EXPERIMENTAL

General Remarks

i) Percentage yield, physical constants (MP/BP) elemental analysis(found and calculated) and spectral characteristics of the compounds have been reported.

ii) MP/BP were determined by open capillary method and are uncorrected.

iii) UV spectra were recorded in 95% ethanol on a Hitachi UV-visible spectrophotometer.

iv) IR spectra were recorded in KBr pellets/nujol on a "Perkin-Elmer 297" spectrophotometer.

v) NMR spectra were recorded on "Perkin-Elmer R-32 Spectrometer using T.M.S. as an internal reference and CCl_4/TFA as solvent. The chemical shifts (δ-values) are reported in ppm.

vi) Mass spectra were recorded on "El-MS" computor system.

vii) The purity of the compound was checked by TLC using silica gel as adsorbent.

PART-I : Synthesis of some new thiazolidinone derivatives of N^1-Hydrazido -6-chloro-4-methyl quinolin-2(1H) one.

PART-II : Synthesis of some new thiazolidinone derivatives of N^1-Acetyhydrazido -8-chloro-4-methyl quinolin-2(1H) one.

PART-III : Synthesis of some new thiazolidinone derivatives of N^1-Hydrazido-4,6-Dimethyl quinolin-2(1H) one.

PART-IV : Synthesis of some new thiazolidinone derivatives of N^1-Acetylhydrazido-6-chloro-2-methyl quinolin-4(1H) one.

PART-V : Synthesis of some new thiazolidinone derivatives of N^1-Hydrazido-8-chloro-2-methyl quinolin-4(1H) one.

PART-VI : Antimicrobial screening of the synthesised compounds.

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EXPERIMENTAL

PART-I : Consists of synthesis of some new thiazolidinone derivative of N^1-Hydrazido-6-chloro-4-methyl quinolin-2 (1H)-one.

PREPARATION OF ACETOACETANILIDE (1) :

In a round bottom flask carrying a reflux condenser a mixture of p-chloroaniline (25.4 ml, 0.1 mol) and acetoacetic ester (26.0 ml, 0.1 mol) in benzene (50 ml) was heated for 3-4 hours on heating mentle cooled and neutralised with Na_2CO_3. Heavy liquid separated out was extracted in chloroform and solvent was removed. The heavy liquid obtained was distilled under reduced pressure to give acetoacetanilide 35 gm. (72.61%) B.P. 142°C. at 15 mm.

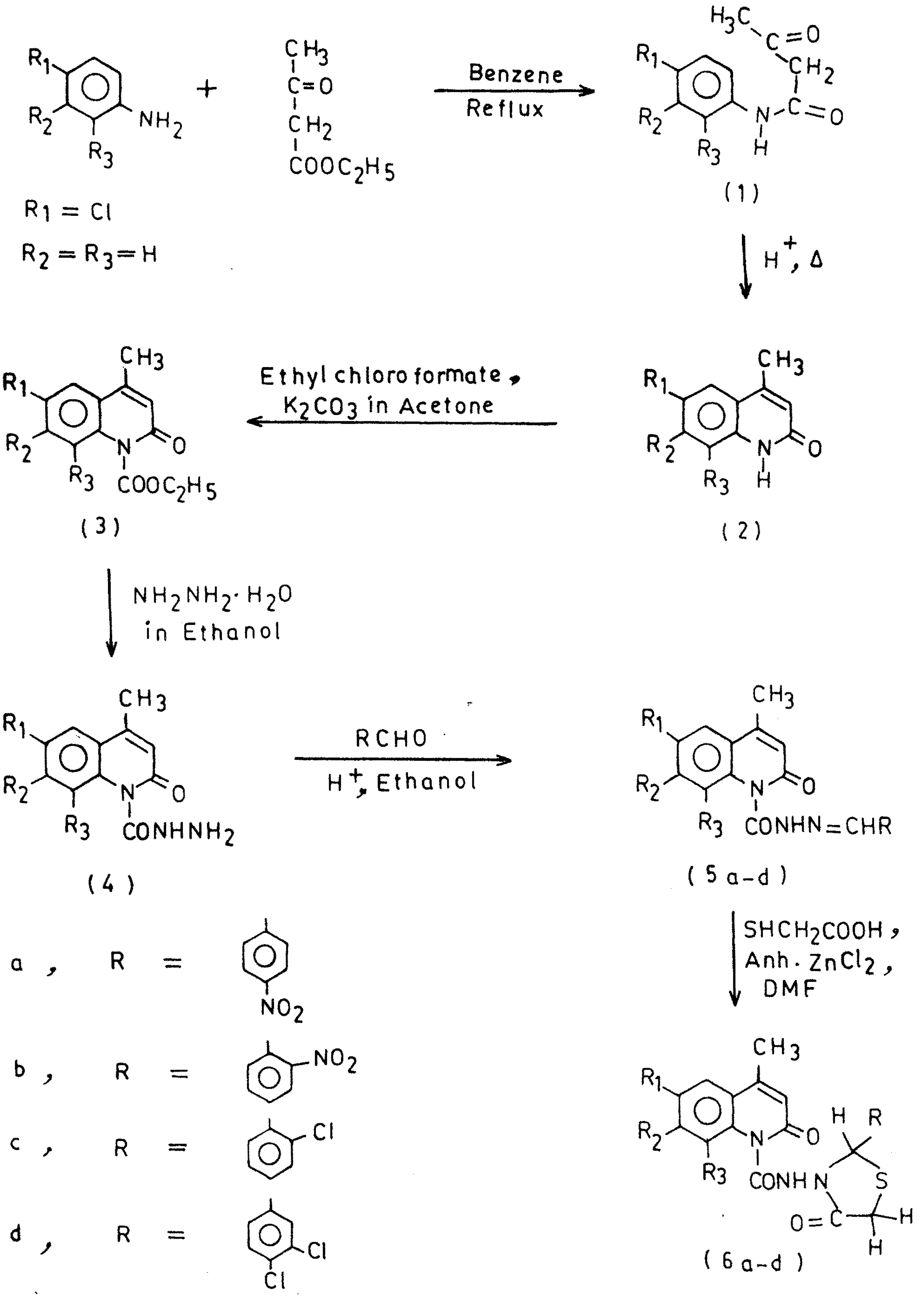
IR (KBR) : ν, 3350-3200 (NH), 1660-1670 (amido >C=O),
1600 (>C=C<), 760 (C - Cl) cm^{-1}.

PMR ($CDCl_3$) :δ, 1.98 (3H, s,-$COCH_3$), 3.3 (2H, s,- $\overset{O}{C}$ - CH_2-$\overset{O}{C}$-).
5.85 (1H,s, exchangable with D_2O, NH), 6.5 - 8
(4H, m, aromaticprotons) ppm.

SYNTHESIS OF 6-CHLORO-4-METHYL QUINOLIN-2(1H)-ONE (2) :

In a round bottom flask a mixture of acetoacetanilide 1 (17.5 gm, 0.1 mol) and conc. H_2SO_4 (75 ml.) was heated on water bath at 70-80°C, cooled and poured in 500 ml. ice cold water with stirring. The separated product was filtered, dried and recrystallised from ethanol to give (2), 14 gm, (72.53%) M.P. 273°C.

SCHEME-I


R1
R2
R3
NH2
+
CH3
C=O
CH2
COOC2H5
Benzene
Reflux
H3C
C=O
CH2
N-C=O
H
(1)
R1 = Cl
R2 = R3 = H
H+, Δ
CH3
N
O
(2)
Ethyl chloro formate,
K2CO3 in Acetone
COOC2H5
(3)
NH2NH2·H2O
in Ethanol
CONHNH2
(4)
RCHO
H+, Ethanol
CONHN=CHR
(5 a-d)
SHCH2COOH,
Anh. ZnCl2,
DMF
CONH N
H R
S
O=C
H
(6 a-d)
a, R =
NO2
b, R =
NO2
c, R =
Cl
d, R =
Cl
Cl

(Found : C, 62.10; H, 4.16; N, 7.20; requires : C, 62.18; H, 4.16; N, 7.23%) Calculated for $C_{10}H_8NOCl$.

IR (Nujol) : ν, 3350-3200 (NH), 1640 (cyclic amido lactone (>C=O), 1600 (>C=C<), 680 (>C - Cl) cm^{-1} .

Fig.-1

PMR ($CDCl_3$) : δ, 2.35 (3H, s, $=/^{CH_3}$), 5.85 (1H,s, exchangable with D_2O NH), 6.6 (1H,s, = CH-), 7.4-8.1 (3H,s, aromatic protons) ppm.

SYNTHESIS OF N^1-CARBETHOXY-6-CHLORO-4-METHYL QUINOLIN-2(1H)-ONE (3) :

In a round bottom flask carrying reflux condenser and a guard tube, a mixture of 6-chloro-4-methylquinolin-2-(1H)-one (10 gm, 0.04 mol) and ethylchloroformate (4.3 gm, 0.04 mole) in dry acetone containing anhydrous, Potassium carbonate (5 gm.) was refluxed for 24 hours, cooled and the solvent was removed under reduced pressure. The resulting white solid was washed with water filtered and recrystalised from ethanol to give (3), 8 gm, 58.2%), M.P. 246 °C.

(Found : C, 58.80%, H, 4.20 N, 5.20 $C_{13}H_{12}NO_3Cl$, requires : C, 58.77 H, 4.55 N, 5.28%).

IR (KBr) : ν, 1770 (ester >C=O), 1670 (acyclic amido lactum >C=O), 1635-1640 (cyclic amido >C=O), 1600 (>C=C<), 760 (C-Cl)cm^{-1}

Fig.-2

PMR ($CDCl_3$) : δ, 1.3(3H,t, J=7.5 Hz, CH_3), 2.45 (3H,s, $=/^{CH_3}$), 4.18 (3H, q, J=7 Hz, OCH_2), 6.6 (1H,s,=CH),

6-CHLORO-4-METHYLQUINOLIN-2(1H)-ONE.

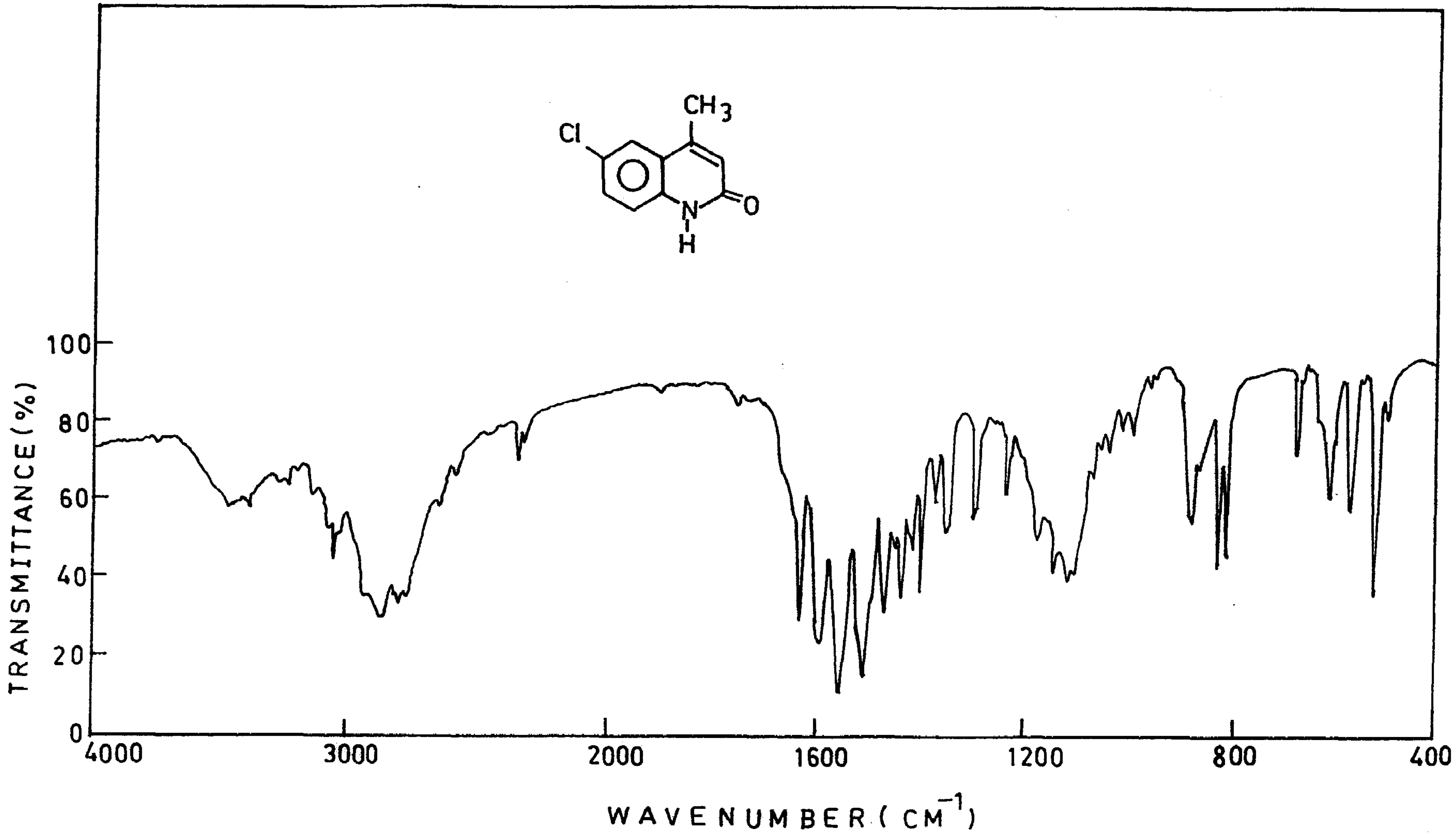


Fig. 1

IR Spectrum of N^1-carbethoxy-6-chloro-4-methyl quinolin-2 (1H) one

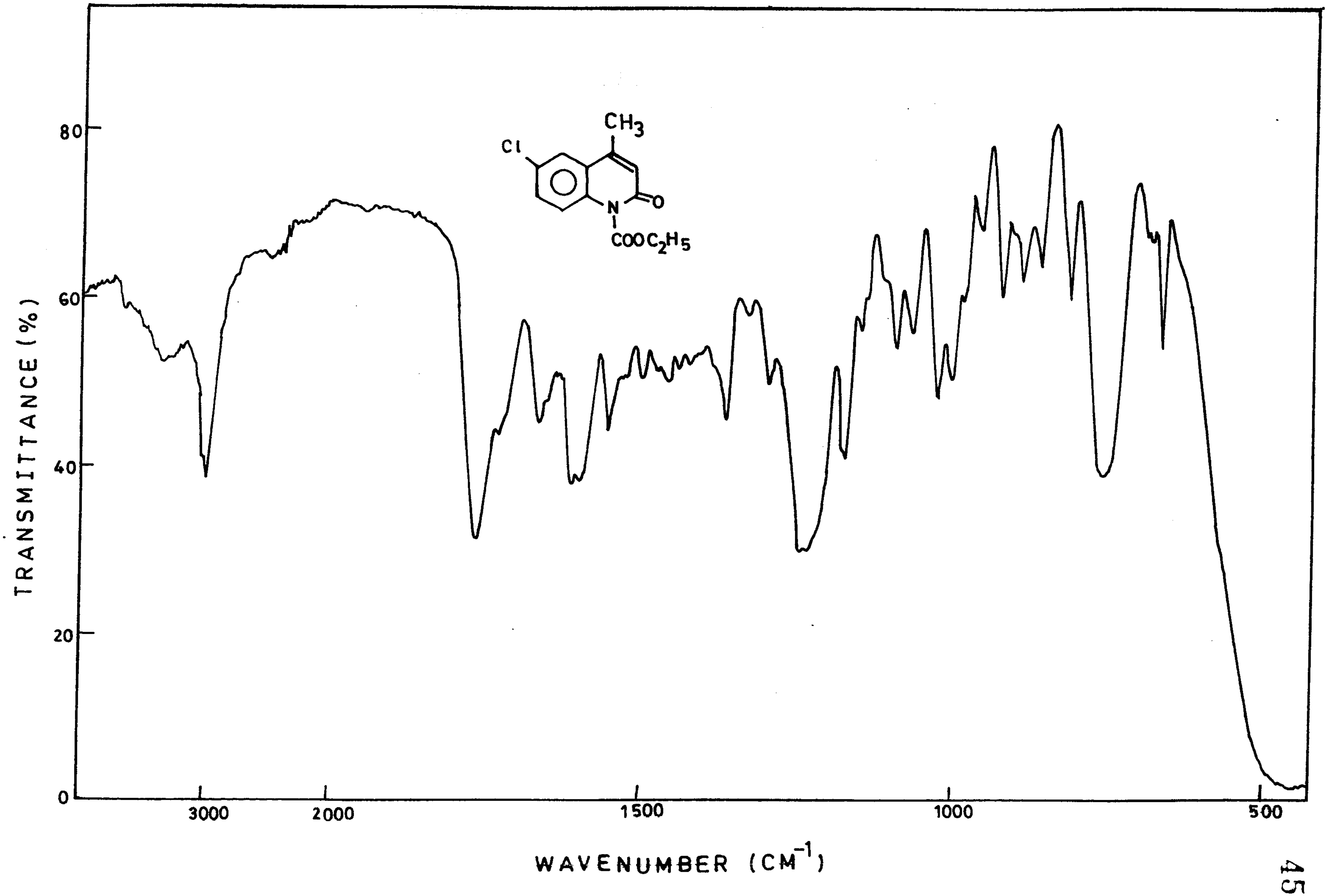


Fig. 2

7.4-8.1) (3H,s, aromatic protons) ppm.

