SYNTHESIS AND REACTION OF COUNTARIN

#### Pak. j. sci. ind. res., vol. 33, no. 12, December 1990

# SOME REACTIONS OF 3-THIOXO-6 - [2-ACYL/ALKYL AMINOPHENYL]– 1,2,4-TRIAZIN-5(2H,4H) ONES

## R.M. ABDEL-RAHMAN

## Chemistry Department, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

#### (Received June 6, 1989; revised January 21, 1991)

A series of some new 3-thioxo-6-(2- acyl/alkylaminophenyl)-1,2,4-triazin-5-(2H,4H) ones (II,XIV) have been synthesized. Behaviour of these products towards amine, hydrazine, thiosemicarbazide, gl. acetic acid, halogenated acetic acid and acetylenetetrachloride have been discussed. The important bands of the UV absorption, IR spectra and main H<sup>1</sup>-NMR signals are assigned and discussed in relation to molecular structure.

Key words: Acyl/alkylaminophenyl-1,2,4- triazinones.

## Introduction

In continuation of our earlier work on some 3-thioxo-1,2,4- triazine derivatives [1-5] the present work reports the synthesis of some new 3-thioxo-6-(2-acyl/alkylaminophenyl)-5(2H,4H) ones and their reaction with substituted amines acetic acid resulting in the formation of fused or condensed 1,2,4-triazine systems.

## Experimental

Melting points reported are uncorrected. UV spectra were recorded in ethanol on a Perkin Elmer (Type 550 S)UVvis spectrophotometer ( $\lambda_{max}$  in nm). IR spectra in KBr were recorded on a Pye Unicam SP 1100 spectrophotometer ( $U_{max}$  in cm<sup>-1</sup>) and PMR spectra in CDCl<sub>3</sub> on varian EM-390 90 MHz NMR spectrometer using TMS as internal standard ( $\delta = 0$  ppm). Compound I was prepared by the procedure described by Doleschal *et al.* [6].

3-Thioxo-6-(2-acylaminophenyl)-1,2,4-triazin-5(2H,4H)ones (IIa-e). An equimolar mixture of I and the appropriate acid chloride with a few drops of dry pyridine was refluxed for 5 min. cooled and acidified with dil. HCl. The solid obtained was filtered and recrystallized from the proper solvent to give IIa-e (Table 1); UV (IId) $\lambda_{max}$  465, 240 and 195.

Aminolysis of IIa-formation of IIIa-c. An equimolar mixture of IIa and the appropriate primary aromatic amine in

dry benzene (100 ml) was refluxed for 1 hr, cooled and the solid obtained filtered and recrystallized to give IIIa-c (Table 1); IR(IIIa): 3550(OH),  $3450(NH_2)$ , 3380, 3310, 3280, 3180 (NH), 1690 (C=O cyclic), 1650-1630 (CO-NH), 1610 (def. NH), 1350 (NCSN) and 1160 (C=S); IIIc: 3520(OH), 3450, 3350, 3300, 3200 (NH), 1700 (C=O cyclic), 1640 (CO-NH), 1470 (def. CH<sub>2</sub>), 1350 (NCSN), 1170 (C-S).

2-(Arylamino)-3H(benzimidazole)(IV). A mixture of IIIa (0.01 mol) and sodium ethylate (0.01 mol, 0.23 gm Na in 50 ml abs. ethanol) was heated under reflux for 1 hr, cooled, acidified with dil. HCl and the resultant solid filtered and recrystallized gave IV (Table 1); IR: 3400 (OH), 3310, 3280, and 3180 (NH), 1710-1670 (C=O), 1610, 1580 (C=N), 1450 (imidazole), 1150-1130 (C=S) and 850 (phenyl).

3-Substituted amino-6-(2-substituted aminophenyl)-1,2,4-triazin-5(4H) one(V). A mixture of IIa (0.01 mol) and 2-aminothiophenol (0.02 mol) was heated at 130-150° in an oil-bath for 1 hr. The solid obtained was triturated with methanol to give V (Table 1), IR(V): 3380, 3290 and 3180 (NH), 3020 (CH aromatic) 2600 (SH), 1700 (cyclic C=O), 1670 (acyclic C=O) [7], 1610, 1580 (C=N), 1470-1450 (NH-CO- NH), and 1020, 970, 940, 870, 850 (phenyl groups).

