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Synthesis of Fused Heterocyclic Derivatives from 5-Ethyl-3-Hydrazino-5H-1,2,4-Triazino[5,6-b]Indole[1]

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5-Ethyl-3-hydrazino-5*H*-1,2,4-triazino[5,6-*b*]indole II was used for the synthesis of various heterocyclic derivatives. This was performed by reaction of its 3-hydrazino group with different reagents such as acid anhydrides, ethylacetate, diethyl oxalate, thioglycolic acid, aroyl esters and acid chlorides. The structure of the products was confirmed by different spectroscopic and analytical methods.

When 5-ethyl-3-hydrazino-4*H*-1,2,4-triazino[5,6-*b*]indole[2] II was reacted with aromatic or aliphatic acid andhydrides[3] in dry benzene as solvent, the open structures III and IV resulted, respectively. Heating III or IV over their melting points gave the cyclic products: 2-(5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl) 2,3-dihydro-1-4-phthalazinedione V and 1-(5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)tetrahydro-3,6-pyridazinedine VI, which could be obtained by heating II with aromatic or aliphatic anhydrides in glacial acetic acid.[4–6] The structures of compounds III–VI were confirmed by elemental and spectral analysis (cf. Table I).

Fusion of II with ethyl cyano acetate for 1 hour at 140–160°C leads to 5-amino-1-(5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)-1*H*-pyrazol-3-ol VII (Chart I). The chemical structure of VII was established by elemental analysis as well as spectral data. The IR spectrum showed the following absorption bands at ν3500–3350 cm^{-1} (NH_2 and OH) and ν2950 cm$_{-1}$ (C–H, Aromatic). ^{1}H-NMR spectrum in DMSO added additional confirmation for the chemical structure of VII and showed a triplet at δ1.1 (3H.CH_3, J=6Hz), a quartet at δ3.6 (2H, CH_2, J=6Hz), a single at δ3.9 (1H, OH), multiplet at δ7.8–2 (4H, Ar-H) and a singlet at 8.2 (1H, CH of pyrazole ring).

TABLE I

Reaction of 5-Ethyl-3-hydrazino-5H-1,2,4-triazino[5,6-b]indole II with Acid Anhydrides

Comp. No.	M.P.°C Solvent	Yield (%)	Formula (M.W.)	Analysis Found/Cald. C	H	N	^{1}H-NMR (PPM) (DMSO)
III	256–258 Ethanol	80	$C_{19}H_{16}N_6O_3$ 376	60.60 60.63	4.20 4.25	22.50 22.34	a triplet at δ1.3(3H, CH_3, J=6Hz) a quartet at δ4.2(2H,CH_2, J=6Hz); a multiplet at δ7.2–8.2 (8H, Ar-H) a singlet at δ7.9(2H,2NH) and a singlet at δ10.3(1H,–OH).
IV	201–202 Benzene/ethanol (1:1)	85	$C_{15}H_{16}N_6O_3$ 376	54.65 54.87	4.80 4.87	25.08 25.60	a triplet at δ1.3(3H,CH_3, J=6Hz) a multiplet at δ3–3.7(4H,2CH_2, J=6Hz), a quartet at δ4.2 (2H,CH_2, J=6Hz); a multiplet at δ7.2–8.2 (4H, Ar-H); a singlet at δ8.0(1H,NH) a singlet at δ8.15(1H, OH) and singlet at δ9.8(1H, OH).
V*	261 Ethyl acetate	86	$C_{19}H_{14}N_6O_2$ 376	63.50 63.68	3.90 3.91	23.50 23.46	a triplet at δ1.35(3H, CH_3, J=6Hz) a quartet at δ4.35(2H, CH_2, J=6Hz) and a multiplet at δ7.65–8.40 (8H, Ar-H)
VI*	322–323 Benzene	84	$C_{15}H_{14}N_6O_2$ 376			27.69 27.09	a triplet at δ1.35(3H,CH_3, J=6Hz) a multiplet at δ3.1–3.7(4H, 2CH_2) a quartet at δ4.3(2H, CH_2, J=6Hz) and a multiplet at 7.2–8.2(4H, Ar-H)

IR-spectra exhibited the characteristic absorption bands for (NH) at ν3300–3200 cm^{-1}; (C=O) at ν1750–1700 cm^{-1}.

