PART : I

OXIDATION OF N-LIGANDS

INTRODUCTION
(OXIDATION)

I. INTRODUCTION

I. 1. General :

Transition metal ions and oxides occupy a central place in the organic chemist's arsenal of oxidants. They are for the most part stable, inexpensive reagents that are easily handled. Because of their desirable properties, transition metal oxidants have been extensively employed in synthetic organic chemistry. Through constant use has come the observation that considerable selectivity with respect to functional groups can be achieved by the choice of the proper oxidant and the conditions.

As a consequence of the great popularity of these reagents, it is difficult to give details for all of the ways in which they have been employed. Instead an attempt has been made to indicate the products that are likely to result from the use of a particular oxidant under various conditions.

I.2. Oxidation of hydrocarbons :

2 (a) Oxidation of alkanes :

The oxidation of saturated hydrocarbons by inorganic oxidants requires quite vigorous conditions and since the initial products of these reactions are usually susceptible to oxidation under milder conditions, considerable second-stage oxidation is often obtained. The versatile reagents for alkane oxidation are

permanganate ion in aqueous solution and chromium (VI) compounds in aqueous acetic acid or aqueous pyridine solution. Usually, methylene group is oxidised to a ketone through the intermediate formation of a secondary alcohol and is associated with C-C bond cleavage under sufficiently vigorous conditions ; and tertiary C-H bond is converted to tertiary alcohol and isolated methylene to a ketone.[1-6]

2 (b) Oxidation of alkenes :

Alkenes readily reduce oxidants. Reaction can take place either at the double bond or at an α-C-H bond. In the former case, diols, α-ketols or cleavage products are obtained, while in the latter α,β-unsaturated ketones or alcohol derivatives are the common products. Both permanganate ion and osmium tetroxide react with the double bond exclusively. Addition of periodate results in C-C bond cleavage.[7-11] Ruthenium tetroxide converts alkenes vigorously to dicarbonyl compounds through the cleavage of C-C double bonds. Selenium dioxide is the most effective reagent for allylic oxidation.[12,13]

2 (c) Oxidation of alkynes :

Vigorous conditions are usually required to attack alkynes and the formation of cleavage products is more likely. The chief products of non-cleavage reactions are α-diketones and α,β-unsaturated alcohols and are obtained with neutral permanganate or selenium dioxide.[14] Oxidative coupling of acetylene and its monosubstituted

derivatives is observed to take place with cupric ion in organic solvents.[15]

2 (d) Oxidation of arenes :

Chromium (VI) is a versatile reagent for the oxidation of arenes. Under proper conditions, it selectively converts side chains to carboxylic acids, aldehydes, ketones or diacetates or attacks polynuclear arenes, leaving the side chains intact.[16-20] Permanganate ion is more vigorous but less selective than chromium(VI).[21] Lead tetra-acetate is unique since it oxidises benzylic C-H bonds to alcohol derivatives.[22] Osmium tetroxide,[10,11] ruthenium tetroxide,[12] vanadium pentoxide,[23] copper (II) ion,[24] cerium (IV) ion,[25] etc. are also used as arene oxidants.

I. 3. Oxidation of O-containing compounds :

3 (a) Oxidation of ethers :

Ruthenium tetroxide[26,27] and chromium trioxide[28,29] oxidise ethers under mild conditions to give esters, while the use of lead tetra-acetate[30] leads to the substitution of one or more of the α-hydrogens with acetoxy groups.

3 (b) Oxidation of alcohols and glycols :

Chromium (VI) compounds[31,32,33] convert primary alcohols to aldehydes or carboxylic acids and secondary alcohols to ketones. Permanganate ion[34,35] is more vigorous than chromium (VI) compounds and carboxylic acids are usually the only products obtained from the oxidation

of primary alcohols.

Manganese dioxide[36,37,38] exhibits considerable selectivity and is a specific oxidant for α,β-unsaturated alcohols. However, in absence of unsaturation, it will attack primary and secondary alcohols to give aldehydes and ketones.

Oxidation of alcohols by lead tetra-acetate[39] often leads to the formation of cyclic ethers.

Cupric ion and platinum metal catalyse the dehydrogenation of alcohols by oxygen.[40,41] Bismuth tetroxide[42] is a specific oxidant for acyloins. Ruthenium tetroxide, vanadium pentoxide and tetravalent cerium are also used for the oxidation of alcohols.[43,44]

Lead tetra-acetate and per-iodate are capable of cleaving C-C bond of vic-diol and related types of groups.[45,46,47]

3 (c) Oxidation of aldehydes :

Dichromate and permanganate ions readily oxidise aldehydes to the corresponding carboxylic acids in aqueous solutions.[48,49] With both reagents, however, particularly under strongly acidic or basic conditions, enolisable aldehydes suffer C-C bond cleavage.[50] Aldehydes are also oxidised by manganese dioxide above 100° and by lead tetra-acetate.[51,52,53]

3 (d) Oxidation of ketones :

Selenium dioxide[54,55] converts ketones to the corresponding α-diketones. Oxidation of ketones with either

dichromate or permanganate ion usually results in the formation of a carboxylic acid by cleavage of an adjacent C-C bond.[56] Lead tetra-acetate, however, leaves the C-skeleton intact and simply acetoxylates ketones.[57]

I. 4. Oxidation of N-containing compounds :

4 (a) Oxidation of amines :

Manganese dioxide converts primary aliphatic amines to the corresponding aldehydes and primary aromatic amines to azo compounds. The reactions of secondary and tertiary amines with the reagents are complex and result in the formation of amides, aldehydes or enamines.[58,59,60]

Lead tetra-acetate[61] converts primary aliphatic amines to nitriles and mercuric acetate[62] converts cyclic tertiary amines to cyclic enamines.

Cupric ion[63] dehydrogenates amines to the corresponding imines. Permanganate ion[64,65] converts amines readily to highly oxidised compounds.

4 (b) Oxidation of oximes :

Glyoximes are oxidised to furoxans by ferricyanide ion,[66,67,68] oxides of nitrogen,[66,69-72] halogens[66,67] etc.

4 (c) Oxidation of osazones and oxime-hydrazones :

Hudson[73] developed copper sulphate as a reagent for converting phenyl osazones of sugars into sugar osotriazoles.

Oxime -hydrazones of α-diketones are oxidised to triazole oxides by mercuric acetate and oxides of nitrogen.[74]

Present Work :

Considerable work has been carried out in our laboratories on the oximino compounds and their interactions with transition metal ions. Talati[75] prepared the dioxime of 2,3-dioxo butyr (aryl) amides, studied their analytical applications as reagents for the estimations of copper, nickel and palladium and investigated some physical properties of the dioximes and their metal chelates. Desai[76] prepared various hydrazones of 2,3-dioxo butyr (aryl) amide 2-oxime and their metal chelates and studied their physical properties. He observed that the phenyl-hydrazone of 2,3-dioxobutyranilide 2-oxime was oxidised in presence of copper (II) ions. Patel[77] prepared the Schiff bases (aryl imines) of 2,3-dioxobutyr(aryl)amides and their metal chelates and studied their properties. Kapadia[78] attempted to prepare the metal chelates of tetradentate ligands that can be obtained from diamines and 2,3-dioxobutyr(aryl)amide 2-oxime. Shah[79] has prepared different Schiff bases (alkyl)cycloalkyl imines and their derivatives of 2,3-dioxobutyranilide 2-oxime and their metal complexes. All these studies led us to believe that bivalent copper is specific for the oxidation of vic-oxime-hydrazone. A search through literature showed that vic-oxime-hydrazone is oxidised by mercuric oxide or oxides of nitrogen to

oxy-triazole and is condensed to ν-triazole by acetic acid, phosphorus pentachloride etc. Similarly it was found from literature that glyoximes were condensed to furazans by ammonia, acetic anhydride, phosphorus oxychloride etc. and oxidised to furoxans by halogens, oxides of nitrogen etc. Hence it was considered interesting to study the ability of various oxidising agents towards the oxidation of vic-oxime-hydrazones and vic-dioximes. It was planned, therefore,

(1) to prepare vic-oxime-hydrazone and vic-dioxime ;

(2) to study their oxidation by different oxidising agents ; and

(3) to study the side reactions (condensation reactions) that may take place during the oxidation reactions.

When the work was initiated, it was believed that the infra-red spectrophotometer and the polarograph available in the department would be quite helpful in the investigations. But the instruments remained out of order during the investigations.

EXPERIMENTAL
(OXIDATION)

II. EXPERIMENTAL

II. 1. General :

1 (i). Reagents and solvents :

All reagents and solvents used were of C.P. grade or better.

1 (ii). Analysis of new products :

Analysis of new products was obtained for nitrogen by micro method.

1 (iii). Melting points :

All melting points recorded herein are uncorrected.

1 (iv). UV absorption spectra :

The ultra-violet absorption spectra of the compounds in solution were prepared from the readings of the Beckman Spectrophotometer model DU using 10 mm matched quartz cells.

1 (v). Kinetic experiments :

Kinetic experiments were carried out using a small water-bath placed in a large water-bath and a temperature was maintained within 1-2^{0}.

II.2. Oxidation (and condensation reactions) of oxime-hydrazone :

2 (a) Preparation of the phenyl hydrazone of 2,3-dioxobutyranilide 2-oxime :

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

Preparation of 2,3-dioxobutyranilide 2-oxime was carried out by nitrous acid method of Knorr[80] as adopted by Dave and Talati.[81]

Acetoacetanilide (10 g.) and sodium nitrite (5 g.) were dissolved in 10 % 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. 2,3-Dioxobutyranilide 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°.

It is soluble in various organic solvents and sparingly soluble in water.

(ii) Preparation of the phenylhydrazone of 2,3-dioxo-butyranilide 2-oxime :

The method employed by Knorr and Reuter[82] was adopted for the preparation of the phenylhydrazone of 2,3-dioxobutyranilide 2-oxime.

2,3-Dioxobutyranilide 2-oxime (10 g.) was dissolved in a little alcohol and was treated with phenylhydrazine (5 g.); the solution became warm, was stirred and kept aside. After about 10 minutes, crystals appeared gradually. The solution was allowed to stand for about 2 hours. The yellow crystalline product was filtered, washed with little dilute alcohol and recrystallised from aqueous alcohol, m.p. 181°.

It is soluble in alcohol, acetone, ethyl acetate, dioxane etc and sparingly soluble in water, ether, petroleum ether etc.

2 (b) Oxidation with potassium permanganate :

2.0 gms. of the phenylhydrazone of 2,3-dioxobutyranilide 2-oxime in 20 ml. of 10 % sodium hydroxide was placed in a boiling water bath. 5 gms. of potassium permanganate were added in small quantities at a time to the mixture. The reaction mixture was kept on a boiling water bath for 2½ hours. Manganese dioxide was removed by filtration and washed with hot water. Sodium bisulphite was added to discharge the purple colour of the permanganate from the filtrate. The solution was acidified with hydrochloric acid and extracted with ether. Crude product was obtained on evaporating ether. For purification it was dissolved in the sodium bicarbonate solution. The solution was acidified and extracted with petroleum ether. The extract was evaporated. The product was recrystallised from petroleum ether. It melts at 94°.

Analysis Found : N, 18.87 %.

$C_{10}H_9N_3O_3$ requires : N, 19.18 %.

It is soluble in hot water and all common organic solvents except petroleum ether in which it is sparingly soluble.

The E-values of the compound in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table-1.

2(c) Oxidation with manganese dioxide :

1 gm. of phenylhydrazone of 2,3-dioxobutyranilide 2-oxime dissolved in 20 ml. glacial acetic acid was mixed with excess of manganese dioxide and allowed to stand for 24 hours at room temperature. The reaction mixture was poured into water and the solution was filtered. The filtrate was extracted with ether. Black brown solid was obtained on evaporating ether. On repeated crystallisation from dilute alcohol in presence of charcoal, it gave white yellow needles melting at 137°.

The compound has been prepared and identified by Desai[76] by the oxidation of the phenylhydrazone of 2,3-dioxobutyranilide 2-oxime.

Alkaline hydrolysis of the product :

The above product (0.5 g.) was refluxed with ethanolic sodium hydroxide (30 % ; 25 ml.) for 25 hours on a low flame. The reaction mixture on acidification with concentrated hydrochloric acid gave the compound.

