Technology Section

Pak. j. sci. ind. res., vol. 38, no. 1, January 1995

SYNTHESIS OF NITROGENOUS COMPOUNDS. *Part -V*

H.M. MOKHTAR AND O.O. FARAHAT
Chemistry Department, Alexandria University, Alexandria - Egypt

(Received May 24, 1992; revised July 10, 1994)

Condensation of 3,4-disubstituted-but-3-en-2-ones (3) with hydrazines produced the hydrazones (4) which with ethanolic HCl underwent cyclization to the pyrazolines (5). Oxidation of (5) with bromine-water furnished the pyrazoles (6). Similarly, condensation of (3) with acylhydrazines generated the acylhydrazones (7).

Ethyl 6-aryl-2, 4-dioxo-5-substituted hexenoates (8) has been synthesized by condensation of 3,4-disubstituted-but-3-en-2-ones (3) with ethyl oxalate. Esters (8) on reaction with hydroxylamine afforded the isoxazole esters (9), whereas, with acylhydrazines furnished the acylhydrazones (10) which were cyclized to N-acylpyrazoles (11). With hydrazines, compounds (8) underwent cyclization to the pyrazole esters (12) which were converted either to the acids (13; $R^2 = OH$) or to the acid hydrazides (13; $R^2 = NHNH_2$). Reaction of (12; $R' = C_6H_4SO_2NH_2$(p)) with the appropriate isothiocyanate derivatives produced benzenesulphonylthioureas which with ethyl bromoacetate and ethyl β-bromopropionate furnished 2-iminothiazolidinones (15) and 2-iminothiazinones (16) respectively. Moreover, esters (8) with o-phenylenediamine yielded the oxyquinoxalines (17).

Key words: Synthesis, Heterocyclic compounds.

Introduction

Substituted pyrazoles are biologically important compounds and have a wide variety of pharmacological properties [1-5] and many of them possess high hypoglycemic activities [6-15]. The present study which is a continuation of previous work [16-25], describes the preparation of new substituted pyrazolesulphonylthiourea derivatives.

Experimental

Melting points were determined in open glass capillaries and are uncorrected. IR absorption spectra were recorded with a Unicam Sp 3-100 recording spectrophotometer using potassium bromide pellets (υ_{max} in cm^{-1}). U.V. spectra were measured with a Unicam Sp 1750 instrument (λ_{max} in nm) in ethanol and ^1H NMR spectra in $CDCl_3$ were taken with a Varian EM-390-90 MHz instrument. Microanalysis were performed in the Faculty of Science, Assuit University and mass spectra were measured on a Kratos MS 30 instrument.

4-[2-(4-Chlorophenyl)triazol-4-yl]-3-substituted-but-3-en-2-ones(3). Dry hydrogen chloride was passed into a mixture of 2-(4-chlorophenyl)-4-formyltriazole (1 mmol) [25] and ethyl methyl ketone or benzyl methyl ketone (1.2 mmol) at -5°C till saturation. Thereafter, the mixture was left in an ice chest for 48 hrs, treated with water and extracted several times with ether. The combined ether extracts were shaken with dil. NaOH solution till just alkaline, washed repeatedly with water till neutral and dried. Removal of ether gave the desired α,β-unsaturated ketone which recrystallized from benzene-methanol mixture in yellow needles (yield 60%). (Table).

4-[2-(4-Chlorophenyl)triazol-4-yl]-3-substituted-but-3-en-2-one-2-arylhydrazones (4). A mixture of the foregoing ketones (3: 1 mmol) and the appropriate aryl/methylhydrazines (1 mmol) in ethanol (25 ml) was refluxed for 1 hr. Concentration and cooling of the reaction mixture furnished the hydrazone that was recrystallized from methanol in needles, (yield 30-40%) (Table).

1-Aryl-3-methyl-4,5-disubstituted-2-pyrazolines (5). A solution of compound (3: 1 mmol) in ethanol (50 ml) was refluxed with the desired aryl/methylhydrazines (1 mmol) and HCl (0.5 ml) for 3 hrs, then concentrated and cooled. The product was filtered off and recrystallized from ethanol in needles,(yield 30-40%) (Table 1). Furthermore, these pyrazolines (5) were obtained in 60-70% yields when a solution of hydrazone (4: 1 mmol) in ethanol (25 ml) was refluxed with HCl (0.5 ml) for 3 hrs.

1-Aryl-3-methyl-4,5-disubstituted pyrazoles (6). To an aqueous suspension of (5:1 mmol) in water (10 ml), 5% bromine water (30 ml) was gradually added with stirring during 1 hr. and stirring was continued for another 20 hrs. The deposited pyrazole derivative was filtered off, washed successively with water and recrystallized from ethanol in needles, (yield 60-68%) (Table).

4-[2-(4-Chlorophenyl)triazol-4-yl]-3-substituted-but-3-en-2-one-2-acylhydrazones (7). A solution of the α,β-unsaturated ketone (3: 1 mmol) in ethanol (50 ml) was refluxed with the desired acylhydrazine (1 mmol) for 1 hr, worked up as in (4) and recrystallized from benzene-methanol mixture in needles, (yield 30-40%) (Table).

Ethyl 6-[2-(4-chlorophenyl) triazol-4-yl]-2, 4-dioxo-5-substituted-hex-5-enoates (8). A mixture of 4-[2-(4-chlorophenyl) triazol-4-yl]-3-substitute-but-3-en-2-one (3: 1 mmol) and ethyl oxalate (1 mmol) in dry ether (100 ml) was gradually added with shaking to an ice cold suspension of sodium ethoxide (1 mmol) in dry ether (150 ml). After keeping the reaction mixture at room temperature for one day, the separated yellow sodium salt was filtered off, washed with ether dried then acidified with cold dil H_2SO_4. It was recrystallized from benzene-methanol mixture in yellow needles, (yield 65%) (Table).

Ethyl 5-[α-substituted-β-2-(4-chlorophenyltriazol-4-yl) vinyl]-isoxazole-3-carboxylates (9). These compounds were prepared by boiling the foregoing 1,3-diketo ester (8; 1 mmol) in ethanol (20 ml) with hydroxylamine hydrochloride (1 mmol) and sodium acetate (1 mmol) in water (2 ml) for 2 hrs. Upon concentration, cooling the isoxazole ester was separated out and filtered off. It was recrystallized from ethanol in colourless needles, (Yield 50-55%) (Table).

Ethyl 6-[2-(4-chlorophenyl) triazol-4-yl]-2,4-dioxo-5-substituted-hex-5-enoate-2-acylhydrazones (10). An ethanolic solution (50 ml) of the appropriate acylhydrazine (1 mmol) was added to a cold solution of ester (8: 1 mmol); in ethanol (100 ml) containing a few drops of glacial acetic acid and the reaction mixture left at room temperature for 24 hrs. They were recrystallized from chloroform-light petroleum (b.p. 40-60°C) in yellow needles (yield 35-38%) (Table).

Ethyl 1-acyl-5-[α-substituted-β-2-(4-chlorophenyltriazol-4-yl) vinyl] pyrazole-3-carboxylates (11). These compounds were prepared by boiling the foregoing acylhydrazone (10: 1 mmol) with ethanol (100 ml) containing two drops of HCl for 2 hrs. The N-acylpyrazole ester that separated out from the reaction mixture on concentration, cooling and dilution with water was recrystallized from dilute ethanol in red-brown needles (yield 30-40% (Table).

Ethyl 1-H/CH/Aryl-5-[α-substituted-β-2-(4-chlorophenyltriazol-4-yl)vinyl] pyrazole-3-carboxylates (12). An ethanolic solution (50 ml) of the ethyl hexenoate (8: 1 mmol) and the appropriate hydrazine, methyl or arylhydrazines (1 mmol) was refluxed for 3 hr. Upon concentration, cooling the pyrazole ester separated out and was recrystallized from ethanol in needles, (yield 45-55%) (Table).