* ^{1}H-NMR Spectra in (TFA)

By reaction of II with phenylisothiocyanate[3] in dry ether, 2-(5-ethyl- 5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)-N-phenylhydrazin-carbothioamide VIII was formed. Treatment of VIII with 1N NaOH leads to 10-ethyl-2,10-dihydro-1*H*[1,2,4]triazolo[3',4':3,4] [1,2,4]triazino-[5,6-*b*]indol-1-thione IX or X. Authentic samples of IX or X were obtained by reaction of II with carbon disulphide in methanolic KOH [2]. The chemical structure of VIII was confirmed using elemental analysis as well as spectral data. The IR showed absorption bands at ν3300 cm^{-1} (NH) and at ν1580 cm^{-1} (CNH of the group $-\overset{\overset{\displaystyle S}{||}}{C}-NHR$) [7]. ^{1}H-NMR spectrum in DMSO added additional confirmation for the chemical structure of VIII and showed a triplet at δ1.3 (3H.CH_3, J=6Hz), a quartet at δ4.3 (2H, CH_2, J=6Hz); multiplet at δ7−8.2 (9H.Ar-H); a singlet at δ9.5 (1H, NHPh) and a singlet at δ9.75 (2H, 2NH). The latter bands disappear by deteration. The UV spectrum in dioxane gave absorption bands at λ_{max} 500 nm (log ε=2.78), λ_{max} 385 nm (log ε=4.56), λ_{max} 330 nm (log ε=4.02) and λ_{max} 277 nm (log ε=4.57). ^{1}H-NMR spectrum of IX or X in DMSO showed a triplet at δ1.35 (3H.CH_3, J=6Hz), a quartet at δ4.35 (2H,CH_2, J=6Hz) and a multiplet at 7.1−8.3 (4H. Ar-H).

Refluxing of II with diethyl oxalate in absolute ethanol gave 11-ethyl-3,11-dihydro[1,2,4]triazino[3',4':3,4] [1,2,4]triazino-[5,6-*b*]indole-1,2-dione XI or XII. The structure of XI or XII was verified using elemental as well as spectral analysis. The IR spectrum showed bands at ν3580 cm^{-1} (OH); at ν3210 cm^{-1} (NH); and at ν1700 cm^{-1} (C=O). ^{1}H-NMR spectrum of XI or XII in (TFA) showed a triplet at δ1.55 (3H, CH_3, J=6Hz); a quartet at δ1.45 (2H, CH_2, J=6Hz) and a multiplet at δ7.50−8.30 (4H, Ar-H).

Treatment of II with thioglycolic acid in dry benzene gives 11-ethyl-3,11-dihydro[1,2,4]triazino[3',4':3,4] [1,2,4]triazino-[5,6-*b*]indole-1-one XIII or XIV. Their chemical structure was confirmed by elemental as well as spectral analysis. The IR spectrum showed absorption bands at ν3200 cm^{-1} (NH) and ν1670 cm^{-1} [amidic C=O]. ^{1}H-NMR spectrum in DMSO showed a triplet at 1.35 (3H,CH_3, J=6Hz); a doublet at δ3.4 (2H,CH_2, J=6Hz); a quartet δ4.3 (2H,CH_2, J=6Hz) and a multiplet at δ7.2−8.15 (4H, Ar-H).

II reacted with aroyl esters in boiling 1,2-dichlorobenzene to give the corresponding hydrazides of 2-hydrooxybenzoic acid, 2-(5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)hydrazide XVa and of 4-aminobenzoic acid, 2-(5-ethyl-5*H*-1,2,4-triazino [5,6-*b*]indol-3-yl)hydrazide XVb. The IR spectrum of XVa showed a broad band at ν3350 cm^{-1} (NH and OH). The IR spectrum of XVb showed a broad band at ν3500 cm^{-1} (NH_2) and at ν3200 cm^{-1} (NH).

^{1}H-NMR spectrum in DMSO added additional confirmation for the chemical structure of XVa and showed a triplet at δ1.0 (3H, CH_3, J=6Hz); a quartet at δ3.6 (2H, CH_2, J6Hz), a singlet at δ3.8 (1H, OH) and a multiplet at δ6.8−8.2 (8H, Ar-H). The UV spectrum of XV_a in ethanol gave absorption bands at λ_{max} 338 nm (log ε=4.13); 278 nm (log ε=4.51); 268 nm (log ε=4.53) (sh) and at 228 nm (log ε=4.56).

