), 10.099 (br.s, 1, NH exchangeable). EI-MS *m*/*z*: 462 ($M^{+\cdot}$, 3), 391 ($M^{+\cdot}$ + 2-$CO_2C_2H_5$, 12), 289 ($M^{+\cdot}$ – $CO_2C_2H_5$, 36), 261 (64), 233 (84), 205 (10), 170 (57), 115 (13), 89 (20), 63 (23), 54 (base). Anal. calcd. for $C_{21}H_{23}N_4O_6Cl$ (%): C 54.49, H 5.01, N 12.01; found: C 54.61, H 5.28, N 12.31.

***6-(4-Chloro-3-methyl)phenyl-3-[(3,5-dimethylpyrazole-1-yl)carbonylmethoxypyridazine (14)***

Yield: 38%; white crystals, mp 164–166 °C (from petroleum ether 60–80 °C – benzene). IR ($cm^{-1}$): 3047, 3011 ($CH_{aryl}$), 2968, 2925, 2854 ($CH_{alkyl}$), 1739 (C=O), 1668, 1591 (C=N and (or) C=C). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 2.257, 2.274 (two singlets, $CH_{3a'}$, $CH_{3a}$), 2.407, 2.421 (two singlets, $CH_3$ (aryl)), 2.529 (s, 3, $CH_{3b}$), 5.765 (s, 2, $OCH_2$), 6.001 (s, 1, CH=), 7.057–7.734 (m, 5, ArH). EI-MS *m*/*z*: 356 ($M^{+\cdot}$, 2), 260 (base), 261 (26), 233 (40), 170 (79), 151 (20), 116 (24), 89 (13), 63 (14). Anal. calcd. for $C_{18}H_{17}N_4O_2Cl$ (%): C 60.59, H 4.80, N 15.70, Cl 9.94; found: C 60.67, H 4.91, N 15.89, Cl 10.02.

**Reactions of 1a with piperidine, morpholine, or piperazine and 40% formaldehyde**

A mixture of **1a** (5 mmol), formaldehyde (15 mL) and piperidine (5 mmol), morpholine (5 mmol), or piperazine (5 mmol) in dioxane (20 mL) was refluxed for 20 h. The reaction mixture was concentrated, cooled, and poured into ice-cold water. The precipitated solid was filtered off, then recrystallized from a suitable solvent to give **15a**, **15b** and **16**, **17** as a mixture.

***6-(4-Chloro-3-methyl)phenyl-2-piperidin-1-yl-methyl-4-(3,5-dimethyl-pyrazol-1-yl)-2,3,4,5-tetrahydropyridazin-3-one (15a)***

Yield: 42%; white crystals, mp 188–190 °C (from petroleum ether 80–100 °C). IR ($cm^{-1}$): 1672 (C=O), 1596, 1557 (C=N and (or) C=C). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 1.391 (m, 2, $CH_2CH_2CH_2$), 1.523 (m, 4, $CH_2CH_2CH_2$), 2.229, 2.257 (two singlets, $2CH_3$ of pyrazol ring), 2.413 (s, 3, $CH_3$), 2.570 (m, 4, $N(CH_2)_2$), 3.444 (dd, $H_b$, $J_{bc}$ = 16.9 Hz, $J_{ba}$ = 7 Hz), 3.881 (dd, $H_c$, $J_{cb}$ = 16.8 Hz, $J_{ca}$ = 13.8 Hz), 4.682, 4.925 (ABq, -$CH_2$-N, $J$ = 13 Hz), 4.842 (q, $H_a$, $J_{HaHb}$ = 6.4 Hz, $J_{HaHc}$ = 13.8 Hz), 5.897 (s, 1, $H_d$), 7.385 (d, $H_y$, $J_o$ = 8.4 Hz), 7.599 (dd, $H_x$, $J_o$ = 8.4 Hz, $J_m$ = 2 Hz), 7.64 (d, $H_{x'}$, $J_m$ = 2 Hz). EI-MS *m*/*z*: 317 ($M^{+\cdot}$ – dimethylpyrazole, 1), 221 (3), 220 (2), 163 (2), 109 (3), 99 (7), 98 (base), 97 (12). Anal. calcd. for $C_{22}H_{28}N_5OCl$ (%): C 63.83, H 6.82, N 16.92; found: C 63.94, H 6.97, N 17.02.

***6-(4-Chloro-3-methyl)phenyl-2-morpholin-4-yl)methyl-4-(3,5-dimethyl-pyrazol-1-yl)-2,3,4,5-tetrahydropyridazin-3-one (15b)***