SYNTHESIS OF N^1-HYDRAZIDO-6-CHLORO-4-METHYL-QUINOLINE-2(1H)-ONE (4) :

To a solution of compound 3 in a round bottom flask (6.0 gm, 0.02 mol) in ethanol (25 ml.) hydrazine hydrate (1.0 gm, 0.02 mol) was added and the same reaction mixture was refluxed on water bath using reflux condenser for 2 hr., cooled. The resulting solid was filtered and recrystallised from ethanol to furnish (4), M.P. 257^{0}C.

(Found : C, 52.50 H, 3.90 N, 16.70, $C_{11}H_{10}O_2N_3Cl$ requires C, 52.49 H, 4.00 N, 16.69 %)

IR (KBr) : ν, 3350-3250 (NH), 1670 (acyclic amido >C=O), 1660 (cyclic amido >C=O), 1600 (>C=C<), 760(C-Cl)cm^{-1}

PMR($CDCl_3$) : δ, 2.45 (3H, s, $=/^{CH_3}$), 2.75-2.8 (3H,s, - NH_2), 6.6 (1H,s, = CH-), 7.4-8.1 (3H,s, aromatic protons),8.2(1H,s, - CONH) ppm.

SYNTHESIS OF N^1-(4-NITROBENZYLIDENE HYDRAZIDO,-6-CHLORO-4-METHYL QUINOLIN-2(1H) - ONE : (5b)

A solution of compound 4 (0.251 gm, 0.001 mol), in ethanol (20 ml) containing few drops of galcial acetic acid was taken in a round bottom flask. To this solution p-nitrobenzaldehyde (0.151 gm, 0.001 mol) was added and the reaction mixture was refluxed on steam bath for 3 hr. The solvent was distilled off under vacuum and the semisolid separated was treated with water. The solid obtained was filtered and further crystallised from ethanol to yield 5b, yield 0.7 gm, (61.13%), M.P. 224°C.

ANALYSIS : Found : C, 56.20; H, 3.40; N, 14.50;

Calculated for $C_{18}H_{13}N_4O_4$: C, 56.18; H, 3.41; N, 14.56 %

IR (KBr) : ν, 3350–3200 (NH), 1670 (acyclic amido >C=O),
1640–1645 (cyclic amido >C=O), 1620 (–C=N–),
1600 (>C=C<), 760 (C–Cl) cm^{-1}
Fig–3

PMR ($CDCl_3$) : δ, 2.45 (3H,s, $=/^{CH}{}_3$), 6.6 (1H,s, – CH =),
7.8 (7H,s, aromatic protons and = CH–),
8.2 (1H,s, – CONH) ppm.

The physical constant (M.P.) percentage yield elemental analysis (found and calculated) of the compounds (5a,5c,5d) have been reported in table–1.

N^1-(4-NITROBENZYLIDENE HYDRAZIDO)-6-CHLORO-4-METHYL QUINOLIN-2(1H)-ONE.

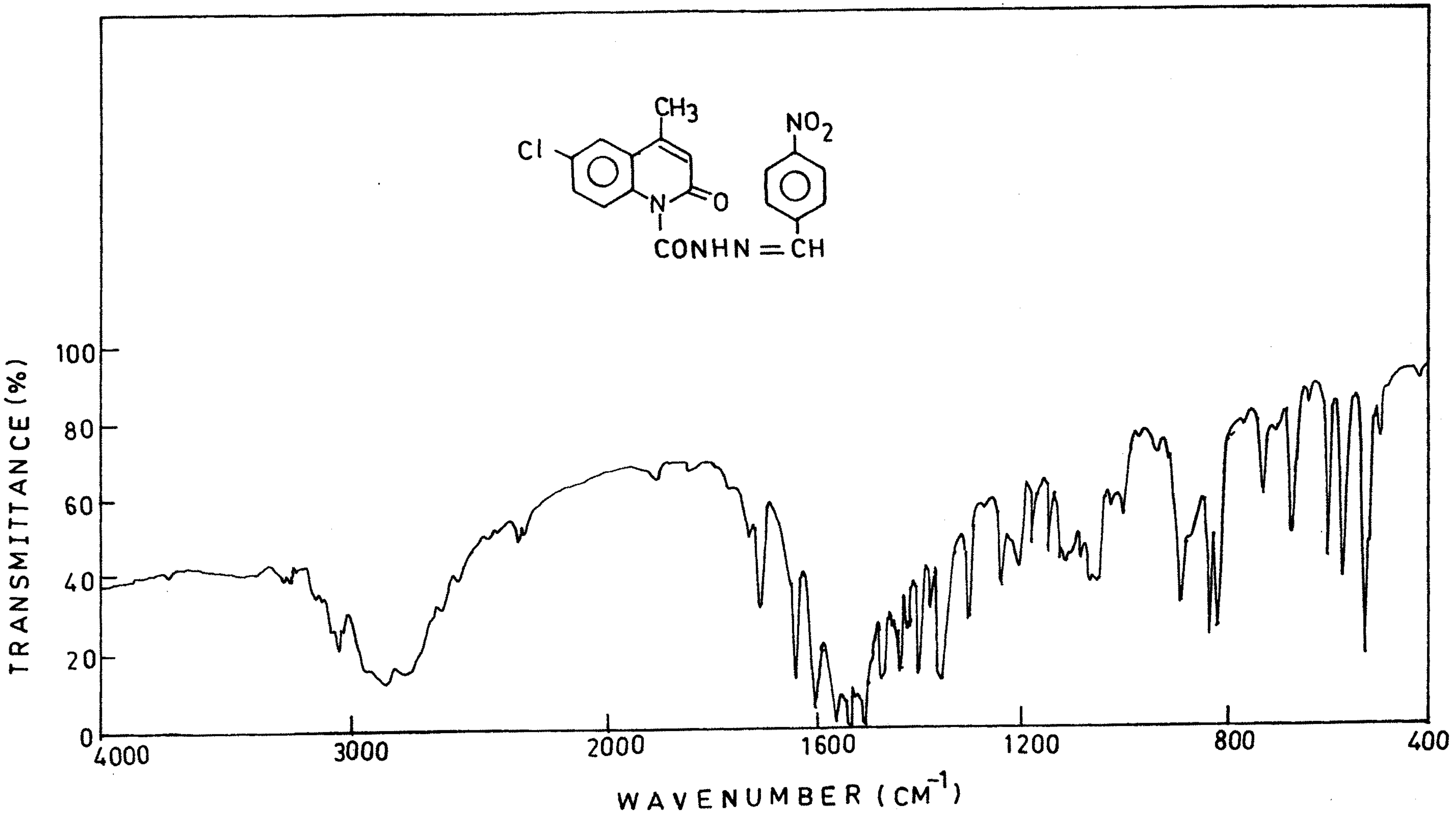


Fig. 3

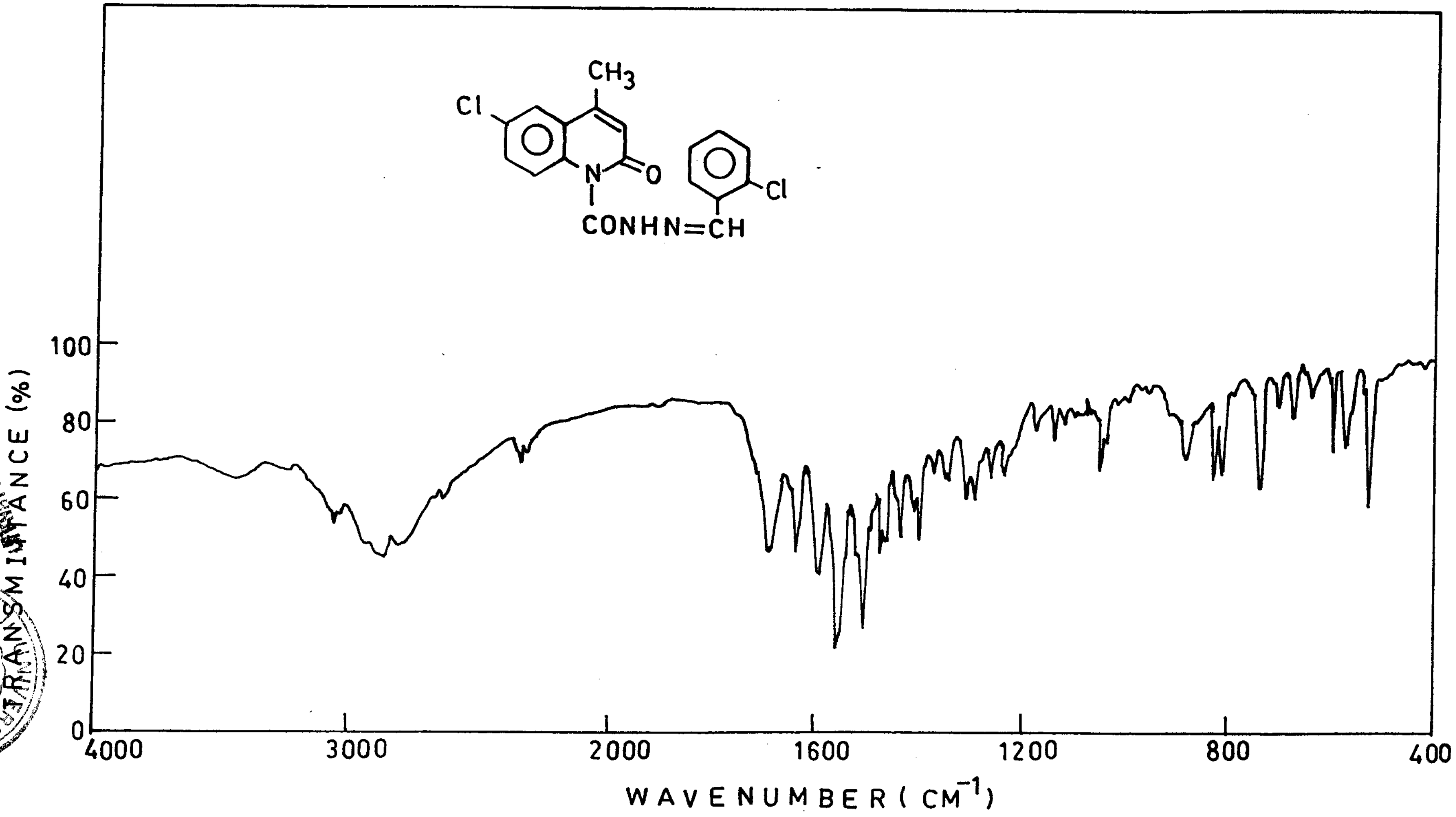
TABLE-1

PHYSICAL AND ANALYTICAL DATA OF THE SCHIFF'S BASE (V)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
5a	205	64.34	$C_{18}H_{13}N_4O_4Cl$	56.20 56.18	3.30 3.41	14.50 14.56
5c	197	65.00	$C_{18}H_{13}N_3O_2Cl_2$	57.80 57.77	3.60 3.56	11.20 11.24
5d	247	57.37	$C_{18}H_{12}N_3O_2Cl_3$	52.90 52.90	2.90 2.95	10.30 10.28

All the above compounds gave satisfactory IR and PMR spectral analysis.

N^1–(2-CHLOROBENZYLIDENE HYDRAZIDO)-6-CHLORO-4-METHYL QUINOLIN-2 (1H)-ONE.



SYNTHESIS OF 3-(6-CHLORO-4-METHYL-2-OXAQUINOLINO-1-AMIDYL)-2-(4-NITROPHENYL)-1,3-THIAZOLIDIN-4-ONE : (6b)

To a solution of compound 5 b (0.4 gm.0.001 mol) in DMF (15 ml) in a round bottom flask, a pinch of anhydrous zinc chloride and mercapto acetic acid (1 gm, 0.001 mol) were added. The same reaction mixture was further refluxed on stem bath for 8 hr. then cooled and poured in ice cold water. The separated solid was filtered and recrystallised from DMF to furnish 6b, yield, 0.31 gm, (65.95%), M.P. > 300^{o}C.

Analysis : Found : C, 52.30, H, 3.30, N, 12.20

Calculated for $C_{19}H_{14}N_4O_5$ Sol, C, 52.34, H, 3.29, N, 12.20%.

<u>IR (KBr)</u> : ν, 3350-3250 (NH), 1690-1700 (five membered cyclic amido >C=O), 1670 (acyclic amido >C=O), 1640-1645 (six membered cyclic amido >C=O), 760 (C-Cl) cm^{-1}.

<u>PMR (CDCl$_3$)</u> : δ, 2.45 (3H, s, $=/^{CH_3}$), 3.2 (1H,s,-CH), 3.5 (2H,s, -CH=), 7-5.2 (7H, m, aromatic protons), 8.2 (1H,s, - CONH) ppm.

The physical constant (M.P.) percentage yield, elemental analysis (found and calculated) of the compounds 6a, 6c, 6d have been reported in Table-2.

TABLE-2

PHYSICAL AND ANALYTICAL DATA OF THE THIAZOLIDINONES (6)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
6a	above 300	62.5	$C_{20}H_{15}N_4O_5SCl$	52.30	3.30	12.20
				52.34	3.29	12.20
6c	above 300	54.71	$C_{20}H_{15}N_3O_3SCl_2$	53.60	3.40	9.40
				53.58	3.37	9.37
6d	above 300	68.08	$C_{20}H_{14}N_3O_3SCl_3$	49.70	3.10	8.70
				49.73	3.12	8.70

All the above compounds gave satisfactory IR and PMR spectral analysis.

PART-II : Consists of synthesis of some new thiazolidinone derivatives of N^1-Acetylhydrazido-8-chloro-4-methyl quinolin-2(1H)-one.

SYNTHESIS OF ACETOACETANILIDE (1)

In a round bottom flask carrying a reflux condenser a mixture of o-chloroaniline (25.4, 0.1 mol.) and acetoacetic ester (26 ml. 0.1 mol) in benzene (50 ml.) was heated for 3-4 hours on heating mentle cooled and neutrilised with Na_2CO_3. Heavy liquid separated out was extracted in chloroform and solvent was removed. The heavy liquid obtained was distilled under reduced pressure to give acetoacetanilide 35 gm. B.P. 139°C at 15 mm.

IR (KBr) : ν, 3300-3250 (NH), 1660-1700 (>C\O), 760 (C-Cl) cm^{-1}

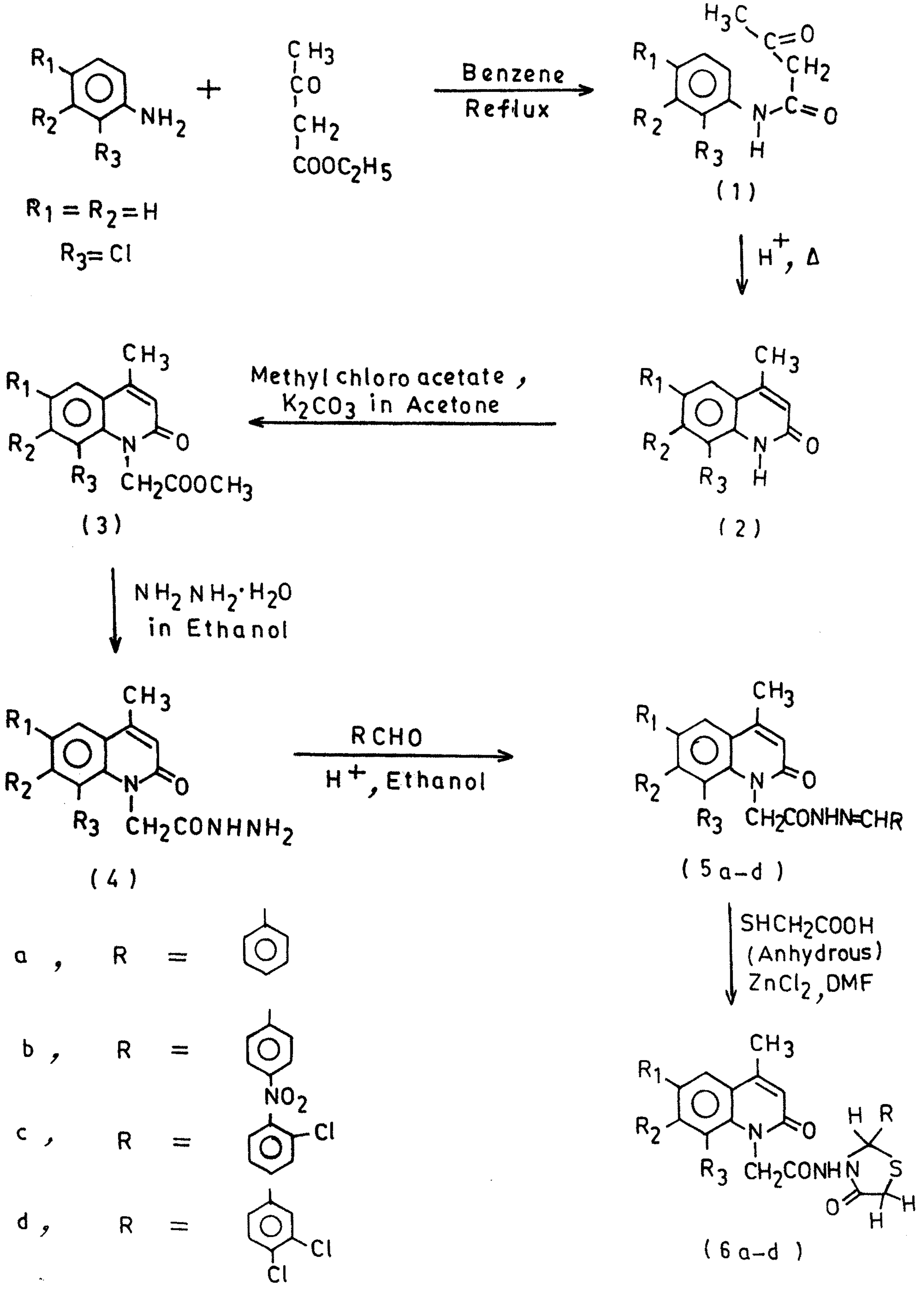
PMR ($CDCL_3$) δ, 1.98 (3H,s, - $COCH_3$), 3.2 (2H,s,- C-CH_2-C-),
4.6 (1H,s,-NH, exchangable with D_2O),
6.4-7.4 (3H, m, aromatic protons ppm.