TABLE

Comp.	R	R[1]	Yield %	m.p. (°C)	Mol. formula	Analyses Calcd/Found C	H	N	U.V. absorption λmax(loge ε)	KBr υ_{max} (cm^{-1})	^{1}H NMR data δ/ppm
3a	CH_3	–	60	148	$C_{13}H_{12}N_3OCl$	59.7	4.6	16.1	204(3.4),	1670(CO),	2.35(S, 3H, C<u>H</u>$_3$CO),
						59.8	4.5	16.0	298(3..6)	1590(C=C)	2.25(s, 3H, CH_3), 7.15-8.05(m,6H,CH=and ArH)
3b	C_6H_5	–	60	136	$C_{18}H_{14}N_3OCl$	66.8	4.3	13.0	206(3.3),	1670(CO),	2.45(s, 3H, C<u>H</u>$_3$CO), 6.45-
						66.8	4.5	12.9	312(3.5)	1595(C=C)	7.9(m,11H,CH= and ArH)
4a	CH_3	CH_3	40	150	$C_{14}H_{16}N_5Cl$	58.0	5.5	24.2	206(3.9)	1595(C=N),	
						58.0	5.7	24.0	298(3.9)	3195(NH)	
4b	CH_3	C_6H_5	35	130	$C_{19}H_{18}N_5Cl$	64.9	5.1	19.9	204(4.2),	1590(C=N),	
						65.5	5.2	20.0	296(4.3)	3170(NH)	
4c	CH_3	$C_6H_4CH_3$(p)	35	161	$C_{20}H_{20}N_5Cl$	65.7	5.5	19.2	204(3.7)	1600(C=N)	
						65.4	5.5	19.2	298(4.1)	3210(NH)	
4d	CH_3	C_6H_4Br(p)	35	140	$C_{19}H_{17}N_5BrCl$	53.1	4.0	16.3	204(3.9),	1600(C=N),	
						52.7	4.4	16.3	298(4.1)	3140(NH)	
4e	CH_3	$C_6H_4NO_2$(p)	30	153	$C_{19}H_{17}N_6O_2Cl$	57.5	4.3	21.2	204(4.3),	1590(C=N),	
						57.2	4.4	21.0	298(4.2)	3110(NH), 890,1335 (NO_2)	
4f	CH_3	$C_5H_4N(O)$	30	138	$C_{18}H_{17}N_6Cl$	61.3	4.8	23.8	206(4.3),	1600(C=N),	
						61.4	4.9	23.8	300(4.2)	3200(NH)	
4g	CH_3	$C_6H_4SO_2NH_2$(p)	30	198	$C_{19}H_{19}N_6O_2SCl$	53.0	4.4	19.5	204(4.1),	1595(C=N),	
						53.0	4.6	19.3	290(4.1)	3195(NH) 1190, 1350 (SO_2)	
4h	C_6H_5	CH_3	35	116	$C_{19}H_{18}N_5Cl$	64.9	5.1	19.9	–	1595(C=N),	
						64.9	5.4	19.8		3190(NH)	

(Continue...)

(Tab. continued)

4i	C_6H_5	C_6H_5	35	147	$C_{24}H_{20}N_5Cl$	69.7	4.8	16.9	206(4.7),	1600(C=N),	
						69.7	4.9	16.7	284(4.5)	3200(NH)	
4j	C_6H_5	$C_6H_4CH_3(p)$	30	158	$C_{25}H_{22}N_5Cl$	70.2	5.2	16.4	204(4.5),	1590(C=N),	
						70.0	5.5	16.3	312(4.6)	3220(NH)	
4k	C_6H_5	$C_6N_4Br(p)$	30	155	$C_{24}H_{19}N_5BrCl$	58.6	3.9	14.2	–	1600(C=N0,	
						58.6	4.2	14.0		32000(NH)	
4l	C_6H_5	$C_6H_4NO_2(p)$	35	161	$C_{24}H_{19}N_6O_2Cl$	62.8	4.1	18.3	211(4.4),	1595(C=N),	
						62.9	4.0	18.4	310(4.5)	3210(NH),	
										870, 1340 (NO_2)	
4m	C_6H_5	$C_5H_4N(O)$	40	145	$C_{23}H_{19}N_6Cl$	66.6	4.6	20.3	212(4.3),	1600(C=N),	
						66.6	4.8	20.1	310(4.4)	32000(NH)	
4n	C_6H_5	$C_6H_4SO_2NH_2(p)$	35	172	$C_{24}H_{21}N_5O_2SCl$	60.2	4.4	14.6	214(4.5),	1590(C=N),	
						60.0	4.6	14.6	312(4.6)	3190(NH),	
										1180, 1335	
										(SO_2N)	
5a	CH_3	CH_3	36	115	$C_{14}H_{16}N_5Cl$	58.0	5.5	24.2	215(4.4),	2900(C-H)	
						57.8	5.5	24.6	280(4.6)		
5b	CH_3	C_6H_5	30	109	$C_{19}H_{18}N_5Cl$	64.9	5.1	19.9	206(3.9),	2905(C-H)	2.15(s,3H,CH_3),2.40(s, 3H,CH_3),4.75(m, 1H,H-4) 5.37(m,1H,H-5) 6.70-8.10 (m, 10H, ArH).
						64.9	5.2	19.8	274(4.0		
5c	CH_3	$C_6H_4CH_3(p)$	35	145	$C_{20}H_{20}N_5Cl$	65.7	5.5	19.2	214(4.6),	2900(C-H)	
						65.5	5.7	19.0	282(4.8)		
5d	CH_3	$C_6H_4Br(p)$	35	130	$C_{19}H_{17}N_5BrCl$	53.1	4.0	16.3	206(3.3),	2905(C-H)	2.13(s,3H,CH_3), 2.42 (s, 3H,CH_3),4.72(m,1H,H-4), 5.40(m,1H,H-5),7.05-8.12 (m, 9H, ArH).
						53.0	4.4	16.3	300(3.5)		
5e	CH_3	$C_6H_4NO_2(p)$	30	171	$C_{19}H_{17}N_6O_2Cl$	57.5	4.3	21.2	204(4.0,	2910(C-H),	
						57.1	4.5	21.3	286(4.1)	870, 1355	
										(NO_2)	
5f	CH_3	$C_5H_4N(O)$	35	119	$C_{18}H_{17}N_6Cl$	61.3	4.8	23.8	212(4.5),	2900(C-H)	
						61.0	4.9	23.6	279(4.6)		
5g	CH_3	$C_6H_4SO_2NH_2(p)$	30	235	$C_{19}H_{19}N_6O_2SCl$	53.0	4.4	19.5	213(4.9),	2905(C-H),	
						52.7	4.6	19.5	292(4.9)	1145, 1300	
										(SO_2N)	
5h	C_6H_5	CH_3	35	99	$C_{19}H_{18}N_5Cl$	64.9	5.1	19.9	214(4.6),	2900(C-H)	2.40(s,3H,CH_3), 3.90 (s,3H,N-$C\underline{H}_3$),4.15(m,1H, H-4),5.40(m,1H,H-5), 6.65-8.10(m,10H,ArH)
						64.8	5.5	19.9	312(4.8)		
5i	C_6H_5	C_6H_5	35	127	$C_{24}H_{20}N_5Cl$	69.7	4.8	16.9	216(4.3),	2850(C-H)	
						69.8	4.8	16.7	280(4.4)		
5j	C_6H_5	$C_6H_4Br(p)$	35	119	$C_{24}H_{19}N_5BrCl$	58.6	3.9	14.2	217(4.4),	2900(C-H)	
						58.3	4.0	14.3	315(4.5)		
5k	C_6H_5	$C_6H_4NO_2(p)$	30	147	$C_{24}H_{19}N_6O_2Cl$	62.8	4.1	18.3	214(4.5),	2900(C-H),	
						62.6	4.2	18.3	308(4.3)	870, 1345	
										(NO_2)	
5l	C_6H_5	$C_6H_4SO_2NH_2(p)$	35	159	$C_{24}H_{21}N_5O_2SCl$	60.2	4.4	14.6	214(4.3),	2900(C-H),	
						60.1	4.6	14.5	290(4.3)	1165, 1335	
										(SO_2N)	
6a	CH_3	C_6H_5	60	93	$C_{19}H_{16}N_5Cl$	65.2	4.6	20.0	204(4.2),		2.02(s,3H,CH_3), 2.30 (s,3H,CH_3), 6.55-8.12 (m, 10H, ArH)
						64.9	4.7	20.1	270(4.2)		

(Continue...)

