CHAPTER -II

EXPERIMENTAL

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EXPERIMENTAL

Synthetic Methodology and General Remarks

Experimental work is divided in to three parts

PART-I(a)

Synthesis of N^1-(Substituted quiniolin-2-one-1-ylmethyloxo)-oxopyrano[4,3-c]pyrazoles

PART-I(b)

Synthesis of N^1-(Substituted quinolin-2-one-1-ylmethyloxo) pyrazoles

PART-II(a)

Synthesis of N^1-(Substituted quinolin-4-ylmethyloxo) oxopyrano[4,3-c]pyrazoles

PART-II(b)

Synthesis of N^1-(Substituted quinolin-4-one-1-ylmethyloxo) pyrazoles

PART-III

Synthesis of new pyranopyrazole derivatives

GENERAL REMARKS :

I Percentage yield, physical constants (M.P/B.P.),Elemental analysis (found and calculated) and spectral characteristics of the synthesised compounds have been reported.

II M.P/B.P.were determined by open capillary method and are uncorrected.

III UV spectra were recorded in 95% ethanol on a "Beckmann DK-1" spectrophotometer.

IV I.R.spectra were recorded in KBr Pellets/Nujol on "Perkin-Elmer-237"/Shimadzu I.R.437"spectrometer.

V ^{1}H NMR spectra were recorded on "Perkin-Elmer R-32" 90 MHz/200 MHz .Spectrometer" using TMS as an internal reference and CCl_4 /$CDCl_3$ /TFA/DMSO as solvent.The chemical shift (δ values) were reported in ppm.

VI The purity of the compounds in addition to the elemental analysis was checked by TLC using silica gel as an adsorbent.

VII Mass spectra were recorded on "EL-MS computer"system.

EXPERIMENTAL PROCEDURE

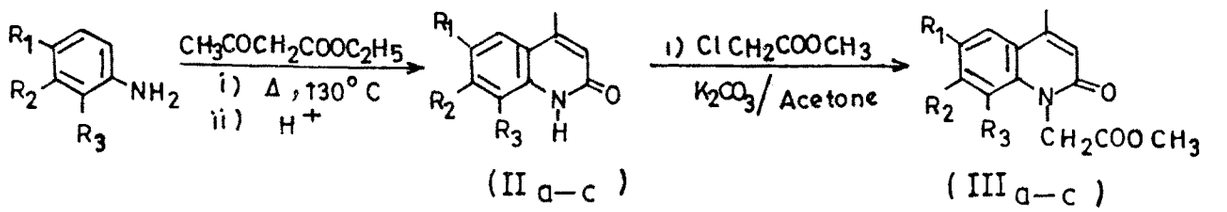
PART-I(a) SYNTHESIS OF N^1-SUBSTITUTED QUINOLIN-2-ONE-1-YL METHYLOXO 4-OXOPYRANO [4,3-c]PYRAZOLES

Synthesis of N^1 -substituted cyclic quinolin-2(1H) One derivatives has been reported. The strategy employed for the preparation of desired compounds involved the acid catalysed cyclisation of acetoacetanilide to yield 4-methyl quinolin-2 (1H)ones (II_{a-c})which when reacted with methyl chloroacetate gave N^1-carbmethoxymethyl 4-methyl quinolin-2(1H) one(III_{a-c}) Compound (III) when reacted with hydrazine hydrate in ethanol formed N^1 -hydrazidomethyl quinolin-2(1H) ones(VI_{a-c}). The reaction of IV_{a-c} with 3-acetyl, 6-methyl, Pyran-2,4-dione in methanol yielded N^1-substituted quinolinopyrazoles(V_{a-c}). The reaction of(IV_{a-c})with acetylacetone furnished 3',5'-Dimethyl-1-(8-chloro-4-methyl quinolin-2-one-1-yl methyloxo) pyrazoles. (VI_{a-c}) as shown in reaction Scheme-1. The structures of these compcund werre confirmed by UV,IR,NMR and mass spectral analysis.

1) PREPARATION OF 4-CHLOROACETOACETANILIDES (I_a) :

In round bottomed flask carring reflux condenser, a mixture of aniline (9.2 gm, 0.001 mole) and acetoacetic ester (12.6 ml, 0.001 mole) in methanol (25 ml) was heated for 4 hours, cooled and neutralised with Na_2CO_3 .Heavy liquid separated out was extracted in chloroform and the solvent was removed. The heavy liquid was distilled under reduced pressure

SCHEME–I

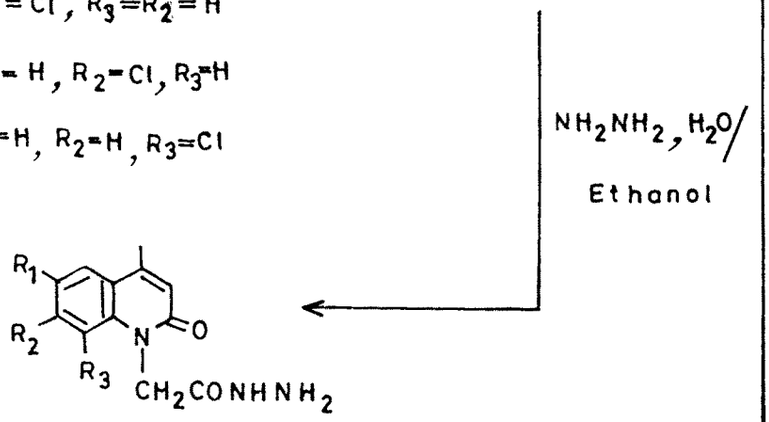


(II a–c) (III a–c)

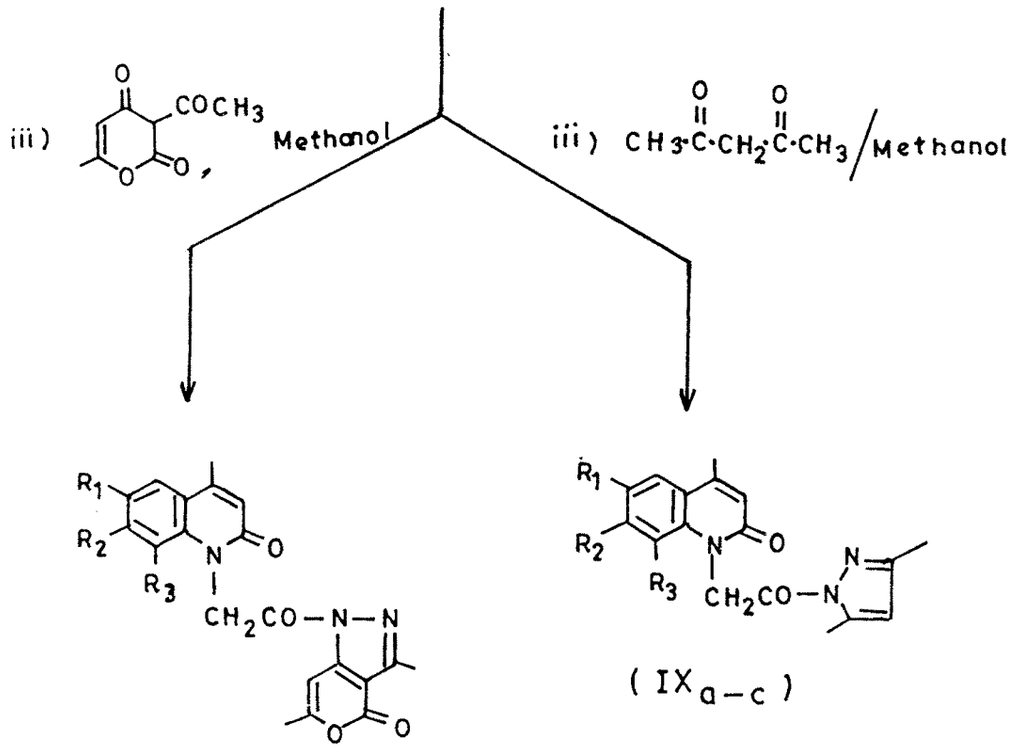
a, $R_1 = Cl$, $R_3 = R_2 = H$

b, $R_1 = H$, $R_2 = Cl$, $R_3 = H$

c $R_1 = H$, $R_2 = H$, $R_3 = Cl$



(V a–c)



(VII a–c) (IX a–c)

to give acetoacetanilide yield 35 gm (85%), B.P.-139^{o}C at15 mm.

IR(Nujol) : ν 3450-3200(-NH),1700 (Ketone, > C=O) 1670-1660 (amido >C=O), 1600 cm^{-1} (> C=C<)

^{1}H NMR ($CDCl_3$) : δ 2.15(3H,s,-$COCH_3$), 3.3 (2H,s,$COCH_2$), 4.55(1H,s,-NH exchangable with D_2O), 6.9-7.35 (5H,m, aromatic protons) ppm

Fig.No. 1

Other substituted acetoacetanilides I_b and I_c were prepared by similar method I_b(R_1=R_3=H,R_2=Cl) B.P. 125^{o}C at 15 mm. I_c(R_1=Cl, R_2=R_3=H).their structures were confirmed by ^{1}H NMR and IR spectral data.

IR (Nujol) I_b, : ν , 3350-3250(-NH), 1685(Ketone>C=O) 1665-1655 (amido,>C=O), 1600(>C=C),760 cm^{-1} (C-Cl).

^{1}H NMR(CCl_4) : I_b, δ, 2.12 (3H,s,-$COCH_3$), 2.2(3H,s,Ar-CH_3) 3.4(2H,s,-CH_2),6.8-7.3(4H,m,aromatic protons) ppm.

2 PREPARATION OF 8-CHLORO-4-METHYL QUINOLIN-2(1H) ONE(II_a)

In round bottom flask a mixture of acetoacetanilide I_a(17.7gm, 0.1 mole) and Conc.H_2SO_4 (AR) (40 ml) was heated on water bath at 80-85^{o}C for 0.5 hr. initially and for 1.0 hr.at 100^{o}C , cooled and poured in 500 ml ice cold water with constant stirring. the separated product was filtered, dried and recrystallised from ethanol to give II_a, 13.0 gm (81.75%),

M.P.227 ^{o}C (Found: C,62.05; H, 4.05; N, 7.10 requires :C,62.8 ; H, 4.15; N,7.25).

IR (KBr) : ν 3200-3100 broad-NH, 1670(cyclic amido >C=O), 1600 cm^{-1}(>C=O) Fig. No. 2

^{1}H NMR(TFA) : δ 2.45 (3H,s,4-CH_3), 6.6(1H,s,=CH-),6.8-7.0 (1H dd ,J_{ortho}=8Hz,J_{meta} =2.5 Hz,C -H), 7.5-7.15 (1H,d J_{ortho} =8Hz C_5-H),7.15-7.35 (1H,dd,J_{ortho} =8Hz ,J_{meta} 2.5 Hz C_8-H) ppm

(Other substituted quinolones were prepared by similar method and their m.pts yields and analytical data have been incorporated in Table -I (a)

TABLE-I (a)

PHYSICAL AND ANALYTICAL DATA OF COMPOUNDS

Sr. No.	Groups R_1	R_2	R_3	M.P ^{o}C	Yield %	Molecular formula	Experimental Analysis found (%) & (Calculated %) C	H	N
II_b	H	Cl	H	213	68.39	$C_{10}H_8ONCl$	62.10 (61.18)	4.00 (4.15)	7.00 (7.25)
II_c	Cl	H	H	205	70.25	$C_{10}H_8ONCl$	62.00 (62.8)	4.05 (4.15)	7.05 (7.25)

TABLE-I (b)

IR AND ^{1}H NMR SPECTRAL DATA OF COMPOUNDS $II_{a(a-c)}$

Sr.No.	IR (Nujol)ν,cm^{-1}	^{1}H NMR ($CDCl_3$) δ, ppm
II_b	3250-3100(-NH),1665-1660 (cyclic amido >C=O,) 1600(>C=C<)	2.4(3H,s-CH_3),6.4-6.5(1H,s,=CH-) 6.8-7.35(3H,m.aromatic protons) 8.25(1H,s,broad exchangable with D_2O,-CONH)
II_c	3200-3150(-NH),1665 (cyclic amido >C=O,), 1605(>C=O). Fig.No.3	2.43(3H,s,=-CH)6.4(1H,s,=CH-) 6.7-7.3(3H,m,aromatic protons), 8.2 (1H,s,broad-CONH).

3 SYNTHESIS OF N^1- CARBMETHOXYMETHYL8CHLORO-4-METHYL-QUINOLIN-2-(1H) One (III_a) :

In round bottomed flask carrying a reflux condenser and a guard tube, a mixture of 8-chloro-4-methyl quinolin-2(1H)one (II_a), 5.9 gm 0.02 mole) methyl chloroacetate(2.2gm. 0.02 mole) in dry acetone containing unhydrous potassium carbonate (2 gm) was refluxed for 24 hr., cooled and the solvent was removed under reduced pressure. The resulting white solid washed with water, filtered & recrystallised from ethanol to yield III_a yield 5.1 gm (55%), m.p. 118°C.

IR (KBr) : ν , 1760 (ester >C=O),1660 (broad cyclic amido >C=O), 1600 (>C=O) cm^{-1}.

^{1}H NMR($CDCl_3$) : δ, 2.43 (3H,s,C-CH_3),3.7 (3H,s,-OCH_3 ester), 3.95 (2H,s,-N-CH_2), 6.8-7.3(3H,m,aromatic protons) Fig.No.4

The physical analytial and spectral data of the other compounds III_{b-c} have been incorporated in Table 3 (a) and 3 (b) respectively.

TABLE 3(a)
PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS (III)

Sr No.	Group R_1	R_2	R_3	M.P. °C	Yield %	Molecular formula	Elemental analysis found % (calculated %) C	H	N
II_a	H	H	Cl	118	55	$C_{13}H_{12}O_3NCl$	56.90 (56.80)	4.70 (4.80)	5.60 (5.70)
II_b	H	Cl	H	111	53,5	$C_{13}H_{12}O_3NCl$	56.90 (56.80)	4.70 (4.80)	5.60 (5.75)
III_c	Cl	H	H	107	54.5	$C_{13}H_{12}O_3NCl$	56.90 (56.95)	4.70 (4.75)	5.60 (5.73)

TABLE 3(b)

IR AND ^{1}HNMR SPECTRAL CHARACTERISATION DATA OF THE COMPOUNDS (III)

Sr No.	IR (Nujol), ν cm^{-1}	^{1}H NMR ($CDCl_3$), δ ppm
III_b	1760(easter >C=O), 1660 (cyclic amido >C=O), 1605(>C=O)	2.65(3H,s,=C-CH_3),3.85 (3H,s,-OCH_3 ester),4.15(2H,s,N-CH_2), 6.7-7.35(3H,m,aromatic protons)
II	1760-1750 (ester C=O), 1665-1660(cyclic amido C=O), 1595 (>C=C<). Fig.No. 5	2.62(3H,s,=C-CH_3)3.87 (3H,s,OCH_3 ester), 4.1 (2H,s,N-CH_2) 6.7-7.3(3H,m,aromatic protons)

4 SYNTHESIS OF N^1 -METHYLHYDRAZIDO-8-CHLORO-4-METHYL-QUINOLIN-2(1H) ONE (IV_a) :

The solution of compound III_a in a flat bottomed Flask (6 gm, 0.01 mole) in ethanol (40 ml) 80% hydrazine hydrate 0.8 ml, 0.01 mol) was added and the same reaction mixture refluxed on a water bath using reflux condensor for 3 hr., cooled & the resulting solid was filtered and recrystallised from ethanol to furnish IV_a yield, 4 gm (74%) m.p.=198^{0}C (found; C 52.60; H 4.10; N,16.70; $C_{12}H_{10}O_2N_3Cl$ requires C, 52.45; H,4.05; N, 16.70;

IR (KBr) : ν, 3350-3200 (-$NHNH_2$),1680-1670 (acyclic amido >C=O), 1660-50 (cyclic amido >C=O),1600(>C=C<), 760 cm^{-1} (C-Cl) Fig.No. 6

Mass(M/e %) : 265(0.5),207(100),192(10)177(10),175(25),164(40) 143(10),99(20),75(10).Fig.No.7.

Mass fragmentation pattern .Scheme-A

^{1}H NMR ($CDCl_3$): δ ,2.4(3H,s,=C-CH_3),2.5(2H,s,-NH_2) 3.9 (2H,s,-N-CH_2), 7.0-7.5 (4H,m,Ar-H) ppm

UV(ethanol) : λ_{max} 328 and 321 nm.

Other compounds were prepared by similar method and their yields, molecular formula, and elemental analysis data have been incorporated in Table 4 (a) and IR, ^{1}H NMR spectral data in Table 4(b).