Table 1

E-Values of the oxy-triazole-carboxylic acid derivative in the ultra-violet region (360-240 mμ)

Wave-length λ(mμ)	E-value	
	in methanol	in alkali
360	38.26	75.60
352	51.01	75.60
344	56.11	69.77
336	56.11	55.25
328	63.77	55.25
320	66.33	55.25
312	89.92	66.86
304	219.4	139.5
296	357.1	261.6
288	510.1	372.1
280	640.3	485.5
272	724.5	523.4
264	719.4	514.6
256	637.7	447.4
248	533.1	325.6
240	576.5	-

For purification it was dissolved in the sodium bicarbonate solution and reprecipitated with concentrated hydrochloric acid. It was recrystallised from petroleum ether in white needles. It melts at 94°.

2(d) Oxidation with lead dioxide :

A suspension of phenylhydrazone of 2,3-dioxobutyranilide 2-oxime (1 g.) in 25 % acetic acid (40 ml.) was stirred at room temperature and lead dioxide (9 g.) was gradually added in small quantities at a time over a period of 1 hour. The resulting mixture was stirred for 3 hours more and filtered. The filtrate was extracted with ether and the ether was evaporated. The residue was recrystallised from dilute alcohol using charcoal. It gave white needles melting at 137°.

2(e) Oxidation with potassium ferricyanide :

Solutions of the phenylhydrazone of 2,3-dioxobutyranilide 2-oxime (1 g.) in 20 ml. alcohol, of potassium ferricyanide (0.6 g.) in 20 ml. water and of sodium hydroxide (3 ml. ; 10 %) were mixed and refluxed for 1/2 hour. The resulting mixture was filtered hot (no residue). The product separated on cooling from the filtrate. It was recrystallised from dilute alcohol using charcoal as white crystals melts at 137°.

2(f) Oxidation with acidic iron (III) chloride :

A solution of iron (III) chloride (1 g.) in 20 ml. water was added to the phenylhydrazone of

2,3-dioxobutyranilide 2-oxime (1 g.) in 20 ml. alcohol. Ten drops of concentrated hydrochloric acid were added drop by drop with stirring. The precipitates separated immediately. The whole reaction mixture was heated to 60-70° for 1 hour. The precipitates were filtered, washed with water and dried. The product was recrystallised from dilute alcohol as white crystals. It melts at 137°.

The filtrate was concentrated at room temperature in an evaporating dish. The residue was filtered and washed with little water and dried. The product was recrystallised from benzene + petroleum ether as orange crystals. It melts at 157°.

Analysis : Found : N, 20.96 %.

$C_{10}H_9N_3O_2$ requires : N, 20.69 %.

The E-values of the compound in methanolic and alkali solutions in the ultra-violet region of the spectrum are presented in table 2.

Preparation of N-phenyl 3-methyl 4-isonitroso pyrazol-5-one:(oxime-pyrazolone) :

It was prepared by the method of Knorr and Reuter.[82]

When the phenylhydrazone of 2,3-dioxobutyranilide 2-oxime (1 g.) was boiled with acetic acid (5 ml.) for about 15 minutes, orange crystals separated out in a quantitative yield. It was recrystallised from benzene+ petroleum ether, m.p. 157°.

Table 2

E-Values of the 4-isonitroso pyrazol-5-one derivative in different solvents in the ultraviolet region (360-240 mμ)

Wave-length λ (mμ)	E-value	
	in methanol	in alkali
360	178.6	153.6
352	214.3	160.7
344	214.3	189.3
336	312.5	285.8
328	558.1	489.4
320	781.1	767.9
312	946.5	1018.0
304	982.1	1086.0
296	834.7	985.8
288	692.0	782.1
280	598.3	635.9
272	607.1	550.0
264	741.1	660.9
256	991.6	853.7
248	1071.0	860.8
240	1009.0	-

Mixed m.p. of the two products was not depressed.

It is soluble in hot water and all common organic solvents except petroleum ether in which it is sparingly soluble.

2(g) Oxidation with copper sulphate :

Phenylhydrazone of 2,3-dioxobutyranilide 2-oxime (1 g.) and copper sulphate (3 g.) in iso-propyl alcohol (60 ml.) and water (90 ml.) were refluxed for 2 hours, using pieces of porous plate to ensure even boiling. The reaction mixture was filtered hot, washed with little water and dried. The precipitates were recrystallised from dilute alcohol as white crystals. It melts at 137°.

2(h) Oxidation with lead tetra-acetate:

(i) Preparation of lead tetra-acetate :

The preparation of lead tetra-acetate was carried out as suggested in "Preparation of organic intermediates".[83]

A stream of dry chlorine was introduced into a rapidly stirred mixture of glacial acetic acid(150 ml.) and acetic anhydride (40 ml.) held at 65°. Red lead (30 g. ; 0.175 mole) which has been dried at 150° for 2 hours was added in five equal portions, each addition taking place only after the dicharge of colour of the reaction mixture from the preceding addition. The temperature was maintained at 60-85° and the time

required for the addition is 60-90 minutes. The hot mixture was decanted through a heated filter and the filtrate on being cooled precipitates about 12 g. of lead tetra-acetate of greater than 90 % purity. It was kept in brown bottle because it rapidly turns brown at the surface on exposure to moist air.

(ii) Oxidation :

In a conical flask was taken the phenyl hydrazone of 2,3-dioxobutyranilide -2-oxime (0.5 g.) in 5 ml. of glacial acetic acid. The mixture was stirred rapidly and one spoon of freshly prepared lead tetra-acetate was added over a period of about 20 minutes. The solution remained clear in the beginning gradually precipitates were obtained. After the addition was complete, the mixture was stirred for 15 minutes more. The precipitates were filtered,washed with small amount of glacial acetic acid and dried. The product was recrystallised from dilute alcohol as white crystals. It melts at 137°.

2 (i) Oxidation with potassium dichromate :

Potassium dichromate (0.5 g.) was added to a suspension of phenylhydrazone of 2,3-dioxobutyranilide 2-oxime (0.5 g.) in 50 ml. 2N sulphuric acid. The reaction mixture was refluxed for 10 minutes. Gummy product was obtained. It could not be crystallised and no definite product could be extracted from it.

2(j) Oxidation with hydrogen peroxide :

Phenylhydrazone of 2,3-dioxobutyranilide 2-oxime (0.5 g.) was dissolved in 5% sodium hydroxide solution (10 ml.). To this solution was added hydrogen peroxide (5 ml.) and the reaction mixture was heated on a water bath for 1 hour at 60-65°. Original(starting) substance was recovered.

2(k) Oxidation with potassium persulphate :

A suspension of phenylhydrazone of 2,3-dioxobutyranilide 2-oxime (1 g.) was prepared in ice cold sulphuric acid (4 ml.) and water (1 ml.). While the suspension was stirred at room temperature, a solution of Caro's acid was prepared as follows : to ice-cold sulphuric acid (3.5 ml.) in a beaker was added pulverised potassium persulphate (6 g.). The mixture was throughly stirred with a glass rod and to it was added crushed ice (18 g.) and water (6 ml.). The well-stirred solution of Caro's acid thus obtained was poured into the suspension of phenylhydrazone of 2,3-dioxobutyranilide 2-oxime in sulphuric acid. The mixture was stirred and warmed and as soon as the temperature reached 40°, heating was discontinued. After the solution was stirred for 1 hour more. Powdered potassium persulphate (2 g.) were added. The heat of reaction was sufficient to maintain the temperature at 40°. Stirring was continued for 1 hour more. The suspension was then diluted with water. The solid was filtered, washed with water and dried. It was identified as the original(starting)material.

2 (1). Kinetic experiments :

Oxidation with iron (III) chloride :

Some experiments were carried out at different concentrations of the reactants and at different temperatures. The following experimental conditions were then selected.

A solution of iron (III) chloride (1 g.) in 20 ml. water and containing 10 drops of hydrochloric acid was added to the phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime (1 g.) in 20 ml. alcohol. The mixture was well-stirred and kept for a definite time at a fixed temperature. At the end of the interval the solution was cooled and precipitates were rapidly filtered off. The precipitates were washed with water, dried and weighed (W_1). (m.pt. 135-37°). The filtrate was evaporated under vaccum and extracted with benzene + petroleum ether. The extract was evaporated. The residue was dried and weighed (W_2). (m.pt. 155-57°).

The results of the experiments carried out for one hour at different temperatures are given in table (3a).

The subsequent experiments were carried out for different intervals of time at 55-60°. The results (average value) are presented in table 3(b).

Table 3 (a)

Oxidation of oxime-hydrazone by acidified iron(III) chloride at different temperatures.

Temperature (^{o}C)	40	60	80	100
Wt. of precipitates (W_1) (mg.)	550	290	245	Gummy mass
Wt. of residue (W_2) (mg)	100	120	145	60

Table 3 (b)

Oxidation of oxime-hydrazone by acidified iron (III) chloride at 55-60^{o}.

Time (hours)	1/4	1/2	3/4	1	2	3
Wt. of precipitates (A) (W_1) (mg)	335	340	330	310	330	350
Wt. of residue (B) (W_2) (mg)	100	120	120	120	120	120

II.3. Oxidation (and other reactions) of the dioxime :

3 (a) Preparation of 2,3-dioxobutyranilide dioxime :

It was prepared by the method of Knorr and Reuter.[82]

2,3-Dioxobutyranilide 2-oxime(4 g.) were dissolved in the minimum quantity of alcohol. Hydroxylamine hydrochloride (2 g.) dissolved in the minimum quantity of water were added to the above solution. The mixture was kept at 35-40°. After some time white crystalline mass appeared, it was kept for an hour. The precipitates were filtered, washed with water and dried. It was recrystallised from dilute alcohol, m.p.190-92°.

It is soluble in water, alcohol, acetone, dioxane, benzene, ether etc. and sparingly soluble in petroleum ether.

3(b) Oxidation with potassium permanganate :

Potassium permanganate (1 g.) in water (50 ml.) was added in small quantities at a time over a period of 1 hour to 2,3-dioxobutyranilide dioxime (0.5 g.) in 10 % sodium hydroxide solution (3 ml.). The reaction mixture was kept for three hours more at room temperature. The resulting mixture was filtered and the solid was extracted with ether. The ether extract was evaporated. The residue was recrystallised from dilute acetic acid

as white crystals. It melts at 149°.

Analysis : Found : N, 18.8 %.

$C_{10}H_9N_3O_3$ requires : N, 19.2 %.

It is insoluble in water but soluble in all common organic solvents except petroleum ether in which it is sparingly soluble.

The E-values of the compound in methanolic, acid and alkali solutions in the ultra-violet region of the spectrum are presented in table -4.

3 (c) Oxidation with potassium ferricyanide :

A solution of potassium ferricyanide (0.8 g.) in 5 ml. water was added dropwise to 2,3-dioxobutyranilide dioxime (0.5 g.) in 2 ml. 10 % sodium hydroxide. The mixture was kept at room temperature for 1/2 hour. The precipitates were filtered, washed carefully with water and dried. The product was recrystallised from dilute acetic acid as white crystals. It melts at 149°.

3 (d) Oxidation with lead dioxide :

A suspension of 2,3-dioxobutyranilide dioxime (0.5 g.) in 25 % acetic acid (20 ml.) was stirred at room temperature for 4 hours. lead dioxide (6 g.) was gradually added during the first hour. The resulting mixture was filtered and the residue was extracted with ether. The ether extract was evaporated. The residue was crystallised from dilute acetic acid using charcoal as white crystals. It melts at 149°.

Table 4

E-Values of the furoxan derivative in the ultra-violet region (360-230 mμ)

Wave-length λ (mμ)	E-value		
	in methanol	in acid	in alkali
360	50.00	21.88	97.92
352	58.34	37.51	127.1
344	70.84	56.26	158.3
336	91.68	71.88	210.4
328	116.7	96.90	252.2
320	158.3	128.1	308.4
312	229.2	175.0	364.6
304	316.6	240.6	400.0
296	416.7	325.1	429.2
288	516.8	400.0	450.2
280	560.8	459.4	473.0
272	547.6	460.2	508.4
264	487.5	450.1	500.0
256	441.7	462.6	487.5
248	491.7	518.8	516.8
240	602.2	618.9	-
232	677.2	700.0	-

3 (e) Oxidation with acidic iron (III) chloride :

A solution of iron (III) chloride (2 g.) in 45 ml. water was added to 2,3-dioxobutyranilide dioxime (1 g.) in 15 ml. alcohol. Ten drops of concentrated hydrochloric acid were added to the mixture drop by drop with stirring. The resulting mixture was refluxed for one hour and filtered hot. The product separated on cooling from the filtrate. The product was recrystallised from dilute acetic acid as white crystals. It melts at 149°.

