EXPERIMENTAL

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1. Preparation of N-aryl 2,3-dioxobutyramide 2-oxime.

(Where aryl amide may be anilide,methyl anilide o-toluidide or o-chloranilide) :

For the preparation of N-aryl 2,3-dioxobutyramide 2-oxime, acetoacetanilide, N-methyl acetoacetanilide (196), o-acetoacetotoluidide and 2'-chloro acetoacetanilide were used as starting materials.

Preparation of 2,3-dioxobutyranilide 2-oxime was carried out by two methods (a) nitrosyl chloride method of Naik et al. (185) with modifications and (b) nitrous acid method of Knorr (184) as adopted by Dave and Talati (186).

1.(a) Nitrosyl chloride method :

(i) Preparation of nitrosyl chloride.

Mankad (197) prepared nitrosyl chloride by the action of nitrosyl sulphuric acid on sodium chloride.

$$HSO_4NO + NaCl = NaHSO_4 + NOCl$$

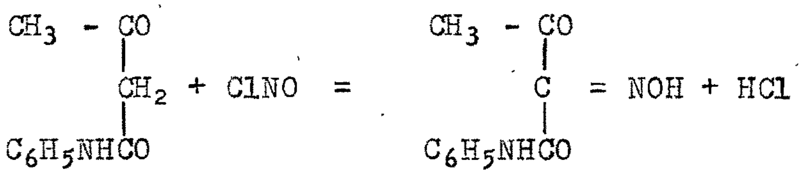
We prepared it by the interaction of sodium nitrite and anhydrous aluminium chloride.

$$3\ NaNO_2 + 2\ AlCl_3 = 3\ NOCl + Al_2O_3 + 3\ NaCl$$

The reaction was carried out as follows : Dry sodium nitrite (4.2 g.) was mixed with anhydrous aluminium chloride (5.4 g.) in a small distillation flask and the mixture was strongly heated. Nitrosyl chloride gas was liberated and was led through calcium chloride tube to the reaction flask.

(ii) Preparation of 2,3-dioxobutyranilide 2-oxime :

Acetoacetanilide (1.8 g.) was dissolved in dry benzene (20 ml.) in a flask and was kept cool by ice during the preparation. Dry nitrosyl chloride gas was passed through the solution, until it was saturated with nitrosyl chloride gas. During the reaction, hydrochloric acid gas evolved ; the solution gradually attained yellow colour and at the point of saturation assumed a deep reddish yellow colour. Acetoacetanilide reacts with nitrosyl chloride as follows :



$$\begin{array}{c} CH_3-CO \\ | \\ CH_2 \\ | \\ C_6H_5NHCO \end{array} + ClNO = \begin{array}{c} CH_3-CO \\ | \\ C \\ | \\ C_6H_5NHCO \end{array} = NOH + HCl$$

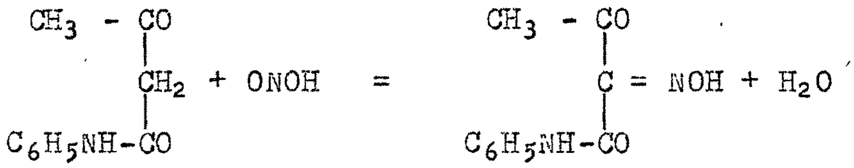
The solution was refluxed on a water bath to remove excess of nitrosyl chloride and hydrochloric acid gas. It was then transferred to an evaporating dish and allowed to crystallise when yellow crystalline mass was obtained. The product was recrystallised from dilute alcohol as yellow needles melting at 99-100°C. Yield 60-65 %. Naik et al. (185) recrystallised the crude mass from light petroleum ether + chloroform and obtained pale yellow needles melting at 100°C.

We tried benzene,chloroform,carbon tetrachloride, ether,etc. as solvents for the preparation of 2,3-dioxobutyranilide 2-oxime and found benzene preferable.

It is easily soluble in chloroform,benzene, carbon tetrachloride,alcohol,acetone,p-dioxane,ether and ethyl acetate and sparingly soluble in water and light petroleum ether.

1. (b) Nitrous acid method :

Acetoacetanilide (10 g.) and sodium nitrite (5 g.) were dissolved in dilute sodium hydroxide solution (60 ml.) and the solution was added drop by drop, to the dilute sulphuric acid solution (600 ml.) which was kept cool by ice and well stirred during the reaction. Acetoacetanilide reacts with nitrous acid as follows :



$$\underset{C_6H_5NH-CO}{\overset{CH_3-CO}{CH_2}} + ONOH = \underset{C_6H_5NH-CO}{\overset{CH_3-CO}{C}} = NOH + H_2O$$

2,3-Dioxo butyranilide 2-oxime was obtained as yellow precipitates. Stirring was continued for half an hour more after the addition of the mixture was over. The precipitates were filtered, washed with water and dried. The product was recrystallised from dilute alcohol as yellow crystals melting at 99-100°C. M.Pt.(lit.) 99-100°C. (184,186) Yield 75-80 %. Its solubility in different solvents is the same as that of the product obtained in 1 (a).

The products obtained in the above two processes are similar in their properties and lowering of the mixed melting point is not observed. Hence the two products are considered to be the same.

In nitrosyl chloride method, tarry products were often obtained which were difficult to work out ; on the other hand, no tarry products were obtained in the nitrous acid method and the yield of the product was better. Hence for the preparation of other 2-oximes of N-aryl 2,3-dioxo-butyramides, nitrous acid method was employed. The products obtained together with their colour, m.pt., analysis (micro), etc. are recorded in Table 1.

2. Preparation of the derivatives of the oxime of 2-cyano glyoxylic acid :

2.(a) Preparation of the oxime of 2-cyano glyoxylanilide :

(i) Preparation of cyanoacetanilide :

Cyanoacetanilide was prepared by the method of Price et al. (198) by heating ethyl cyanoacetate with aniline. It was recrystallised from ethyl acetate ; M.Pt. 198-200°C ; M.Pt.(lit.) 198-200°C.

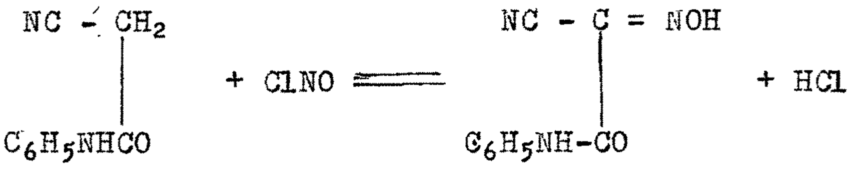
(ii) Preparation of the oxime of 2-cyano glyoxylanilide :

It was prepared by two methods : nitrosyl chloride method and nitrous acid method.

Nitrosyl chloride method :

Nitrosyl chloride gas obtained by heating a mixture of anhydrous aluminium chloride (5 g.) and sodium nitrite (4 g.) was passed through a solution of cyanoacetanilide (0.8 g.) in ethanol (20 ml.) kept below 15°C. The solution turned yellow with the evolution of fumes of hydrochloric acid.

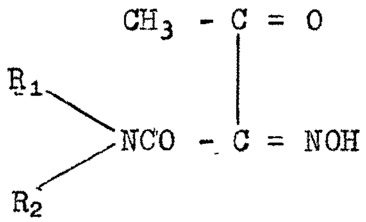
The reaction may be represented as follows :



$$\begin{array}{c} NC - CH_2 \\ | \\ C_6H_5NHCO \end{array} + ClNO = \begin{array}{c} NC - C = NOH \\ | \\ C_6H_5NH-CO \end{array} + HCl$$

TABLE I

N-aryl 2,3-dioxo butyramide 2-oxime



No.	Substance		Formula	Colour	M.Pt.	M.Pt.	% N	% N	References
	R_1=	R_2=			obs.	lit.	found	reqd.	
1.	H -	o-$CH_3C_6H_4$-	$C_{11}H_{12}N_2O_3$	Yellow	130°C	130°C	-	-	185,186
2.	H -	o-ClC_6H_4-	$C_{10}H_9N_2O_3Cl$	Yellow	122°C	122°C	-	-	186
3.	CH_3-	C_6H_5-	$C_{11}H_{12}N_2O_3$	White	205°C	-	12.71	12.72	-

when no more fumes were formed, the solution was removed and kept for crystallisation. The pale yellow crystals were filtered and dried. The product was recrystallised repeatedly from aqueous alcohol to get purer product ; yield 60 % ; M.Pt. 217-19°C.

Analysis :
Found :: N, 20.76 ;
$C_9H_{17}O_2N_3$ requires : N, 22.22.

It is soluble in alcohol, acetone, ethyl acetate and chloroform, partly soluble in water, benzene and ether and sparingly soluble in n-hexane and petroleum ether.

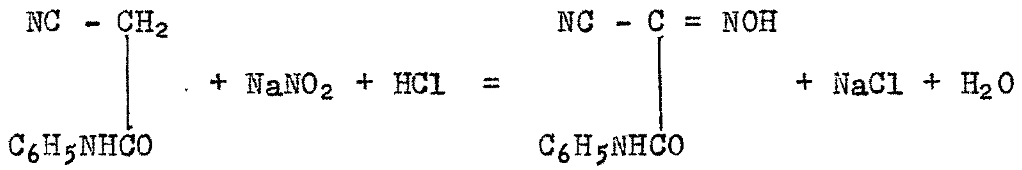
Its reactions with some transition metal ions are :

Fe (II)	brownish violet colouration in slightly alkaline solution ;
Fe (III)	Orange yellow colouration in slightly alkaline solution ;
Co (II)	Orange red colouration in slightly alkaline solution ;
Ni (II)	reddish yellow colouration in slightly alkaline solution ;
Cu (II)	brown colouration in slightly alkaline solution.