TABLE 4(a)
PHYSICAL AND ANALYTICAL DATA OF OTHER COMPOUNDS (IV)

Sr. No.	Group R_1	R_2	R_3	M.P. °C	Yield %	molecule formula	Elemental analysis- found % & (calculated)% C	H	N
IV_b	H	Cl	H	196	70	$C_{12}H_{12}O_2N_3Cl$	52.40 (52.60)	4.00 (4.10)	16.50 (16.70)
IV_c	Cl	H	H	197	72	$C_{12}H_{12}O_2N_3Cl$	52.45 (52.60)	4.05 (4.10)	16.7 (16.70)

TABLE 4(b)
SPECTRAL CHARACTERISATION DATA OF THE COMPOUND (IV)

Sr. No.	IR (Nujol)ν, cm^{-1}	^{1}H NMR ($CDCl_3$)δ, ppm
IV_b	3350-3250(NH), 1670(acyclic amido), 1660-1665(cyclic amido) 1600 (>C=C<).	2.4(3H,s,=C-CH_3),2.5(2H,s,-NH_2) 6.7-7.3(3H,m,aromatic protons), 8.2(1H,s,-CO-NH).
IV_c	3260-3250 (-NH), 1670(acyclic amido), 1600 (>C=C<)	2.45(3H,s,=C-CH_3),2.52(2H,s, -NH_2) 6.7-7.3(3H,m,aromatic protons), 8.25(1H,s,-CONH)

5 SYNTHESIS OF 3,6-DIEMTHYL-1(8-CHLORO-4-METHYL QUINOLIN -2-ONE-1-YL-METHYLOXO)4-OXYOPYRANO[4,3-c] PYRAZOLES(V_a)

The mixture of compound IV_a (0.251 gm, 0.001 mole) and 3-acetyl, 6-methyl pyran-2,4-dione (0.168gm, 0.001 mole) in methanol was refluxed for 3-4 hr. and concentrated. The separated solid was filtered and recrystallised from methanol to yield (V_a) yield 64%, m.p.=212°C (Found;C,60.4;H,4.0,N,10.5; $C_{20}H_{16}O_4N_3Cl$ requires; C,60.5, H,4.1;N,10.6%).

IR(KBr) : ν ,1760(lactone >C=O),1685 (cyclic and acylic amido >C=O), 1630 (>C=N),755 cm^{-1} (-C-Cl).

^{1}H NMR CDCl$_3$) : δ ,2.15 (3H,s,-N=C-CH_3),2.35 (6H,s,2 X-CH_3), 6.15(2H,s,2 X =C<u>H</u>-),3.90(2H,s,-N-CH_2), 7.0-7.3(3H,m,Ar-H).

Other compounds i.e. V_b and V_c were prepared by similar method. Their physical, analytical and spectral data have been incorporated in Table 5(a) and Table 5(b) respectively.

TABLE 5(a)
PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS(V)

Sr No	Group			M.P. °C	Yield %	Molecular formula	Elemental analysis found/(calculated.)%		
	R_1	R_2	R_3				C	H	N
V_b	H	Cl	H	204	65	$C_{20}H_{16}O_4N_3Cl$	60.40 (60.50)	4.10 (4.19)	10.50 (10.60)
V_c	Cl	H	H	201	62	$C_{20}H_{16}O_4N_3Cl$	60.4 (60.5)	4.00 (4.1)	10.5 (10.6)

TABLE 5(b)
IR AND ^{1}H NMR SPECTRAL DATA OF THE COMPOUNDS (V)

Sr No	IR (Nujol), ν cm^{-1}	^{1}H NMR ($CDCl_3$), δ , ppm
V_b	1770(lactone >C=O),1680-1685 (cyclic and acyclic amido >C=O),1620(>C=N), 760(C-Cl)	2.18(3H,s,-N=C-CH_3), 2.35(6H,s, 2 X -CH_3),6.12(2H,s,2 X -CH=) 3.8(2H,s,N-CH_2),6.8-7.3(3H,m, aromatic protons).
V_c	1770-1780(lactone >C=O), 1685(cyclic and acyclic amido >C=O)1620(>C=N-) 760,(C-Cl)	2.16(3H,s,-N=C-CH_3),2.35(6H,s, 2X -CH_3),6.15(2H,s,2 X=CH-) 3.82(2H,s,-N-CH_2),6.7-7.35(3H,m, aromatic protons).

6 SYNTHESIS OF 3,5-DIMETHYL-1(8-CHLORO-4-METHYL QUINOLIN -2-ONE -1-YLMETHYLOXO) PYRAZOLES

The compounds (IV_a) (0.251 g,0.001 mole) and acetylacetone (0.10 g; 0.001 mole) in methanol refluxed on a steam bath for 5 hr., cooled and the solvent was removed under vacuum. The residual mass then treated with ice-water to give a solid which when recrystallised from ethanol furnished (VI_a) yield 0.20 gm (40%) m.p. 42 ^{0}C, (found C;59.8;H,4.8;N,12.7; $C_{17}H_{16}N_3O_2Cl$ requires C, 60.0; H,4.9 N,12.8 %).

IR(KBr) : ν ,1680-60 (borad cyclic and acyclic >C=O), 1620(>C=N), 760 cm^{-1} (C-Cl) Fig.No.

^{1}H NMR ($CDCl_3$) : δ ,2.5(3H,s,-N=C-CH_3),2.35(6H,s,2 X=-CH_3) 3.78(2H,s,-N-CH_2), 6.2(1H,s,=CH-),7.0-7.3(3H,m,Ar-H)ppm

Other compounds VI_b and VI_c were prepared by similar method.

Their physical and analytical data have been furnished in Table No. 6(a) and spectral data in Table 6(b) respectively.

TABLE 6(a)

PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS

Sr No	Group R_1	R_2	R_3	M.P. ^oC	Yield %	Mol.Formula	Elemental analysis found/(calculated) % C	H	N
VI_b	H	Cl	H	48	45	$C_{17}H_{16}N_3O_2Cl$	59.90 (60.00)	4.85 (4.90)	12.70 (12.80)
VI_c	Cl	H	H	52	41	$C_{17}H_{16}N_3O_2Cl$	59.80 (60.0)	4.80 (4.90)	12.80 (12.80)

TABLE 6(b)

IR AND ^1H NMR SPECTRAL DATA OF THE COMPOUNDS (VI)

Sr. No.	IR (Nujol) ν, cm^{-1}	^1H NMR ($CDCl_3$) δ, ppm
VI_b	1665-1680(cyclic and acyclic amido),1620(>C=N-),1605 (>C=C<),760(-C-Cl)	2.15(3H,s,-N=C-CH_3),2.35 (6H,s,2 X-CH_3),3.8(2H,s,N-CH_2) 6.2(1H,s,=CH-),6.8-7.3(3H,m, Ar-H),
VI_c	1660-1685(cyclic and acyclic amido >C=O),1620(>C=N), 1600(>C=C<),755(C-Cl). Fig.No.8	2.18(3H,s,N=C-CH_3),2.35(6H,s, 2 X CH_3),3.82(3H,s,N-CH_2) 6.18 (1H,s,=CH-),6.7-7.3(3H,m,Ar-H).

7 IR, ^1H NMR AND MASS SPECTRA

IR, ^{1}H NMR AND MASS SPECTRA

^{1}H NMR SPECTRUM OF o-CHLORO ACETOACETANILIDE .

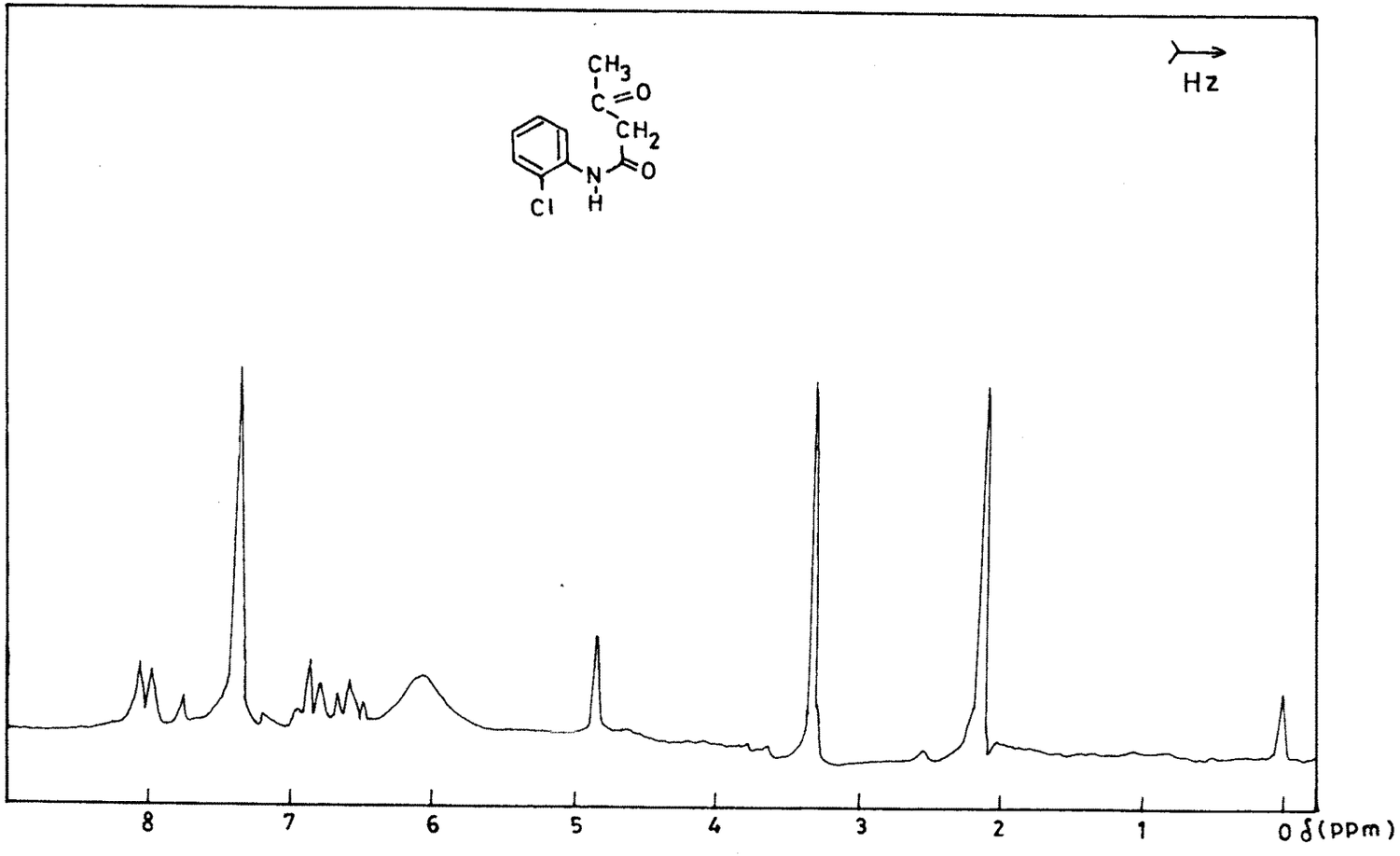


FIG. NO. 1

I R SPECTRUM OF 4-METHYL , 8-CHLORO QUINOLIN -2(1H) ONE .

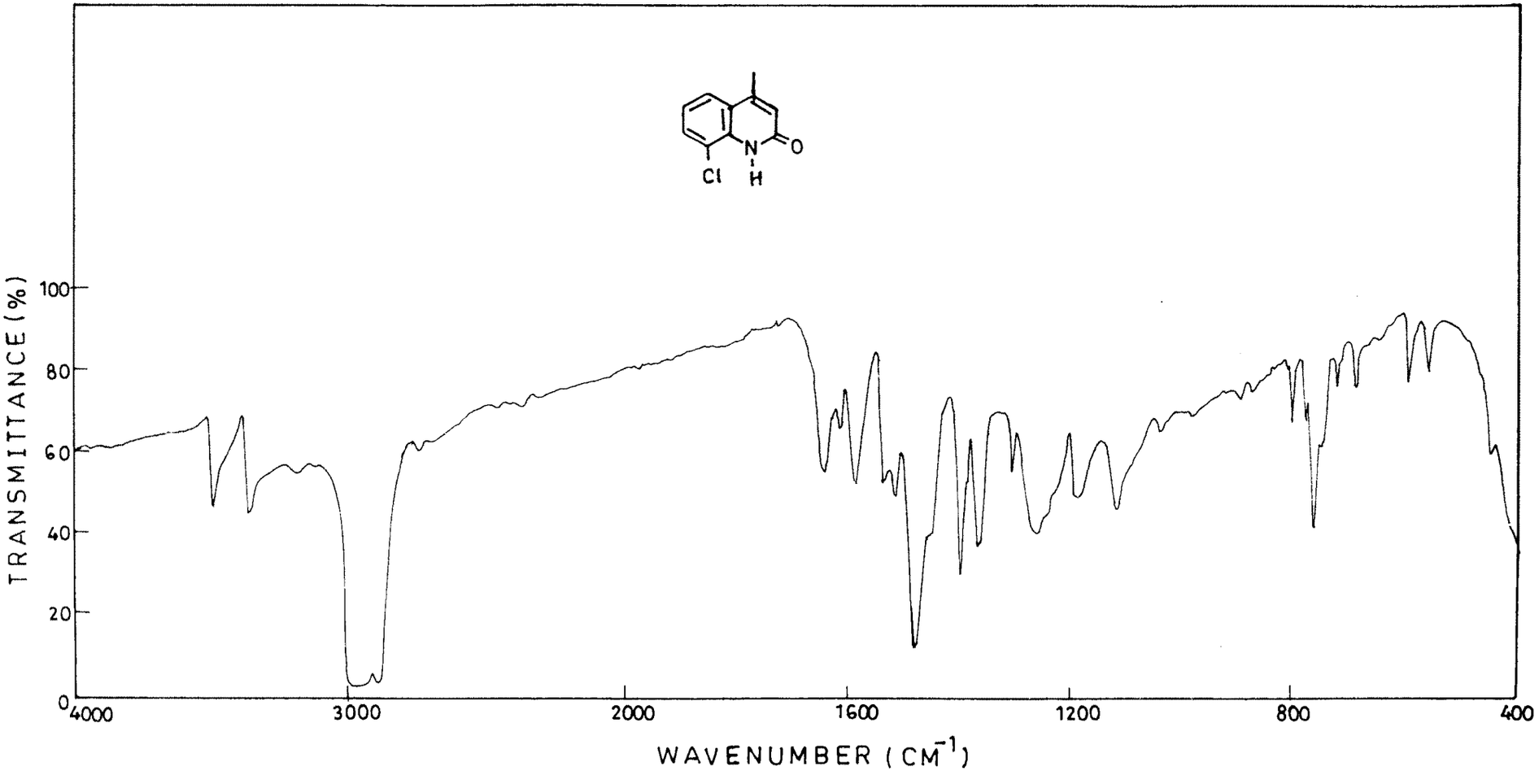


FIG. NO. 2

IR Spectrum of 6-Chloro-4-methyl quinoline-2(H) one .

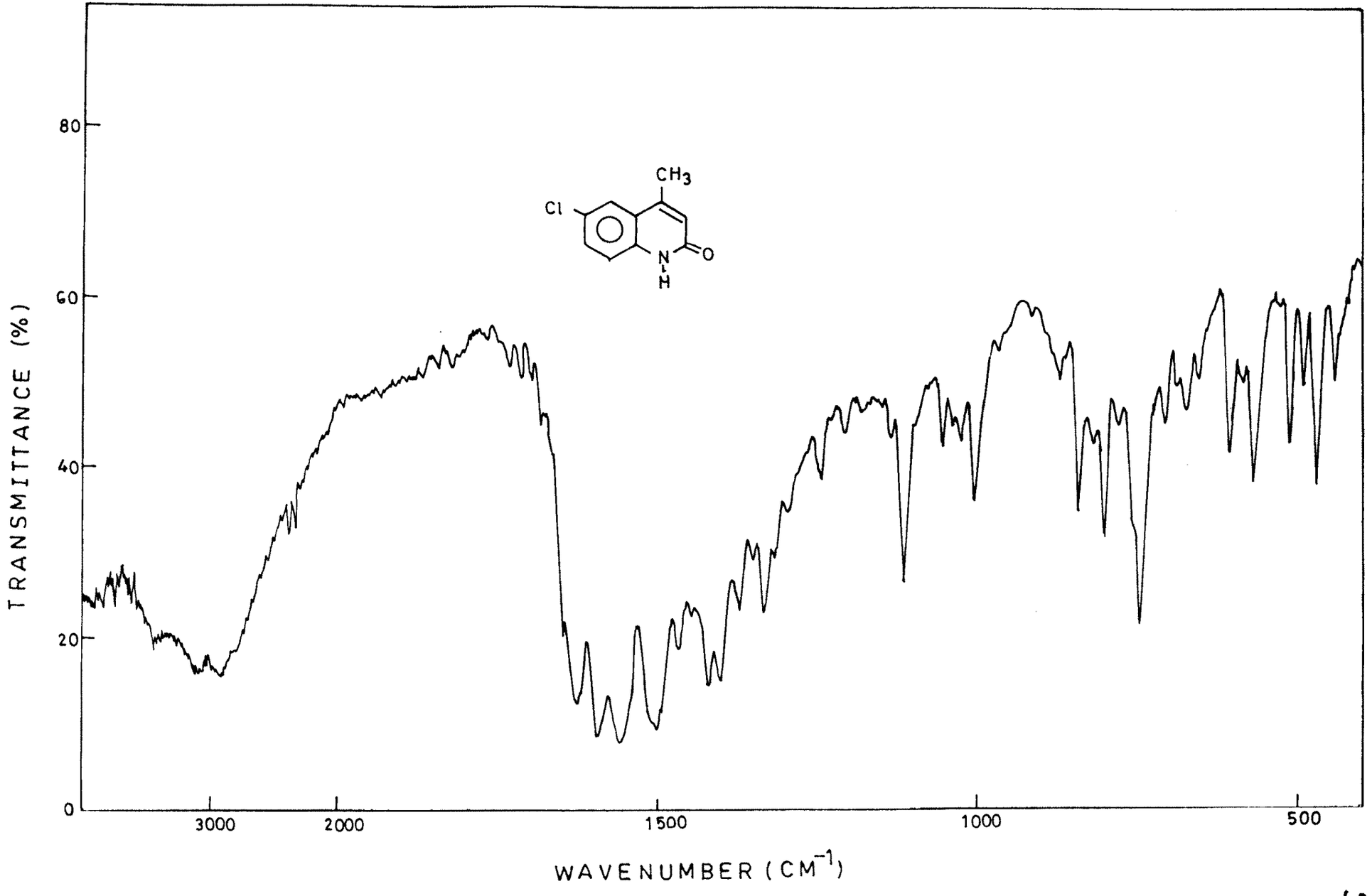


Fig. 3

^1H NMR Spectrum of N^1-Carbmethoxy methyl-8-chloro-4-methyl quinolin-2 (1H) one .