3 (f) Oxidation with red lead :

A suspension of 2,3-dioxobutyranilide dioxime (0.5 g.) in 25 % acetic acid (20 ml.) was stirred at room temperature for 4 hours. Red lead (5 g.) was gradually added during the first hour. The resulting mixture was filtered and the residue was extracted with ether. The ether extract was evaporated. The residue was recrystallised from dilute acetic acid as white crystals. It melts at 112°.

Analysis : Found : N, 20.5 %.

$C_{10}H_9N_3O_2$ requires : N, 20.7 %.

The E-values of the compound in methanolic, acid and alkali solutions in the ultra-violet region of the spectrum are presented in table-5.

3 (g) Oxidation with lead tetra-acetate :

In a conical flask 2,3-dioxobutyranilide dioxime (1 g.) in 20 ml. glacial acetic acid were taken. The

Table 5

E-Values of the furazan derivative in the ultra-violet region (360-240 mμ)

Wave-length λ (mμ)	E-value		
	in methanol	in acid	in alkali
360	49.34	1.98	53.28
352	49.34	1.98	69.68
344	65.77	8.93	83.99
336	72.36	17.86	98.35
328	88.81	39.69	122.9
320	138.1	69.45	157.8
312	213.8	110.1	206.9
304	279.6	161.7	258.2
296	353.4	215.3	322.9
288	427.6	269.9	362.7
280	476.9	311.6	403.7
272	532.8	323.4	424.2
264	532.8	311.6	442.7
256	509.8	280.8	459.0
248	480.3	249.2	465.2
240	506.5	281.8	497.9

mixture was stirred rapidly and 3/2 spoons of freshly prepared lead tetra-acetate was added in 1/2 hour. After the addition was complete, the mixture was stirred for 30 minutes more. The resulting solution was filtered and the filtrate poured into water. The precipitates were filtered and recrystallised from dilute acetic acid as white crystals. It melts at 149°.

3(h) Oxidation with manganese dioxide :

2,3-Dioxobutyranilide dioxime (0.2 g.) dissolved in glacial acetic acid (10 ml.) was mixed with excess of manganese dioxide and allowed to stand for 15 hours at room temperature. The reaction mixture was poured into water and the solution was filtered. The filtrate was extracted with ether. Original substance was obtained on evaporating ether.

3(i) Oxidation with chlorine gas :

Chlorine gas was bubbled into the solution of 2,3-dioxobutyranilide dioxime (1 g.) in ethanol(10 ml.) until the solution became colourless. The temperature was kept under 40°. On cooling and dilution with water,gummy product was obtained from which no definite substance could be isolated.

3(j) Oxidation with sodium hypochlorite :

A solution of sodium hypochlorite was prepared by bubbling chlorine gas into 10 % sodium hydroxide solution (25 ml.) until the solution was neutral or slightly acidic.This solution was added dropwise to a well-stirred,cold

(0-10°) solution of 2,3-dioxobutyranilide dioxime(0.5 g.) in 5 % sodium hydroxide (10 ml.). The mixture was stirred for 1 hour. Black gummy mass was obtained from which no definite compound could be isolated.

3(k) Oxidation with bleaching powder :

(i) A suspension of bleaching powder (0.5 g.) in water (10 ml.) was added slowly to a solution of 2,3-dioxobutyranilide dioxime (0.5 g.) in alcohol(10 ml.). The reaction mixture was stirred for 2 hours.Original substance was recovered.

(ii) Bleaching powder (0.5 g.) was added to a suspension of 2,3-dioxobutyranilide doxime (0.5 g.) in water(5 ml.). Concentrated hydrochloric acid (2.5 ml.) was added with stirring. The reaction mixture was refluxed on a wire gauze for 3 hours. Reddish yellow liquid was obtained ; it was not worked out further.

3(l) Oxidation with potassium persulphate :

A solution of Caro's acid was prepared as follows : to ice-cold sulphuric acid (2 ml.) in a beaker was added pulverised potassium persulphate (3 g.).The mixture was throughly stirred with a glass rod and to it was added ice-cold water (10 ml.).

The well-stirred solution of Caro's acid was poured into the suspension of 2,3-dioxobutyranilide dioxime (1 g.) in ice-cold sulphuric acid (3 ml.). The mixture was stirred and warmed at (35-50°) for 2 hours. The heat of reaction was sufficient to maintain the temperature at 40°.

Stirring was continued for 1 hour more and the suspension was then diluted with water. The solid was filtered and washed with water and dried. The solid was extracted with ether. Identifiable products could not be isolated from it.

(ii) Solutions of the 2,3-dioxobutyranilide dioxime(1 g.) in sodium hydroxide (10 ml. ; 10 %) and of potassium persulphate (1.5 g.) in 30 ml. water were mixed and stirred for 4 hours at 7°. The resulting mixture was kept overnight. Concentrated hydrochloric acid was added till congo red paper turns blue. Black gummy substance was obtained after filtering it. No definite compound could be obtained from it.

3(m) Oxidation with potassium dichromate :

(i) A solution of potassium dichromate (0.2 g.) in 5 ml. water was added to 2,3-dioxobutyranilide dioxime in acetic acid (5 ml. ; 50 %) . The reaction mixture was kept on a boiling water bath for 7 hours. Original substance was recovered.

(ii) A solution of potassium dichromate (0.2 g.) in 5 ml. water was added to the 2,3-dioxobutyranilide dioxime in sodium hydroxide (2 ml. ; 10 %) . The reaction mixture was refluxed for 6 hours. Original substance was recovered.

(iii) Potassium dichromate (0.2 g.) was added to the 2,3-dioxobutyranilide dioxime in water (25 ml.). The reaction mixture was refluxed for 1 hour. Original substance was recovered.

(iv) A suspension of potassium dichromate (0.2 g.) in concentrated sulphuric acid (1 ml.) was added to the 2,3-dioxobutyranilide dioxime (0.2 g.) in 5 ml. water. The reaction mixture was refluxed for 10 minutes. The reaction mixture was poured into water. The solution was extracted with ether. Gummy mass was obtained on evaporating ether. No definite product could be isolated from it.

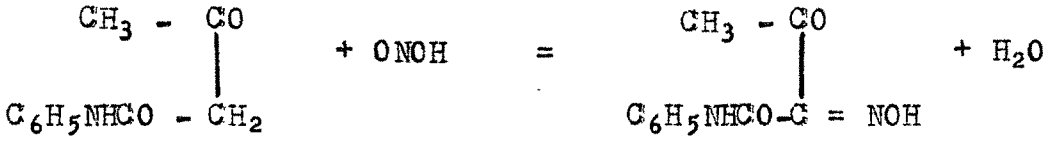
RESULTS AND DISCUSSION (OXIDATION)

III. Discussion :

III. 1. vic-Oxime-hydrazone and its oxidation :

1 (a). vic-Oxime hydrazone :

2,3-Dioxobutyranilide 2-oxime was prepared from acetoacetanilide by the action of nitrous acid as follows :

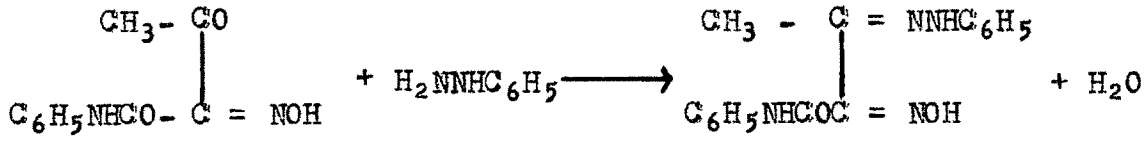


It can exist in two stereoisomeric forms (I-a,b) . Only one form has been isolated by various investigators and syn-amide structure has been attributed to it by them.[75,76,77,84]

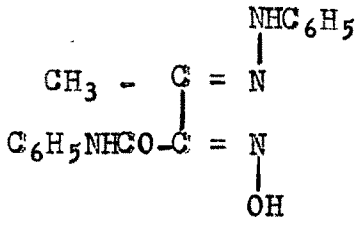
Syn-amide (I-a)

anti-amide (I-b)

Desai[76] obtained its phenyl hydrazone by treating it with phenyl hydrazine.



He has attributed anti-oxime-hydrazone structure (II) to it.

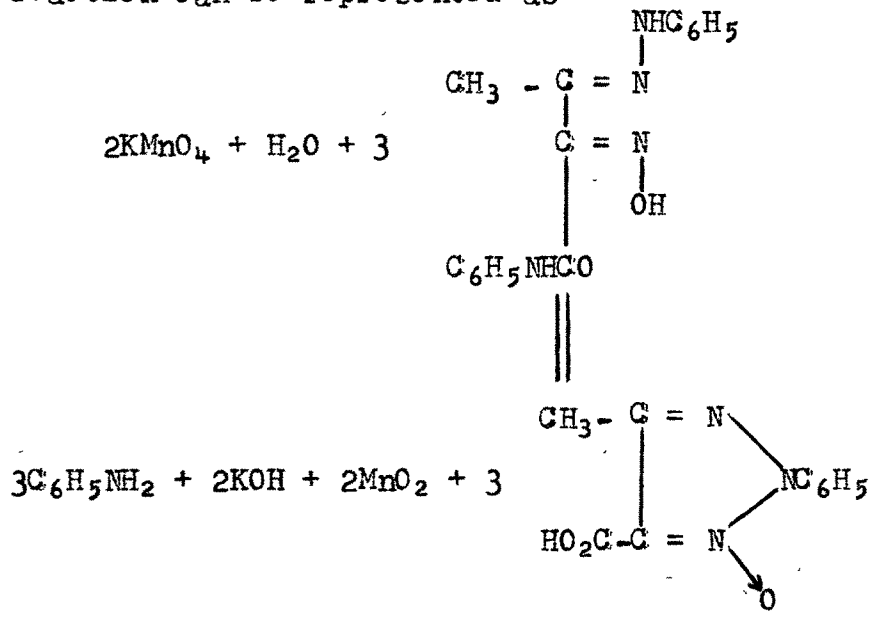


(II)

The ultra-violet absorption spectra of the oxime-ketone and its hydrazone have been studied by Talati[75] and Desai[76]. They are presented in fig. 1. The oxime-ketone has a two band spectrum, whereas the oxime-hydrazone has a characteristic three-band spectrum.

