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SYNTHESIS OF SOME MORE HETEROBICYCLIC DERIVATIVES BEARING A 1, 2, 4-TRIAZINE MOIETY AND THEIR ANTIBACTERIAL ACTIVITY

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Some new monohydrazones (IIa-e) and monoacyl 1, 2, 4-triazine derivatives (XIIa 1) have been prepared by reacting 3-hydrazino-5, 6-diphenyl-1, 2, 4-triazine (I) with some oxo-compounds. These products have been used to synthesize some new fused heterobicyclic derivatives by cyclization under acidic and neutral medium. UV, IR, PMR spectra and antibacterial activity of the new products have been recorded.

Key words: Heterobicyclic 1, 2, 4-Triazines, Antibacterial activity.

INTRODUCTION

In continuation of our studies on the chemistry of 3-hydrazino-5, 6-diphenyl, 1, 2, 4-triazine (I) [1-3] and in view of possible pharmacological activity of new pyrazole analogues [4], the synthesis of some more heterobicyclic derivatives bearing 1, 2, 4-triazine moiety has been made in our present study. All the reactions sequences have been reported in the schemes 1, 2.

EXPERIMENTAL

Melting points reported are uncorrected UV spectra were recorded in pure Et OH on a Perkin Elmer 550 S uv vis spectrophotometer (λ_{max} in nm), IR spectra in KBr on a Pye Unicam SP 1100 Infrared spectrophotometer (υ_{max} in cm^{-1}) and H^{-1}nmr spectra in DMSO-d_6 solution with $(CH_3)_4$ Si as internal standard (δ, ppm) are recorded in Varian instrument division EM 390 90 MHz NMR spectrometer. 3-hydrazino-5, 6-diphenyl-1, 2, 4-triazine (I) was prepared by reported method [13].

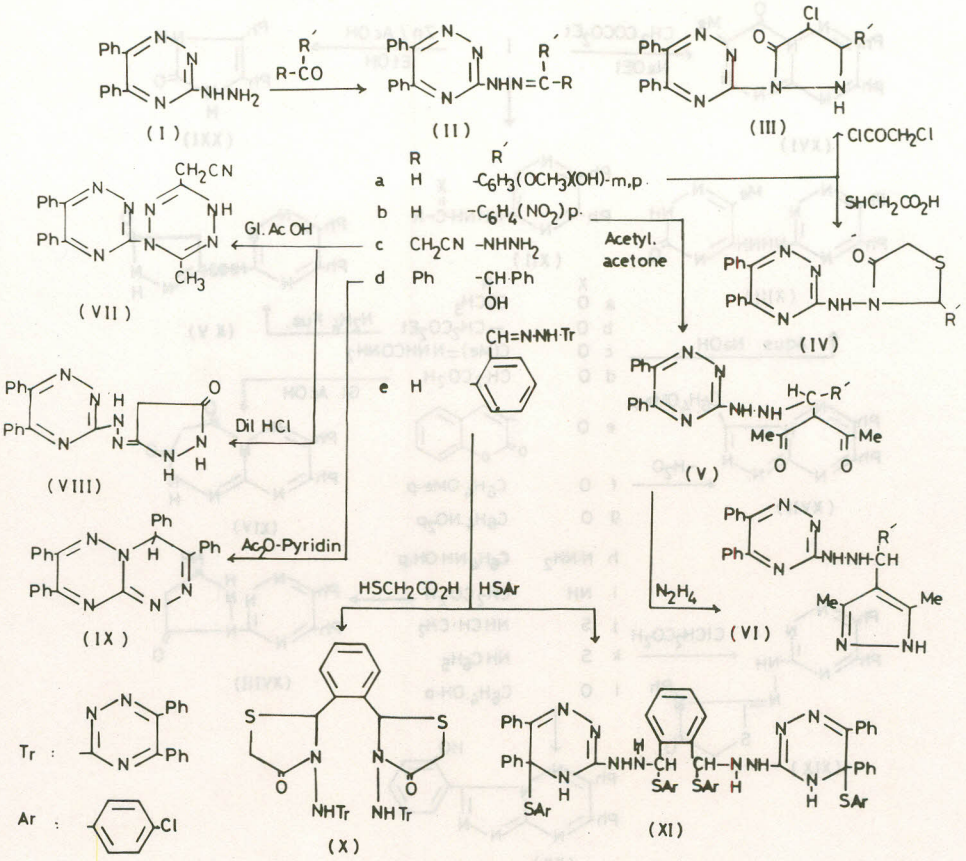
1. *Preparation of the hydrazones (IIa-e).* A mixture of I(0.0 1 mol) and the appropriate aldehyds and ketones (0.015 mol) was heated under reflux for 30 min and diluted with cold water. The solid obtained was filtrated and crystallized from ethanol to give IIa-e (Table 1), IR (IIa) 3400 (OH), 3200 (NH), 3050 (aromati CH), 2900 (aliphatic CH), 1590 (C = N), 1480 (def. CH_2) and 1050 (R-O-CH_3; UV: 195 and 330, PMR 2.5 (s, 3H, OCH_3), 3.3 (s, 1H, CH), 6.8-7.4 (m, 13 H, aromatic protons), 9.2 (s, 1H, OH phenolic) and 11.7 (s, 1H, NH). The OH and NH peaks exchangeable with D_2O. IR (IIc): 3400 (NH_2), 3300-3200 (NH-NH), 3020 (aromatic CH), 2900 (aliphatic CH), 2250 (C = N), 1610 (C = N), 1500 (def. CH_2) and 1020 (phenyl groups).