^{1}H-NMR spectrum of XVb in (TFA) showed a triplet at δ1.5 (3H, CH_3, J=6Hz), a quartet at δ4.45 (2H, CH_2, J=6Hz) and a multiplet at δ7.5−8.2 (8H, Ar-H).

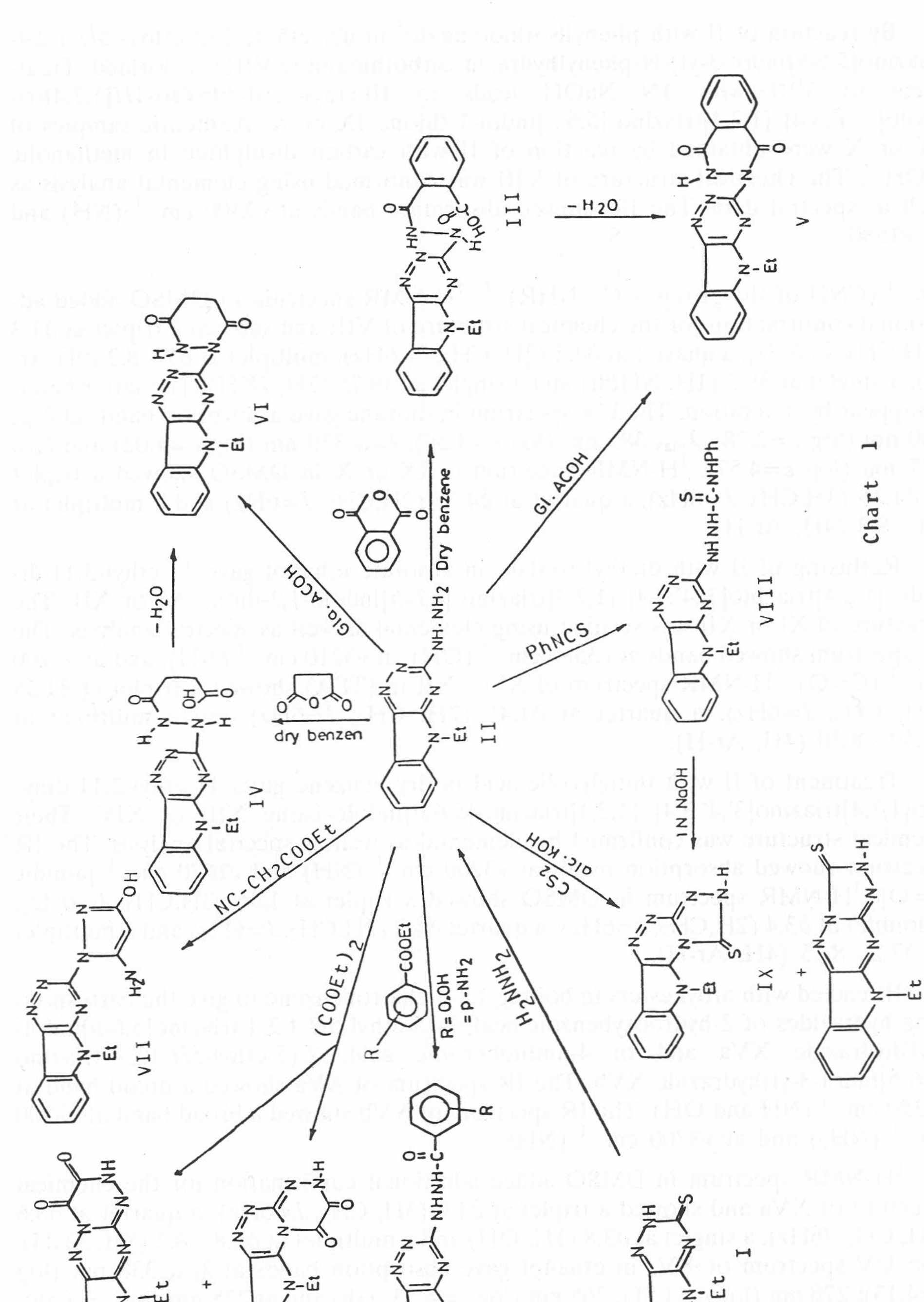


Chart 1

Treatment II with acid benzoyl chloride in chloroform containing anhydrous potassium carbonate yielded benzoic acid, 2-(5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)hydrazide XVI. The structure of XVI was confirmed by elemental as well as spectral data. The IR spectrum showed absorption bands at $\nu 3430\ cm^{-1}$ (2NH) and at $\nu 1720\ cm^{-1}$ (C=O). ^{1}H-NMR spectrum in DMSO showed a triplet at 1.3 (3H,CH_3, J=6Hz); a quartet at $\delta 4.2$ (2H,CH_2, J=6Hz); a multiplet at $\delta 7.1-8.2$ (10H, Ar-H and amidic H) and a singlet at $\delta 9.4$ (1H.NH).