I. (b) <u>Oxidation with potassium permanganate</u> :

The oxime-hydrazone was oxidised by potassium permanganate under alkaline conditions. The overall reaction can be represented as



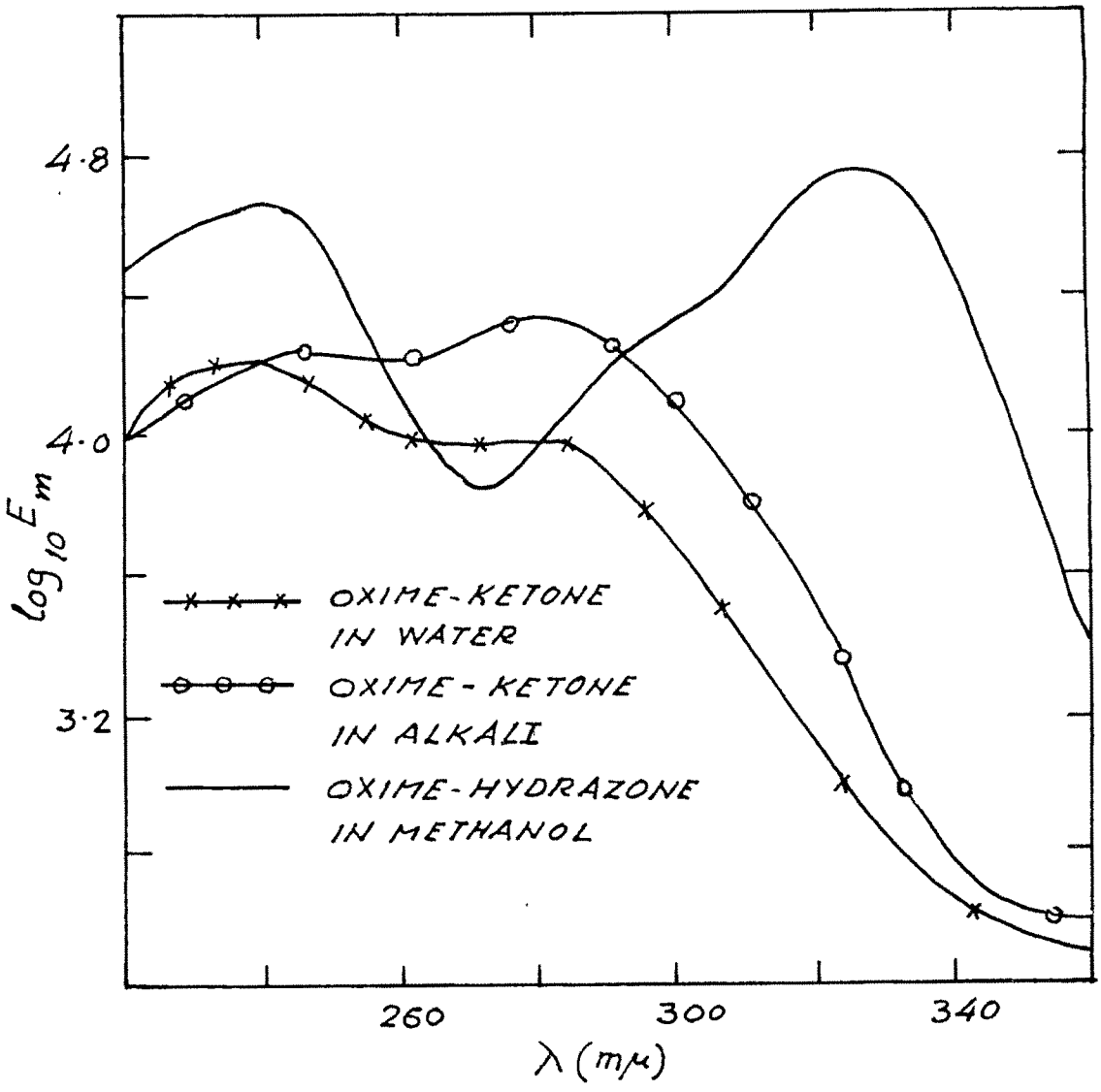


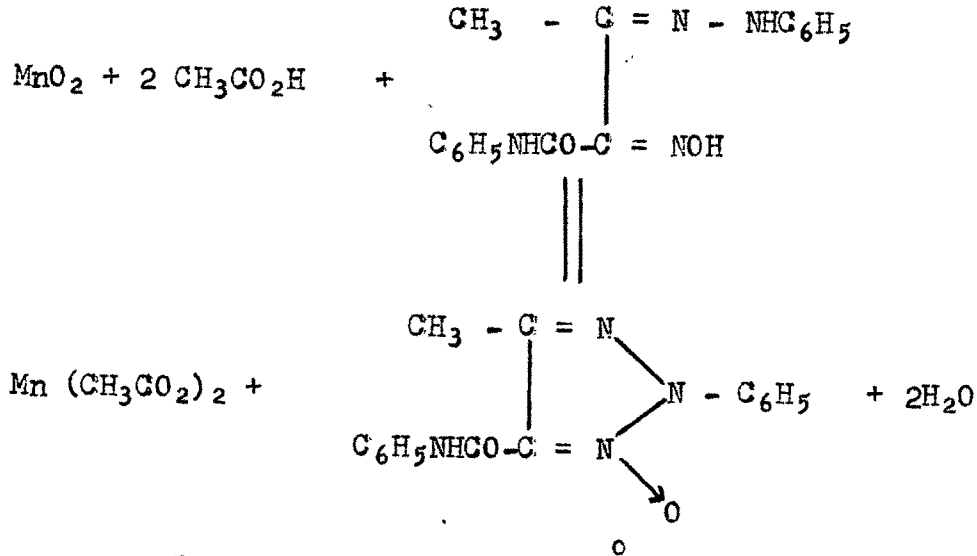
FIG. 1 ULTRAVIOLET ABSORPTION SPECTRA OF 2,3-DIOXOBUTYRANILIDE 2-OXIME (OXIME-KETONE) AND ITS PHENYL HYDRAZONE.

The structure of the product is in agreement with its analysis. It is acidic in character and gives effervescence with sodium bicarbonate. It was also prepared from its anilide derivative as will be referred to below in 1 (c).

The ultra-violet absorption spectra of the compound in methanolic and alkali solutions are presented in fig. 2. It has an absorption band at 266-68 mμ (or 268-70 mμ) in solution. The three-band structure of the spectrum of the oxime-hydrazone has changed to a one-band structure of the spectrum for the product.

1 (c). Oxidation with manganese dioxide :

The oxime-hydrazone was oxidised with manganese dioxide in presence of acetic acid. The overall reaction is represented as follows :



The product melts at 137°. It has been identified by Desai[76] as the oxy-triazole derivative. The product on alkaline hydrolysis produces the acid

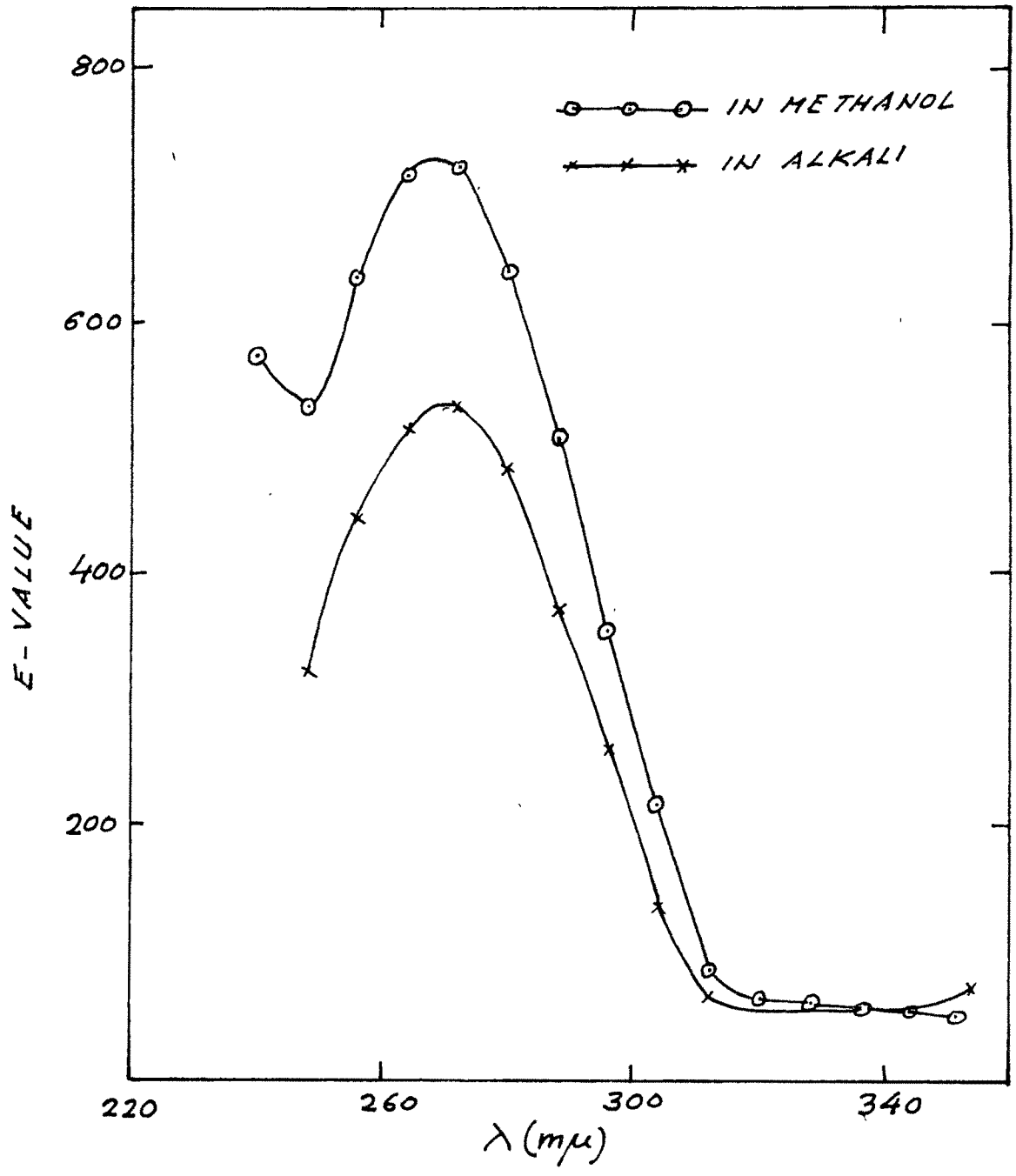
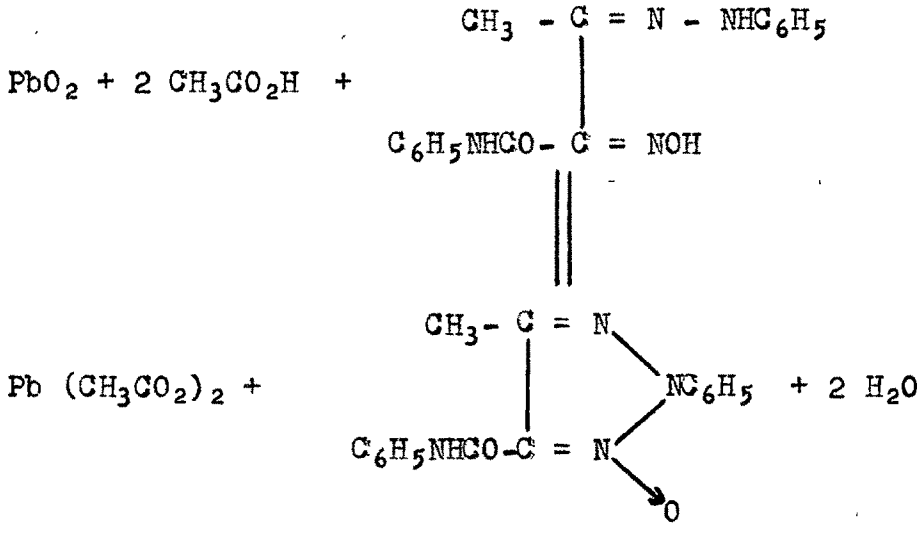


FIG. 2 UV ABSORPTION SPECTRA OF THE OXY-TRIAZOLE - CARBOXYLIC ACID DERIVATIVE

derivative melting at 94°. Its mixed m.pt. with the product obtained in 1(b) is not lowered.

1 (d). Oxidation with lead dioxide :

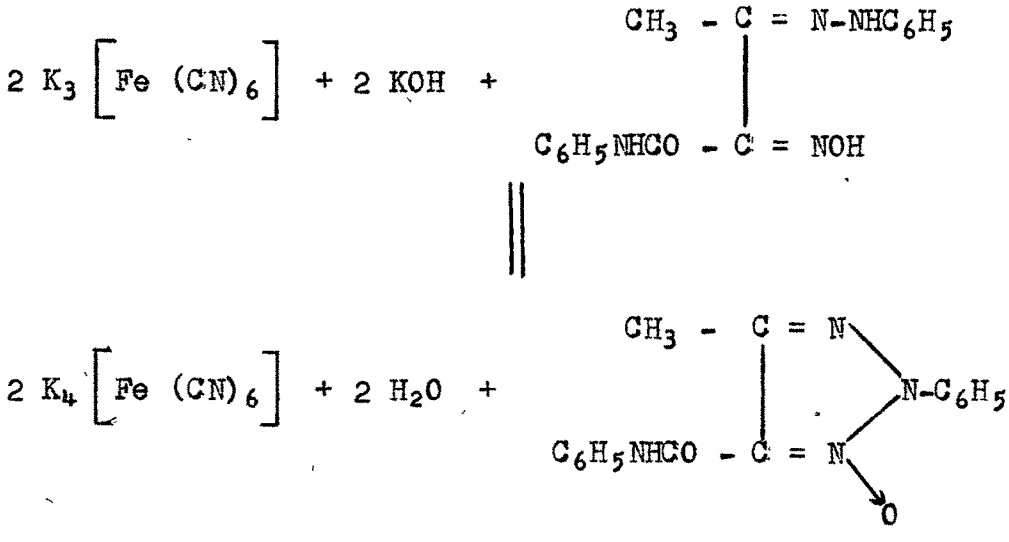
The oxime-hydrazone was oxidised by lead dioxide in presence of acetic acid. The overall reaction is represented as follows :



The product is identical with the one obtained in the oxidation with manganese dioxide.