2. *Ring closure reactions of the hydrazones.* (i). *Reactions of IIa with chloroacetyl chloride. Formation of III.* To a well stirred solution of IIa (0.01 mol) and triethylamine (0.1 mol) in dry benzene, an equimolar amount of chloroacetyl chloride was added dropwise at room temp. The mixture was then stirred for 8 hr and left standing overnight. The precipitated Et_3N HCl was filtered was washed with dil. HCl, then with water and dried over fused Na_2SO_4. The solvent was evaporated and the reaction residue which solidifies with methanol was crystallized from DMF to give III, PMR, 2.5 (s, 3H, OCH_3), 3.4 (s, 1H, CHCl). 7-7.4 (m, 13H, aromatic protons), 11.2 (s, 1H, OH) and 12.3 (s, 1H, NH). The OH and NH peaks exchangeable with D_2O. (m.p. 165-167°, yield 65%; Found, Cl: 7.0. $C_{25}H_{20}N_5ClO_3$ requires Cl: 7.6%).

(ii). *Action of mercaptoacetic acid on IIa: Formation of IV.* Mercaptoacetic acid (0.15 mol) was added to a well stirred solution of IIa (0.01 mol) in dry benezene (100 ml). The mixture was stirred for 4 hr and then refluxed for 6 hr with fused Na_2SO_4 (100 g). Filter will hot. The precipitated product was filtered off and crystallized from ethylbenzene to give IV, (m.p. 230-232°, yield 86%, Found, S 6.0, $C_{25}H_{21}N_5SO_3$ requires S 6.8%), IR, 3500-3300 (OH, NH), 3050 (aromatic CH), 2910 (aliphatic CH), 1650 (C = O), 1470 (def. CH_2), UV: 220 (1, 2, 4-triazine), 260 (thiazolidin-4-one) and 330 (vanilline moiety); P M R: 1,9 (s, 3H, CH_3 O), 2.5 (s, 2H, CH_2), 6.8 (s, 1H, CH), 7-7,7 (m, 13H, aromatic protons) and 11.1 (s, 1H, OH), 12.4 (s, 1H, NH exchangeable with D_2O).

(iii). *Addition of acetylacetone to IIb. Formation of V.* A mixture of equimolar amounts of IIb and acetylacetone in ethanol (100 ml) with a few drops of piperidine, was refluxed for 2 hr, cooled acidified with dil. HCl and the resultant solid filtered and crystallized from ethanol to give V, (m.p. 280°, yield 75%), (Found, 16.3, $C_{27}H_{24}N_6O_4$ requires, N, 16.93%); IR; 3400 (NH), 3200 (NH), 3020 (aromatic CH), 2970-2850 (aliphatic CH_3, CH-CH), 1650-1620 (C = O), (C = N), 1480 (def. CH_2), 1550, 1330 (asy. NO_2, sy. NO_2) and 1020 (phenyl groups).