Reaction of 2,4-dinitrophenylhydrazine with IIa-formation of 1,4- disubstituted semicarbazide (VI). A mixture of IIa(0.01 mol) and 2,4-dinitrophenylhydrazine (0.01 mol) in

	IIa	II . Younes,	lc	1	IId	
IR:	3450(OH), 3380, 3300, 3200 (NH),	3500(HO), 3380	, 3290, 3	190(NH)	3600 3450 (OH), 3390 (OH cyclic), 3240	-
	2990 (CH <sub>3</sub> ), 1680 (C=O cyclic),	1710(C=0 cyclic	), 1640(0	CO-NH)	3090 (NH), 1720 (C=O cyclic), 1650	
	1650(CO-NH), 1470 (def. CH) 1550, 1350(NO <sub>2</sub> )		), 1140(C	C=S)	(CO-NH), 1350 (NCSN), 1180 (C=S). 1050, 1000, 9000 (substituted phenyl).	
	and 1170 (C=S).	1020 (substituted phenyl)		Pharm		
PMR	: 2.5(t,3H, CH <sub>3</sub> ), 3.8(q,2H, CH <sub>2</sub> ), 7-7.2 (m,4H	,ph), 2 g	PMR:	6.7-7.1(m,4	H,phenyl), 7.3-7.5 (d,2H, trihydroxyphenyl),	
	8.7 (s,1H, OH, cyclic),	(1973).		7.8 (s,1H,	OH acyclic)	
Па	9.2 (s, 1H, NH-COOEt), 11.2, 12.4(s,1H,NH)		IId	<ul> <li>8-8.4 (m,3H, 3(OH) phenolic), 8.6 (s,1H, OH cyclic),</li> <li>9(A, 1H, NH-CO-R) and 10.6 (s, 1H, NH cyclic) of N<sup>2</sup>-H<sup>4</sup> of 1,2,4- triazine moiety.</li> </ul>		
	of N <sup>2</sup> H 1,2,4-triazine moiety and at 7.7 (s,1H,-C=N acyclic amide).					

DMF (20 ml) was refluxed for 1 hr. cooled and neutralized with dil. HCl. The resultant solid was filtered off and recrystallized to give VI (Table 1); IR: 3400-3300 (NH-NH), 3110-3090 (NH), 1720, 1650 (cyclic and acyclic C=O) [7], 1610, 1580 (C=N), 1520, 1330 (asy. and sy NO<sub>2</sub>), 1140-1100 (C=S).

2-Thioxo-5-aroyl-1,2,4-triazino[5,6-b]indoles (VIIa,b). Compounds IId,e were suspended in gl. acetic acid (100 ml) and refluxed for 3 hr. The solid precipitated after dilution with cold water and were crystallized from the proper solvent to give VIIa,b(Table 1); IR(VIIa): 3550-3050 (broad OH, NH), 1680 (C=0 aroyl), 1630, 1600 (C=N), 1350 (NCSN), 1150 (C-S), 1000, 890, 850 and 800 (substituted phenyl).

Addition of substituted thioisocyanates to I-formation of 1,3-disubstituted thioures (VIII). Compound I (0.01 mol) was suspended in DMF (20 ml) and the appropriate substituted thioisocyanate (0.01 mol) was added. The reaction mixture was refluxed for 1 hr. and then cooled. The solids precipitated after dilution with cold water and were recrystallized from the proper solvent to give VIIIa,b (Table 1); IR(VIIIa): 3520 (OH), 3410, 3340, 3280, 3180 (NH), 2800 (CH,), 1700-1670 (C=O), 1620, 1590 (C=N, C=C), 1500 1460 (def. CH\_), 1350 (NCSN), 1200, 1150 (C=S); IR(VIIIb): 3570(OH), 3470, 3380, 3300, 3200(NH), 1710-1680 (C=O), 1630, 1600 (C=N), 1350(NCSN), 1210, 1160, 1140 (C-S). PMR(VIIIa [8]: 2,6(d,2H,CH,), 3.4 (m,2H,CH,), 5.5- 6.1 (t,1H,CH:) 6.9-7.5(m,4H,phenyl), 7.7-7.8 (d,1H,NH-CH:CH), 8.7 (s,1H,OH cyclic), 9.1 (s,1H,NH-CS), and 11.2 (s,1H,NH) 12.5 (s,1H,NH) of 1,2, 4- triazine ring.

