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TRIAZOLE - PYRAZOLE COMPOUNDS WITH POSSIBLE BIOLOGICAL ACTIVITY
Part –I. Synthesis and Spectra

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Condensation of the new chalcones (1) with different arylhydrazines, leads either to hydrazones (3) or pyrazolines (4) depending upon the reaction condition. Oxidation of (4) with bromine water affords pyrazole derivatives (5). Reaction of (4) and (5) with isothiocyanate derivatives leads to thioureas (6 and 7). Cyclization of (6 and 7) with ethyl bromoacetate affords the corresponding thiazolidine derivatives (8 and 9).

Key words: Triazoles, Chalcones, Pyrazoles.

Introduction

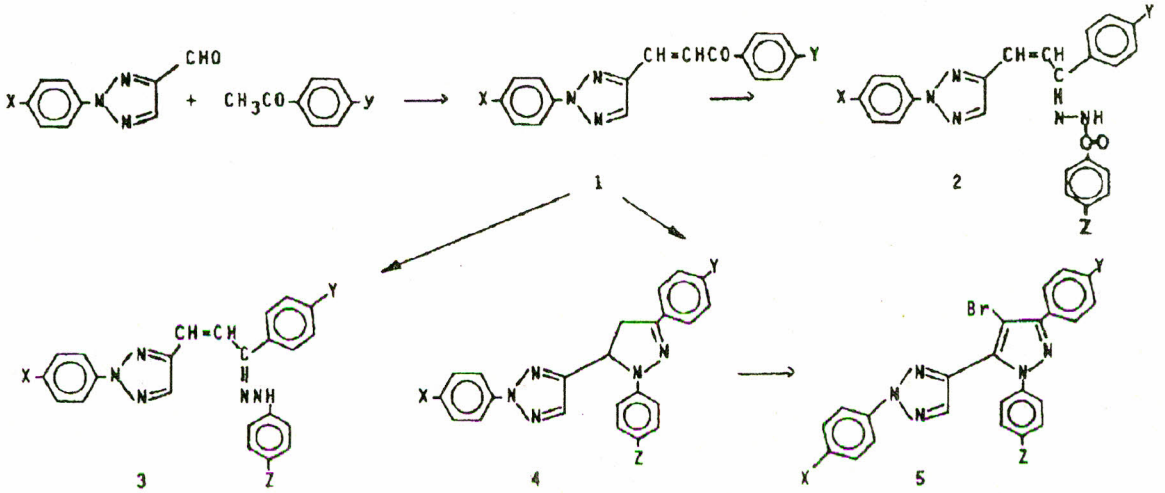
1,2,3-Triazole derivatives are biologically important compounds. Some of these triazoles have better antibacterial activity than carbencillin against gram-negative bacteria [1], while others are used as antimicrobial agents [2-4]. On the other hand a wide variety of pharmacological properties have been encountered with di- and trisubstituted pyrazoles [5-10]. These observations have prompted the synthesis of compounds possessing both triazole and pyrazole moieties in the hope that they might be of potential pharmacological and/or biological importance.

Results and Discussion

Chalcones are useful intermediates in the synthesis of certain di- and trisubstituted pyrazoles [11-15]. In this report, previously prepared [16-18] 4-formyl-2-aryl-1,2,3-triazoles were reacted with substituted acetophenones to give the corresponding α, β-unsaturated ketones [1] (Scheme 1). The IR spectra of these compounds exhibited a carbonyl stretching absorption band at 1656- 1660 cm^{-1} as well as an olefinic C=C stretching in the region 1606-1610 cm^{-1} [19] (Table 1). The structure of the foregoing chalcones was further supported by their ^1H and ^{13}C NMR spectra (Table 2) Fig. 1. The ^1H nmr of (1) showed the olefinic and the aromatic protons as a multiplet in the δ7.2-8.7 region. The H-5' of the triazole moiety appeared either at 9.2 or with the aromatic multiplets depending on the solvent used. On the other hand, the ^{13}C NMR spectra of (1) exhibited 10 signals in the aromatic region for the aromatic and triazole carbons as well as two signals in the δ138.6-138.8 and 129.6-129.7 regions for C_α and C_β respectively [20a]. The carbonyl carbon (CO) appeared at δ 187.6- 188.8. The mass spectra of 1-*p*-tolyl-3-(2'-phenyl-1',2',3'- triazole-4'-yl)-prop-2-en-1-one (1b) showed the molecular ion peak at *m/z* 289 and all the expected fragments (Fig. 2).

Condensation of chalcones (1) with the appropriate aroylhydrazines in presence of acid catalyst afforded the corresponding aroylhydrazones (2) in good yield. Their IR spectra revealed an amide carbonyl band at 1654-1665 cm^{-1}, NH at 3118-3135 cm^{-1} and C=N at 1640-1645 cm^{-1} (Table 1).

Similarly condensation of the prepared chalcones with arylhydrazines yielded the corresponding arylhydrazones (3), which underwent cyclization to the corresponding pyrazolines



Scheme 1.