Heating of XVI above its melting point for 15 min gave 10-ethyl-2-phenyl-10*H*-[1,2,4]triazolo[4'1':3,4] [1,2,4]triazino-[5,6-*b*]indole XVII or XVIII, which were obtained directly by heating a mixture of II and benzoyl chloride at 200 °C for 2 hours (cf. Chart 2). The chemical structures of both isomers were confirmed by elemental as well as spectral data. ^{1}H-NMR spectrum in DMSO showed a triplet at $\delta 3.25$ (3H,CH_3, J=6Hz); a quartet at $\delta 4.2$ (2H, CH_2, J=6Hz); and multiplet at $\delta 7-8.15$ (9H, Ar-H). The UV spectrum in dioxane showed an absorption band at λ_{max} = 375 (log ε=4.01).

Treatment of XVI with thionyl chloride in dry benzene gave *N*-2-(5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)benzenecarbohydrazonyl chloride XIX. Heating of XIX with excess thionyl chloride gave XVII or XVIII, which were also obtained by heating 5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)-3-benzaldhydrazone[2] XX over its melting point. Refluxing XVI with excess thionyl chloride gave 10-ethyl-1-phenyl-10*H*- 1,2,4 triazolo[3',4':3,4] [1,2,4]triazino[5,6-*b*]indole XXI or XXII, which were also obtained by refluxing XX with thionyl chloride (cf. Chart 2).

