EXPERIMENTAL

II EXPERIMENTAL

I General :

(i) Reagents and Solvents :

All the reagents and solvents used were of C.P. grade or better unless otherwise stated.

(ii) Analysis of new products :

Analyses of new products were carried out for metal, nitrogen, carbon and hydrogen as required by known micro or semi-micro methods.

(iii) Melting points :

All melting points recorded herein are uncorrected.

(iv) UV Spectra :

Ultraviolet absorption spectra of the compounds in methanol were obtained from the readings of the Beckman Spectrophotometer Model DU using 10 mm. matched quartz cells.

(v) Visible Spectra :

Absorption spectra in the visible region (800-400 mμ) were obtained for a few compounds in suitable solvents from the readings of the Carl Zeiss Spectrophotometer.

(vi) Electrical conductivity (in solution) :

Electrical conductivity of a few compounds in solution was measured on Toshniwal's conductivity Bridge Model Cl-01 using platinum electrodes.

(vii) Magnetic susceptibility :

Magnetic susceptibility of the transition metal complexes was determined on Gouy's magnetic balance at 29-32°C. temperature by using pyrex glass tubes calibrated with ferrous ammonium sulphate.

The observations and results of the various determinations for different compounds are given at appropriate places in the following pages.

II. 2. vic-Oxime ketone and its metal complexes.

(i) 2,3-Dioxobutyranilide-2-oxime (OK)

It was prepared by the method of Talati(224).

Acetoacetanilide (10 g.) and sodium nitrite (5 g.) were dissolved in dilute sodium hydroxide solution and the solution was added, drop by drop, to the dilute sulphuric acid solution which was kept cool by ice and well stirred during the reaction. 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.

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

(ii) Transition metal complexes of 2,3-dioxobutyranilide-2-oxime under different conditions

(a) Acetate method : (Cu, Ni, Co)

2,3-Dioxobutyranilide-2-oxime dissolved in ether was mixed with cold aqueous solution of metal acetate (metal: ligand : : 1 : 4) and agitated. Precipitates were obtained at the interface. These were kept for four to six hours. The ether layer was separated and the precipitates were filtered, washed with water, dilute alcohol and ether and dried. The products were recrystallised from chloroform + petroleum ether.

They are soluble in chloroform, pyridine, acetic acid and dimethyl formamide and sparingly soluble in water, alcohol, acetone, benzene, ether and petroleum-ether. Metal sulphides are not precipitated from the solutions of copper and cobalt complexes by hydrogen sulphide . However slight colouration is observed when the solution of metal complex is treated with hydrogen sulphide.

Further, when the metal complex dissolved in chloroform was shaken with hydroxylamine dissolved in water and left over, the nickel complex was precipitated out on standing as the complex of 2,3-dioxobutyranilide dioxime.

(b) Sulphate method : (Fe, Mn, Zn)

2,3-Dioxobutyranilide-2-oxime dissolved in ether was treated with metal sulphate (metal: ligand : : 1 : 4) dissolved in 1 N sodium acetate and agitated. Precipitates were obtained at the interface ; these were kept for four to six hours. The ether layer was separated and the precipitates were filtered, washed with water, dilute alcohol and ether and dried. The products were recrystallised from chloroform + petroleum ether. Iron complex is freely soluble in benzene, acetone and chloroform while manganese and zinc complexes are much less soluble in those solvents.

Metal sulphides are precipitated from the solutions of these complexes by hydrogen sulphide. The iron complex gives the precipitates of barium sulphate with a solution of barium salt.

(c) Chloride method: (Sr)

2,3-Dioxobutyranilide-2-oxime dissolved in ether was mixed with cold aqueous ammoniacal solution of metal chloride (metal : ligand : : 1 : 4) and agitated. Precipitates were obtained at the interface ; these were kept for four to six hours. The ether layer was separated and the precipitates were filtered, washed with water, dilute alcohol and ether and dried. The product was recrystallised from chloroform + petroleum ether. It is soluble in pyridine, acetic acid and dimethyl formamide and sparingly soluble in water,alcohol,acetone,benzene,chloroform,ether and petroleum ether.

(d) Metal foil method: (Cu, Mg)

Metal foil was added to 2,3-dioxobutyranilide-2-oxime in alcohol (metal : ligand 1 :: 4) and was stirred for 2 days. The product was filtered,washed with water,alcohol and ether and dried. Solubility of copper complex is the same as that of the complex prepared by the acetate method. Magnesium complex is soluble in pyridine and dimethyl formamide and sparingly soluble in water,alcohol,ether,petroleum ether, benzene,acetone,chloroform.

(e) Carbonate method: (Cu,Co,Ni)

Metal carbonate was added to 2,3-dioxobutyranilide-2-oxime dissolved in alcohol (metal carbonate : ligand :: 1:4) and was refluxed for 2 days ; it was filtered and the filtrate was evaporated to dryness. The product was recrystallised from chloroform + petroleum ether.

The products were tested for the absence of carbonate after purification. The solubilities of these complexes are the same as those of the complexes prepared by the acetate method.

The colour, m.p. analyses etc. of these complexes are presented in table (1). Mass magnetic susceptibilities and dimagnetic corrections of some of these complexes are given in table (2). E-values (or optical densities) of some compounds in methanol in the ultraviolet region are given in table (3) and optical densities of the compounds in dimethyl formamide in the visible region of the spectrum are presented in table (4). The electrical resistances and the molar concentrations of some of these complexes in methanol are given in table (5).