Yield: 44%; white crystals, mp 186 to 187 °C (from petroleum ether 80–100 °C). IR ($cm^{-1}$): 1672 (C=O), 1597, 1557 (C=N and (or) C=C). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 2.219, 2.555 (two sinlgets, $2CH_3$ of pyrazol ring), 2.409 (s, 3, $CH_3$), 2.715 (m, 4, N $(CH_2)_2$), 3.442 (dd, $H_b$, $J_{bc}$ = 16.7 Hz, $J_{ba}$ = 7.0 Hz), 3.675 (m, 4, $O(CH_2)_2$), 3.892 (dd, $H_c$, $J_{cb}$ = 15.3 Hz, $J_{ca}$ = 14.4 Hz), 4.691, 4.869 (ABq, $CH_2$-N, $J$ = 13.1 Hz), 4.858 (m, 1, $H_a$), 5.895 (s, 1, $H_d$), 7.383 (d, $H_y$, $J_o$ = 8.2 Hz), 7.554 (dd, $H_x$, $J_o$ = 8.4 Hz, $J_m$ = 2 Hz), 7.628 (d, $H_{x'}$, $J_m$ = 1.8 Hz). EI-MS *m*/*z*: 415 ($M^{+\cdot}$, 1), 397 ($M^{+\cdot}$ – $H_2O$, 1), 319 ($M^{+\cdot}$ – dimethylpyrazole, 1), 221 (4), 220 (4), 100 (base), 99 (4), 97 (15), 96 (4), 56 (19), 54 (4). Anal. calcd. for $C_{21}H_{26}N_5O_2Cl$ (%): C 60.64, H 6.30, N 16.84, Cl 8.52; found: C 60.75, H 6.44, N 16.96, Cl 8.68.

***3-Hydroxymethoxy-6-(4-chloro-3-methyl)phenylpyridazine (16) and 2-hydroxymethyl-6-(4-chloro-3-methyl)phenyl-2,3-dihydropyridazin-3-one (17)***

Yield: 30%; white crystals, mp 152 to 153 °C (from aqueous ethanol). IR ($cm^{-1}$): 3335 ($OH_{br.}$), 3072 ($CH_{aryl}$), 2958, 2918, 2852 ($CH_{alkyl}$), 1652 (C=O), 1601, 1515 (C=N and (or) C=C). For **16**: $^1H$ NMR (200 MHz, DMSO-$d_6$) δ: 2.421 (s, 3, $CH_3$), 5.418 (d, 2, $OCH_2$), 6.802 (t, 1, OH, exchangeable), 7.061 (d, 1, $H_a$, $J_{ab}$ = 10.1 Hz), 7.529 (d, 1, $H_d$, $J_o$ = 8.48 Hz), 7.742 (dd, 1, $H_{c'}$, $J_o$ = 8.4 Hz, $J_m$ = 2.8 Hz), 7.862 (d, 1, $H_c$, $J_m$ = 2.9 Hz), 8.042 (d, 1, $H_b$, $J_{ba}$ = 9.7 Hz). For **17**: $^1H$ NMR (200 MHz, DMSO-$d_6$) δ: 2.400 (s, 3, $CH_3$), 4.464 (d, 2, $NCH_2$), 6.802 (t, 1, OH, exchangeable), 7.061 (d, 1, $H_a$, $J_{ab}$ = 10.1 Hz), 7.529 (d, 1, $H_d$, $J_o$ = 8.48 Hz), 7.742 (dd, 1, $H_{c'}$, $J_o$ = 8.4 Hz, $J_m$ = 2.8 Hz), 7.862 (d, 1, $H_c$, $J_m$ = 2.9 Hz), 8.042 (d, 1, $H_b$, $J_{ba}$ = 9.7 Hz). EI-MS *m*/*z*: 252 ($M^{+\cdot}$ + 2, 4), 250 ($M^{+\cdot}$, 12), 185 ($M^{+\cdot}$ – $CH_2O$-Cl, 19), 163 (61), 128 (37), 89 (12), 63 (39). Anal. calcd. for $C_{12}H_{11}N_2O_2Cl$ (%): C 57.49, H 4.42, N 11.17, Cl 14.14; found: C 57.58, H 4.57, N 11.01, Cl 14.20.

**Reaction of 1a with 3-bromopropanoic acid**

A mixture of **1a** (5 mmol) and 3-bromopropanoic acid (5 mmol) in dry dioxane (20 mL), in the presence of potassium carbonate (3 g), was refluxed for 10 h. The reaction mixture was concentrated, cooled, and poured into ice-cold water. The precipitated solid was filtered off, washed, dried, and recrystallized from methanol to give a mixture of **18** and **19**.

***6-(4-Chloro-3-methyl)phenyl-2-(2-carboxy)ethyl-2,3-dihydropyridazin-3-one (18) and 6-(4-chloro-3-methyl) phenyl-3-(2-carboxy)ethoxypyridazine (19)***

Yield: 68%; yellowish white crystals, mp > 300 °C. IR ($cm^{-1}$): 3197 ($OH_{br.}$), 1710, 1668 (C=O). $^1H$ NMR (200 MHz, DMSO-$d_6$) δ: 2.095 (t, 2, $CH_2COOH$, $J$ = 6.8 Hz), 2.408 (two singlets, $2CH_3$), 3.496 (t, 2, $NCH_2CH_2$, $J$ = 6.8 Hz),