(Tab. continued)

6b	CH_3	$C_6H_4Br(p)$	65	100	$C_{19}H_{15}N_5BrCl$	53.3	3.5	16.4	206(4.6),		2.28(s,3H,CH_3), 2.52(s,
						53.0	3.5	16.6	302(4.9)		3H,CH_3), 7.16-8.12
											(m, 9H, ArH).
6c	CH_3	$C_6H_4SO_2NH_2(p)$	60	166	$C_{19}H_{17}N_6O_2SCl$	53.2	4.0	19.6	204(4.1),	1190, 1345	
						52.9	4.4	19.7	286(4.2)	(SO_2N).	
6d	C_6H_5	C_6H_5	60	87	$C_{24}H_{18}N_5Cl$	70.0	4.4	17.0	206(3.9),		2.42(s,3H,CH_3), 7.12-
						70.0	4.6	16.8	312(4.0)		8.15(m, 15H, ArH).
6e	C_6H_5	$C_6H_4Br(p)$	66	106	$C_{24}H_{17}N_5BrCl$	58.8	3.5	14.3	206(4.4),		2.40(s, 3H, CH_3), 7.05-
						58.7	3.5	14.4	286(4.3)		8.05(m, 14H, ArH).
6f	C_6H_3	$C_6H_4SO_2NH_2(p)$	68	183	$C_{24}H_{19}N_6O_2SCl$	58.7	3.9	17.1		1170, 1335	
						58.7	4.2	17.0		(SO_2 N)	
7a	CH_3	C_6H_5	35	175	$C_{20}H_{18}N_5OCl$	66.0	5.0	19.3	204(3.9),	1605(C=N)	
						66.1	5.3	19.2	233(2.7),	1645(CO),	
									323(4.0)	3200(NH)	
7b	CH_3	$C_6H_4CH_3(p)$	35	200	$C_{21}H_{20}N_5OCl$	64.0	5.1	17.8	–	1595(C=N)	
						63.8	5.3	17.5		1650(CO),	
										3210(NH)	
7c	CH_3	$C_6H_4Cl(p)$	40	193	$C_{20}H_{17}N_5OCl_2$	58.0	4.1	16.9	206(3.8),	1600(C=N)	
						57.8	4.3	17.0	232(3.7),	1660(CO),	
									310(3.3)	3200(NH)	
7d	CH_3	$C_6H_4Cl(m)$	35	165	$C_{20}H_{17}N_5OCl_2$	58.0	4.1	16.9	204(3.7),	1600(C=N)	
						57.7	4.5	16.9	230(3.6),	1650(CO),	
									270(3.2)	3210(NH)	
7e	CH_3	$C_6H_4NH_2(p)$	30	210	$C_{20}H_{19}N_6OCl$	60.8	4.8	21.3	204(4.4),	1600(C=N)	
						61.0	4.9	21.3	212(4.4),	1655(CO),	
									328(4.7)	3220(NH)	
7f	CH_3	$C_6H_4NO_2(p)$	35	222	$C_{20}H_{17}N_6O_3Cl$	56.5	4.0	19.8	203(4.2),	1690(C=N)	
						56.1	4.4	19.6	265(4.1)	1660(CO),	
										3300(NH),	
										860, 1345 (NO_2)	
7g	C_6H_5	C_6H_5	36	203	$C_{25}H_{20}N_5OCl$	68.0	4.5	15.9	203(4.0),	1600(C=N)	
						67.8	4.8	16.0	228(3.9),	1675(CO),	
									300(3.4)	3190(NH)	
7h	C_6H_5	$C_6H_4CH_3(p)$	34	197	$C_{26}H_{22}N_5OCl$	68.5	4.8	15.4	204(3.8),	1605(C=N),	
						68.2	4.9	15.4	228(3.8),	1650(CO),	
									306(3.3)	3200(NH)	
7i	C_6H_5	$C_6H_4Cl(p)$	30	230	$C_{25}H_{19}N_5OCl_2$	63.0	4.0	14.7	204(4.1),	1695(C=N),	
						63.0	4.4	14.6	228(4.0),	1645(CO),	
									306(3.6)	3190(NH)	
7j	C_6H_5	$C_6H_4Cl(m)$	30	187	$C_{25}H_{19}N_5OCl_2$	63.0	4.0	14.7	206(3.9),	1605(C=N),	
						63.2	3.8	14.7	234(3.9),	1650(CO),	
									302(3.5)	3195(NH)	
7k	C_6H_5	$C_6H_4NH_2(p)$	35	225	$C_{25}H_{21}N_6OCl$	65.7	4.6	18.4	206(3.5),	1600(C=N),	
						65.7	4.6	18.2	234(3.6),	1645(CO),	
									300(3.2)	3200(NH)	
7l	C_6H_5	$C_6H_4NO_2(p)$	33	241	$C_{25}H_{19}N_6O_3Cl$	61.7	3.9	17.3	205(4.5),	1600(C=N),	
						61.6	4.0	17.3	313(4.6)	1645(CO),	
										3200(NH).	
										860,1340(NO_2)	
8a	CH_3	–	65	104	$C_{17}H_{16}N_3O_4Cl$	56.4	4.4	11.6	204(3.9),	1730(CO),	1.28(t,3H,$CH_2C\underline{H}_3$),
						56.2	4.6	11.5	294(3.9)	3480(OH)	2.38(s,3H,CH_3), 4.25
											(q,2H,$C\underline{H}_2CH_3$),6.67(s,

(Continue...)

(Tab. continued)