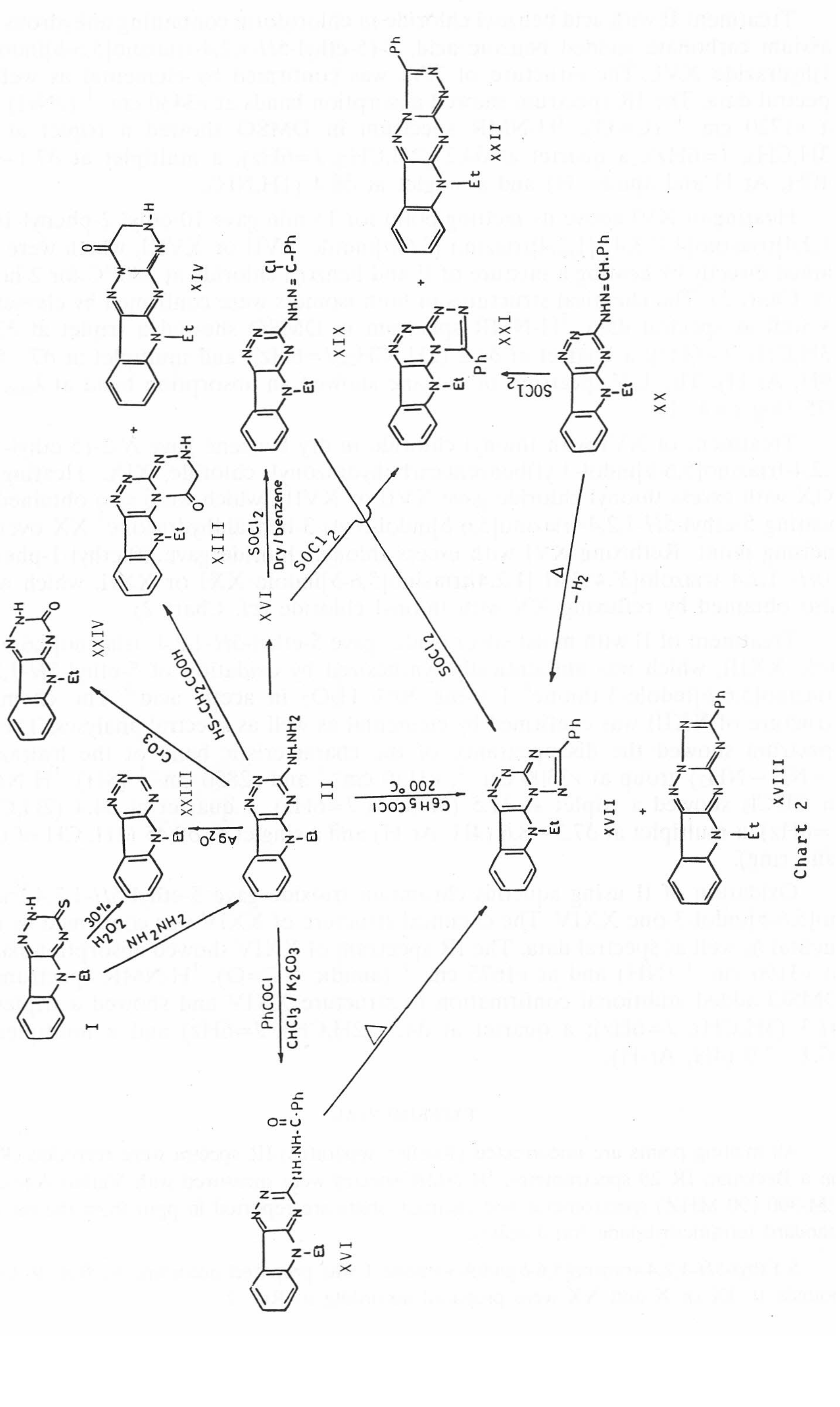
Treatment of II with moist silver oxide[7] gave 5-ethyl-5*H*-1,2,4- triazino[5,6-*b*]indole XXIII, which was authentically synthesized by oxidation of 5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indole-3-thione[8] I using 30% H_2O_2 in acetic acid.[9] The chemical structure of XXIII was confirmed by elemental as well as spectral analyses. The IR spectrum showed the disappearance of the characteristic band of the hydrazino ($-NH-NH_2$) group at $\nu 3300\ cm^{-1}$; $\nu 3110\ cm^{-1}$ and $\nu 2850\ cm^{-1}$ (SH). ^{1}H-NMR in $CDCl_3$ showed a triplet at $\delta 1.5$ (3H,CH_3, J=6Hz), a quartet at $\delta 4.4$ (2H,CH_2, J=6Hz), a multiplet at $\delta 7.3-8.6$ (4H, Ar-H) and a singlet at $\delta 9.45$ (1H, CH of triazine ring).

Oxidation of II using aqueous chromium trioxide gave 5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-one XXIV. The chemical structure of XXIV was confirmed by elemental as well as spectral data. The IR spectrum of XXIV showed absorption bands at $\nu 3190\ cm^{-1}$ (NH) and at $\nu 1675\ cm^{-1}$ (amidic >C=O). ^{1}H-NMR spectrum in DMSO added additional confirmation to structure XXIV and showed a triplet at $\delta 1.3$ (3H,CH_3, J=6Hz); a quartet at $\delta 4.1$ (2H,CH_2, J=6Hz) and a multiplet at $\delta 7.1-7.9$ (4H, Ar-H).

EXPERIMENTAL

All melting points are uncorrected (Koefler apparatus)-IR spectra were recorded (KBr) on a Beckman IR 20 spectrometer, ^{1}H-NMR spectra were measured with Varian Associate EM-390 (90 MHZ) spectrometer and chemical shifts are reported in ppm from the internal standard tetramethylsilane (on δ scale).

5-Ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-thione I was prepared according to Ref. 9. Compounds II, IX or X and XX were prepared according to Ref. 2.



I
30% H_2O_2
NH_2NH_2
XXIII
XXIV
CrO_3
Ag_2O
II
XIII
XIV
$HS-CH_2COOH$
XVI
$SOCl_2$
Dry / benzene
$SOCl_2$
XIX
XX
XXI
XXII
$SOCl_2$
Δ
$-H_2$
PhCOCl
$CHCl_3$ / K_2CO_3
C_6H_5COCl
200 °C
XVII
XVIII

Chart 2

Reaction of 5-ethyl-3-hydrazino-5H-1,2,4-triazino[5,6-b]indole II with Acid Anhydride. General procedure.

a) In Dry Benzene:

A mixture of 5-ethyl-3-hydrazino-5*H*-1,2,4-triazino[5,6-*b*]indole II (2.28 g; 0.01 mol) and the acid anhydrides (0.012 mol) in dry benzene (100 ml) was heated under reflux for 4 hrs. After cooling, the solid product was filtered off and crystallized from the proper solvent. The results are listed in Table I.

b) In glacial Acetic Acid:

A mixture of 5-ethyl-3-hydrazino-5*H*-1,2,4-triazino[5,6-*b*]indole II (2.28 g, 0.01 mol) and the acid anhydride (0.012 mol) in glacial acetic acid (50 ml) was heated under reflux for 3 hrs., the mixture was cooled, poured onto an ice-water mixture, dried and crystallized from the proper solvent (cf. Table I).

Synthesis of 5-Amino-1-(5-ethyl-5H-1,2,4-triazino[5,6-b]indol-3-yl)-1H-pyrazol-3-ol (VII):

A mixture of 5-ethyl-3-hydrazino-5*H*-1,2,4-triazino[5,6-*b*]indole II (2.28 g., 0.01 mol), ethyl cyanoacetate (1.06 ml, 0,01 mol) and a few drops of piperidine was heated at 100–120°C for 3 hrs. The reaction product was filtered, washed with benzene and crystallized from dioxane into yellow needles, 1.8 g (61%) of VII; m.p. 262–264°C.

Anal. $C_{14}H_{13}N_7O$ (295) ; calc'd.: C, 56.94; H, 4.40: N, 33.22.

found: C, 57.10; H, 4.26; N; 32.50

Synthesis of 2-(5-Ethyl-5H-1,2,4-triazino[5,6-b]indol-3-yl)-N-phenylhydrazinecarbothioamide (VIII):

A mixture of 5-ethyl-3-hydrazino-5*H*-1,2,4-triazino[5,6-*b*]indole II (5.7 g., 0.025 mol) and phenyl isothiocyanate (3 ml, 0.025 ml) in dry ether (75 ml) was heated under reflux for 3 hrs. After cooling, the buff precipitate obtained was filtered and crystallized from ethanol into buff needles, 4.8 g (58%) of VIII; m.p. 193–195°C.

Anal. $C_{18}H_{17}N_7S$ (363): calc'd.: C, 59.59; H, 4.48; N, 26.99; S, 8.81.

found: C, 59.67; H, 5.0; N, 26.65; S, 8.60

Synthesis of IX or X:

2-(5-Ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)-N-phenylhydrazinecarbothioamide (VIII) (3.63 g, 0.01 mol) was heated in 1M sodium hydroxine (50 ml) for 10 min, the reaction mixture was filtered and the filtrate was neutralized with acetic acid to give a solid product, which was filtered, washed with water and crystallized from ethanol into red fibrous crystals, 2.1 g (78%), m.p. 229–230°C.

Anal. $C_{12}H_{10}N_6S$ (270): calc'd.: C, 53.33; H, 3.70; N, 31.11; S, 11.85.

found: C, 53.40; H, 3.60; N, 31,30; S, 12.10.

Formation of XI or XII:

A mixture of II (2.28 g, 0.01 mol) and diethyl oxalate (3 ml) in absolute ethanol (50 ml) was heated under reflux for 8 hrs. The solvent, as well as the excess ester, was distilled off under reduced pressure and the remaining solid product was crystallised from dioxane-water (1:1) to give fine white crystals, 1.6 g (57%), m.p. 249–250°C.

Anal. $C_{13}H_{16}N_6O_2$ (288): calc'd.: N, 29,16.

found: N, 28.70.

Reaction of 2 with Thioglycolic Acid. Formation of XIII or XIV:

To a well stirred solution of II (2.28 g, 0.01 mol) in dry benzene thioglycolic acid was added (1.38 g, 0.015 mol) and the mixture was refluxed on water bath for 4 hrs. The solvent was removed under reduced pressure to give a yellow solid which was triturated with diethyl ether, then crystallized from ethanol into pale yellow fibrous crystals, 1.6 g (60%), m.p. 215°C.

Anal. $C_{13}H_{12}N_6O$ (268): calc'd.: C, 58.20; H, 4.47; N, 31.34.

found: C, 57.66; H, 4.90; N, 31.70.