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TABLE 1. MICROANALYSIS AND ELECTRONIC SPECTRAL DATA OF COMPOUND 1-5

Comp. No.	IR νmax. (cm^{-1}) C=O&/or C=N	C=C	NH_2&/ or NH	^1H NMR (δ/ppm) H-5' (s)	H-4 (m)	H-5 (m)	ArH (m)	NH_2 &/ or CH_3 (s)	^{13}C NMR(δ/ppm) CO	C-α	C-β	Pyrazoline C C-3	C-4	C-5	Ar & pyrazole C
1a	1660	1608		9.2			8.0-8.7		188.8	138.8	129.6				118.6, 125.7, 128.1, 128.4, 128.7, 131.1,133.21, 136.3, 137.0, 145.6.
1b	1658	1610		a			7.2-8.2	2.38							
1c	1656	1607		9.2			7.6-8.6		187.6	138.6	129.7				187.6,138.6,129.7,120.5, 125.6,128.7,130.6,131.7, 132.5,136.9,136.3,137.1, 145.9.
1d	1659	1606		9.2			7.7-8.7		187.9	138.7	129.6				187.9,138.7,129.6,118.6, 125.4,127.4,128.1,130.3, 131.4,131.80,135.9,136.4, 145.6.
2a	1663,1642	1609	3118												
2b	1665,1645	1600	3131												
2c	1664,1644	1602	3130												
2d	1660,1642	1600	3125												
2e	1658,1644	1602	3128												
2f	1655,1645	1600	3125												
2g	1655,1644	1603	3135												
2h	1654,1640	1602	3121												
3a	1661	1607	3119	a			7.1-8.0								
3b	1662	1595	3115	a			7.5-8.4								
3c	1662	1595	3118	9.2			7.6-8.6								
3d	1660	1607	3115	a			7.1-8.0								
3e	1650	1598	3078,3380 3260	9.2			7.7-8.5	6.8							
3f	1655	1599	3118												
3g															
3h	1660	1608	3118	a			7.1-8.0								
3i				9.2			7.5-8.6	6.7							
3j	1656	1604	3116	a			7.3-8.4								
3k	1658	1599	3118	9.2			7.5-8.7	6.9							
3l	1656	1604	3116	a			7.2-8.1								
3m	1644	1594	3055,3370	9.2			7.4-8.7	6.8							
4a	1554			a	3.9	5.3	7.2-8.2					155.2	40.7	55.8	114.6,118.2,118.4,124.1, 125.8,126.8,127.9,128.5, 130.9,132.6,133.6,135.1, 138.7,145.8.
4b	1555			9.2	4.2	6.3	7.7-8.7					150.1	40.7	55.6	114.7,118.2,118.5,122.7, 125.8,127.6,128.6,129.5, 131.7,134.1,136.3,138.9, 143.1,145.6.
4c	1558		3383,3266	a	3.8	5.5	7.3-8.3	a				149.1	40.8	56.0	111.8,118.0,124.4,125.4 127.0,128.0,128.6,130.9, 132.6,133.7,135.1,133.7, 145.8
4d	1556			a	3.7	5.4	7.2-8.2	2.4							
4e	1558			9.1	4.1	6.3	7.7-8.6	2.4,6.8							
4f	1556														
4g	1550		3380,3260	a	3.8	5.3	7.3-8.3	6.8							
4h	1560			a	3.8	5.6	7.2-8.2					150.5	40.1	55.8	114.5,118.3,118.6,121.5, 126.0,127.7,129.0,129.1 131.6,134.4,136.6,139.9, 144.1,145.6.
4i	1562			9.2	4.2	6.3	7.6-8.6					149.9	40.5	55.7	114.7,118.3,118.6,122.9, 125.3,127.7,128.5,129.5, 131.5,134.2,136.4,138.9 142.8,145.5.
4j	1564			9.3	4.3	6.3	7.6-8.5								
4k	1560		3375,3255	a	3.8	5.5	7.1-8.3	6.7							
5a	1560			9.2			8.1-8.6								111.9,120.2,124.4,126.1,

(Table 1, Contd...)

(Contd. Table 1)

						128.4,129.9,130.6,130.9 132.7,133.6,135.6,135.5, 137.6,138.9,140.7,145.4.
5b	1562	3370,3260	9.1	8.0-8.5		
5c	1558		a	7.7-8.2	2.5	
5d	1565	3380,3265	9.2	7.6-8.7	2.6	
5e	1564		a	7.2-8.1		
5f	1560	3382,3264				
5g	1555		9.2	7.5-8.5		
5h	1554	3385,3268				112.3,120.1,123.9,125.7, 127.6,128.6,129.6,130.5, 131.2,132.7,133.6,134.6, 135.9,136.2,138.9,142.5, 146.1.

a Overlapped by aromatic protons.

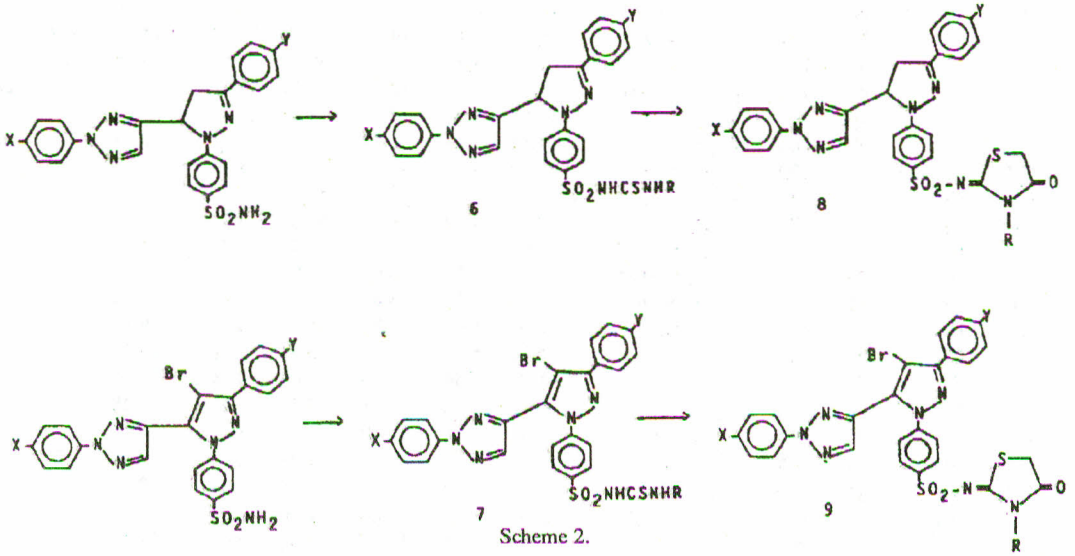
TABLE 2. IR AND NMR SPECTRAL DATA OF COMPOUND 1-5.