2-Arylidin-5-[2-(thiazolidin-3-yl)phenyl]-3,6-dioxothiazolo [3,2-b][1,2,4] triazine (IX). A mixture of equimolar amounts of VIIIa, 3-nitrobenzaldchyde, monochloroacetic acid and anhyd. sodium acetate (0.05 mol) in gl. acetic (100 ml) was refluxed for 6 hr., cocled and poured onto crushed ice. The solid obtained was filtered off washed several times with cold water and crystallized to give IX(Table 1); IR: 2820 (CH<sub>2</sub>), 1750, 1700 (2 C=O), 1650 (CO-NH cyclic) 1620-1600 (C=N, C=C), 1530 (asy. NO<sub>2</sub>), 1465 (def. CH<sub>2</sub>), 1360 (sy. NO<sub>2</sub>) and 1050, 1020, 900, 835 (substituted phenyl). UV:  $\lambda_{max}$  470, 370, 245 and 195 [9].

Reaction of IIa and IIb with thiosemicarbazide - formation of  $N^1$  substituted thiosemicarbazides X and XI. Compound IIa or IIb (0.01 mol) and thiosemicarbazide (0.01 mol, in hot water) in DMF (50 ml) was refluxed for 1 hr., cooled and acidified with very dil. HCl. The solid obtained was recrystallized to give X or XI respectively (Table 1); IR(X): 3550 (OH), 3450 (NH<sub>2</sub>), 3390-3300, 3220, 3170 (NH- NH), 1680 (C=O cyclic), 1630 (CO-NH), 1600 (def. NH<sub>2</sub>), 1350 (NCSN), 1170-1140 (C- S) and 850,800 (substituted phenyl); IR(XI): 3450(OH), 3380(NH<sub>2</sub>), 3300, 3220, 3190 (NH-NH), 2810 (CH<sub>2</sub>), 1710-1680 (C=O cyclic), 1630 (C=O-NH), 1600(def. NH<sub>2</sub>), 1480 (def. CH<sub>2</sub>), 1350 (NCSN), 1210, 1150 (C-S) and 900, 850 (substituted phenyl).

*Basic cyclization of X and XI - formation of XII and XIII*. To X or XI (2 gm) aq. solution of sodium hydroxide (10%, 100 ml) was added. The reaction mixture was refluxed for 4 hrs., cooled, neutralized with very dil. HCl and the precipitated solid was recrystallized to give XII and XIII respectively (Table 1);*IR(XII)*: 3300-3100 (broad OH,NH), 1650(C=O), 1590 (C=N), 1350 (NCSN), 1210, 1170 (C-S) and 1000, 850, 800 (substituted phenyl).*IR(XIII)*: 3500-3400 (broad OH,NH), 3380-3120 (NH-NH), 2900 2800 (CH<sub>2</sub>), 1720(C=O), 1620, 1590 (C=N), 1470 (def. CH<sub>2</sub>), 1350 (NCSN), 1220, 1180