<u>Nitrous acid method</u> :

Hydrochloric acid gas was passed through the ice-cold solution of cyanoacetanilide (0.8 g.) and sodium nitrite

(0.4 g.) in alcohol (20 ml.). Yellow solution was obtained . The reaction may be represented as



$$\begin{array}{l} NC - CH_2 \\ \quad\;\, | \\ C_6H_5NHCO \end{array} + NaNO_2 + HCl = \begin{array}{l} NC - C = NOH \\ \quad\;\;\, | \\ C_6H_5NHCO \end{array} + NaCl + H_2O$$

The solution was allowed to crystallise when pale yellow crystals were obtained. They were filtered, washed with water and a little dilute alcohol and dried. The product was repeatedly recrystallised from aqueous alcohol to get pure product ; yield 60 % ; M.Pt. 217-19°C.

Its solubility in different solvents is the same as that of the product obtained by nitrosyl chloride method. The products obtained by the above two processes are similar in their properties and no lowering of the mixed melting point of the two products was observed.

Dimroth (159) prepared it by the action of silver cyanide on the oxime of 2-chloro glyoxyl anilide and Darapsky and Hillers (160) obtained it by the action of aniline on the oxime of 2-cyano glyoxyl azide. They found that it melts at 218-20°C.

2.(b) Preparation of the oxime of N-methyl 2-cyano glyoxyl anilide :

(i) Preparation of N-methyl cyanoacetanilide.

It was prepared by condensing methyl aniline with ethyl cyanoacetate by the method of Price et al. (198). M.Pt. 86-88°C. M.Pt. (lit.) 86-88°C.

(ii) Preparation of the oxime of N-methyl-2-cyano glyoxylanilide :

Nitrosyl chloride gas was passed through a solution of N-methyl cyanoacetanilide (0.8 g.) in alcohol (20 ml.) as described above. Yellowish white product was obtained, and was filtered, washed with water and a little dilute alcohol and dried. It was recrystallised from alcohol as pale yellow crystals ; yield 65 % ; M.Pt. 126-28 °C.

Analysis :

Found : N, 20.13 ;

$C_{10}H_9O_2N_3$ requires : N, 20.68.

It is soluble in acetone, alcohol, ether, and chloroform, partly soluble in benzene and water and sparingly soluble in petroleum ether.

Its reactions with some transition metal ions are :

Fe (II)	deep violet colouration in neutral or slightly alkaline solution ;
Fe (III)	orange yellow colouration in neutral or slightly alkaline solution ;
Co (II)	blood red colouration in slightly alkaline solution ;
Ni (II)	yellowish colouration in slightly alkaline solution ;
Cu (II)	deep green colouration in slightly alkaline solution.

2.(c) Preparation of the oxime of ethyl 2-cyano-glyoxylate :

It was prepared from ethyl cyanoacetate and nitrous acid by the method of Conrad and Schulze (152). To the ice-cold solution of sodium nitrite (2.5 g.) in water (13 ml.) was added ethyl cyanoacetate (3.4 g.), followed by acetic acid (2.5 g.). The mixture was kept in ice-bath for about 8 hours. Yellowish white product (sodium salt) was obtained. It was filtered, dried and treated with hydrochloric acid. Ether extract of the solution gave the oxime of ethyl 2-cyanoglyoxylate. It was recrystallised from hot water; yield 80 % . M.Pt. 133°C ; M.Pt.(lit.) 133°C.

It is soluble in hot water, acetone, alcohol, hot benzene, ether, chloroform, dioxane, n-hexane, etc.

Its reactions with some transition metal ions are :

Fe (II)	reddish violet colour in neutral solution ;
Fe (III)	Orange yellow colouration in slightly alkaline solution ;
Co (II)	reddish yellow colouration in slightly alkaline solution ;
Ni (II)	yellowish colouration in slightly alkaline solution ;
Cu (II)	No colouration.

2.(d) Preparation of the oxime of 2-cyano glyoxylamide :

(i) Preparation of cyanoacetamide :

It was prepared by the action of ammonia on ethyl cyanoacetate as described in organic synthesis (199). M.Pt. 119-20°C ; M.Pt.(lit.) 119-20°C.

(ii) Preparation of the oxime of 2-cyano glyoxylamide:

It was prepared from cyanoacetamide and nitrous acid by the method of Conrad and Schulze (152).

Acetic acid (2.4 g.) was added to the ice-cold solution of cyanoacetamide (1.7 g.) and sodium nitrite (1.7 g.) in water (7 ml.). White precipitates of the sodium salt of the oxime were obtained. On treatment with hydrochloric acid and extracting with ether it gave the oxime of 2-cyano glyoxylamide. It was recrystallised from alcohol as white crystals, melting at 184°C. M.Pt.(lit.) 184°C.

It is soluble in water, alcohol, acetone, n-hexane, benzene and ether and partly soluble in carbon tetrachloride, petroleum ether and dioxane.

Its reactions with some transition metal ions are :

Fe (II)	violet colour in slightly alkaline solution ;
Fe (III)	No colouration ;
Co (II)	red colouration in slightly alkaline solution ;
Ni (II)	reddish,yellow colouration in slightly alkaline solution ;
Cu (II)	No colouration.

2.(e) Preparation of the dioxime of N,N'-ethylene bis (2-cyano glyoxylamide) :

(i) Preparation of N,N'-ethylene bis(cyanoacetamide) :

It was prepared by the method of Guareschi (200) by heating ethylene diamine with ethyl cyanoacetate. It was recrystallised from hot water. M.Pt. 190-92°C. M.Pt. (lit.) 190-92°C.

(ii) Preparation of the dioxime of N,N'-ethylene bis (2-cyano glyoxylamide) :

Nitrosyl chloride gas was passed through the solution of N,N'-ethylene bis(cyanoacetamide) (0.5 g.) in alcohol (20 ml.) kept below 15°C. The solution turned deep yellow with the evolution of hydrochloric acid gas. On crystallisation it gave pale yellow crystals. They were filtered, washed with little dilute alcohol and dried. The product was recrystallised from aqueous alcohol ; yield 60 % ; M.Pt. 236°C.

Analysis :
Found : N, 33.35 ;
$C_8H_8O_4N_6$ requires : N, 33.33.

It is soluble in alcohol, acetone, ethyl acetate, p-dioxane and chloroform and sparingly soluble in water, benzene, n-hexane, ether and petroleum ether.

Its reactions with some transition metal ions are :

Fe (II)	violet precipitates in slightly alkaline solution ;
Fe (III)	No colouration ;
Co (II)	orange red precipitates in slightly alkaline solution ;
Ni (II)	orange yellow precipitates in slightly alkaline solution ;
Cu (II)	reddish brown precipitates in slightly alkaline solution.

2.(f) Preparation of the oxime of 2(hydroxyamidino) glyoxylamide :

It was prepared from the oxime of 2-cyano glyoxylamide by the method of Conrad and Schulze (152). The oxime of 2-cyano glyoxylamide (0.7 g.) in alcohol (10 ml.) was added to the solution of sodium carbonate (0.8 g.) and hydroxylamine hydrochloride (1 g.) in alcohol (10 ml.). The solution turned yellow and was kept on water bath at about 40°C for 4 hours. On crystallisation, pale yellow crystals were obtained. They were filtered, washed with little dil.alcohol and dried. The product was recrystallised from alcohol ; yield 60 % ; M.Pt. 170°C ; M.Pt.(lit.) 170°C.

It is soluble in alcohol, partly soluble in benzene and sparingly soluble in carbon tetrachloride, ethyl acetate, ether and petroleum ether.

Its reaction with some transition metal ions are :

Fe (II)	brownish blue precipitates in slightly alkaline solution ;
Fe (III)	brown precipitates in slightly alkaline solution ;
Co (II)	bluish colouration in slightly alkaline solution ;
Ni (II)	red colouration in hot slightly alkaline solution.

2.(g) Preparation of the oxime of ethyl 2-(hydroxyamidino) glyoxylate :

All attempts to prepare it by the action of hydroxylamine on the oxime of ethyl 2-cyano-glyoxylate failed.

3. Preparation of vic-oxime-ketones :

For comparative studies, 2,3-butane dione oxime, 1,2-propane dione 1-phenyl 2-oxime and 1,2-cyclohexane dione monoxime were also prepared.

3.(a) Preparation of 2,3-butane dione oxime :

(i) Preparation of n-amyl nitrite :

It was prepared by treating an ice-cold aqueous solution of sodium nitrite with a previously cooled mixture of sulphuric acid, n-amyl alcohol and water (201).

(ii) Preparation of 2,3-butane dione oxime :

It was prepared from n-amyl nitrite and methyl ethyl ketone according to the process of Diels and Jost (202).

Methyl ethyl ketone (85 g.) was mixed with concentrated hydrochloric acid (3 ml.) and amyl nitrite (100 ml.) was added to it dropwise over a period of two hours with stirring and cooling. The temperature was kept below 50°C during the addition of nitrite. Next ice (80 g.) and sodium hydroxide solution (800 g. of 33 % solution) were added to the mixture and amyl alcohol formed was extracted with a large quantity of ether. The alkaline solution was acidified with dilute sulphuric acid at 10°C. The precipitates were filtered, washed with a little water and melted over a water-bath. After the mass solidified, the product was removed as a crystalline lump from the mother liquor. It was recrystallised from water. White crystals melting at 74°C were obtained. M.Pt. (lit.) 74°C (203).

3.(b) Preparation of 1,2-propane dione 1-phenyl 2-oxime :

(i) Preparation of methyl nitrite :

Gaseous methyl nitrite was produced by adding sulphuric acid to a solution of sodium nitrite in aqueous methanol.

(ii) Preparation of 1,2-propane dione 1-phenyl 2-oxime :

It was prepared by passing gaseous methyl nitrite and hydrochloric acid through the solution of propiophenone in ether, according to the method given in Organic Synthesis (199). The product was recrystallised from toluene as white crystals melting at 112-13°C. M.Pt.(lit.) 112-13°C.