Compd.				Yield	M.P.	Molecular	Found			Calc.			UV
No.	X	Y	Z	%	°C	formula	C	H	N	C	H	N	λmax.(log ε)
1a	H	H		85	127	$C_{17}H_{13}N_3O$	73.88	5.15	15.61	74.17	4.76	15.26	272, 322(4.2,4.3)
1b	H	CH_3		82	190	$C_{18}H_{15}N_3O$	74.38	5.44	14.35	74.72	5.22	14.52	278, 324(4.1,4.1)
1c	H	Cl		80	160	$C_{17}H_{12}N_3OCl$	65.81	3.39	13.56	65.92	3.90	13.56	268, 326(4.0,4.1)
1d	H	Br		83	162	$C_{17}H_{12}N_3OBr$	57.98	3.76	12.25	57.64	3.41	11.86	374, 326(3.8,3.9)
2a	H	H	H	70	115	$C_{24}H_{19}N_5O$	72.91	4.86	17.70	73.27	4.87	17.80	
2b	H	H	Cl	72	160	$C_{24}H_{18}N_5OCl$	67.55	4.53	16.47	67.37	4.24	16.37	
2c	H	CH_3	H	75	130	$C_{25}H_{21}N_5O$	74.07	5.29	17.54	73.69	5.12	17.19	
2d	H	CH_3	Cl	70	182	$C_{25}H_{20}N_5OCl$	68.31	4.28	15.62	67.95	4.56	15.85	
2e	H	Cl	H	71	77	$C_{24}H_{18}N_5OCl$	67.59	4.59	15.57	67.37	4.24	16.37	
2f	H	Cl	Cl	74	145	$C_{24}H_{17}N_5OCl_2$	62.02	3.59	15.47	62.35	3.71	15.15	
2g	H	Br	H	73	135	$C_{24}H_{18}N_5OBr$	61.06	3.68	15.04	61.03	3.84	14.83	
2h	H	Br	Cl	75	145	$C_{24}H_{17}N_5OBrCl$	56.63	3.38	13.88	6.88	3.38	13.82	
3a	H	H	H	77	140	$C_{23}H_{19}N_5$	75.94	5.61	18.81	75.60	5.24	19.16	
3b	H	H	CH_3	75	180	$C_{24}H_{21}N_5$	76.37	5.19	18.08	75.97	5.58	18.46	
3c	H	H	Cl	76	122	$C_{23}H_{18}N_5Cl$	68.74	4.46	17.16	69.08	4.54	17.51	
3d	H	H	NO_2	79	136	$C_{23}H_{18}N_6O_2$	66.98	4.12	20.81	67.31	4.42	20.48	
3e	H	H	SO_2NO_2	80	165	$C_{23}H_{20}N_6O_2S$	62.49	4.88	18.80	62.15	4.54	18.90	
3f	H	CH_3	NO_2	81	185	$C_{24}H_{20}N_6O_2$	67.60	5.10	19.59	67.91	4.75	19.80	
3g	H	CH_3	SO_2NH_2	79	180	$C_{24}H_{22}N_6O_2S$	62.66	4.64	18.40	62.68	4.84	18.33	
3h	H	Cl	NO_2	80	155	$C_{23}H_{17}N_6O_2Cl$	61.90	3.91	19.20	62.10	3.85	18.89	
3i	H	Cl	SO_2NH_2	84	166	$C_{23}H_{19}N_6O_2ClS$	57.35	4.13	17.89	57.68	4.00	17.55	
3j	H	Br	H	75	165	$C_{23}H_{18}N_5Br$	61.91	4.30	15.79	62.17	4.08	15.76	
3k	H	Br	Cl	76	147	$C_{23}H_{17}N_5BrCl$	58.09	3.79	14.57	57.70	3.58	14.63	
3l	H	Br	NO_2	78	170	$C_{23}H_{17}N_6O_2Br$	56.86	3.86	17.50	56.45	3.50	17.17	
3m	H	Br	SO_2NH_2	80	92	$C_{23}H_{19}N_6O_2BrS$	52.39	3.95	15.78	52.78	3.66	16.06	
4a	H	H	H	65	123	$C_{23}H_{19}N_5$	75.52	4.88	19.48	75.60	5.24	19.16	
4b	H	H	Cl	67	139	$C_{23}H_{18}N_5Cl$	69.09	4.18	17.66	69.08	4.54	17.51	
4c	H	H	SO_2NH_2	75	175	$C_{23}H_{20}N_6O_2S$	61.92	4.79	18.90	62.15	4.54	18.90	210, 268, 350(4.4,4.4,4.4)
4d	H	CH_3	H	65	145	$C_{24}H_{21}H_5$	76.27	5.46	18.53	75.97	5.58	18.46	210, 276(4.5,4.5)
4e	H	CH_3	SO_2NH_2	69	180	$C_{24}H_{22}N_6O_2S$	62.62	4.53	18.13	62.86	4.84	18.33	210, 274(4.4,4.3)
4f	H	Cl	H	68	115	$C_{23}H_{18}N_5Cl$	69.03	4.78	17.70	69.08	4.54	17.51	244sh, 280(4.1,4.3)
4g	H	Cl	SO_2NH_2	70	152	$C_{23}H_{19}N_6O_2ClS$	57.55	4.06	17.31	57.68	4.00	17.55	220, 270, 316(4.3,4.4,4.3)
4h	H	Br	H	66	110	$C_{23}H_{18}N_5Br$	62.45	3.71	16.01	62.17	4.08	15.76	210, 264(4.5,4.4)
4i	H	Br	Cl	67	125	$C_{23}H_{17}N_5BrCl$	57.46	3.31	14.74	57.70	3.58	14.63	
4j	H	Br	NO_2	65	210	$C_{23}H_{17}N_6O_2Br$	56.49	3.19	17.14	56.45	3.50	17.17	
4k	H	Br	SO_2NH_2	74	176	$C_{23}H_{19}N_6O_2BrS$	52.91	4.02	15.72	52.78	3.66	16.06	210, 274sh(4.4,4.3)
5a	H	H	H	75	80	$C_{23}H_{16}N_5Br$	62.40	3.88	15.70	62.46	3.65	15.83	242, 280(4.4,4.5)
5b	H	H	SO_2NH_2	79	172	$C_{23}H_{17}N_6O_2BrS$	52.73	3.62	16.32	52.98	3.29	16.12	210, 270, 352(4.4,4.3,4.2)
5c	H	CH_3	H	77	125	$C_{24}H_{18}N_5Br$	62.97	4.37	15.55	63.17	3.98	15.35	208, 272(4.5,4.4)
5d	H	CH_3	SO_2NH_2	80	152	$C_{24}H_{19}N_6O_2BrS$	53.87	3.96	15.55	53.84	3.58	15.70	220, 280(4.1,4.3)
5e	H	Cl	H	77	120	$C_{23}H_{15}N_5BrCl$	58.29	3.49	14.52	57.94	3.17	14.69	250sh, 276(4.5,4.6)
5f	H	Cl	SO_2NH_2	76	188	$C_{23}H_{16}N_6O_2BrClS$	49.65	3.15	14.79	49.70	2.90	15.12	205, 280(4.0,3.8)
5g	H	Br	H	78	172	$C_{23}H_{15}N_5Br_2$	52.67	3.11	13.71	53.00	2.90	13.44	248, 276(4.3, 4.4)
5h	H	Br	SO_2NH_2	80	145	$C_{23}H_{16}N_6O_2Br_2S$	45.91	2.46	13.90	46.02	2.69	14.00	210, 270, 330(4.4,4.3,4.1)