7.017 (d, $H_a$, $J_{ab}$ = 9.6 Hz), 7.528 (d, $H_d$, $J_o$ = 8.6), 7.761 (dd, $H_c$, $J_o$ = 8.6 Hz, $J_m$ = 1.8 Hz), 7.904 (d, $H_c'$, $J_m$ = 1.9 Hz), 8.043 (d, $H_b$, $J_{ba}$ = 9.6 Hz), 11.5 (br.s, 1, OH exchangeable). EI-MS *m/z*: 222 ($M^{+\cdot}$ + 2-$CH_2$=CHCOOH, 38), 220 ($M^{+\cdot}$ – $CH_2$=CH-COOH, base), 192 ($M^{+\cdot}$ – $CH_2$=CHCOOH-CO, 19), 185 ($M^{+\cdot}$ – $CH_2$=CHCOOH-Cl, 20), 165 (34), 163 (76), 157 (14), 128 (36), 102 (16), 89 (18), 72 (50), 63 (46), 55 (61). Anal. calcd. for $C_{14}H_{13}N_2O_3Cl$ (%): C 57.44, H 4.48, N 9.57; found: C 57.62, H 4.53, N 9.74.

**Acetylation of 1a with acetic anhydride**

A solution of **1a** (5 mmol) in acetic anhydride (15 mL) was heated for 3 h. The reaction mixture was cooled and then poured into ice-cold water. The precipitated solid was filtered off, washed, dried, and then recrytallized from benzene to give a mixture of **20** and **21**.

***2-Acetyl-6-(4-chloro-3-methyl)phenyl-2,3-dihydropyridazin-3-one (20) and 3-acetoxy-6-(4-chloro-3-methyl)phenylpyridazine (21)***

Yield: 72%; white crystals, mp 167 to 168 °C. IR ($cm^{-1}$): 1764, 1674 (C=O), 1616, 1595 (C=N and (or) C=C). $^1$H NMR (200 MHz, $CDCl_3$) δ: 2.424, 2.442 (two singlets, $2CH_3$), 2.75 (s, 3, $NCOCH_3$), 7.044 (d, $H_a$, $J_{ab}$ = 9.8 Hz), 7.437 (d, $H_d$, $J_o$ = 8.4 Hz), 7.547–7.601 (m, 2, $H_c$, $H_c'$), 7.65 (d, $H_b$, $J_{ba}$ = 9.8 Hz). EI-MS *m/z*: 222 ($M^{+\cdot}$ + 2-$CH_2$=C=O, 36), 220 ($M^{+\cdot}$ – $CH_2$=C=O, base), 185 ($M^{+\cdot}$ – $CH_2$=C=O-Cl, 17), 163 (88), 157 (14), 128 (49), 89 (14), 63 (75). Anal. calcd. for $C_{13}H_{11}N_2O_2Cl$ (%): C 59.44, H 4.22, N 10.66; found: C 59.61, H 4.35, N 10.81.

**Reaction of 1a with *p*-toluenesulphonyl chloride, succinyl chloride, oxalyl chloride, ethanolamine, or ethyl chloroacetate**

A mixture of **1a** (5 mmol) and ethyl chloroacetate (5 mmol) in DMF (10 mL) or *p*-toluene sulphonyl chloride (5 mmol), succinyl chloride (5 mmol), oxaylchloride (5 mmol), or ethanolamine (5 mmol) in pyridine (10 mL) was heated for 12 h. The reaction mixture was cooled then poured into ice-cold water in the former case or ice-cold HCl in the latter cases. The precipitated solid was filtered, washed, dried, and then recrystallized from ethanol to give **22**.

***6-(4-Chloro-3-methyl)phenyl-2,3-dihydropyridazin-3-one (22)***

Yield: 50%; white crystals, mp 232 to 233 °C, lit. value (17) mp 238 °C. IR ($cm^{-1}$): 3189, 3146 (NH), 3041 ($CH_{aryl}$), 2929, 2836 ($CH_{alkyl}$), 1679 (C=O), 1592, 1548 (C=N and (or) C=C). $^1$H NMR (200 MHz, DMSO-$d_6$) δ: 2.358, 2.380 (two singlets, $2CH_3$), 6.998, 7.009 (two doublets, $H_a$, $J_{ab}$ = 9.8 Hz), 7.446, 7.496 (two doublets, $H_d$, $J_o$ = 8.4 Hz), 7.696, 7.736 (two doublet doublets, $H_c$, $J_o$ = 8.2 Hz, $J_m$ = 2.0 Hz), 7.847, 7.879 (two doublets, $H_c'$, $J_m$ = 1.8 Hz), 8.034, 8.059 (two doublets, $H_b$, $J_{ba}$ = 9.8), 13.271 (br.s, 1, NH exchangeable). EI-MS *m/z*: 222 ($M^{+\cdot}$ + 2, 28), 221 ($M^{+\cdot}$ + 1, base), 220 ($M^{+\cdot}$, 88), 206 (15), 192 ($M^{+\cdot}$ – CO, 10), 185 (17), 166 (20), 165 (19), 163 (55), 157 (12), 129 (44), 128 (30), 127 (23), 78 (18), 77 (27), 75 (15), 64 (23), 63 (45), 50 (20). Anal. calcd. for $C_{11}H_9N_2OCl$ (%): C 59.87, H 4.09, N 12.69, Cl 16.07; found: C 59.96, H 4.27, N 12.76, Cl 16.25.

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