# New Triazinoindoles through the Action of 3-Hydrazino[1,2,4]triazino[5,6-*b*]indole on *α*,*β*-Unsaturated Compounds

AHMED S. A. YOUSSEF

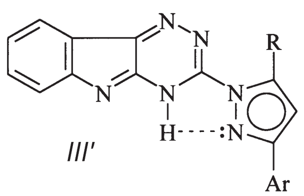
*Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt*
*e-mail: ahmedy67@hotmail.com*

Received 16 November 2000
Accepted for publication 24 September 2001

3-Hydrazino[1,2,4]triazino[5,6-*b*]indole (*I*) reacted with 1-aryl-3-phenylprop-2-yn-1-ones *IIa*—*IIc* to give 3-(5-aryl-3-phenylpyrazol-1-yl)[1,2,4]triazino[5,6-*b*]indoles *IIIa*—*IIIc*. *ω*-(*p*-Chlorobenzoyl)acetophenone ([1,2,4]triazino[5,6-*b*]indol)-3-ylhydrazone was isolated in case of *IIb* only. On the other hand, methyl (*p*-chlorophenyl)prop-2-ynoate (*IId*) gave 3-[3-(*p*-chlorophenyl)-5-hydroxypyrazol-1-yl][1,2,4]triazino[5,6-*b*]indole (*IIId*). *I* reacted with diethyl but-2-ynedioate to give 3-((4*H*)-3-ethoxycarbonyl-5-oxopyrazol-1-yl)[1,2,4]triazino[5,6-*b*]indole and diethyl oxaloacetate ([1,2,4]triazino[5,6-*b*]indol)-3-ylhydrazone. Similar treatment of *I* with 2-cyano- or 2-cyano-3-methylcinnamonitriles afforded 3-((4*H*)-3,5-dioxo-4-phenylmethylenepyrazol-2-yl)- and 3-[(4*H*)-3,5-dioxo-4-(1-phenylethylene)pyrazol-2-yl][1,2,4]triazino[5,6-*b*]indoles, respectively. Structures of all products are evidenced by microanalytical and spectral data.