3.(c) Preparation of 1,2-cyclohexane dione monoxime :

(i) Preparation of ethyl nitrite :

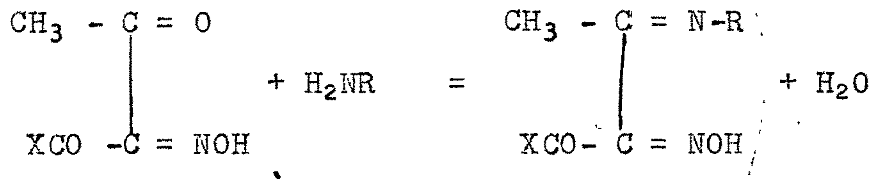
Ethyl nitrite gas was generated by allowing the solution of sulphuric acid in ethyl alcohol + water to flow into a solution of sodium nitrite in ethyl alcohol + water.

(ii)Preparation of 1,2-cyclohexane dione monoxime:

It was prepared by the method of Murakami and Yukawa (204). Ethyl nitrite gas was passed through a mixture of cyclohexanone and hydrochloric acid at 10-15°C. The product was filtered, washed with little water and dried. It was recrystallised from dilute alcohol as yellow crystals melting at 227°C (d). M.Pt.(lit.) 227°C (d).

4. Preparation of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime :

N-aryl 2,3-dioxobutyramide 2-oxime (10^{-2} mole) was dissolved in alcohol (20-25 ml.) and primary amine (10^{-2} mole) was added to it. (The amines used were aniline,p-toluidine,p-phenetidine and benzyl amine) The mixture was warmed gently for a short time and then kept at room temperature for a long period. Crystals appeared after keeping the mixture for about 4 days. The reaction may be represented as



$$\begin{array}{l} CH_3 - C = O \\ \qquad | \\ XCO - C = NOH \end{array} + H_2NR = \begin{array}{l} CH_3 - C = N\text{-}R \\ \qquad | \\ XCO - C = NOH \end{array} + H_2O$$

The product was filtered, washed with aqueous alcohol and dried. It was recrystallised from aqueous alcohol. The products obtained together with their colour, m.pt., analysis (micro), etc. are given in Table II.

They are soluble in alcohol, acetone, benzene, p-dioxane and petroleum-ether, partly soluble in ether, carbon tetrachloride and chloroform and sparingly soluble in water.

Their reactions with some transition metal ions (in neutral solutions) are :

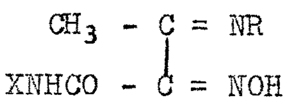
Fe (II)	violet-blue precipitates ;
Fe (III)	no colouration or precipitates ;
Co (II)	orange yellow precipitates ;
Co (III)	orange red precipitates ;
Ni (II)	brown green precipitates ;
Cu (II)	greenish brown precipitates ;
Pd (II)	orange red precipitates ;
Ti (IV)	no colouration or precipitates ;
Th (IV)	no colouration or precipitates ;

5. Preparation of nickel (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime :

The Schiff base from N-aryl 2,3-dioxobutyramide 2-oxime (0.003 moles) was dissolved in alcohol(20-25 ml.) and was mixed with warm aqueous solution of nickel chloride (0.00075 mole). Brown green precipitates were obtained. These were digested on water bath for about half an hour, filtered, washed with water and dilute alcohol and dried. The product was recrystallised from benzene + petroleum ether. The

TABLE II

Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime



$$\begin{array}{l} CH_3 - C = NR \\ \qquad\quad | \\ XNHCO - C = NOH \end{array}$$

No.	Substance X =	 R =	Formula	Colour	M.Pt. °C	% N found	% N reqd.
1	2	3	4	5	6	7	8
1.	C_6H_5	C_6H_5	$C_{16}H_{15}O_2N_3$	White	187	15.38	14.94
2.	o-$CH_3C_6H_4$	C_6H_5	$C_{17}H_{17}O_2N_3$	White	155	13.99	14.23
3.	o-ClC_6H_4	C_6H_5	$C_{16}H_{14}O_2N_3Cl$	White	160	13.67	13.31
4.	C_6H_5	$C_6H_5CH_2$	$C_{17}H_{17}O_2N_3$	Red	137	14.60	14.23
5.	o-$CH_3C_6H_4$	$C_6H_5CH_2$	$C_{18}H_{19}O_2N_3$	Red	135	14.13	13.59
6.	o-ClC_6H_4	$C_6H_5CH_2$	$C_{17}H_{16}O_2N_3Cl$	Red	145	12.36	12.74

TABLE II (CONTD)

1	2	3	4	5	6	7	8
7.	C_6H_5	p-$CH_3C_6H_4$	$C_{17}H_{17}O_2N_3$	White	163	13.88	14.23
8.	o-$CH_3C_6H_4$	p-$CH_3C_6H_4$	$C_{18}H_{19}O_2N_3$	White	164	13.39	13.58
9.	o-ClC_6H_4	p-$CH_3C_6H_4$	$C_{17}H_{16}O_2N_3Cl$	White	160	12.53	12.74
10.	C_6H_5	p-$C_2H_5OC_6H_4$	$C_{18}H_{19}O_3N_3$	White	163	13.0	12.92
11.	o-$CH_3C_6H_4$	p-$C_2H_5OC_6H_4$	$C_{19}H_{21}O_3N_3$	White	144	11.83	12.38
12.	o-ClC_6H_4	p-$C_2H_5OC_6H_4$	$C_{18}H_{18}O_3N_3Cl$	White	172	11.79	11.68

products obtained together with their m.pt., analysis (micro), etc. are given in table III.

They are soluble in alcohol, acetone, benzene, ether, p-dioxane, carbon tetrachloride and chloroform and sparingly soluble in water and petroleum ether.

6. Preparation of nickel (II) complexes of Schiff bases from N-aryl 2,3-dioxo-butyramide 2-oxime in presence of ammonia :

The Schiff base from N-aryl 2,3-dioxobutyramide 2-oxime (0.003 mole) was dissolved in ethyl alcohol (20-25 ml.) and mixed with aqueous solution of nickel chloride(0.00075 mole). Excess of liquor ammonia was added to the mixture. Brownish green precipitates formed immediately. These were digested on the water bath when the brownish green precipitates turned yellowish orange. They were filtered, washed with water and alcohol and dried.

It was not possible to recrystallise them from the usual solvents. The products obtained together with their m.pt., analysis (micro), etc. are given in table IV.

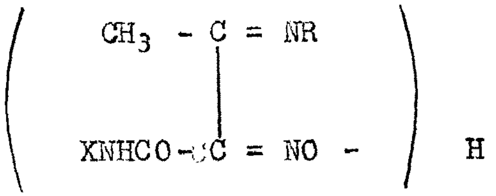
7. Preparation of the copper (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime :

The Schiff base from N-aryl 2,3-dioxobutyramide 2-oxime (0.003 mole) was dissolved in alcohol (20-25 ml.) and mixed with warm aqueous solution of copper chloride (0.00075 mole). Brown green precipitates were obtained. These were digested on water bath for half an hour, filtered, washed with water and dil. alcohol and dried. The product was recrystallised from benzene+ petroleum-ether. The

TABLE · III

Nickel (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime

Reagent :



$$\left(\begin{array}{l} CH_3 - C = NR \\ \qquad\; | \\ XNHCO - C = NO - \end{array} \right) H$$

No.	Reagent R =	 X =	Formula of the complex	M.Pt. °C	% Ni found	% Ni reqd.	% N found	% N reqd.
1	2	3	4	5	6	7	8	9
1.	C_6H_5	C_6H_5	$Ni_2C_{48}H_{49}O_{10}N_9$	> 300	11.16	11.42	12.39	12.25
2.	C_6H_5	$o\text{-}CH_3C_6H_4$	$Ni_2C_{51}H_{61}O_{13}N_9$	235	10.00	10.42	11.16	11.18
3.	$C_6H_5CH_2$	C_6H_5	$NiC_{34}H_{32}O_4N_6$	143-45	9.25	9.10	12.80	13.03
4.	$C_6H_5CH_2$	$o\text{-}CH_3C_6H_4$	$NiC_{36}H_{36}O_4N_6$	185	9.62	8.74	12.27	12.49

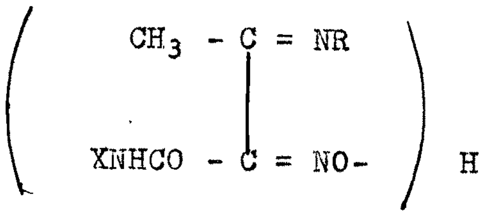
TABLE III (CONTD.)

1	2	3	4	5	6	7	8	9
5.	$C_6H_5CH_2$	o-ClC_6H_4	$NiC_{34}H_{30}O_4N_6Cl_2$	198-200	9.00	8.20	11.65	11.73
6.	p-$CH_3C_6H_4$	C_6H_5	$NiC_{34}H_{32}O_4N_6$	> 300	9.46	9.10	12.42	13.03
7.	p-$CH_3C_6H_4$	o-$CH_3C_6H_4$	$NiC_{36}H_{36}O_4N_6$	> 300	8.80	8.74	12.08	12.49
8.	p-$C_2H_5OC_6H_4$	C_6H_5	$NiC_{36}H_{36}O_6N_6$	210-12	9.33	8.30	11.57	11.88
9.	p-$C_2H_5OC_6H_4$	o-$CH_3C_6H_4$	$NiC_{38}H_{40}O_6N_6$	120	7.92	7.99	10.78	11.43

TABLE IV

Nickel (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime in ammonia.