1 (e). Oxidation with potassium ferricyanide :

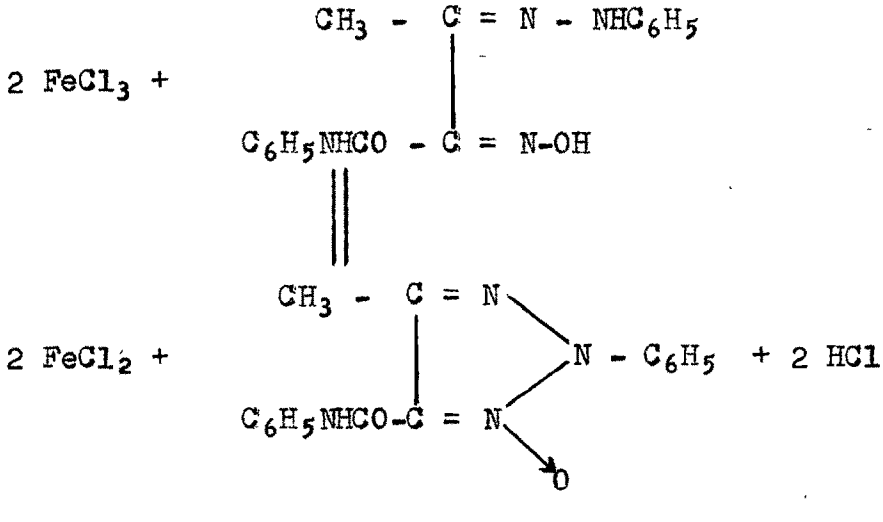
The oxime-hydrazone was oxidised with potassium ferricyanide in presence of alkali. The overall reaction can be represented as follows :



The product is identical with the one obtained in 1 (d).

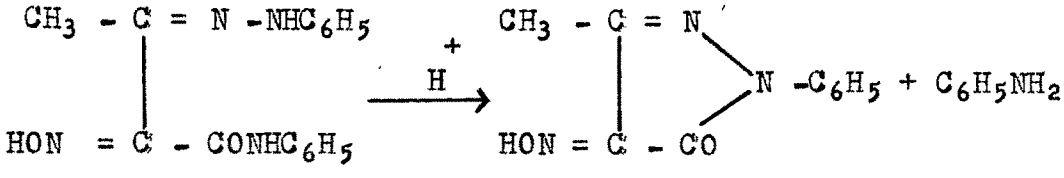
1 (f). Oxidation with iron(III) chloride :

The oxime-hydrazone was oxidised with iron(III) chloride in presence of hydrochloric acid. The oxidation reaction is presented as follows :



Besides oxidation, the oxime-hydrazone also undergoes condensation. Both reactions take place

simultaneously. The other product which is isolated from the filtrate melts at 157° and is formulated as N-phenyl 3-methyl 4-isonitroso pyrazol-5-one, on the basis of reaction and properties. Its formation can be represented as follows :



The condensation reaction is facilitated by hydrochloric acid.

The ultra-violet absorption spectra of the product in methanolic and alkali solutions are presented in fig. 3. It has absorption bands at 248-50 mμ and 304-8 mμ in methanol and at 252 mμ and 302-4 mμ in alkali solution. The three-band spectrum of the oxime-hydrazone is converted into a two-band spectrum for the oxime-pyrazolone. It is comparable to a two-band spectrum of the oxime-ketone.

1 (g). Oxidation with copper sulphate :

The oxime-hydrazone was oxidised by copper sulphate. The solvent selected after various experiments was aqueous iso-propyl alcohol. The product was the same as obtained by Desai[76] (same as in 1-c).

1 (h). Oxidation with lead tetra-acetate :

The oxime-hydrazone was oxidised by lead tetra-acetate in presence of acetic acid. The overall reaction is represented as follows :

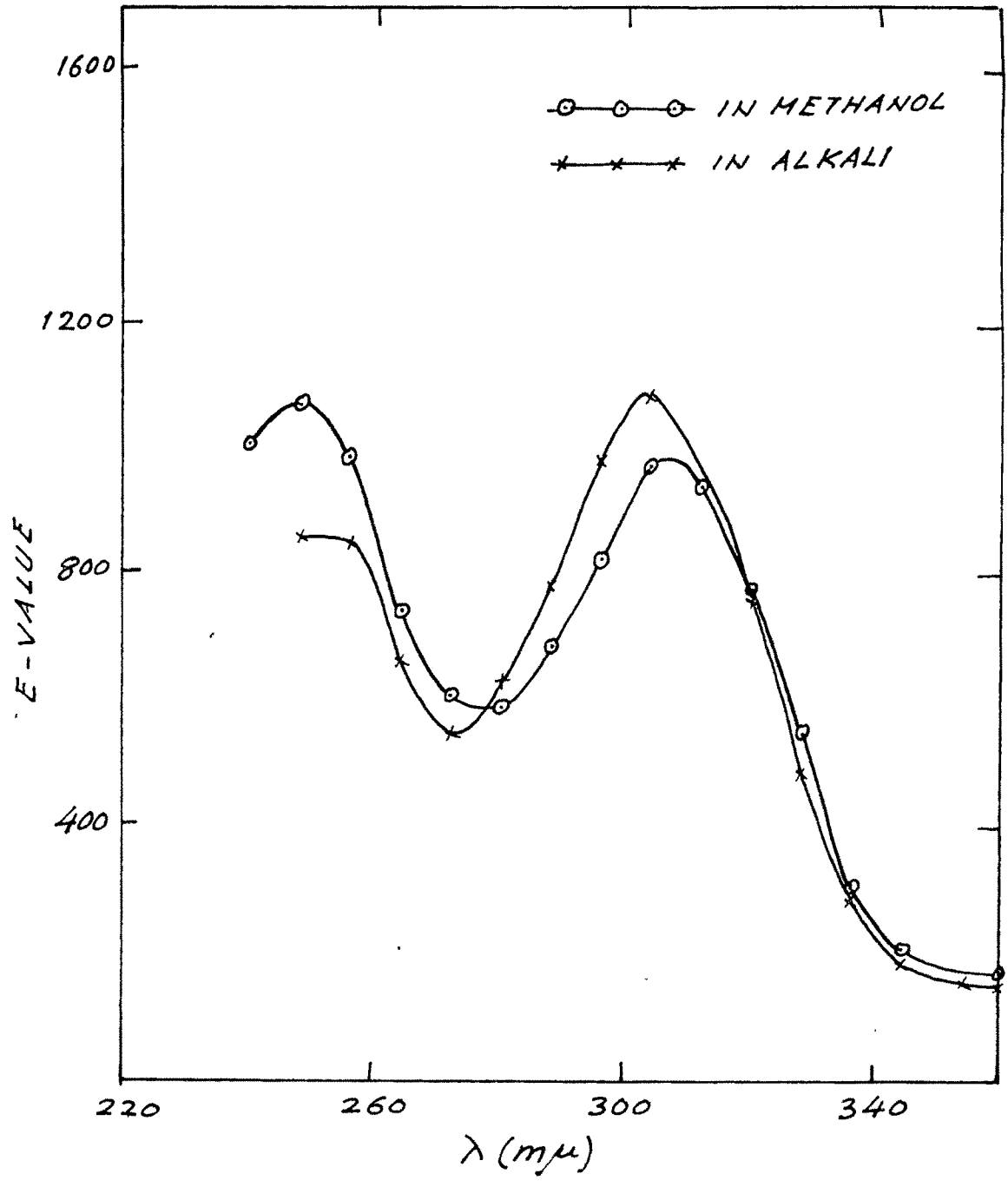
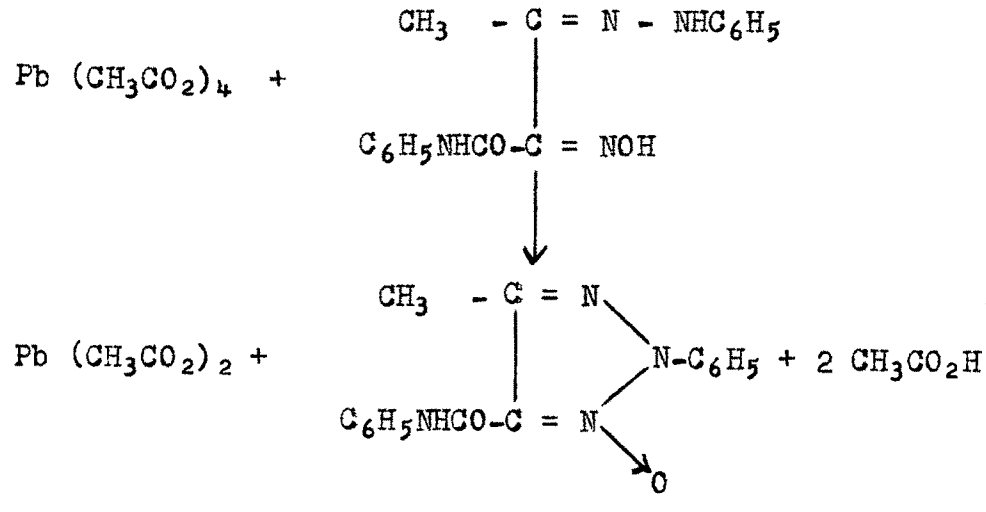


FIG. 3 UV ABSORPTION SPECTRA OF THE 4-ISONITROSO PYRAZOL-5-ONE DERIVATIVE



The product is the same as obtained in 1 (c).

1 (i) Oxidation with potassium dichromate :

Oxidation of the oxime-hydrazone was attempted with potassium dichromate. The reaction was very vigorous and a gummy mass was obtained. No definite compound was isolated from it.

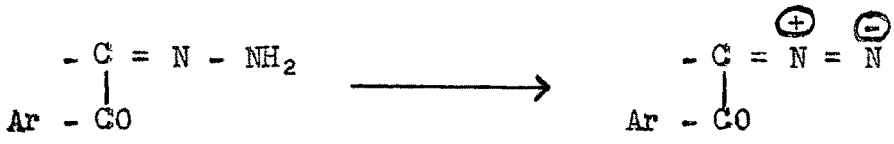
1 (j) Oxidation with other oxidising agents :

Attempts were made to oxidise the oxime-hydrazone with (i) hydrogen peroxide under alkaline conditions and (ii) per-sulphuric acid. In both the cases, large amounts of the unreacted starting material were recovered.

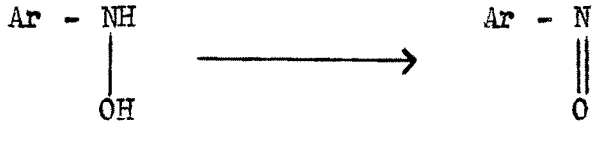
1 (k) Oxidation of the oxime-hydrazone-general :

When the hydrazones are oxidised with mercuric oxide, diazo compounds are obtained.[85]

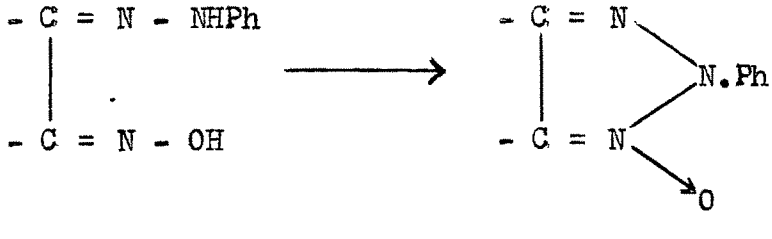
Glyoxal monohydrazones are oxidised by manganese dioxide to diazo ketones.[86]



Further, hydroxyl amines are oxidised by potassium dichromate to nitroso compounds.[85]



Bensen and Savell[74] showed that oxime-hydrazone undergoes oxidation with mercuric oxide or oxides of nitrogen forming triazole oxide.



Desai[76] carried out the oxidation of the phenyl-hydrazone of 2,3-dioxobutyranilide 2-oxime with (a) mercuric oxide and (b) copper sulphate and obtained the same triazole oxide derivative in both cases.