(4) when heated with conc. HCl. However, the pyrazoline derivatives (4) were also obtained from the corresponding chalcones and the appropriate arylhydrazine in presence of HCl. In agreement with the suggested structures, the IR spectra of the above pyrazolines lacked the olefinic C=C band which exists in the starting hydrazones (3, Table 1). The ^{1}H NMR spectra of (4, Table 2) showed in addition to the aromatic protons at δ7.05-8.70, two other multiplets at δ5.3-6.3 and 3.7-4.2 the first multiplet integrated for 2 protons (H-4) and the second for 1 proton (H-5) [21]. The ^{13}C NMR spectra of the above pyrazolines (4, Table 2, Fig. 3) exhibited the expected number of signals for these compounds as well as 3 signals at δ149.9-155.2, 40.7-40.8 and 55.6-55.8 for C-3, C-4 and C-5 of the pyrazoline ring respectively [22].

Oxidation of pyrazoline derivatives (4) with excess of bromine water afforded the corresponding bromopyrazoles (5). Their ^{1}H NMR (Table 2) displayed the aromatic protons as multiplet in the δ7.2-8.7 region and lacked the two signals characteristic of H-4 and H-5 of the corresponding pyrazoline derivatives. The ^{13}C NMR spectra of the above pyrazoles (5) (Table 2, Fig. 4) are consistent with the assigned structures. It showed the expected number of signals for the aromatic carbons and lacked the two signals of C-4 and C-5 existing in the corresponding pyrazoline derivatives. The appearance of the molecular ion peaks for compounds (4d) at *m/z* 379 and (5b) at *m/z* 520/522 supported their molecular formula and they were followed by all expected fragments (Figs. 5 and 6).

p-(3,5-Disubstituted-2-pyrazolin-1-yl) benzenesulfonylureas (6) as well as *p*-(3,5-disubstituted-pyrazol-1-yl)- benzenesulfonylureas (7) were prepared from the reaction of the corresponding sulfamylphenylpyrazolines (4) or pyrazoles (5) with the appropriate isothiocyanate (Scheme 2). Their



Scheme 2.

TABLE 3. MICROANALYSIS AND SPECTRAL DATA OF BENEZENESULFONYLTHIOUREAS (6, 7) AND 4-OXOTHIAZOLIDINES (8, 9).