(iv). *Fusion of V with hydrazine hydrate. Formation of VI.* A mixture of V (0.01 mol) and hydrazine hydrate (0.01 mol) was heated at 180-200° in oil-bath for 20 min. The



Scheme 1

solid obtained was triturated with methanol to give VI, crystallized from ethanol, (m.p. 270-272°, yield 68%, Found, N: 22, $C_{27}H_{25}N_8O_2$, requires N: 22.7%; IR: 3500-3300 (NH-NH), 3050 (aromatic CH), 2850 (aliphatic CH), 1600-1570 (C = N), 1510, 1350 (asy. NO_2, sy NO_2), 1470 (def. CH_3) and 1050 (phenyl groups).

(v). *Acidic cyclization of IIc: Formation of VII.* Compound IIc (0.01 mol) in glacial acetic acid (100 ml) was heated under reflux for 8 hr, cooled, diluted with cold water. The solid obtained was crystallized from ethanol to give VII (Table 2); IR 3200 (NH), 3000 (aromatic CH), 2980 2850 (aliphatic CH), 2250 (C = N), 1600-1580 (C = N), 1480 (def. CH_2), 1335 (NCN cyclic) and 1050 (phenyl groups), PMR, 2.5 (s, 3H, CH_3), 3.2 (s, 2H, CH_2), 7.2-7.4 (m, 10H, aromatic protons) and 8 (s, 1H, NH exchangeable with D_2O).

(vi). *Acidic hydrolysis of IIc: Formation of VIII.* A mixture of IIc (0.01 mol) and dil. HCl (20%, 20 ml) was heated under reflux for 4 hr, cooled and filtered. The solid obtained was recrystallized from acetic acid to give VII (Table 2); IR: 3220-3180 (NH NH), 3000 (aromatic CH), 2820 (aliphatic CH), 2680 (OH), 1620 (CO-NH), 1570 (acyclic C = N), 1480-1460 (def. CH_2, 1350 (NCN) and 1100-1050 (phenyl groups).

(vii). *Cyclization of IId: Formation of IX.* A mixture of IId and pyridine-Ac_2 0 (1.1, 100 ml) was refluxed for 2 hr, colded, poured into ice HCl and filtered. The solid obtained was crystallized from acetic acid to give IX (Table 2); IR: 3020 (aromatic CH), 1640 (C = N), 1590 (C = N), 1440 (def. CH), 1000, 900 and 830 (phenyl groups).

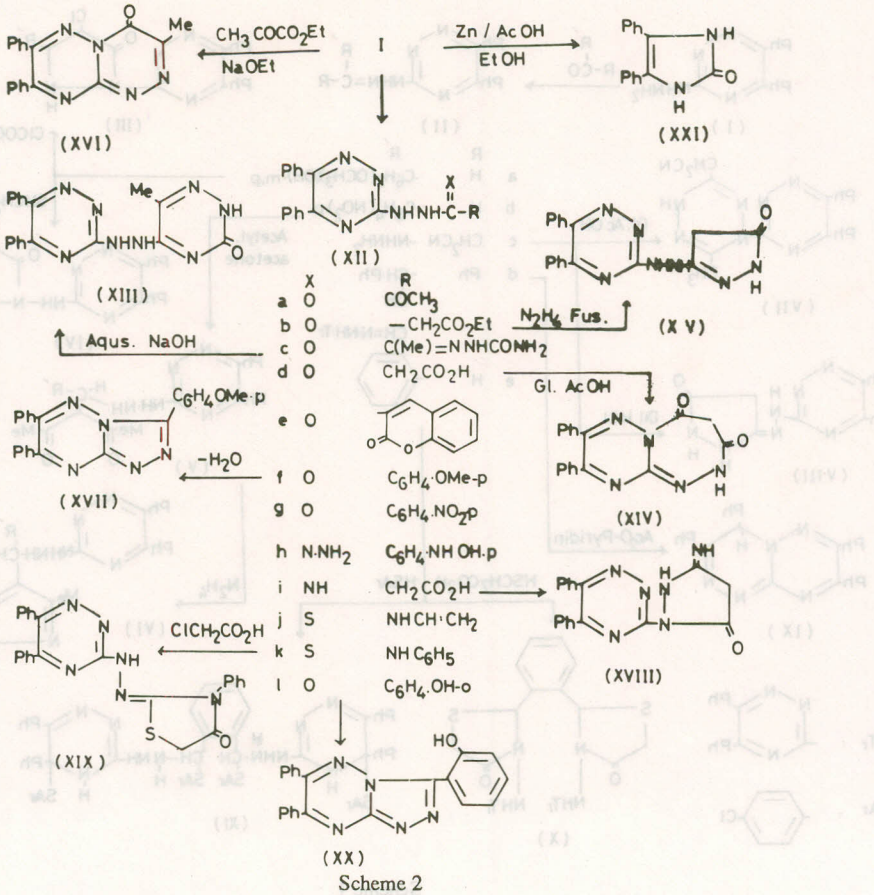
Table 1.