											1H, =CH),7.07-7.88(m, 7H, CH=, OH and ArH)
8b	C_6H_5	–	60	119	$C_{22}H_{18}N_3O_4Cl$	62.3 62.3	4.3 4.6	9.9 9.7	202(3.7), 310(3.8)	1730(CO), 330(OH)	1.28(t,3H,CH_2CH_3), 4.26(q.2H,CH_2CH_3), 6.43 (s,1H,CH=), 7.01-7.98 m, 12H, CH=, OH and ArH)
9a	CH_3	–	50	148	$C_{17}H_{15}N_4O_3Cl$	56.9 56.9	4.2 4.4	15.6 15.4	204(3.4), 298(3.6)	1585(C=C), 1745(CO)	1.21(t,3H,CH_2CH_3), 2.26 (s,3H,CH_3), 3.66 (q, 2H, CH_2CH_3), 7.11-8.00 (m, 7H, ArH).
9b	C_6H_5	–	50	170	$C_{22}H_{17}N_4O_3Cl$	62.8 62.6	4.0 4.4	13.3 13.1	206(3.8) 300(3.8)	1580(C=C), 1735(CO)	1.22(t, 3H, CH_2CH_3), 4.12(q,2H,CH_2CH_3), 7.0-8.00(r, 12H, ArH).
10a	CH_3	C_6H_5	37	180	$C_{24}H_{22}N_5O_4Cl$	60.1 60.1	4.6 4.4	14.6 14.4	–	1640,1720 (2CO) 3200 (NH)	
10b	CH_3	$C_6H_4CH_3$(p)	38	175	$C_{25}H_{24}N_5O_4Cl$	60.8 60.7	4.9 5.1	14.2 14.0	210(4.6), 320(4.7)	1645,1715(2CO) 3200(NH)	
10c	CH_3	C_6H_4Cl(p)	36	201	$C_{24}H_{21}N_5O_4Cl_2$	56.0 56.1	4.1 4.3	13.6 13.7	211(4.4), 316(4.5)	1650,1715(2CO) 3225(NH)	
10d	C_6H_5	C_6H_5	35	179	$C_{29}H_{24}N_5O_4Cl$	64.3 64.3	4.4 4.3	12.9 13.0	204(3.4), 326(3.5)	1630,1725(2CO) 3220 (NH)	
10e	C_6H_5	$C_6H_4CH_3$(p)	38	143	$C_{30}H_{26}N_5O_4Cl$	64.8 64.8	4.7 4.9	12.6 12.3	206(4.2), 324(4.3)	1640,1720(2CO) 3200(NH)	
10f	C_6H_5	C_6H_4Cl(p)	38	164	$C_{29}H_{23}N_5O_4Cl_2$	60.4 60.1	4.0 4.3	12.2 12.0	206(3.9), 326(4.1)	1630,1715(2CO) 3190(NH)	
11a	CH_3	C_6H_5	40	161	$C_{24}H_{20}N_5O_3Cl$	62.4 62.2	4.3 4.6	15.2 15.2	206(4.0), 300(4.1)	1690,1730(2CO)	
11b	CH_3	$C_6H_4CH_3$(p)	36	156	$C_{25}H_{22}N_5O_3Cl$	63.1 62.9	2.6 2.8	14.7 14.7	204(3.9), 280(4.0)	1655,1725(2CO)	
11c	CH_3	C_6H_4Cl(p)	35	176	$C_{24}H_{19}N_5O_3Cl_2$	58.1 58.0	3.8 3.8	14.1 14.3	204(3.8), 280(3.9)	1695,1730(2CO)	
11d	C_6H_5	C_6H_5	30	163	$C_{29}H_{22}N_5O_3Cl$	66.5 66.4	4.2 4.4	13.4 13.4	204(4.4), 314(4.3)	1690,1725(2CO)	
11e	C_6H_5	$C_6H_4CH_3$(p)	35	122	$C_{30}H_{24}N_5O_3Cl$	67.0 67.0	4.5 4.6	13.0 13.0	204(4.3), 316(4.2)	1690,1725(2CO)	
11f	C_6H_5	C_6H_4Cl(p)	40	140	$C_{29}H_{21}N_5O_3Cl_2$	62.4 62.1	3.8 3.9	12.5 12.4	204(4.3), 316(4.2)	1695,1730(2CO)	
12a	CH_3	H	50	120	$C_{17}H_{16}N_5O_2Cl_2$	57.1 56.9	4.5 4.7	19.6 19.6	206(3.7), 330(3.0	1725(CO), 3190(NH)	1.31(t,3H,CH_2CH_3), 2.10 (s,3H,CH_3), 4.32(q,2H, CH_2CH_3), 6.91-8.05 (m,8H,NH and ArH)
12b	CH_3	CH_3	55	114	$C_{18}H_{18}N_5O_2Cl$	58.1 58.0	4.9 5.2	18.8 18.8	206(3.9), 326(4.0)	1720(CO)	1.32(t,3H,CH_2CH_3), 2.16(s,3H,CH_3),4.1 (s,3H,NCH_3), 4.22 (q, 2H, CH_2CH_3), 6.92-8.12(m, 7H, ArH)
12c	CH_3	C_6H_5	55	143	$C_{23}H_{20}N_5O_3Cl$	63.7 63.5	4.6 4.7	16.2 16.0	204(4.4), 284(4.3)	1715(CO)	1.18(t,3H,CH_2CH_3), 2.12 (s, 3H, CH_3), 4.12 (q, 2H, CH_2CH_3), 6.79-8.1 (m, 12H, ArH).
12d	CH_3	$C_6H_4CH_3$(p)	50	131	$C_{24}H_{22}N_5O_2Cl$	64.4 64.4	4.9 4.7	15.6 15.6	204(4.1), 300(4.2)	1720(CO)	

(Continue...)

(Tab. continued)

12e	CH_3	$C_6H_4Cl(p)$	53	123	$C_{23}H_{19}N_5O_2Cl_2$	59.0 58.8	4.1 4.3	15.0 15.0	206(4.2), 300(4.3)	1730(CO)	
12f	CH_3	$C_6H_4Br(p)$	50	135	$C_{23}H_{19}N_5O_2BrCl$	54.0 54.2	3.7 3.6	13.7 13.6	204(4.2), 300(4.3)	1725(CO)	
12g	CH_3	$C_6H_4NO_2(p)$	55	185	$C_{23}H_{19}N_6O_4Cl$	57.7 57.5	4.0 4.1	176 17.6	204(3.5), 306(3.2)	1735(CO), 1345(NO_2)	
12h	CH_3	$C_5H_4N(O)$	50	142	$C_{22}H_{19}N_6O_2Cl$	60.8 60.8	4.4 4.6	19.3 19.1	–	1720(CO)	
12i	CH_3	$C_6H_4SO_2NH_2(p)$	55	183	$C_{23}H_{21}N_6O_4SCl$	53.9 53.9	4.1 4.2	16.4 16.2	–	1725(CO),1130, 1175(SO_2N)	
12j	CH_3	Phthalazinyl	50	190	$C_{25}H_{20}N_7O_2Cl$	61.8 61.7	4.1 4.1	20.2 20.1	204(3.7), 300(3.3)	1725(CO)	
12k	C_6H_5	H	50	130	$C_{22}H_{18}N_5O_2Cl$	62.9 63.1	4.3 4.4	16.7 16.6	204(3.8), 316(3.8)	1720(CO), 3300((NH)	1.37(t,3H,$CH_2\underline{CH_3}$), 4.35 (q,2H,$\underline{CH_2}CH_3$), 6.36-8.18(m,13H,NH and ArH)
12l	C_6H_5	CH_3	50	97	$C_{23}H_{20}N_5O_2Cl$	63.7 63.5	4.6 4.9	16.2 16.0	220(4.9), 301(4.9)	1715(CO)	1.30(t,3H,CH_2CH_3), 4.12 (s,3H,N-CH_3), 4.20 (q,2H,$\underline{CH_2}CH_3$), 6.52-8.15 (m, 12H, ArH)
12m	C_6H_5	C_6H_5	55	144	$C_{28}H_{22}N_5O_2Cl$	67.8 67.8	4.4 4.5	14.1 14.0	206(4.8), 280(4.7)	1725(CO)	1.30(t,3H,$CH_2C\underline{H}_3$), 4.32 (q,2H,CH_3CH_2), 6.72-8.10 (m, 18H, ArH)
12n	C_6H_5	$C_6H_4CH_3(p)$	48	130	$C_{29}H_{24}N_5O_2Cl$	68.3 68.0	4.7 4.9	13.7 13.9	–	1715(CO)	
12o	C_6H_5	$C_6H_4Cl(p)$	50	145	$C_{28}H_{21}N_5O_2Cl_2$	63.4 63.0	4.0 4.2	13.2 13.3	204(4.4), 310(4.4)	1725(CO)	
12p	C_6H_5	$C_6H_4Br(p)$	45	128	$C_{28}H_{21}N_5O_2BrCl$	58.6 58.6	3.7 3.9	12.2 12.1	204(4.4), 308(4.4)	1715(CO)	
12q	C_6H_5	$C_6H_4NO_2(p)$	48	173	$C_{28}H_{21}N_6O_4Cl$	62.2 62.0	3.9 3.9	15.5 15.6	204(3.8), 304(3.6)	1735(CO),870 1380(NO_2)	
12r	C_6H_5	$C_5H_4N(O)$	50	128	$C_{27}H_{21}N_6O_2Cl$	65.3 65.1	4.2 4.4	16.9 16.9	215(4.5), 312(4.6)	1725(CO)	
12s	C_6H_5	$C_6H_4SO_2NH_2(p)$	50	180	$C_{28}H_{23}N_6O_4SCl$	60.4 60.3	4.1 4.4	15.1 15.0	204(4.2), 304(4.1)	1725(CO),1165 1335(SO_2N)	
12t	C_6H_5	Phthalazinyl	45	200	$C_{30}H_{22}N_7O_2Cl$	65.8 65.8	4.0 4.3	17.9 17.8	206(4.2), 308(3.9)	1730(CO)	