Table 1 (a)

Metal complexes of 2,3-dioxobutyranilide-2-oxime (OK)

No.	Complex	Colour	M.P. °C	Formula	Analysis %M found	%N found	%M reqd.	%N reqd.
1.	OKCu	Green	198(d)	$C_{20}H_{18}N_4O_6Cu$	14.42	11.75	13.43	11.82
2.	OKNi	brownish green	> 300	$C_{20}H_{18}N_4O_6Ni$	12.80	11.28	12.52	11.94
3.	OKCo	orange red	225(d)	$C_{30}H_{28}N_6O_9Co$	10.28	13.55	8.95	12.44
4.	OKFe	bluish violet	> 300	$C_{30}H_{28}N_6O_{13}SFe_2$	14.27	10.22	13.55	10.21
5.	OKMn	violet	> 300	$C_{30}H_{28}N_6O_9Mn$	8.69	11.74	8.19	12.50
6.	OKZn	pale yellow	200(d)	$C_{30}H_{40}N_6O_{15}Zn$	8.30	11.48	8.22	10.55
7.	OKSr	pale yellow	245(d)	$C_{20}H_{22}N_4O_8Sr$	16.78	10.48	16.42	10.56
8.	OKMg	pale yellow	> 300	$C_{20}H_{22}N_4O_8Mg$	5.13	11.28	5.17	11.91

Table 1 (b)

Metal complexes of 2,3-dioxobutyranilide-2-oxime

No.	Complex	Colour	M.P. °C	Formula	Analysis %N found	%N reqd.
1.	$OKCu(CO_3)$	Green	198 (d)	$C_{20}H_{18}N_4O_6Cu$	11.36	11.82
2.	$OKNi(CO_3)$	Brownish green	> 300	$C_{20}H_{18}N_4O_6Ni$	11.65	11.94
3.	$OKCo(CO_3)$	Orange red	224-5(d)	$C_{30}H_{28}N_6O_9Co$	13.32	12.44
4.	OKCu(foil)	Green	195-8(d)	$C_{20}H_{18}N_4O_6Cu$	11.39	11.82

Table-2

Magnetic susceptibility of the complexes.

No.	Complex	Mass magnetic susceptibility $X_g \times 10^6$	Temp. ^oC	Diamagnetic corrections per metal atom $X \times 10^6$
1.	OK Cu	2.55	33	-190
2.	OK Ni	6.33	31	-190
3.	OK Co	1.7	31	-279
4.	OK Fe	12.1	30.5	-327

Table 3

E-Values of the compounds in methanol in the ultraviolet region (360-230 mµ)

Wavelength	E-Value			
(mµ)	OKCu	OK-Ni	OK-Co	OK-Sr
360	185.2	140.6	169.2	3.3
352	201.9	187.5	169.2	6.2
344	230.2	218.8	195.4	10.0
336	263.1	255.7	202.5	10.0
328	276.1	296.9	208.4	16.1
320	282.9	340.7	221.4	26.9
312	316.3	359.3	231.8	40.3
304	336.6	381.9	260.4	57.1
296	363.5	406.2	281.3	71.0
288	403.9	435.7	306.6	96.8
280	444.3	459.4	377.7	134.5
272	488.1	500.0	455.7	177.4
264	555.4	578.2	481.9	245.3
256	673.1	718.8	533.9	369.7
248	804.8	875.2	612.0	530.9
240	905.7	969.0	677.4	633.6
232	925.8	969.0	713.7	618.3

Table 3 (Contd)

Optical densities of the compounds in methanol in the ultraviolet region (360-220 mμ)

Wavelength (mμ)	Optical density			
	OK-Mg	OK-Fe	OK-Zn	OK-Mn
360	0.01	0.05	0.02	0.04
352	0.01	0.06	0.04	0.05
344	0.01	0.06	0.05	0.06
336	0.02	0.07	0.06	0.07
328	0.02	0.09	0.08	0.08
320	0.03	0.09	0.09	0.10
312	0.05	0.11	0.11	0.12
304	0.09	0.13	0.14	0.14
296	0.14	0.15	0.15	0.18
288	0.21	0.18	0.17	0.23
280	0.26	0.20	0.18	0.25
272	0.31	0.24	0.20	0.29
264	0.39	0.30	0.26	0.33
256	0.59	0.39	0.34	0.42
248	0.84	0.52	0.46	0.54
240	1.05	0.62	0.51	0.60
232	1.07	0.66	0.48	0.59

Table 4

Optical densities of the compounds in dimethyl formamide in the visible region (400-800 mμ)

Wave length (mμ)	Optical density			
	OK-Cu	OK-Ni	OK-Co	OK-Fe
800	0.08	0.01	-	0.06
780	0.08	0.01	-	0.08
760	0.09	0.02	0.00	0.08
740	0.09	0.02	0.00	0.08
720	0.09	0.02	0.00	0.11
700	0.10	0.02	0.01	0.16
680	0.10	0.02	0.02	0.27
660	0.13	0.02	0.06	0.48
640	0.13	0.03	0.07	0.77
620	0.13	0.03	0.08	1.10
600	0.13	0.03	0.09	1.30
580	0.11	0.04	0.08	1.40
560	0.09	0.04	0.08	1.16
540	0.10	0.04	0.09	0.85
520	0.13	0.05	0.10	0.54
500	0.22	0.06	0.13	0.33
480	0.30	0.10	0.19	0.25
460	0.54	0.14	0.32	0.24
440	0.89	0.22	0.52	0.24
420	-	0.41	0.80	0.31
400	-	0.80	1.10	0.48

Table 4 (Contd)

Optical densities of the compound in dimethyl formamide or methanol in the visible region (400-800 mμ)

Wavelength (mμ)	optical density		
	OK-Sr (in methanol)	OK-Mn (in DMF)	OK-Zn (in DMF)
800	-	0.045	0.008
780	-	0.051	0.006
760	-	0.044	0.004
740	-	0.046	0.004
720	-	0.055	0.004
700	-	0.051	0.004
680	-	0.061	0.004
660	-	0.071	0.004
640	-	0.084	0.009
620	-	0.109	0.009
600	0.000	0.141	0.013
580	0.000	0.168	0.013
560	0.004	0.157	0.018
540	0.004	0.187	0.018
520	0.009	0.215	0.018
500	0.022	0.237	0.022
480	0.051	0.268	0.027
460	0.086	0.310	0.041
440	0.119	0.377	0.061

Table - 5

Electrical resistance of the complexes of 2,3-dioxobutyranilide-2-oxime in solution.

No.	Complex	Concentration (g/L)	Resistance (meg-ohms)
1 .	OK Cu	0.04	0.84
2..	OK Ni	0.04	0.40
3 .	OK Co	0.05	0.19

II-3. 2,3-Dioxobutyranilide dioxime and its metal complexes :

(i) 2,3-Dioxobutyranilide dioxime (OO)

It was prepared by the method of Knorr and Reuter(230).

2,3-Dioxobutyranilide-2-oxime(4 g.) dissolved in a little alcohol was treated with hydroxylamine hydrochloride (2 g.) in a little water with gentle warming ; abundant crystals appeared gradually. The product was filtered, washed with water and recrystallised from aqueous alcohol. It melts at 192°C.