We have obtained the triazole oxide derivative with a number of oxidising agents. The reagents successfully used are lead dioxide, manganese dioxide, potassium permanganate, potassium ferricyanide, iron(III)

chloride, copper sulphate and lead tetra-acetate. The reagents with which the reaction could not be effected are hydrogen peroxide and per-sulphuric acid. And the reagent with which the reaction took place beyond control is potassium dichromate.

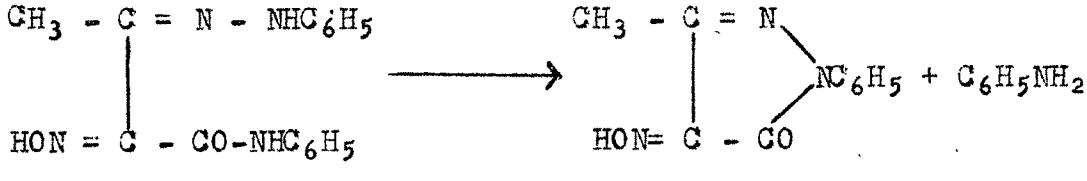
If we compare the relative yield of the product obtained with different oxidising agents, we find that the yield increases in order

$$Cu^{2+} < Pb^{4+} < PbO_2 \sim MnO_2 < Fe^{3+} < \left[Fe(CN)_6\right]^{3-}$$

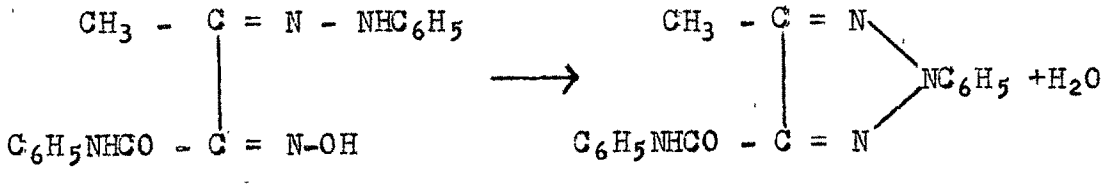
The yield varied from about 20 to 50 %.

We consider that trivalent iron both in the cationic and anionic forms is selective and can be considered suitable for preparative purposes.

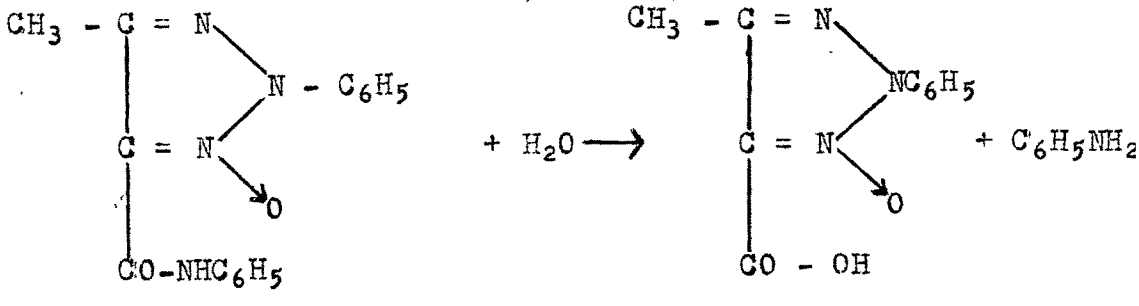
We further, observed that in the presence of hydrochloric acid, the oxime hydrazone undergoes condensation reaction.



The other condensation reaction yielding triazole is considered feasible[74] but could not be confirmed.



The pyrazolone oxime was isolated in the oxidation of the oxime-hydrazone with iron(III) chloride. Hence an attempt was made to study the oxidation by iron (III) chloride in more details. The reaction was carried out at different temperatures. It was found that higher temperatures would be unsuitable because of the formation of gummy mass. A small temperature range of 40-80^{o} was considered suitable. Hence a temperature of 55-60^{o} was adopted for the remaining experiments. The results are shown in fig. 4. We find that the yield of pyrazolone oxime reaches a maximum in 30 minutes and remains so for the remaining period of the experiment. On the other hand the yield of triazole oxide reaches a maximum in 30 minutes and thenafter decreases for another 30 minutes. It is curious to observe that if the reaction is continued further the yield once again increases. The decrease in the yield can be attributed to the dissolution of the precipitate resulting from the hydrolysis of the anilide.



However, to explain the subsequent slow increase in the yield, one has to assume various possibilities :

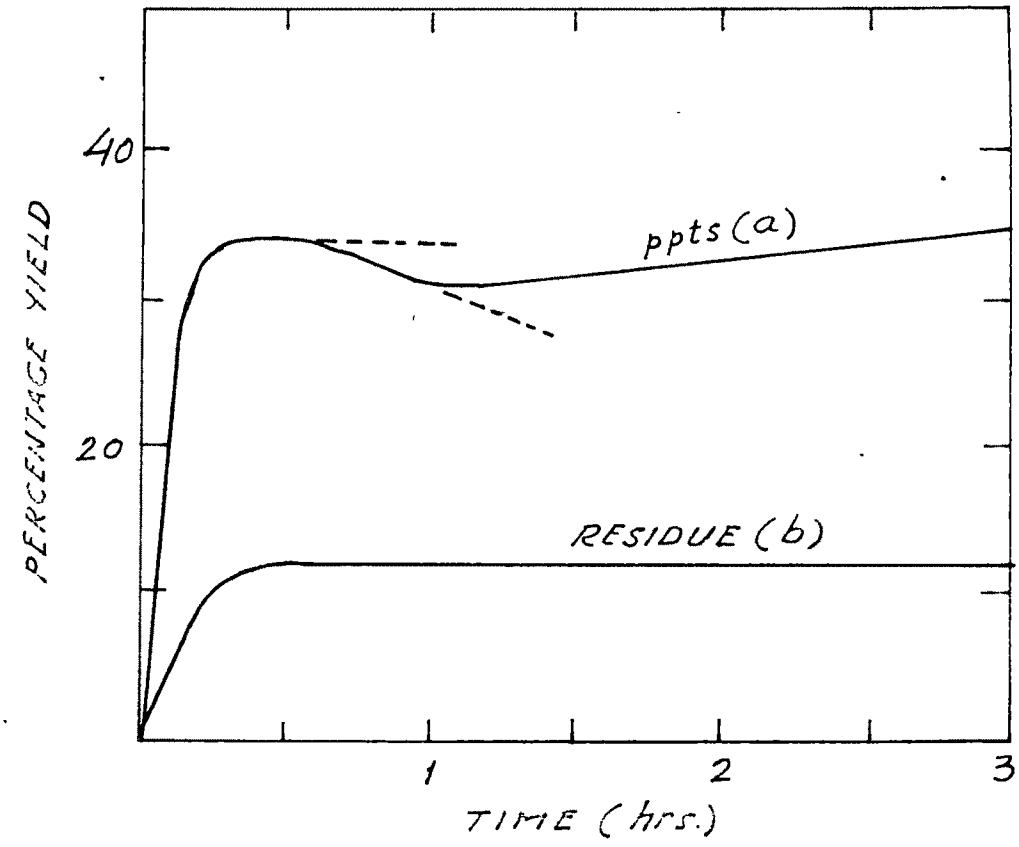


FIG.4 KINETIC STUDIES OF THE REACTION BETWEEN OXIME-HYDRAZONE, IRON (III) CHLORIDE AND HYDROCHLORIC ACID.

(i) Oxygen of the atmosphere surrounding the solution may assist in the oxidation of the oxime-hydrazone ;

(ii) Oxygen of the atmosphere may help in the oxidation of the reduced product ;

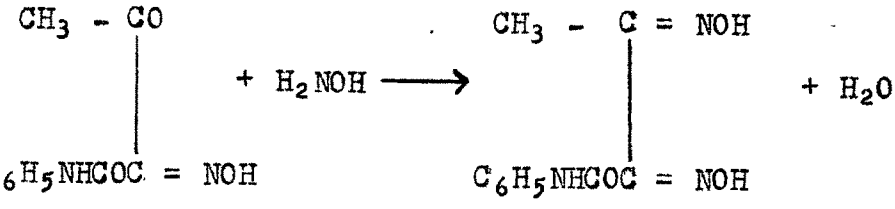
(iii) Aniline formed in the other reaction may lead to the mass effect and favour the reverse reaction.

The complex nature of the reaction can be resolved by further investigations.

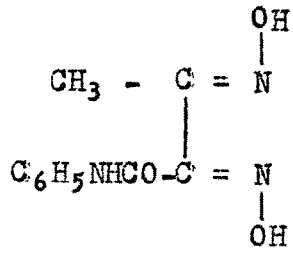
III. 2. vic-Dioxime and its oxidation :

2(a). vic-Dioxime :

The dioxime of 2,3-dioxobutyranilide was prepared from 2,3-dioxobutyranilide 2-oxime by the action of hydroxylamine as follows :



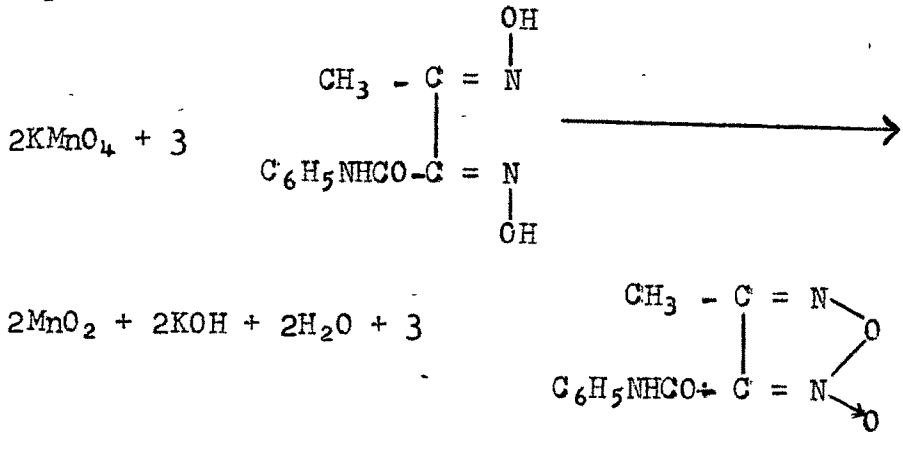
Talati[75] attributed anti-dioxime structure (III) to it.



(III)

2(b). Oxidation with potassium permanganate :

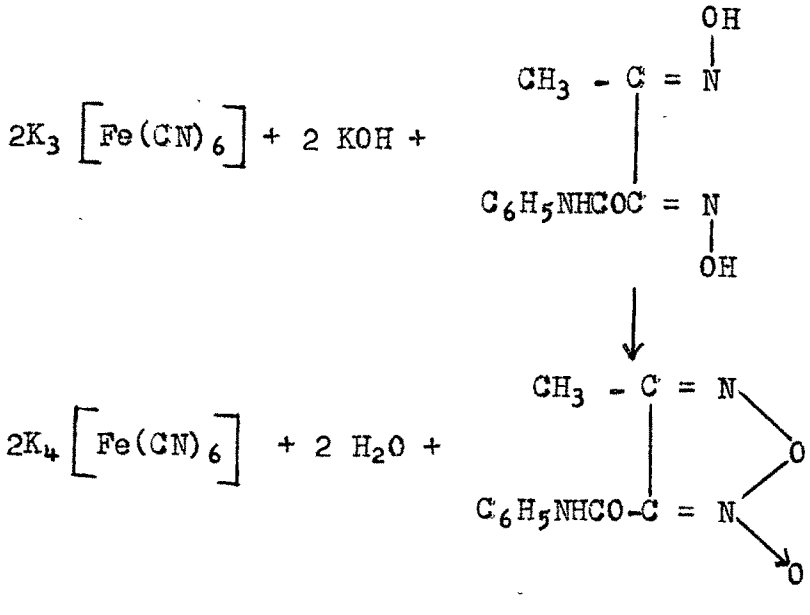
The dioxime was oxidised by potassium permanganate under alkaline conditions. The overall reaction can be represented as



The structure of the compound is in agreement with its analysis. The ultra-violet absorption spectra of the compound in methanolic, acidic and alkali solutions are presented in fig. 5. It has an absorption band at 278 mμ, 278 mμ and 271 mμ in methanolic, acidic and alkali solutions respectively. The spectrum has a one-band structure.