Reagent :



$$\left(\begin{array}{l} CH_3 - C = NR \\ \quad\quad\quad\;\; | \\ XNHCO - C = NO- \end{array}\right)_H$$

No.	Reagent R =	 X =	Formula of the complex	M.Pt. °C	% Ni found	% Ni reqd.	% N found	% N reqd.
1	2	3	4	5	6	7	8	9
1.	C_6H_5	C_6H_5	$NiC_{16}H_{23}O_4N_5$	269-72	13.97	14.40	17.54	17.17
2.	$C_6H_5CH_2$	C_6H_5	$NiC_{17}H_{36}O_8N_6$	216	11.65	11.50	16.52	16.45
3.	$C_6H_5CH_2$	$o\text{-}CH_3C_6H_4$	$NiC_{18}H_{36}O_7N_6$	282	11.70	11.58	16.77	16.58

TABLE IV (CONTD.)

1	2	3	4	5	6	7	8	9
4.	$C_6H_5CH_2$	o-ClC_6H_4	$NiC_{17}H_{19}O_3N_4$	282	13.10	13.94	13.75	13.30
5.	p-$CH_3C_6H_4$	C_6H_5	$NiC_{17}H_{28\cdot5}O_4N_{5\cdot5}$	270-73	13.36	13.10	17.43	17.18
6.	p-$CH_3C_6H_4$	o-$CH_3C_6H_4$	$NiC_{18}H_{36}O_7N_6$	> 300	12.06	11.58	16.17	16.58
7.	p-$C_2H_5OC_6H_4$	C_6H_5	$NiC_{18}H_{30}O_5N_6$	266-68	12.90	12.51	18.00	17.92

products obtained together with their m.pt., analysis (micro), etc. are given in table V.

They are soluble in alcohol, acetone, benzene, p-dioxane, ether and carbon tetrachloride and sparingly soluble in water and petroleum ether.

8. Preparation of the palladium (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime :

The Schiff base from N-aryl 2,3-dioxobutyramide 2-oxime (0.003 mole) was dissolved in alcohol and was mixed with acidic solution of palladium chloride (0.00075 mole). Orange red precipitates were obtained. These were digested on water bath for half an hour, filtered, washed with water and dilute alcohol and dried. The product was recrystallised from benzene + petroleum ether. The products obtained together with their m.pt., analysis (micro), etc. are given in table VI.

They are slightly soluble in benzene and alcohol and sparingly soluble in water, ether and petroleum ether.

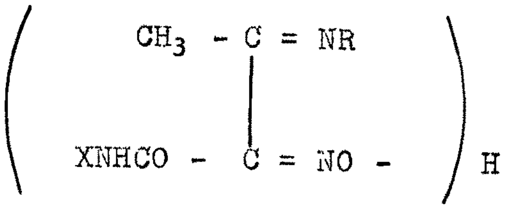
9. Preparation of iron (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime :

The Schiff base from N-aryl 2,3-dioxobutyramide 2-oxime (0.0015 mole) dissolved in alcohol (20 ml.) and 1 N sodium acetate (30 ml.) was treated with ferrous ammonium sulphate (0.0005 mole) in water (5 ml.). Violet blue precipitates appeared. These were kept for a day (in solution), then filtered, washed with water and dilute alcohol and dried. The product was recrystallised from benzene + petroleum ether. The products obtained together

TABLE V

Copper (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime

Reagent :



$$\left(\begin{array}{l} CH_3 - C = NR \\ \quad\quad\;\; | \\ XNHCO - C = NO - \end{array}\right)H$$

No.	Reagent R =	X =	Formula of the complex	M.Pt. °C	% Cu found	% Cu reqd.	% N found	% N reqd.
1	2	3	4	5	6	7	8	9
1.	C_6H_5	C_6H_5	$CuC_{16}H_{21}O_6N_3$	158	15.20	15.32	10.30	10.13
2.	C_6H_5	o-$CH_3C_6H_4$	$Cu_2C_{51}H_{51}O_8N_9$	160	12.20	12.17	12.06	12.07
3.	$C_6H_5CH_2$	C_6H_5	$Cu_2C_{51}H_{55}O_{10}N_9$	137	11.73	11.76	11.70	11.67
4.	$C_6H_5CH_2$	o-$CH_3C_6H_4$	$CuC_{18}H_{25}O_6N_3$	158	13.56	14.35	10.20	9.50

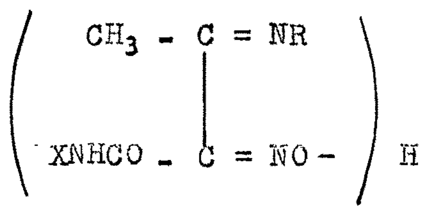
TABLE V (CONTD.)

1	2	3	4	5	6	7	8	9
5.	p-$CH_3C_6H_4$	C_6H_5	$CuC_{17}H_{22}O_5N_3$	172-75	15.10	15.47	10.39	10.23
6.	p-$CH_3C_6H_4$	o-$CH_3C_6H_4$	$CuC_{18}H_{23}O_5N_3$	160	15.17	14.96	9.90	9.90
7.	p-$CH_3C_6H_4$	o-ClC_6H_4	$Cu_3C_{68}H_{66}O_{16}N_{12}Cl_4$	170-72	12.67	12.10	10.01	10.66
8.	p-$C_2H_5OC_6H_4$	C_6H_5	$Cu_3C_{72}H_{82}O_{18}N_{12}$	161-63	12.10	11.96	10.40	10.54
9.	p-$C_2H_5OC_6H_4$	o-$CH_3C_6H_4$	$Cu_3C_{76}H_{92}O_{19}N_{12}$	162	11.71	11.42	9.74	10.08

TABLE VI

Palladium complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime

Reagent :



$$\left(\begin{array}{l} CH_3 - C = NR \\ \qquad\;\; | \\ XNHCO - C = NO - \end{array} \right) H$$

No.	Substance R =	X =	Formula of the complex	M. Pt. °C	% Pd found	% Pd reqd.	% N found	% N reqd.
1.	C_6H_5	C_6H_5	$Pd_2C_{48}H_{51}O_{11}N_9$	172	18.37	18.80	11.60	11.14
2.	$C_6H_5CH_2$	C_6H_5	$Pd_3C_{68}H_{70}O_{12}N_{12}$	166	20.52	20.40	10.53	10.71
3.	p-$CH_3C_6H_4$	C_6H_5	$Pd_3C_{68}H_{68}O_{11}N_{12}$	175	20.70	20.63	10.94	10.86
4.	p-$C_2H_5OC_6H_4$	C_6H_5	$Pd_3C_{72}H_{74}O_{14}N_{12}$	183-84	20.20	19.36	10.80	10.20

with their m.pt., analysis (micro), etc. are given in table VII.

They are soluble in acetone, p-dioxane, benzene, and carbon tetrachloride, partly soluble in alcohol and ether and sparingly soluble in water and petroleum ether.

10. Preparation of cobalt (III) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime :

The Schiff base from N-aryl 2,3-dioxobutyramide 2-oxime (0.003 mole) dissolved in alcohol was mixed with hexamminecobalt(III)chloride (0.00062 mole) in water. Orange red precipitates were obtained. These were digested on water bath for about half an hour, filtered, washed with water and dilute alcohol and dried. The products were recrystallised from benzene + petroleum ether. The products obtained together with their m.pt. analysis (micro), etc. are given in table VIII.

They are soluble in alcohol, acetone, benzene and carbon tetrachloride and sparingly soluble in water, ether and petroleum ether.

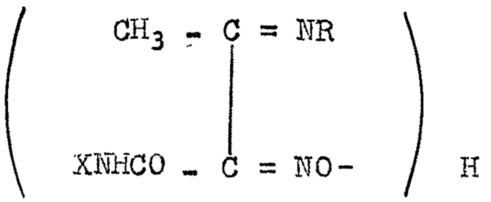
11. (a) Preparation of Schiff base from 2,3-butane dione oxime and p-phenetidine :

p-Phenetidine (0.003 mole) was added to 2,3-butane dione oxime (0.003 mole) in alcohol (20-25 ml.). The mixture was refluxed for about one hour and kept for 4 days when pale yellow crystals were obtained. These were filtered, washed with little dilute alcohol and dried. It was recrystallised from alcohol as pale yellow crystals ; m.pt. 166 °C.

TABLE VII

Iron (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime

Reagent :



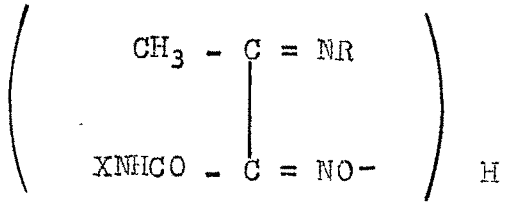
$$\left(\begin{array}{l} CH_3 - C = NR \\ \qquad\quad | \\ XNHCO - C = NO- \end{array} \right) H$$

No.	Substance R =	X =	Formula of the complex	M. Pt. °C	% Fe found	% Fe reqd.	% N found	% N reqd.
1.	C_6H_5	C_6H_5	$Fe_2C_{16}H_{15}O_7N_3S$	>300	22.02	22.13	9.20	8.32
2.	$C_6H_5CH_2$	C_6H_5	$Fe_2C_{17}H_{17}O_7N_3S$	>300	21.18	21.83	8.92	8.10
3.	$C_6H_5CH_2$	o-$CH_3C_6H_4$	$Fe_3C_{36}H_{38}O_{10}N_6S$	>300	18.80	18.34	9.14	9.19
4.	p-$CH_3C_6H_4$	C_6H_5	$FeC_{34}H_{36}O_6N_6$	115	8.90	8.23	11.50	12.36
5.	p-$CH_3C_6H_4$	o-$CH_3C_6H_4$	$FeC_{36}H_{4}0O_6N_6$	130	8.06	7.89	11.58	11.86

TABLE VIII

Cobalt (III) complexes of Schiff bases of N-aryl 2,3-dioxobutyramide 2-oxime

Reagent :



$$\left(\begin{array}{l} CH_3 - C = NR \\ \quad\quad\;\; | \\ XNHCO - C = NO- \end{array}\right)H$$

No.	Reagent R =	X =	Formula of the complex	M. Pt. °C	% Co found	% Co reqd.	% N found	% N reqd.
1.	C_6H_5	C_6H_5	$CoC_{48}H_{42}O_6N_9$	166-72	7.06	6.55	13.63	14.02
2.	$C_6H_5CH_2$	C_6H_5	$CoC_{51}H_{48}O_6N_9$	155-62	6.16	6.26	13.07	13.40
3.	$C_6H_5CH_2$	o-ClC_6H_4	$CoC_{34}H_{44}O_{10}N_7Cl_2$	120	6.99	7.02	11.87	11.66
4.	p-$CH_3C_6H_4$	C_6H_5	$CoC_{34}H_{42}O_8N_7$	160-65	8.35	8.02	13.11	13.33
5.	p-$C_2H_5OC_6H_4$	C_6H_5	$CoC_{36}H_{44}O_9N_7$	155-60	7.20	7.59	12.90	12.61

Analysis :

Found :: N, 12.40 ;
$C_{12}H_{16}N_2O_2$ requires : N, 12.72 .