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

(ii) Iron (II) complex of 2,3-dioxobutyranilide dioxime :

2,3-Dioxobutyranilide dioxime dissolved in ether was treated with ferrous ammonium sulphate dissolved in 1 N sodium acetate (metal: ligand :: 1:4) and agitated. Precipitates were obtained at the interface. These were kept for four to six hours. The ether layer was separated and the precipitates were filtered,washed with water,dilute alcohol and ether and dried. The product was recrystallised from chloroform + petroleum ether. It is blue in colour and does not melt upto 300°C.

Analysis : Found : Fe : 12.73 ; N : 13.65 %.
$C_{30}H_{35}N_9O_{15}SFe_2$ requires : Fe : 12.33 ; N : 13.93 %.

It is soluble in alcohol,acetone,chloroform, dimethyl formamide and pyridine and sparingly soluble in water,ether,[illegible] petroleum ether and benzene.

The mass magnetic susceptibility of the complex was determined as 11.5 x 10^{-6} at 31.3°c and its diamagnetic correction per metal atom has been calculated as - 323 x 10^{-6}. E-values of the complex in methanol in the ultraviolet region of the spectrum are presented in table (6) and the optical densities of the complex in solution in the visible region of the spectrum are presented in table (7).

Table 6

E-Values of the compound (OO-Fe) in methanol in the ultraviolet region (360-240 mμ)

(mμ)	E-values	(mμ)	E-values	(mμ)	E-values
360	347.2	320	510.3	280	781.2
352	399.3	312	527.7	272	867.0
344	416.7	304	556.5	256	1111.0
336	451.3	296	607.8	248	1215.0
328	486.1	288	694.4	240	1230.0

Table 7

Optical density of the compound (OO-Fe) in methanol in the visible region (800-440 mμ)

(mμ)	- O.D.	(mμ)	O.D.	(mμ)	O.D.
800	0.057	680	0.071	560	0.284
780	0,056	660	0.086	540	0.377
760	0.056	640	0.097	520	0.420
740	0.046	620	0.119	500	0.432
720	0.051	600	0.168	480	0.444
700	0.056	580	0.229	460	0.444
				440	0.495

II-4. Phenyl Hydrazone of 2,3-dioxobutyranilide-2-oxime and its metal complexes :

(i) Phenyl Hydrazone of 2,3-dioxobutyranilide-2-oxime (OZ)

It was prepared by the method of Knorr and Reuter(230).

2,3-Dioxobutyranilide-2-oxime (10 g.) dissolved in a little alcohol was treated with phenyl hydrazine (5 g.). The solution became warm ; it was stirred and allowed to stand for 2 hours. The product was filtered, washed with little dilute alcohol and recrystallised from aqueous alcohol. It crystallises with a molecule of alcohol and melts at 181°C. When it is dried on water bath for 48 hours, melting point of the product becomes 169-70°C. Recrystallisation from ethyl alcohol gives the product melting at 168-69°C.

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

(ii) Metal complexes of the phenyl hydrazene of 2,3-dioxobutyranilide-2-oxime :

(a) Acetate method :(Cu, Zn)

Phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime dissolved in ether was mixed with cold aqueous solution of metal acetate (metal:ligand::1:4) and agitated. Precipitates were obtained at the interface. These were kept for 14 to 16 hours. The ether layer was separated and the precipitates were filtered, washed with water, dilute alcohol and ether and dried. The products were recrystallised from chloroform + petroleum ether. (The ligand in the complex OX Cu appears to have undergone dehydrogenation).

They are soluble in benzene, acetone, chloroform, alcohol, pyridine, dimethyl formamide and sparingly soluble in water, petroleum ether and ether.

The mass magnetic susceptibility of the copper complex has been determined as 2.8×10^{-6} at $34^{\circ}C$ and its diamagnetic correction is -152×10^{-6}.

The metal sulphide was precipitated from the solution of the complex by hydrogen sulphide in case of zinc but not in case of copper.

(b) Acetate method : (Al)

Phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime was dissolved in dry methanol, aluminium basic acetate was added to it (metal:ligand::1:4) and the mixture was refluxed on water bath for about 10 hours. It was filtered and the filtrate was evaporated to dryness. The residue was washed with water and dilute alcohol and dried. The product was recrystallised from methanol.

It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide and sparingly soluble in water and petroleum ether.

(c) Chloride method : (Ba)

Phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime dissolved in ether was treated with cold aqueous solution of barium chloride (metal:ligand::1:4), liquor ammonia was added to the mixture and agitated. Precipitates were obtained at the interface by adding petroleum ether. These were kept for 4 to 6 hours. The ether layer was separated and the precipitates were filtered,washed with water and dried.

It is soluble in alcohol,acetone,benzene, chloroform,ether,pyridine and dimethyl formamide and sparingly soluble in water and petroleum ether.

The colour,m.p. analysis etc. of these complexes are given in table (8). E.values of the compounds in methanol in the ultraviolet region of the spectrum are presented in table (9) and optical densities of the compounds in p-dioxane or dimethyl formamide in the visible region of the spectrum are presented in table (10). The electrical resistance of these complexes in methanol solution and their molar concentrations are given in table (11).

Table 8

Metal complexes of 2,3-dioxobutyranilide-2-oxime-3-phenyl hydrazone and its derivatives .

No.	Complex	Colour	M.P. °c	Formula	Analysis			
					% M found	% N found	% M reqd.	% N reqd.
1.	OZBa	Yellow	189(d)	$C_{32}H_{30}N_8O_4Ba$	18.04	15.07	18.87	15.40
2.	OZAl	Pale yellow	180(d)	$C_{16}H_{21}N_4O_6Al$	7.10	14.77	7.08	14.70
3.	OZZn	Pale yellow	200(d)	$C_{20}H_{22}N_4O_6Zn$	13.89	10.98	13.65	11.68
4.	OXCu	green	155(d)	$C_{16}H_{16}N_4O_4Cu$	16.55	14.11	16.28	14.36

Table 9

E-Values of the compounds in methanol in the ultraviolet region (360-220 mμ)

Wavelength (mμ)	E-Value		
	OX-Cu	OZ-Ba	OZ-Zn
360	54.7	159.0	149.5
352	62.6	264.9	284.6
344	82.0	402.6	475.5
336	109.4	550.9	693.1
328	156.3	656.8	822.2
320	218.8	656.8	822.2
312	300.8	599.4	665.8
304	367.3	497.9	543.5
296	420.9	487.3	516.4
288	433.6	453.4	448.3
280	437.5	423.7	380.5
272	424.2	428.1	346.4
264	429.7	487.3	394.1
256	453.1	635.6	536.7
248	523.6	794.5	733.6
240	617.2	879.2	794.9
232	625.2	-	773.1