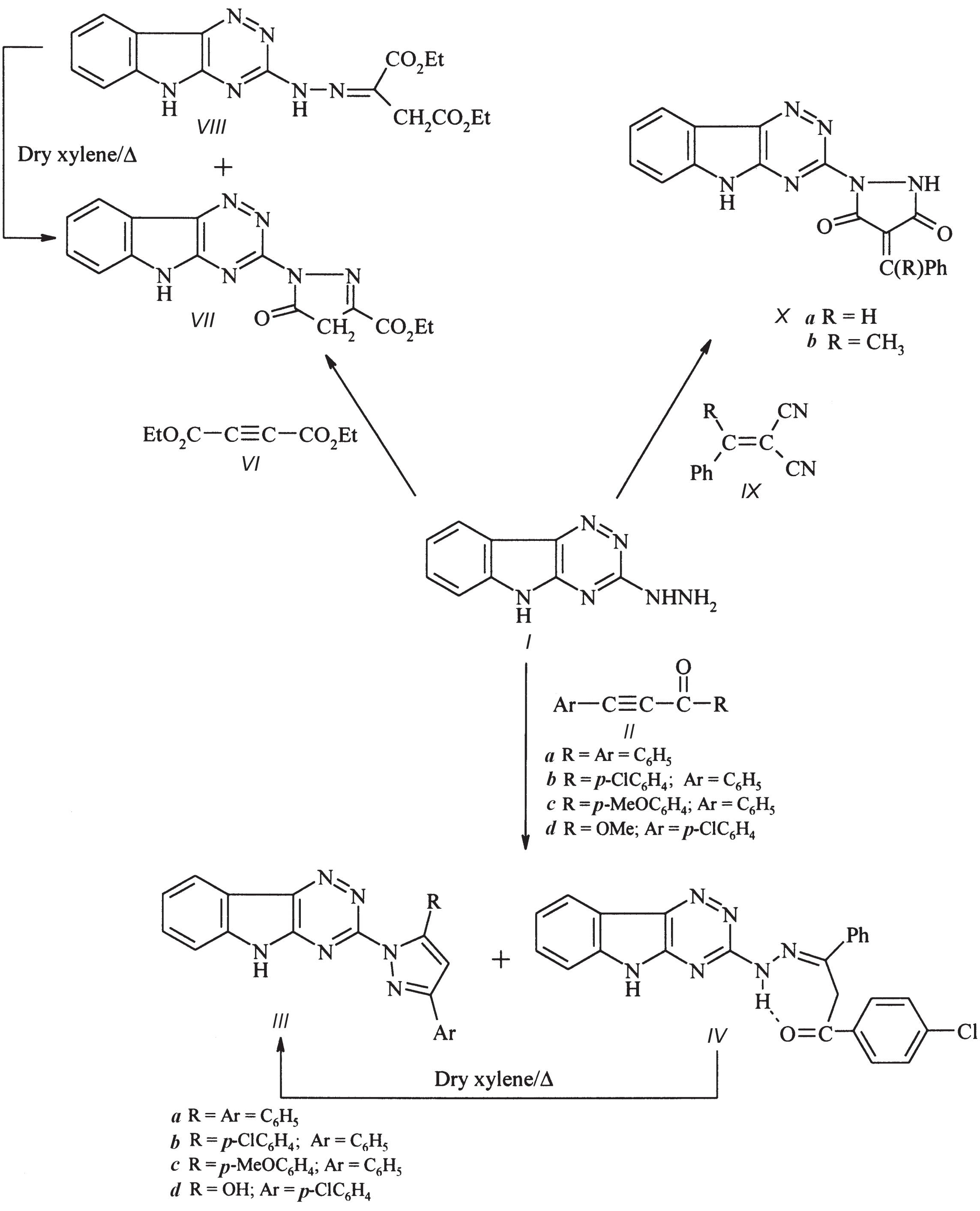
The wide range of pharmacological and medicinal activities exhibited by *as*-triazines [1—10] promoted the author to prepare 3-hydrazino[1,2,4]triazino[5,6-*b*]indole (*I*) and to study its reaction with *α*,*β*-unsaturated ketones, esters, and nitriles hoping the involvement of ring nitrogen would give new heterocyclic compounds of anticipated biological activities. The ring nitrogen has been involved in the reaction of *I* with carbon disulfide [5, 11], aldehydes, and carboxylic acids [8]. The reaction of arylhydrazines [12—15] with acetylenic ketones and esters is well known and involves the formation of pyrazole derivatives, whereas the reaction of heterocyclic hydrazines with acetylenic ketones and esters is rather limited. *Brugger et al.* [16] and *Nair* [17] have reported that the reaction of 2-hydrazinopyridine with dimethyl acetylenedicarboxylate gave the hydroxypyrazole derivative. However, in further study of this reaction, *Le Count* and *Greer* [18] obtained the succinate derivative and cyclized it with acetic anhydride to pyrido[2,1-*c*][1,2,4]triazinone derivative. Similarly 2-hydrazinobenzimidazole [18] reacted with dimethyl acetylenedicarboxylate to give the hydroxypyrazole and the benzimidazolo[2,1-*c*]triazinone derivatives.

*I* reacted with 1-phenyl- (*IIa*), 1-*p*-chlorophenyl- (*IIb*) or 1-*p*-methoxyphenyl-3-phenylprop-2-yn-1-ones (*IIc*) in refluxing dioxane to give 3-(5-aryl-3-phenylpyrazol-1-yl)[1,2,4]triazino[5,6-*b*]indoles *IIIa* and *IIIb* (Scheme 1). *ω*-(*p*-Chlorobenzoyl)acetophenone ([1,2,4]-triazino[5,6-*b*]indol)-3-ylhydrazone (*IV*) was isolated in case of *IIb* only. The reaction seems to proceed by Michael addition of hydrazino derivative *I* to the triple bond of the acetylenic ketones to give the cyclized products *IIIa*—*IIIc* and the open chain adduct *IV*. The assigned structure for *IIIa*—*IIIc* was substantiated from analytical and spectral data. Thus their IR spectra reveal the absence of $\nu_{C\equiv C}$, $\nu_{C=O}$ and the presence of a broad band at 3440 $cm^{-1}$ (NH). The $^1H$ NMR spectra showed a broad signal in the region of $\delta$ = 11.0—13.6 (1H, NH) which suggests the existence of structure *III* in its tautomer *III′* as shown. Further support for the assigned structure was gained from mass spectra, which showed the correct molecular ions beside some of the abundant peaks.