It is soluble in alcohol, acetone, benzene, p-dioxane, carbon tetrachloride, petroleum-ether, etc.

Its reactions with some transition metal ions (in neutral or slightly alkaline solution) are :

Fe (II)	violet precipitates ;
Co (II)	orange colouration ;
Ni (II)	red colouration ;
Cu (II)	greenish brown precipitates.

11. (b) <u>Preparation of copper (II) complex of the Schiff base from 2,3-butane dione oxime and p-phenetidine</u> :

The Schiff base (0.003 mole) in alcohol (20-25 ml.) was mixed with aqueous solution of copper chloride (0.00075 mole). Brown green precipitates were obtained. These were digested on water-bath for half an hour, filtered, washed with water and dilute alcohol and dried. The product was recrystallised from benzene + petroleum ether ; m.pt. 150°.

Analysis :
Found : N, 8.07 ; Cu, 17.5 ;
$CuC_{12}H_{22}O_6N_2$ requires : N, 7.90 ; Cu, 17.9.

It is soluble in alcohol, benzene,p-dioxane, acetone and carbon tetrachloride and sparingly soluble in water and petroleum ether.

11. (c) Preparation of iron (II) complex of the Schiff base from 2,3-butane dione oxime and p-phenetidine :

The Schiff base (0.0015 mole) dissolved in ethyl alcohol (20 ml.) and 1 N sodium acetate (30 ml.) was treated with ferrous ammonium sulphate (0.0005 mole) in water (5 ml.). Violet precipitates were obtained and allowed to stand for a day. They were filtered, washed with little water and dilute alcohol and dried. The product was recrystallised from benzene + petroleum ether ; m.pt. 205-8°C.

Analysis :
Found : Fe, 16.63 ; N, 7.29 ;
$Fe_2C_{24}H_{36}N_4O_{11}S$ requires : Fe, 15.96 ; N,8.00 .

It is soluble in alcohol, acetone, benzene carbon tetrachloride and p-dioxane and sparingly soluble in ether, water and petroleum ether.

12. Ultra-violet absorption spectra :

All the measurements of optical density (O.D.) of N-ligands and their metal complexes in solution in the ultra-violet region were carried out on Beckmann Spectrophotometer Model DU at room temperature using 1 cm. matched quartz cells.

The solvents used were distilled water, methanol and 0.1 N alcoholic sodium hydroxide solution.

Different workers have used different terms for presenting their absorption spectroscopic data. The terms used in the present investigation (with their definitions) are :

I_0 : Intensity of incident light ;

I : Intensity of transmitted light after passage through cell of length b ;

b : length of the cell (cm) ;

c : concentration (gm. mole. per litre) ;

T : transmittance = I / I_0 ;

A : absorbance (optical density , O.D.) = $-\log_{10} T$;

E : molar extinction coefficient = A / (b x c) ;

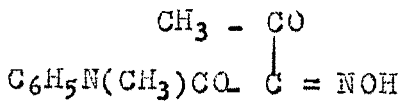
E — value = $E^{1\%}_{1\,cm}$ = A / (b x c') ;

c' = concentration (gm / 100 ml of solution)

E-values observed for the compounds in solution (using the corresponding solvent as reference) at a few selected wave-lengths are given in tables IX to XIV.

TABLE IX

E-values of N-methyl 2,3-dioxobutyranilide 2-oxime

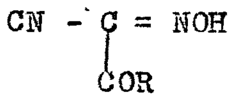


$$\begin{array}{l} \qquad\qquad\quad CH_3 - CO \\ \qquad\qquad\qquad\qquad\ | \\ C_6H_5N(CH_3)CO\text{-}C = NOH \end{array}$$

λ mμ	E-values in water	E-values in methanol	E-values in alkali
228	430.0	437.3	214.8
240	301.4	339.7	146.1
252	194.3	172.4	121.9
264	174.3	91.37	166.4
276	229.3	65.51	259.3
288	257.1	47.42	326.6
300	179.3	28.44	227.5
315	60.01	18.10	75.11
330	19.29	112.93	21.10
345	11.43	11.20	10.93
360	10.72	10.35	8.59

TABLE X

E-values of the oximes of 2-cyano glyoxylic acid derivatives

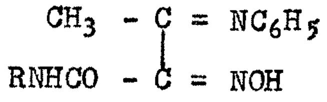


$$CN - \underset{\displaystyle COR}{\underset{|}{C}} = NOH$$

λ (mμ)	R = NHC_6H_5 E-values in water	NHC_6H_5 E-values in methanol	OC_2H_5 E-values in water	OC_2H_5 E-values in methanol	NH_2 E-values in water	NH_2 E-values in methanol
220	485.0			365.0	665.1	731.9
230	575.4	447.8	581.2	380.9	682.7	779.4
240	504.7	365.7	581.2	354.8	500.0	561.0
250	344.3	293.3	371.8	261.0	335.1	318.4
260	356.6	218.7	215.4	252.2	320.5	270.9
270	392.4	225.8	203.4	382.6	401.7	232.8
280	403.7	229.5	235.1	556.5	491.5	410.7
290	416.8	240.7	249.6	621.8	465.8	444.8
300	424.5	250.0	196.5	504.3	299.1	327.9
310	367.9	329.5		273.9	144.3	166.3
320	264.1	187.2		100.0	51.29	58.93
330	174.6	136.2		30.44	25.64	
340	99.06	89.56		18.26	27.35	

TABLE XI A

E-values of the Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime and aniline

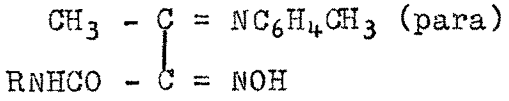


$$\begin{array}{l} CH_3 - C = NC_6H_5 \\ \quad\quad\ \ | \\ RNHCO - C = NOH \end{array}$$

λ(mμ)	R =	C_6H_5 E-values in methanol	C_6H_5 E-values in alkali	o-$CH_3C_6H_4$ E-values in methanol	o-$CH_3C_6H_4$ E-values in alkali	o-ClC_6H_4 E-values in methanol	o-ClC_6H_4 E-values in alkali
228		855.1		634.8	380.1	525.0	
240		814.3	394.5	439.3	374.0	298.5	334.4
252		513.4	468.8	267.7	446.7	220.0	384.7
264		315.6	483.4	178.5	455.2	224.4	381.8
276		231.1	517.5	143.7	467.2	231.2	412.3
288		179.2	557.7	110.8	438.4	211.6	463.5
300		145.5	511.3	81.8	343.5	160.4	440.9
312		116.1	353.1	60.3	225.9	118.7	314.7
324		88.5	168.1	43.8	115.9	69.3	150.9
336		66.0	63.3	32.2	54.4	36.4	52.3
348		46.8	25.5	24.7	25.4	22.3	19.7
360		34.6	15.8	19.9	13.5	18.8	11.8

TABLE XI B

E-values of the Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime and p-toluidine

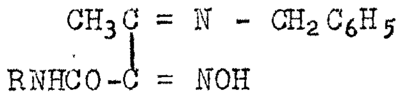


$$\begin{array}{l} CH_3 - C = NC_6H_4CH_3 \text{ (para)} \\ \qquad\quad\;\, | \\ RNHCO - C = NOH \end{array}$$

λ mμ	R = C_6H_5 E-values in methanol	C_6H_5 E-values in alkali	o-$CH_3C_6H_4$ E-values in methanol	o-$CH_3C_6H_4$ E-values in alkali	o-ClC_6H_4 E-values in methanol	o-ClC_6H_4 E-values in alkali
228	833.5	-	555.5	527.8	595.0	-
240	800.4	389.6	329.6	347.6	319.8	316.6
252	537.9	434.2	241.3	378.7	211.3	354.9
264	318.2	440.4	220.1	398.2	226.8	359.6
276	240.5	471.5	207.1	415.8	237.4	389.1
288	185.7	499.5	178.8	409.3	219.0	446.6
300	149.6	445.7	143.6	338.0	174.4	412.3
312	122.2	308.9	111.8	222.2	129.8	307.0
324	97.5	152.7	78.8	114.8	85.2	149.1
336	76.7	59.0	54.1	49.1	52.3	47.8
348	58.7	26.9	43.5	21.3	38.7	18.3
360	43.5	16.5	-	12.9	24.2	4.8

TABLE XI C

E-values of the Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime and benzylamine

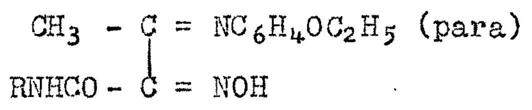


$$\begin{array}{l} \quad CH_3C = N - CH_2C_6H_5 \\ \qquad\ \ | \\ RNHCO-C = NOH \end{array}$$