TABLE 1. PHYSICAL AND ANALYTICAL DATA OF THE NEW

COMPOUNDS.									
Compound	I. Crystalized	M. P.	Yield	Mol. formula <sup>+</sup>					
No.	from	[°C]	(%)						
IIa	Ethyl benezn	245-46	70	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> S O <sub>3</sub>					
IIb	Me OH	235-37	60	C1, H, N, S CIO,					
IIc	Et OH	205-07	60	C, H, N, SO					
IId	Et OH	295-96	70	C16 H12 N4 SO					
IIe	Me OH	238-40	70	C, H, N, SO,					
Ша	Et OH	260-61	65	C <sub>16</sub> H <sub>14</sub> N <sub>6</sub> SO <sub>2</sub>					
IIIb	Aceton	254-55	60	C, H, N, S,O,					
IIIc	Et OH	249-50	60	C16 H14 N6 SO					
IV	Ac OH	242-45	70	C <sub>16</sub> H <sub>12</sub> N <sub>6</sub> SO					
V	Et OH	120-122	50	C, H, N, S, O,					
VI	DMF	ab. 300	60	C16 H1, N. S O6					
VIIa	Ac OH	ab. 300	80	CIE HIN SO					
VIIb	AcOH	255-56	76	C10 H16 NAS OA					
VIIIa	Ethyl benzen	260-62	85	C., H., N. S. O					
VIIb	Et Oh	265-67	90	C. H. N. S.O					
IX	DMF	185-86	60	C, H, N, S,O,					
X	Et OH	199-200	70	C., H., N. S.O.					
XI	Et OH	248-50	65	C, H, N, S,O,					
XII	Me OH	ab. 300	60	C, H, N, S,O					
XIII	Me OH	ab. 300	50	C, H, N, S,O					
XIVa	Et OH	220-22	60	C., H., N. SO.					
XIVb	Me OH	235-36	60	C., H., N. SO,					
XIVc	Et OH	255-56	75	C, H, N, SO,					
XIVd	Me OH	245-46	70	C., H., N. S.O.					
XIVe	Et OH	224-25	75	C., H., N. S.O.					
XV	Dil. Et OH	155-56	67	C, H, N, SO,					
XVIa	Ac OH	259-60	60	C. H. N. S.O.					
XVIb	Ac OH	225-26	75	C., H., N. S.O.					
XVIIa	Ac OH	190-92	60	C. H. N. S.O.					
XVIIb	Et OH	185-86	67	C. H. N. S.O.					
XVIIIa	Me OH	250-51	50	C., H., N. S.O.					
XVIIIb	Et OH	210-12	60	C.H.N.S.O.					
XIX	Et OH	189-90	80	C., H., N. SO.					
XX	Et OH	225-26	75	C., H., N. SO.					
XXI	DMF	289-300	90	C H N S.O.					

\*All the new compounds gave satisfactory C, H, N, S and Cl analysis.

(C-S) and 1010, 870, 800 (substituted phenyl).

3-Thioxo-6-(2-alkylaminophenyl)-1,2,4-triazin-5(2H,4H)ones (XIVa-e) An equimolar mixture of I and the appropriate alkyl halides in sodium ethylate and left overnight. The solid obtained was filtered, dried and crystallized from the proper solvent to give XIVa-e (Table 1).

*IR(XIVa)* 3450 (OH), 3390, 3200, 3100(NH), 2900 (CH<sub>2</sub>), 1720, 1640 (2 C=O), 1600 (C=N), 1470 (def. CH<sub>2</sub>), 1350(NCSN), 1145 (C=S) and 890, 860, 795 (substituted phenyl).

IR(XIVb) 3600-3400 (broad OH,NH), 3250, 3200, 3070 (NH,NH), 2790 (CH<sub>2</sub>), 1720-1700 (C=O), 1620 (C=N), 1540, 1330 (NO<sub>2</sub>), 1460 (def. CH<sub>2</sub>), 1350 (NCSN), 1180 (C=S) and 1030, 900, 800 (substituted phenyl).

IR(XIVc) 3570-3470 (broad OH), 3380, 3300, 3200 (NH), 2900 (CH<sub>2</sub>), 1700, 1680 (2 C=O), 1630, 1600 (C=N), 1485 (def, CH<sub>2</sub>), 1350 (NCSN), 1150 (C=S) and 890, 860, 790 (substituted phenyl).