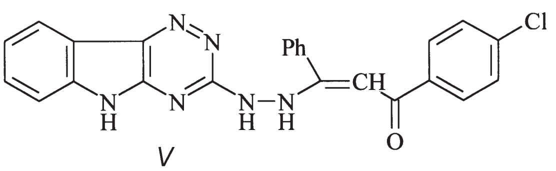


*III′*

The structure of *IV* was established from analytical and spectral data. The IR spectrum reveals the absence of $\nu_{C\equiv C}$ and the presence of two bands at 3440 $cm^{-1}$, 3340 $cm^{-1}$ ($\nu_{NH}$), it also shows a shoulder at 1690 $cm^{-1}$ ($\nu_{C=O}$). This indicates that the compound has structure *IV* or the structure of its tautomer *V*. Its $^1H$ NMR spectrum, however, shows a




*Scheme 1*

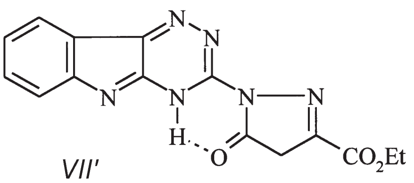


*V*

quartet (2H) representing an AB system ($J_{AB} = 9$ Hz) due to the $CH_2CO$ protons [19—21] indicating that the compound has the structure *IV* and not *V*. The fact that this methylene group behaves as an AB system can be attributed either to the large anisotropic effect of the C═N group and the nitrogen lone pair or to the restriction of rotation at the $p$-$ClC_6H_4CO$ group by the weak hydrogen bonding between the NH and the carbonyl group [21]. Further proof for the proposed structure was gained from mass spectrum which showed a peak at $m/e = 422$ ($M^{+\bullet} - 18$) arising from the loss of $H_2O$ in addition to some of abundant peaks. A chemical proof for the assigned structure *IV* was gained from its conversion to the pyrazole derivative *IIIb* in refluxing xylene.

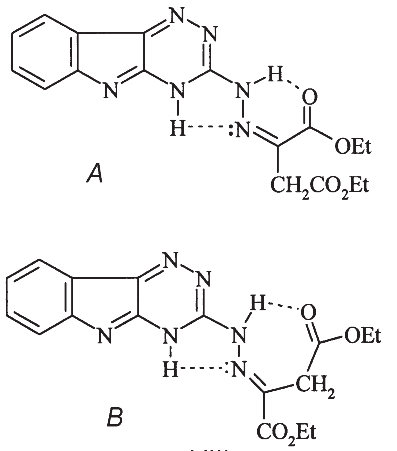
Similar treatment of *I* with methyl *p*-chlorophenylprop-2-ynoate (*IId*) afforded 3-[3-(*p*-chlorophenyl)-5-hydroxypyrazol-1-yl][1,2,4]triazino[5,6-*b*]indole (*IIId*). The suggested structure for *IIId* was elucidated from spectral and chemical data. IR spectrum is devoid of a band which is characteristic of the C═O group of pyrazolones [22]. However, it shows an absorption band for OH at 3460 $cm^{-1}$ which is consistent with the proposed structure. The reaction of the acetylenic ester *IId* with the hydrazine *I* seems to take place *via* the initial attack on the $\beta$-acetylenic carbon atom followed by cyclization. This postulate is consistent with the previous finding [23, 24] that aroyl hydrazines add to the acetylenic bond of methyl arylpropiolate and dimethyl acetylenedicarboxylate to give the pyrazole and derivatives of ester of oxaloacetic acid, respectively. Further insight concerning the exact structure of the reaction product may be gleaned out from $^1$H NMR spectrum which shows a singlet signal at $\delta$ = 6.26 (1H, OH) and a broad signal in the region of $\delta$ = 12.3—13.6 (1H, NH), which reveals the existence of *IId* in its respective 3-hydroxy chelated tautomer *III′*. The mass spectrum of *IIId* also lends further support for the assigned structure as it shows the correct molecular ion as a base peak beside some of abundant peaks. Further proof for its existence as an enol tautomer was gained chemically, as its alcoholic solution gives a violet colour with ferric chloride solution.

On the other hand, diethyl but-2-yndioate *VI* reacted with *I* in refluxing 1,4-dioxane to afford a mixture of 3-((4*H*)-3-ethoxycarbonyl-5-oxopyrazol-1-yl)[1,2,4]triazino[5,6-*b*]indole (*VII*) (major) and diethyl oxaloacetate ([1,2,4]triazino[5,6-*b*]indole)-3-hydrazone (*VIII*) (minor). The structure of the pyrazolone derivative *VII* was substantiated from its analytical and spectral data. The IR spectrum shows absorptions at $\tilde{\nu}$ = 1730 $cm^{-1}$ ($\nu_{C=O}$ ester), 1670 $cm^{-1}$ ($\nu_{C=O}$ pyrazolone), and 3180 $cm^{-1}$ (NH), the lower value of absorption of the C═O group of pyrazolone [22] suggests that it most probably chelated with NH group of triazine ring. The assigned structure was evidenced also from $^1$H NMR spectrum which showed a singlet at $\delta$ = 3.97 (2H, $CH_2CO$) and a broad signal in the range of $\delta$ = 12.5—13.2 (1H, NH). The downfield value for NH infers the existence of *VII′* as its chelated tautomer as shown