SYNTHESIS OF 8-CHLORO-4-METHYLQUINOLIN-2(H)-ONE

In a round bottom flask a mixture of acetoacetanilide (1) (17 gm, 0.1 mol) and conc. H_2SO_4 (75 ml) was heated on water bath at 70-80°C for 0.5 hr initially and for 1.0 hr at 100°C, cooled and poured in 500 ml ice cold water weith stirring. The separated product was filtered, dried and recrystallised from ethanol to give (2), 13 gm (67.37 %), M.P. = 229°C.

Analysis : Found : C, 62.00; H, 4.10; N, 7.30, calculated for $C_{10}H_8NOCl$: C, 62.02; H, 4.23; N, 7.23 %

SCHEME-II


R1
R2
R3
NH2
+
CH3
CO
CH2
COOC2H5
R1 = R2 = H
R3 = Cl
Benzene
Reflux
H3C
C=O
CH2
N-C=O
H
(1)
H+, Δ
CH3
N
H
O
(2)
Methyl chloro acetate ,
K2CO3 in Acetone
CH2COOCH3
(3)
NH2NH2·H2O
in Ethanol
CH2CONHNH2
(4)
RCHO
H+, Ethanol
CH2CONHN=CHR
(5a–d)
SHCH2COOH
(Anhydrous)
ZnCl2, DMF
CH2CONH
H R
N
S
H
H
(6a–d)
a , R =
b , R =
NO2
c , R =
Cl
d , R =
Cl
Cl

IR(KBr) : ν, 3350-3200 (NH), 1640-1645 (cyclic amido >C=O, 1600 (>C=C<), 760 (C-Cl) cm^{-1}.

Fig.-4

PMR($CDCl_3$) : δ, 2.45 (3H,s, = $/^{CH_3}$), 5.85 (1H,s, exchangable with D_2O, NH), 6.6 (1H, s, = CH-), 7.4-8.1 (3H,s, aromatic protons)ppm.

SYNTHESIS OF N^1-METHOXYCARBONYL METHYL-8-CHLORO-4-METHYL-QUINOLIN-2-(1H)-ONE (3)

In a round bottom flask, carrying a reflux condenser and a guard tube, a mixture of 8-chloro-4-methylquinolin-2(1H)-one (6 gm. 0.03 mol) and methyl chloroacetate (4.1 gm. 0.03 mol) in dry acetone containing anhydrous Potassium carbonate (5 gm) was refluxed for 24 hours, cooled and the solvent was removed under reduced pressure. The resulting white solid was washed with water, filtered and recrystallised from ethanol to give (3). 8.4 gm. (61.17%) M.P. 241 °C.

Analysis : Found : C, 58.80; H, 4.50; N, 5.20

Calculated for $C_{13}H_{12}NO_3Cl$.

Requires : C, 58.76; H, 4.55; N, 5.27%

IR (KBr) : ν, 1770 (ester >C=O), 1650 (cyclic amido >C=O), 1600 (>C=C<), 760 (-C-Cl) cm^{-1}.

PMR ($CDCl_3$) : δ, 2.45 (3H,s, = $/^{CH_3}$), 3.8 (3H,s, $-OCH_3$), 4.2 (2H, s, - NCH_2), 6.6 (1H,s, = CH-), 7.4-8.1 (3H,s, aromatic protons) ppm.

8 — CHLORO-4—METHYLQUINOLIN—2(1H)—ONE .

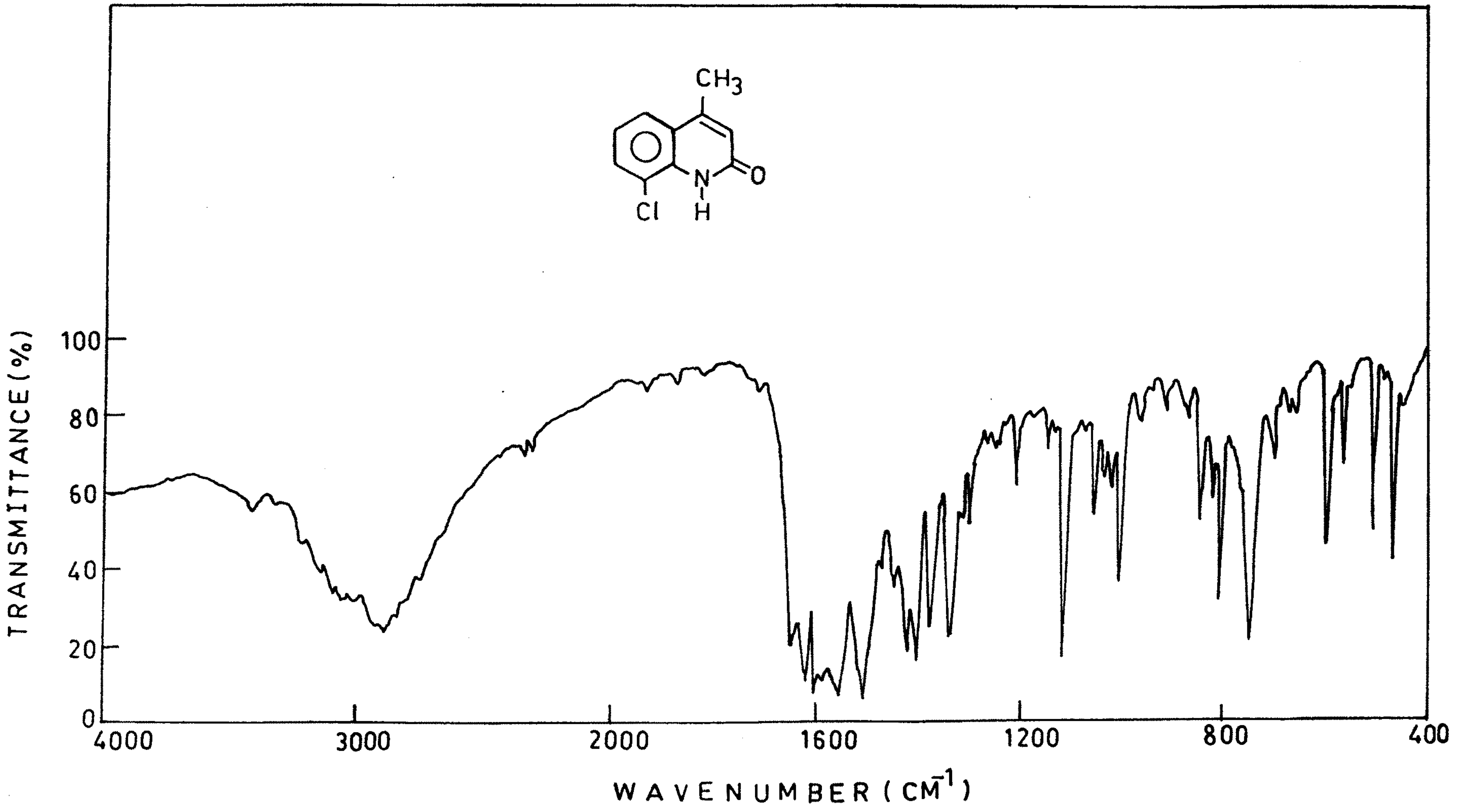


Fig. 4

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

To a solution of compound 3 in a round bottom flask (8 gm., 0.03 mole) in ethanol (25 ml.) hydrazine hydrate (1.5 gm,. 0.03 mole) was added and the same reaction mixture was refluxed on water bath using reflux condenser for 2 hr. cooled. The resulting solid was filtered and recrystallised from ethanol to furnish (4), 56 gm. 80%). M.P. 178 °C.

Analysis : Found : C, 54.20; H, 4.50, N, 15.80

Calculated for $C_{12} H_{12}N_3O_2Cl$.

Requires : C, 54.23; H, 4.52; N, 15.81%.

<u>IR (KBr)</u> : ν, 3300-3100 ($NHNH_2$), 1665-1645 (broad cyclic and acyclic amido >C=O), 1605 (>C=O), 750 (C-Cl)cm^{-1}.

Fig.-5

<u>PMR (DMSO)</u> : δ, 2.65 (3H,s, $=/^{CH}{}_{3}$), 4.45 (2H,s,$-NH_2$), 4.8(2H,s,$-NCH_2$), 7 (7H,s, = CH-), 7.4-8.1(3H,s, aromatic protons), 8.2 (1H,s,-CONH) ppm.

Fig.-6

<u>Mass spectrum</u> : $\frac{M}{e}$ (M+); 265, 267 (28.5); 234, 236 (2.86%); 206, 208 (17.80%); 193, 195 (100%); 164, 166 (12.3%); 124,126 (4.6%).

Fig.-7

N^1 – ACETYLHYDRAZIDO-8-CHLORO – 4-METHYLQUINOLIN – 2 (1'H') ONE .

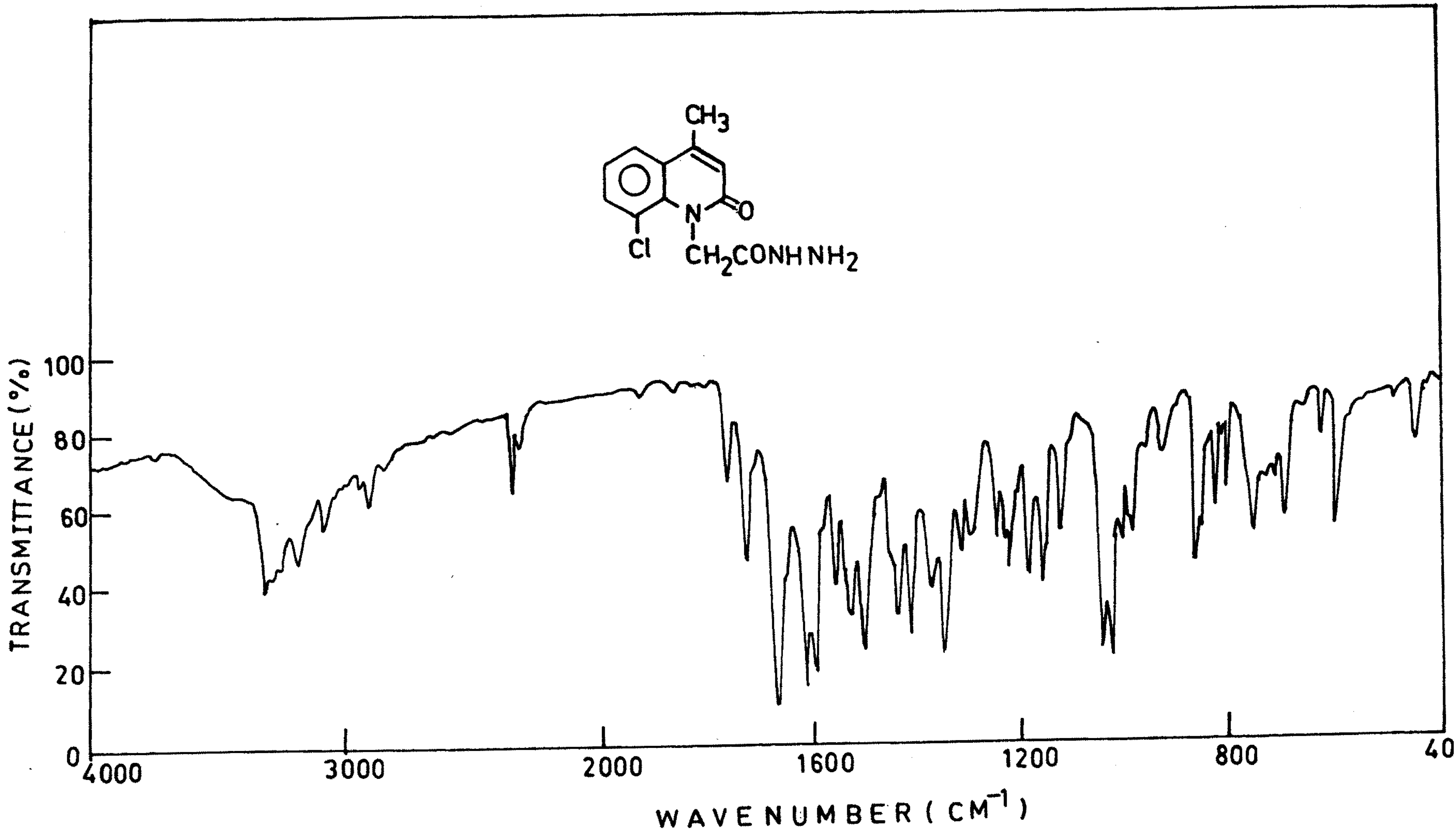


Fig. 5

N^1–ACETYLHYDRAZIDO – 8 – CHLORO – 4 – METHYLQUINOLIN – 2 (1H)-ONE .

