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Synthesis and Characterization of Certain Pyrazolin-5-Ones

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ABSTRACT

A new series of Pyrazolin-5-ones were synthesized. The structures for all the compounds have been established by elemental analysis, IR spectral, ^{1}H NMR spectral and Mass spectral studies.

Keywords: Pyrazolin-5-ones, characterization**,** elemental analysis, IR Spectral data, ^{1}H NMR spectral data, mass spectral data.

INTRODUCTION

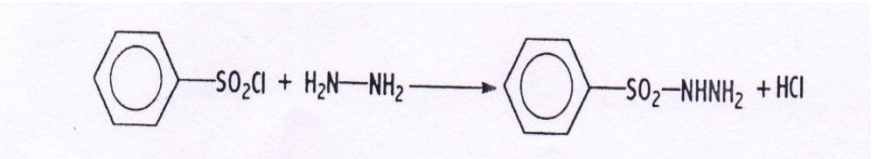
The chemistry of pyrazoline derivatives has received much attention, because of their interesting structural properties and applications to diverse areas [1]. Pyrazolin-5-ones are very important class of heterocycles, due to their potential pharmacological and biological applications [2-4]. Heterocyclic azo Schiff base and their complexes with transition metal ions are important due to their complexing, catalytically biological properties[5,6] These exhibit chemotherapeutic and antiseptic properties[7]. They also have variety of applications such as redox indicator dyeing food stuff and preserving food grains[8]. It is well known fact that they have been used as therapeutic agents, such as anti-inflammatory, antibacterial, antifungal, analgesic, antipyretic [9-11] and cerebral infarction (Free radical Scavenger) [12-15].The diversified applications of pyrazolin-5-ones in different fields have inspired the authors to synthesize the new pyrazolin-5-ones.

MATERIALS AND METHODS

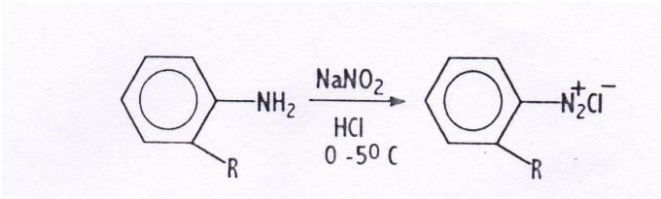
Instruments and Chemicals employed: pH measurements were made using the ELICO Private Limited, Hyderabad, India. IR Spectral details were obtained from a Perkin-Elmer 283 spectrometer. All reagents used were of analytical grade procured from Merck, India. The working solutions were prepared using double distilled water. The Britton-Robinson buffer was prepared from appropriate amounts of 0.04M o-phosphoric acid, 0.04M Boric acid and 0.04M acetic acid. The solutions of desired pH values were prepared by the addition of an appropriate volume of 0.2M sodium hydroxide solution.

Synthesis of N-(Benzene sulfonyl)-3-methyl-4-(2'-substituted aryl hydrazino)-pyrazolin-5-ones: The synthesis involves the following steps:

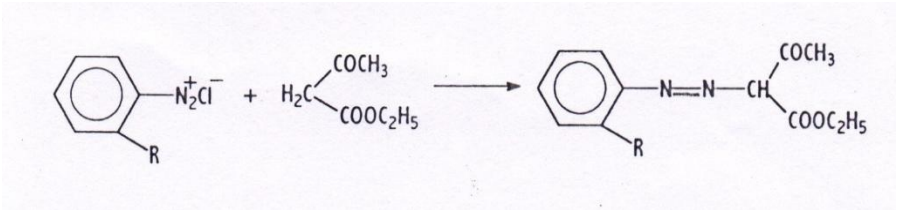
Synthesis of Benzene sulfonyl hydrazide: A solution of benzene sulfonyl chloride in acetone and an appropriate amount of hydrazine hydrate were treated with 5% NaOH solution. The mixture is shaken vigorously for 10 minutes, cooled and poured into 1:1 HCl. The precipitate is filtered off, washed with water and recrystalised from methanol. Melting point of the compound is 104-106^{0}C.