*VII′*

The structure of diethyl oxaloacetate hydrazone derivative *VIII* was elucidated from its analytical and spectral data. IR spectrum shows two bands at $\tilde{\nu}$ = 1735 $cm^{-1}$, 1690 $cm^{-1}$ attributable to $\nu_{C=O}$ of the two ester groups. The appearance of the latter absorption at lower value is due to chelation between C═O and NH groups and/or conjugation with —NH—N═C— system, which suggests either structure *VIIIA* (*Z*-isomer) or *VIIIB* (*E*-isomer) as shown



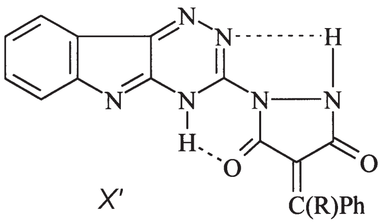

*VIII*

The configurational assignment to *VIII* was based on $^1$H NMR spectrum which showed signals characteristic of two $OCH_2CH_3$ groups, broad signal at $\delta$ = 11.27 (1H, HN—N), a broad singlet at $\delta$ = 12.8 (1H, NH indolo), and a singlet at $\delta$ = 3.28 (2H, $CH_2CO$). The appearance of the two protons of $CH_2CO$ group as a singlet rather than two doublets characteristic of an AB system infers that *VIII* has the *Z*-configuration (*A*) rather than the *E*-configuration (*B*). Its structure was also confirmed chemically by cyclization to *VII* in refluxing xylene.

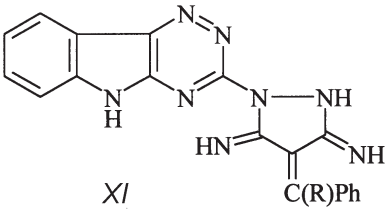
However, when *I* was allowed to react with 2-cyano- (*IXa*) or 2-cyano-3-methylcinnamonitriles (*IXb*) in refluxing 1,4-dioxane it gave 3-((4*H*)-3,5-dioxo-4-phenylmethylenepyrazol-2-yl)- (*Xa*) or 3-[(4*H*)-3,5-dioxo-4-(1-phenylethylene)pyrazol-2-yl][1,2,4]triazino[5,6-*b*]indoles (*Xb*). The structure of pyrazol-3,5-dione derivatives *Xa* and *Xb* was established from analytical and spectral data. IR spectra show $\nu_{HN}$ in the regions of $\tilde{\nu}$ = 3230—3260 $cm^{-1}$, 3130—3150 $cm^{-1}$ and $\nu_{C=O}$ in the region of $\tilde{\nu}$ = 1610—1620 $cm^{-1}$ corresponding to dihydrazides [25]. The $^1$H NMR spectra which are in accord with the assigned structure show a broad singlet in the range $\delta$ = 10.67—11.84 (1H, HN—N), broad singlet at $\delta$ = 12.3 (1H, NH indolo) and are devoid of signals characteristic of protons of the two imino groups which exclude structure *XI*. The downfield value for (NH indolo) suggests the existence of *X* as its chelated tautomer *X′*.

## EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded using a Unicam SP 1200 spectrometer



*X'*



*XI*

(potassium bromide). $^1$H NMR spectra were recorded on Varian Gemini 200 MHz using TMS as internal standard. Mass spectra were recorded on Shimadzu GC-MS-QP 1000 Ex operating at 70 eV. The purity of the analytical samples was checked by the TLC (Silica gel).

1-Aryl-3-phenylprop-2-yn-1-ones *IIa*—*IIc* were prepared according to the method outlined by *Parker et al.* [26]. Methyl (*p*-chlorophenyl)prop-2-ynoate *IId* was synthesized according to *Benghiat* and *Becker* [27] method. Cyanocinnamonitriles *IXa* and *IXb* were prepared according to *David* [28] method. 3-Hydrazino[1,2,4]triazino[5,6-*b*]indole (*I*) was prepared according to the method outlined by *Joshi* and *Chand* [29].