Reaction of (5-Ethyl-5H-3-hydrazino-5H-1,2,4-triazino[5,6-b]indole II with Aroyl Esters, Model Procedure:

A mixture of II (2.28 g, 0.01 mol) and the aromatic acid esters (0.015 mol) in 1,2-dichlorobenzene was heated under reflux for 6 hrs. After cooling the solid product was filtered off and cristallized from the proper solvent. The results are summarized as follows:

2-(5-ethyl-5H-1,2,4-triazino[5,6-b]indol-3-yl)-hydrazide (XVa):

Red needles from ethanol, 2.1 g (60%) of XVa, m.p. 120–122°C.

Anal. $C_{18}H_{16}N_6O_2$ (332): calc'd.: C, 62.06; H, 4.59.

found: C, 62.60; H, 4.90.

4-Aminobenzoic Acid, 2-(5-Ethyl-5H-1,2,4-triazino[5,6-b]indol-3-yl)-hydrazide (XVb):

Yellow needles from benzene, 2.4 g (69%) of (XVb), m.p. 116–117°C.

Anal. $C_{18}H_{17}N_7O$ (347): calc'd.: C, 62.24; H, 4.89; N, 28.24.

found: C, 62.40; H, 4.90; N, 28.40.

Synthesis of Benzoic Acid, 2-(5-Ethyl-5H-1,2,4-triazino[5,6-b]indol-3-yl)-hydrazide (XVI):

To a solution of II (5.7 g, 0.025 mol) in dry chloroform (100 ml), containing anhydrous potassium carbonate (0.5 g), benzoyl chloride (2.34 ml, 0.02 mol) was slowly added. After the addition was completed, the reaction mixture was stirred at room temperature for 30 min and then heated on a steam bath for one hour. The mixture was filtered from potassium carbonate. After cooling, the yellow precipitate separated was filtered and crystallized from ethanol to give yellows needles, 7.2 g (87%) of XVI, m.p. 222–224°C.

Anal. $C_{18}H_{16}N_6O$ (322) calc'd.: C, 65.1; H, 4.8; N, 25.3.

found: C, 65.9; H, 4.53; N, 25.9.

Synthesis of N-(5-Ethyl-5H-1,2,4-triazino[5,6-b]indol-3-yl)-benzenecarbhydrazonoyl Chloride (XIX):

A mixture of XVI (3.32 g, 0.01 mol) and thionyl chloride (5 ml) was stirred at room temperature for 2 hrs. The excess of thionyl chloride was removed and the remaining yellow solid was crystallized from benzene to give orange flakes, 2.6 g (74%) of XIX, m.p. 193–194°C.

Anal. $C_{18}H_{15}N_6Cl$ (350.5): calc'd.: C, 61.62; H, 4.27; N, 23.96; Cl, 10.12.

found: C, 61.40; H, 4.40; N, 23.80; Cl, 10.30.

Formation of (XVII) or (XVIII):

A) From II. – A mixture of II (2.28 g, 0.01 mol) and benzoyl chloride (4.7 ml, 0,04 mol) was heated at 200°C in an oil bath for 2 hours, whereby a solid product was formed. It was triturated with dry benzene (3 ml), filtered and crystallized from ethanol into orange flakes, 1.7 g (81%), m.p. 180–183°C.

Anal $C_{18}H_{14}N_6$ (314): calc'd.: C, 68.78; H, 4.45.

found: C, 69.35; H, 4.93.

B) From XVI. – XVI (3.3 g, 0.01 mol) was heated at 240°C in an oil bath for 1 hour. After cooling, the solid product was washed with diethyl ether and crystallized from ethanol to give orange flakes, 2.3 g (74%), m.p. 180–183°C.

Anal. $C_{18}H_{14}N_6$ (314): calc'd.: C, 68.78; H, 4.45; N, 27.07.

found: C, 68.70; H, 4.40; N, 27.20.

C) From XIX. – A mixture of *N*-(5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)-benzenecarbohydrazonoyl chloride XIX (3.5 g, 0.01 mol) and thionyl chloride (5 ml) in dry benzene was heated under reflux for 3 hrs. The excess of thionyl chloride was removed and the remaining orange precipitate was crystallized from ethanol to give orange flakes, 2.6 g (80%), m.p. 180–183°C.

Anal. $C_{18}H_{14}N_6$ (314): calc'd.: C, 68.78; H, 4.45; N, 27.07;

found: C, 68.60; H, 4.60; N, 27.30.