Final Comp.	M.P. C°		Yield (%)	Cryst. solvent	Mol formula	Found. N (%)	Requires N (%)
iia	245	246	85	Et OH	$C_{23}H_{19}N_5O_2$	17	17.6
IIb	298	300	82	Et OH	$C_{22}H_{16}N_6O_2$	20.0	21.2
IIc	105	106	95	Et OH	$C_{18}H_{16}N_8$	32.0	32.6
IId	215	216	75	Et OH	$C_{29}H_{23}N_5O$	14.4	15.3
IIe	205	206	85	Et OH	$C_{38}H_{28}N_{10}$	21.5	22.4

Table 2.

Comp.	M.P. C°		Yield (%)	Cryst.	Mol formula	N (%) Found	N (%) Requires
VII	175	177	65	Ethanol	$C_{20}H_{16}N_8$	29.5	30.4
VIII	120	122	60	Acetic	$C_{18}H_{15}N_7O$	27.7	28.4
IX	205	208	67	Acetic	$C_{29}H_{21}N_5$	15.4	15.9
X	110	112	78	Ethyl-benzene	$C_{46}H_{20}N_{10}S_2O_2$	18.0	18.2
XI	80	85	68	IMF	$C_{56}H_{48}N_{10}S_4Cl_4$	11.8	12.4

*Found, (X):S, 8.1, Cacl. 8.3 (%). **Found, (XI): S, 13.0, Cacl. 13.1 (%). Cl, 12.0, Cacl. 12.4 (%).



Scheme 2

(viii). *Formation of the bis compounds X and XI.* (a) A mixture of IIe (0.01 mol) and thioglycollic acid (0.2 mol) in dry benzene (100 ml) and fused Na_2SO_4 (100 g) was refluxed for 10 hr, filtered while hot and the excess solvent removed. The oily residue was solidify with pet. ether 40-60°. The solid thus obtained was filtered and crystallized from ethylbenzene to give X (Table 2).

(b) A mixture of IIe (0.01 mol) and *p*-chloro thiophenol (0.04 mol) was heated at 200° in an oil-bath for 6 hr. The solid obtained was triturated with pet. ether 40-60 and the solid resultant crystallized from DMF to give XI (Table 2); IR: (XI). 3300-3100 (broad NH-NH), 3030 (aromatic CH), 2820 (aliphatic CH), 1460 (def. CH), 1370 (CNS), 1080 (C-S) and 1000, 800 (phenyl groups) and 600-550 (C-Cl).

3. *Acylation of I: Formation of monoacyl derivatives (XIIa-l).* (i). *Reaction of I with oxo-esters: Formation of XIIa and XIIb.* A mixture of I(0.01 mol) and ethylpyruvate or diethylmalonate (0.01 mol) in dry benzene (100 ml) was heated under reflux for 2 hr, cooled and the solid obtained crystallized and from ethanol to give XIIa and XIIb (Table 3); IR (XIIa) 3500-3350 (NH-NH), 3050 (aromatic CH), 2800 (aliphatic CH), 1720-1650 (CO-CO), 1490 (def. CH_2) and 1050 (phenyl groups). IR (XIIb): 3300-3200 (NH NH), 3040 (aromatic CH), 2950 (aliphatic CH), 1700-1600 (NH $COCH_2$, $COOC_2H_5$), 1510-1480 (def. CH_2), 1050 and 950 (phenyl groups); UV (XIIb): 350 and 270.