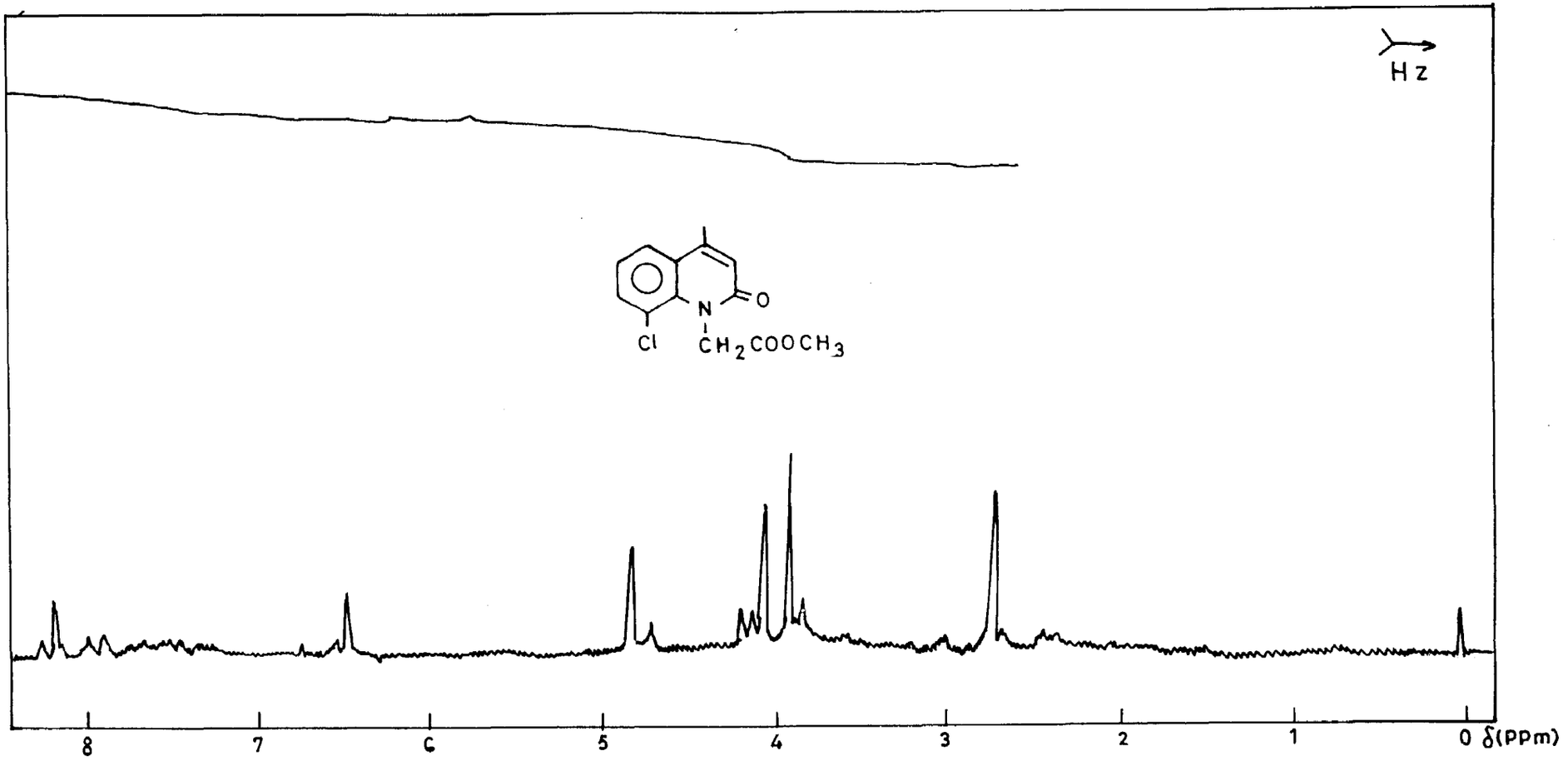


Fig. 4

IR Spectrum of N^1- Carbomethoxy methyl 6-Chloro-4-Methyl quinoline-2 (1H) one .

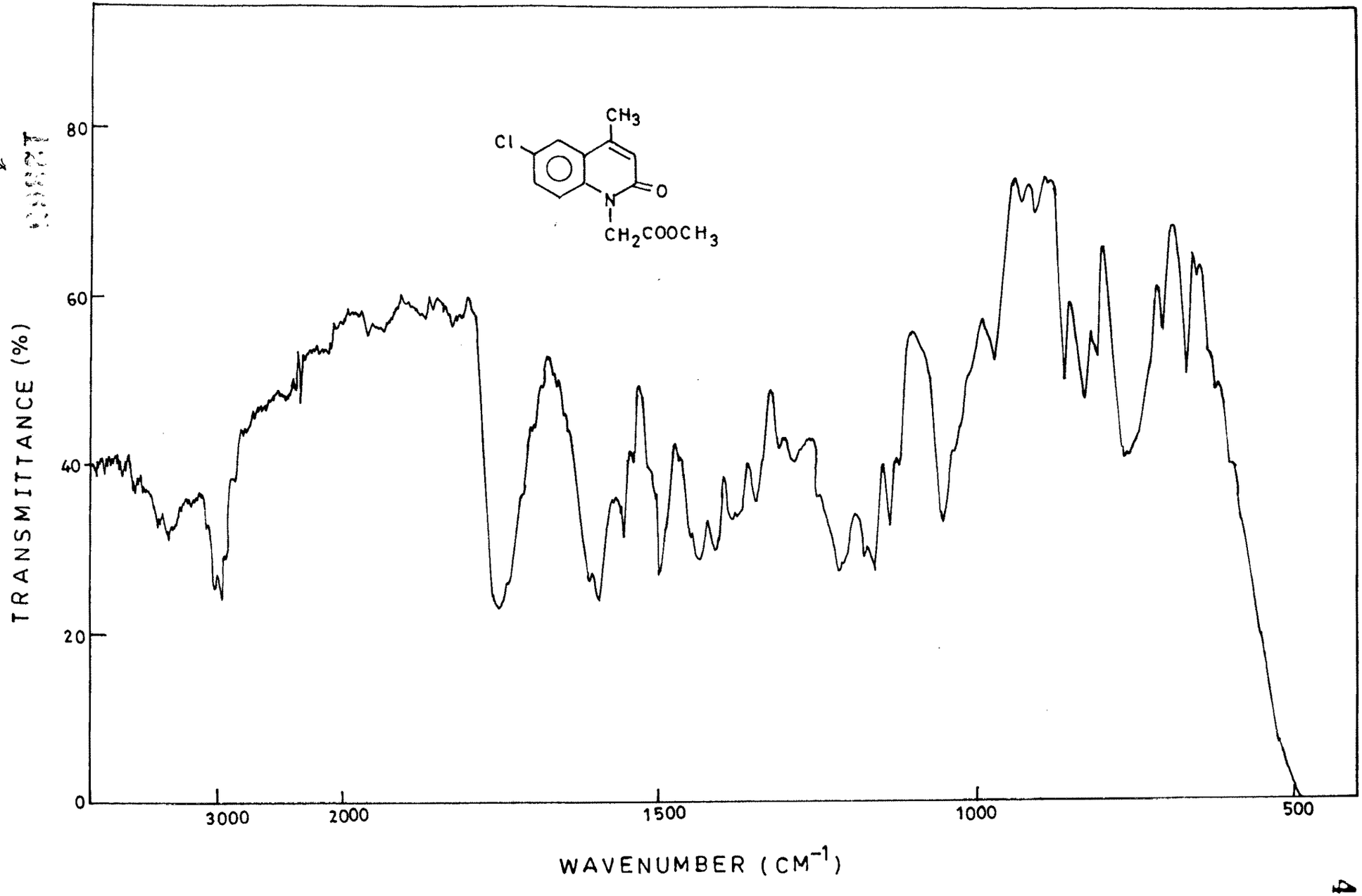


Fig. 5

IR Spectrum of N^1- Methoxyhydrazido-8-Chloro-4-Methyl quinolin-2 (1H) one.

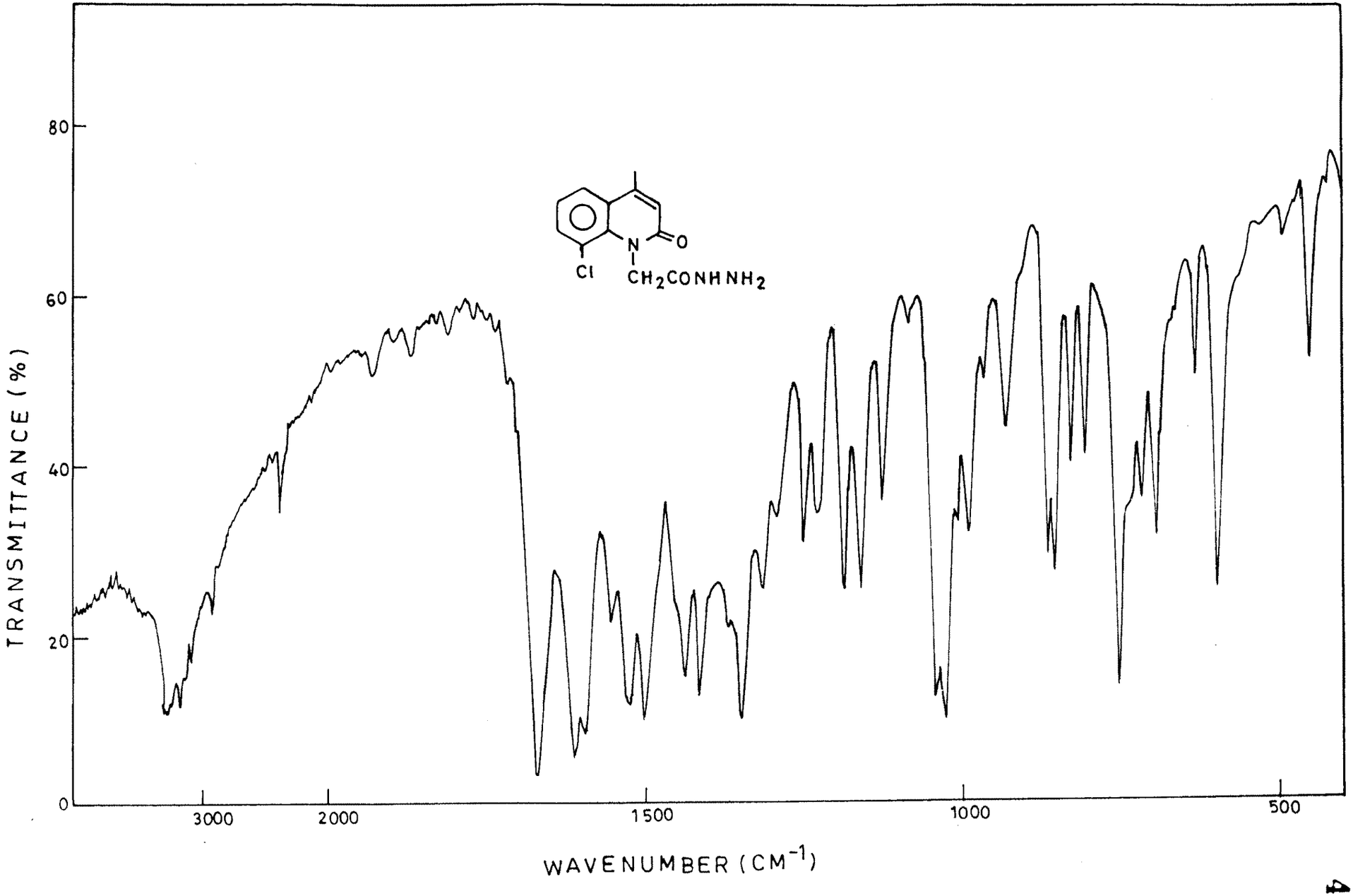


Fig. 6

. MASS SPECTRUM OF N^1- ACETYLHYDRAZIDO - 8 - CHLORO QUINOLIN - 2 (1H) ONE .

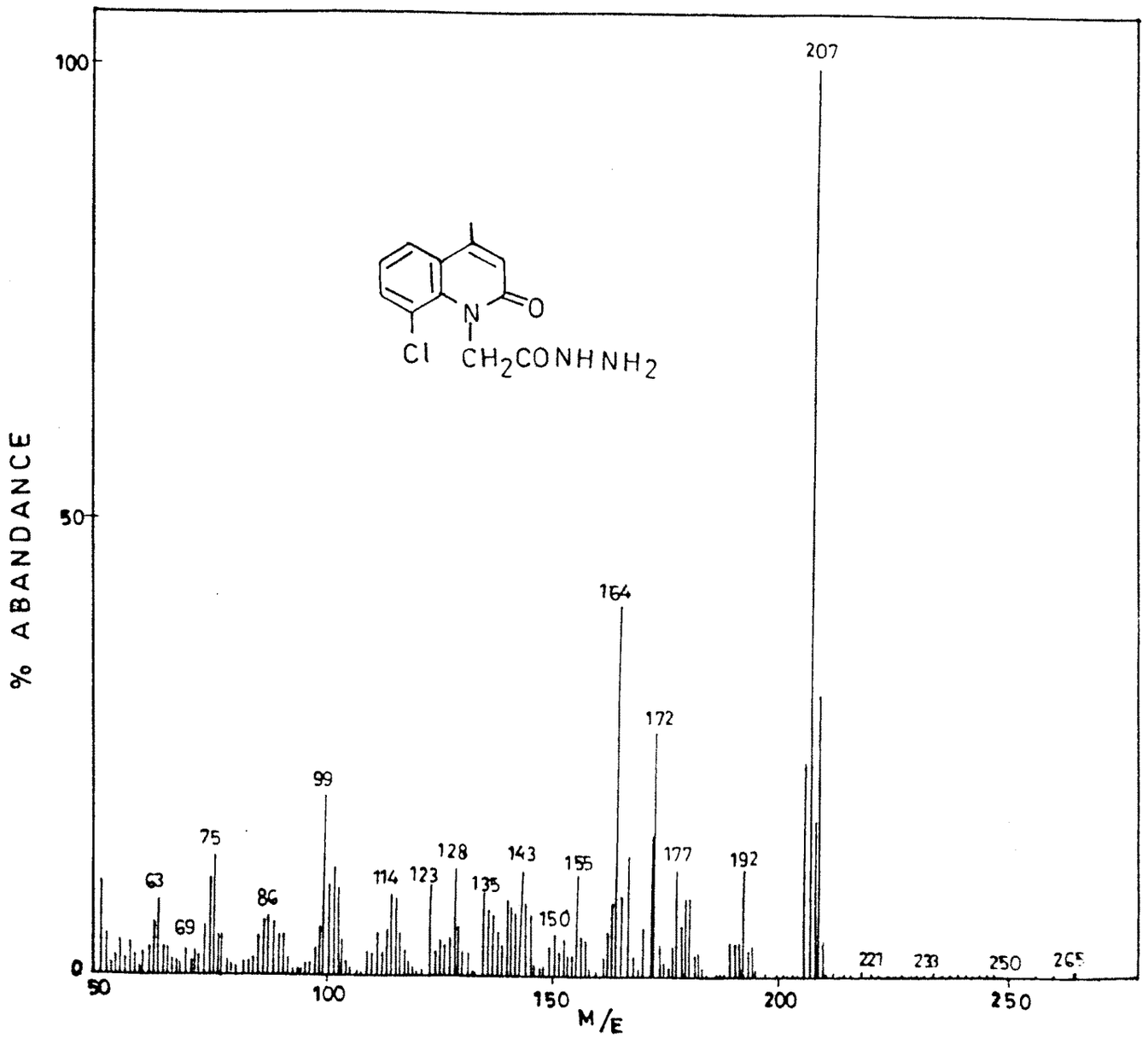
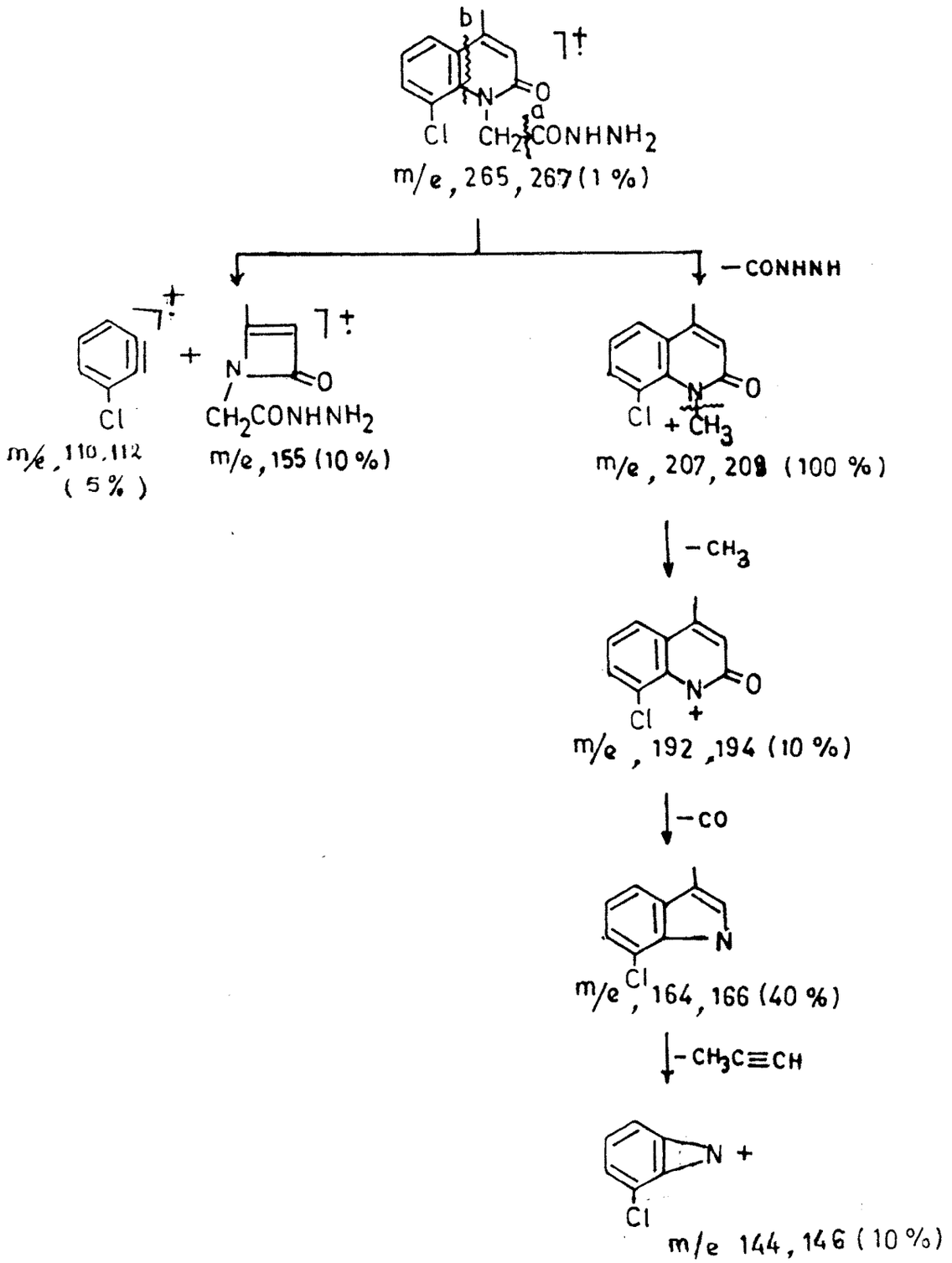


FIG. NO. 7

SCHEME-A

MASS SPECTRAL FRAGMENTATION OF

N^1-ACETYLHYDRAZIDO-8-CHLORO-QUINOLIN-2(1H) ONE.