Compd. No.	X	Y	R	Yield %	M.P. °C	Molecular formula	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	IR max.(cm^{-1}) C=o	C=S	SO_2N	NH
6a	H	H	n-C_4H_9	60	122	$C_{28}H_{29}N_7O_2S_2$	59.71	5.49	17.56	60.09	5.22	17.52		1092	1334,1153	3062,3264
6b	H	H	C_6H_5	63	95	$C_{30}H_{25}N_7O_2S_2$	61.91	7.70	16.56	62.16	4.35	16.91		1090	1335,1154	3118,3255
6c	H	H	$C_6H_4CH_2$	65	117	$C_{31}H_{27}N_7O_2S_2$	63.10	4.40	16.91	62.71	4.58	16.51		1094	1335,1153	3062,3264
6d	H	Br	CH_2=CH-CH_2	67	140	$C_{27}H_{24}N_7O_2BrS_2$	51.90	4.21	15.98	52.09	3.88	15.75		1090	1332,1150	3060,3262
6e	H	Br	n-C_4H_9	69	137	$C_{28}H_{28}N_7O_2BrS_2$	52.37	4.64	15.68	52.66	4.42	15.35		1046	1334,1152	3065,3266
6f	H	Br	C_6H_5	80	138	$C_{30}H_{24}N_7O_2BrS_2$	54.50	3.36	15.29	54.71	3.67	14.89		1092	1334,1153	3060,3262
6g	H	Br	$C_6H_4CH_2$	66	128	$C_{31}H_{26}N_7O_2BrS_2$	55.37	3.78	14.73	55.36	3.90	14.58		1094	1335,1152	3066,3266
7a	H	H	n-C_4H_9	62	85	$C_{28}H_{26}N_7O_2BrS_2$	52.60	3.77	15.18	52.83	4.12	15.40		1087	1337,1152	3063,3274
7b	H	H	C_6H_5	64	115	$C_{30}H_{22}N_7O_2BrS_2$	55.12	3.69	14.67	54.88	3.38	14.93		1084	1338,1149	3061,3260
7c	H	H	$C_6H_4CH_2$	61	80	$C_{31}H_{24}N_7O_2BrS_2$	55.78	4.00	15.01	55.52	3.61	14.62		1089	1335,1153	3062,3280
7d	H	Br	CH_2=CH-CH_2	68	118	$C_{27}H_{21}N_7O_2Br_2S_2$	46.38	3.28	14.18	46.36	3.03	14.02		1088	1338,1154	3068,3264
7e	H	Br	n-C_4H_9	70	105	$C_{28}H_{25}N_7O_2Br_2S_2$	46.86	3.87	13.54	47.00	3.52	13.70		1086	1336,1150	3060,3280
7f	H	Br	C_6H_5	69	123	$C_{30}H_{21}N_7O_2Br_2S_2$	49.27	2.62	13.20	48.99	2.88	13.33		1088	1338,1152	3062,3275
7g	H	Br	$C_6H_4CH_2$	67	100	$C_{31}H_{23}N_7O_2Br_2S_2$	49.32	2.85	13.34	49.68	3.09	13.08		1086	1336,1154	3064,3276
8a	H	Br	CH_2=CH-CH_2	70	122	$C_{29}H_{24}N_7O_3BrS_2$	52.21	3.82	15.01	52.57	3.65	14.80	1748		1334,1152	
8b	H	Br	C_6H_5	68	130	$C_{32}H_{24}N_7O_2BrS_2$	54.97	3.62	15.98	55.02	3.46	14.03	1750		1332,1154	
9a	H	H	C_6H_5	66	90	$C_{32}H_{22}N_7O_3BrS_2$	55.53	3.58	14.37	55.17	3.18	14.07	1746		1332,1153	
9b	H	Br	CH_2=CH-CH_2	65	110	$C_{29}H_{21}N_7O_3Br_2S_2$	47.38	2.68	12.97	47.10	2.86	13.26	1752		1330,1152	

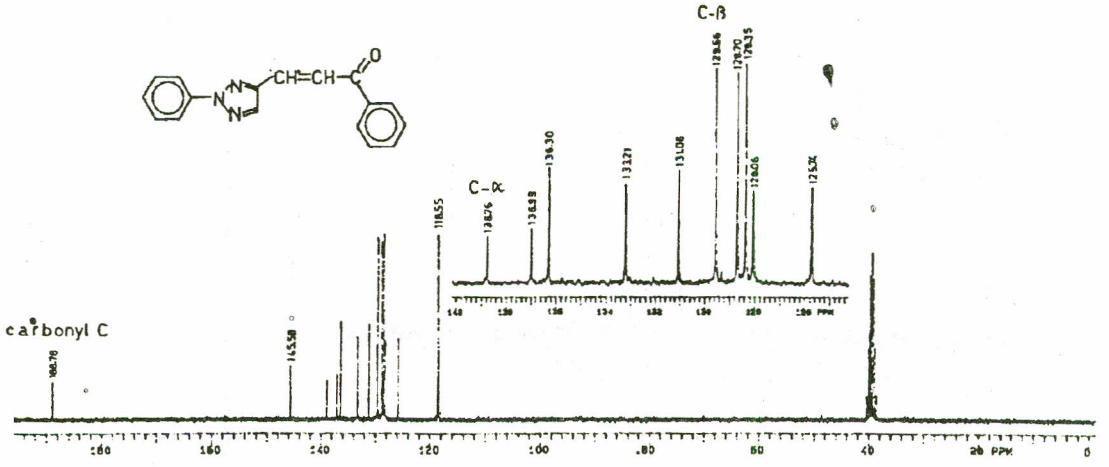


Fig. 1. ^{13}C NMR Spectrum of: 1-Phenyl-3-(2'-phenyl-1',2', 3'-triazol-4-yl) prop-2-en-1-one.