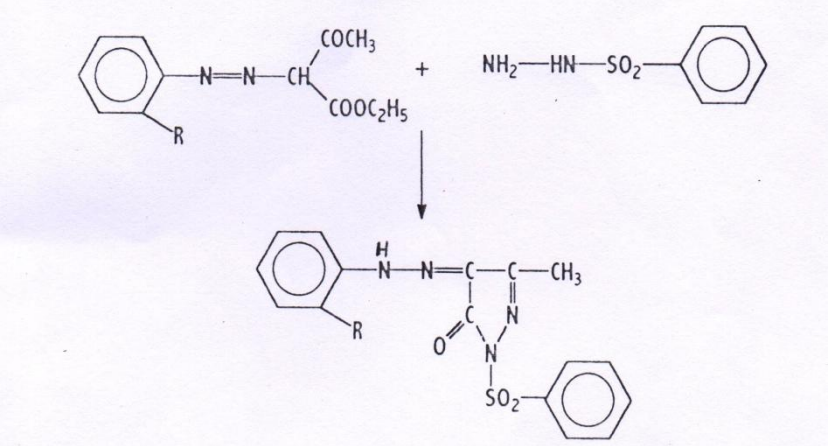
Synthesis of aryl diazonium chloride: The required amount of substituted aryl amine was dissolved in a suitable volume of dilute HCl. The solution obtained is cooled to 0^{0}C, a little amount of an aqueous solution of sodium nitrite was added slowly. The addition of an excess of sodium nitrite solution stabilizes the diazonium chloride.



Synthesis of aryl diazonium aceto acetic ester: The appropriate diazonium chloride solution was added to an ice cold solution of the mixture of sodium acetate and aceto acetic acid solutions in methanol. The addition of corresponding diazonium chloride was continued till yellow crystals were separated out, the crystals were filtered, washed with water and dried. It was recrystalised from 1:1 DMF. Yield is 3.9 g.



Synthesis of N-(Benzene sulfonyl)-3-methyl-4-(2'-substituted aryl hydrazino)-pyrazolin-5-ones: A mixture of appropriate amounts of diazonium acetoacetic ester and benzene sulfonyl chloride was refluxed for 4 hours and cooled. The crystalline solid separated was filtered, washed with water, dried and recrystalized from 1:1 DMF.



RESULTS AND DISCUSSION

Elemental Analysis data: The compounds are analyzed for carbon, hydrogen, nitrogen and sulfur and the results are presented in table-1. The melting points of the synthesized compounds are also presented in table-1.

Table-1: Analytical Data for the compounds synthesized

Sample Number	Substituent	Color	Melting Point (^{0}C)	Elemental Analysis Found (Cal) %			
				C	H	N	S
I	-H	Orange	117-120	56.14 (55.89)	4.09 (4.81)	16.37 (16.01)	9.35 (9.19)
II	2'-CH_3	Yellow	243-245	57.30 (57.00)	4.49 (4.21)	15.73 (15.40)	8.90 (8.71)
III	2'-OCH_3	Yellow	215-217	54.83 (54.51)	4.84 (4.59)	15.05 (57.00)	8.60 (14.70)
IV	2'-OH	Black	260-263	53.63 (53.31)	4.47 (4.21)	15.64 (15.31)	8.94 (8.73)
V	2'-Cl	Yellow	210-212	50.99 (50.62)	3.98 (3.71)	14.87 (14.51)	8.50 (8.30)
VI	2'-NO_2	Orange	224-226	49.61 (49.27)	3.36 (3.12)	18.09 (17.70)	8.27 (8.01)

Infrared spectral studies: The infrared spectral data for N-(Benzene sulfonyl)-3-methyl-4-(2'-substituted aryl hydrazino)-pyrazolin-5-ones were recorded. It is revealed from the study of infrared spectral data that a weak >C=N stretching frequency band is present in the compounds around 1565cm^{-1}. The characteristic absorption band for –NH- group in –NH-N=C< is observed in the region 3448cm^{-1}[16]. Sulphone (O=S=O) group noticed in the region of 1270 cm^{-1} and 1165-1685 cm^{-1}. The (cyclic) C=O group is observed in the region 1686-1701 cm^{-1}[17]. The detailed IR data pertaining to different compounds are given in the table-2. IR Spectra are shown in figures 1-3.