Table 10

Optical densities of the compounds in dimethylformamide in the visible region (400-800 mμ)

Wavelength (mμ)	Optical density		
	OX-Cu	OZ-Zn	OZ-Ba
800	1.20	0.00	-
780	0.19	0.00	0.02
760	0.20	0.00	0.01
740	0.17	0.00	0.00
720	0.17	0.00	0.00
700	0.17	0.00	0.00
680	0.19	0.00	0.01
660	0.20	0.00	0.01
640	0.23	0.00	0.02
620.	0.23	0.01	0.03
600	0.24	0.01	0.03
580	0.24	0.02	0.04
560	0.23	0.02	0.04
540	0.28	0.03	0.04
520	0.33	0.02	0.05
500	0.42	0.03	0.06
480	0.57	0.04	0.07
460	0.77	0.05	0.11
440	1.05	0.09	0.19
420	1.23	0.18	0.44
400	1.48	0.50	0.80

Table 11

Electrical resistance of the complexes in solution

No.	Complex	Electrical resistance (mag-ohms)	Concentration (g/1)
1.	OZ Ba	0.05	0.04
2.	OZ Zn	0.12	0.10

II. 5 Schiff base from 2,3-dioxobutyranilide-2-oxime and methylamine and its transition metal complexes :

(i) Schiff base from 2,3-dioxobutyranilide-2-oxime and methyl amine (OA)

2,3-Dioxobutyranilide-2-oxime (10.3 g.) dissolved in ether was treated with methylamine (33 % ; 4.7 g.) ; the mixture was cooled and stirred for 10 minutes. The precipitates were obtained and kept for 2 hours. They were filtered,washed with water and ether and dried. The product was recrystallised from chloroform + petroleum ether. M.P. 115°C.

Analysis : Found : N, 19.18 %.

$C_{11}H_{13}N_3O_2$ requires : N, 19.17 %.

It is soluble in alcohol,acetone,benzene,chloroform, pyridine,dimethyl formamide and sparingly soluble in water, ether and petroleum ether.

(ii) Transition metal complexes of Schiff base from 2,3-dioxobutyranilide-2-oxime and methylamine

(a) Acetate method (ether) (Cu,Ni,Co)

The Schiff base from 2,3-dioxobutyranilide-2-oxime and methylamine dissolved in ether was mixed with cold aqueous solution of metal acetate (metal:ligand::1:4) and agitated. Precipitates were obtained at the interface. They were left overnight. The ether layer was separated and the precipitates were filtered,washed with water and ether and dried. The products were recrystallised from chloroform + petroleum ether.

They are soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide and sparingly soluble in water, ether and petroleum ether.

(b) Acetate method (alcohol) (Mn)

The Schiff base from 2,3-dioxobutyranilide-2-oxime and methylamine dissolved in alcohol was mixed with the dilute alcoholic solution of the metal acetate (metal : ligand::1:4). The mixture was left overnight. The precipitates were filtered, washed with water, dilute alcohol and ether and dried.

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

The metal sulphide was precipitated from the solution of the complex by hydrogen sulphide.

(c) Sulphate method (Fe)

The Schiff base from 2,3-dioxobutyranilide-2-oxime and methylamine dissolved in alcohol was treated with ferrous ammonium sulphate dissolved in 1 N sodium acetate (metal : ligand::1:4); bluish violet solution was obtained. It was allowed to evaporate to dryness at room temperature. The residue was washed with water and dilute alcohol and dried. The product was recrystallised from chloroform + petroleum ether.

It is soluble in alcohol, acetone, benzene, chloroform, ether, pyridine and dimethyl formamide and sparingly soluble in water and petroleum ether.

The m.p., colour, analysis, etc. of these complexes are given in table (12). The mass magnetic susceptibilities and dimagnetic corrections of these complexes are given in table (13). E-values of the compounds in methanol in the ultraviolet region of the spectrum are presented in table (14) and optical densities of the compounds in methanol in the visible region of the spectrum are presented in table (15).

Table 12

Metal complexes of the Schiff base of 2,3-dioxobutyranilide-2-oxime and methyl amine

No.	Complex	Colour	M.P. °C	formula	Analysis			
					% M found	% N found	% M reqd.	% N reqd.
1.	OANi	brownish green	> 300	$C_{22}H_{28}N_6O_6Ni$	10.68	16.12	11.04	15.88
2.	OACo	orange red	295 (d)	$C_{33}H_{37}N_9O_6Co$	8.47	17.88	8.25	17.64
3.	OAFe	bluish violet	128 (d)	$C_{22}H_{26}N_6O_8\,5Fe$	9.60	14.09	9.50	14.29
4.	OAMn	violet	> 300	$C_{15}H_{19}N_3O_6Mn$	13.93	11.57	14.00	10.70
5.	OKCu	brownish green	195 (d)	$C_{20}H_{18}N_4O_6Cu$	13.18	12.29	13.43	11.82

Table 13

Magnetic susceptibility of the complexes

No.	Complex	Mass magnetic susceptibility x_g x 10^6	Temp. (^oC)	Diemagnetic correction per metal atom x x 10^6
1.	OA-Ni	8.4	32	- 232
2.	OA-Co	1.6	33	- 313
3.	OA-Fe	8.7	32.9	- 244
4.	OA-Mn	37.2	33.5	- 169
5.	OK-Cu	2.5	32	- 190

Table 14

E-Values of the Schiff base from 2,3-dioxobutyranilide-2-oxime and methylamine in the ultraviolet region (360-224 mμ)

Wavelength (mμ)	E-value	
	in methanol	in alkali
360	35.3	10.8
352	55.5	16.3
344	80.7	29.9
336	161.3	57.6
328	195.5	157.6
320	287.3	182.1
312	383.1	277.4
304	458.6	377.8
296	514.1	451.4
288	574.6	532.6
280	640.4	592.4
272	690.5	625.0
264	704.7	603.3
256	635.1	586.9
248	534.3	559.8
240	478.8	486.4
232	466.8	408.6
224	443.6	408.6

Table 14 (Contd)

E-Values of the compounds in methanol in the ultraviolet region (360-240 mμ)