Comp.	R	R[1]	R[2]	Yield (%)	m.p. (°C)	Mol. formula	Analyses Calcd/found C	H	N	KBr υ_{max}(cm^{-1})	[1]H NMR data δ/ppm
13a	CH_3	H	OH	60	157	$C_{15}H_{12}N_5O_2Cl$	54.6 54.6	3.6 3.7	21.2 21.0	1730(CO), 3320(OH),	
13b	CH_3	CH_3	OH	65	146	$C_{16}H_{14}N_5O_2Cl$	55.9 56.6	4.1 4.1	20.4 20.3	1725(CO), 3310(OH)	
13c	CH_3	C_6H_5	OH	60	169	$C_{21}H_{16}N_5O_2Cl$	62.2 62.0	4.0 4.3	17.3 17.3	1735(CO), 3390(OH)	
13d	CH_3	$C_6H_4CH_3(p)$	OH	63	177	$C_{22}H_{18}N_5O_2Cl$	62.9 62.9	4.3 4.5	16.7 16.6	1730(CO), 3350(OH)	
13e	CH_3	$C_5H_4N(O)$	OH	65	189	$C_{20}H_{15}N_6O_2Cl$	59.0 58.8	3.7 3.8	20.7 20.7	1730(CO), 3360(OH)	
13f	CH_3	$C_6H_4SO_2NH_2(p)$	OH	65	204	$C_{21}H_{17}N_6O_4SCl$	52.0 51.9	3.5 3.7	17.3 17.4	1715(CO), 3330(OH),1130 1165(SO_2N)	

(Continue...)

(Tab. continued)

13g	C_6H_5	H	OH	60	158	$C_{20}H_{14}N_5O_2Cl$	61.3	3.6	17.9	1720(CO),	
							61.5	3.6	17.7	3400(OH)	
13h	C_6H_5	CH_3	OH	65	125	$C_{21}H_{16}N_5O_2Cl$	62.2	4.0	17.3	1725(CO),	
							62.0	4.1	17.0	3380(OH)	
13i	C_6H_5	C_6H_5	OH	70	161	$C_{26}H_{18}N_5O_2Cl$	66.7	3.9	15.0	1705(CO),	
							66.7	3.6	15.1	3500(OH)	
13j	C_6H_5	$C_6H_4CH_3$(p)	OH	65	143	$C_{27}H_{20}N_5O_2Cl$	67.3	4.2	14.5	1710(CO),	
							67.0	4.4	14.5	3450(OH)	
13k	C_6H_5	C_6H_4Cl(p)	OH	65	171	$C_{26}H_{17}N_5O_2Cl_2$	62.2	3.4	13.9	1710(CO),	
							62.1	3.6	13.6	3500(OH)	
13l	C_6H_5	C_6H_4Br(p)	OH	70	161	$C_{26}H_{17}N_5O_2BrCl$	57.2	3.1	12.8	1705(CO),	
							57.3	3.0	12.9	3450(OH)	
13m	C_6H_5	$C_5H_4N(O)$	OH	65	140	$C_{25}H_{17}N_6O_2Cl$	64.0	3.6	17.9	1715(CO),	
							64.2	3.4	17.9	3450(OH)	
13n	C_6H_5	$C_6H_4SO_2NH_2$(p)	OH	70	194	$C_{26}H_{19}N_6O_4SCl$	57.1	3.5	15.4	1716(CO), 3450	
							56.9	3.6	15.6	(OH),1165,1335 (SO_2N)	
13o	CH_3	C_6H_5	$NHNH_2$	50	162	$C_{21}H_{18}N_7OCl$	60.1	4.3	23.4	1615(CO),3295	2.21(s,CH_3),4.08
							60.0	4.5	23.3	($NHNH_2$)	(s,NH_2),6.61-8.24 (m,NH and ArH)
13p	C_6H_5	C_6H_5	$NHNH_2$	50	174	$C_{26}H_{20}N_7OCl$	64.8	4.2	20.4	1625(CO),3250	
							64.7	4.4	20.4	($NHNH_2$)	

Comp.	R	R^3	Yield (%)	m.p. (°C)	Mol. formula	Analyses Calcd/Found C	H	N	S	KBr $\upsilon_{max}(cm^{-1})$
14a	H	C_4H_9	70	184	$C_{27}H_{28}N_7O_4S_2Cl$	52.8	4.6	16.0	10.4	1095(CS),1180 and 1330 (SO_2N)
						52.8	4.7	16.1	10.3	
14b	H	C_6H_5	65	205	$C_{29}H_{24}N_7O_4S_2Cl$	55.0	3.8	15.5	10.1	1135(CS), 1190 and 1335 (SO_2N)
						55.1	3.8	15.6	10.0	
14c	H	$CH_2C_6H_5$	60	166	$C_{30}H_{26}N_7O_4S_2Cl$	55.4	4.2	15.0	9.9	1140(CS), 1180 and 1335 (SO_2N)
						55.6	4.0	15.1	10.0	
14d	CH_3	C_4H_9	75	178	$C_{28}H_{30}N_7O_4S_2Cl$	53.6	4.8	15.6	10.2	1145(CS), 1170 and 1330 (SO_2N)
						53.5	4.8	15.6	10.1	
14e	CH_3	C_6H_5	60	140	$C_{30}H_{26}N_7O_4S_2Cl$	55.6	4.0	15.1	9.9	1135(CS), 1190 and 1330 (SO_2N)
						55.6	4.2	14.9	10.0	
14f	CH_3	$CH_2C_6H_5$	65	163	$C_{31}H_{28}N_7O_4S_2Cl$	56.2	4.2	14.8	9.7	1140(CS), 1170 and 1335 (SO_2N)
						56.2	4.3	14.6	9.5	
14g	C_6H_5	C_4H_9	70	225	$C_{33}H_{32}N_7O_4S_2Cl$	57.4	4.6	14.2	9.3	1145(CS),1180 and 1335 (SO_2N)
						57.4	4.5	14.1	9.4	
14h	C_6H_5	C_6H_5	75	182	$C_{35}H_{28}N_7O_4S_2Cl$	59.2	4.0	13.8	9.0	1145(CS), 1190 and 1330 (SO_2N)
						59.0	4.0	13.6	9.2	
14i	C_6H_5	$CH_2C_6H_5$	65	170	$C_{36}H_{30}N_7O_4S_2Cl$	59.7	4.2	13.6	8.9	1135 (CS), 1185 and 1330 (SO_2N)
						59.6	4.4	13.5	8.8	
15a	H	C_4H_9	60	155	$C_{29}H_{28}N_7O_5S_2Cl$	53.3	4.3	15.0	9.8	1730(CO), 1165 and 1340 (SO_2N)
						53.1	4.4	15.1	9.6	
15b	H	C_6H_5	65	175	$C_{31}H_{24}N_7O_5S_2Cl$	55.2	3.6	14.6	9.5	1725(CO), 1170 and 1330 (SO_2N)
						55.2	3.6	14.7	9.6	
15c	H	$CH_2C_6H_5$	63	170	$C_{32}H_{26}N_7O_5S_2Cl$	55.9	3.8	14.3	9.3	1725(CO), 1180 and 1335 (SO_2N)
						55.9	3.7	14.4	9.4	
15d	CH_3	C_4H_9	70	140	$C_{30}H_{30}N_7O_5S_2Cl$	53.9	4.5	14.7	9.6	1730(CO), 1185 and 1330 (SO_2N)
						53.9	4.6	14.8	9.6	

(Continue...)