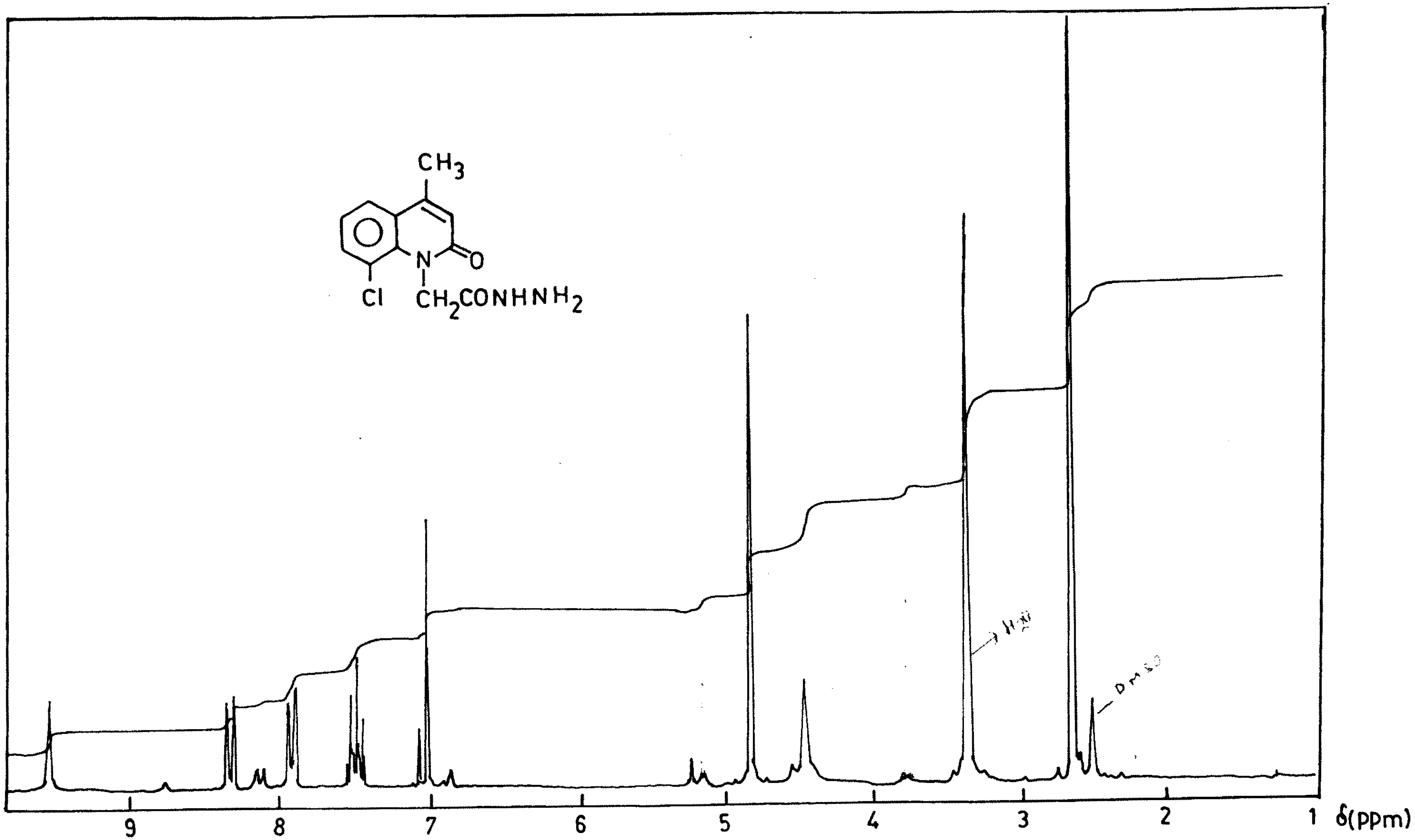


Fig . 6

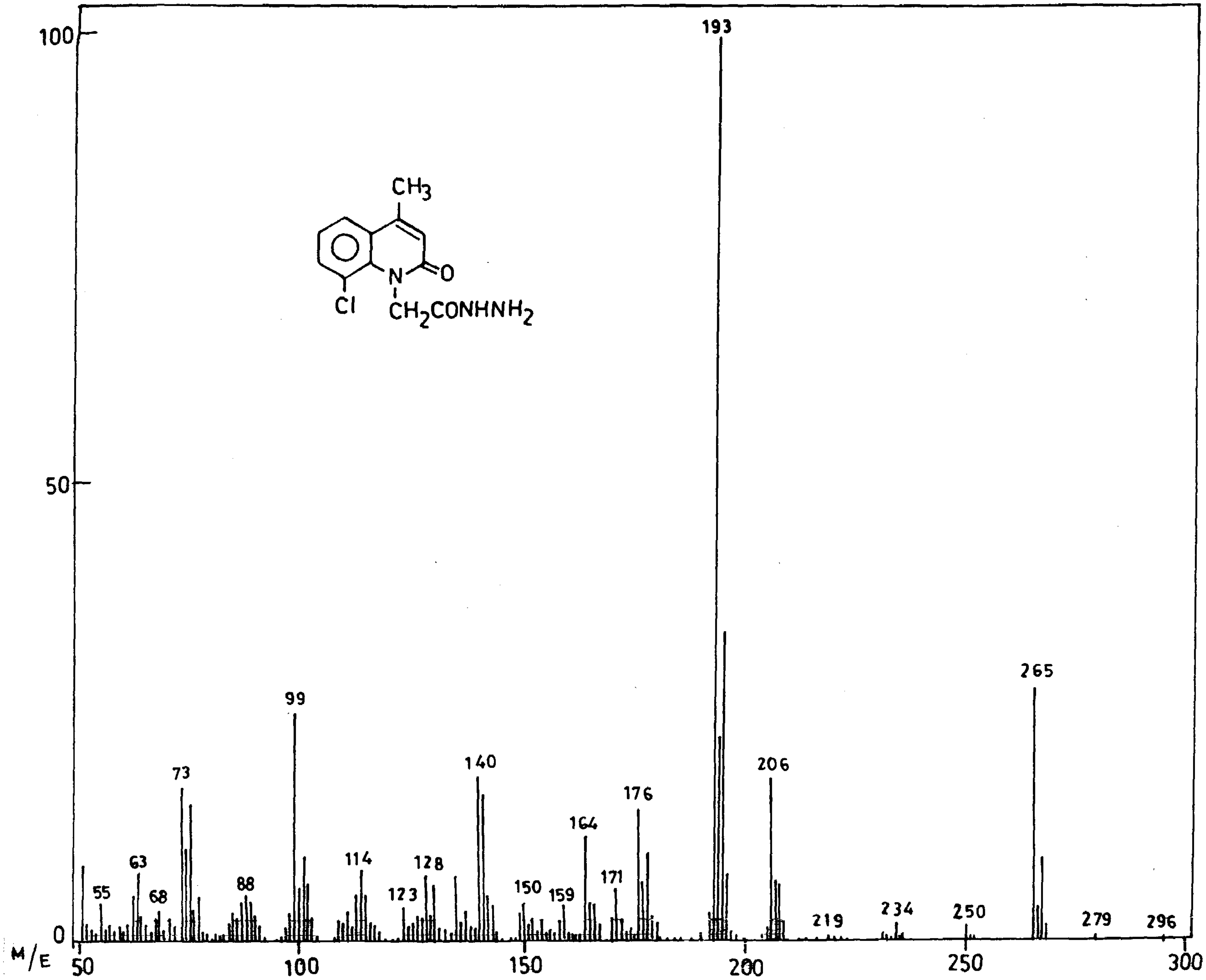


Fig. 7 — N^1– ACETYLHYDRAZIDO–8–CHLORO–4–METHYLQUINOLIN–2 (1H)–ONE.

FRAGMENTATION PATTERN OF COMPOUND
N'-ACETYLHYDRAZIDO-8-CHLORO-4-METHYLQUINOLIN-2(1H)-ONE.

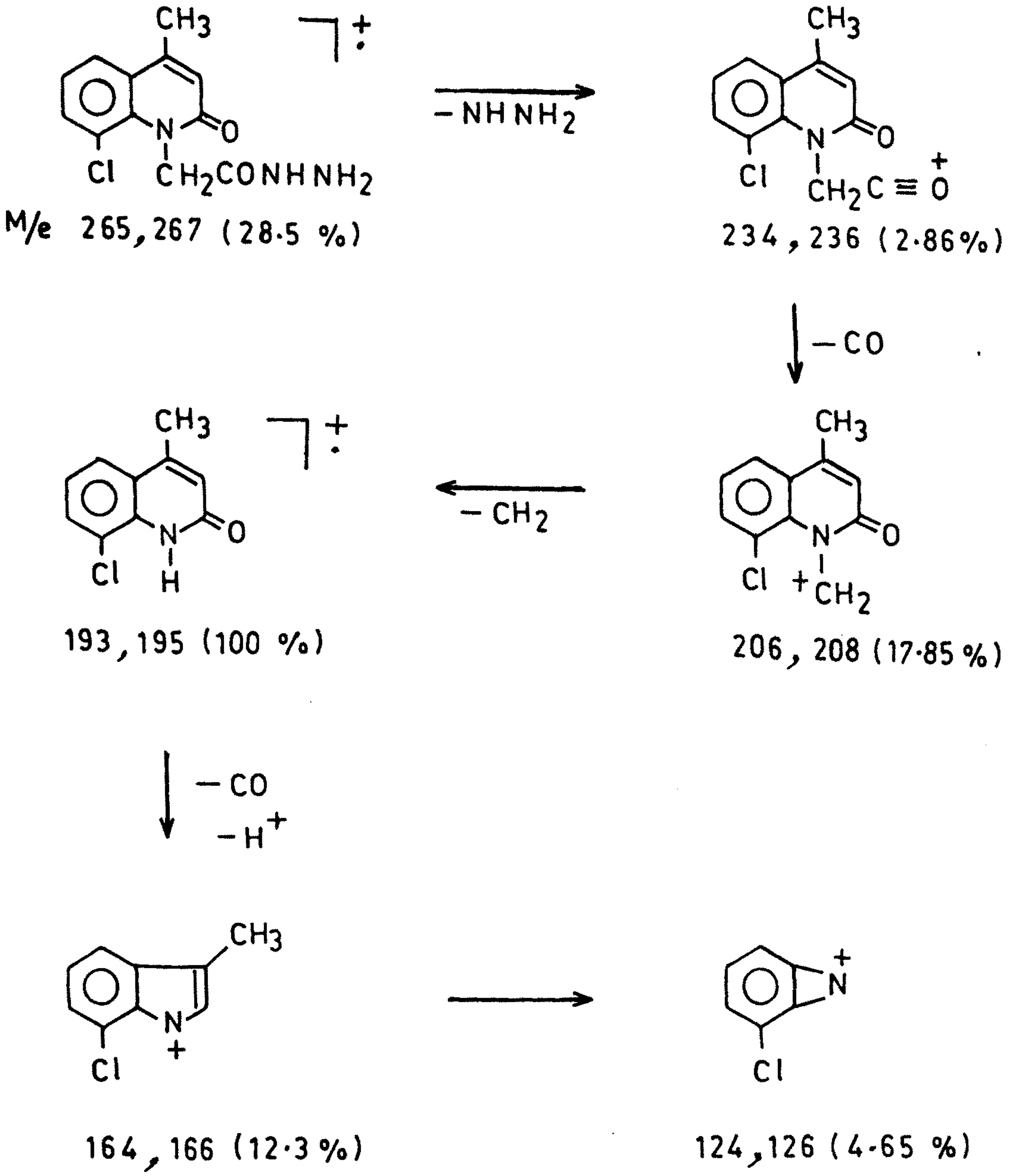


Fig. 8

SYNTHESIS OF N^1-BENZYLIDENEACETYLHYDRAZIDO-8-CHLORO-4-METHYLQUINOLIN-2-ONE (5a)

A solution of compound 4 (0.26 gm, 0.001 mol) in ethanol (20 ml) containing few drops of glacial acetic acid was taken in a round bottom flask. To this solution benzaldehyde (0.106 gm, 0.001 mol) was added and the reaction mixture refluxed on steam bath for 3 hr. The solvent was distilled off under vacuum and the semi-solid separated was treated with water. The solid obtained was filtered and further crystallised from ethanol to yield 5a.

Yield 0.8 gm. (60.15%), M.P. 212 °C.

Analysis :

Found : C, 64.50; N, 4.50; N, 12.00

Calculated for $C_{19}H_{10}N_3OCl$: C, 61.49; H, 4.53; N, 11.88%.

<u>IR</u> <u>(KBr)</u> : ν, 3350-3250 (NH), 1660-1680 (acyclic amido >C=O),
1640-1645 (six membered cyclic amido >C=O),
1600 (>C=C<), 760 (-C-Cl) cm^{-1}.

<u>PMR</u> <u>($CDCl_3$)</u> : δ, 2.45 (3H, s, $=/^{CH}{}_{3}$), 4.2 (2H,s, - NCH_2),
6.6 (1H,s, = CH), 7.4-8.1 (9H,s, aromatic protons
and -CH=), 8.2 (1H,s,-CONH) cm^{-1}.

The physical constant (M.P.), percentage yield elemental analysis (found and calculated) of the compounds (5b, 5c, 5d) have been reported in table-1.

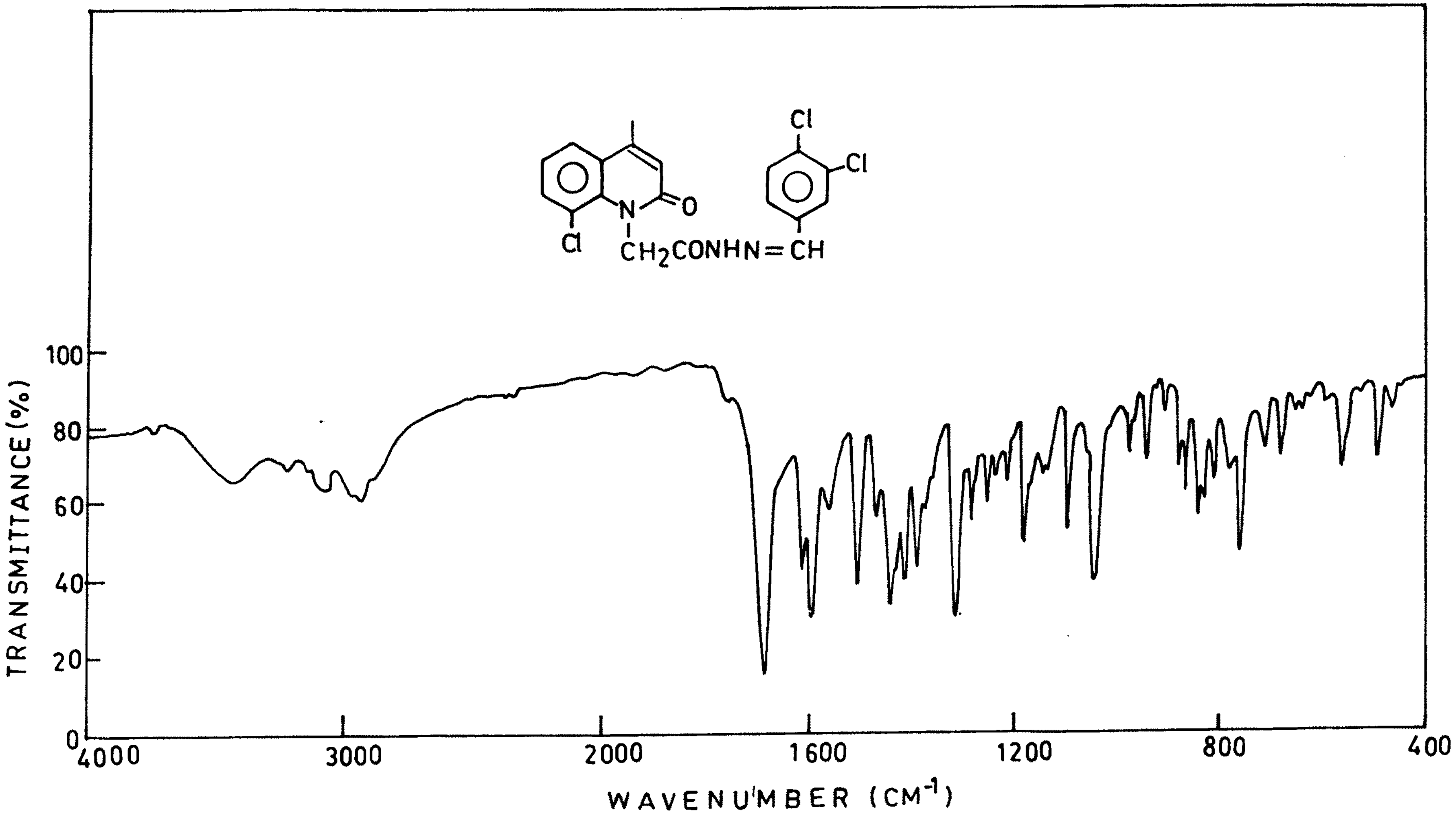
TABLE-1

PHYSICAL AND ANALYTICAL DATA OF THE SCHIFF'S BASES (5)

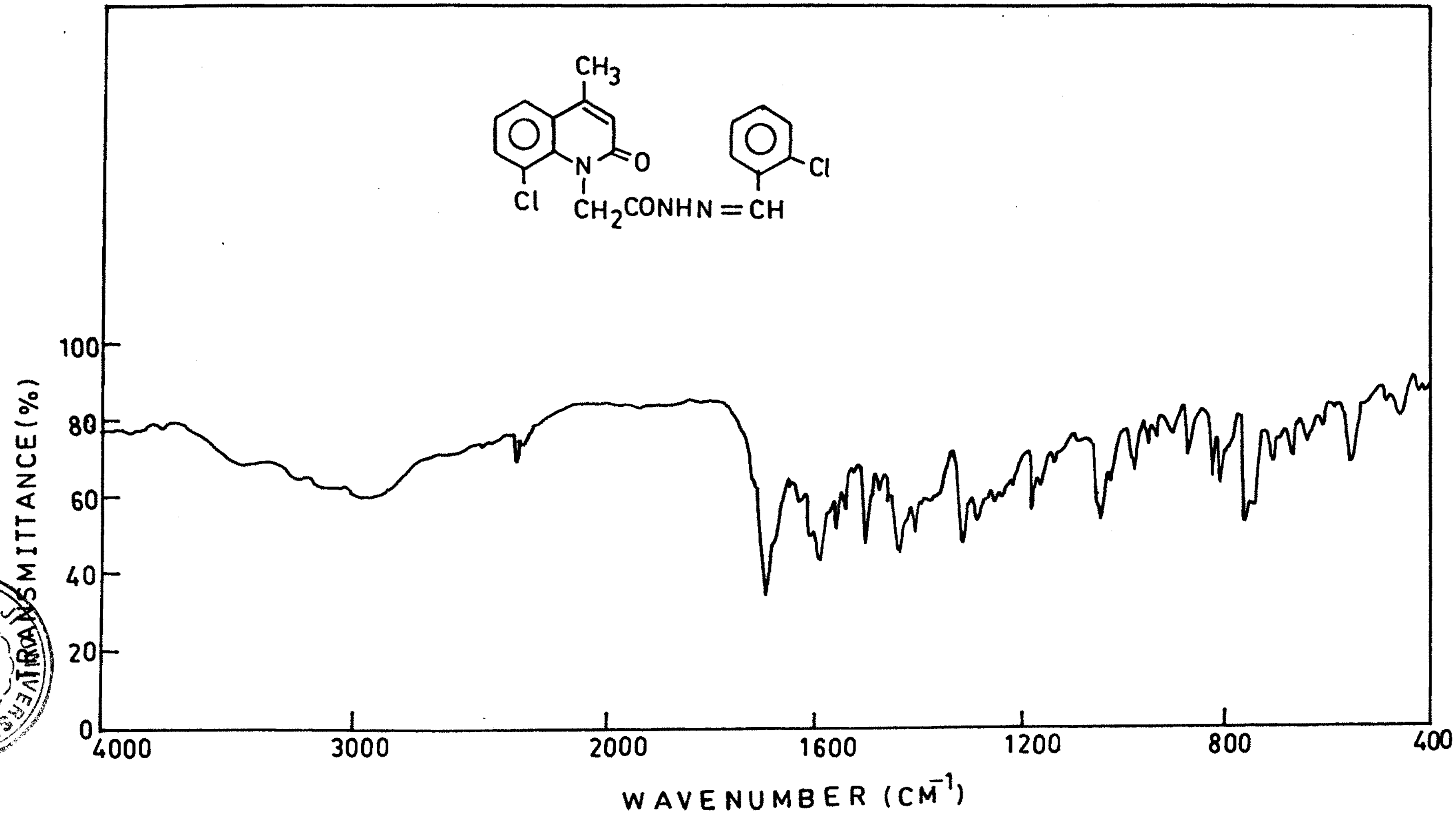
Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
5b	203	60.12	$C_{19}H_{15}N_4O_4Cl$	57.20	3.80	14.00
				57.22	3.79	14.05
5c	208	59.58	$C_{19}H_{15}N_3O_2Cl_2$	58.90	3.80	10.80
				58.77	3.87	10.82
5d	217	63.29	$C_{19}H_{14}N_3O_2Cl_3$	54.10	3.30	9.90
				53.98	3.33	9.94

All above compounds gave satisfactorily IR and PMR spectral analysis.

N^1-(3,4-DICHLOROBENZYLIDENEACETYLHYDRAZIDO)-8-CHLORO-4-METHYLQUINOLIN-2(1H)-ONE.



N¹-(2-CHLOROBENZYLIDENE ACETYLHYDRAZIDO)-8-CHLORO-4-METHYLQUINOLIN-2 (1H)-ONE .