Wave length (mμ)	E-Value		
	OA-Ni	OA-Co	OA-Fe
360	23.4	230.4	90.6
352	46.9	238.9	126.9
344	62.5	259.9	154.0
336	85.9	274.0	181.1
328	109.3	281.0	186.6
320	132.8	288.0	217.4
312	156.3	298.6	234.4
304	171.9	309.1	261.5
296	192.2	326.5	278.9
288	211.0	372.3	307.9
280	266.6	484.8	335.2
272	289.1	688.5	380.5
264	320.2	913.3	452.9
256	359.3	955.4	552.6
248	406.2	843.1	579.7
240	414.0	730.7	561.6

Table 15

Optical densities of the compounds in methanol in the visible region (400-800 mμ)

Wavelength (mμ)	Optical density		
	OA-Ni	OA-Co	OA-Fe
800	0.05	0.01	0.05
780	0.04	0.01	0.04
760	0.05	0.01	0.05
740	0.05	0.00	0.05
720	0.06	0.00	0.06
700	0.07	0.00	0.08
680	0.09	0.01	0.11
660	0.12	0.01	0.18
640	0.16	0.01	0.36
620	0.20	0.01	0.59
600	0.25	0.01	0.89
580	0.29	0.01	1.22
560	0.34	0.01	1.40
540	0.42	0.01	1.40
520	0.57	0.03	1.22
500	0.80	0.07	0.92
480	1.05	0.10	0.67
460	1.30	0.25	0.38
440	1.52	0.70	0.30
420	1.49	1.36	0.32
400	1.35	1.80	0.43

II. 6 Schiff base from 2,3-dioxobutyranilide-2-oxime and cyclohexylamine and its transition metal complexes

(i) Schiff base from 2,3-dioxobutyranilide-2-oxime and cyclohexylamine (OC)

2,3-Dioxobutyranilide-2-oxime (10.3 g.) dissolved in ether was treated with cyclohexylamine (4.65 g.). The mixture was cooled and stirred for 6 hours. The precipitates were filtered,washed with water and ether and dried ; the product was recrystallised from chloroform + petroleum ether. M.P. 143 °C.

Analysis : Found : N, 14.07 %.

$C_{16}H_{21}N_3O_2$ requires : N, 14.62 %.

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

(ii) Transition metal complexes of the schiff base from 2,3-dioxobutyranilide-2-oxime and cyclohexylamine

(a) Acetate method (Ni,Co)

The Schiff base from 2,3-dioxobutyranilide-2-oxime and cyclohexylamine dissolved in alcohol was mixed with dilute alcoholic solution of metal acetate (metal:ligand::1:4). The solution with precipitates was left overnight. The precipitates were filtered,washed with water,dilute alcohol and ether and dried. The products were recrystallised from chloroform + petroleum ether.

They are soluble in acetone, benzene, chloroform, alcohol, pyridine, dimethyl formamide, p-dioxane and ether and sparingly soluble in water and petroleum ether.

(b) Sulphate method (Fe)

The Schiff base from 2,3-dioxobutyranilide-2-oxime and cyclohexylamine dissolved in alcohol was treated with ferrous ammonium sulphate (metal:ligand::1:4) dissolved in 1 N sodium acetate. Bluish violet solution was obtained. It was evaporated at room temperature. The residue was washed with water and dilute alcohol and dried. The product was recrystallised from chloroform + petroleum ether.

It is soluble in alcohol, acetone, benzene, chloroform, pyridine, dimethyl formamide and ether and sparingly soluble in water, petroleum ether.

The colour, m.p. analyses etc. of these complexes are given in table (16).

Mass magnetic susceptibilities and dimagnetic corrections of these complexes are given in table (17).

E-Values of some compounds in methanol in the ultra-violet region are given in table (18) and optical densities of the compounds in dimethyl formamide in the visible region of the spectrum are presented in table (19).

Table 16

Metal complexes of the Schiff base of 2,3-dioxobutyranilide-2-oxime and cyclohexylamine

No.	Complex	Colour	M.P. °C	Formula	Analysis			
					% M found	% N found	% M reqd.	% N reqd.
1.	OCNi	brownish green	> 300	$C_{16}H_{23}N_3O_4Ni$	16.00	10.47	15.19	11.06
2.	OKCo(C)	orange red	> 300	$C_{20}H_{22}N_4O_8Co$	11.54	10.97	11.66	10.83
3.	OCFe	bluish violet	198 (d)	$C_{16}H_{27}N_3O_6Fe$	13.90	9.76	13.01	9.57

Table 17

Magnetic susceptibility of the complexes

No.	Complex	mass magnetic susceptibility $X_g \times 10^6$	Temp. (^oC)	Diamagnetic correction per metal atom $X \times 10^6$
1.	OC-Ni	9.3	32.9	-185
2.	OK-Co (C)	6.0	32.9	-211
3.	OC-Fe	8.6	32.9	-206

Table 18

E-Values of the Schiff base from 2,3-dioxobutyranilide-2-oxime and cyclohexylamine in the ultraviolet region (360-224 mμ)

Wavelength (mμ)	E-Value	
	in methanol	in alkali
360	17.7	0.00
352	23.6	0.00
344	47.2	2.90
336	94.3	36.60
328	188.7	115.00
320	300.7	209.30
312	377.3	297.80
304	424.5	359.60
296	448.1	383.30
288	465.8	395.10
280	485.9	386.20
272	485.9	368.50
264	454.0	350.90
256	395.0	389.10
248	330.2	392.10
240	311.3	340.90
232	347.6	283.00
224	406.8	199.10

Table 18 (Contd)

E-Values of the compound in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E-Value	
	OK-Co (c)	OC-Fe
360	177.7	75.12
352	186.9	93.26
344	189.9	112.60
336	189.9	131.20
328	189.9	153.10
320	196.1	178.10
312	211.3	203.20
304	220.6	225.00
296	239.0	243.80
288	269.7	262.50
280	318.6	281.30
272	379.9	306.30
264	435.1	343.80
256	477.7	387.60
248	502.4	431.20
240	496.4	437.50

Table 19

Optical densities of the compounds in p-dioxane in the visible region (400-800 mμ)

Wave length (mμ)	Optical density	
	OC-Ni	OK-Co(C)
800	0.05	0.03
780	0.03	0.03
760	0.02	0.03
740	0.01	0.03
720	0.01	0.04
700	0.01	0.05
680	0.01	0.06
660	0.02	0.09
640	0.03	0.10
620	0.04	0.12
600	0.05	0.13
580	0.05	0.14
560	0.05	0.14
540	0.05	0.17
520	0.05	0.20
500	0.05	0.24
480	0.07	0.34
460	0.11	0.47
440	0.23	0.67
420	0.53	1.02
400	1.06	1.15

II. 7. Schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diamino hexane and its transition metal complexes :

(i) Schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diaminohexane (OD) :

2,3-Dioxobutyranilide-2-oxime (10.3 g.) dissolved in ether was treated with 1,6-diamino hexane (4.65 g.) and the mixture was cooled and stirred for 2 hr. The precipitates were filtered, washed with water, little dilute alcohol and ether and dried. The product was recrystallised from chloroform + petroleum ether, m.p. 130°C.