IR Spectrum of 3,5-Dimethyl-1(6 chloro-4-methyl quinolin-2-one-1-yl methyloxo) pyrazole .

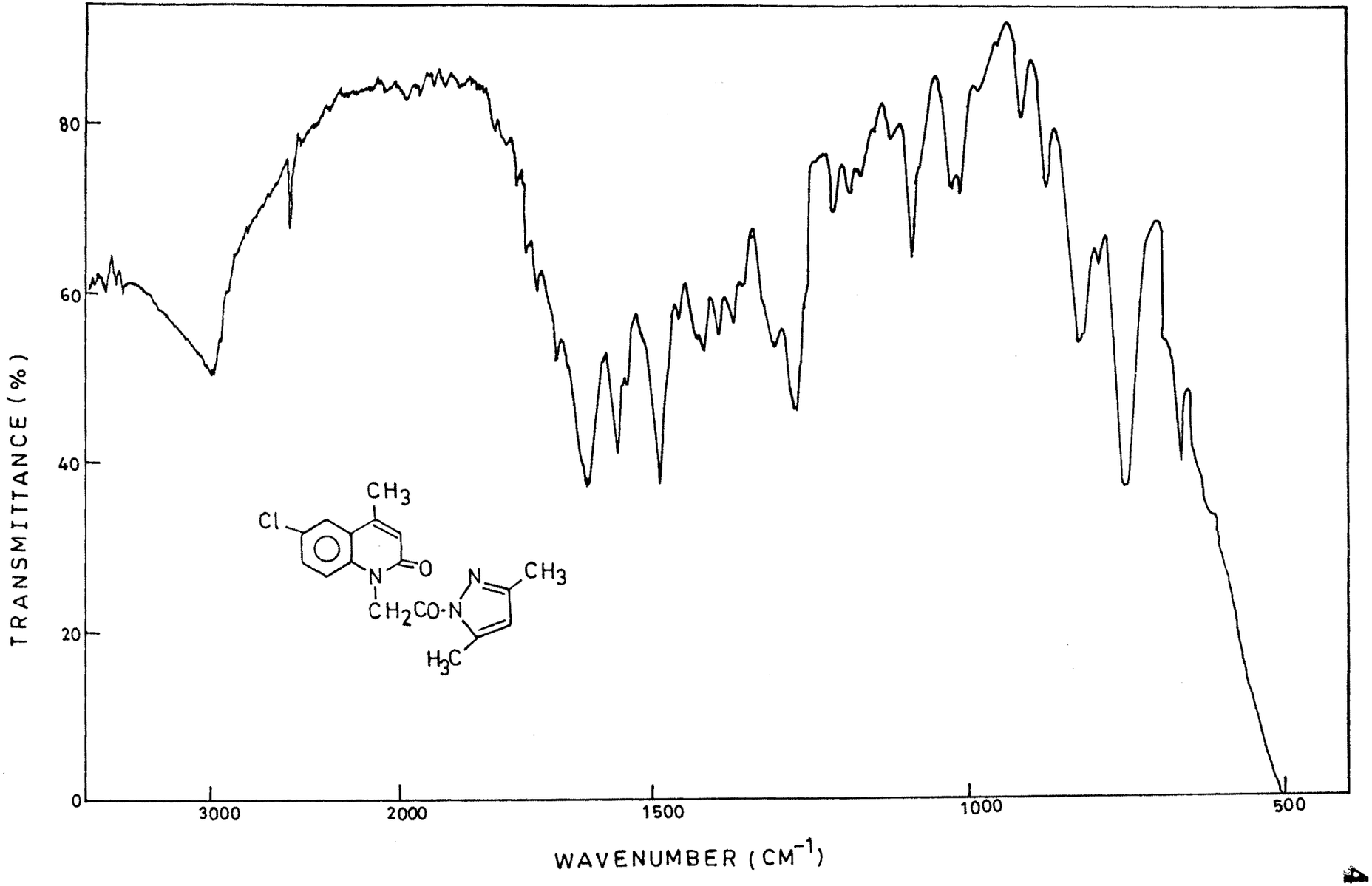


Fig. 8

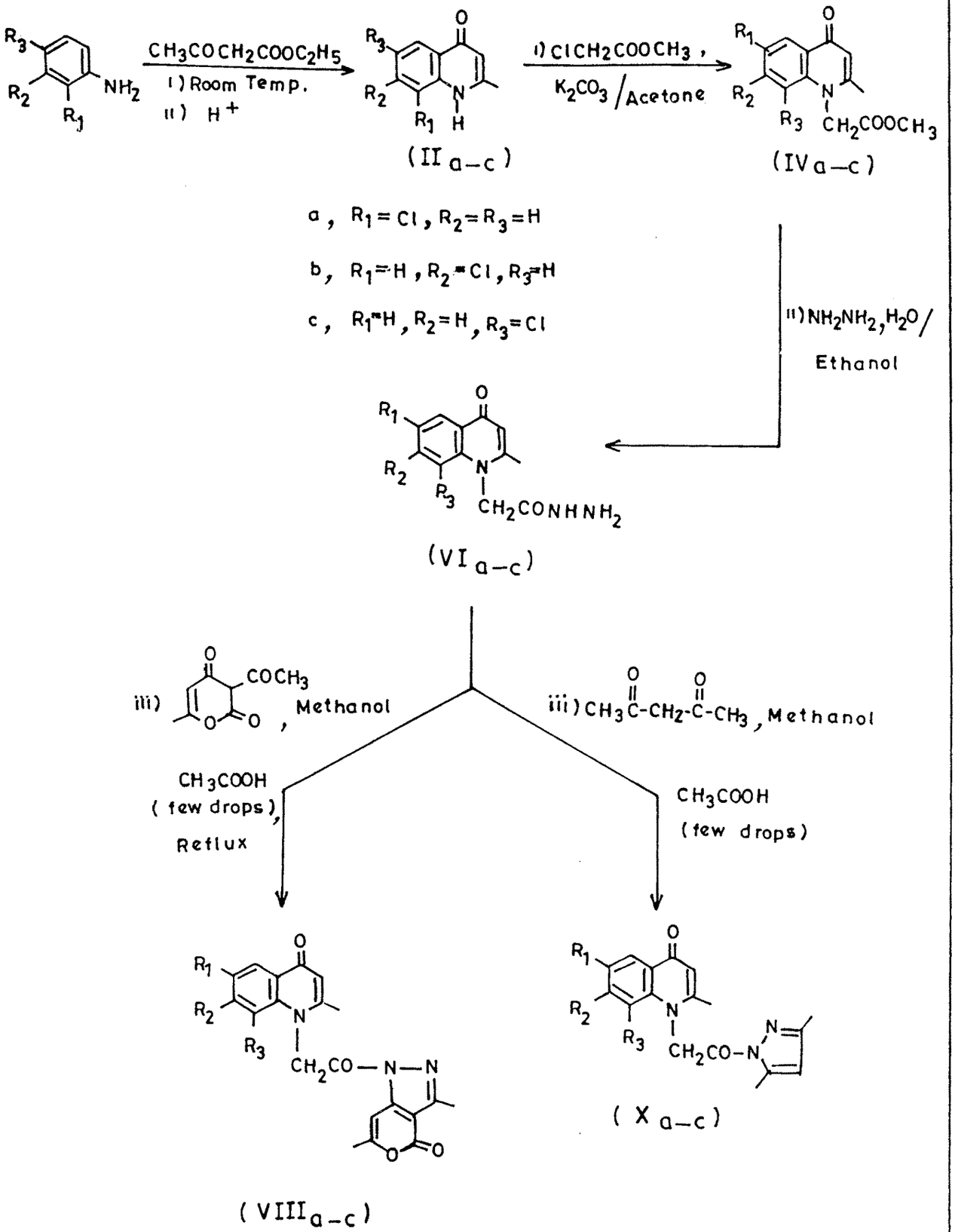
PART-II SYNTHESIS OF N^1-(SUBSTITUTED CHLOROQUINOLIN-4-ONE -1- YLMETHYLOXO)OXOPYRANO PYRAZOLES

The strategy employed for the synthesis of N^1- substituted quinolinoyl pyrazole derivative has been reported. It involved the acid catalysed cyclisation of ethyl butyrate-2-aroyl-hydrazone (VII_{a-c}) at room temperature to yield ($VIII_{a-c}$) 2-methyl,6,7,8-chloro-quinolin-4-(1H)ones ($VIII_a$) when reacted with methylchloroacetate gave N^1-carbmethoxymethyl,2-methyl-8-chlorro-quinolin-4-(1H) ones (IX_{a-c}). These compounds on refluxation with hydrazine hydrate in ethanol formed N^1-hydrazidomethyl-2-methyl quinolin-4-(1H)ones (X_{a-c}). The reaction of (X_{a-c}) with 3-acetyl, 6-methyl pyran-2,4-dione in methanol yielded N^1-substituted quinolino-4(1H)ones. Pyrazole derivatives [$XI_{(a-c)}$] .Further the reaction of (X) with acetylacetone yielded N-(3',5'-dimethyl pyrazolomethyloxo-)8-chloro-2-methyl quinolin-4-(1H)ones (XII_{a-c})(Scheme-II). The structures of the synthesised compounds have been confirmed by UV,IR and ^1H NMR spectral analysis.

8 PREPARATION OF ETHYL BUTRATE-2-AROYL HYDRAZONE(VII)

In conical flask a mixture of aniline (9.2 gm,0.001 mole) and acetoacetic ester (12.6 ml 0.001 mole) in methanol (25 ml) was placed for 5 days at room temperature and neutralised with Na_2CO_3 . The separated heavy liquid was extracted in chloroform and the solvent was removed under vacuum. The heavy liquid obtained was distilled under reduced pressure

SCHEME—II


CH3COCH2COOC2H5
i) Room Temp.
ii) H+
i) ClCH2COOCH3 ,
K2CO3 /Acetone
(II a–c)
(IV a–c)
a , R1 = Cl , R2 = R3 = H
b , R1 = H , R2 = Cl , R3 = H
c , R1 = H , R2 = H , R3 = Cl
ii) NH2NH2,H2O/
Ethanol
(VI a–c)
iii) , Methanol
iii) , Methanol
CH3COOH
(few drops),
Reflux
CH3COOH
(few drops)
(VIII a–c)
(X a–c)

to give ethyl butryate 2-aroylhydrazone (VII_a), yield 30 gm (72%) m.p. 132°C.

IR (KBr) : ν ,1760(easter >C=O),1620 (>C=N),1600 cm^{-1} (>C=C<)

^1H NMR($CDCl_3$) : δ ,1.1(3t,t,J=8.5Hz,ester-CH_3),2.18(3H,s,-N= C- CH_3), 3.3(2H,s,-CH_2),4.2(2H,q,J=8.5 Hz,ester-O-CH_2), 7.0-7.3(5H,m,aromatic protons).

Other compounds VII_b and VII_c were prepared by adopting similar procedure.

9 PREPARATION OF 8-CHLORO-2-METHYL,QUINOLIN-4-(1H) ONE ($VIII_a$) :

The substituted quinolones were prepared by the method discribed in Part-I of this chapter-II. Yield, melting points, molecular formula and elemental analysis data have been incorporated in Table 7(a) and IR, ^1H NMR in Table 7(b).

TABLE 7(a)

PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS(VIII)

Sr.No.	Group R_1	R_2	R_3	M.P. °C	Yield %	Mole.formula	Elemental analysis found/(calculated) % C	H	N
$VIII_a$	H	H	Cl	168	74.5	$C_{10}H_8ONCl$	62.10 (61.18)	4.10 (4.15)	7.20 (7.25)
$VIII_b$	H	Cl	H	205	82.1	$C_{10}H_8ONCl$	62.05 (62.18)	4.00 (4.15)	7.15 (7.25)
$VIII_c$	Cl	H	H	163	70.3	$C_{10}H_8ONCl$	62.00 (62.18)	4.05 (4.15)	7.05 (7.25)

TABLE 7(b)

IR AND ^{1}H NMR DATA OF THE COMPOUNDS (VIII)

Sr.No.	IR (Nujol)ν, cm^{-1}	^{1}H NMR($CDCl_3$),δ ppm
$VIII_a$	3300-3200(-NH),1635-1625 cyclic amido >C=O),1600 (>C=O),755 (C-Cl)	2.25(3H,s,C_2-CH_3),6.5(1H,s,-CH=), 6.8-7.15(3H,m,aromatic protons), 8.2-8.3(1H,s,exchangable with D_2O -CONH)
$VIII_b$	3350-3200(-NH),1635-1640 cyclic amido >C=O),1600 (>C=C<), 760 (C-Cl)	2.25(3H,s,C_2-CH_3),6.6(1H,s, -CH=), 6.8-7.2(3H,m,aromatic protons), 8.2-8.3(1H,s,exchangable with D_2O -CONH)
$VIII_c$	3300-3150(-NH),1635-1625 (cyclic amido >C=O),1600 (>C=C<), 765 (C-Cl)	2.27(3H,s,C_2-CH_3),6.6(1H,s, -CH=), 6.8-7.35(3H,m,aromatic protons), 8.2-8.35(1H,s,exchangable with D_2O,CONH-)

10 **SYNTHESIS OF N-1-CARBOMETHOXYMETHYL-8-CHLORO-2-METHYL QUINOLIN-4-(1H)ONE (IX_a) :**

In a round bottomed flask carrying reflux condenser and a guard tube, a mixture of 8-chloro-2-methyl quinolin-4-(1H) one ($VIII_a$) (5.9 gm, 0.02 mole) and methyl chloroacetate (2.2 gm 0.02 mole) in dry acetone, containing unhydrous potassium carbonate (2 gm) was refluxed for 24 hr. cooled and the solvent was removed under reduced pressure. The resulting white solid washed with water, filtered recrystallised from

ethanol to yield IX_a, 7.59 gm (80%) m.p.121 °C (found C,56.9; H,4.7; N,5.6; $C_{13}H_{12}O_3NCl$ requires C,56.9; H,4.7; N,5.7 %).

IR (KBr) : ν ,1760-1640(>C=O), 1665-1650 (cyclic amido >C=O), 1600 cm^{-1} (>C=C<).

^1H NMR ($CDCl_3$) : ,2.25(3H,s,$-CH_3$) ,3.85(3H,s,$-OCH_3$) ,6.15 (1H,s,$-\underline{C}H=C-$),6.8-7.4(3H,m,Ar-H)ppm

Other compounds IX_b and IX_c have been prepared by similar method and their physical and analytical data have been incorporated in Table 8(a) and spectral data depicted in Table 8(b) respectively.