SYNTHESIS OF N^1-3-(8-CHLORO-4-METHYL-2-OXOQUINOLINO-1-ACETAMIDYL-2-(PHENYL)-1,3-THIAZOLIDIN-4-ONE(6a)

To a solution of compound 5a, (0.354 gm,0.001 mol) in DMF (15 ml.) in a round bottom flask, a pinch of anhydrous zinc chloride and mercapto acetic acid (1gm.0.001 mol) were added. The same reaction mixture was further refluxed on steam bath for 8 hr. then cooled and poured into ice-cold water. The separated solid was filtered and recrystallised from DMF to furnish 6a, yield .43 gm. (59.72%), M.P. above 300^{o}C.

Analysis : Found : C, 59.00; H, 4.20; N, 9.80

Calculated for $C_{21}H_{18}N_3O_3SCl$: C, 58.94; H, 4.24; N, 9.81%.

IR (KBr) : ν, 3300-3250 (NH), 1700-1690 (five membered cyclic amido >C=O), 1670 (acyclic amido >C=O), 1640 (six membered cyclic amido >C=O), 760 (C-Cl) cm^{-1}

PMR ($CDCl_3$) : δ, 2.45 (3H,s, =/^{CH}s), 3.2 (1H,s, -CH), 3.5 (1H,s, -SCH_2), 4.25 (2H,s,- NCH_2), 6.25 (1H,s, = CH), 7-7.2 (8H, m, aromatic protons) ppm.

The physical constant (M.P.) percentage yield, elemental analysis (found and calculated) of the compounds 6b, 6c, 6d have been reported in table-2.

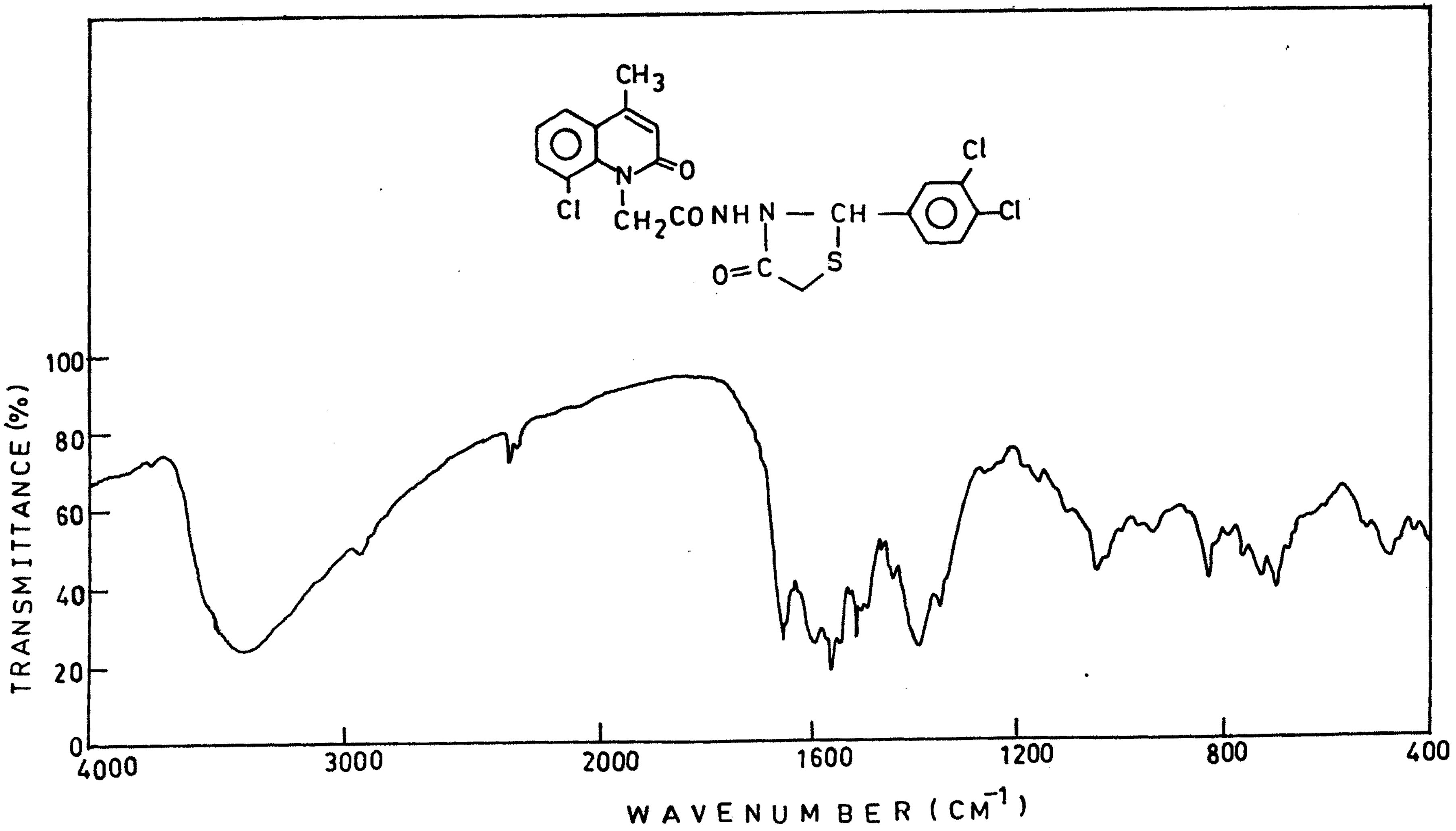
TABLE-2

PHYSICAL AND ANALYTICAL DATA OF THE THIAZOLIDINONES (6)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
6b	above 300	59.15	$C_{21}H_{17}N_4O_5SCl$	52.30 53.33	3.50 3.62	11.80 11.84
6c	above 300	63.38	$C_{21}H_{17}N_3O_3SCl_2$	54.60 54.55	3.60 3.70	9.10 9.08
6d	above 300	58.57	$C_{21}H_{16}N_3O_3SCl_3$	50.80 50.76	3.20 3.23	8.40 8.45

All above compounds gave satisfactory IR and PMR spectral analysis.

N^1-3 –(8–CHLORO–4–METHYL–2–OXOQUINOLINO–1–ACETAMIDYL)–2–(3,4–DICHLOROPHENYL)–1,3–THIAZOLIDIN–4(1H)–ONE.



PART-III Consists of synthesis of some new thiazolidinone derivatives of N^1-Hydrazido-4,6-dimethylquinolin-2(1H)-one.

PREPARATION OF ACETOACETANILIDE (1)

In a round bottom flask carrying a reflux condenser, a mixture of p-toluidine (21.4 ml, 0.1 mol.) and acetoacetic ester (26 ml, 0.1 mol.) in benzene (50 ml.) was heated for 3-4 hours on heating mentle cooled and neutrilised with Na_2CO_3. heavy liquid separated out was extracted in chloroform and solvent was removed. The heavy liquid obtained was distilled under reduced pressure to give acetoacetanilide 33 gm. (74.66%) B.P. 141°C, at 15 mm.

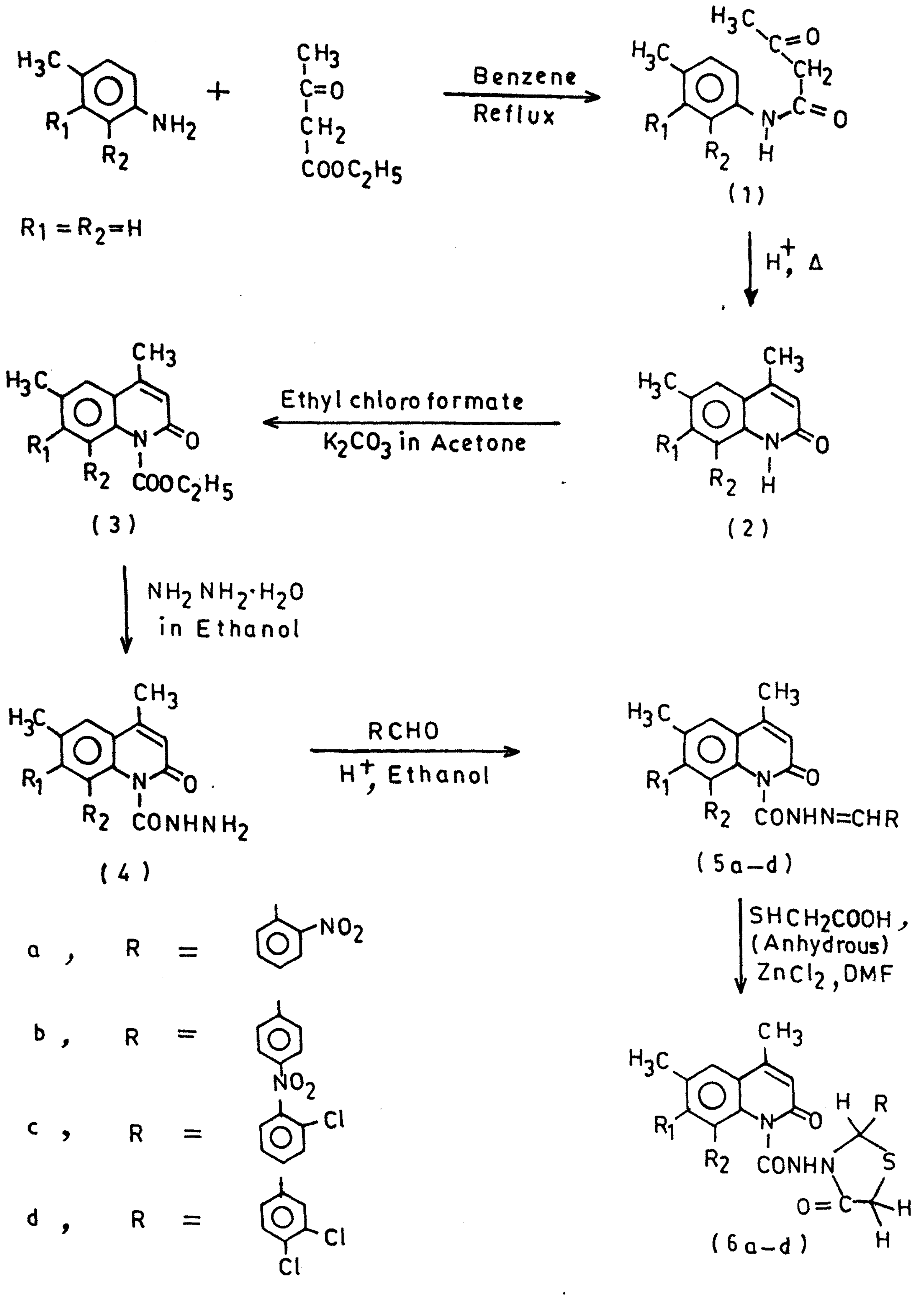
IR (KBr) : ν, 3350-3200 (NH), 1660-1670 (amido >C=O),
1600 (>C=C<) cm^{-1}.

PMR ($CDCl_3$) δ, 1.98 (3H,s, - $COCH_3$), 3.3 (2H,s, - C - CH_2-C-),
5.85 (1H,s, exchangable with D_2O NH),
6.5-8 (4H,m, aromatic protons)ppm.

SYNTHESIS OF 4,6-DIMETHYLQUINOLIN-2 (1H)-ONE (2)

In a round bottom flask a mixture of acetoacetanilide 1(17.2 gm, 0.1 mol) and conc. H_2SO_4 (75 ml.) was heated on water bath at 70-80°C for 0.5 hr. initially and for 1.0 hour at 100°C cooled and poured in 500 ml. ice-cold water with stirring. The separated

SCHEME-III


$R_1 = R_2 = H$
Benzene
Reflux
(1)
H^+, Δ
Ethyl chloro formate
K_2CO_3 in Acetone
(2)
(3)
$NH_2NH_2 \cdot H_2O$
in Ethanol
(4)
RCHO
H^+, Ethanol
(5a–d)
$SHCH_2COOH$,
(Anhydrous)
$ZnCl_2$, DMF
(6a–d)
a , R =
b , R =
c , R =
d , R =

product was filtered, dried and recrystallised from ethanol to give (2), 13 gm. (75.58%) M.P. 251^{0}C.

Analysis : Found : C, 76.30; H, 6.30; N, 8.10,

Claculated for $C_{11}H_{10}NO$

Requires : C, 76.27; H, 6.39; N, 8.08%.

IR (KBr) : ν, 3300-3200 (NH), 1660 (cyclic amido >C=O), 1600 (>C=C<) cm^{-1}.

PMR ($CDCl_3$) δ, 3.35 (3H,s, Ar-CH_3), 2.5 (3H,s, $=/^{CH_3}$), 5.85(1H,s, exchangable with D_2O,NH), 6.5 (1H,s, = CH), 7.1 to 7.7 (3H,m, aromatic protons) ppm.

SYNTHESIS OF N^1-CARBETHOXY-4,6-DIMETHYLQUINOLIN-2(1H)-ONE(3)

In a round bottom flask carrying a reflux condenser and a guard tube, a mixture of 4,6-Dimethylquinolin-2(1H) one (10 gm, 0.04 mol) and ethyl chloroformate (4.1 gm, 0.04 mol) in dry acetone containing anhydrous potassium carbonate (5 gm.) was refluxed for 24 hrs. cooled and the solvent was removed under reduced pressure. The resulting white solid was washed with water filtered and recrystalised from ethanol to give (3). 8.5 gm, (60.12%), M.P. 263^{0}C.

Analysis : Found : C, 68.50; H, 6.20; N, 5.70

Calculated for $C_{14}H_{15}NO_3$. C, 68.55; H, 6.16; N, 5.71%

IR (KBr) : ν, 1760-1740 (ester >C=O), 1640 (six membered cyclic amido >C=O), 1600 (>C=C<) cm^{-1}.

Fig.-9

N^1– CARBETHOXY – 4,6 – DIMETHYLQUINOLIN-2 (1H)-ONE .

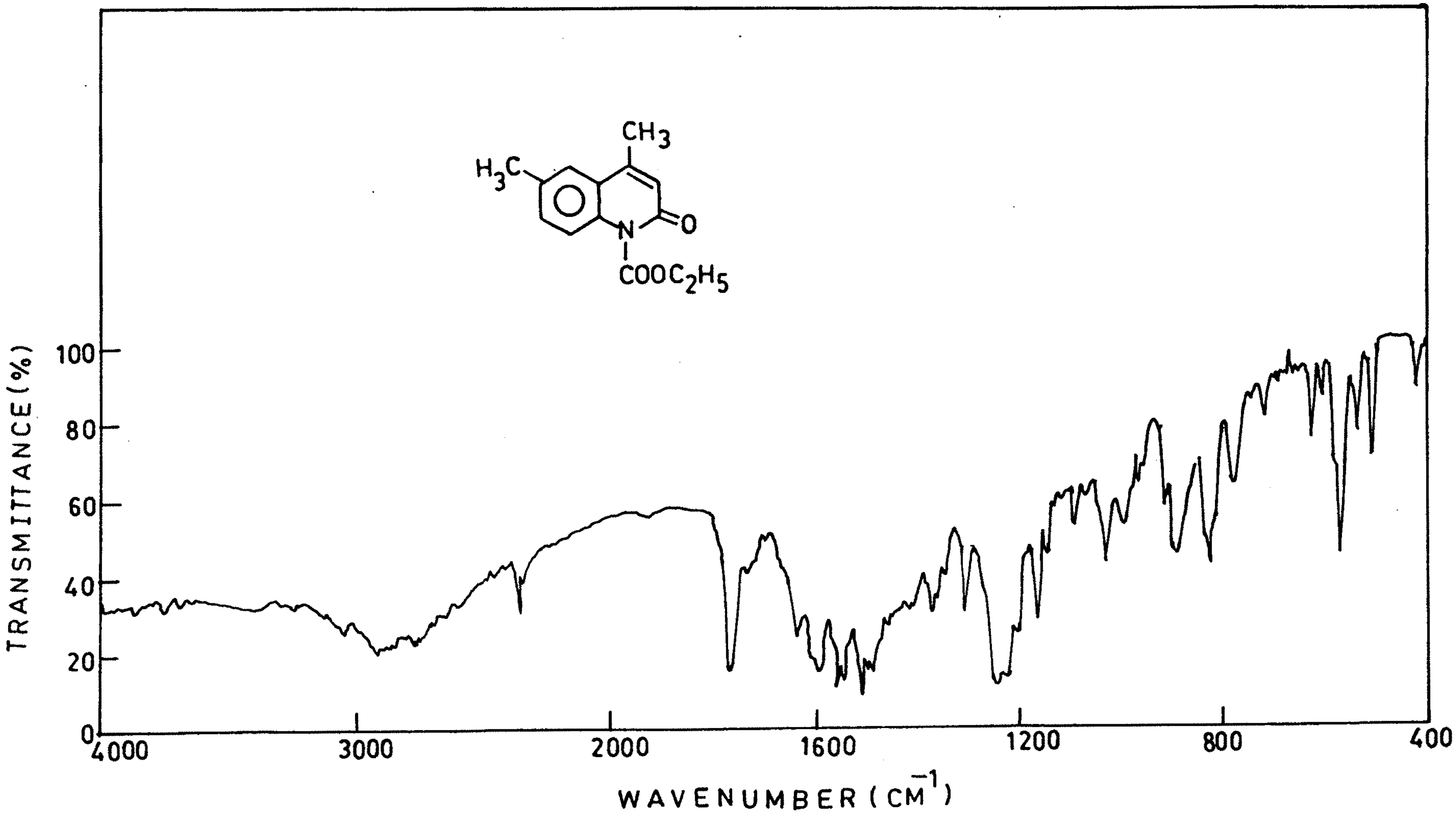


Fig. 9

PMR ($CDCl_3$) δ, 1.3 (3H,t, J=8.5 H_3, CH_3 ester), 2.35 (3H,s, Ar-CH_3), 2.45 (3H,s, $=/^{CH_3}$), 4.15 (2H,s, - OCH_2), 6.4 (1H,s, = CH-), 7.15-7.5 (3H,m, aromatic protons)ppm.