2(c) Oxidation with potassium ferricyanide :

The dioxime was oxidised by potassium ferricyanide under alkaline conditions as represented below



The product is identical with the one obtained in 2(b).

2(d) Oxidation with iron(III) chloride :

The dioxime was oxidised by iron (III) chloride in presence of hydrochloric acid as follows :

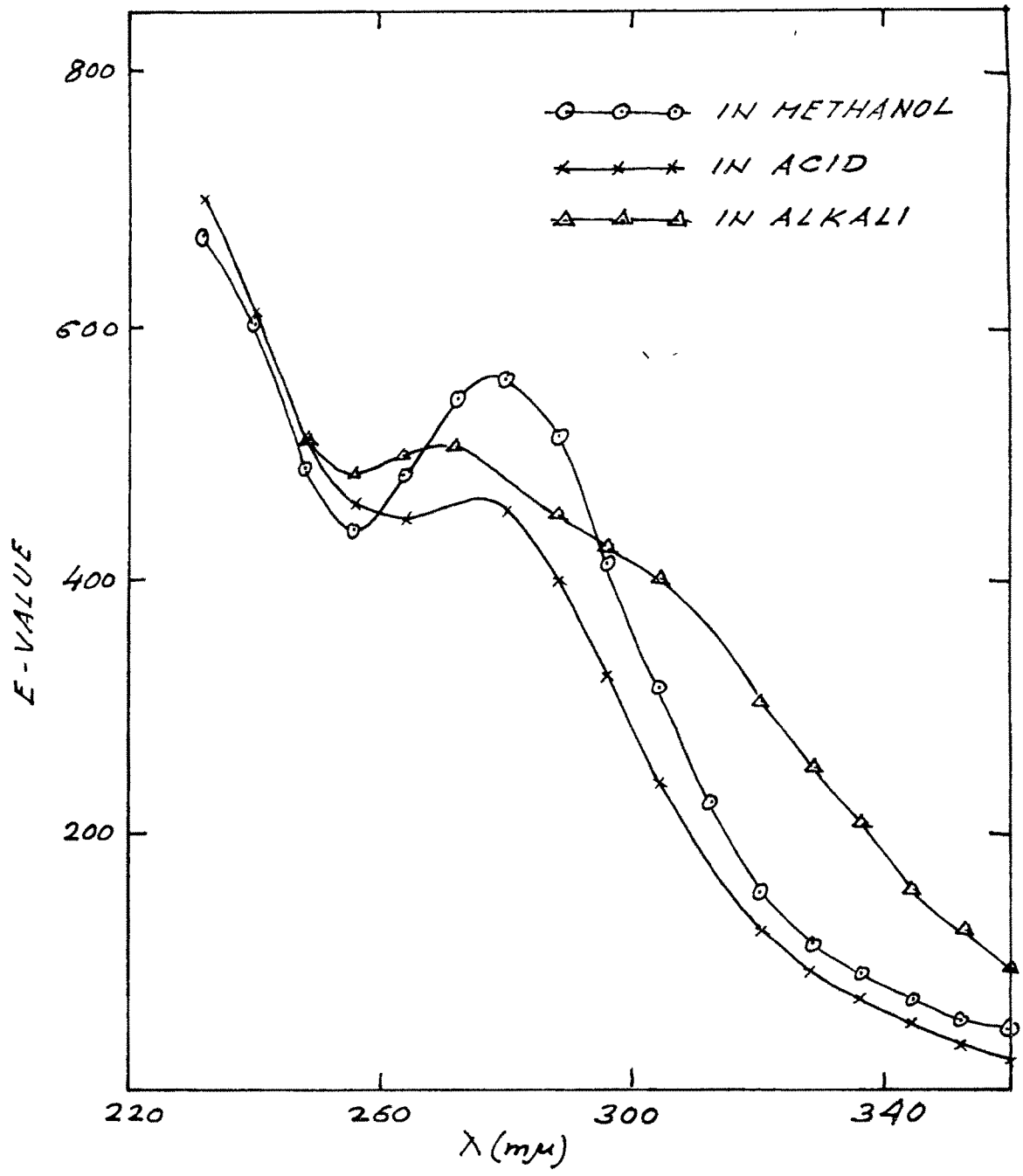
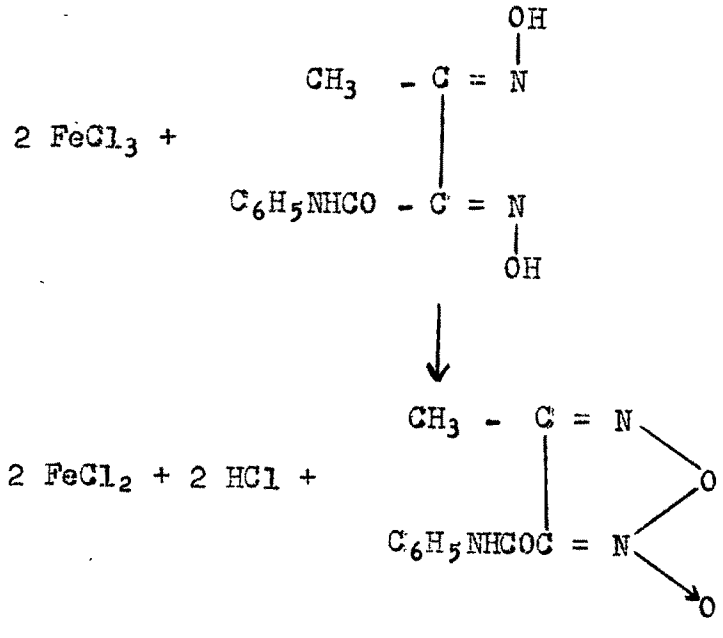


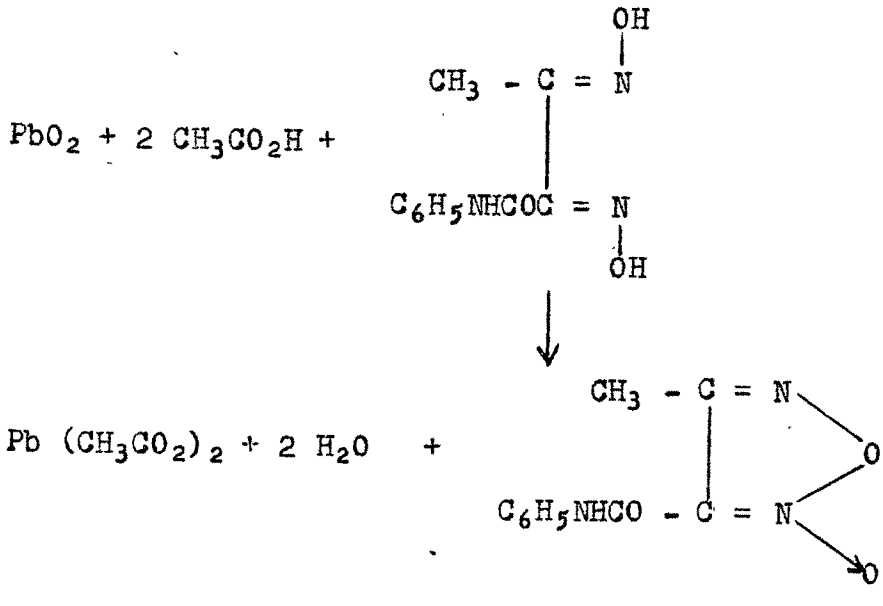
FIG. 5 UV ABSORPTION SPECTRA OF THE FUROXAN DERIVATIVE



The product is identical with the one obtained in 2(b).

2(e) <u>Oxidation with lead dioxide</u> :

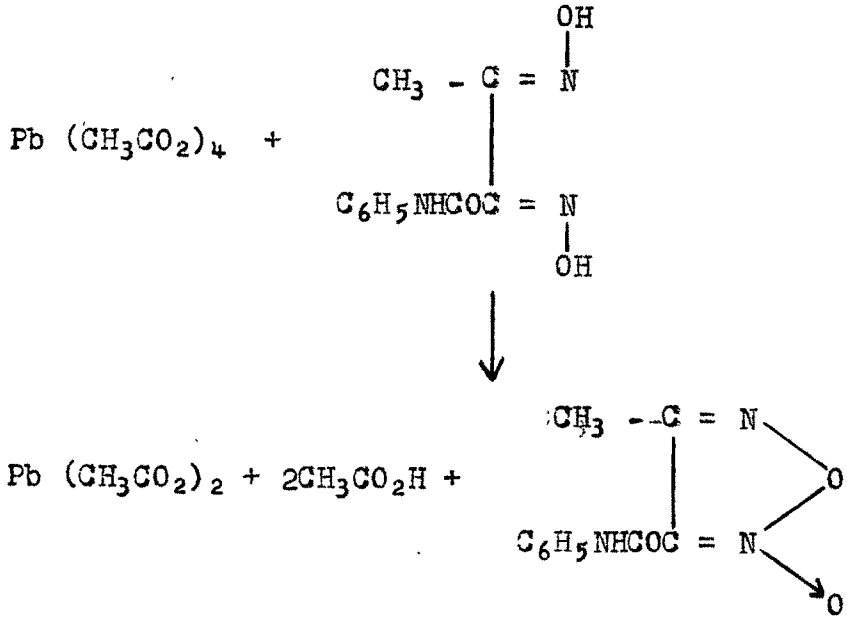
The dioxime was oxidised by lead dioxide in presence of acetic acid as follows :



The product is the same as obtained in 2 (b).

2(f) Oxidation with lead tetra-acetate :

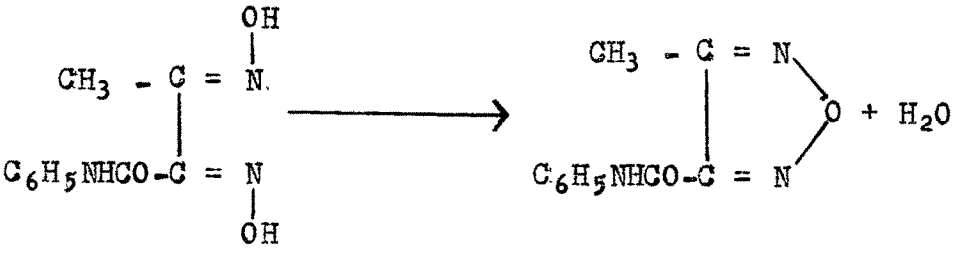
The dioxime was oxidised by lead tetra-acetate in presence of acetic acid as follows :



The product is the same as obtained in 2 (b).

2(g) Oxidation with red lead and acetic acid :

Oxidation product of the dioxime with red lead could not be obtained ; instead only a condensation product was obtained as represented below :



The structure of the product is in agreement with its analysis. The ultraviolet absorption spectra of the compound in methanol, acid and alkali are presented in fig. 6. It has an absorption band at 270-72 mμ with a shoulder at 330 mμ in methanolic solution. It has an absorption band at 270-72 mμ in alkali solution but no band in acid solution. Thus the spectrum is considerably affected by the pH of the solution.

2(h) Oxidation with manganese dioxide :

Oxidation of the dioxime was attempted with manganese dioxide ; only original substance was obtained.

2(i) Oxidation with chlorine, sodium hypochlorite, bleaching powder or per-sulphuric acid :

Oxidation of the dioxime by chlorine, sodium hypochlorite, bleaching powder or per-sulphuric acid led to the formation of a (gummy) mass from which no product could be isolated.

2(j) Oxidation with potassium dichromate :

When the dioxime was oxidised with potassium dichromate in presence of alkali or acetic acid, the original substance was recovered ; however, when the oxidation was carried out in presence of sulphuric acid, gummy mass was obtained.