(Tab. continued)

15e	CH_3	C_6H_5	66	112	$C_{32}H_{26}N_7O_5S_2Cl$	55.9	3.8	14.3	9.3	1730(CO), 1170 and 1340 (SO_2N)
						55.8	3.9	14.2	9.0	
15f	CH_3	$CH_2C_6H_5$	75	137	$C_{33}H_{28}N_7O_5S_2Cl$	56.5	4.0	14.0	9.1	1725 (CO), 1165 and 1330 (SO_2N)
						56.5	4.2	14.1	9.1	
15g	C_6H_5	C_4H_9	70	160	$C_{35}H_{32}N_7O_5S_2Cl$	57.6	4.4	13.4	8.8	1725 (CO), 1180 and 1335 (SO_2N)
						57.7	4.3	13.5	8.6	
15h	C_6H_5	C_6H_5	60	162	$C_{37}H_{28}N_7O_5S_2Cl$	59.2	3.7	13.1	8.5	1730 (CO), 1190 and 1340 (SO_2N)
						59.0	3.8	13.1	8.5	
15i	C_6H_5	$CH_2C_6H_5$	65	125	$C_{38}H_{30}N_7O_5S_2Cl$	59.7	3.1	12.8	8.4	1730 (CO), 1160 and 1330 (SO_2N)
						59.5	4.0	12.9	8.3	
16a	H	C_4H_9	60	130	$C_{30}H_{30}N_7O_5S_2Cl$	53.9	4.5	14.7	9.6	1730(CO), 1165 and 1330 (SO_2N)
						53.9	4.6	14.8	9.6	
16b	H	C_6H_5	66	110	$C_{32}H_{26}N_7O_5S_2Cl$	55.9	3.8	14.3	9.3	1725 (CO), 1170 and 1340 (SO_2N)
						55.7	3.9	14.1	9.3	
16c	H	$CH_2C_6H_5$	70	138	$C_{33}H_{28}N_7O_5S_2Cl$	56.5	4.0	14.0	9.1	1725 (CO), 1160 and 1330 (SO_2N)
						56.6	4.3	14.0	9.0	
16d	CH_3	C_4H_9	65	165	$C_{31}H_{32}N_7O_5S_2Cl$	54.6	4.7	14.4	9.4	1730 (CO), 1170 and 1335 (SO_2N)
						54.6	4.0	14.5	9.3	
16e	CH_3	C_6H_5	70	204	$C_{33}H_{28}N_7O_5S_2Cl$	56.5	4.0	14.0	9.1	1725 (CO), 1185 and 1335 (SO_2N)
						56.3	4.1	14.2	9.0	
16f	C_6H_5	C_4H_9	60	143	$C_{36}H_{34}N_7O_5S_2Cl$	58.1	4.6	13.2	8.6	1725 (CO), 1190 and 1330 (SO_2N)
						58.2	4.6	13.1	8.7	
16g	C_6H_5	C_6H_5	65	153	$C_{38}H_{30}N_7O_5S_2Cl$	59.7	3.9	12.8	8.4	1730 (CO), 1180 and 1335 (SO_2N)
						59.7	4.0	12.9	8.3	
16h	C_6H_5	$CH_2C_6H_5$	65	190	$C_{39}H_{32}N_7O_5S_2Cl$	60.2	4.1	12.9	8.3	1730 (CO), 1165 and 1340 (SO_2N)
						60.0	4.3	12.5	8.5	
17a	CH_3	–	75	173	$C_{21}H_{16}N_5O_2Cl$	62.2	4.0	17.3	–	1685 (OCN), 3190 (NH), 3400 (OH)
						62.0	4.3	17.1		
17b	C_6H_5	–	75	201	$C_{26}H_{18}N_5O_2Cl$	66.7	3.9	15.0	–	1680 (OCH), 3100 (NH), 3450 (OH)
						66.9	4.3	15.0		

1-H-CH_3/Aryl-5-[α-substituted-β-2-(4-chlorophenyltriazol-4-yl)-vinyl]pyrazole-3-carboxylic acids (13; R^2 = OH). The foregoing trisubstituted pyrazole esters (12: 0.5 g) was refluxed with ethanolic 2N KOH solution (25 ml) for 3 hrs. The reaction mixture was concentrated, diluted with water and then acidified with dilute hydrochloric acid. The solid mass that deposited was filtered off and recrystallized from dilute ethanol in needles, (yield 60-70%) (Table).

1-Phenyl-5-[α-substituted-β-2-(4-chlorophenyltriazol-4-yl)-vinyl] pyrazole-3-carboxylic acid hydrazides (13; R^2 = $NHNH_2$). These derivatives were obtained by heating a mixture of ethyl-1-phenyl-5-substituted vinyl pyrazole-3-carboxylates (12: R^1 = C_6H_5; 1 mmol) and hydrazine hydrate (3 mmol) in an oil bath at 100°C for 8 hr. The reaction mixture was cooled then diluted with water. The product that separated out was filtered off, washed thoroughly with water till free alkalinity, dried and recrystallized from ethanol in colourless needles, (yield 50%) (Table).

Substituted p-[3-carbethoxy-5-[α-substituted-β-2-(4-chloro-phenyltriazol-4-yl) vinyl) pyrazol-1-yl] benzenesulphonyl-thioureas (14). A mixture of (12: 0.005 mol), anhydrous potassium carbonate (0.01 mol) in dry acetone (50 ml) was stirred and treated with appropriate isothiocyanate (0.006 mol). After the mixture was stirred and refluxed for 10 hr. acetone was removed under reduced pressure. The resulting solid residue was dissolved in water and the mixture was acidified with 2N HCl. The product was purified by recrystallization from ethanol in needles, (yield 65-80%) (Table).

3-Substituted2-[p-(3-carbethoxy-5-(α-substituted-β-2-(4-chlorophenyltriazol-4-yl) vinyl) pyrazol-1-yl) benzene-sulphonyl-imino]-4-oxothiazolidines (15). A mixture of (14: 0.01 mol) and ethyl bromoacetate (0.01 mol) in absolute ethanol (50 ml) was refluxed with stirring for 6 hr. concentrated and allowed to cool. The product obtained was recrystallized from ethanol as needles, (yield 60-70%) (Table).

3-Substituted 2-[p-(3-carbethoxy-5-(α-substituted-β-2-(4-chlorophenyltriazol-4-yl) vinyl) pyrazol-1-yl) benzene-sulphonylimino]-4-oxo-5, 6-dihydro-1,3-thiazines (16). A mixture of (14: 0.01 mol) and ethyl β-bromopropionate (0.011

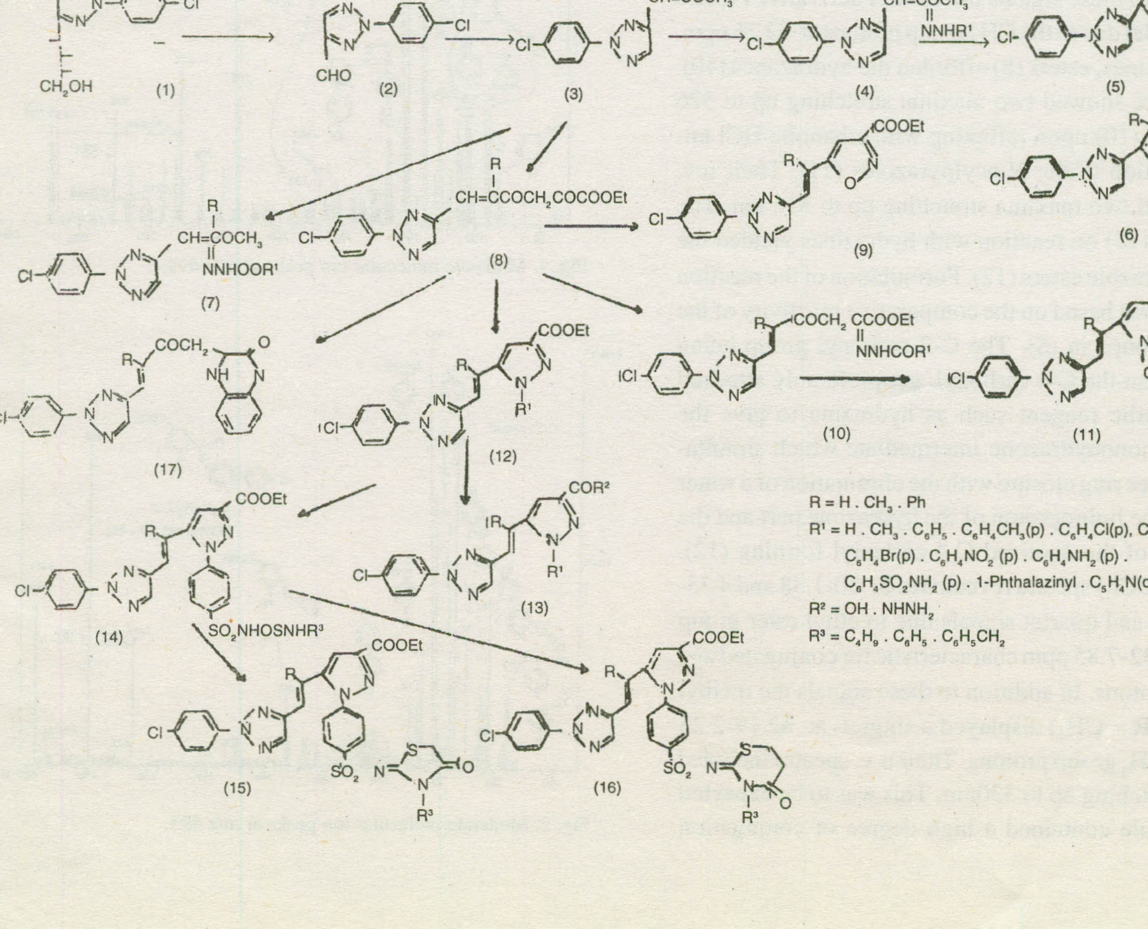
mol.) in absolute ethanol (50 ml) was refluxed with stirring for 8 hrs. worked up as in (15), (yield 55-75%) (Table).