### Reaction of *I* with *IIa*—*IId* to Pyrazole Derivatives *IIIa*—*IIId*

A mixture of *I* (2.5 mmol) and *IIa*—*IId* (2.5 mmol) was refluxed in 1,4-dioxane (20 cm$^3$) for 20 h. The reaction mixture was filtered while hot from insoluble materials, recrystallization from DMF gave *I* recovered unchanged (0.05—0.1 g). The filtrate was concentrated, filtered from the precipitated solid and recrystallized from the proper solvent to give *IIIa*—*IIId,* respectively. In case of *IIb* the filtrate gives first *IV* as yellow crystals from ethanol—benzene. On leaving the mother liquor at room temperature for 48 h, a crystalline product was obtained. Upon filtration and recrystallization from benzene, *IIIb* was obtained as orange crystals.

*3-(3,5-Diphenylpyrazol-1-yl)[1,2,4]triazino[5,6-b]-indole* (*IIIa*), yield = 0.65 g (83 %), orange crystals, m.p. = 257—259 ℃ (ethanol—benzene). For $C_{24}H_{16}N_6$ ($M_r$ = 388.42) $w_i$(calc.): 74.21 % C, 4.15 % H, 21.63 % N; $w_i$(found): 74.53 % C, 4.22 % H, 21.49 % N. IR spectrum, $\tilde{\nu}$/cm$^{-1}$: 3240 $\nu$(NH), 3090 $\nu(H_{aryl})$, 1620 $\nu$(C=C and/or C=N). $^1$H NMR spectrum ($CDCl_3$), $\delta$: 7.01—8.35 (m, $15H_{arom}$), 13.08 (brs, 1NH indolo, exchangeable).

*3-[5-(p-Chlorophenyl)-3-phenylpyrazol-1-yl][1,2,4]-triazino[5,6-b]indole* (*IIIb*), yield = 0.1 g (10 %), orange crystals, m.p. = 267—269 ℃ (benzene). For $C_{24}H_{15}N_6Cl$ ($M_r$ = 422.87) $w_i$(calc.): 68.16 % C, 3.57 % H, 19.87 N; $w_i$(found): 67.98 % C, 3.44 % H, 19.22 % N. IR spectrum, $\tilde{\nu}$/cm$^{-1}$: 3230 $\nu$(br, NH), 3070 $\nu(H_{aryl})$, 1640 $\nu$(C=C and/or C=N). $^1$H NMR spectrum (DMSO-$d_6$), $\delta$: 7.34—8.44 (m, 14, $H_{arom}$), 13.05 (brs, 1NH indolo, exchangeable). EI MS $m/z$ ($I_r$/%): 423 ($M^{+\bullet}$ + 2 − H, 48.5), 422 ($M^{+\bullet}$, 73.3), 421 ($M^{+\bullet}$ − H, base), 295 (27.7), 294 (27.2), 129 (10.7), 128 (12.1), 114 (15.5), 111 (15.5), 108 (18), 102 (22.3), 101 (20.4), 89 (18.4), 88 (12.1), 78 (12.6), 77 (49), 76 (24.3), 75 (20.4), 73 (16.5), 64 (11.7), 63 (11.2), 56 (15.5), 55 (16), 51 (33.5), 50 (10.2).

*3-[5-(p-Methoxyphenyl)-3-phenylpyrazol-1-yl][1,2,4]triazino[5,6-b]indole* (*IIIc*), yield = 0.8 g (95 %), orange crystals, m.p. = 276—278 ℃ (ethanol—benzene). For $C_{25}H_{18}N_6O$ ($M_r$ = 418.47) $w_i$(calc.): 71.75 % C, 4.33 % H, 20.08 % N; $w_i$(found): 71.52 % C, 4.18 % H, 20.15 N. IR spectrum, $\tilde{\nu}$/cm$^{-1}$: 3250 $\nu$(br, NH), 3060 $\nu(H_{aryl})$, 2980 $\nu(H_{alkyl})$, 1640 $\nu$(C=C and/or C=N). $^1$H NMR spectrum (DMSO-$d_6$), $\delta$: 3.74 (s, 3OMe), 6.87—8.44 (m, $14H_{arom}$), 12.3 (brs, 1NH indolo, exchangeable). EI MS $m/z$ ($I_r$/%): 418 ($M^+$, base), 291 (24.9), 290 (24.2), 77 (16.9), 51 (9.5).