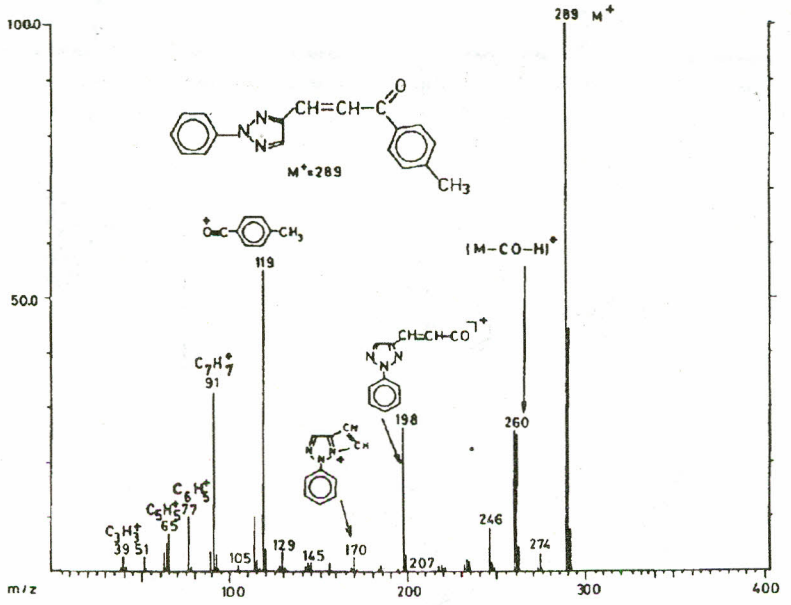


Fig. 2. Mass spectrum of: 1-p-tolyl-3(2'-phenyl-1',2',3'-triazol-4'-yl)prop-2-en-1-one.

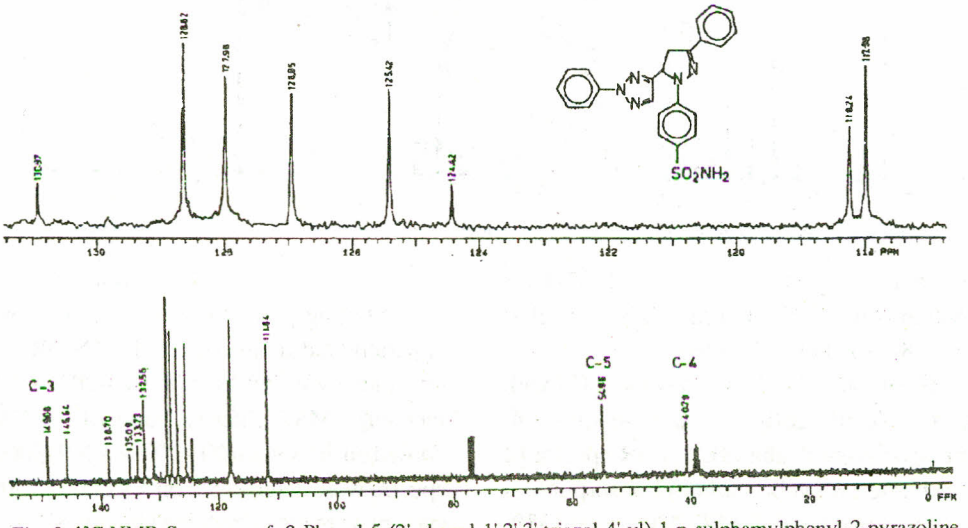


Fig. 3. ^{13}C NMR Spectrum of: 3-Phenyl-5-(2'-phenyl-1',2',3' triazol-4'-yl)-1-p-sulphamylphenyl-2-pyrazoline.