TABLE 8(a)

PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS (VIII)

Sr No.	Group R_1	R_2	R_3	M.P. °C	Yield %	Mol.formula	Elemental analysis C	H	N
IX_b	H	Cl	H	109	60	$C_{13}H_{12}O_3NCl$	56.90 (56.80)	4.70 (4.80)	5.60 (5.70)
IX_c	Cl	H	H	117	62	$C_{13}H_{12}O_3NCl$	56.90 (56.90)	4.70 (4.75)	5.60 (5.73)

TABLE 8(b)

IR and ^1H NMR DATA OF THE COMPOUNDS (IX)

Sr.No.	IR (KBr) ν cm^{-1}	^1H NMR($CDCl_3$) δ ppm
IX_b	1750-1710(ester >C=O),1635 (cyclic amido >C=O), 1605(>C=C<), 760 (-C-Cl). Fig.No.9	2.38(3H,s,C_2-CH_3),3.77(3H,s, ester-OCH_3),3.85(2H,s,N-CH_2) 6.65 (1H,s,$-\underline{C}H=$),6.8-7.3(3H, m, aromatic protons).
IX_c	1745-1735(ester>C=O), 1635(Cyclic amido, >C=O), 1600(>C=C<),755(C-Cl), Fig.No.10.	2.4(3H,s,C_2-CH_3),3.78(3H,s, ester-OCH_3),3.87(2H,s,N-CH_2) 6.6(1H,s,$-\underline{C}H=$),6.7-7.3(3H,m, aromatic protons).

11 SYNTHESIS OF N-1-METHYLHYDRAZIDO-8-CHLOROQUINOLIN-4(1H) ONE(X_a) :

To the solution of compound (IX_a) in a flat bottomed flask (6 gm,0.01 mole)in ethanol (40 ml),80% hydrazine hydrate (0.01mole) was added and the same reaction mixture refluxed on a steam bath using reflux condensor for 3 hr. cooled. the resulting solid was filtered and recrystallised from ethanol to furnish (X_a), yield 70%, m.p. 262° C. (Found C,52.4,N,4.0;N,16.7; $C_{12}H_{10}N_3O_2Cl$ requires C,52.6; H,4.1; N,16.7 %).

IR (KBr) : ν,3250-3100(-NH-NH_2),1600-60, (broad cyclic >C =O),1605(>C=C<),760 cm^{-1} (C-Cl),.

^{1}H NMR($CDCl_3$) : δ ,2.3(3H,s,-CH_3),3.82(2H,s,-N,CH_2),6.1 (1H,s,=C<u>H</u>-),6.9-7.5(3H,m,Ar-H),8.2(1H,s,-CON<u>H</u>) ppm.

Other compounds X_b and X_c were prepared by adopting same procedure and their physical and analytical spectral data have been furnished in Table 9(a) and 9(b).

TABLE 9
PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS

Sr. No.	Group R_1	R_2	R_3	M.P. °C	Yield %	Mol.formula	Elemental analysis Found/(calculated) % C	H	N
X_b	H	Cl	H	250	72	$C_{12}H_{10}N_3O_2Cl$	52.5 (52.6)	4.0 (4.1)	16.8 (16.7)
X_c	Cl	H	H	234	75	$C_{12}H_{10}N_3O_2Cl$	52.7 (52.6)	4.1 (4.1)	16.6 (16.7)

TABLE 9(b)
IR AND ^{1}H NMR SPECTRAL DATA OF THE COMPOUNDS

Sr.No.	IR (KBr)ν cm^{-1}	^{1}H NMR ($CDCl_3$) δ, ppm
X_b	3350-3300(-NH),1670-1630 (acyclic amido >C=O), 1640(>C=O),760 (C-Cl). Fig.No.10	2.25(3H,s,C_2-CH_3),3.5(2H,s,-NH_2) 3.85(2H,s,-N-CH_2),6.8-7.3(3H,m , aromatic protons),8.2(1H,s,-CONH)
X_c	3300-3150(-NH),1665-1670 (acyclic amido >C=O), 1640 (>C=O),755(C-Cl) Fig.No.11.	2.4(3H,s,C_2-CH_3),3.55(2H,s, -NH_2),3.83(2H,s,N-CH_2), 6.8-7.25(3H,m,aromatic protons), 8.2(1H,s,-CONH).

12 SYNTHESIS OF 3,6-DIMETHYL-1-8-CHLORO-2-METHYLQUINOLIN -4-ONE-1-YLMTHYLOXO)-4-OXOPYRANO[4-3-c]PYRAZOLE(XI_a)

The mixture of compound (X_a) (0.251 gm,0.001 mole) and 3-acetyl,6-methylpyran-2,4-dione (0.168 gm,0.001 mole) in methanol was refluxed for 4 hr., and concentrated. The separated solid was filtered and recrystallised from methanol to yield (XI_a), yield 0.26 gm (72%) m.p. 249 ^oC (Found C,60.3; H,4.0;N,10.5; $C_{20}H_{16}N_3O_4Cl$ requires C,60.5;H,4.1;N,10.6 %),

IR (Nujol) : ν ,1735-1710(lactone >C=O), 1680(acyclic >C=O), 1640(cyclic >C=O),1620(>C=N-),760 cm^{-1} (C-Cl).

^{1}H NMR($CDCl_3$) : δ ,2.20(3H,s,-N=C=CH_3),2.35(6H,s,2 X-CH_3) 3.8(2H,s,N-CH) 6.2(2H,s,2 X-CH=C)7.0-7.3 (3H,m,Ar-H) ppm.

Other compounds were prepared by adopting same procedure and their physical and analytical data have been incroporated in Table 10(a) and spectral data depicted in Table 10(b).

TABLE 10(a)
PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS

Sr. No.	Group R_1	R_2	R_3	M.P. ^oC	Yield %	Mol.Formula	Elemental analysis found/(calculated)% C	H	N
XI_b	H	Cl	H	247	68	$C_{20}H_{16}N_3O_4Cl$	60.4 (60.5)	4.15 (4.1)	10.5 (10.6)
XI_c	Cl	H	H	231	76	$C_{20}H_{16}N_3O_4Cl$	60.4 (60.5)	4.0 (4.1)	10.7 (10.6)

TABLE 10(b)
IR AND ^1H NMR SPECTRAL DATA OF THE COMPOUNDS

Sr.No.	IR(Nujol) ν cm^{-1}	^1H NMR ($CDCl_3$) δ ppm
XI_b	1760(latone >C=O),1680 (acyclic >C=O),1635 amido),1620(>C=N-),1605 (>C=C<) 760(C-Cl)	2.27(3H,s,C_2-CH_3),2.35(6H,s, 2 X-CH_3),6.0-6.2(2H,s,2 X-CH=), 3.8(2H,s,N-CH_2),6.8-7.3(2H,m, aromatic protons).
XI_c	1765(lactone >C=O),1670-1680 (acyclic amido >C=O), 1635 (cyclic amido),1620 (>C=N-)1605(>C=C<), 760(C-Cl). Fig.No.11	2.25(3H,s,C_2-CH_3),2.37(6H,s , 2 X -CH_3),6.0-6.2(2H,s,2 X-CH=) 3.82(2H,s,N-CH_2),6.7-7.3(2H,m , aromatic protons).

13 SYNTHESIS OF 3,5-DIMETHYL-1-8-CHLORO-2-METHYLQUINOLI N-4-ONE-1-YLMETHYLOXO)PYRAZOLE (XII_a) :

The compound (X_a), (0.251 g, 0.001 mole) and actytacetone (0.10 g,0.001 mole) in methanol refluxed on a steam bath for 5 hr.,cooled and the solvent was removed under vacuum. The

residual mass then treated with ice-water to give a solid, which was recrystallised from ethanol furnished (XII_a), yield 0.20gm (40%) m.p. 83°C (Found C,60.00, H,4.70;N,12.7; $C_{17}H_{16}N_3O_2Cl$ requires C,60.0;H,4.9; N,12.8;

IR (Nujol) : ν,1680 (acyclic >C=O),1635(cyclic amido >C=O), 1620 (>C=N-),760 cm^{-1} (C-Cl)

NMR ($CDCl_3$) : δ,2.18(3H,s,N=C-CH_3),2.35(6H,s,2 X-CH_3) ,3.90 (2H,s,-N-CH_2)6.35(1H,s,=C<u>H</u>),7.0-7.3(3H,m,Ar-H)ppm

Other compounds were prepared by the similar method and their physical, analytical and spectral data have been incorporated in Table 11(a) and Table 11(b) respectively.

TABLE 11(a)
PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS (XII)

Sr No.	Group R_1	R_2	R_3	M.P °C	Yield %	Mol.formula	Elemental analysis found/(calculated)% C	H	N
XII_b	H	Cl	H	55	40	$C_{17}H_{16}N_3O_2Cl$	61.90 (62.0)	4.70 (4.90)	12.60 (12.80)
XII_c	Cl	H	H	142	38	$C_{17}H_{16}N_3O_2Cl$	61.90 (62.0)	4.80 (4.90)	12.60 (12.70)

TABLE 11(b)
IR AND ^{1}H NMR SPECTRAL DATA OF THE COMPOUNDS (XII)

Sr.No.	IR (Nujol) ν, cm^{-1}	^{1}H NMR($CDCl_3$) δ, ppm
XII_b	1680(acyclic amido >C=O), 1635(cyclc amido >C=O), 1620(>C=N),1600(>C=C<) 760 (C-Cl)	2.2(3H,s,C_2-CH_3),2.3(6H,s, 2 X-CH_3),3.87(2H,s,N-CH_2), 6.4(2H,s, 2 X CH=C),6.7-7.3 (3H,m,aromatic protons)
XII_c	1680-1670(acyclic amido >C=O)1620(>C=N-),1600 (>C=C<),755 (C-Cl)	2.18(3H,s,C_2-CH_3),2.3(6H,s, 2 X-CH_3),3.85(2H,m,N-CH_2) 6.4(2H,s,2 X-CH=C-)6.7-7.3 (3H,m,aromatic protons).

14 IR AND ^{1}H NMR SPECTRA :

IR, ^{1}H NMR SPECTRA

IR Spectrum of N^1- Methylhydrazido-7-chloro quinolin-4(1H) one (Xb).

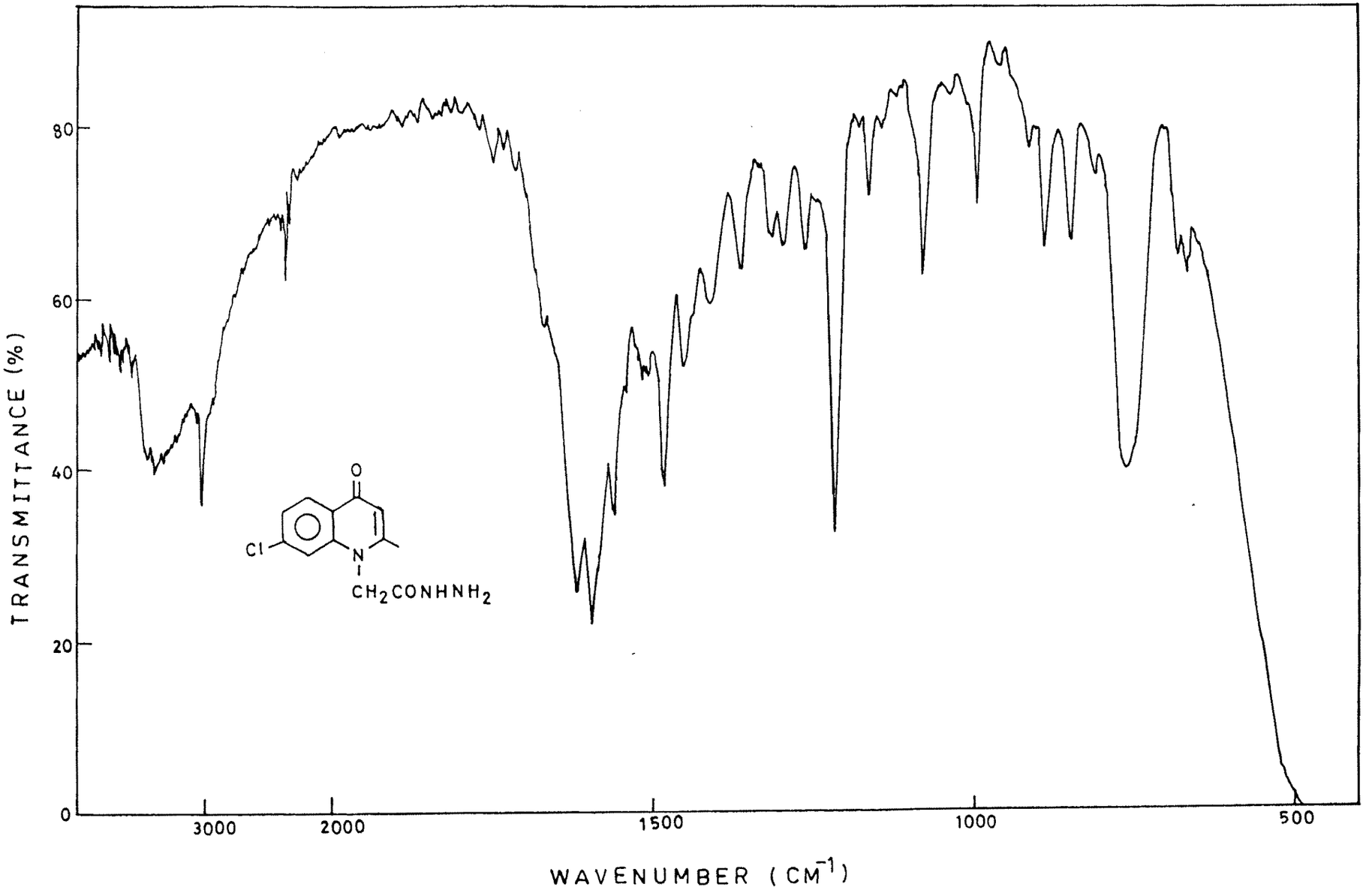


Fig. 9

IR Spectrum of N-Carbmethoxy methyl-6-Chloro-2-Methyl quinolin-4 (1H) one (IV).

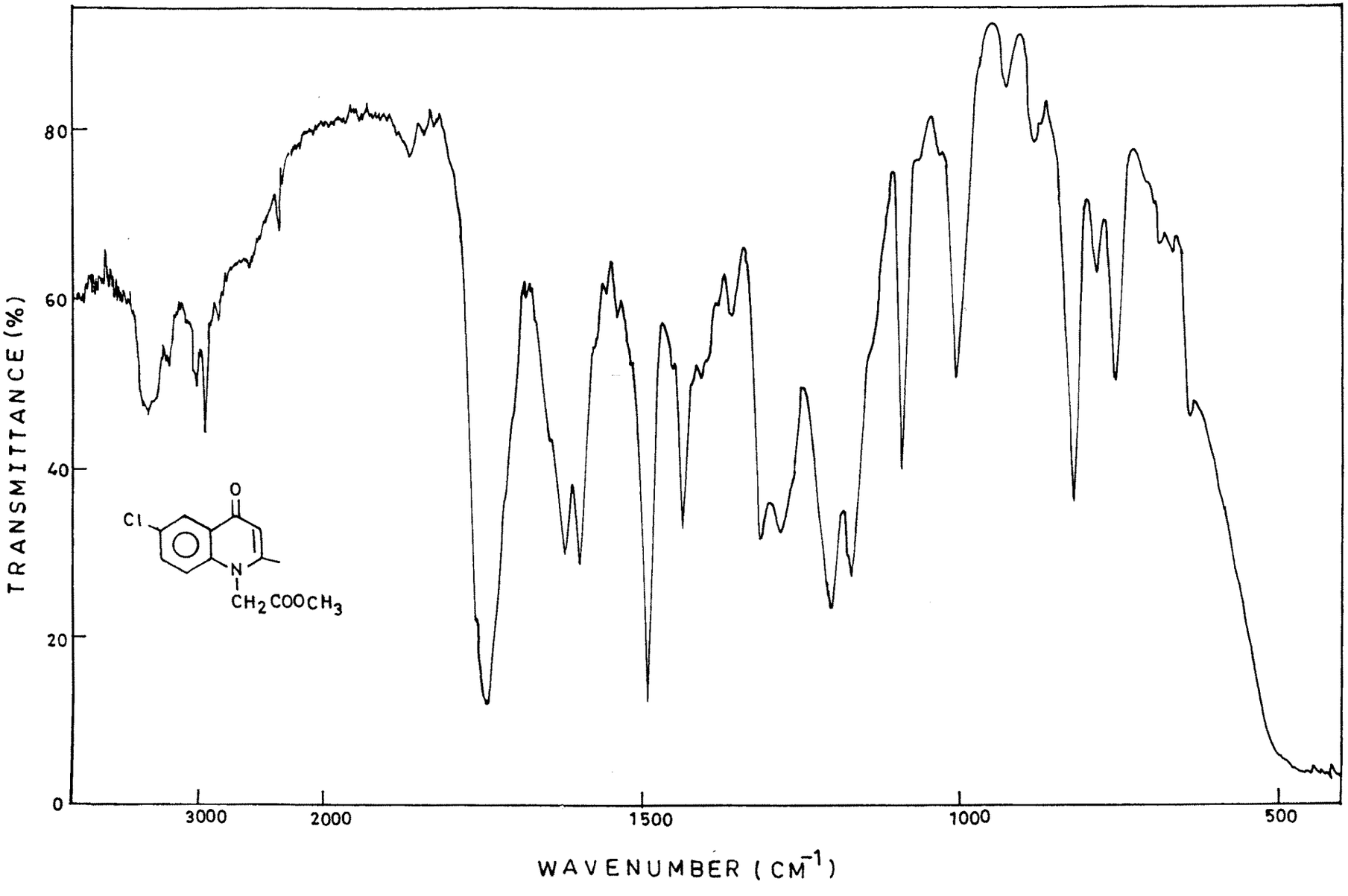


Fig.10

IR Spectrum of N^1-Methylhydrazido-6-chloroquinolin-4(1H)one (X_{II})