IR(XIVd) 3430(OH), 3380, 3290, 3190 (NH), 1700-1670 (C=O), 1630, 1600 (C=N, C=C), 1370-1340 (SO<sub>2</sub>), 1170(C=S), 1060 (S=O) and 890, 850, 785 (substituted phenyl).

*PMR(XIVc)* 3.4-3.6(d,2*H*,CH<sub>2</sub>), 6.8-7.5 (m, 6*H*, aromatic protons), 7.6-7.8 (d, 2*H*, 2HO,m,m,C<sub>6</sub>H<sub>2</sub>), 8.7 (s,1H,OH,  $p-C_6H_2$ ), 9.1, 11.0 and 12.3 (s,*1H*,NH of 1,2,4-triazine and NH of ArNH-CO-Ar).

UV of XIVc :  $\lambda_{max}$  355, 300, 260, 240 and 190.

1,2-Disubstituted hydrazine (XV). A mixture of XIVe (0.01 mol) and 2,4-dinitrophenylhydrazine (0.01 mol) in isopropanol (100 ml) was heated under reflux for 6 hrs and the solvent removed to give a solid which on recrystallization afforded XV (Table 1); IR: 3300-3200 (NH-NH), 3100-3080(NH), 1700-1600 (cyclic C=O), 1660-1640 (-CO-NH acyclic), 1610-1580 (C=N), 1530, 1340 (NO<sub>2</sub>) and 1380 (SO<sub>2</sub>).

Acidic cyclization of XIVd,e-formation of XVIa,b. A mixture of XIVd or XIVe (0.01 mol) and gl. acetic acid (100 ml) was heated under reflux for 2 hr, cooled, diluted with cold water and filtered. The solid obtained was crystallized from a proper solvent to give XVIa or XVIb (Table 1); IR(XVIa): 3250-3150 (NH), 1620, 1580 (C=N), 1350 (SO<sub>2</sub>), 1140 (C=S) and 890, 850, 800 (phenyls).

Cyclocondensation of XIVd, e with m-nitrobenzaldehyde and monochloroacetic acid - formation of XVIIa, b. A mixture of XIVd or XIVe (0.01 mol), m-nitrobenzaldehyde (0.01 mol), monochloroacetic acid (0.01 mol) and anhyd. sodium acetate (0.05 mol) in gl. acetic (100 ml) was refluxed for 2 hrs, cooled and poured onto crushed ice. The solid obtained was filtered off washed several times with cold water and crystallized to give XVIIa, b(Table 1); IR(XVIIa): 3400-3200 (NH broad), 2780 (CH), 1750-1700 (2 C=O), 1640-1620 (C=N, C=C), 1550 (asy. NO<sub>2</sub>), 1460 (def, CH), 1360 (SO<sub>2</sub>), 1330 (sy. NO<sub>2</sub>), 1070 (S=O) and 940, 820 (substituted phenyl). *PMR (XVIIa*): 4.2 (s,1H, CH=C), 6.7 (m, 5H,C<sub>6</sub>H<sub>5</sub> SO<sub>2</sub>), 7.2-7.4 (m,4H, C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>), 7.7-8 (m,4H, C<sub>6</sub>H<sub>4</sub>-NH), and 10.2 (s,1H, NH proton). UV (XVIIa):  $\lambda_{max}$  360,245 and 195.

Reaction of XVIId,e with phenylhydrazine-formation of triheterocyclic derivatives (XVIIIa,b). An equimolar mixture of XVIId or XVIIe, phenylhydrazine in pepridine (1 ml) and abs. ethanol (100 ml) was refluxed for 8 hrs, cooled, acidified with dil. HCl and the resultant solid filtered and crystallized gave XVIIIa,b (Table 1); IR(XVIIIa): 3380 (NH), 1730 (C=O), 1630-1610 (C=N), 1560 (asy. NO<sub>2</sub>), 1360 (SO<sub>2</sub>), 1060 (S=O) and 900, 830, 800 (substituted). *PMR(XVIIIa)*: 3(s,1H, of CH pyrazole at C<sub>3</sub>) 3.5-3.6 (S, 1H, pyrazole protone at C<sub>4</sub>) 6.7-7.1 (m, 5H, C<sub>6</sub>H<sub>5</sub> SO<sub>2</sub>), 7.2-7.5 (m, 4H, C<sub>6</sub>H<sub>4</sub> NO<sub>2</sub>), 7.7-8(m, 5H, C<sub>6</sub>H<sub>5</sub>-N), 8.2-8.5 (m,4H, C<sub>6</sub>H<sub>4</sub>-NH-triazine moiety), and 10.5 (s, 1H, NH of substituted amino).