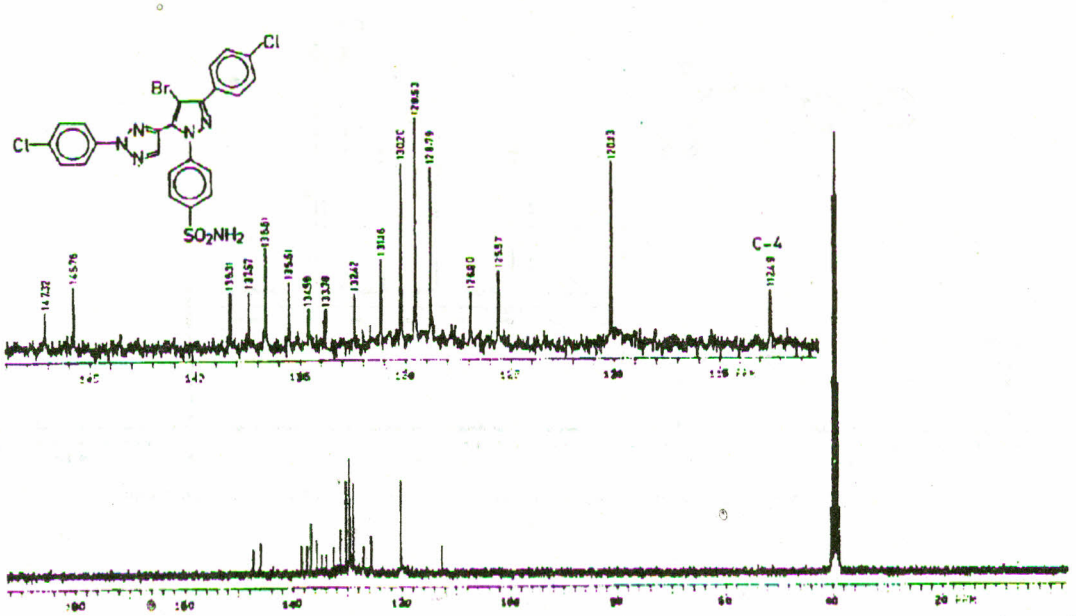


Fig. 4. ^{13}C NMR Spectrum of: 4-Bromo-3-p-chlorophenyl-5-(2'-p-chlorophenyl-1',2',3'-triazol-4'-yl)-1-p-sulphamylphenyl pyrazole

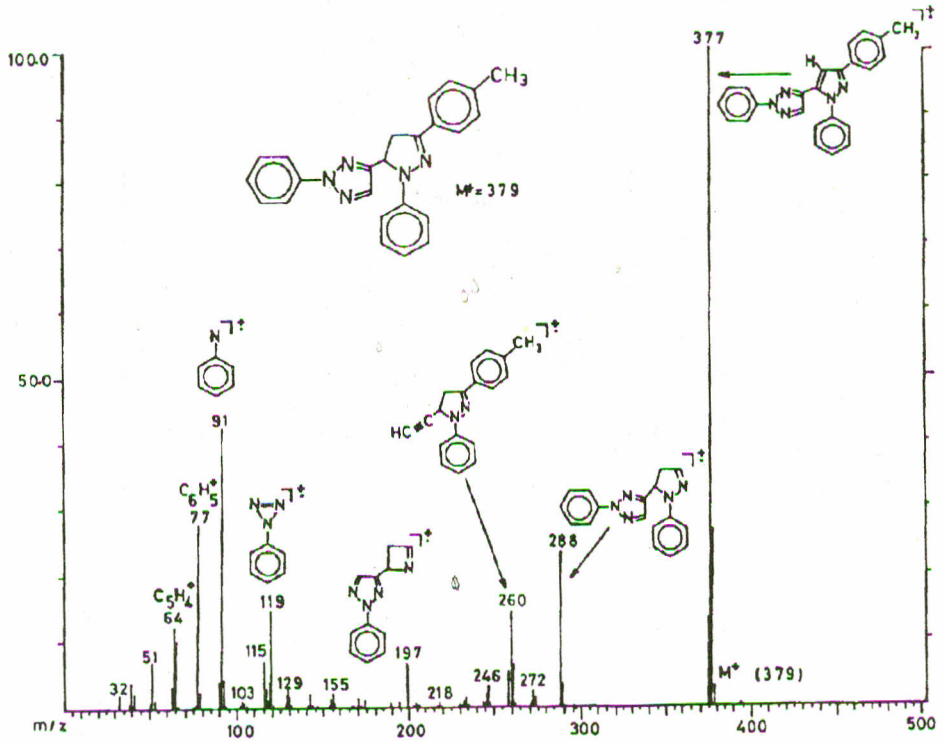


Fig. 5. Mass Spectrum of: 1-Phenyl-5-(2'-phenyl-1',2',3'-triazol-4'-yl)-3-p-tolyl-2-pyrazoline.

spectra of these compounds exhibited two bands at 1332-1338 cm^{-1} and 1149-1154 cm^{-1} due to SO_2N group [20b] as well as a C=S stretching at 1084-1094 cm^{-1} (Table 3).

Cyclization of the thiourea derivatives (6) and (7) with ethyl bromoacetate afforded the corresponding 4-oxothiazolidines (8) and (9) respectively (Table 3). The IR spectra of these compounds exhibited a cyclic carbonyl absorption at 1746-1750 cm^{-1} as well as two bands for SO_2N group at 1330-1334 and 1152-1154 cm^{-1}.

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. ^1H NMR spectra were recorded on either a Varian EM 360L, XL-200 or VXR-300 spectrometer using TMS as internal standard. ^{13}C NMR spectra were recorded on the Varian XL-200 or VXR-300 spectrometer. Mass spectra were determined on a Kratos M 30 instrument. The IR spectra were measured on a Unicam SP 1025 spectrophotometer using KBr pellets. Electronic spectra were recorded on a