(ii). *Condensation of XIIa with semicarbazide. HCl: Formation of XIIc.* A mixture of XIIa (0.01 mol) and semicarbazide. HCl (0.01 mol, in 10 ml water) in abs. ethanol (50 mol) was stirred for 1 hr. The solid resultant was filtered and crystallized from ethanol to give XIIc (Table 3).

(iii). *Basic cyclization of XIIc: Formation of 5 (substituted hydrazino)-6-methyl-1, 2, 4-triazin-3(2H)one(XIII).* A mixture of XIIc (0.01 mol) and aq. sodium hydroxide (10%, 50 ml) was heated under reflux for 2 hr and acidified. The solid obtained was crystallized from ethanol to give XIII (Table 3); IR: 3500-3400 (OH), 3200-3150 (NH-NH), 3010 (aromatic CH), 2850 (aliphatic CH), 2700 (def. OH), 1730 (C = O), 1610-1590 (C = N), 1440 (def. CH_2), 1320 (NCN) and 1050 (phenyl groups).

(iv). *Basic hydrolysis of XIIb. Formation of acetic acid hydrazide derivative (XIId).* A solution of XIIb (0.01 mol) and sodium hydroxide (80 mg, 0.002 mol) in ethanol H_2O (1:1, 20 ml) was refluxed for 4 hr. The reaction mixture was acidified with dil. HCl. The solid obtained was filtered and crystallized from ethanol to give XIId (Table 3). Compound XIId give acidity with aq. sodium bicarbonate.

(v). *Acidic cyclization of XIId: Formation of XIV.* A suspention of XIId (0.2 g) in glacial acetic acid (50 ml) was refluxed for 3 days. The solvent was evaporated and the residue crystallized from ethanol to give XIV (Table 3);

Table 3. Physical data of the compounds XII-XXI.

Compd.	M.P. °C	Yield (%)	Mol. formula*	N (%) Found	N (%) Calc.
XIIa	16-162	60	$C_{18}H_{15}N_5O_2$	20.0	21.0
XIIb	170-171	76	$C_{20}H_{19}N_5O_3$	17.7	18.6
XIIc	182-185	86	$C_{19}H_{18}N_8O_2$	28.1	28.7
XIId	100-102	67	$C_{18}H_{15}N_5O_3$	19.2	20.1
XIIe	270-271	87	$C_{25}H_{17}N_5O_3$	15.3	16.1
XIIf	105-107	76	$C_{23}H_{19}N_5O_2$	16.9	17.3
XIIg	280-281	67	$C_{22}H_{16}H_6O_3$	19.5	20.4
XIIh	115-118	76	$C_{22}H_{20}N_8O$	26.2	27.2
XIIi	125-126	88	$C_{18}H_{16}N_6O_2$	23.4	24.1
XIIj	145-147	75	$C_{18}H_{16}N_6S^*$	23.5	24.1
XIIk	195-196	65	$C_{22}H_{18}N_6S^{**}$	20.2	21.1
XIII	215-218	86	$C_{22}H_{17}H_5O_2$	17.5	18.3
XIII	230-233	89	$C_{19}H_{16}N_8O$	29.3	30.1
XIV	130-133	76	$C_{18}H_{13}N_5O_2$	20.3	21.1
XV	160-161	86	$C_{18}H_{15}N_7O$	27.5	28.4
XVI	235-237	76	$C_{18}H_{13}N_5O$	21.7	22.2
XVII	155-156	65	$C_{23}H_{17}N_5O$	17.8	18.5
XVIII	115-117	75	$C_{18}H_{14}N_6O$	33.1	33.9
XIX	180-181	70	$C_{24}H_{18}N_6SO$	18.3	19.2
XX	260-262	65	$C_{22}H_{15}N_5O$	18.5	19.2
XXI	255-256	90	$C_{15}H_{12}N_2O$	11.2	11.9

* Found, S. 8.5 Calc, 9.2 % ** S. 76 8.0 % *** S. 6.8 7.3%
*All the compounds gave satisfactory C, H analysis.