Reaction of I with 1,1-dichloroacetic acid or  $\alpha, \alpha$ -dibromoacetophenone-formation of arylidine derivatives XIX and XX. An equimolar mixture of I and 1,1-dichloroacetic acid or  $\alpha, \alpha$ -dibromoacetophenone in sodium ethylate and left overnight. The solid obtained was filtered, dried and crystallized from the proper solvent to give XIX and XX (Table 1).

Acetylene tetrasubstitutedamino derivative XXI. A mixture of I (0.04 mol) and acetylenetetrachloride (0.01 mol) in ethano pyridine (50:50 ml) was stirred for 2 hrs, cooled, diluted with water and dil. HCl added. The solid precipitated was filtered and crystallized to give XXI (Table 1); UV: 365, 270, 240 and 195.

#### **Results and Discussion**

Acylation of 3-thioxo-6-(2-aminophenyl)-1,2,4-triazin-5 (2H, 4H) one (I) with haloesters and haloacids such as, ethyl chloroformate, chloroacetyl chloride, p-nitrobenzoyl chloride, m,m,p-trihydroxybenzoyl chloride, m,m,p-trimethoxybenzoyl chloride in pyridine led to the formation of 3-thioxo-6-(2-acylaminophenyl)-1,2,4-triazin-5 (2H,4H) ones (IIa-e). Heating IIa with primary aromatic amines such as, o-phenylenediamine, o-amino-thiophenol and o-aminop-methylpyridine in the presence of dry benzene gave 1,3disubstituted ureas (IIIa-c). Cyclocondensation of IIIa by refluxing with sodium ethylate [10] led to the direct formation of 3-thioxo-6-[2-(benzimidazol-2-yl)aminophenyl]-1,2,4triazin-5(2H,4H) one (IV). On the other hand, fusion of IIa with o-amino thiophenol, 3-substituted amino-6-[2-(1,3-disubstituted urea)phenyl]-1,2,4-triazin-5(4H) one (V) was isolated, while treatment of IIa with 2,4-dinitrophenylhydrazine in the presence of DMF gave 1,4-disubstituted semicarbazide (VI). Heating IId, e with gl. acetic acid resulted in the formation of 3-thioxo-5- aroyl[1,2,4] triazino [5,6-b] indoles (VIIa,b).



Acylation of I using substituted thioisocyanates such as, allyl thioisocyanate and phenyl thioisocyanate as acylating agents in the presence of DMF gave 1,3-disubstituted thioureas (VIIIa,b). Reaction of VIIIa with monochloroacetic acid, mnitrobenzaldehyde in the presence of gl. acetic acid-fused sodium acetate [11] led to the direct formation of 2-arylidin-5-[2-(thiazolidin-3-yl) phenyl]-3,6-dioxo-thiazolo[3,2b][1,2,4] triazine (IX).

The reactivity of ethylcarboxylate group in IIa,b promoted us to investigate their behaviour towards the action of thiosemicarbazide followed by alkalin cyclization. Thus, IIa and IIb when heated with thiosemicarbazide in the presence of DMF, produced N<sup>1</sup>-substituted thiosemicarbazide X and XI, while alkalin cyclization of both X and XI using [12] aq. NaOH yielded 3-thioxo-5-substituted amino-s-(1H, 3H) triazole (XII) and 3-thioxo-5- substituted amino-1,2,6-tetrahydro-1,2,4-triazine (XIII) derivatives (Scheme 1).