Table-2: IR Spectral data for the Compounds (I to VI)

S. No	Group	ν (cm^{-1})					
		I	II	III	IV	V	VI
1	-N-H	3452	3448	3448	3440	3448	3447
2	C-H (Aromatic)	3050	3030	3028	3020	3084	3042
3	C=O (in pyrazolin ring)	1689	1686	1685	1680	1687	1701

4	C---C(in aromatic nucleus)	1656, 1549, 1480	1654, 1544, 1475	1650, 1543, 1486	1640, 1560, 1488	1540, 1545, 1453	1614, 1575, 1501
5	>C=N	1569	1565	1560	1559	1559	1593
6	C-H (def)	1439	1436	1433	1431	1420	1448
7	N-----O (stre)	-	-	-	-	-	1384
8	S=O (sym &Asym)	1269,1167	1270,1169	1269,1165	1260,1170	1269,1189	1301,1164
9	S-aryl	1088,1045	1086,1040	1087,1040	1080,1030	1109,1085	1048
10	C-H (def) (mono substituted)	757,726	759,724	751,725	748,721	763,725	726,681
11	C-H (def)	762	759	752	749	758	777
12	C----C (def) (out of plane ring)	685	683	680	668	680	678
13	C-Cl (stre) (Aromatic ring)	-	-	-	-	590	-

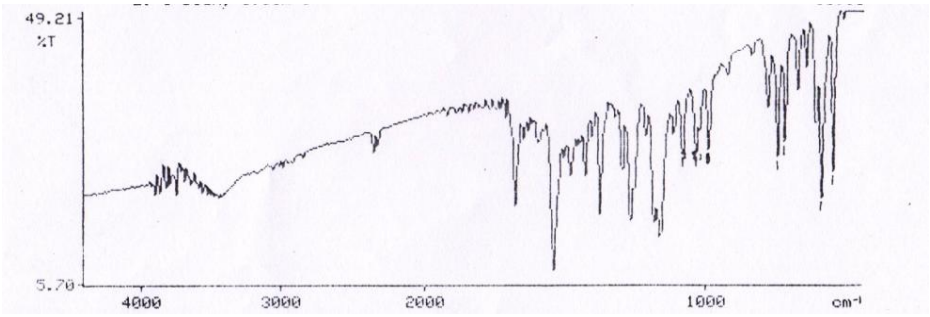


Figure-1: IR Spectrum of compound I

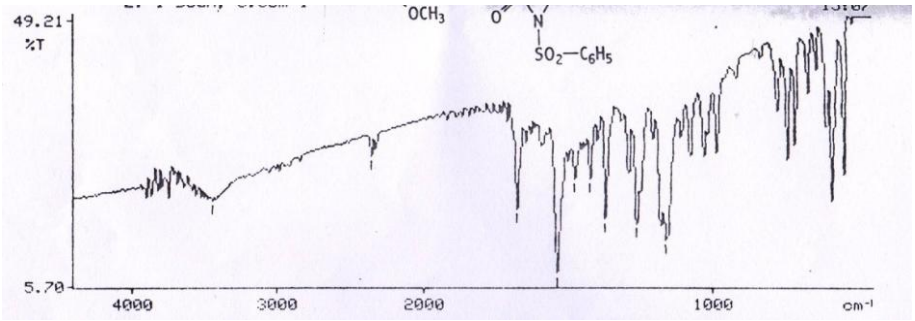


Figure-2: IR Spectrum of compound III

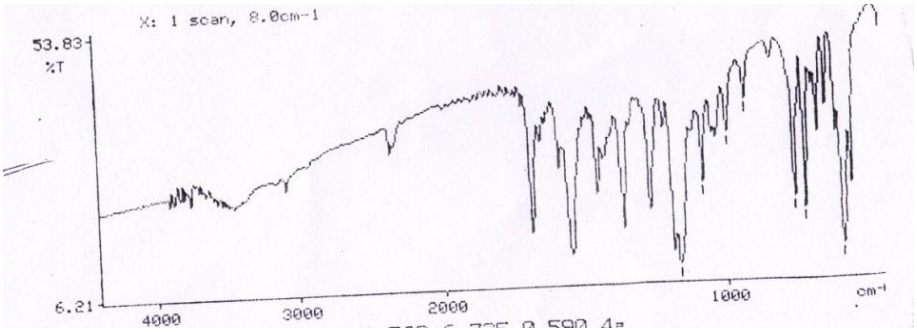


Figure-3: IR Spectrum of compound V

^{1}H NMR spectral data: The ^{1}H NMR spectra were recorded for all the synthesized compounds (I to VI). The chemical shift for N-H proton is observed at 13.4 ppm. The $–CH_3$ group (in pyrazoline) is appeared at 1.4 ppm, phenyl group in $–SO_2$-C_6H_5 is observed at 7.1 to 7.8 ppm. The results relating to ^{1}H NMR data is presented in table-3 and spectra are shown in figures 4 and 5.