PMR: 2.5 (s, 2H, CH_2), 7.2-7.4 (m, 10 H, aromatic protons) and 7. (s, 1H, NH exchangeable with D_2O).

(vi). *3-Substituted hydrazino-4-dihydro-pyrazol-5 (1H) one (XV).* A mixture of XIIb (0.01 mol) and hydrazine hydrate (0.01 mol) was heated under reflux at 200° in an oil-bath for 2 hr. The solid obtained was triturated with methanol and crystallized from acetic acid to give XV (Table 3); IR: 3300-3150 (NH-NH), 3120 (NH), 3010 (aromatic CH), 2850 (aliphatic CH), 1675 (C = O), 1600 (C = N), 1430 (def. CH) and 1000-900 (phenyls).

(vii). *Formation of 3-substituted-coumarin (XIIe).* The mixture of XIIb (0.01 mol) and salicylaldehyde (0.01 mol) in ethanol (50 ml), piperidine (1 ml) was refluxed for 6 hr, cooled, acidified with dil. HCl. The solid obtained was crystallized from DMF to give XIIe (Table 3); IR: 3300 (NH-NH), 3020 (aromatic CH), 1700-1650 (C = O), 1590 (C = C), 1050, 1000 and 950 (phenyl groups); UV: 330 and 280.

4. *Cyclocondensation of I with ethylpyruvate: Formation of XVI.* A mixture of I(0.01 mol) and ethylpyruvate (0.01 mol) in sodium ethylate (0.23 g Na in 100 ml abs. ethanol) was refluxed for 3 hr, cooled and diluted with cold water. The solid resultant was crystallized from ethanol to give XVI (Table 3); IR: 3050 (aromatic CH), 2900 (aliphatic CH), 1700-1650 (C = O), 1560 (C = N), 1480 (def. CH_2), 1000 and 880 (phenyl groups); UV: 350 and 250.

Acylation of I. Formation of acid hydrazides XIIf and XIIg. An equimolar mixture of I and *p*-methoxybenzoyl chloride or *p*-nitrobenzoyl chloride in DMF (100 ml) was refluxed for 20min, cooled and acidified. The solid resultant filtered and crystallized from ethanol to give XIIf and XIIg (Table 3).

Dehydration of XIIf. Formation of 3-(p-methoxyphenyl)-5, 6-diphenyl-1, 2, 4-triazolo [4, 3-b] [1, 2, 4] triazine (XVII). Compound XIIf (0.2 g) was heated above melting points (50° higher) for 30 min and cooled. The solid obtained was triturated with methanol, filtered and crystallized from methanol to give XVII (Table 3).

Fusion of XIIg with hydrazine hydrate: Formation of substituted hydroxyl amine XIIh. Compound XIIg (0.01 mol) and hydrazine hydrate (0.01 mil) was heated at 180° in an oil-bath for 2 hr. The solid obtained was triturated with methanol to give XIIh (Table 3); IR; 3400 (NH_2), 3100 (NH), 2700 (OH), 1580 (C = N), 1350 (NCN) and 1050, 850 (phenyl groups).

5. *Addition of cyanoacetic acid to I: Formation of XIIi.* A mixture of I(0.01 mol) and cyanoacetic acid (0.01 mol) in ethanol (50 ml), piperidine (1 ml) was heated under reflux for 8 hr, cooled, and acidified. The solid obtained was filtered and crystallized from ethanol to give XIIi (Table 3); IR: 3500-3200 (OH, NH) (aromatic CH), 2850 (aliphatic CH), 1650 (C = O), 1570 (C = N), 1440 (def. CH_2), 1330 (NCN) and 980-950 (phenyl groups).

Basic cyclization of XIIi: Formation of N^1 (5, 6-diphenyl-1,2,4-triazin-3-yl)-3-imino-4-dihydro-pyrazol 5(2H) one (XVIII). A mixture of XIIi (0.01 mol) and aq. sodium hydroxide (10%, 50 ml) was heated under reflux for 2 hr and acidified with dil. HCl. The solid obtained was crystallized from ethanol togive (Table 3).