Analysis : Found : N, 15.59 %.

$C_{26}H_{38}N_6O_7$ requires : N, 15.38 %.

(ii) Transition metal complexes of the schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diaminohexane :

(a) Acetate method (Cu,Ni,Co,Zn,Mn)

Schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diamino hexane dissolved in alcohol was mixed with dilute alcoholic solution of metal acetate(metal:ligand:: 1:4). The mixture was left overnight. The precipitates were filtered,washed with water,dilute alcohol and ether and dried. The products were recrystallised from chloroform + petroleum ether.

They are soluble in alcohol,acetone,benzene, chloroform, pyridine, dimethyl formamide and sparingly soluble in water, ether and petroleum ether.

(b) Sulphate method (Fe)

Schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diamino hexane dissolved in chloroform was treated with ferrous ammonium sulphate (metal:ligand:: 1:4) dissolved in 1 N sodium acetate. Bluish violet solution was obtained. It was kept for 4 to 6 hours. The chloroform layer was separated and evaporated at room temperature. The residue was washed with water and dilute alcohol and dried. The product was recrystallised from chloroform + petroleum ether.

It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide and sparingly soluble in water, ether and petroleum ether.

The colour, m.p. analyses etc. of these complexes are recorded in table 20. The mass magnetic susceptibilities and dimagnetic corrections of these complexes are given in table 21. E-values of the compounds in methanol in the ultraviolet region of the spectrum are presented in table 22 and optical densities of the compounds in p-dioxane or methanol in visible region of the spectrum are presented in table 23.

Table 20

Metal complexes of the Schiff base of 2,3-dioxobutyranilide-2-oxime and hexamethylene diamine

No.	Complex	Colour	M.P. (°c)	Formula	Analysis			
					% M found	% N found	% M reqd.	% N reqd
1.	ODCu	Green	208(d)	$C_{13}H_{18}N_3O_4Cu$	19.70	12.00	19.03	12.11
2.	ODNi	Brownish green	210(d)	$C_{26}H_{40}N_6O_9Ni$	8.57	13.16	9.18	13.15
3.	ODCo	orange red	250(d)	$C_{26}H_{38}N_6O_8Co$	8.91	14.09	9.73	13.56
4.	ODFe	bluish violet	100(d)	$C_{13}H_{18}N_3O_4Fe$	17.00	12.54	16.65	12.50
5.	ODMn	violet	215(d)	$C_{26}H_{34}N_6O_6Mn$	9.70	14.55	9.43	14.43
6.	ODZn	pale yellow	210(d)	$C_{17}H_{23}N_3O_7Zn$	14.80	9.68	15.70	10.09

Table 21

Magnetic susceptibility of the complexes

No.	Complex	Mass magnetic susceptibility X_g x 10^6	Temp. (^{o}C)	Diamagnetic correction per metal atom X x 10^6
1.	OD-Cu	2.5	32.8	- 150
2.	OD-Ni	5.5	32.5	- 304
3.	OD-Co	2.4	33.0	- 293
4.	OD-Fe	9.0	33.9	- 150

Table 22

E-Values of Schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diamino hexane in the ultra-violet region (360-224 mμ)

Wavelength (mμ)	E-Value	
	in methanol	in alkali
360	18.7	9.8
352	31.9	9.8
344	57.4	19.5
336	101.4	48.8
328	223.2	175.8
320	357.2	327.1
312	452.8	439.4
304	503.9	493.2
296	512.8	468.6
288	525.5	420.0
280	542.1	346.6
272	548.6	278.3
264	523.0	146.5
256	468.1	185.6
248	413.1	287.9
240	392.9	258.1
232	401.8	43.9

Table 22 (Contd)

E-values of the compounds in methanol in the ultra-violet region (360-220 mµ)

Wave-length (mµ)	E-value			
	OD-Cu	OD-Ni	OD-Co	OD-Fe
360	41.6	15.6	6.6	19.5
352	47.4	23.4	8.8	31.3
344	56.8	29.7	11.1	39.0
336	64.4	35.2	12.0	58.6
328	77.7	55.0	15.5	85.9
320	89.0	74.2	20.0	113.3
312	102.3	85.9	24.4	132.8
304	109.8	93.8	25.3	144.5
296	113.6	105.4	25.8	152.4
288	121.2	113.3	28.9	161.7
280	129.6	132.8	31.0	179.7
272	149.6	156.3	35.5	201.0
264	178.0	199.2	46.6	254.0
256	223.6	273.4	57.7	328.1
248	253.8	359.4	66.6	390.6
240	246.2	398.5	64.8	398.5

Table 23

Optical densities of the compounds in the visible region (400-800 $m\mu$)

Wave-length ($m\mu$)	Optical density			
	OD-Cu	OD-Ni	OD-Co	OD-Fe
800	0.11	0.03	0.00	0.03
780	0.12	0.03	0.00	0.03
760	0.13	0.03	0.00	0.05
740	0.14	0.03	0.00	0.05
720	0.14	0.03	0.00	0.07
700	0.17	0.05	0.01	0.09
680	0.19	0.06	0.02	0.14
660	0.24	0.10	0.03	0.24
640	0.27	0.16	0.05	0.40
620	0.29	0.26	0.07	0.57
600	0.31	0.35	0.11	0.65
580	0.31	0.42	0.14	0.68
560	0.31	0.46	0.19	0.60
540	0.35	0.54	0.28	0.54
520	0.40	0.64	0.40	0.37
500	0.52	0.77	0.54	0.24
480	0.74	0.96	0.82	0.15
460	1.10	1.22	1.30	0.13
440	1.52	1.40	1.70	0.14
420	1.61	1.67	1.91	0.17

II 8. Transition metal complexes of tridentate ligands :

(i) Di-glycinato-copper monohydrate :

It was prepared by the method of Aberhalden and Schnizler (241)

Copper sulphate (5 g.) dissolved in cold water was added to the aqueous solution of sodium hydroxide (1.7 g.). The precipitated copper hydroxide was filtered, washed thoroughly with cold water until free from alkali and then dissolved in warm aqueous solution of glycine (3.0 g.). The solution was warmed on the water bath at 60°C for about 30 minutes and filtered . On concentration and cooling, blue crystals of diglycinato copper (II) monohydrate were obtained. They were twice recrystallised from water and finally dried in a dessicator over conc. sulphuric acid for several days.