*3-[3-(p-Chlorophenyl)-5-hydroxypyrazol-1-yl][1,2,4]triazino[5,6-b]indole* (*IIId*), yield = 0.6 g (80 %), yellow crystals, m.p. = 294—296 ℃ (1,4-dioxane). For $C_{18}H_{11}N_6OCl$ ($M_r$ = 362.36) $w_i$(calc.): 59.59 % C, 3.05 % H, 23.16 % N, 9.77 % Cl; $w_i$(found): 59.21 % C, 2.98 % H, 22.97 % N, 9.24 % Cl. IR spectrum, $\tilde{\nu}$/cm$^{-1}$: 3460, 3260 $\nu$(OH and/or NH), 3060 $\nu(H_{aryl})$, 1625 $\nu$(C=C and/or C=N). $^1$H NMR spectrum (DMSO-$d_6$), $\delta$: 6.26 (s, 1OH exchangeable), 7.47—8.14 (m, $9H_{arom}$), 12.95 (1NH indolo, exchangeable). EI MS $m/z$ ($I_r$/%): 364 ($M^{+\bullet}$ + 2, 26.7), 362 ($M^{+\bullet}$, 95), 170 (38.3), 169 (12.2), 156 (19.4), 155 (15), 143 (27.8), 138 (27.2), 137 (29.4), 102 (40), 101 (24.4), 91 (11.7), 90 (15.6), 89 (11.7), 88 (23.9), 87 (10.6), 77 (27.8), 76 (32.2), 75 (48.3), 74 (13.3), 73 (11.1), 68 (16.1), 64 (20), 52 (12.8), 51 (31.1), 50 (17.2).

*ω-(p-Chlorobenzoyl)acetophenone ([1,2,4]-triazino[5,6-b]indol)-3-ylhydrazone* (*IV*), yield = 0.8 g (80 %), orange crystals, m.p. = 280—282 ℃ (ethanol—benzene). For $C_{24}H_{17}N_6OCl$ ($M_r$ = 440.86) $w_i$(calc.): 65.38 % C, 3.88 % H, 19.06 % N; $w_i$(found): 65.29 % C, 3.56 % H, 19.17 % N.

IR spectrum, $\tilde{\nu}$/cm$^{-1}$: 3440, 3340 $\nu$(NH), 3080 $\nu(H_{aryl})$, 2960 $\nu(H_{alkyl})$, 1690 $\nu$(sh)(C=O), 1620 $\nu$(C=C and/or C=N). $^1$H NMR spectrum (DMSO-$d_6$), $\delta$: 3.66, 3.76 (q, $2CH_2$—C=O, $J$ = 9 Hz), 7.15 (brs, 1NH—N exchangeable), 7.31—8.15 (m, 13 $H_{arom}$), 12.34 (brs, 1NH indolo, exchangeable). EI MS $m/z$ ($I_r$/%): 423 ($M^{+\bullet}$ + 2 − $H_2O$ − H, 37.1), 422 ($M^{+\bullet}$ − $H_2O$, 75.2), 421 ($M^{+\bullet}$ − $H_2O$ − H, base), 294 (38.1), 254 (16.8), 225 (11.9), 136 (10), 129 (15.8), 127 (16.3), 104 (14.9), 103 (19.8), 102 (24.3), 101 (18.8), 89 (76.3), 88 (12.4), 77 (39.1), 76 (19.2), 75 (25.2), 64 (10.4), 63 (14.4), 51 (30.2).

### Conversion of the Hydrazone *IV* to the Pyrazole Derivative *IIIb*

Hydrazone *IV* (0.2 g; 0.5 mmol) was dissolved in dry xylene (10 $cm^3$) and the mixture was refluxed for 2 h. The solution was concentrated, cooled and filtered from the precipitated solid. Recrystallization from benzene gave orange crystals which proved to be *IIIb* by TLC, melting point, and mixed melting point.

### Reaction of *I* with Diethyl But-2-ynedioate (*VI*)

*I* (0.5 g; 2.5 mmol) and *VI* (0.42 g; 2.5 mmol) were refluxed in 1,4-dioxane (20 $cm^3$) for 30 h. The reaction mixture was filtered off while hot from the precipitated solid. Recrystallization from DMF gave *VII* (major). The filtrate was concentrated, left to stand at room temperature overnight. The precipitated solid was recrystallized from dioxane to give *VIII* (minor).

*3-((4H)-3-Ethoxycarbonyl-5-oxopyrazol-1-yl)[1,2,4]-triazino[5,6-b]indole* (*VII*), yield = 0.5 g (62 %), orange crystals, m.p. = 297—299 ℃ (DMF). For $C_{15}H_{12}N_6O_3$ ($M_r$ = 324.29) $w_i$(calc.): 55.55 % C, 3.73 % H, 25.91 % N; $w_i$(found): 55.68 % C, 3.80 % H, 25.89 % N. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3180 $\nu$(br, NH), 3050 $\nu(H_{aryl})$, 2920 $\nu(H_{alkyl})$, 1730, 1670 $\nu$(C═O ester and pyrazolone), 1610 $\nu$(C═C and/or C═N). $^1H$ NMR spectrum (DMSO-$d_6$), $\delta$: 1.21 (t, 3, $\underline{CH_3}$—$CH_2$, $J$ = 7 Hz), 3.97 (s, $2CH_2CO$), 4.14 (q, $2CH_3\underline{CH_2}$, $J$ = 7 Hz), 7.4—8.27 (m, $4H_{arom}$), 12.85 (brs, 1NH indolo, exchangeable).