λ (mμ)	R = C_6H_5 E-values in methanol	C_6H_5 E-values in alkali	o-$CH_3C_6H_4$ E-values in methanol	o-$CH_3C_6H_4$ E-values in alkali	o-ClC_6H_4 E-values in methanol	o-ClC_6H_4 E-values in alkali
228	482.6	346.1	363.9	356.7	303.8	438.0
240	447.0	345.4	293.9	338.3	273.3	395.7
252	396.6	428.8	302.0	400.4	370.6	460.7
264	423.3	490.8	410.4	444.1	577.1	495.8
276	427.3	485.1	456.7	446.4	658.3	188.7
288	385.8	407.5	450.1	381.9	369.4	429.7
300	330.3	320.6	418.6	303.0	485.6	352.3
312	261.1	218.7	317.4	214.8	370.6	247.9
324	171.1	119.0	202.9	128.0	252.2	134.3
336	91.9	53.4	96.8	62.1	119.3	60.9
348	44.5	23.5	51.3	29.9	47.8	32.0
360	25.7	14.9	29.0	16.8	21.1	20.6

TABLE XI D

E-values of the Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime and p-phenetidine



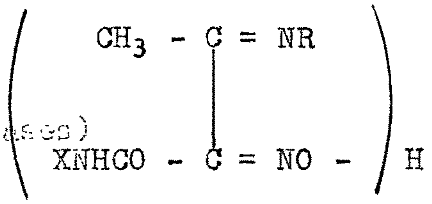
$$\begin{array}{l} CH_3 - C = NC_6H_4OC_2H_5 \text{ (para)} \\ \quad\quad\quad\;\, | \\ RNHCO - C = NOH \end{array}$$

λ(mμ)	R = C_6H_5 E-values in methanol	C_6H_5 E-values in alkali	o-$CH_3C_6H_4$ E-values in methanol	o-$CH_3C_6H_4$ E-values in alkali	o-ClC_6H_4 E-values in methanol	o-ClC_6H_4 E-values in alkali
228	664.5	-	376.8	516.4	614.2	605.9
240	389.6	464.1	615.9	381.4	385.8	387.2
252	290.5	477.2	331.9	369.8	263.5	388.1
264	279.4	499.9	184.8	417.5	235.4	390.4
276	298.4	545.5	137.7	434.3	242.5	433.3
288	287.2	597.1	123.2	402.5	232.0	501.2
300	233.1	539.2	106.9	333.6	183.6	470.2
312	172.3	380.6	93.2	238.3	139.7	347.6
324	119.3	192.1	94.1	148.4	105.4	188.1
336	76.5	81.2	95.8	82.1	79.9	80.9
348	49.5	33.2	88.9	44.4	58.8	34.5
360	29.2	17.2	75.2	26.5	43.1	23.8

TABLE XII

E-values of copper (II) complexes of Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime (in methanol)

Reagent
(Schiff base)



$$\left(\begin{array}{c} CH_3 - \underset{|}{C} = NR \\ XNHCO - C = NO - \end{array} \right) H$$

	Copper complexes of Schiff bases				
R =	C_6H_5	C_6H_5	$C_6H_5CH_2$	$C_6H_5CH_2$	$C_6H_5CH_2$
X =	C_6H_5	o-$CH_3C_6H_4$	C_6H_5	o-$CH_3C_6H_4$	o-ClC_6H_4
λ(mμ)	E-values	E-values	E-values	E-values	E-values
228	456.3	460.2	417.4	371.3	346.4
240	523.0	435.9	507.1	361.4	364.8
252	573.5	411.8	547.5	361.4	397.4
264	496.8	382.3	477.9	353.0	371.8
276	378.6	308.8	369.2	300.5	308.2
288	308.0	253.1	318.6	254.2	258.3
300	291.8	234.3	295.1	237.4	234.1
312	290.8	219.6	274.5	230.0	211.8
324	288.8	207.9	235.6	205.3	183.1
336	259.5	184.9	195.2	175.4	147.3
348	216.0	153.3	154.8	140.7	-

TABLE XII (Continued)

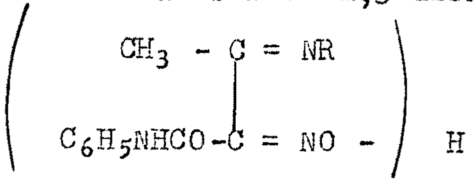
Copper complexes of Schiff bases

	R = $p\text{-}CH_3C_6H_4$	$p\text{-}CH_3C_6H_4$	$p\text{-}CH_3C_6H_4$	$p\text{-}C_2H_5OC_6H_4$	$p\text{-}C_2H_5OC_6H_4$	$p\text{-}C_2H_5OC_6H_4$
	X = C_6H_5	$o\text{-}CH_3C_6H_4$	$o\text{-}ClC_6H_4$	C_6H_5	$o\text{-}CH_3C_6H_4$	$o\text{-}ClC_6H_4$
λ (mμ)	E-values	E-values	E-values	E-values	E-values	E-values
228	432.0	397.9	365.2	437.9	351.9	416.3
240	505.1	377.0	372.8	481.4	325.9	395.0
252	558.0	355.2	403.1	486.6	300.0	400.7
264	470.0	339.5	385.8	413.2	289.8	391.0
276	344.1	308.0	309.9	316.7	255.6	326.9
288	290.0	266.7	262.2	263.2	220.4	258.7
300	278.9	254.2	237.3	246.5	201.8	216.2
312	270.1	234.4	215.5	234.9	181.5	183.7
324	260.0	209.3	190.7	216.1	156.8	163.4
336	236.0	182.1	163.6	195.1	142.6	139.1
348	210.0	157.3	132.9	175.1	129.6	-
360	166.0	134.3	111.4	159.4	116.6	-

TABLE XIII

E-values of Co(III)complexes of Schiff bases from 2,3-dioxobutyranilide 2-oxime(in methanol)

Reagent
(Schiff base) :

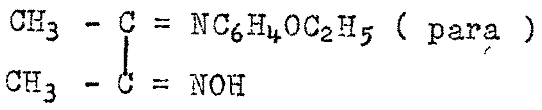


$$\left(\begin{array}{l} CH_3 - C = NR \\ \quad\quad\quad\;\; | \\ C_6H_5NHCO-C = NO - \end{array}\right) H$$

	Cobalt (III) complexes of Schiff bases			
R =	p-$CH_3C_6H_4$	$C_6H_5CH_2$	C_6H_5	p-$C_2H_5OC_6H_4$
λ(mμ)	E-values	E-values	E-values	E-values
228	838.1	507.0	570.5	690.8
240	1006.0	582.2	679.5	796.0
252	1059.0	633.9	749.5	801.5
264	972.5	649.6	759.1	696.3
276	738.7	547.4	613.7	520.4
288	519.8	408.3	426.1	364.4
300	390.7	323.3	340.1	290.0
312	343.0	275.0	318.2	257.4
324	322.5	251.4	310.2	249.3
336	314.8	244.9	304.5	239.3
348	308.0	231.9	295.3	223.0
360	293.3	220.1	280.6	-

TABLE XIV

E-values of the Schiff base from 2,3-butane dione oxime and p-phenetidine



$$\begin{array}{l} CH_3 - C = NC_6H_4OC_2H_5 \text{ (para)} \\ \quad\quad\quad | \\ CH_3 - C = NOH \end{array}$$

λ(mμ).	E-values in methanol	E-values in alkali
228	869.0	571.8
240	999.3	558.5
252	416.2	486.7
264	182.2	666.1
276	126.5	737.8
288	144.2	520.6
300	133.5	286.9
312	124.0	214.1
324	133.5	194.7
336	127.2	158.8
348	105.0	116.8
360	75.26	76.86

13. Infra-red absorption spectra:

All infra-red spectroscopic investigations were carried out (at Bombay) using Perkin-Elmer model 21 equipped with calcium fluoride optics. Potassium bromide pellet technique was followed in obtaining the spectra.

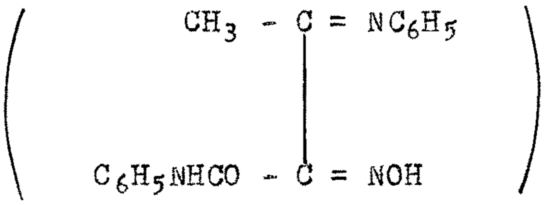
Infra-red absorption bands (cm $^{-1}$) of the Schiff bases obtained from 2,3-dioxobutyranilide 2-oxime and aniline or benzylamine and their copper, nickel, palladium and cobalt complexes (potassium bromide pellets) are given in tables XV and XVI.

The abbreviations used in the body of the table to indicate the relative intensities of absorptions are : vs, very strong ; s, strong ; m, medium strong; w, weak ;vw, very weak. The symbols used in parentheses to describe the nature of absorption are : (b) broad ; (sh),shoulder on a band of higher intensity.