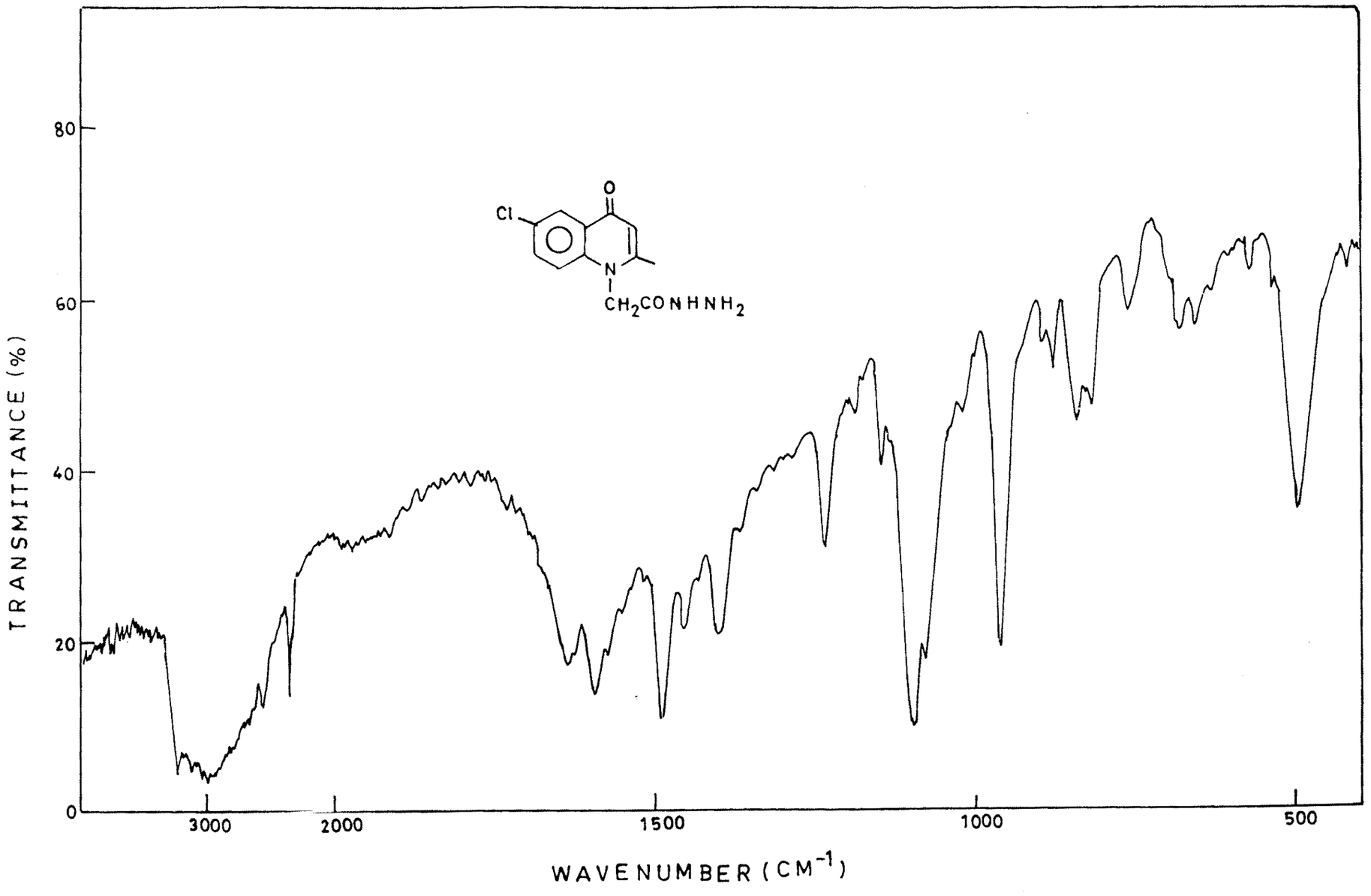


Fig.11

IR Spectrum of 3,6-Dimethyl-1(6-Chloro-2-Methylquinolin-4-one-1-yl methyloxo)-4-oxopyrano [4,3-c] Pyrazole (XIc).

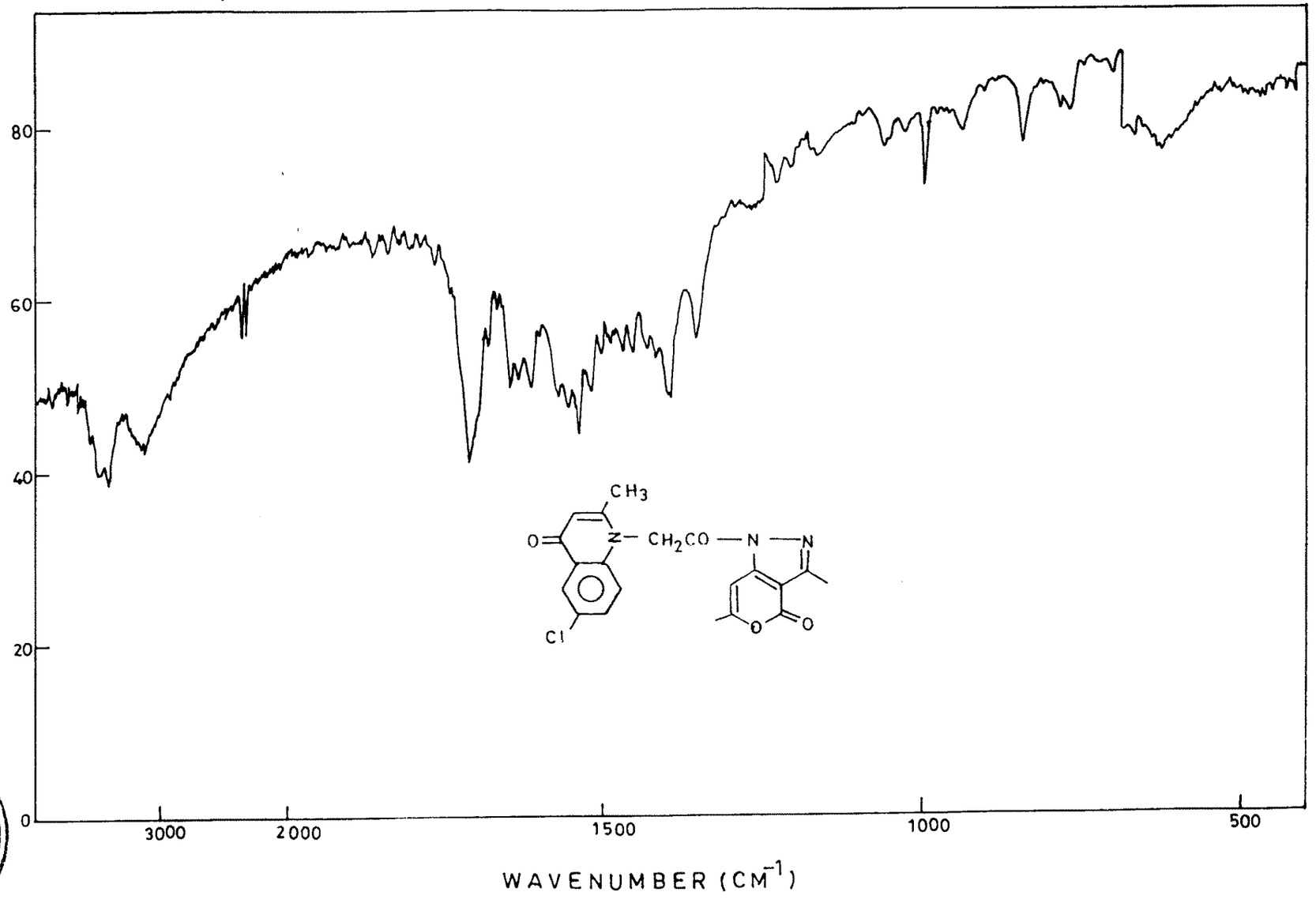


Fig. 12

PART-III SYNTHESIS OF 3,6-DIMETHYL-1-ARYL-4-OXOPYRANO[4,3-c] PYRAZOLE DERIVATIVES

Pyrazole derivative posses wide ranging biological activities such as pesticidal, antifungal, antibacterial and antiinflammatory etc. Recently, it has been pointed out that when benzopyran ring is directly attached to the hetrocyclic ring enhances the pesticidal activity, so it was considered worthwhile to synthesise fused pyrazoles containing pyran ring.

the strategy employed for the synthesis of desired pyrazoles involved the self condensation of acetoacetic ester to form 3-acetyl,6-methyl pyran-2,4-dione(II)'.This when reacted witth variously substituted aryl hydrazides gave targetted pyranopyrazoles. Scheme-III.

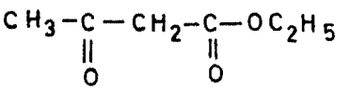
1(a) SYNTHESIS OF 3-ACETYL,6-METHYL PYRAN-2,4-DIONE(II')

In the round bottomed flask carrying a reflux condenser, acetoacetic ester (0.2 mole) was refluxed in the presence of $NaHCO_3$ (0.5 gm) for about 5 hr. and uncondensed acetoacetic ester was removed by distillation under vacuum. The residual solution was cooled in ice to get white solid which was recrystallised from ethanol to furnish (II'). Yield 12.6 gm (75%) m.p. $94^{o}C$.

IR (KBr) : ν, 1760-1730(pyrone >C=O), 1700-1680(cyclic and acyclic >C=O),1600 cm (>C=C<) Fig.No.13

NMR ($CDCl_3$) : δ ,2.23(3H,s,C-CH_3),2.55(3H,s,-$COCH_3$).5.87(1H,s , =C<u>H</u>-). Fig.No.14.

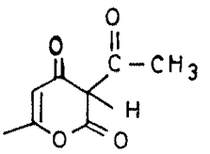
SCHEME-III



(I')

Self condensation ,

$NaHCO_3$



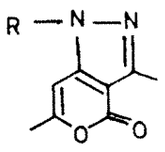
3-Acetyl-6-methyl Pyran 2,4-dione

(II')

$R\text{-}NH\text{-}NH_2$,

AcOH ,

Methanol



(III')

1.(b) PREPARATION OF HYDRAZIDES :

(II_a) Preparation of esters :

SYNTHESIS OF ETHYL-2(4-CHLOROPHENOXY) PROPIONATE:

In 250 ml round bottom flask a mixture of P-chloro-phenoxpropionic acid and ethanol (70 ml) containing 8 ml conc. H_2SO_4 (A.R.) was refulxed for 17 hrs. cooled and pour in ice water. The neutralisation of the same mixture by sodium biicarbonate heavy liquid separated out which was extracted in the ether. Removal of ether by evaporation gave heavy liquid which was distilled under reduced pressure yielded desired ester yield 15 gm (66.1%)BP: .150^{o}C.

IR(KBr) : ,1710-1740(ester-$COOC_2H_5$),1600(>C=C<),1070(C-O-C), 755 (C-Cl), cm^{-1}

^1H NMR (TFA) : ,1.2(3H,t,ester-CH_3),1.6(3H,d,~~CH-CH~~$_3$)4.15(2H,q, ester-OCH_2)4.65(1H,q-O<u>C</u>H-CH_3),6.65-6.75(2H, d, J=8.0 Hz,Ar-H)7.1-7.2(2H,d,J=8.5 Hz,Ar-H)

<u>Fig.No. 15.</u>

Other esters were prepared by similar method and characterised.

(II_b) SYNTHESIS OF 2-(4-CHLOROPHENOXYPROPIONIC ACID HYDRIZIDE:

In round bottomed flask carring a reflux condenser a mixture of compound (II_a),11.3(0.05 mole) in 25 ml ethanol and 2.5 ml(0.05 mole) hydrazine hydrate (80%) was refluxed on a steam bath for 3 hr., cooled. The separated solid was recrystallised from ethanol to yield (II_a),7.0 gm(65.4%),m.p. 128^{o}C .

IR(KBr) : ν ,3350-3300(NH),1670(amido >C=O),1070(C-O-C)760 (C-Cl) cm^{-1} Fig.No. 16.

^{1}H NMR(TFA) : δ ,1.65(3H,s,-CHCH$_3$),2.7(2H,s,-NH$_2$),4.65(1H,q, -O-CH-CH$_3$)6.7-6.8(2H,d,J= 8.5 Hz,Ar-H), 7.1-7.2(2H,d,J=8.5 Hz,Ar-H)8.4(1H,s, exchangable with D_2O,-CONH).

Other hydrazides were prepared similarly and characterised and their M.Ps' were compared with the literature[156] values which were found to be correct.

2 SYNTHESIS OF 3,6-DIMETHYL-1-PHENYLACETYL-4-OXOPYRANO-[4,3-c]PYRAZOLE (III'$_a$) :

A mixture of compound 3-acetyl,6-methyl pyran-2,4-dione (II') (0.001 mole) and phenylacetic hydrazide (0.001 mole) in methanol was refluxed on steam bath for 5 hr. in the presence of acetic acid, cooled and the solvent removed under vacuum. The separated solid recrystallised from methanol to furnish pyrazole (III'$_a$),yield 0.25 gm(93%)m.p.144^{o}C.

IR(KBr) : ν ,1730(lactone >C=O),1665,(amido >C=O),1620(>C=N) cm^{-1}

^{1}H NMR($CDCl_3$) δ ,2.15(3H,s,=C-CH$_3$),2-2.3(3H,s,=C-CH$_3$) 4.2(2H,s,-CH)5.9(1H,s,=CH),6.9-7.5(5H,s,Aromatic protons).

Other compounds were prepared by adopting same procedure. Their melting points, yield, molecular formula, elemental analysis, Table 12(a) and spectral data in Table 12(b).

TABLE 12(a)
PHYSICAL AND ANALYTICAL DATA OF THE COMPOUND

Compound No.	Group	M.P. °C	Yield %
III'_a	$C_6H_5-CH_2$	144	93.3
III'_b	$4-NO_2;C_6H_5-O-CH_2$	98	90.0
III'_c	$3,5-(NO_2)C_6H_3$	226	81.9
III'_d	$3-CH_3;C_6H_4-O-CH_2$	159	69.4
III'_e	$4-NO_2;C_6H_4-O$	241	92.8
III'_f	$2-ClC_6H_4-O-CH_2$	192	94.7
III'_g	$4-CH_3;C_6H_4-O-CH_2$	147	77.8
III'_h	$3-Cl\cdot 4-CH_3;C_6H_3-O-CH_2$	164	88.5
III'_i	$4-ClC_6H_4-O-CH-CH_3$	167	97.5
III'_j	$2-OH,5-ClC_6H_3$	223	93.8
III'_k	$2-CH_3;C_6H_4-O$	215	91.7
III'_l	$2-ClC_6H_4$	170	73.7
III'_m	3-Pyridyl	152	84.0
III'_n	$C_6H_5-CH=CH-$	88	60.4
III'_o	$2-CH(CH_3)_2 4-CH_3C_6H_3-O-CH_2$	131	77.5
III'_p	C_6H_5	195	84.5
III'_q	$C_6H_5-CH_2$	156	83.0
III'_r	$4-CH_3OC_6H_4$	221	63.3
III'_s	$2-CH(CH_3)_2,4-CH_3;C_6H_3-O-CH(CH_3)$	126	38.0
III'_t	$C_6H_5-O;CH(CH_3)$	146	44.4
III'_u	$4-NO_2;C_6H_4O-CH_2$	82	87.7

(Contd....Table 12(a)

Compound No.	Group	M.P. °C	Yield %
III'_v	4-CH_3;C_6H_4-$CH(CH_3)$	129	56.7
III'_w	2-CH_3;C_6H_4	167	90.0
III'_x	2,4-Br_2;C_6H_3-O-CH_2	93	54.5
III'_y	2,6-Br_2;4-ClC_6H_2-O-CH_2	89	74.5
III'_z	4-ClC_6H_4-O-CH_2	208	42.5

TABLE 12(b)
ANALYTICAL DATA OF THE COMPOUNDS

Compound No	Molecular formula	Elemental analysis found/ (calculated) % C	H	N
III'_a	$C_{16}H_{14}N_2O_3$	68.00 (68.08)	4.85 (4.96)	9.82 (9.92)
III'_b	$C_{16}H_{13}N_3O_6$	55.00 (55.90)	3.70 (3.79)	12.10 (12.2)
III'_c	$C_{15}H_{10}N_4O_7$	49.5 (50.2)	2.70 (2.79)	15.55 (15.6)
III'_d	$C_{17}H_{16}N_2O_4$	65.20 (65.38)	5.10 (5.12)	8.75 (8.9)
III'_e	$C_{15}H_{11}N_3O_5$	57.40 (57.5)	3.45 (3.51)	13.35 (13.41)
III'_f	$C_{16}H_{13}N_2O_4Cl$	57.65 (57.74)	3.85 (3.90)	8.35 (8.42)
III'_g	$C_{17}H_{13}N_2O_4$	65.30 (65.38)	5.10 (5.12)	8.85 (8.97)
III'_h	$C_{17}H_{15}N_2O_4Cl$	58.80 (58.87)	4.25 (4.30)	8.00 (8.08)
III'_i	$C_{17}H_{15}N_2O_4Cl$	58.80 (58.87)	4.27 (4.30)	7.95 (8.08)
III'_j	$C_{15}H_{11}N_2O_4Cl$	56.10 (56.51)	3.40 (3.45)	8.80 (8.79)
III'_k	$C_{16}H_{12}N_2O_6$	58.45 (58.53)	3.65 (3.65)	8.50 (8.53)

(Contd....Table 12(b)