Table-3: 1H NMR spectral data for the compounds I to VI (δ ppm)

Compound	$–CH_3$ (singlet)	$–CH_3$/$–OCH_3$/-OH attached to the aromatic ring	$–C_6H_4$(-R) (multiplet)		
I	1.4	---	6.9-7.1	7.4-8.1	13.4
II	1.4	2.4	7.1-7.3	7.6-8.2	13.4
III	1.4	4.0	6.8-7.2	7.5-8.2	13.4
IV	1.4	5.2	7.1-7.4	7.6-8.3	13.4
V	1.4	---	7.0-7.4	7.6-8.2	13.4
VI	1.4	---	7.3-7.7	8.0-8.3	13.4

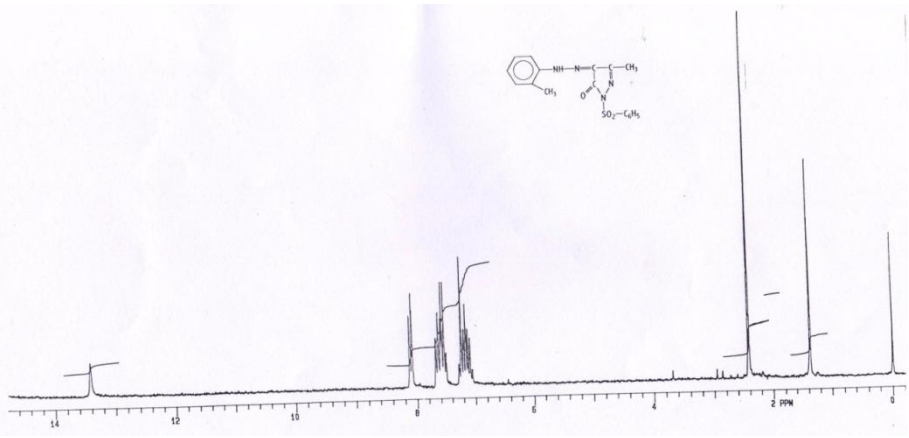


Figure-4: 1H NMR spectrum of compound II

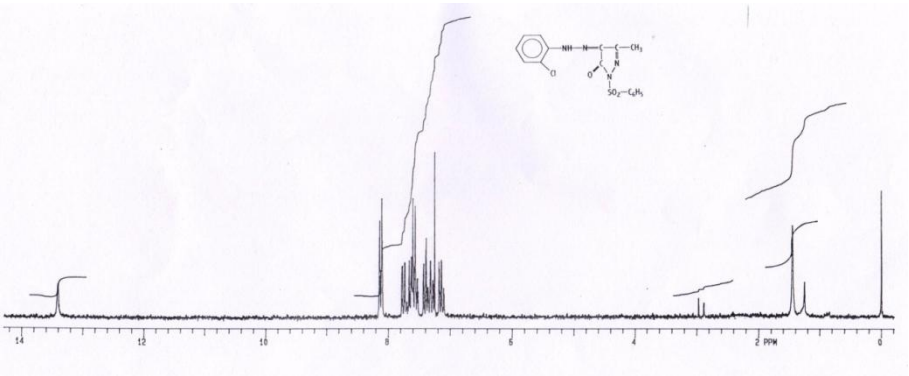


Figure-5: 1H NMR spectrum of compound V

Mass spectral data: Mass spectral studies for N-(Benzene sulfonyl)-3-methyl-4-(2'-substituted aryl hydrazino)-pyrazolin-5-ones were recorded. Molecular ion peaks (M^+) were present in all compounds (Compounds I to VI). Major fragmentation patterns observed are due to loss of C_6H_5-SO_2, N_2, CO, C_6H_5. The fragmentation pattern is shown in figure 6 and spectra are shown in figures 7and 8.