(ii) Di-glycinato nickel dihydrate :

The procedure used by Stosick (242) was followed.

The aqueous solution of glycine (7.5 g.) was digested on the water bath at 70° with nickel carbonate (7 g.). On concentration and cooling, blue crystals were obtained. There were filtered and recrystallised from water.

(iii) Condensation of vic-oxime ketone with diglycinato metal (Cu Ni) :

2,3-Dioxobutyranilide-2-oxime dissolved in ether was mixed with cold aqueous solution of diglycinato metal (metal complex : ligand : 1:4) and agitated ; precipitates were obtained at the interface. These were kept for four to six hours. The ether layer was separated and the precipitates were filtered,washed with ether and dried. The products were recrystallised from chloroform + petroleum ether.

They are soluble in pyridine,dimethyl formamide,chloroform and sparingly soluble in water, ether,petroleum ether. The colour, m.p. analysis etc. of these complexes are given in table 24. The mass magnetic susceptibility and dimagnetic correction of these complexes are given in table 25 and optical density of the compounds in dimethylformamide in the visible region of the spectrum is presented in table 26.

Table 24

Metal complexes obtained from (di-glycinato) metal and 2,3-dioxobutyranilide-2-oxime

No.	Complex	Colour	M.P. (°C)	Formula	Analysis			
					M.Found %	N.Found %	M.Reqd. %	N.Reqd. %
1.	(Gly)O-Cu	Brownish green	192(d)	$C_{22}H_{27}O_{10}N_5Cu$	10.77	12.24	10.84	11.95
2.	(Gly)O-Ni	Brownish	>300	$C_{14}H_{24}O_{10}N_4Ni$	13.05	11.83	12.64	11.99

Table 25

Magnetic susceptibility of the diglycinato metal and of the metal complexes obtained from (di-glycinato) metal and 2,3-dioxobutyranilide-2-oxime

No.	Complex	Mass magnetic susceptibility $X_g \times 10^6$	Temp. °C	Dimagnetic correction $X \times 10^6$
1.	(Gly) O-Cu	2.4	32.8	-244
2.	(Gly) O-Ni	7.0	32.5	-183
3.	(Gly) -Cu	6.9	32.5	- 85
4.	(Gly) -Ni	18.1	33.5	- 95

Table 26

Optical density of the compounds in dimethyl formamide in the visible region (400-800 mμ)

Wavelength (mμ)	Optical density	
	(Gly) O-Cu	(Gly) O-Ni
800	0.09	0.02
780	0.11	0.02
760	0.12	0.03
740	0.13	0.03
720	0.14	0.03
700	0.16	0.03
680	0.19	0.03
660	0.24	0.04
640	0.28	0.05
620	0.31	0.06
600	0.34	0.08
580	0.34	0.09
560	0.32	0.09
540	0.38	0.11
520	0.60	0.14
500	1.16	0.21
480	1.70	0.51
460	2.00	1.10
440		1.22

II.9 3-phenyl-2,3-dioxo-propion anilide 2-oxime and related compounds :

(i) Benzoyl acetanilide :

It was prepared by the method given in organic syntheses (243).

A 250 ml. three-necked round bottom flask was fitted with a dropping funnel, mechanical stirrer and a condenser set for downward distillation. In a flask were placed ethyl benzoylacetate (42.2 g.) and dry xylene (50 ml.) and the flask was immersed in an oil bath heated to 145-50°c. Stirring was started and aniline (18.6 g.) was added dropwise,during 30 minutes. Alcohol formed distilled over and was collected.

The reaction flask was removed from the oil bath and the solution was poured into 250 ml. beaker to crystallise. The crystals were filtered and washed with a small quantity of xylene. Powdery white product was obtained. M.P. (observed) 104- 5°c. M.P. (literature) 106°C.

(ii) 3-Phenyl-2,3-dioxopropioanilide-2-oxime :

It was prepared by the method developed by Talati (224) for preparing 2,3-dioxobutyranilide-2-oxime.

The benzoyl acetanilide (10 g.) and sodium nitrite (5 g.) were dissolved in dilute sodium hydroxide solution and the solution was added, drop by drop, to the dilute sulphuric acid solution which was kept cool by ice and well stirred during the reaction. 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 pale yellow crystals. M. P. (observed) 190°C ; M.P.(literature) : 190°C.

E-Values of the compound in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table 27.

(iii) Ethyl ester of 3-phenyl-2,3-dioxo-propionic acid-2-oxime :

It was prepared by the method similar to the one used above.

Ethyl benzyoyl acetate (10 g.) and sodium nitrite (5 g.) were dissolved in dilute sodium hydroxide solution and the solution was added, drop by drop, to the dilute sulphuric acid solution which was kept cool by ice and well stirred during the ~~x~~ reaction. 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 pale yellow crystals. M.P. (observed) 121°C ; M.P.(literature) 120-21°C. (244).

E-Values of the compound in different solvents in the ultra-violet region of the spectrum are presented in table 28.

(iv) α-Benzil monoxime :

It was prepared by the method of Dunn and Forster (245).