Compound No.	Molecular formula	Elemental analysis found/(Calculated) % C	H	N
III'_l	$C_{15}H_{11}N_2O_3Cl$	59.35	3.45	9.20
		(59.5)	(3.63)	(9.25)
III'_m	$C_{14}H_{11}O_3N_3$	62.25	4.00	15.50
		(62.45)	(4.08)	(15.61)
III'_n	$C_{16}H_{14}N_2O_3$	67.80	4.85	9.82
		(68.08)	(4.96)	(9.92)
III'_o	$C_{20}H_{22}N_2O_4$	67.4	6.10	7.80
		(67.79)	(6.21)	(7.90)
III'_p	$C_{15}H_{12}N_2O_3$	67.10	4.37	10.42
		(67.16)	(4.47)	(10.44)
III'_q	$C_{16}H_{14}N_2O_5$	68.0	4.80	9.82
		(68.08)	(4.96)	(9.92)
III'_r	$C_{16}H_{14}N_2O_4$	64.00	4.55	9.25
		(64.42)	(4.69)	(9.39)
III'_s	$C_{21}H_{24}N_2O\ Cl$	68.20	6.42	7.55
		(68.47)	(6.52)	(7.60)
III'_t	$C_{17}H_{16}N_2O_4$	65.25	5.00	8.88
		(65.38)	(5.12)	(8.97)
III'_u	$C_{16}H_{13}N_3O_6$	55.90	3.85	12.20
		(55.97)	(3.79)	(12.24)
III'_v	$C_{16}H_{18}N_2O_4$	66.15	5.42	8.50
		(66.25)	(5.52)	(8.58)
III'_w	$C_{16}H_{14}N_2O_3$	67.55	4.90	9.82
		(68.08)	(4.96)	(9.92)
III'_x	$C_{16}H_{14}N_2O_4Br_2$	41.90	2.55	6.10
		(42.10)	(2.63)	(6.14)
III'_y	$C_{16}H_{11}N_2O_4Br_2Cl$	39.05	2.20	5.60
		(39.14)	(2.24)	(5.70)
III'_z	$C_{16}H_{13}N_2O_4Cl$	57.65	3.80	8.35
		(57.74)	(3.90)	(8.42)

TABLE 12(b)
IR, ^{1}NMR SPECTRAL DATA OF THE COMPOUNDS (III)

Sr.No.	IR (KBr)ν, cm^{-1}	^{1}H NMR (DMSO) δ ,ppm
III'_g	1740-30(lactone >C=O),1670 amido >C=O),1620(>C=N-) 1060(C-O-C) Fig.No.17.	2.15(3H,s,-N=C-CH_3),2.3(3H,s Ar-CH_3),2.45(3H,s,=-CH_3) 4.7(2H,s,-OCH_2-),5.9(1H,s,=CH-), 6.8-6.9(2H,d,J_{ortho}=8.5 Hz, ArH),7.1-7.2(2H,d,J_{ortho} = 8.5 Hz,Ar-H),Fig.No. 18
III'_i	1735(lactone>C=O),1670 amido >C=O),1615(>C=N-), 1060(C-O-C),760(C-Cl)	1.6(3H,d,-CH_3),2.15(3H,s, -N=C-CH_3),2.35(3H,s,Ar-CH_3), 5.05(1H,q,OCH-),5.9(1H,s,-CH=) 7-7.1(2H,d,J_{ortho}=8.5 Hz, Ar-H),7.25-7.35(2H,d,J_{ortho} = 8.5 Hz,Ar-H)Fig.No.19.
III'_k	1740-30(Pyrone >C=O), 1670-60(amido >C=O),1620 >C=N),1070 (C-O-C) Fig.No.20.	2.18(3H,s,N=C-CH_3),2.3(3H,s, Ar-CH_3),2.45(3H,s,=-CH_3), 4.65(2H,s,-OCH_2-),5.9(1H,s,-CH=), 6.9-7.35(4H,m,aromatic protons)

IR, ^{1}H NMR SPECTRA

IR Spectrum of 3-Acetyl, 6-methyl Pyran-2,4-dione (II')

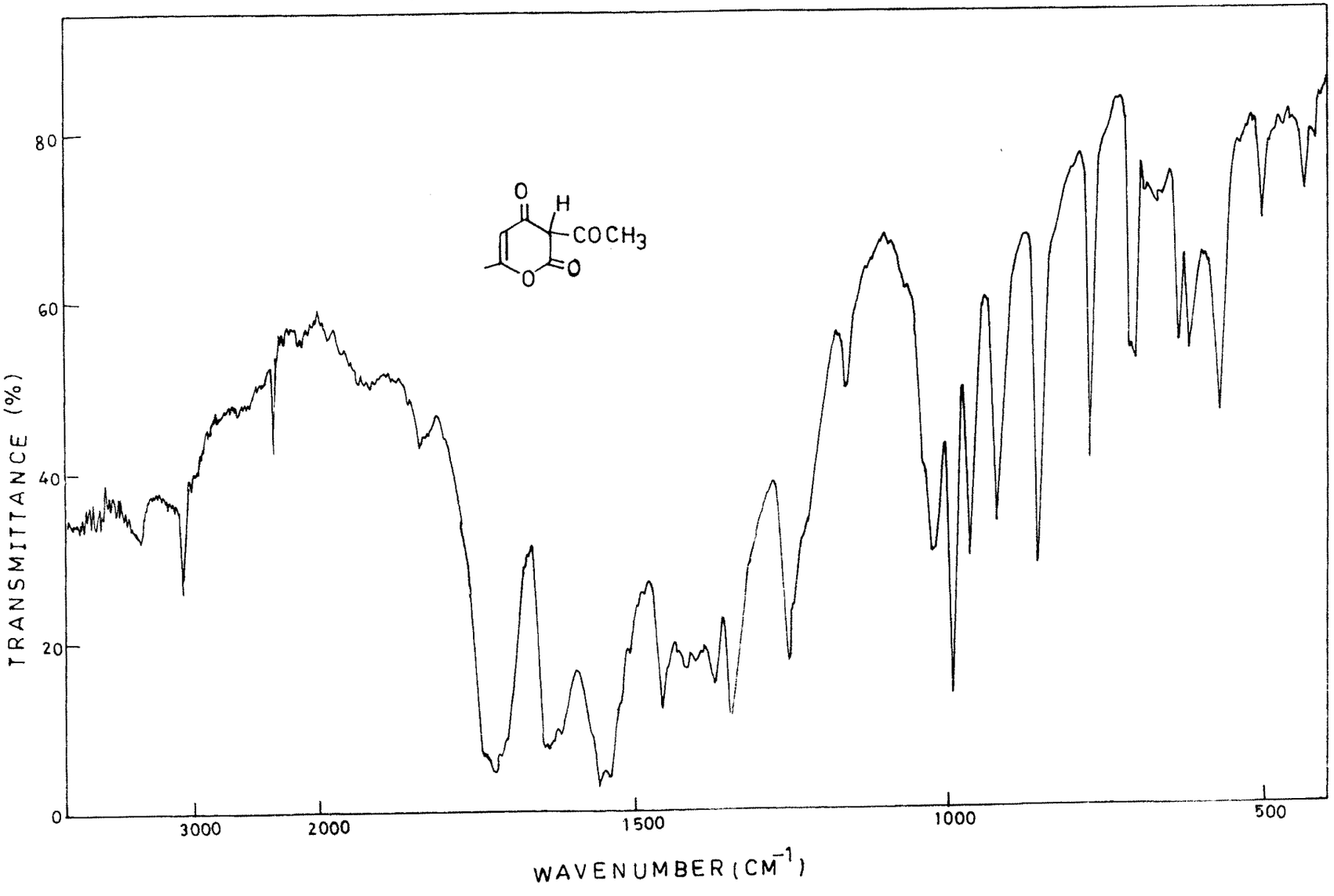


Fig. 13

^{1}H NMR Spectrum of 3-Acetyl 6-methyl pyran-2,4-dione (III')

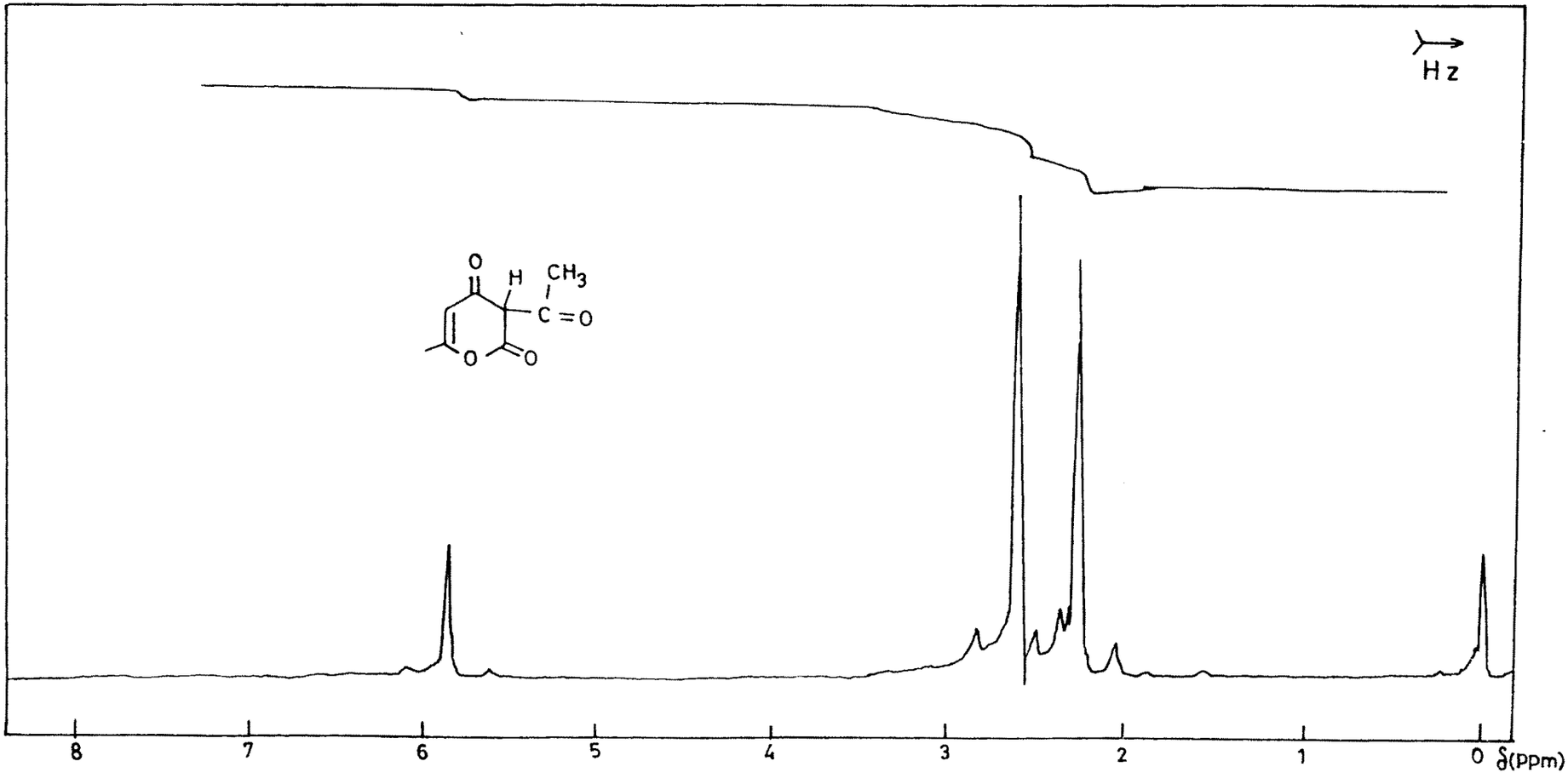


Fig. 14

^1H NMR Spectrum of Ethyl 2 (4-chlorophenoxy) propionate .(IIa)

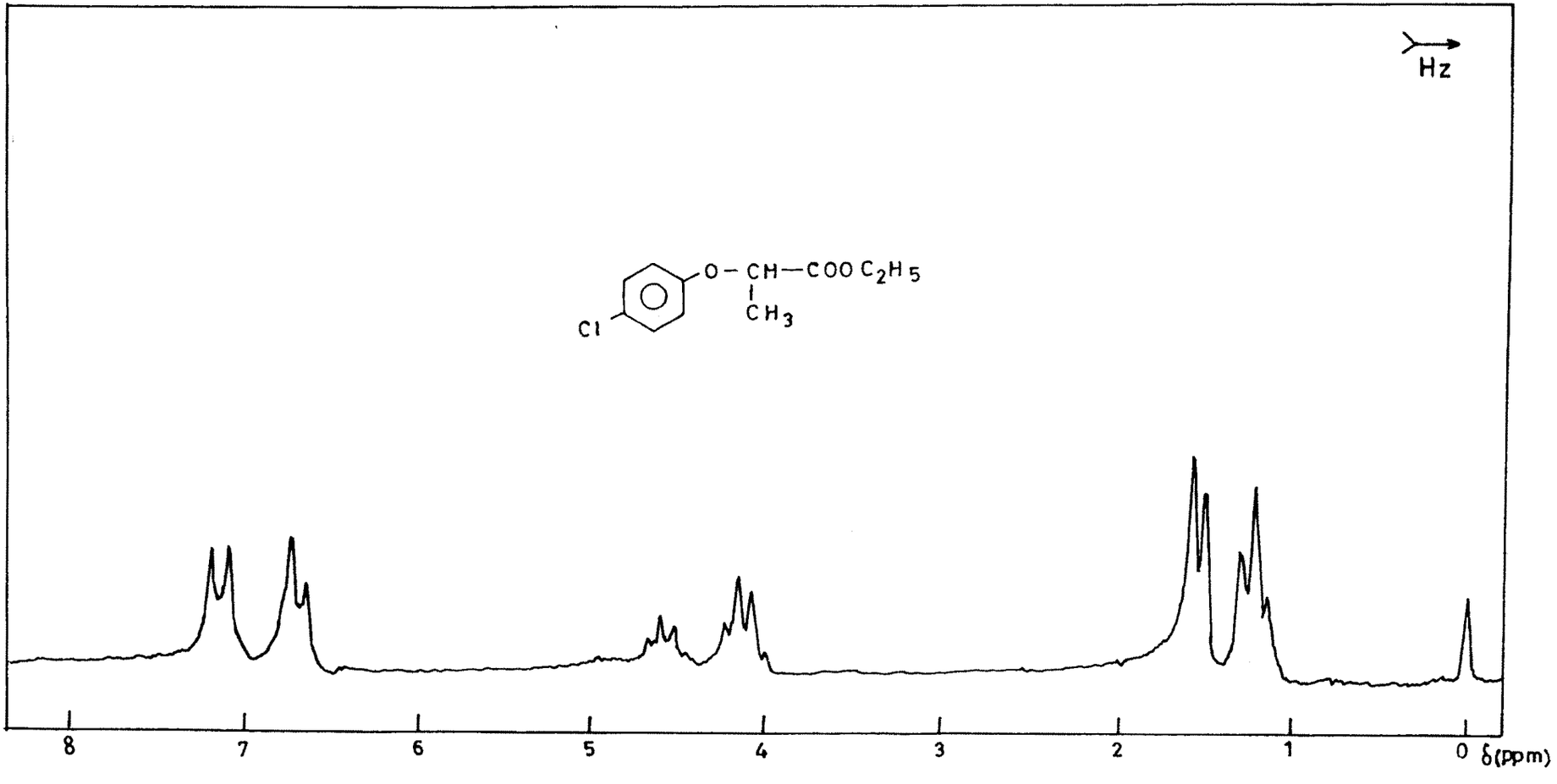


Fig. 15

IR Spectrum of 2 (4-Chlorophenoxy) propionic acid hydrazide (II_b) .