2(k) Oxidation of the dioxime-general :

The glyoxime is known to be oxidised to furoxan by various oxidising agents[66,67,68], such as potassium

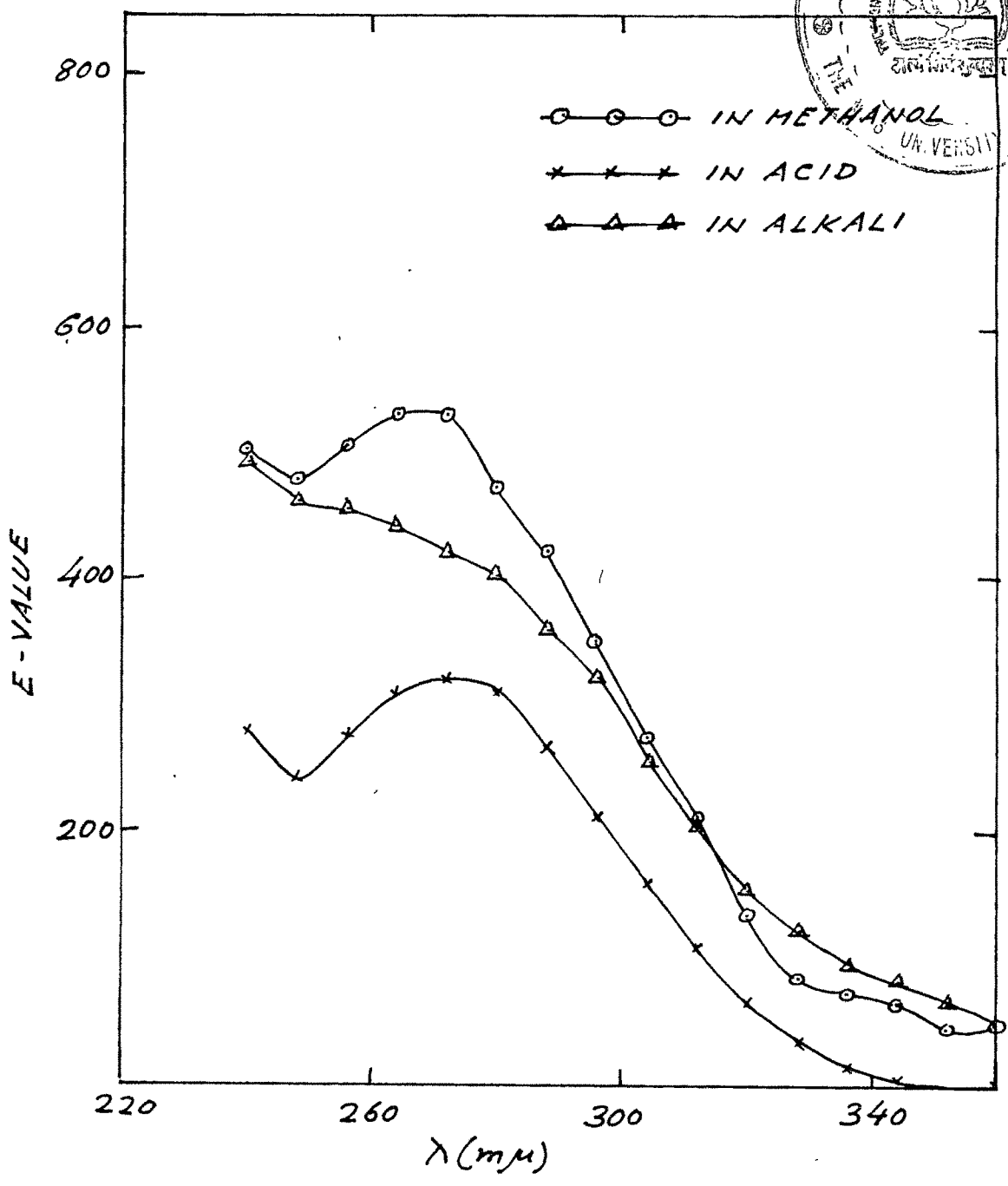


FIG. 6 UV ABSORPTION SPECTRA OF THE FURAZAN DERIVATIVE

ferricyanide, halogens etc. and to furazan by condensing agents such as acetic anhydride,[85] alkali[86] etc.

Ponzio[87] found that the dioxime of 2,3-dioxo-butyranilide is oxidised to furoxan derivative, melting at 150°. We have oxidised the dioxime of 2,3-dioxo-butyranilide to its furoxan derivative melting at 149° by various oxidising agents. The reagents with which oxidation can be successfully carried out are potassium ferricyanide, potassium permanganate, lead dioxide, lead tetra-acetate, iron(III) chloride. The reagents with which the reaction could not be effected were manganese dioxide, potassium dichromate under alkaline, neutral and acetic acid conditions. Gummy mass was obtained with chlorine, sodium hypochlorite, bleaching powder (in presence of acid) and per-sulphuric acid.

If we compare the relative yield of the product obtained with different oxidising agents, we find that the yield increases in order

$$K_3\left[Fe(CN)_6\right] < PbO_2 < FeCl_3 < KMnO_4 \sim Pb(CH_3CO_2)_4$$

The yield varied from 20 to 60 % .

The results show that lead tetra-acetate and alkaline potassium permanganate can be considered more suitable for the oxidation of the dioxime to furoxan.

We attempted to oxidise the dioxime by red lead.

We could not isolate the product of oxidation. Instead, a small quantity of the condensation product (furazan derivative) was obtained.

Patel, Patel and Mankad[88] obtained the furazan derivative as the condensation product of the dioxime of 2,3-dioxobutyranilide. The furazan derivative prepared by them is identical in analysis and ultra-violet absorption spectra to the one prepared by us.

- X - - X - - X -

It may be noted here that a paper has appeared in the January,1971 issue of the Journal of Organic Chemistry wherein Burkevich[89] studied the oxidation of the glyoxime to furazan oxide.

REFERENCES

(OXIDATION)

REFERENCES

1. Eastman and Quinn, J.Am.Chem.Soc., 82, 4249 (1960).
2. Wiberg and Fox, ibid., 85, 3487 (1963).
3. Kwart and Null, ibid., 82, 2348 (1960).
4. Wiberg and Foster, ibid., 83, 423 (1961).
5. Sagar and Bradley, ibid., 78, 1187 (1956).
6. Wiberg and Evans, Tetrahedron., 8, 313 (1960).
7. Snyder, J.Chem.Educ., 43, 141 (1966).
8. Lemieux and Von Rudloff, Can.J.Chem., 33, 1701, 1710 (1955).
9. von Rudloff, ibid., 34, 1413 (1956).
10. Crieger, Ann., 522, 75 (1936).
11. Barton and Elad, J.Chem.Soc., 2085 (1956).
12. Oberender and Dixon, J.Org.Chem., 24, 1226 (1959).
13. Djerassi and Engle, J.Am.Chem.Soc., 75, 3838 (1953).
14. Khan and Newman, J.Org.Chem., 17, 1063 (1952).
15. Eglinton and McCrae, Advan.Org.Chem., 4, 225 (1963).
16. Fuson, J.Am.Chem.Soc., 48, 2937 (1926).
17. Linstead and Doering, ibid., 64, 1991 (1942).
18. Schroeter, Ber., B 57, 2003 (1924).
19. Bavin, Can.J.Chem., 38, 911 (1960).
20. Wheeler, ibid., 36, 667, 949 (1958).
21. Gardner, J.Am.Chem.Soc., 49, 1831 (1927).
22. Bokadia, Brown and Cummings, J.Chem.Soc., 3308 (1960).
23. Landen and Simon, Chem.Ind.(London)., 70 (1962).
24. Nonhebel, J.Chem.Soc., 1216 (1963).

25. Ramaswamy, Venkatachalapathy and Udupa, Bull.Chem. Soc. Japan ., 35, 1751 (1962).
Chem.Abstr., 58, 11256 (1968).
26. Berkowitz and Rylander, J.Am.Chem.Soc., 80, 6682 (1958).
27. Wolff, Kerwin, Owings, Lewis and Blank, J.Org.Chem., 28, 2729 (1963).
28. Henbest and Nicholls, J.Chem.Soc., 227 (1959).
29. Harrison and Harrison, Chem.Commun., 752 (1966).
30. Kharasch, Friedlander and Urry, J.Org.Chem., 16, 533 (1951).
31. Westheimer, Chem.Rev., 45, 419 (1949).
32. Rocek, Westheimer, Eshermoser, Moldovanyi and Schrieber, Helv.Chim.Acta., 45, 2554 (1962).
33. Holum, J.Org.Chem., 26, 4814 (1961).
34. Link and Sell, Biochem.Prep., 2, 74 (1953).
35. Dayton, J.Org.Chem., 21, 1535 (1956).
36. Highet and Wildman, J.Am.Chem.Soc., 77, 4399 (1955).
37. Gritter and Wallace, J.Org.Chem., 24, 1051 (1959).
38. Harrison, Proc.Chem.Soc., 110 (1964).
39. Criegee, Kraft and Rank, Ann., 507, 159 (1933).
40. Optiz and Urbanski, Ger.Pat., 1097969.
Chem.Abstr., 55, 25757 (1961).
41. Heyns and Stockel, Ann., 558, 192 (1947).
42. Ridby, J.Chem.Soc., 793 (1951).
43. Little and Waters, ibid., 1299, 4046 (1959).
44. Hintz and Johnson, J.Org.Chem., 32, 556 (1967).
45. Criegee, Ber., 64, 260 (1931).
46. Malaprade, Compt.Rend., 186, 382 (1928).

47. Fleury and Langè, ibid., 195, 1395 (1932).

48. Hurd, Garrett and Osborne, J.Am.Chem.Soc., 55, 1082 (1933).

49. Wiberg and Stewart, ibid., 77, 1786 (1955).

50. Conant and Aston, ibid., 50, 2783 (1928).

51. Barakat, Abdel-Wahab and El-Sadr, J.Chem.Soc., 4685 (1956).

52. Mihailovic et al., Tetrahedron., 21, 1395 (1965).

53. Riehl, Compt.rend., 250, 4174 (1960).

54. Riley, Morley and Friend, J.Chem.Soc., 1875 (1932).

55. Hatt, Pilgrim and Hurran, ibid., 93 (1936).

56. Mares, Rocek and Sicher, Collection Czech.Commun., 26, 2355 (1961).

57. Cavill and Solomon, J.Chem.Soc., 4426 (1955).

58. Pelletier and Jacobs, J.Am.Chem.Soc., 76, 4496 (1954).

59. Hight and Wildman, ibid., 77, 4399 (1935).

60. Henbest and Thomas, J.Chem.Soc., 3132 (1957).

61. Mihailovis et al., Tetrahedron letters., 461 (1965).

62. Leonard et al., J.Am.Chem.Soc., 77, 1552 (1955).

63. Bradley and Lute, J.Chem.Soc., 2129, 2147 (1951).

64. Shechter, Rawalay and Tubis, J.Am.Chem.Soc., 86, 1701 (1964).

65. Shechter and Rawalay, ibid., 86, 1706 (1964).

66. Boyer and Toggweiler, ibid., 79, 295 (1957).

67. Koreff, Ber., 19, 176 (1886).

68. Borsche, ibid., 40, 737 (1907).

69. Beckmann, ibid., 22, 1501, 1588 (1889).

70. Scholl, ibid., 21, 506 (1888).

71. Ponzio, Gazz.Chim.ital., 66, 119 (1936).

72. Milone, ibid., 59, 257 (1929).

73. Hann and Hudson, J.Am.Chem.Soc., 66, 735 (1944).

74. Benson and Savell, Chem.Rev., 46, 1 (1950).

75. Talati, Ph.D.thesis, M.S.University of Baroda(1958).

76. Desai, Ph.D.thesis, M.S.University of Baroda(1965).

77. Patel, Ph.D.thesis, M.S.University of Baroda (1965).

78. Kapadia, Ph.D.thesis, M.S.University of Baroda(1970).

79. Shah, Ph.D.thesis, M.S.University of Baroda (submitted).

80. Knorr, Ann., 236, 80 (1887).

81. Dave and Talati, J.Indian Chem.Soc., 37, 578 (1960).

82. Knorr and Reuter, Ber., 27, 1170 (1894).

83. Shirley, Preparation of organic intermediates, John Wiley and Sons. (1951). p. 187.

84. Taylor, J.Chem.Soc.Japan., 74, 153 (1953) ;
76, 1007 (1955).

85. March, Advanced Organic Chemistry, McGraw Hill Co. (1968). p. 867.

86. Hauptmann, Kluge, Seidig and Wilde, Angew.Chem.Intern Ed. 4, 688 (1965).

87. Ponzio, Gazz.chim.ital., 66, 819-26 (1936).

88. Patel, Patel and Mankad, Indian J.Chem., 5, 545 (1967).

89. Burkevich, J.Org.Chem., 36, 5 (1971).