SYNTHESIS OF N^1-HYDRAZIDO-4,6-DIMETHYLQUINOLIN-2(1H)-ONE (4)

To a solution of compound 3 in a round bottom flask (7 gm, 0.03 mole) in ethanol (25 ml.) hydrazine hydrate (1.5 gm, 0.03 mol) was added and the same reaction mixture was refluxed on water bath using reflux condenser for 2 hr. cooled. The resulting solid was filtered and recrystallised from ethanol to furnish (4) 4.7 gm. (71.21%) M.P. 268°C.

Analysis : Found : C, 62.30; H, 5.60; N, 18.20

Calculated for $C_{12}H_{13}N_3O_2$, C, 62.33; H, 5.66; N, 18.18 %

IR (KBr) : ν, 3050, 3140, 3250 (NH), 1685 (acyclic amido >C=O), 1640 (six membered cyclic amido >C=O), 1600 (>C=C<), 1595 (>C=N) cm^{-1}.

Fig.-10

PMR ($CDCl_3$) δ, 2.3 (3H,s $=/^{CH_3}$), 2.55-2.8 (3H,s,-NH_2), 6.1 (1H,s, = CH), 7-7.4 (3H,m, aromatic protons), 8.7 (1H, broad s, -CONH) ppm.

N^1- HYDRAZIDO - 4,6 - DIMETHYLQUINOLIN - 2(1H) - ONE .

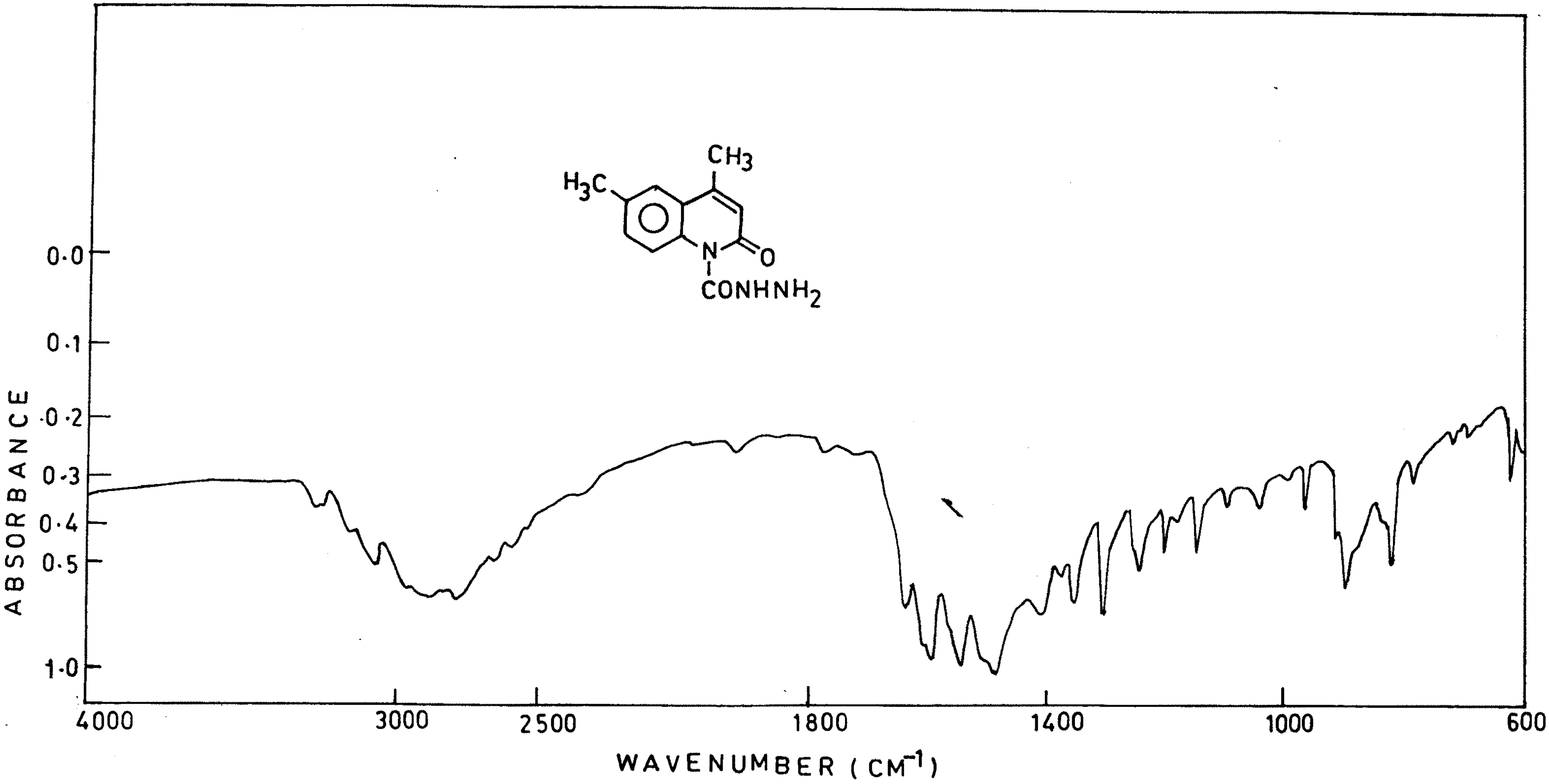


Fig. 10

SYNTHESIS OF N^1-(2-NITROBENZYLIDENEHYDRAZIDO)-4,6-DIMETHYL QUINOLIN-2(1H)-ONE (5a)

A solution of compound 4 (0.23 gm, 0.001 mol) in ethanol (20 ml.) containing few drops of glacial acetic acid was taken in a round bottom flask. To this solution o-nitrobenzaldehyde (.151 gm., 0.001 mol) was added and the reaction mixture was refluxed on steam bath for 3 hr. The solvent was distilled off under vacuum and the semisolid separated was treated with water. The solid obtained was filtered and further crystallised from ethanol to yield 5a, yield 0.9 gm. (57.32%) M.P. 217°C.

ANALYSIS : Found : C, 62.60; H, 4.40; N, 11.40

Calculated for $C_{19}H_{16}N_4O_4$; C, 62.63; H, 4.42; N, 15.37%

<u>IR (KBr)</u> : ν, 3350-3200 (NH), 1670 (acyclic amido >C=O), 1660 (cyclic amido >C=O), 1600 (>C=C<) cm^{-1}.

<u>PMR ($CDCl_3$)</u> : δ, 2.3 (3H,s, Ar-CH_3), 6.1 (1H,s, = CH), 7-7.4 (3H,m, aromatic protons), 8.2(1H,s,-CONH)ppm

The physical constant (M.P.) percentage yield, elemental analysis (found and calculated) of the compounds (5b,5c,5d) have been reported in the table-1.

N^1-(4-NITROBENZYLIDENEHYDRAZIDO)-4,6-DIMETHYLQUINOLIN-2(1H)-ONE .

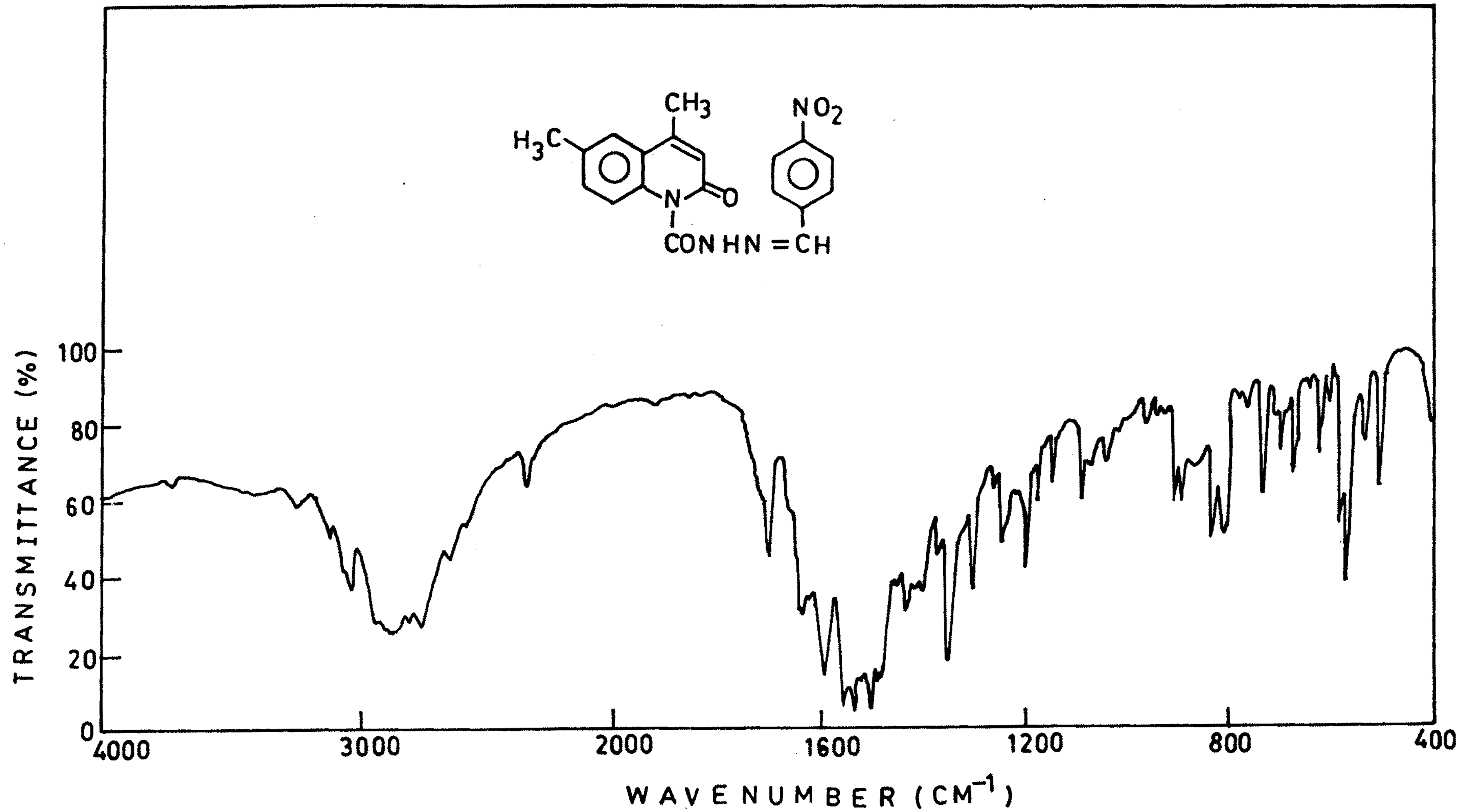


TABLE-1 : PHYSICAL AND ANALYTICAL DATA OF THE SCHIFF'S BASES (5)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
5b	223	63.05	$C_{19}H_{16}N_4O_4$	62.60 62.63	4.40 4.42	11.40 15.37
5c	209	63.81	$C_{19}H_{16}N_3O_2Cl$	64.50 64.49	4.50 4.56	11.80 11.87
5d	207	65.48	$C_{19}H_{15}N_3O_2Cl_2$	58.80 58.77	3.90 3.89	10.80 10.82

All the above compounds gave satisfactory IR and PMR spectral analysis.

SYNTHESIS OF 3-(4,6-DIMETHYL-2-OXOQUINOLINO)-1-AMIDYL-2-(2-NITROPHENYL)-1,3-THIAZOLIDIN-4-ONE (6a)

To the solution of compound 5a (0.438 gm, 0.001 mol.) in DMF (15 ml.) in a round bottom flask, a pinch of anhydrous zinc chloride and mercaptoacetic acid (1 gm,0.001 mol.) were added. The same reaction mixture was further refluxed on steam bath for 8 hr., then cooled and poured in ice cold water. The separated solid was filtered and recrystallised from DMF to furnish 6a, yield 0.4 gm. (55.55%), above 300°C.

ANALYSIS : Found : C, 57.50; H, 4.10; N, 12.70

Calculated for $C_{21}H_{18}N_4O_5S$ C, 57.53; H, 4.13; N, 12.78 %

IR (KBr) : ν, 3250-3350 (NH), 1700 (five membered cyclic amido >C=O), 1670 (acyclic amido >C=O), 1640-1645 (six membered cyclic amido >C=O), 1600 (>C=C<) cm^{-1}.

PMR ($CDCl_3$) δ, 2.45 (3H,s, =/^{CH}3), 3.2 (1H,s, -CH), 3.5 (2H,s,- SCH_2), 6.9(1H,s, = CH), 7-8 (7H,m, aromatic protons), 8.25 (1H, broad s, - CONH) ppm.

Physical constant (M.P.), percentage yield, elemental analysis (found and calculated) of the compounds 6b,6c,6d have been reported in table-2.

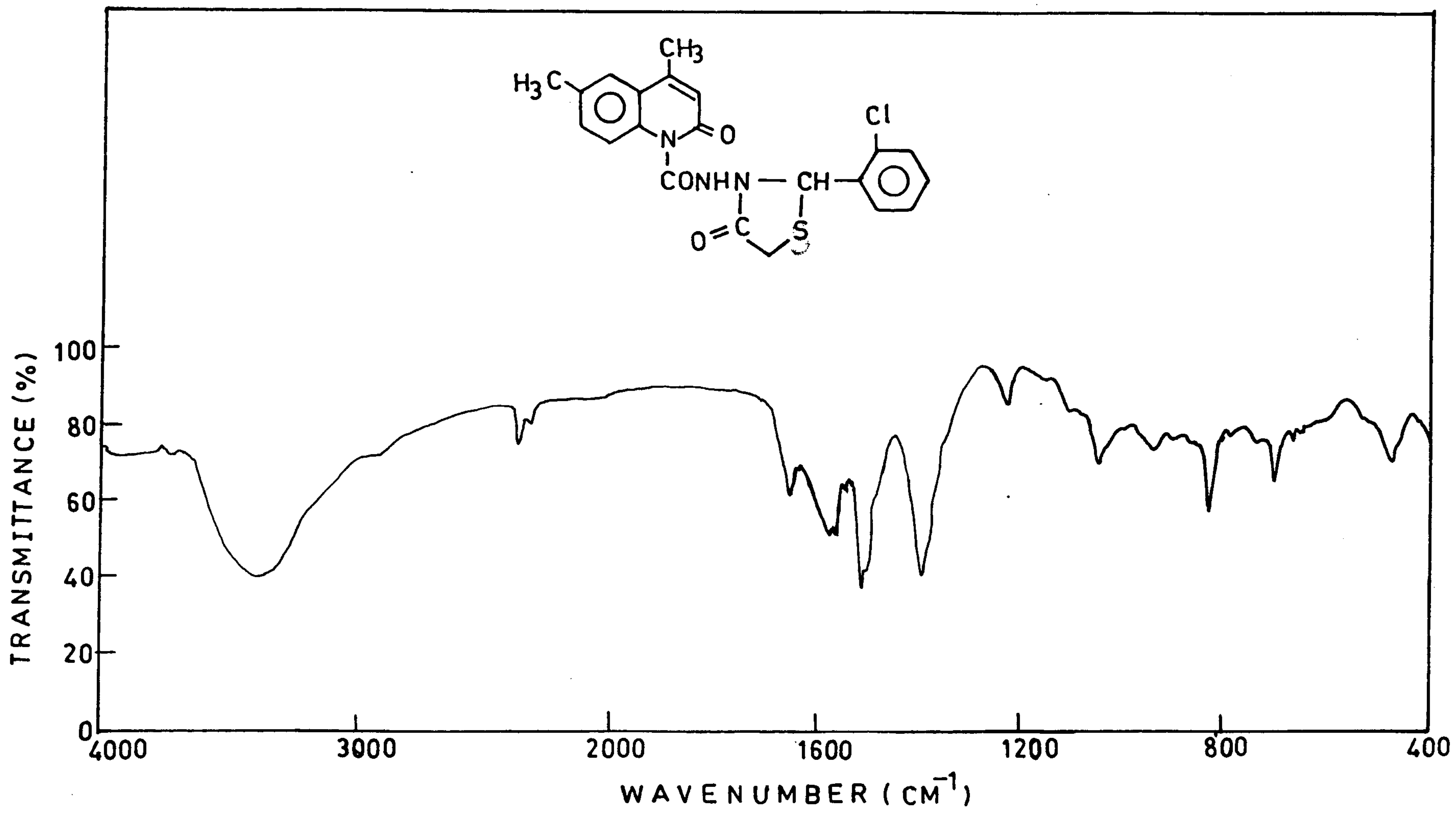
TABEL-2

PHYSICAL AND ANALYTICAL DATA OF THE THIOZOLIDINONES (6)