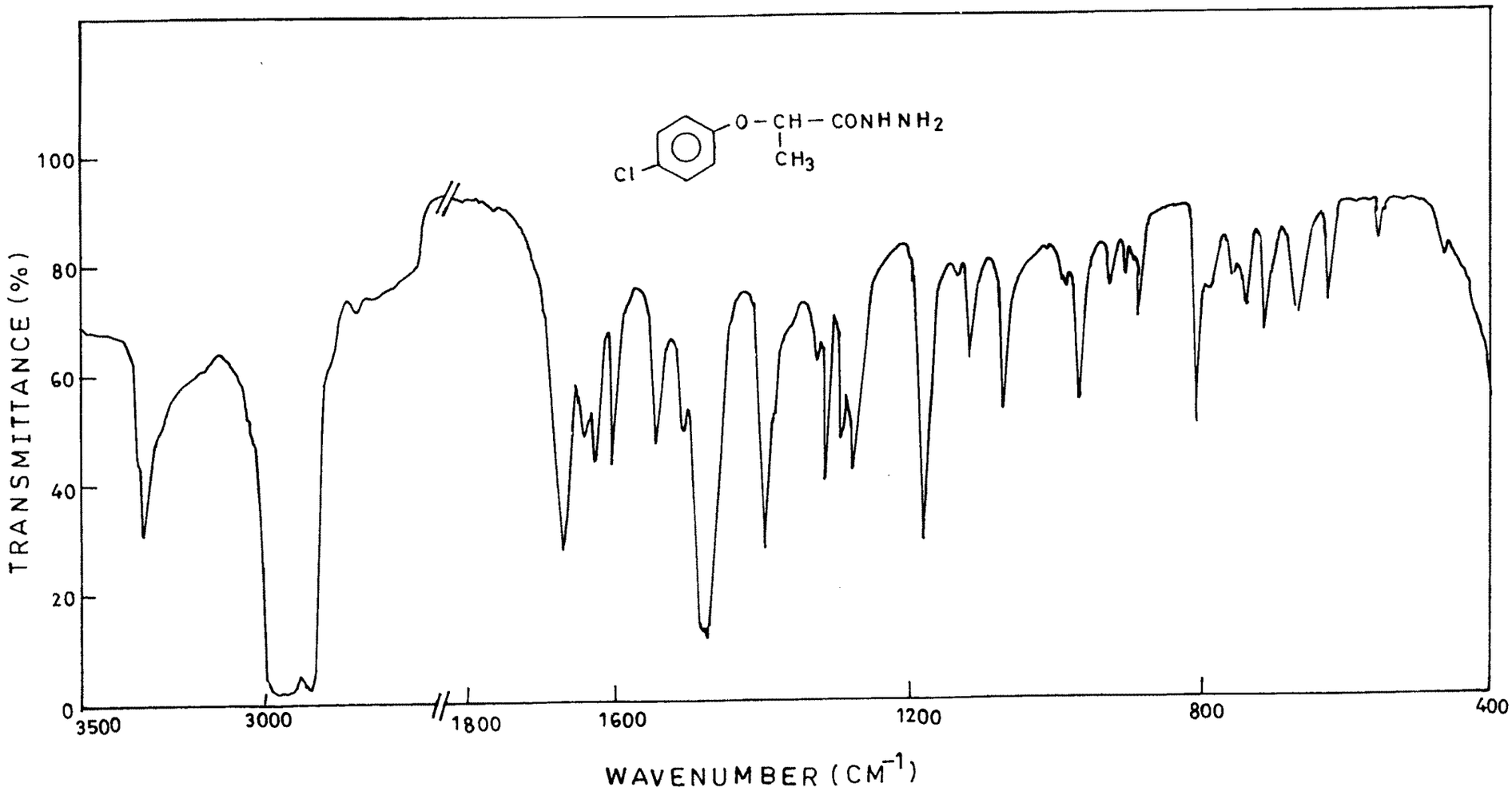


Fig. 16

IR Spectrum of 3,6-Dimethyl-1-(4-Methylphenoxy acetyl)-4-oxopyrano [4,3-c] Pyrazole (III'g)

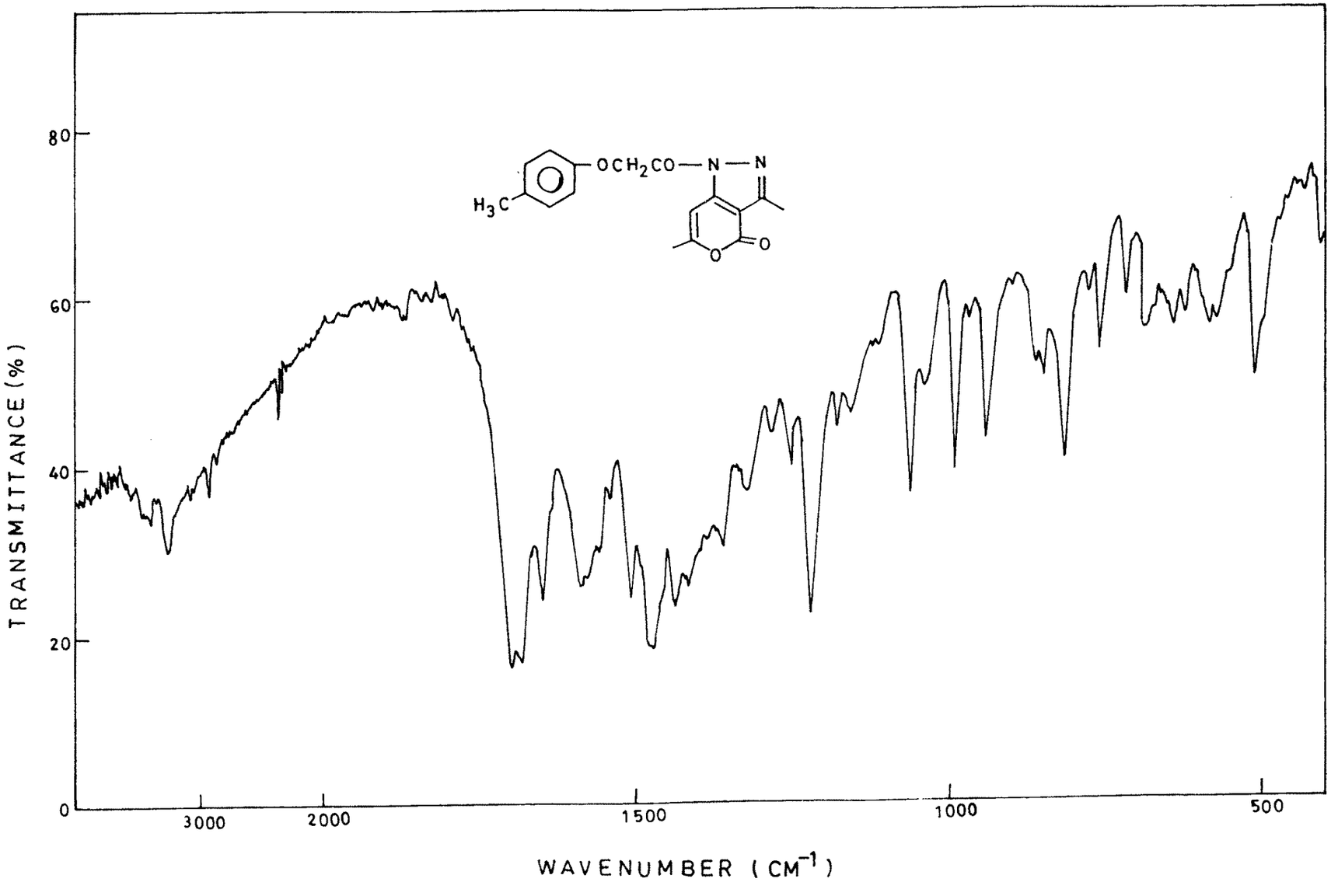


Fig. 17

^{1}H NMR Spectrum of 3,6 – Dimethyl-1-(4-Methylphenoxyacetyl)-4-oxopyrano[4,3-c] Pyrazole (III′g) .

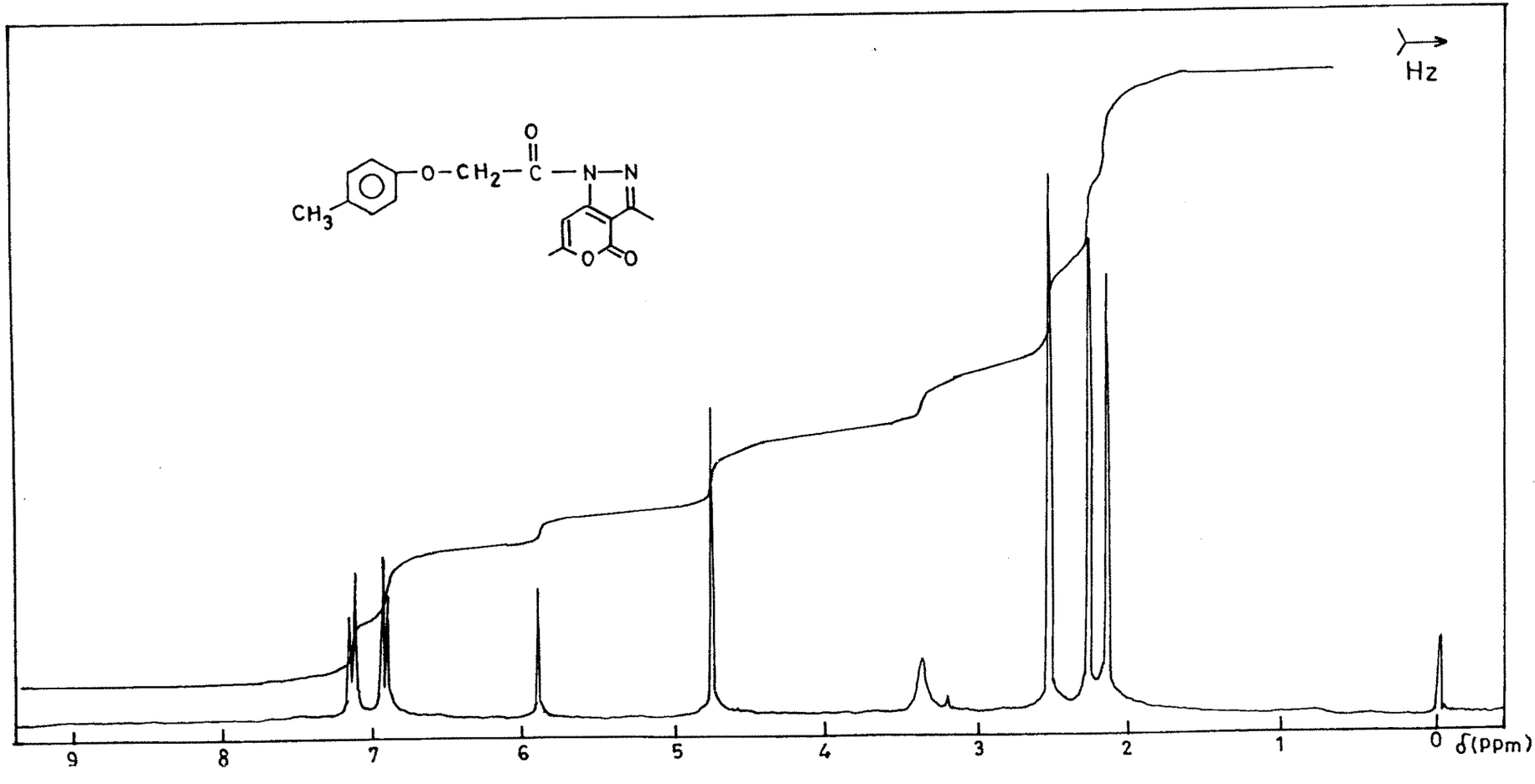


Fig. 18

1 H NMR Spectrum of 3,6-Dimethyl – 1-[2-(4-Chlorophenoxypropionyl)] – oxopyrano [4 3-c] Pyrazole (III'i)

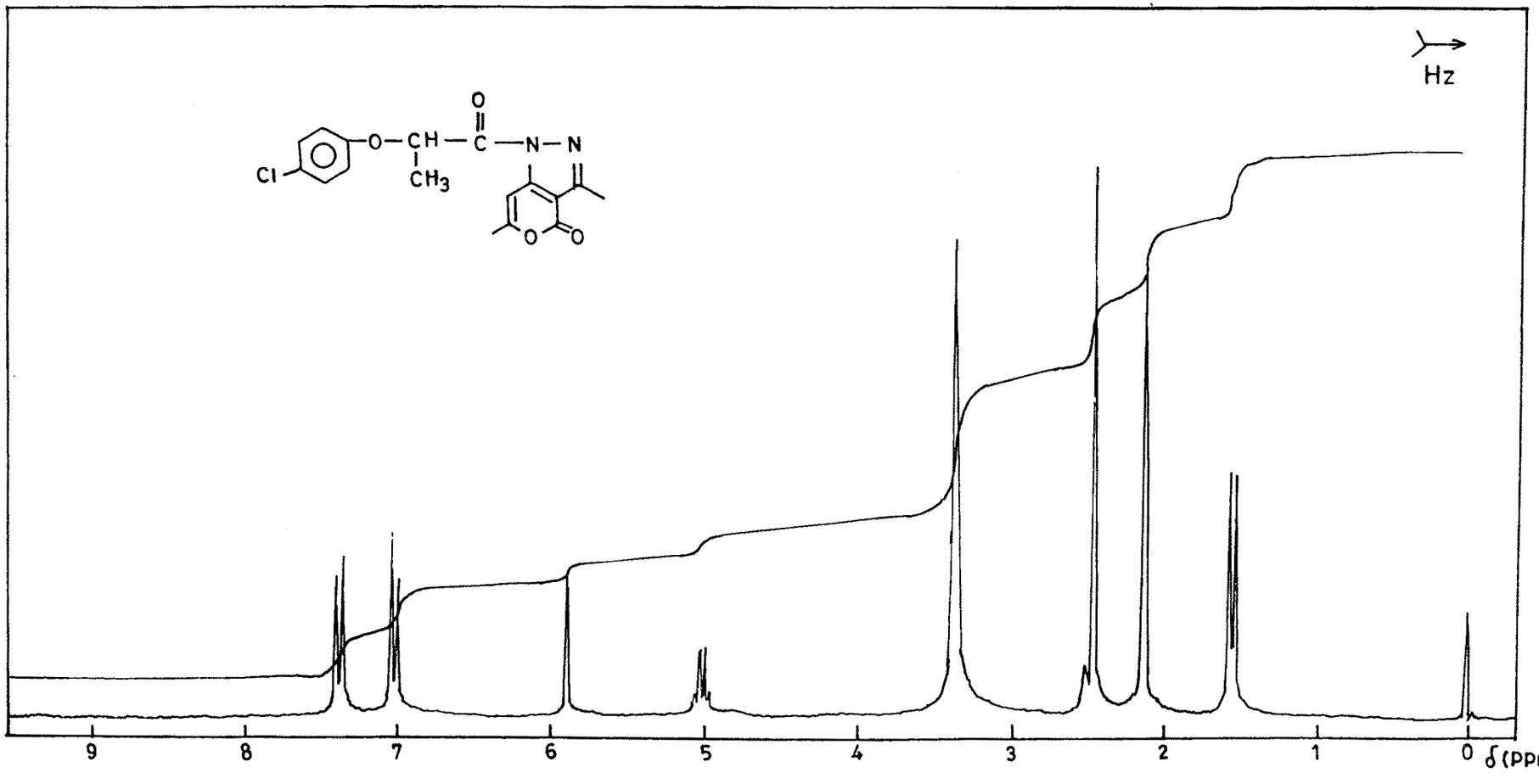


Fig. 19

IR Spectrum of 3,6-Dimethyl-1-(2-methylphenoxyacetyl)-4-oxopyrano pyrazole (III'k).

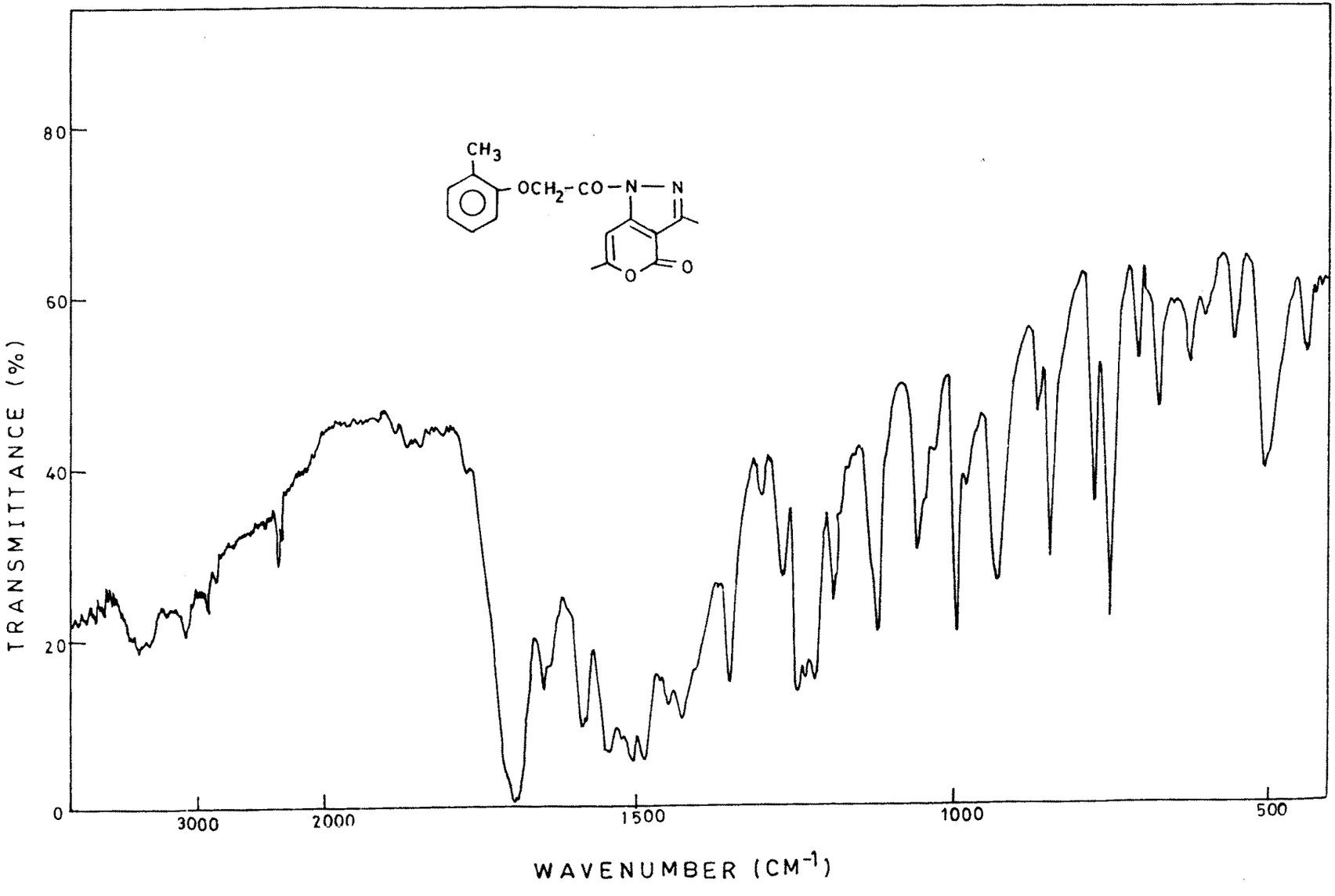


Fig. 20