Table XV

Infra-red absorption bands (cm^{-1}) of the Schiff base from 2,3-dioxobutyranilide 2-oxime and aniline and its transition metal complexes

Reagent :



$$\left(\begin{array}{l} CH_3 - C = NC_6H_5 \\ \quad\quad\quad\;\; | \\ C_6H_5NHCO - C = NOH \end{array}\right)$$

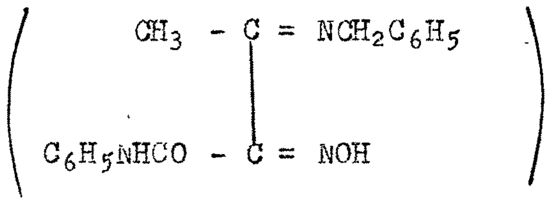
$C_{16}H_{15}O_2N_3$ 1	Ni- $C_{48}H_{49}O_{10}N_9$ 2	Cu- $C_{16}H_{21}O_6N_3$ 3	Pd_2- $C_{48}H_{51}O_{11}N_9$ 4	Co- $C_{48}H_{42}O_6N_9$ 5
		3430 m(b)		3430 m(b)
	3390 m(b)		3320 m	3370 m(b)
3260 vs(b)				
3220 vs(b)	3220 s(b)	3235 s		3220 s(b)
3180 vs(b)	3180 s	3190 s	3200 s	3180 s(b)
3160 s(sh)	3135 s	3130 s	3140 s	
3110 s				3100 s(b)
3052 s	3062 s	3060 s	3060 s	3058 s
3032 s	3032 s	3035 s	3035 s	3032 s
3008 s			3003 s	
2975 m	2975 m	2975 m		
2930 w	2920 m	2925 m	2920 m	2925 m
2855 m	2850 w	2850 w	2870 w	2850 w
2780 w				
1675 s(sh)	1670 vs	1670 vs		1670 vs

1	2	3	4	5
1660 vs	1658 vs			
1652 vs	1650 vs			1640 vs
1632 vs		1620 s		
1600 vs	1600 vs	1600 vs	1600 vs(b)	1600 vs
1580 s	1562 vs	1565 vs	1575 vs	1565 vs
1548 vs	1550 vs	1555 vs	1550 vs	1550 vs
1540 vs			1530 vs	1530 vs
	1500 s		1502 s	1500 vs
1490 vs	1488 s	1495 s	1470 vs	1488 vs
1448 vs	1448 vs	1448 vs	1452 vs	1445 vs
1428 s	1415 vs	1425 s	1415 m	
			1402 m	1405 vs
1390 m	1388 s	1392 s	1388 m	1390 vs
1370 m	1370 s	1370 s	1370 vs	1368 vs
1338 s	1340 s	1345 m		
1325 m		1325 m	1320 s	1390 s
1305 w				1302 s
1292 w		1295 m	1292 vs	
1285 s	1275 m	1280 m		
1245 s	1245 m	1245 m	1250 m	1245 m

Table XVI

Infra-red absorption bands (cm^{-1}) of the Schiff base from 2,3-dioxobutyranilide 2-oxime and benzylamine and its transition metal complexes

Reagent :



$$\left(\begin{array}{rl} CH_3 - & C = NCH_2C_6H_5 \\ & | \\ C_6H_5NHCO - & C = NOH \end{array}\right)$$

$C_{17}H_{17}O_2N_3$ 1	Ni- $C_{34}H_{32}O_4N_6$ 2	Cu_2- $C_{51}H_{55}O_{10}N_9$ 3	Pd_3- $C_{68}H_{70}O_{12}N_{12}$ 4	Co- $C_{51}H_{48}O_6N_9$ 5
3430 w(b)	3375 w(b)	3365 w(b)	3440 w(b)	3365 w(b)
3230 w(b)	3225 m(b)	3245 w	3250 w(sh)	3225 m
	3180 m	3190 w	3192 m	3185 m
		3130 w	3140 m	
3060 m	3062 m	3058 m	3060 m	3060 m
3035 m	3028 m	3028 m	3035 m	3030 m
			3008 m	
2962 s	2968 w	2965 w(b)		2970 w
2920 m	2915 w	2925 w	2920 w	2922 w
1655 (sh)	1668 vs	1665 vs	1668 s	1668 vs
	1652 vs			1640 s
1620 vs(b)		1618 s(sh)	1625 s	
1592 vs	1595 vs	1595 vs	1598 vs	1600 vs
1562 vs	1565 vs	1560 vs	1572 vs	1562 s
1550 vs	1548 vs	1545 vs	1545 vs	1548 vs

1	2	3	4	5
1535 vs	1535 vs	1535 vs	1530 vs	1538 vs
1492 s	1498 vs	1495 vs	1495 s	1498 s
1468 vs			1470 vs	
1448 vs	1445 vs	1442 vs	1452 vs	1445 vs
1417 vs	1420 s(b)	1415 s	1405 s	1412 s
1370 s	1370 s	1368 m	1368 s	1368 m
1335 vs	1338 s	1345 m	1320 s	1332 m
1308 vs				
1295 vs	1272 m	1290 w	1298 vs	1302 m
1225 s	1242 m	1240 w	1245 w	1245 w

14. Magnetic measurements :

Magnetic susceptibilities of some of the metal complexes were determined by the Gouy's method .

The cleaned specimen tube was suspended in the pole gap and its weights were determined at constant temperature in absence and in presence of the magnetic field (obtained by passing a current of 3 amperes through the electromagnet).

According to the theory,

$$X_g = \frac{\left(\frac{2 \times g \times v}{A \times H^2}\right) dw + X_2 \times \rho_2 \times V}{m}$$

where dw is the change in weight of the cylindrical specimen of mass m, volume V, cross-sectional area A and magnetic mass susceptibility X_g , H is the magnetic field, g the gravitational constant and X_2 and ρ_2 the mass susceptibility and density of the medium respectively.

Since g, X_2 and ρ_2 are constant, H is maintained constant and A and V are constants for a particular tube,

$$X_g = \frac{\alpha + \beta \times dw}{m}$$

where $\alpha = X_2 \times \rho_2 \times V = 0.029 \times V \times 10^{-6}$

$$\beta = \frac{2 \times g \times V}{A \times H^2}$$

For the determination of the tube constant "α" the tube was filled with distilled water upto the mark and the weight of the water was determined. For the determination of the tube constant "β", the tube was filled with ferrous ammonium sulphate or mercuric cobalt thiocyanate upto the mark and weights were determined before and during the passage of the current (i.e. in absence and in presence of the magnetic field). The change in weight was calculated and corrected for the change in weight due to the tube.

For the purpose of determining the tube constant "β", mercuric cobalt thiocyanate was prepared by the method of Figgis and Nyholm (205) as follows :

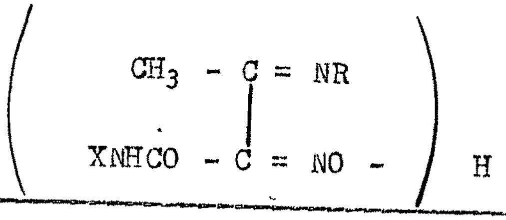
A solution of cobalt sulphate heptahydrate (28 g.) and ammonium thiocyanate (30 g.) in distilled water (50 ml.) was added, at the boiling point and in one lot, to a boiling filtered solution of mercuric chloride (27 g.) in distilled water (300 ml.) with vigorous stirring. Boiling was continued for 1 to 2 minutes more with vigorous stirring. The product was washed several times by decantation and then dried at 120°C.

For the purpose of determining the magnetic susceptibilities of the unknown samples, measurements were made with two tubes and usually with two fillings for each tube. The magnetic susceptibilities (X_g) obtained for some of the metal complexes under investigation are presented in <u>table XVII</u>.

TABLE XVII

Magnetic susceptibilities of transition metal complexes

Reagent :



$$\left(\begin{array}{c} CH_3 - C = NR \\ | \\ XNHCO - C = NO - \end{array}\right) H$$

S.No. 1	Metallic ion. 2	Reagent R = 3	X = 4	Formula of the Complex 5	X_g x 10^6 6	Temperature ^oC 7
1.	Ni (II)	$C_6H_5CH_2$-	C_6H_5-	$NiC_{34}H_{32}O_4N_6$	+ 4.42	34.5
2.	Ni (II)	$C_6H_5CH_2$-	o-$CH_3C_6H_4$-	$NiC_{36}H_{36}O_4N_6$	+ 5.40	34.0
3.	Ni (II)	p-$CH_3C_6H_4$-	C_6H_5 -	$NiC_{34}H_{32}O_4N_6$	+ 7.01	34.0
4.	Ni (II)	$C_6H_5CH_2$-	o-$CH_3C_6H_4$-	$NiC_{18}H_{36}O_7N_6$	- 0.22	31.5
5.	Ni (II)	p-$CH_3C_6H_4$-	C_6H_5-	$NiC_{17}H_{28}\ {}_5O_5N_5\ {}_5$-	- 0.16	31.0
6.	Ni (II)	p-$CH_3C_6H_4$-	o-$CH_3C_6H_4$-	$NiC_{18}H_{36}O_7N_6$	- 0.75	30.0
7.	Ni (II)	p-$C_2H_5OC_6H_4$-	C_6H_5-	$NiC_{18}H_{30}O_5N_6$	-0.43	30.0

TABLE XVII (Contd.)

1	2	3	4	5	6	7
8.	Cu (II)	C_6H_5-	$o-CH_3C_6H_4-$	$Cu_2C_{51}H_{51}O_8N_9$	+ 2.28	33.0
9.	Cu (II)	$C_6H_5CH_2-$	C_6H_5-	$Cu_2C_{51}H_{55}O_{10}N_9$	+ 2.28	33.0
10.	Cu (II)	$C_6H_5CH_2-$	$o-CH_3C_6H_4-$	$CuC_{18}H_{25}O_6N_3$	+ 2.99	34.0
11.	Pd (II)	C_6H_5-	C_6H_5-	$Pd_2C_{48}H_{51}O_{11}N_9$	- 0.70	30.0
12.	Pd (II)	$C_6H_5CH_2-$	C_6H_5-	$Pd_3C_{68}H_{70}O_{12}N_{12}$	- 0.49	30.5
13.	Pd (II)	$p-CH_3C_6H_4-$	C_6H_5-	$Pd_3C_{68}H_{68}O_{11}N_{12}$	- 0.40	30.0
14.	Fe (II)	C_6H_5-	C_6H_5-	$Fe_2C_{16}H_{15}O_7N_3S$	+12.33	33.5
15.	Fe (II)	$C_6H_5CH_2-$	C_6H_5-	$Fe_2C_{17}H_{17}O_7N_3S$	+10.47	33.0
16.	Fe (II)	$C_6H_5CH_2-$	$o-CH_3C_6H_4-$	$Fe_3C_{36}H_{38}O_{10}N_6S$	+11.08	33.5
17.	Fe (II)	$p-CH_3C_6H_4-$	C_6H_5-	$FeC_{34}H_{36}O_6N_6$	+ 5.69	33.5

TABLE XVII (Contd.)