3-Substituted-2-oxyquinoxalines (17). A mixture of (8: 1 mmol) and 2-phenylenediamine (1 mmol) in ethanol (30 ml) was heated under reflux for 3 hrs. The hydroxyquinoxaline derivative obtained after concentration was filtered off and recrystallized from ethanol in orange needles, (yield 70%) (Table).

Results and Discussion

Condensation of 2-(4-chlorophenyl)-4-formyltriazole (2) [25] with ethyl methyl ketone or benzyl methyl ketone furnished the, α,β-unsaturated ketones (3). Their ^{1}H nmr ($CDCl_3$) spectra displayed the CH_3 protons as singlet- at δ2.35-2.45 and multiplet signals at 6.45-8.00 ppm characteristic for conjugated and aromatic ring protons. In addition to these signals the methyl derivative (3: R = CH_3) revealed the CH_3 group protons as singlet at δ2.25 ppm. Their u.v. spectra exhibited two maxima stretching up to 312 nm (Table). The reaction of (3) with arylhydrazines gave the corresponding arylhydrazones (4). Their u.v. spectra displayed two maxima stretching up to 312 nm. This was due to low degree of conjugation than in (7).

Hydrazones (4) on refluxing with ethanol containing two drops HCl underwent cyclization to the pyrazolines (5). Their ^{1}H nmr ($CDCl_3$) spectra revealed the CH_3 protons as singlet at δ2.05-2.45 and multiplet signals at 4.15-4.75 due to one proton of H-4 pyrazoline, at δ5.37-5.40 for one proton of H-5 pyrazoline and at δ6.65-8.12 ppm due to aromatic ring protons. In addition to these signals the methyl derivatives (5; R=CH_3) exhibited the CH_3 protons as singlet at δ2.40-2.42 ppm. Their u.v. spectra showed two maxima stretching up to 312 nm (Table). Oxidation of the pyrazolines (5) with bromine-water led to the formation of the corresponding pyrazole derivatives (6). The structure of (6) was supported by their ^{1}H nmr ($CDCl^3$) spectra which included the CH_3 protons as singlet- at δ2.30-2.52, the aromatic ring protons as multiplet at 6.55-8.12 ppm and disappearance of the signals observed at the region of 4.15 and 5.35 ppm in the spectra of the pyrazolines (5). In addition to these signals the methyl derivaties (6; R=CH_3) revealed the CH_3 protons as singlet- at δ2.02-2.28 ppm. Their u.v. spectra exhibited two maxima stretching up to 312 nm (Table). With acylhydrazines, the ketones (3) furnished the corresponding acylhydrazones (7). Their u.v. spectra revealed three maxima stretching up to 328 nm. This was to be expected since the



molecule contained a high degree of conjugation between the triazole ring, the phenyl rings, conjugated double bonds and the carbonyl group of the hydrazone part.

The α, β-unsaturated ketones (3) on condensation with ethyl oxalate afforded ethyl 6-[2-(4-chlorophenyl)triazol-4-yl]-2,4-dioxo-5-substituted-hex-5-enoates (8). Their ^1H nmr ($CDCl_3$) spectra included signals at δ1.28-1.31 (triplet, 3H, CH_2CH_3), 4.25-4.28 (quartet, 2H, CH_2CH_3), 6.15 (doublet, ^1H, CH=) 6.47 (singlet, 1H, = CH-) and at 7.15-7.88 (multiplet, 11H, OH and aromatic protons) ppm. The signal at δ6.47 ppm proved the enolic form of esters (8) and this explains their reactions with hydrazines to give the pyrazole-3-esters (12) and not the 5-esters. In addition to these signals the methyl derivative (8; R = CH_3) revealed a singlet at δ 2.38 ppm due to the methyl protons. Their u.v. spectra exhibited two maxima stretching up to 310 nm.. The 1,3-diketo-esters (8) on reaction with hydroxylamine produced the isoxazole esters (9) to which assigned the formula (9). This confirms our experience regarding the reactivity of carbonyl group attached to the ethoxycarbonyl group towards the carbonyl reagents. Their u.v. spectra included two maxima stretching up to 300 nm Their ^1H nmr ($CDCl_3$) spectra exhibited at δ1.21-1.25 and 3.66-4.25 triplet and quartet signals characteristic for ethyl ester group protons and at 6.73-7.98 ppm multiplet corresponding to conjugated and aromatic ring protons.

In addition to these signals the methyl derivative (9; R = CH_3) gave a singlet due to the CH_3 group protons at δ2.26 ppm. With acylhydrazines, esters (8) afforded the hydrazones [10]. Their u.v. spectra showed two maxima stretching up to 326 nm. Hydrazones (10) upon refluxing with ethanolic HCl underwent cyclization to the N-acylpyrazoles (11). Their u.v. spectra displayed two maxima stretching up to 316 nm. The ethyl hexenoates (8) on reaction with hydrazines yielded the trisubstituted pyrazole esters (12). Formulation of the reaction product as (12) was based on the comparative reactivity of the two carbonyl groups in (8). The C-2 carbonyl group being more reactive than the C-4 carbonyl, get preferably attacked by the nucleophilic reagent such as hydrazine to give the corresponding monohydrazone intermediate which simultaneously undergoes ring closure with the elimination of a water molecule from the iminoproton of the hydrazone part and the hydroxyl group of the enolized C-4 carbonyl forming (12). Their ^1H nmr ($CDCl_3$) spectra revealed at δ1.30-1.38 and 4.33-4.35 ppm triplet and quartet signals due to ethyl ester group protons and at 6.32-7.85 ppm characteristic for conjugated and aromatic ring protons. In addition to these signals the methyl derivatives (12; R = CH_3) displayed a singlet- at δ2.19-2.23 ppm due to the CH_3 group protons. Their u.v. spectra included two maxima stretching up to 330nm. This was to be expected since the molecule contained a high degree of conjugation between the pyrazole ring, the triazole ring, the phenyl ring and the carbonyl of the carbethoxy group. In all the spectra, the position and intensity of the different maxima did not change when the spectra were measured in polar solvent as ethanol or non-polar solvents such as cyclohexane. This, together with their high extinction coefficient suggests that these absorption bands are due to π-π* transition The weaker n-π* transition which are usually characterised by a wavy appearance in non-polar solvents and which become blurred in polar solvents were absent. They probably lie below the π-π* transitions, which due to the high degree of conjugation were shifted to longer wavelengths and overlap n-π* transition which are unaffected by conjugation [26]. The structure of the pyrazoles (12) was further supported by measuring the mass spectra of compounds (R; R = C_6H_5; R' =H) and (12; R = C_6H_5; R' = C_6H_5) (Figs. 1&2) where they gave a moderate molecular ion peaks at m/z 419 and 495. The base peak appeared at m/z 154 and was