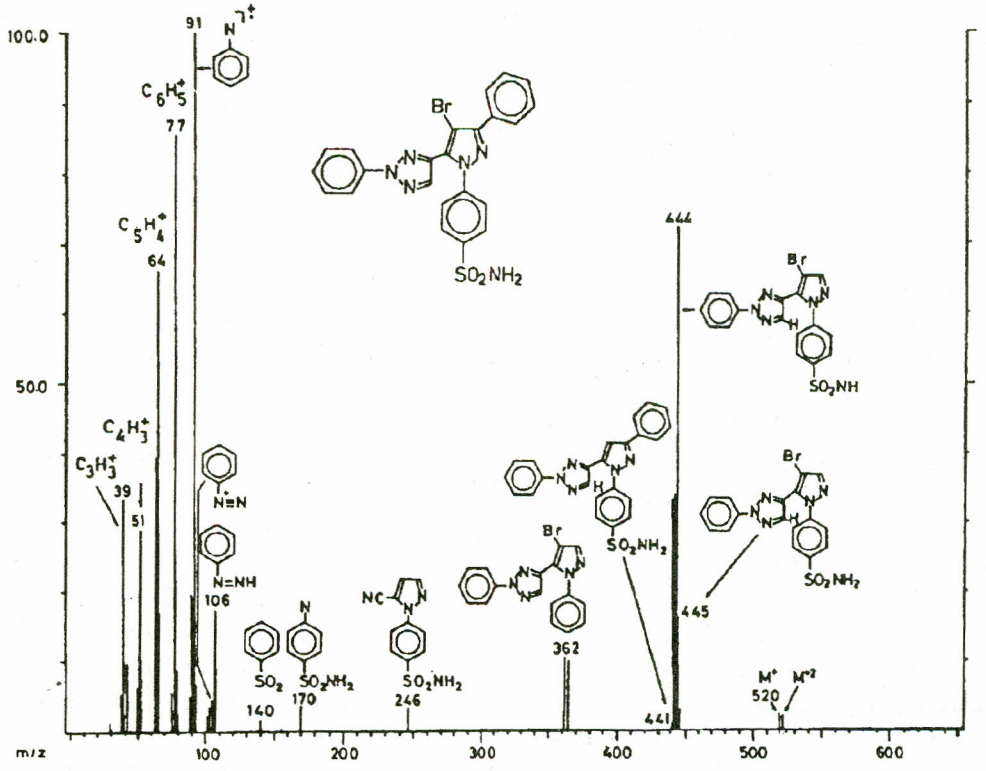


Fig. 6. Mass Spectrum of: 4-Bromo-3-phenyl-5-(2'-phenyl-1',2',3'-triazol-4'-yl)-1-p-sulphamylphenyl-pyrazole.

Unicam 1805 programme controller instrument. Microanalyses were performed at the Microanalytical Unit, Faculty of Science, University of Cairo, Egypt.

Chalcone derivatives (1). A solution of sodium hydroxide (0.055 mol) in water (25 ml) and ethyl alcohol (15 ml) was stirred and cooled. To this solution 4-formyl-2-phenyltriazole [16-18] (0.045 mol) was added followed by the appropriate acetophenone derivative (0.045 mol). The temperature of the mixture was kept at 25° and stirring was continued for 3 hrs. After keeping the reaction mixture in the refrigerator overnight, the solid chalcone that separated out was filtered off, washed with water and crystallised from alcohol (Table 1).

Aroylhydrazone derivatives (2). A solution of the appropriate chalcone (1; 0.01 mol) in toluene (30 ml) was refluxed with the corresponding aroylhydrazine (0.011 mol) in presence of a few drops of glacial acetic acid for 1 hr. Toluene was removed under reduced pressure and the residue was treated with methanol to give the product which was recrystallised from benzene-methanol mixture (Table 1).

Arylhydrazone derivatives (3). A solution of (1; 0.01 mol) in ethanol (30 ml) was refluxed with a mixture of the appropriate arylhydrazine hydrochloride (0.011 mol) and sodium acetate (0.012 mol) in water (5 ml) for 1 hr. The reaction mixture was poured into water, the precipitated product was filtered off and recrystallised from alcohol (Table 1).

1,3,5-Trisubstituted-2-pyrazolines (4). A solution of the appropriate chalcone (1; 0.01 mol) in ethanol (50 ml) was refluxed with the proper arylhydrazine hydrochloride (0.011 mol) for 4 hrs, cooled and diluted with water. The precipitated crude product was filtered off and recrystallised from ethanol in the form of needles (Table 1).

The pyrazolines 4 were also obtained (65% yield) by refluxing the appropriate hydrazone in ethanol with hydrochloric acid for 3 hrs.

4-Bromo-1,3,5-trisubstituted pyrazoles (5). A suspension of 4 (0.01 mol) in water (10 ml) was treated with excess 5% bromine water with stirring until a faint yellow colour was developed. After stirring for 4 hrs, the crude pyrazole was filtered off and recrystallised from methanol as needles (Table 1).

Substituted p-(3,5-diaryl-2-pyrazolin-1-yl)(6)-and p-(3,5-diarylpyrazol-1-yl)(7)-benzenesulfonylthioureas. A mixture of 4 or 5 (0.01 mol) and anhydrous potassium carbonate (0.02 mol) in dry acetone (25 ml) was stirred and refluxed for 1 hr. At this temperature, a solution of the appropriate isothiocyanate (0.015 mol) in dry acetone (5 ml) was added dropwise. After the mixture was stirred and refluxed for 10 hrs, acetone was removed under reduced pressure, the solid mass dissolved in water and acidified with 2N HCl. Recrystallisation of the precipitate from methanol gave needles of pure product (Table 3).

3-Substituted2-[p-(3,5-diaryl-2-pyrazolin-1-yl)benzenesulfonylimino](8)-and2-[p-(3,5-diarylpyrazol-1-yl)benzenesulfonylimino] (9)-4-oxothiazolidines. A mixture of 6 or 7 (0.01 mol) and ethyl bromoacetate (0.011 mol) in absolute ethanol (50 ml) was refluxed with stirring for 6 hrs, concentrated and allowed to cool. The product obtained was recrystallised from ethanol in the form of needles (Table3).

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