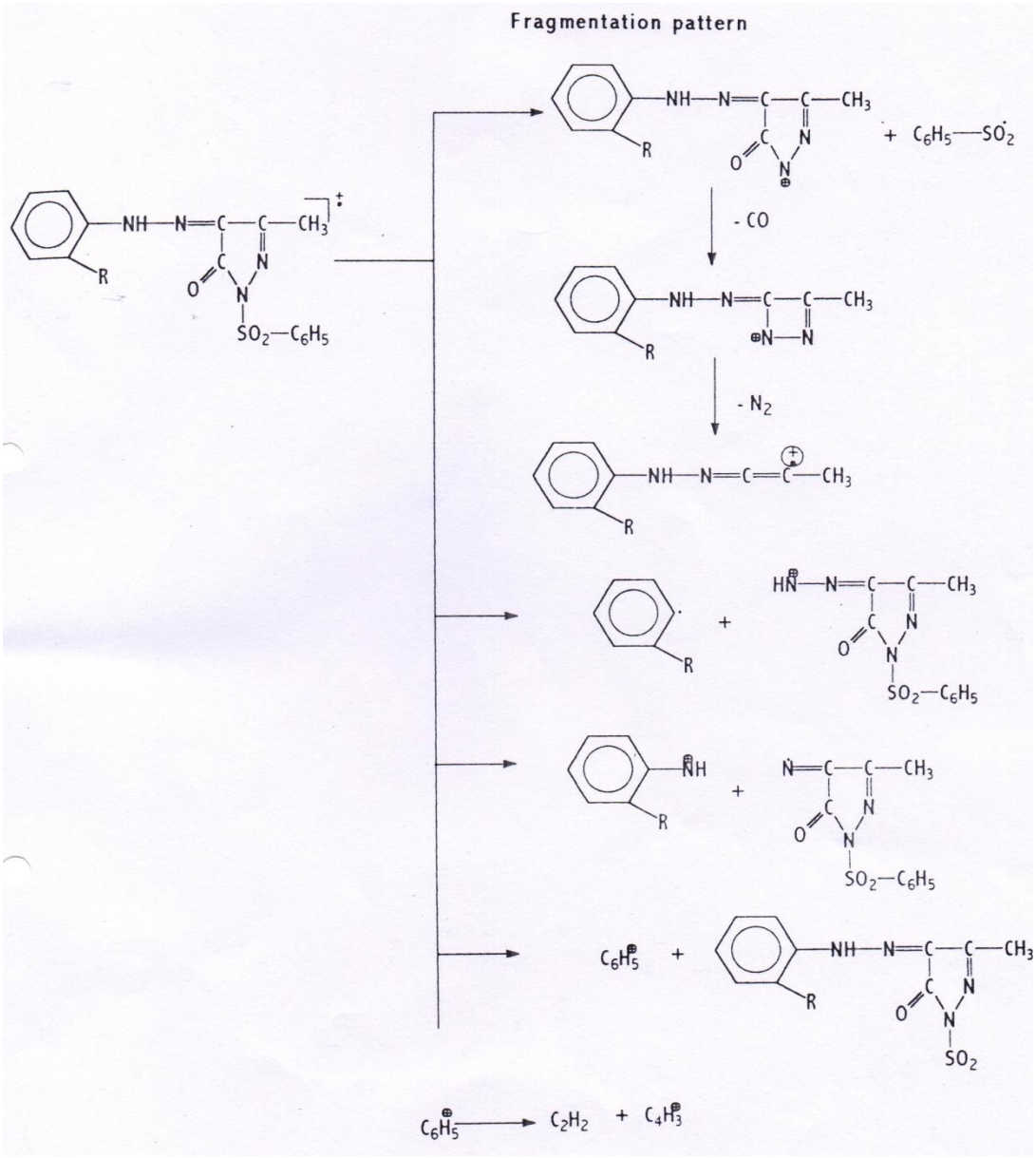


Figure-6: General Fragmentation Pattern for the compounds

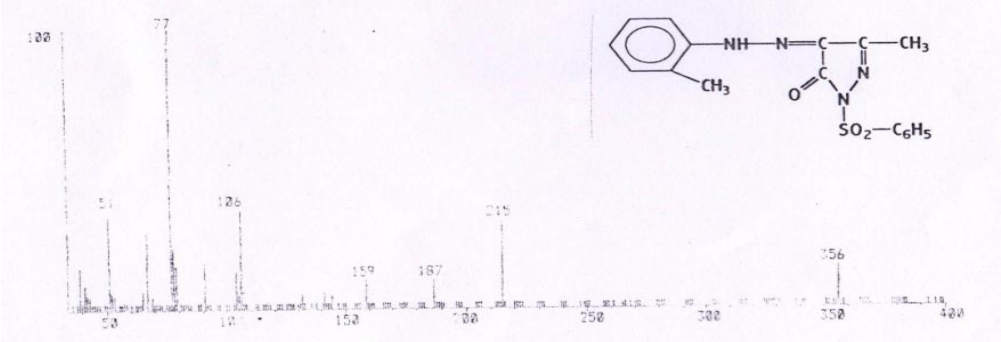


Figure-7: Mass spectrum of compound II

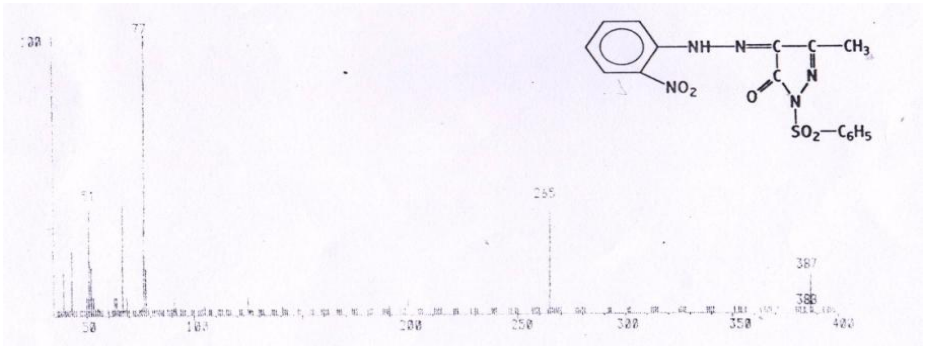


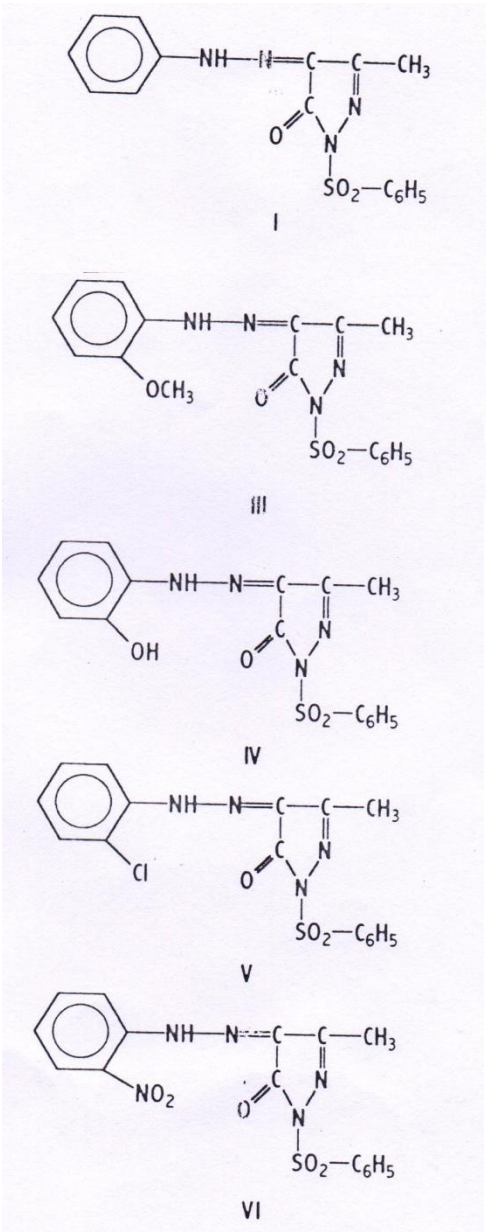
Figure-8: Mass spectrum of compound VI

APPLICATIONS

Synthesized different Pyrazolin-5-Ones compounds and characterized due to its many applications.

CONCLUSIONS

On the basis of elemental analysis, IR, ^{1}H-NMR and mass spectral studies, the following structures were proposed for N-(Benzene sulfonyl)-3-methyl-4-(2'-substituted aryl hydrazino)-pyrazolin-5-ones (Compounds I to VI).



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