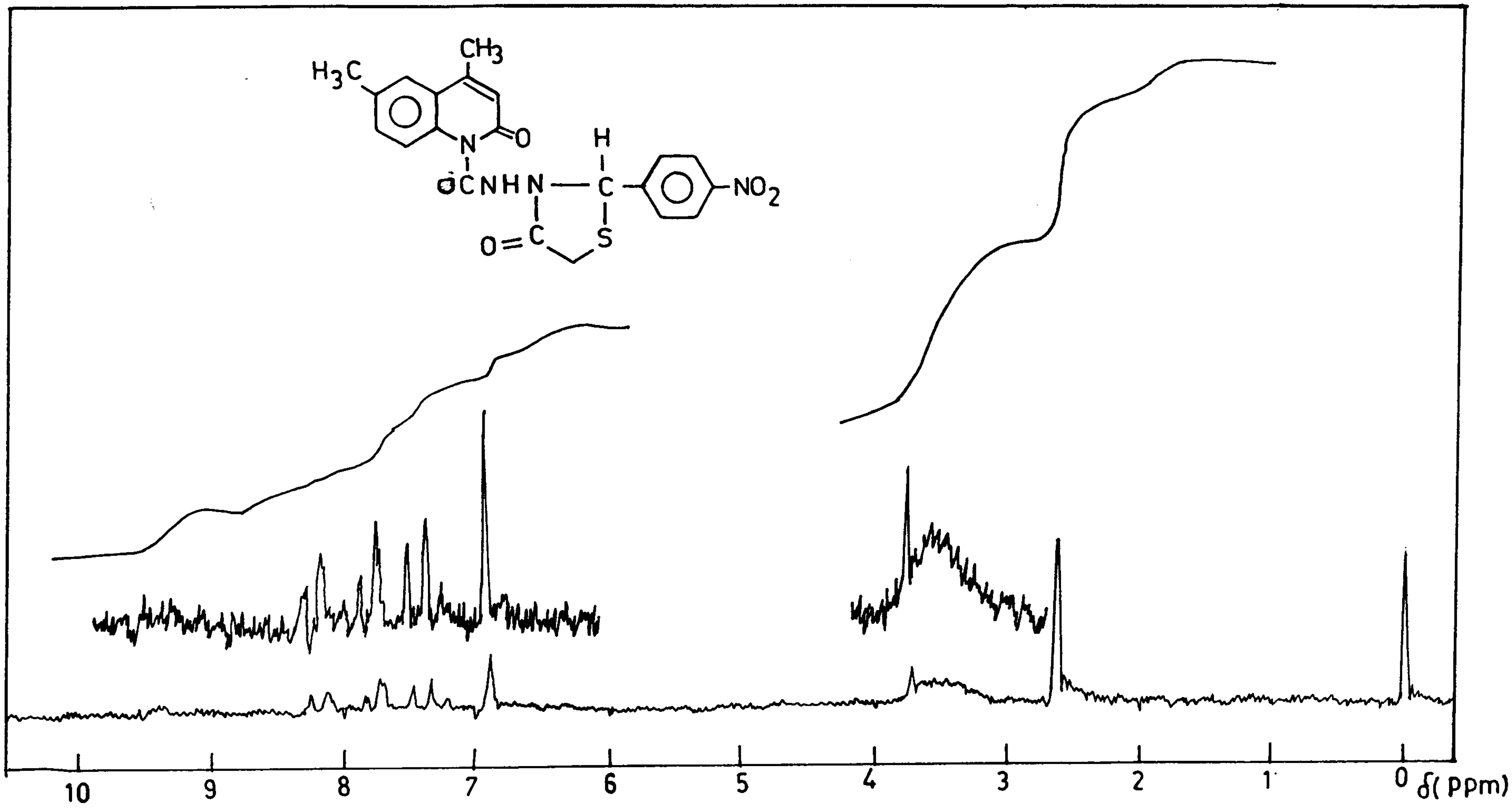
Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated		
				C	H	N
6b	above 300	65.27	$C_{21}H_{18}N_4O_5S$	57.50	4.10	12.70
				57.53	4.13	12.78
6c	above 300	57.53	$C_{21}H_{18}N_3O_3SCl$	59.00	4.20	9.83
				58.94	4.24	9.81
6d	above 300	61.97	$C_{21}H_{17}N_3O_3SCl_2$	54.60	3.68	9.11
				54.55	3.70	9.10

All the above compounds gave satisfactory IR and PMR spectral analysis.

3-(4,6-DIMETHYL-2-OXOQUINOLINO-1-AMIDYL)-2-(2-CHLOROPHENYL)-1,3-THIAZOLIDIN-4(1H)-ONE.



3-(4,6-DIMETHYL-2-OXOQUINOLINO-1-AMIDYL)-2(4-NITROPHENYL)-1,3-THIAZOLIDIN-4(1H)-ONE.



PART-IV Consists of synthesis of some new thiazolidinone derivatives of N^1-Acetylhydrazido-6-chloro-2-methyl quinolin-4 (1H) - one

PREPARATION OF ACETOACETANILIDE (1)

In a round bottom flask carrying a reflux condenser a mixture of p-chloroaniline (25.4 ml, 0.1 mol) and acetoacetic ester (26 ml, 0.1 mol) in benzene (50 ml.) was kept for 36 hours cooled and neutralised with Na_2CO_3. Heavy liquid separated out was extracted in chloroform and solvent was removed. The heavy liquid obtained was distilled under reduced pressure to give acetoacetanilide 35 gm. B.P. 136 °C, at 15 mm.

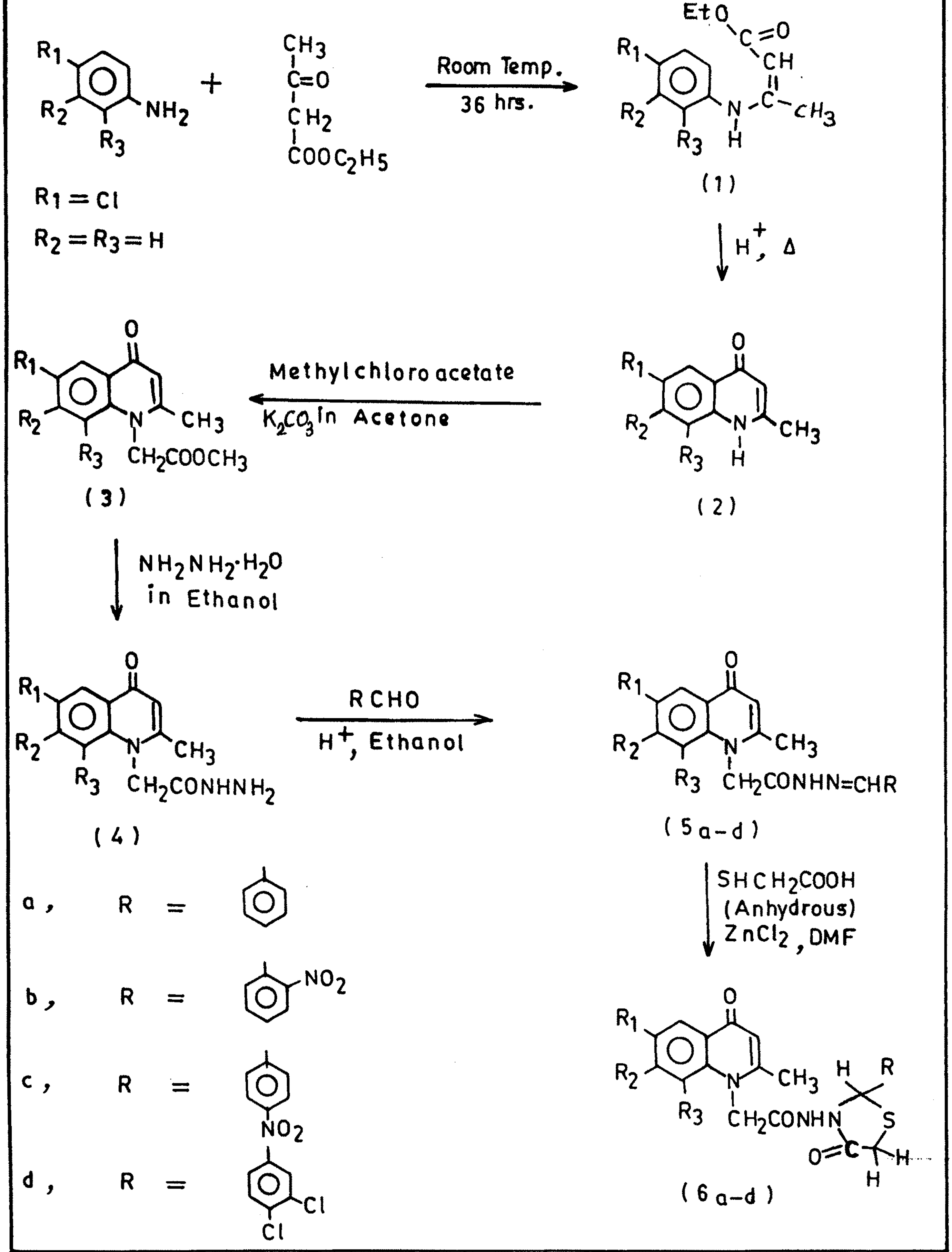
IR (KBr) : ν, 3350-3200 (NH), 1660-1670 (amido >C=O), 1600 (>C=C<), 760 (>C-Cl) cm^{-1}.

PMR ($CDCl_3$): δ, 1.98 (3H,s, - $COCH_3$), 3.3 (2H,s, $-\overset{O}{C}-CH_2-\overset{O}{C}-$), 5.85 (1H,s, exchangable with D_2O, NH), 6.5 - 8 (4H,m, aromatic protons) ppm.

SYNTHESIS OF 6-CHLORO-2-METHYL QUINOLIN-4(1H)-One (2)

In a round bottom flask a mixture of acetoacetanilide 1 (07.7 gm, 0.1 mol) and conc. H_2SO_4 (75 ml.) was heated on water bath at 70-80 °C for 0.5 hr. initially and for 1.0 hour at 100 °C, cooled and poured in 500 ml. ice cold water with constant stirring. The separated product was filtered, dried and

SCHEME-IV


R1
R2
R3
NH2
+
CH3
C=O
CH2
COOC2H5
R1 = Cl
R2 = R3 = H
Room Temp.
36 hrs.
EtO
C=O
CH
C
CH3
N
H
(1)
H+, Δ
O
CH3
(2)
Methylchloroacetate
K2CO3 in Acetone
CH2COOCH3
(3)
NH2NH2·H2O
in Ethanol
CH2CONHNH2
(4)
RCHO
H+, Ethanol
CH2CONHN=CHR
(5a-d)
SHCH2COOH
(Anhydrous)
ZnCl2, DMF
CH2CONHN
S
H
R
O=C
(6a-d)
a, R =
b, R =
NO2
c, R =
NO2
d, R =
Cl
Cl

recrystallised from ethanol to give (3), 15 gm. (77.72%). M.P. 241 °C.

ANALYSIS : Found : C, 62.10; H, 4.10; N, 7.20.

Calculated for $C_{10}H_8NOCl$ requires : C, 62.02; H, 4.16; N, 7.23.

IR (KBr) : ν, 3250-3350 (NH), 1680-1720 (six membered ketone >C=O), 1600 (>C=C<), 760 (C-Cl) cm^{-1}.

PMR ($CDCl_3$) δ, 2.45 (3H,s, $=/^{CH}{}_3$), 5.85 (exchangable with D_2O NH), 6.6 (1H,s, = CH), 7.4-8.1 (3H,s, aromatic protons) ppm.

SYNTHESIS OF N^1-ACETYLCARBMETHOXY-6-CHLORO-2-METHYLQUINOLIN 4(1H) ONE (3)

In a round bottom flask carrying a reflux condenser and a guard tube, a mixture of 6-chloro-2-methylquinolin-4(1H)-one (11 gm, 0.04 mol.) and methyl chloroacetate 4.1 gm. 0.04 mol) in dry acetone containing anhydrous potassium carbonate (5 gm.) was refluxed for 24 hours, cooled and the solvent was removed under reduced pressure. The resulting white solid was washed with water filtered and recrystallised from ethanol to give (3). 9 gm. (59.60%) M.P. 231 °C.

ANALYSIS : Found : C, 58.80; H, 4.60; N, 5.30.

Calculated for $C_{13}H_{12}NO_3Cl$; C, 58.76; H, 4.55; N, 5.27 %

IR (KBr) : ν, 3250-3350 (NH), 1770 (ester >C=O), 1680-1720 (six membered cyclic ketone), 760 (C-Cl) cm^{-1}.

PMR ($CDCl_3$) δ, 2.45 (3H,s, $=/^{CH}{}_3$), 3.8 (3H,s,- OCH_3),
4.2 (2H,s, NCH_2), 6.6 (1H,s = CH),
7.4 - 8.1 (3H,s, aromatic protons) ppm.

SYNTHESIS OF N'-ACETYLHYDRAZIDO-6-CHLORO-2-METHYLQUINOLIN-4(1H)ONE (4)

To a solution of compound 3 in a round bottom flask (8 gm, 0.03 mol) in ethanol (25 ml.) hydrazine hydrate (1.6 ml, .03 mol) was added and the same reaction mixture was refluxed on water bath using reflux condenser for 2 hr.,cooled. The resulting solid was filtered and recrystallised from ethanol to furnish (4); 6.2 gm. (77.21%), M.P.189°C

ANALYSIS : Found : C, 54.30; H, 4.50; N, 15.80

Calculated for $C_{12}H_{12}N_3O_2Cl$: C, 54.24; H, 4.55; N, 15.82 %

IR (KBr): ν, 3300-3100 (NH), 1664-1645 (broad cyclic and acyclic amido), 1605 (>C=O), 750 (C-Cl) cm^{-1}.

PMR (CDC_3) : δ, 2.45 (3H,s, $=/^{CH}{}_3$), 4.45 (2H,s,-NH_2),
4.8 (2H,s,-NCH_2), 6.6 (1H,s, = CH), 7.4-8.1
(3H,s, aromatic protons), 8.2(1H,s,-CONH)ppm.

SYNTHESIS OF N^1-(BENZYLIDENEACETYL HYDRAZIDO)-6-CHLORO-2-METHYL QUINOLIN-4(1H)- ONE (5a):

A solution of compound 4 (0.265 gm, 0.001 mol) in ethanol (20 ml.) containing few drops of glacial acetic acid was taken in a round bottom flask. To this solution benzaldehyde (0.106 gm, 0.001 mol) was added and the reaction mixture was refluxed on steam bath for 3 hr. The solvent was distilled off under vacuum and semisolid separated was treated with water. The solid obtained was filtered and further crystallised from ethanol to yield 5a, yield 0.91 gm. (61.21%) M.P. 103°C.

ANALYSIS : Found : C, 64.50; H, 4.50; N, 11.90

Calculated for $C_{19}H_{16}N_3O_2Cl$: C, 64.58; H, 4.53; N, 11.89 %.

<u>IR (KBr)</u>: ν, 3250–3400 (NH), 1670 (acyclic amido >C=O), 1640 (cyclic ketone >C=O), 1600 (>C=C<), 750 (C–Cl)cm^{-1}

<u>PMR ($CDCl_3$)</u>: δ, 2.45 (3H,s, $=/^{CH_3}$), 4.25 (2H,s, $-NCH_2$), 6.6 (1H,s, = CH–), 7.4–8.1 (8H,s, aromatic protons), 8.2 (1H, broad s, – CONH) ppm.

The physical constant (M.P.), percentage yield elemental analysis (found and calculated) or the compounds (5b, 5c, 5d) have been reported in Table-1.

TABLE-1

PHYSICAL AND ANALYTICAL DATA OF THE SCHIFF'S BASES (5)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
5b	139	61.07	$C_{19}H_{15}N_4O_4Cl$	57.20 57.22	3.40 3.39	14.90 14.89
5c	147	65.10	$C_{19}H_{15}N_4O_4Cl$	57.20 57.22	3.80 3.79	14.80 14.89
5d	131	67.72	$C_{19}H_{14}N_3O_2Cl_3$	53.90	3.30	9.90

All the above compoundsd gave satisfactory IR and PMR spectral analysis.

SYNTHESIS OF 3-(6-CHLORO-2-METHYL-4-OXOQUINOLINO-1-ACETAMIDYL) -2-(PHENYL)-1-3,-THIAZOLIDIN-4(1H) - ONE

To a solution of compound 5a (0.354 gm,0.001 mol.) in DMF (15 ml.) in a round bottom flask, a pinch of anhydrous zincchloride and mercaptoacetic acid (1 gm, 0.001 mol.) were added. The same reaction mixture was further refluxed on steam bath for 8 hr. then cooled and poured in ice cold water. The separated solid was filtered and recrystallised from DMF to furnish 6a, yield 0.49 gm. (67.12%), M.P. >300^{0}C.

ANALYSIS : Found : C, 59.00; H, 4.20; N, 9.80.

Calculated for $C_{21}H_{18}N_3O_3SCl$). C, 58.94; H, 4.24; N, 9.81.

IR (KBr): ν, 3350-3400 (NH), 1680-1720 (six membered ketone >C=O), 1690-1700 (five membered cyclic amido >C=O), 1670 (acyclic amido), 1600 (>C=C<), 760 (C-Cl) cm^{-1}.

PMR ($CDCl_3$): δ, 2.45 (3H,s, =/^{CH}s), 3.2 (1H,s, -CH), 3.5(1H,s, -SCH_2), 4.25 (2H,s,-NCH_2), 6.2 (1H,s,=CH),7-5.2(8H, m, aromatic protons). 8.3(1H,broad s, -CONH) ppm.

Physical constant (M.P.), percentage yield, elemental analysis (found and calculated) of the compounds 6b, 6c, 6d, have been reported in table-2.

3-(6-CHLORO-2-METHYL-4-OXOQUINOLINO-1-ACETAMIDIL)-2-(2-NITRO-PHENYL)-1,3-THIAZOLIDIN-4(1H)-ONE.