*Diethyl oxaloacetate ([1,2,4]triazino[5,6-b]indol)-3-ylhydrazone* (*VIII*), yield = 0.2 g (22 %), pale brown crystals, m.p. = 184—186 ℃ (decomp.) (dioxane). For $C_{17}H_{18}N_6O_4$($M_r$ = 370.36) $w_i$(calc.): 55.13 % C, 4.90 % H, 22.69 % N; $w_i$(found): 54.96 % C, 4.88 % H, 22.45 % N. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3450, 3260 $\nu$(NH), 3080 $\nu(H_{aryl})$, 2980 $\nu(H_{alkyl})$, 1735, 1690 $\nu$(C═O), 1620 $\nu$(C═C and/or C═N). $^1H$ NMR spectrum ($CDCl_3$), $\delta$: 1.15 (t, $3CH_2COOCH_2\underline{CH_3}$, $J$ = 6.8 Hz), 1.29 (t, $3COOCH_2\underline{CH_3}$, $J$ = 7.2 Hz), 3.28 (s, $2CH_2CO$), 3.97 (q, $2CH_2COO\underline{CH_2}CH_3$, $J$ = 6.8 Hz), 4.33 (q, $2COO\underline{CH_2}CH_3$, $J$ = 7.2 Hz), 7.30—8.35 (m, $4H_{arom}$), 11.27 (brs, 1NH—N exchangeable), 12.82 (s, 1NH indolo, exchangeable).

### Conversion of *VIII* to *VII*

Diethyl oxaloacetate derivative *VIII* (0.1 g) was dissolved in 10 $cm^3$ of dry xylene, the mixture was boiled for 3 h and then cooled, concentrated and filtered from the precipitated solid. Recrystallization from DMF gave orange crystals which were proved to be *VII* by TLC, melting point and mixed melting point.

### Reaction of *I* with 2-Cyano- (*IXa*) or 2-Cyano-3-methylcinnamonitriles (*IXb*)

A mixture of *I* (2.5 mmol) and *IXa* or *IXb* (2.5 mmol) was refluxed in dioxane (20 $cm^3$) for 50 h. The reaction mixture was filtered off while hot to give after crystallization 3-((4*H*)-3,5-dioxo-4-phenylmethylenepyrazol-2-yl)- (*Xa*) or 3-[(4*H*)-3,5-dioxo-4-(1-phenylethylene)pyrazol-2-yl][1,2,4]triazino-[5,6-*b*]indoles (*Xb*). The filtrate was concentrated and then left to stand at room temperature overnight. The precipitated solid was filtered, recrystallized from proper solvent to give further amounts of products.

*3-((4H)-3,5-Dioxo-4-phenylmethylenepyrazol-2-yl)-[1,2,4]triazino[5,6-b]indole* (*Xa*), yield = 0.7 g (78 %), yellow canary crystals, m.p. = 300 ℃ (DMSO). For $C_{19}H_{12}N_6O_2$($M_r$ = 356.33) $w_i$(calc.): 64.04 % C, 3.39 % H, 23.58 N; $w_i$(found): 64.23 % C, 3.42 % H, 23.61 % N. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3230, 3130 $\nu$(NH), 3060 $\nu(H_{aryl})$, 2900 $\nu(H_{alkyl})$, 1610 $\nu$(C═O dihydrazide [25]). $^1H$ NMR spectrum (DMSO-$d_6$), $\delta$: 7.36—8.29 (m, $10H_{arom}$ + CH═), 11.84 (brs, 1HN—N exchangeable), 12.3 (brs, 1NH indolo, exchangeable).