Alkylation of I with monochloroacetic acid, p-nitrobenzyl chloride, m,m,p-trihydroxy-phenacyl chloride, benzenesulphonyl chloride and p-acetamidobenzenesulphonyl chloride in presence of sodium ethylate [13], 3-thioxo-6-(2-alkylaminophenyl)-1,2,4-triazin-5 (2H,4H) ones (XIVa-e) were obtained. Hydrazinolysis of XIVe with 2,4-dinitro phenylhydrazine in isopropanol gave 3-substitutedh ydrazino-6-(2-substitutedaminophenyl)-1,2,4-triazin- 5(4H) one (XV).

Investigation of the reaction of XIV with acetic acid, halogenatedacetic acid,  $\alpha$ ,  $\alpha$ - dibromoacetophenone and acetylenetetrachloride indicates that the course of this reaction is governed by the medium and the reaction conditions. Thus, 3- thioxo-5-benzenesulphonyl-1,2,4-triazino[5,6-b] indoles (XVIa,b) were obtained from heating of XIVd,e with gl. acetic, while 2- arylidine-3,6-dioxo-5-(2-substitutedaminophenyl) thiazolo[3,2- b][1,2,4] triazines (XVIIa,b) derived from reaction of XIVd,e with monochloroacetic acid, p-nitrobenzaldehyde in the presence of sodium acetate-gl. acetic acid. Cycloaddition of XVII with phenyl- hydrazine in abs. ethanol with a few drops of pipridine [14], furnished the triheterocyclic system XVIIIa,b.

Treatment of I with 1,1-dichloroacetic acid and  $\alpha$ ,  $\alpha$  dibromoacetophenone in sodium ethylate, [15] the arylidenes of the type XIX and XX were isolated. Finally, addition of acetylenetetrachloride to compound I in the presence of DMF at room temperature yielded acetylenetetrasubstituted amino aryl derivative XXI (Scheme 2). The structure of all the compounds prepared have been established by their IR, UV and *PMR* spectral data (Table 1).

Acknowledgement. The authors are grateful to Mr. H.A. Hassan, Department of Chemistry, Faculty of Education, Ain-Shams University, for providing necessary laboratory facilities and UV, IR and NMR spectra.

#### References

- H. Zaher, H. Jahine, M. Saada and R. Mohammady, Pak. j. sci. ind. res., 4, 34 (1982).
- H. Zaher, R. Mohammady and Y.A. Ibrahim, J. Heterocycl. Chem., 21, 905 (1984).
- R.M. Abdel-Rahman and M. Ghareib, Indian J. Chem., 26B, 496 (1987).
- 4. R.M. Abdel-Rahman, Pak. j. sci. ind. res., 30, 490 (1987).
- R.M. Abdel-Rahman and M.S. Abdel-Malik, Pak. j. sci. ind. res., (1990), In Press.
- Doleschal Gabor, Lempert Karoly, Pallos Laszlo, and Simon Klara, Hung Teljes, 1168 (CI CO 7d), 27 Oct. 1970, Appl. 25 June 1969, Chem. Abstr., 74, 88068q (1971).
- R.M. Abdel-Rahman and Z. El-Gendy, Indian J. Chem., 28B, 1072 (1989).
- 8. R.M. Abdel-Rahman, II Farmaco (In press 1990).
- M.T. Omar and R.M. Abdel Rahman, Indian J. Chem., 20B, 849 (198).
- 10. Z. El-Gendy and F. A. Sherif, Indian J. Chem., 28B, 64(1989).
- Z. El Gendy, R.M. Abdel Rahman and M.S. Abdel Malik, Indian J. Chem., 28B, 479 (1989).
- Z. El Gendy, and R.M. Abdel Rahman, Indian J. Chem., 28B, 654 (1989).
- M.J. Ali, A.M. Abdel-Fattah, H.A. Hammouda and S.M. Hussein, Indian J. Chem., 13 (2), 109 (1975).
- 14. R.M. Abdel Rahman, Indian J. Chem., 27B, 548 (1988).
- 15. R.M. Abdel Rahman, Z. El-Gendy and M.M. Fawzy, Asian J. Chem., (1990), In press.