1	2	3	4	5	6	7
18.	Co (III)	C_6H_5-	C_6H_5-	$CoC_{48}H_{42}O_6N_9$	- 0.48	31.0
19.	Co (III)	$C_6H_5CH_2-$	C_6H_5-	$CoC_{51}H_{48}O_6N_9$	- 0.29	30.0
20.	Co (III)	$p-CH_3C_6H_4-$	C_6H_5-	$CoC_{34}H_{42}O_8N_7$	- 0.48	30.5
21.	Co (III)	$p-C_2H_5OC_6H_4-$	C_6H_5-	$CoC_{36}H_{44}O_9N_7$	- 0.26	31.5

15. Conductivity measurements :

Electrical conductivity was measured in 10^{-3}-10^{-2} M solutions in methanol at room temperature using Mullard Bridge and a cell with cell constant 1.46.

The specific conductance was calculated by the relation

$$K = \frac{C}{R}$$

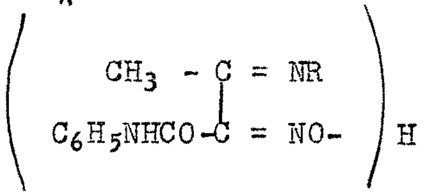
Where K = Specific conductance, C = Cell constant and R = resistance.

Electrical conductivity of the complexes of copper, nickel, palladium and cobalt with the Schiff bases from 2,3-dioxobutyranilide 2-oxime was investigated at room temperature. The results are given in table XVIII.

TABLE XVIII

Electrical conductivity of metal complexes

Reagent :



$$\left(\begin{array}{l} CH_3 - C = NR \\ \quad\quad\;\; | \\ C_6H_5NHCO - C = NO- \end{array}\right)H$$

No.	Reagent R =	formula of the complex	Sp. conductance ($mho\ -cm^{-1}$)
1	2	3	4
1.	C_6H_5	$CuC_{16}H_{22}O_6N_3$	5.32×10^{-6}
2.	C_6H_5	$Ni_2C_{48}H_{52}O_{10}N_9$	1.12×10^{-6}
3.	C_6H_5	$(Co)_2C_{80}H_{82}O_{14}N_{15}$	0.076×10^{-6}

1	2	3	4
4.	C_6H_5	$Pd_2C_{48}H_{52}O_{10}N_9$	0.210×10^{-6}
5.	$C_6H_5CH_2$	$Cu_2C_{57}H_{58}O_{10}N_9$	3.08×10^{-6}
6.	$C_6H_5CH_2$	$NiC_{34}H_{34}O_4N_6$	1.05×10^{-6}
7.	$C_6H_5CH_2$	$(Co)_3C_{51}H_{51}O_6N_9$	1.26×10^{-6}
8.	$C_6H_5CH_2$	$Pd_3C_{68}H_{75}O_2N_{12}$	2.16×10^{-6}

16. Stoichiometry of complexes in solution :

The composition of the complexes formed in solution was investigated by Job's method of continuous variation.

0.001 M solutions of Schiff bases (from N-aryl 2,3-dioxobutyramide 2-oxime), copper chloride,nickel chloride and sodium acetate were prepared in methyl alcohol(E.Merck). The ligand and metal ion solutions were mixed in proportions of 8:2 ; 7:3 ; 6:4 ; 5:5 ; 4:6 ; 3:7 ; 2:8 ;. Thus sets of mixtures were prepared in case of various pairs of metal-ligand solutions. In case of some pairs,additional sets of mixtures were prepared and to each mixture(10 ml.)of the set, 1 ml. of sodium acetate solution was added. The mixtures were kept for about five days and then optical densities of these solutions,after suitable dilutions,were measured at 280,300,320,340 mμ using Beckmann spectrophotometer model DU. These values were corrected for the optical densities of the component solutions. The corrected values are given in tables XIX to XXVI.

TABLE XIX

Corrected optical densities of a mixture of nickel chloride and Schiff base from 2,3-dioxobutyranilide 2-oxime and aniline (in methanol)

(A) : in absence of sodium acetate

Initial volume of ligand in the mixture (ml)	Corrected O. D. at 320 mμ	Corrected O. D. at 340 mμ
7.0	0.182	0.086
6.0	0.204	0.099
5.0	0.227	0.110
4.0	0.222	0.106
3.0	0.219	0.102

(B) : in presence of sodium acetate

Initial volume of ligand in the mixture (ml)	Corrected O. D. at 300 mμ	Corrected O. D. at 320 mμ	Corrected O. D. at 340 mμ
8.0	0.078	0.056	0.025
7.0	0.141	0.115	0.054
6.0	0.177	0.162	0.083
3.0	0.112	0.107	0.057
2.0	0.089	0.084	0.046

TABLE XX

Corrected optical densities of a mixture of nickel chloride and Schiff base from 2,3-dioxo-o-butyrotoluidide 2-oxime and aniline (in methanol.)

(A) : in absence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 280 mμ	Corrected O. D. at 300 mμ	Corrected O. D. at 340 mμ
8.0	0.179	-	0.144
7.0	-	0.374	-
6.0	0.352	0.452	0.249
5.0	0.428	0.519	0.291
4.0	0.351	0.409	0.234
3.0	0.255	0.310	-
2.0	0.153	0.195	0.113

(B) : in presence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 280 mμ	Corrected O. D. at 300 mμ
8.0	0.186	0.195
7.0	-	0.259
6.0	0.234	0.291
5.0	0.290	0.345
3.0	0.169	0.201
2.0	0.125	0.143

TABLE XXI

Corrected optical densities of a mixture of nickel chloride and Schiff base from 2,3-dioxobutyranilide 2-oxime and benzylamine (in methanol)

(A) : in absence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O.D. at 280 mμ	Corrected O.D. at 300 mμ	Corrected O.D. at 320 mμ
8.0	0.060	0.078	0.208
7.0	0.320	0.530	0.578
6.0	0.416	0.670	0.711
4.0	0.235	0.430	0.478
3.0	0.189	0.327	0.372
2.0	0.130	0.236	0.275

(B) : in presence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O.D. at 280 mμ	Corrected O.D. at 300 mμ	Corrected O.D. at 340 mμ
8.0	0.137	0.163	0.165
7.0	0.430	0.552	0.334
6.0	0.494	0.666	0.365
5.0	0.385	0.549	0.319
4.0	0.322	-	0.214
3.0	0.217	0.308	0.177
2.0	-	0.242	0.148

TABLE XXII

Corrected optical densities of a mixture of copper chloride and Schiff base from 2,3-dioxobutyranilide 2-oxime and aniline (in methanol)

(A) : in absence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 280 mμ	Corrected O. D. at 300 mμ
8.0	- 0.020	- 0.001
7.0	-	0.100
6.0	0.090	0.127
5.0	0.160	0.231
4.0	0.161	0.231
3.0	-	0.223
2.0	0.169	-

(B) : in presence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 280 mμ	Corrected O. D. at 320 mμ
8.0	0.080	0.060
7.0	0.115	0.092
6.0	0.155	0.143
4.0	0.195	0.173
3.0	0.196	0.165
2.0	-	0.156

TABLE XXIII

Corrected optical densities of copper chloride and Schiff base from 2,3-dioxo-o-butyro-toluidide 2-oxime and aniline (in methanol)

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 320 mμ	Corrected O. D. at 340 mμ
8.0	0.188	0.168
7.0	0.223	0.187
6.0	0.295	0.227
5.0	-	0.257
4.0	0.301	0.211
3.0	0.278	0.196
2.0	0.235	0.158

TABLE XXIV

Corrected optical densities of copper chloride and Schiff base from 2,3-dioxobutyranilide 2-oxime and benzylamine (in methanol)

(A) : in ansence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O.D. at 320 mμ	Corrected O.D. at 340 mμ
8.0	0.140	0.134
7.0	0.210	0.188
6.0	0.274	0.251
5.0	0.344	0.289
4.0	0.356	0.273
3.0	0.285	0.203
2.0	0.208	0.148

(B) : in presence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O.D. at 280 mμ	Corrected O.D. at 300 mμ	Corrected O.D. at 340 mμ
8.0	0.212	0.173	0.111
7.0	0.245	0.212	-
6.0	-	-	0.168
5.0	-	-	0.187
4.0	0.312	0.253	0.166
3.0	0.289	0.225	0.131
2.0	0.247	0.186	0.100

TABLE XXV

Corrected optical densities of copper chloride and Schiff base from 2,3-dioxobutyranilide 2-oxime and p-toluidine (in methanol)

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 300 mμ	Corrected O. D. at 340 mμ
8.0	0.178	0.158
7.0	0.214	0.202
6.0	0.297	0.249
5.0	0.356	0.286
3.0	0.259	0.179
2.0	0.223	0.165

XXVI

TABLE XXVI

Corrected optical densities of copper chloride and Schiff base from 2,3-dioxobutyranilide 2-oxime and p-phenetidine (in methanol)

(A) : in absence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 280 mμ	Corrected O. D. at 300 mμ
8.0	0.098	0.148
7.0	0.148	0.176
6.0	0.167	0.220
5.0	0.212	0.234
4.0	0.198	0.203
2.0	0.179	0.110

(B) : in presence of sodium acetate

Initial volume of ligand in the mixture (ml.)	Corrected O. D. at 300 mμ	Corrected O. D. at 320 mμ
8.0	-	0.206
7.0	0.144	0.220
6.0	0.196	0.260
5.0	0.238	0.276
4.0	0.250	0.261
3.0	0.244	0.223
2.0	0.228	0.183