Product XVII or XVIII was prepared by the heating of XX above its melting point. This was confirmed by m.p. and m.m.p. determinations with authentic samples.

*Reaction of Benzoic Acid, 2-(5-Ethyl-5H-*1,2,4-*triazino*[5,6-*b*]*indol*-3-yl)-*hydrazide XVI with Thionyl Chloride. Formation of XXI or XXII:*

A mixture of XVI (3.32 g, 0.01 mol) and thionyl chloride (5 ml) was heated under reflux for 4 hours. The excess thionyl chloride was removed and the remaining orange solid was crystallized from ethanol to give orange needles, 2.8 g (80%) of XXI or XXII, m.p. 254–255°C.

Anal. $C_{18}H_{14}N_6$ (314): calc'd.: C, 68.78; H, 4.45; N, 27.07.

found: C, 68.60; H, 4.60; N, 27.10.

Transformation of XX into XXI or XXII:

A mixture of benzaldehyde (5-ethyl-5*H*-1,2,4-triazino[5,6-*b*]indol-3-yl)-hydrazone (0.5 g) and thionyl chloride (10 ml) was heated on a water bath for 8 hours. Excess of thionyl chloride was removed by evaporation. The product was crystallized from methanol, m.p. 255°C, yield, 0.22 g; (73.3%).

Anal. $C_{18}H_{14}N_6$ (314): calc'd.: C, 68.78; H, 4.45; N, 27.07.

found: C, 68.5; H, 4.9; N, 26.9.

Preparation of 5-Ethyl-5H-1,2,4-triazino[5,6-b]indole (XXIII):
Method A: Oxidation of II with Silver Oxide.

A solution of II (7.3 g, 0.032 mol) in water (1000 ml) was stirred at 80°C and silver oxide (20 g, 0.088 mol) was added in portions. The stirring was continued for one hour, whereby nitrogen gas was evolved. The mixture was filtered from excess silver oxide and the filtrate was extracted with diethyl ether. The ether extract was dried over magnesium sulphate and evaporated to give a solid product, which was crystallized from benzene to give brown needles, 4.0 g (63%) of XXIII, m.p. 133–135°C.

Anal. $C_{11}H_{10}N_4$ (198): calc'd.: C, 66.66; H, 5.05; N, 28.29.

found: C, 66.80; H, 5.70; N, 28.90.

Method B: From Oxidation of 5-Ethyl-5H-1,2,4-triazino[5,6-b]indo-3-thione I with H_2O_2:

Compound I (0.23 g, 0.001 mol) was suspended in hot acetic acid and hydrogen peroxide (2.5 ml, 30%) was added with stirring. A clear solution was obtained after the vigorous reaction had ceased. The solution was poured onto cold water and the solid product filtered, washed with water, dried and crystallized from benzene to give brown needles, 0.15 g, (75%) of XXIII, m.p. 133–135°C.

Anal. $C_{11}H_{10}N_4$ (198): calc'd.: C, 66.66; H, 5.05; N, 28.29.

found: C, 66.60; H, 5.20; N, 28.50.

Preparation of 5-Ethyl-5H-1,2,4-triazino[5,6-b]indol-3-one (XXIV):

A solution of II (7.3 g, 0.032 mol) in water (1000 ml) was stirred at 80°C and chromium trioxide (13.3 g, 0.088 mol) was added in portions. The stirring was continued for one hour, whereby nitrogen gas was evolved. After cooling, the mixture was extracted with diethyl ether. The ether extract was dried over magnesium sulphate and evaporated. The solid product was crystallized from benzene to give pale yellow needls, 5.09 (79%) of XXIV, m.p. 290–292°C.

Anal. $C_{11}H_{10}N_4O$ (214): calc'd.: N, 26.16.

found: N, 26.30.

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SAŽETAK

Sinteza prikondenziranih heterocikla iz 5-etil-3-hidrazino-5H-1,2,4-triazino[5,6-b] indol

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5-etil-3-hidrazino-5H-1,2,4-triazino[5,6-b]indol(II) iskorišten je za sintezu različitih heterocikličkih spojeva. Ona je provedena reakcijom 3-hidrazino skupine s različitim reagensima, kao: anhidridi, dieteiloksalat, tioglikolna kiselina, aroil-esteri i kiselinski kloridi. Struktura produkata potvrđena je različitim spektroskopskim analitičkim metodama.