Hydroxylamine hydrochloride (7 g.) was

Table 27

E-Values of 3-phenyl-2,3-dioxopropionanilide-2-oxime in the ultraviolet region.(360-232 mμ)

Wavelength (mμ)	E- Value	
	in methanol	in alkali
360	14.9	30.8
352	14.9	41.6
344	26.9	61.6
336	41.7	92.3
328	64.5	141.6
320	98.3	210.8
312	131.0	300.0
304	178.6	400.0
296	248.7	500.0
288	307.7	576.9
280	357.4	624.6
272	416.9	641.5
264	536.0	692.3
256	645.2	738.4
248	635.3	676.9
240	546.1	538.6
232	496.5	438.4

Table 28

E-Values of the ethyl ester of 2,3-dioxopropionic acid-2-oxime in the ultraviolet region (360-224 mμ)

Wavelength (mμ)	E-Values			
	in methanol	in alkali	in acid	in water
360	27.3	24.8	29.8	14.1
352	31.2	28.2	34.2	16.9
344	31.2	33.8	37.2	20.6
336	32.9	37.9	38.7	23.4
328	42.9	49.5	44.6	26.2
320	58.6	66.0	52.4	39.2
312	97.6	86.6	65.5	51.5
304	117.1	115.5	89.3	84.3
296	144.4	144.4	126.5	121.4
288	178.7	170.8	171.1	173.3
280	226.4	214.5	252.9	248.7
272	320.2	332.5	204.8	374.7
264	460.7	618.9	558.0	505.8
256	601.2	829.0	617.5	561.9
248	670.1	915.8	550.5	487.0
240	620.7	726.1	453.8	421.4
232	554.4	511.6	416.7	395.7
224	-	337.5	414.4	449.4

covered with dry pyridine and stirred with powdered sodium hydroxide (5 g.) until decomposition appeared complete. The liquid was filtered, mixed with benzil (20 g.) dissolved in pyridine, and treated with a drop of 50% solution of potassium hydroxide. After leaving it for twenty four hours at the laboratory temperature* the solution was dilted and nearly neutralised with acetic acid. The product was filtered and recrystallised from 30 % alcohol. M.P. (observed) 137-8°C; M.P. (litreature) 137-38°C.

E-values of the compounds in methanol and alkali solution in the ultra-violet region of the spectrum are presented in table - 29.

(v) β-Benzil monoxoime :

It was prepared by the method of Meyer (246).

One mole of benzil dissolved in dilute alcohol was mixed with one mole of hydroxylamine dissolved in dilute alcohol and reflued on the water bath till it gave oil on adding water. Then water was added when the only mass solidified, It was filtered and recrystallised from benzene.M.P. (observed) 105°C; M.P. (literature) 105°C.

E-Values of the compound in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table 30.(a).

(vi) 1,3-diphenyl pyrazol-5-one :

It was prepared by the method of Knorr and Klotz (247).

Equivalent moles of ethyl benzoylacetate and

Table 29

E-Values of α-benzylimonoxime and β-benzilmonoxime in the ultraviolet region (360-224 mμ)

Wavelength (mμ)	E-Values			
	α-Benzilmonoxime		β-Benzilmonoxime	
	in methanol	in alkali	in methanol	in alkali
360	15.6	34.1	29.4	9.4
352	15.6	62.5	31.9	15.0
344	16.4	103.3	36.1	15.0
336	18.8	162.5	39.2	16.9
328	19.5	245.8	43.1	19.7
320	19.5	349.9	57.6	23.5
312	27.4	450.0	84.6	37.5
304	50.9	524.9	128.6	79.8
296	106.8	516.6	208.3	172.6
288	164.1	474.0	306.3	267.4
280	246.1	433.3	447.3	394.1
272	351.6	445.9	680.1	694.2
264	523.5	516.6	970.1	949.7
256	703.1	574.9	1005.0	938.3
248	765.6	533.3	832.3	750.6
240	687.6	491.7	612.8	628.7
232	562.4	457.5	367.6	431.6
224	-	508.3	-	-

Table - 30 (a)

E-Values of 1,3-diphenyl-4-isonitroso pyrazol-5-one in the ultra-violet region (232-360 mμ)

Wave-length (mμ)	E-Values	
	in methanol	in alkali
360	20.0	40.0
352	146.0	50.0
344	178.5	90.0
336	274.8	195.1
328	403.5	340.0
320	483.2	450.0
312	493.6	490.0
304	463.6	490.0
296	497.9	526.2
288	592.5	590.0
280	712.5	635.1
272	815.7	683.1
264	875.4	722.1
256	824.1	710.1
248	721.1	660.1
240	662.8	630.1
232	609.5	575.2

phenyl hydrazine were mixed and just warmed. Reaction took place readily. The precipitates were filtered, washed with water and dil. alcohol and dried. The product was recrystallised from alcohol. M.P. (observed) 138°C. M.P.(literature) 138°C.

(vii) 1,3-Diphenyl-4-isonitrosopyrazol-5-one :

1,3-Diphenyl pyrazol-5-one and sodium nitrite were dissolved in dilute sodium hydroxide solution and the solution was added drop by drop to the dilute sulphuric acid solution which was kept cool by ice and well stirred during the reaction. Reddish yellow precipitates were obtained. Stirring was continued for half an hour more after the addition was over. The precipitates were filtered, washed with water and dried. The product was recrystallised from alcohol as reddish yellow crystals.M.P.(observed) 199-200°C ; M.P. (literature) 199-200°C.(247)

(viii) 3-Phenyl isoxazol-5-one :

It was prepared by the method of Hantzsch (248). Ethyl benzoyl acetate in hot alcohol was condensed with hot aqueous solution of hydroxylamine hydrochloride.Needles of 3-phenyl isoxazol-5-one were obtained. The product was filtered, washed with water and dried. It was recrystallised from benzene. M.P. (observed) 152°C. M.P.(Literature) 152°C.

(ix) 3-Phenyl-4-isonitroso isoxazol-5-one :

3-Phenyl isoxazol-5-one and excess of sodium nitrite were dissolved in dilute sodium hydroxide solution and the solution was added drop by drop to the dilute sulphuric acid. The solution was kept cool by ice and well stirred during the reaction. Light yellow precipitates were obtained. Stirring was continued for half an hour more. The precipitates were filtered, washed with water and dried. The product was recrystallised from ether + petroleum ether as light yellow crystals. M.P. (observed) 138°C.M.P.(literature) 137-38°C(249)

E-values of the compounds in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table 30 (b).

Table 30 (b)

E-Values of 3-phenyl-4-isonitroso isoxazol-5-one in the ultra-violet region.

Wave-length (m μ)	E-Values	
	in alkali	in methanol
360	227.7	139.0
352	315.6	196.0
344	386.7	235.9
336	436.4	269.6
328	432.2	273.0
320	398.2	252.8
304	335.9	210.5
296	349.5	214.0
288	355.9	232.3
280	349.5	273.8
272	312.5	315.9
264	262.7	311.8
256	217.7	289.8
248	180.1	242.9
240	143.0	328.6
232	-	480.2