*3-[(4H)-3,5-Dioxo-4-(1-phenylethylene)pyrazol-2-yl][1,2,4]triazino[5,6-b]indole* (*Xb*), yield = 0.65 g (70 %), yellow crystals, m.p. = 289—291 ℃ (decomp.) (dioxane). For $C_{20}H_{14}N_6O_2$ ($M_r$ = 370.36) $w_i$(calc.): 64.86 % C, 3.81 % H, 22.69 % N; $w_i$(found): 64.90 % C, 3.79 % H, 22. 72 % N. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3200, 3150 $\nu$(NH), 3060 $\nu(H_{aryl})$, 2960 $\nu(H_{alkyl})$, 1620 $\nu$(C═O dihydrazide [25]). $^1H$ NMR spectrum (DMSO-$d_6$), $\delta$: 2.42 (s, $3CH_3$), 7.36—8.24 (m, $9H_{arom}$), 10.67 (brs, 1NH—N exchangeable), 12.32 (brs, 1NH indolo, exchangeable).

## REFERENCES


1. El-Emary, T. I. and Ahmed, R. A., *7th Ibn Sina International Conference of Pure and Applied Heterocyclic Chemistry.* Faculty of Science, Alexandria University, Alexandria, Egypt, March 25—28, 2000.
2. Abdel-Rahman, R. M., Seada, M., Fawzy, M., and El-Baz, I., *Farmaco 48*, 397 (1993).
3. Abdel-Rahman, R. M., *Farmaco 47*, 319 (1992).
4. Abdel-Rahman, R. M., *Farmaco 46*, 379 (1991).
5. Joshi, K. C., Dandia, A., and Baweja, S., *J. Indian Chem. Soc. 66*, 690 (1989).
6. Holla, B. S. and Udupa, K. V., *J. Indian Chem. Soc. 65*, 524 (1988).
7. Segupta, A. K., Pandey, A. K., Verma, H. N., and Khan, M. M. A. A., *J. Indian Chem. Soc. 62*, 165 (1985).
8. Monge, A., Palop, J. A., Ramirez, C., and Fernandez-Alvarez, E., *Acta Farm. Bonaerense 6*, 157 (1987).
9. Ram, V. J., *Arch. Pharm. 313*, 108 (1980).
10. Boyle, J. J., Ferauto, R. J., Haff, R. F., Kormendy, C. G., Sandfield, F. J., and Stewart, R. C., *J. Med. Chem. 15*, 277 (1972).

11. Ram, V. J., Dube, V., and Vlietinck, A. J., *J. Heterocycl. Chem. 24*, 1435 (1987).
12. El-Rayyes, N. R. and Al-Hajjar, F. H., *J. Heterocycl. Chem. 14*, 367 (1977).
13. Coispeau, G., Elguero, J., and Jacguier, R., *Bull. Soc. Chim. Fr. 2*, 689 (1970).
14. Coispeau, G. and Elguero, J., *Bull. Soc. Chim. Fr. 7*, 2717 (1970).
15. Lown, J. W. and Ma, J. C., *Indian J. Chem. 45*, 953 (1967).
16. Brugger, M., Wamhoff, H., and Korte, F., *Annal. 757*, 100 (1972).
17. Nair, M. D., *Indian J. Chem. 9*, 104 (1971).
18. Le Count, D. J. and Greer, A. T., *J. Chem. Soc., Perkin Trans. 1*, 297 (1974).
19. Al-Farkh, Y. A., Al-Hajjar, F. H., El-Rayyes, N. R., and Hamoud, H. S., *J. Heterocycl. Chem. 15*, 759 (1978).
20. Baddar, F. G., Al-Hajjar, F. H., and El-Rayyes, N. R., *J. Heterocycl. Chem. 15*, 358 (1978).
21. Baddar, F. G., Al-Hajjar, F. H., and El-Rayyes, N. R., *J. Heterocycl. Chem. 13*, 257 (1976).
22. Gagnon, E. P., Boivin, L. J., and Paquin, J. R., *Can. J. Chem. 31*, 1025 (1953).
23. Moussa, G. E. M., Basyouni, M. N., Fouli, F. A., and Kandeel, K. A., *Acta Chim. Hung. 106*, 167 (1981).
24. Gudi, N. M., Hiriyakkanvar, G. J., and George, V. H., *Indian J. Chem. 9*, 743 (1971).
25. Pretsch, E., Clerc, T., Seibl, J., and Simon, W., *Tables of Spectral Data for Structure Determination of Organic Compounds.* Springer-Verlag, Berlin, 1983.
26. Parker, W., Raphael, R. A., and Wilkinson, O. I., *J. Chem. Soc. 1958*, 3871.
27. Benghiat, I. and Becker, E. I., *J. Org. Chem. 33*, 885 (1985).
28. David, T. M., *J. Am. Chem. Soc. 65*, 991 (1943).
29. Joshi, K. C. and Chand, P., *J. Heterocycl. Chem. 17*, 1783 (1980).