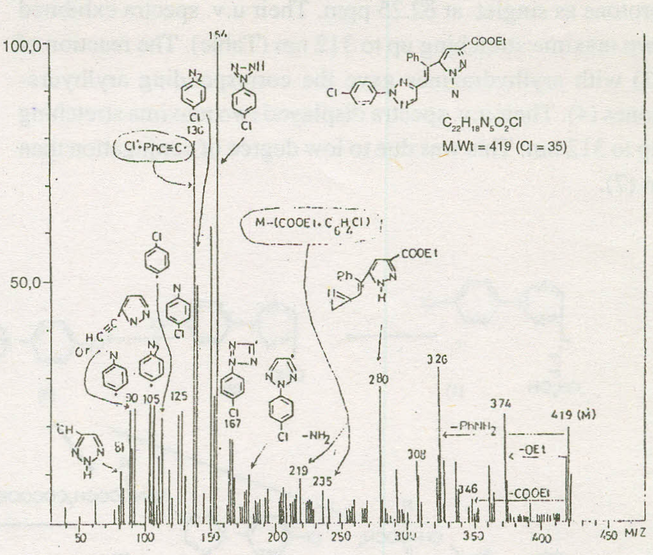


Fig. 1. Moderate molecular ion peaks at m/z 419.

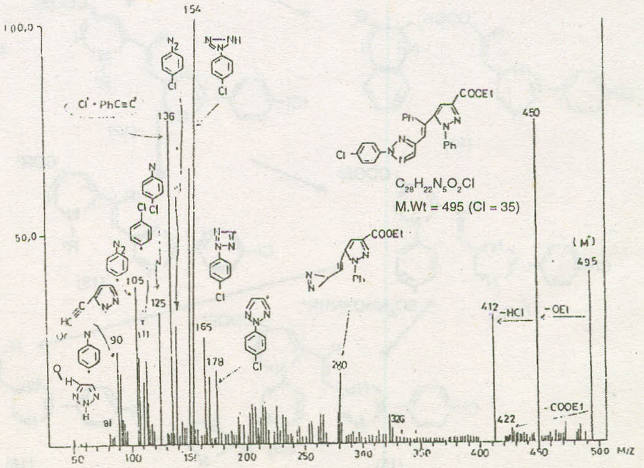


Fig. 2. Moderate molecular ion peaks at m/z 495.

attributed to $C_6H_5N_3Cl^+$ ion followed by all expected fragments produced from their structures. Esters (12) underwent either hydrolysis with ethanolic 2N KOH to give the acids (13; R^2 = OH), or converted to the acid hydrazides (13; R^2 = $NHNH_2$) by fusion with hydrazine hydrate. The structure of these acid hydrazides was confirmed by measuring the ^{1}H nmr ($CDCl_3$) spectra of (13; R = CH_3; R^2 = $NHNH_2$) which included a singlet- at δ2.21 due to CH_3 protons, a singlet- at δ4.08 due to (NH_2) protons and multiplet signals at 6.61-8.24 ppm characteristic for (NH) and aromatic ring protons. Reaction of the p-sulphamylphenyl esters (12; R^1 = $C_6H_4SO_2NH_2$ (p)) with isothiocyanate derivatives yielded the corresponding thioureas (14). It has been reported that condensation of N,N'-disubstituted thioureas with α-halogenoacids or esters afforded 2-imino-4-oxothiazolidines and the reaction proceeds through the intermediate formation of cyclic pseudo-thiohydantoic acid [27-31]. However, in the present study, cyclization of the thioureas (14) with ethyl bromoacetate and ethyl β-bromopropionate afforded the 3-substituted-2-[p-(5-aryl-3-carbethoxypyrazol-1-yl)benzenesulphonylimino]-4-oxothiazolidines (15) and the 3-substituted-2-[p-(5-aryl-3-carbethoxypyrazol-1-yl) benzenesulphonylimino]-4-oxo-5,6-dihydro-1, 3-thiazines (16) respectively (Table). However, with o-phenylenediamine, compounds (8) yielded the oxyquinoxalines [17].

References

1. R. Soliman, H.M. Faid Allah and S.K. El Sadany, J. Pharm. Sci, **76**, 626 (1987).
2. A.M. Farghaly, I. Shaaban, M.A. Khalil and A.A. Behkit, Arch. Pharm., **323**, 311 (1990).
3. M.A.E. Sallam, M.A. Moustafa, N.A.R. Hussein and L.B. Townsend, Alex. J. Pharm. Sci., **4**, 18 (1990).
4. H.V. Patel and P.S. Fernandes, J. Indian. Chem. Soc, **67**, 321, (1990).
5. M.L. Younes, H.H. Abbas and S.A.M. Metwally, Pharmazie, **46**, 48 (1991).
6. J.B. Wright, W..E. Dulin and J.H. Markillie, J. Med. Chem., **7**, 102 (1964).
7. D.L. Smith, A.A. Forist and W.E. Dulin, J. Med. Chem., **8**, 350 (1965).
8. G.C. Gerritsen and W.E. Dulin, Diabetes, **14**, 507 (1965).
9. G.C. Gerritsen and W.E. Dulin, J. Pharmacol. Exp. Ther., **150**, 491 (1965).
10. D.L. Smith, A.A. Forist and G.C. Gerritsen, *Ibid.*, **150**, 315 (1965).
11. R. Soliman, H. Feid Allah and S.K. El-Sadany, J. Pharm. Sci., **70**, 606 (1981).
12. R. Soliman, H. Mokhtar and H.F. Mohamed, *Ibid.*, **72**, 1004 (1983).
13. R. Soliman and H. Feid Allah, *Ibid.*, **70**, 602 (1981).
14. R. Soliman, H. Mokhtar and H.F. Mohamed, *Ibid.*, **72**, 999 (1983).
15. R. Soliman, J. Med. Chem., **22**, 321 (1979).
16. H. M. Mokhtar and J. Wojoanis, Indian J. Chem., **24**, 188, (1985).
17. H.M. Mokhtar, Pak. j. sci.. ind. res., **18**, 85 (1985).
18. H.M. Mokhtar and R. Soliman, Pharmazie, **10**, 649 (1978).
19. R. Soliman, H. Mokhtar and E.S. El Ashry, *Ibid.*, **4**, 184 (1978).
20. H.M. Mokhtar, A.T.F. Tag El Din and M.A.T. Desheash, Pak. j. sci. ind. res., **30**, 1 (1987).
21. H.M. Mokhtar, *Ibid*, **31**, 762 (1988).
22. H.M. Mokhtar, Pakistan J. Chem. Soc., **10**, 414 (1988).
23. H.M. Mokhtar, Pak. j. sci. ind. res., **33**, 30 (1990).
24. H.M. Mokhtar and O.O. Faraht, *Ibid.*, **34**, 9 (1991).
25. H.M. Mokhtar and O.O. Faraht, *Ibid.*, **34**, 16 (1991).
26. A.R. Katritsky, *Physical Methods in Heterocyclic Chemistry*, (Academic Press, New York, 1963) Vol. 2.
27. P. Bhargava, J.. Am. Chem. Soc., **73**, 2353 (1951).
28. W.J. Doran and H.A. Shonle, J. Org. Chem., **3**, 193(1938).
29. E.R.H. Jones, F.A. Robinson and M.N. Starchan, J.. Chem. Soc., **91**, (1946).
30. K.S. Markly and E.E. Reid, J. Am Chem. Soc., **52**, 2137 (1930).
31. a. F.B. Dains, R. Irvin and G.G. Harrel, J. Am. Chem. Soc., **43**, 613 (1921).
    b. F.B. Dains and F.E.. Eberly, J. Am. Chem. Soc.., **55**, 3859 (1933).
    c. J.A. Davis and F.B. Dains, J. Am. Chem.. Soc., **27**, 2627 (1935).
    d. A. Floyd and F..B. Dains, J. Am. Chem. Soc., **57**, 2544 (1936).