6. *Fusion of I with thiocarbamide and carbamide: Formation of thiosemicarbazide and semi-carbazide XIIj-l.* An equimolar mixture of I and N-allylthiourea, N-phenylthiourea or salicylamide was heated at 180-200° in an oil-bath for 30 min. The residue obtained was triturated with methanol and crystallized from ethanol to give XIIj-l (Table 3), IR. 3350-3155 (NH-NH), 3010 (aromatic CH), 2950 (aliphatic CH), 1585 (C = N). 1320 (CNS), 1100-1050 (C-S) and 1000, 950 (phenyl groups).

Cyclization of XIIk with monochloroacetic acid. Formation of 2-imino-3-phenyl-thiazolidin-4-one (XIX). A mixture of XIIk (0.01 mol), monochloroacetic acid (0.01 ml) and fused sodium acetate (0.03 mol) in ethanol (25 ml) was heated under reflux for 6 hr, on a water-bath. The solvent was removed and the reaction mixture was poured onto crushed ice. The solid obtained was filtered, washed with cold water and crystallized from ethanol to give XIX (Table 3); IR: 3550 (OH), 3200-3100 (NH), 3020 (aromatic CH), 2920-2850 (aliphatic CH), 1670 (C = O), 1600 (C = N), 1570 (C = N), 1440 (def. CH_2), 1370 (CNS), 1210-1190 (C-S), and 890 750 (phenyl groups).

Dehydration of XII 1: Formation of 3-(o-hydroxyphenyl)-5, 6-diphenyl-1, 2, 4-triazolo [4,3-b] [1, 2, 4] triazine (XX). Compound XII 1(0.2 g) was heated above melting points (60° higher) for 30 min and cooled. The

solid obtained was crystallized from acetic acid to give XX (Table 3); IR: 3555 (OH), 3020 (aromatic CH), 1570 (C = N), 1550 (C = N), 920, 820 and 720 (phenyl groups).

7. Reduction of I: Formation of XXI. A mixture of 1(2 g) and zinc dust (10 g) in ethanol-acetic acid (1:1, 100 ml) was heated under reflux for 2 hr, filtered while hot and concentrated. The solid obtained was crystallized from acetic acid to give XXI (Table 3); IR; 3500 3100 (OH, NH), 3050 (aromatic CH), 1700-1650 (C = O), 1570 (C = N), 1000 and 950 (phenyl groups); UV 200 and 300.

RESULTS AND DISCUSSIONS

3-Hydrazino-5, 6-diphenyl-1, 2 ,4-triazine (I) condensed with aldehydes and ketones to give the monohydrazones (IIa-e). Treatment of IIa with chloroacetyl chloride in dry benezene-triethylamine [5] gave l-(5,6-diphenyl-1, 2, 4-triazine-3-yl)-3-aryl-4-chloro-2H, 3H, 4H-pyrazol-5-one (III), while addition of mercaptoacetic acid to IIa ane further condensation furnished 3-(substituted amino)-thiazolidin-4-one (IV). The structure of IV was established from IR, UV and PMR spectral data. Michael addition of acetylaceton [6] to IIb in the presence of ethanol-piperidine gave the product V which on treatment with hydrazine hydrate afforded 3, 5-dimethyl-4-substituted methyl-2H-pyrazole (VI).

On the other hand, refluxing IIc with glacial acetic acid led to the direct formation 1-(substituted)-3-cyanomethyl-6-methyl-4H-1, 2, 4, 5-tetrazine (VII), while acidic hydrolysis of its using dil. HCl, 3-hydrazone-1H, 2H-pyrazolin-5-one (VIII) was isolated.

Heating IId with AC_2O-pyridine yielded 1, 2, 4-triazino [4, 3-b] [1, 2, 4] triazine derivative (IX). Treatment of IIe with mercaptoacetic acid in the presence of dry benzene-fused Na_2SO_4, thiazolidin-4-one of the type X was obtained, however aryl thioether XI was produced from fusion of IIe with *p*-chlorothiophenol at 200° for 8 hr.