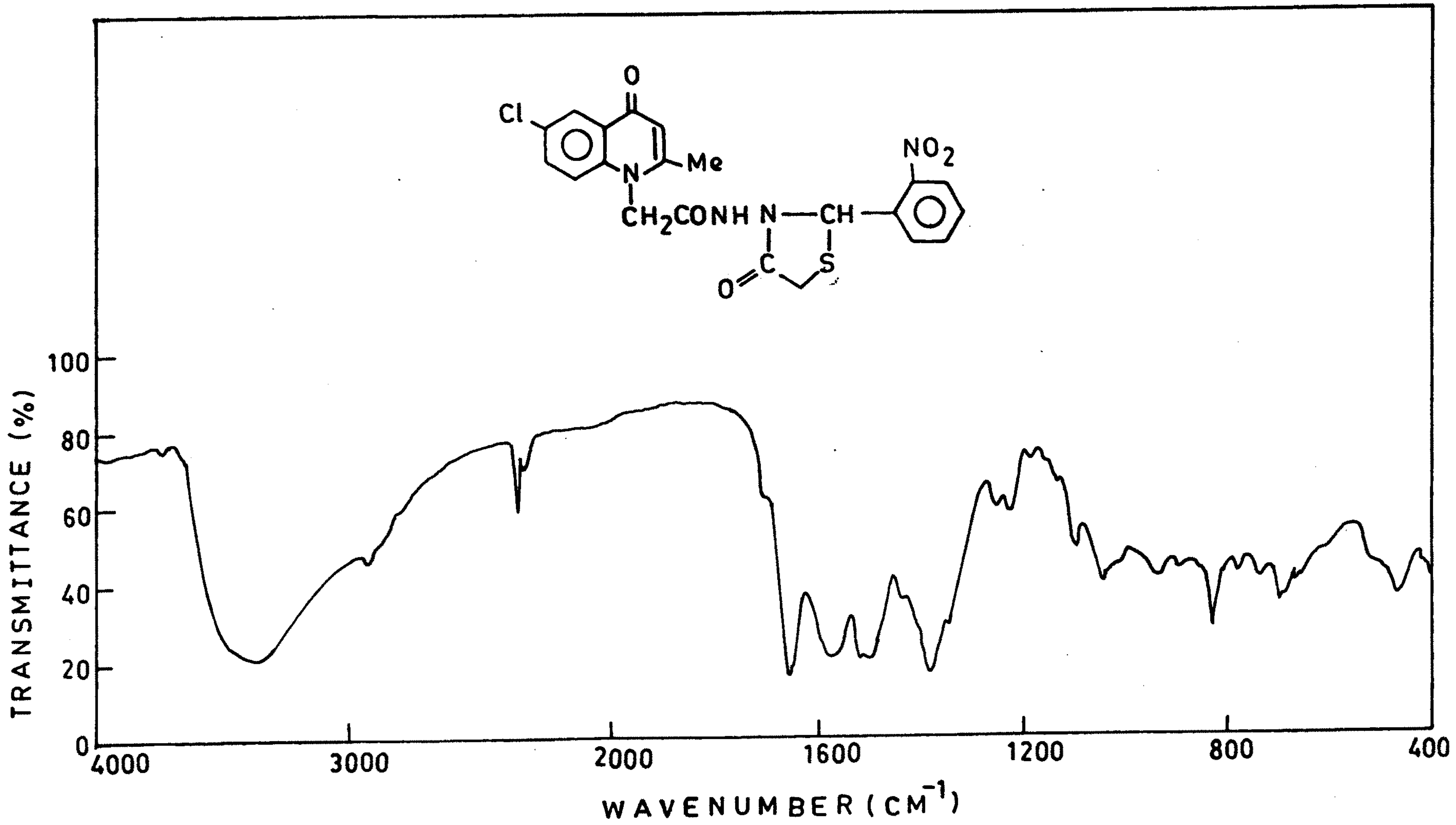


TABLE-2

PHYSICAL AND ANALYTICAL DATA OF THE THIOZOLIDINONES (6)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
6b	above 300	59.08	$C_{21}H_{17}N_4O_5SCl$	53.30 53.33	3.50 3.62	11.80 11.84
6c	above 300	71.83	$C_{21}H_{17}N_4O_5SCl_3$	53.30 53.33	3.50 3.62	11.80 11.84
6d	above 300	66.20	$C_{21}H_{16}N_3O_3SCl$	50.00 50.76	3.20 3.24	8.40 8.45

All the above compounds gave satisfactory IR and PMR spectral analysis.

PART V : Consists of synthesis of some new thiazolidinone derivatives of N^1Hydrazido-8-chloro-2-methyl quinolin-4(1H) - one

PREPARATION OF ACETOACETANILIDE (1)

In a round bottome flask carrying a reflux condenser a mixture of o-chloroaniline (25.4 ml. 0.1 mol.) and acetoacetic ester (26 ml., 00.1 mol) in benzene (50 ml.) was kept for 36 hours cooled and neutrilised with Na_2CO_3. Heavy liquid separated out was extracted in chloroform and solvent was removed. The liquid obtained was distilled under reduced pressure to give acetoacetanilide 35 gm. B.P. 137 ^{o}C, at 15 mm.

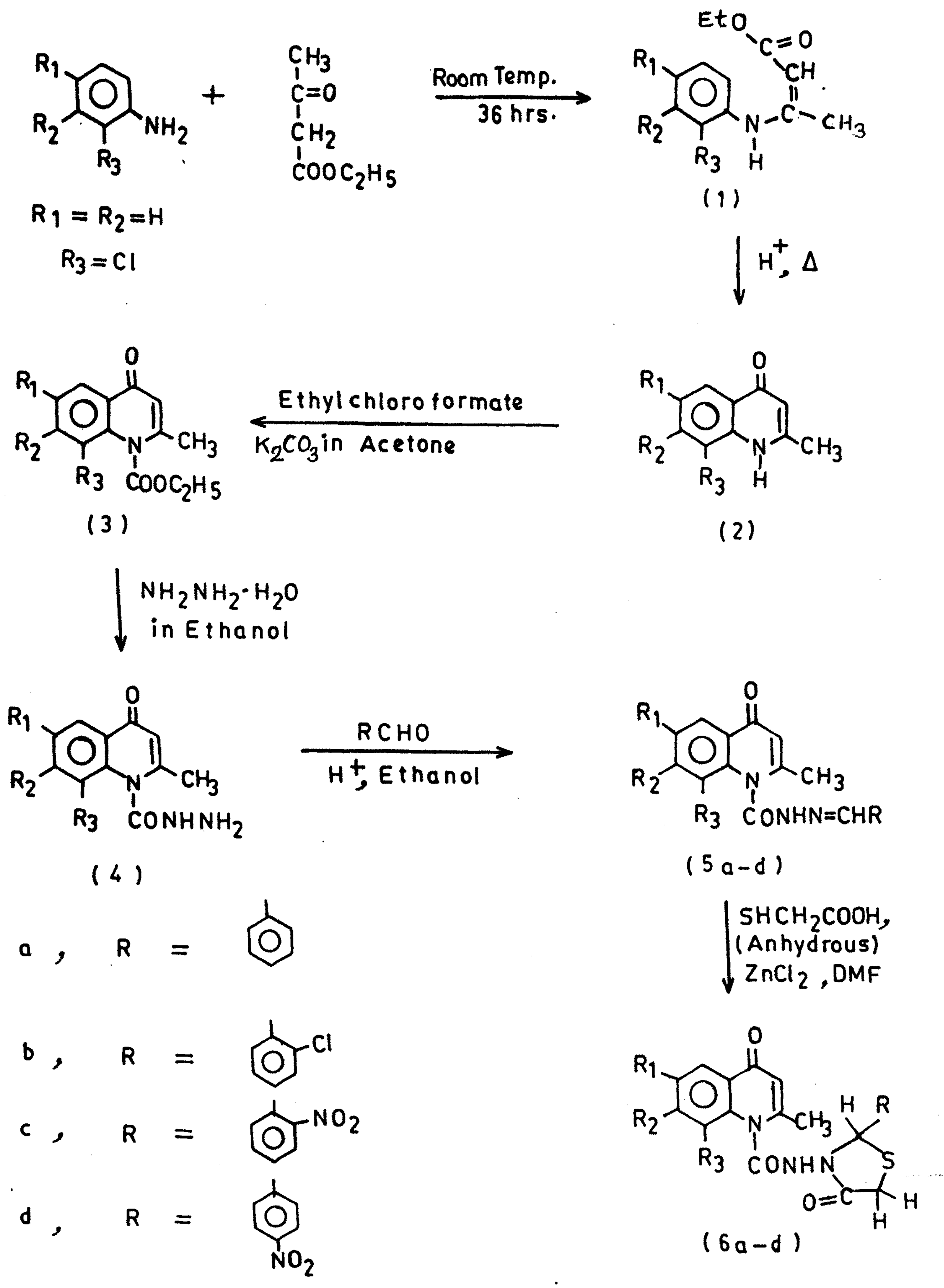
IR (KBr): ν, 3350-3200 (NH), 1660-1670 (>C=O), 1600 (>C=C<), 760 (C-Cl) cm^{-1}.

PMR ($CDCl_3$): δ, 1.98 (3H,s, - $COCH_3$), 3.3 (2H,s, - C - CH_2- C-) 5.85 (1H,s, exchangable with D_2O NH) 6.5-8 (4H,m, aromatic protons) ppm.

SYNTHESIS OF 8-CHLORO-2-METHYLQUINOLIN-4(1H)-ONE (1) :

In a round bottom flask a mixture of acetoacetanilide (17.5 gm, 0.1 mol) and conc. H_2SO_4 (75 ml.) was heated on water bath at 70-80^{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 stirring. The separated products was filtered, dried and recrystallised from ethanol to give (2), 14.8 gm, (76.68%) M.P. 232^{o}C.

SCHEME-V



R_1
R_2
R_3
NH_2
+
CH_3
C=O
CH_2
$COOC_2H_5$
$R_1 = R_2 = H$
$R_3 = Cl$
Room Temp.
36 hrs.
EtO
C=O
CH
C
CH_3
N
H
(1)
H^+, Δ
O
N
H
CH_3
(2)
Ethyl chloro formate
K_2CO_3 in Acetone
$COOC_2H_5$
(3)
$NH_2NH_2 \cdot H_2O$
in Ethanol
$CONHNH_2$
(4)
RCHO
H^+, Ethanol
CONHN=CHR
(5a-d)
$SHCH_2COOH$,
(Anhydrous)
$ZnCl_2$, DMF
H
R
CONHN
S
O=C
H
H
(6a-d)
a, R =
b, R =
Cl
c, R =
NO_2
d, R =
NO_2

ANALYSIS : Found : C, 62.10; H, 4.10; N, 7.20

Calculated for $C_{10}H_8NOCl$

Requires : C, 62.02; H, 4.16; N, 7.23%.

IR (KBr): ν, 3350–3400 (NH), 1680–1700 (six membered cyclic ketone >C=O), 1600 (>C=C<), 760 (C–Cl) cm^{-1}.

PMR ($CDCl_3$): δ, 2.45 (3H,s, $=/^{CH_3}$), 5.85 (1H,s, exchangable with D_2O NH), 6.6 (1H,s, = CH), 7.4–8.1 (3H,s, aromatic protons) ppm.

SYNTHESIS OF N^1-CARBETHOXY-8-CHLORO-2-METHYLQUINOLIN-4(1H) ONE (3)

In a round bottom flask carrying a reflux condenser and a guard tube, a mixture of 8-chloro-2-methylquinolin-4(1H) one (11 gm, .04 mol) and ethylchloroformate (4.1 gm., .04 mol.) in dry acetone containing anhydrous potassium carbonate (5 gm.) was refluxed for 24 hours, cooled and the solvent was removed under reduced pressure. The resulting white solid was washed with water filtered and recrystallised from ethanol to give (3).

ANALYSIS : Found : C, 58.80; H, 4.50; N, 5.30

Calculated for $C_{13}H_{12}NO_3Cl$: C, 58.76; H, 4.55; N, 5.27%.

IR (KBr): : ν, 1670 (ester >C=O), 1680–1720 (six membered ketone >C=O), 1670 (acyclic amido >C=O), 1600 (>C=C<), 760 (C–Cl) cm^{-1}.

PMR ($CDCl_3$): : δ, 2.45 (3H,s, $=/^{CH_3}$), 6.6 (1H,s, = CH–), 7.4–8.1 (3H,s, aromatic protons) ppm.

SYNTHESIS N^1-HYDRAZIDO-8-CHLORO-2-METHYL QUINOLIN-4(1H)-ONE

To a solution of compound 3 in a round bottom flask (8 gm, 0.03 mol.) in ethanol (25 ml), hydrazine hydrate (1.6 gm., 0.03 mol.) was added and the same reaction mixture was refluxed on water bath using reflux condenser for 2 hr cooled. The resulting solid was filtered and recrystallised from ethanol to furnish (4), 5 gm (66.05%) M.P. 198°C.

ANALYSIS: Found : C, 52.50; H, 3.90 ; N, 16.70

Calculated for ($C_{11}H_{10}N_3O_2Cl$) C, 52.49; H, 4.00; N, 16.69%

IR (KBr): ν, 3250-3400 (NH), 1680-1720 (six membered ketone >C=O), 1670 (acyclic amido >C=O), 1600 (>C=C<), 760 (>C=Cl) cm^{-1}.

PMR ($CDCl_3$): δ, 2.45 (3H,s, =/^{CH}3), 2.75-2.8 (3H,s, - NH_2), 6.6 (1H,s, = CH), 7.4-8.1 (3H,s, aromatic protons) 8.2 (1H,s, - CONH) ppm.

SYNTHESIS OF N^1-(BENZILIDENE HYDRAZIDO)-8-CHLORO-2-METHYL-QUINOLINE-4(1H)-ONE (5a)

A solution of compound 4 (0.251 gm, 0.005 mol) in ethanol (20 ml.) containing few drops of glacial acetic acid was taken in a round bottom flask. To this solution benzaldehyde (0.106 gm, 0.001 mol.) was added and the reaction mixture was refluxed on steam bath for 3 hr. The solvent was distilled off under vacuum and semisolid separated was treated with water. The solid obtained was filtered and further crystallised from ethanol to yield 5a, yield 0.9 gm. (66.66%). M.P. 198 ^{o}C.

ANALYSIS : Found : C, 63.60; H, 4.20; N, 12.30

Calculated for $C_{18}H_{15}N_3O_2Cl$: C, 63.62; H, 4.15; N, 12.36 %

IR (KBr): ν, 3250-3400 (NH), 1650-1700 (six membered ketone >C=O), 1670 (acyclic amido >C=O), 1605 (-C=N), 1600 (>C=C<), 760 (>C-Cl) cm^{-1}.

PMR ($CDCl_3$): δ, 2.45 (3H,s, =/^{CH}3), 6.6 (1H,s, = CH), 7.4-8.1 (8H,m, aromatic protons), 8.2 (1H,s, - CONH) ppm.

The physical constant (M.P.) percentage yield elemental analysis (found and calculated) of the compounds (5b, 5c, 5d) have been reported in table-1.

TABLE - 1

PHYSICAL AND ANALYTICAL DATA OF THE SCHIFF'S BASES (5)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
5b	219	59.21	$C_{18}H_{13}N_4O_4Cl$	56.20 56.18	3.30 3.40	14.50 14.56
5c	227	57.89	$C_{18}H_{13}N_4O_4Cl$	56.20 56.18	3.30 3.40	14.50 14.56
5d	239	62.16	$C_{18}H_{13}N_3O_2Cl_2$	57.80 57.77	3.40 3.48	11.20 11.22

All the above compounds gave satisfactory IR and PMR spectral analysis.

SYNTHESIS OF 3-(8-CHLORO-2-METHYL-4-OXOQUINOLINO-1-AMIDYL) 2-(PHENYL)-1,3-THIAZOLIDIN-4(1H)-ONE (6)

To a solution of compound 5a (0.339 gm,0.001 mol.) in DMF (15 ml.) in a round bottom flask, a pinch of anhydrous zinc chloride and mercapto acetic acid (1 gm,0.001 mol.) were added. The same reaction mixture was further refluxed on steam bath for 8 hr. then cooled and poured in ice cold water. The separated solid was filtered and recrystallised from DMF to furnish 6a.

ANALYSIS : Found : C, 58.10; H, 3.80; N, 10.10

Calculated for $C_{20}H_{16}N_3O_3SCl$. C, 58.04; H, 3.89; N, 10.15%

IR (KBr): ν, 3250-3400 (NH), 1680-1720 (six membered ketone >C=O), 1690-1700 (five membered cyclic amido >C=O), 1670 (cyclic amido >C=O), 1600 (>C=C<), 760 (C-Cl)cm^{-1}.

PMR ($CDCl_3$): δ, 2.45 (3H,s, $=/^{CH}{}_{3}$), 3.2 (1H,s, - CH), 3.5 (1H,s,- SCH_2), 6.2(1H,s, = CH), 7-5.2 (8H,m, aromatic protons), 8.3 (1H,broad s, -CONH) ppm.

Physical constant (M.P.) percentage yield, elemental analysis (found and calculated) of the compounds 6b, 6c, 6d, have been reported in table - 2.

TABLE -2

PHYSICAL AND ANALYTICAL DATA OF THE THIOZOLIDINONES (6)

Sr. No.	M.P. °C	Yield %	Molecular formula	Elemental Analysis Found/Calculated C	H	N
6b	above 300	67.79	$C_{20}H_{15}N_4O_5SCl$	52.30 52.34	3.20 3.29	12.20 12.21
6c	above 300	64.10	$C_{20}H_{15}N_4O_5SCl$	52.30 52.34	3.20 3.29	12.20 12.21
6d	above 300	70	$C_{20}H_{15}N_3O_3SCl_2$	53.60 53.69	3.30 3.35	9.30 9.30

All the above compounds gave satisfactory IR and PMR spectral analysis.