The reaction of 1, 2, 4-triazine I with ∝-oxo esters, indicated that the course of this reactions is governed by the reactivity of the neighbouring groups of the ester and the type of medium used. Thus, 3-(1 monoacyl) hydrazino-5, 6-diphenyl-1, 2, 4-triazines (XIIa, b) were obtained from the reaction of I with ethylpyruvate and diethyl-malonate in dry benezene. Condensation of XIIa with semicarbazide hydrochloride gave the semicarbazone XIIc which underwent cyclization by boiling with sq. sodium hydroxide gave 5-substituted hydrazino-6-methyl-1, 2, 4-triazin-3-one (XIII), while saponification of XIIb afforded substituted acetic acid (XIId) which on heating with glacial acetic acid [7] fused Na_2SO_4 gave 1, 2, 4-triazipeneone [4, 3-b] [1, 2, 4] triazine derivative (XIV). Moreover fusion of XIIb with hydrazine hydrate gave 3-substituted-1-Hydrazolin-5-one(XV).

Cyclocondensation of XIIb with salicylaldehyde in the presence of piperidine-ethanol led to the direct formation of 3-substituted coumarin (XIIe). The reaction of I with ethyl pyruvate [8] in the presence of sodium ethoxide resulted in the formation 3-methyl-7, 8-diphenyl-1, 2, 4-triazino [4, 3-b] [1, 2, 4] triazin-4 (H) one (XVI). The structure of XVI was confirmed from UV and IR spectral studies. Its uv spectra showed an intense band at 350 and another less prominent band in the lower wavelength of 250 nm. This is in good agreement with the observation of Dunwell [10] and Rees *et al.* [11], with the 1, 2, 4-triazin-5-one compounds. In addition IR showed bands at 3050 (CH aromatic), 2900 (CH aliphatic), 1700-1650 (C = O), 1560 (C = N), 1480 (def. CH_2) and 1000, 880 (phenyl groups). Acylation of I with p-methoxybenzoyl chloride or p-nitrobenzoyl chloride in DMF gave the monoacyl derivative XIIf,g, dehydration of XIIf with Ac_2 O-pyridine gave the 1,2,4-triazolo [4, 3-b] [1, 2, 4,] triazine derivative (XVII), while fusion of XIIg with hydrazine hydrate, yielded [8]-substituted hydroxyl amine (XIIh).

Addition of cyanoacetic acid to compound I gave 2-(hydrazino)-2-iminopropinic acid (XIIi) which underwent basic cyclization using aq. sodium hydroxide produced 1-(5, 6-diphenyl-1, 2, 4-triazin-3-yl)-3-imino-2H pyrazolin-5-one (XVIII). On the other hand, fusion of I with N-allylthiourea, N-phenylthiourea and salicylamide gave 1, 4-disubstituted thio/semicarbazide (XIIj,k,l) respectively. Cyclization of XIIk with mono-chloroacetic acid led to the direct formation of 2-(hydrazone)-3-phenyl-thiazolidin-4-one (XIX), while dehydration of XIII by heating with Ac_2 O-pyridine gave s-triazolo [4, 3-b] [1, 2, 4] triazine (XX). Finally, reduction of I using zinc dust-glacial acetic acid in the presence of ethanol [11], 4, 5-diphenyl-imidazolin-2-one (XXI) was isolated.

Antibacterial activity. The in vitro antibacterial activity of some new compounds, IIa, IV, X, XI, XIIg, XIIj, XIIk and XIX in 1% methanol was tested by the diffusion method [12], against the gram+ve bacteria *Bacillus subtilis* ATCC 6633 and against *Escherichia coli* as gram-ve bacterium. The presence of methanol caused no visible effect in the bacterial growth. The previous results confirmed the suitability of XI as antibacterial agent against *B. subtilis* and IIa as antibacterial agent *E. coli* while XIIk had agood antibacterial activity against both *B. subtilis* and *E. coli* due to the blocking thiosemicarbazide moiety. An addition almost all the selected compounds, showed promising antibacterial activity (Table 1).

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