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REACTIONS OF α-HYDROXYIMINO DERIVATIVES OF CARBONYL COMPOUNDS WITH BASES—I

DERIVATIVES OF α,β-DIHYDROXYIMINO-BUTYRIC ACID*

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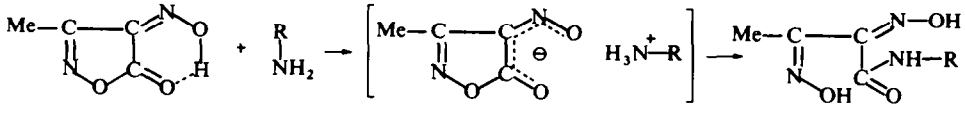
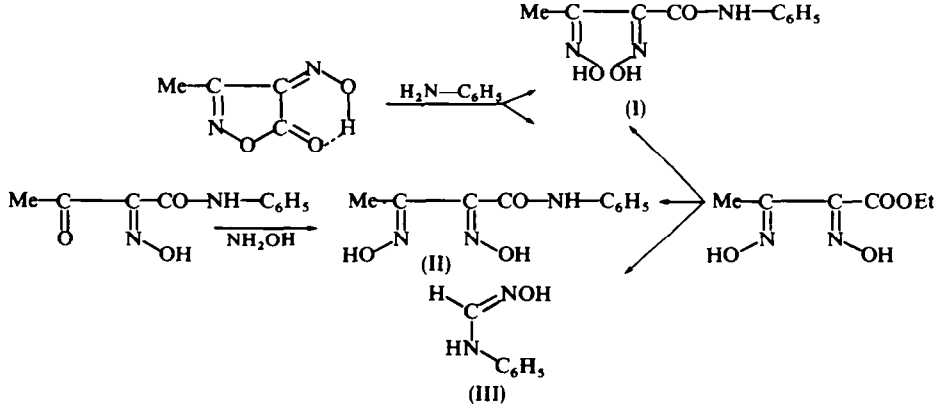
Abstract—The reaction between 3-methyl-4-hydroxyiminoisoxazolin-5-one and amines or hydrazides affords amides and hydrazides of α,β-dihydroxyiminobutyric acid respectively. In the reaction with aromatic amines, an isomeric pair of dioximes is produced, to which *syn* and *anti* configurations have been attributed.

THE products obtained from the action of nucleophilic reagents on 3-methyl-4-hydroxyimino-isoxazolin-5-one[1] have been studied; they are the derivatives of α,β-dihydroxyiminobutyric acid. It was, however, interesting to ascertain which of



the four possible configurations could be ascribed to these dioximes, since in the reaction with aromatic amines (aniline, *o*-toluidine, *o*-chloroaniline) two isomers were obtained. In the case of aniline, the m.ps of the products were 144° (I) and 185° (II); the latter, obtained in about one tenth of the yield of I, is identical with the product obtained by treating α-hydroxyimino-β-oxobutyranilide with hydroxylamine.[2] This product also results from the reaction between aniline and ethyl α,β-dihydroxy-iminobutyrate,[1] together with N-phenylformydroxamamide (III), which is the main product, and a small quantity of I.



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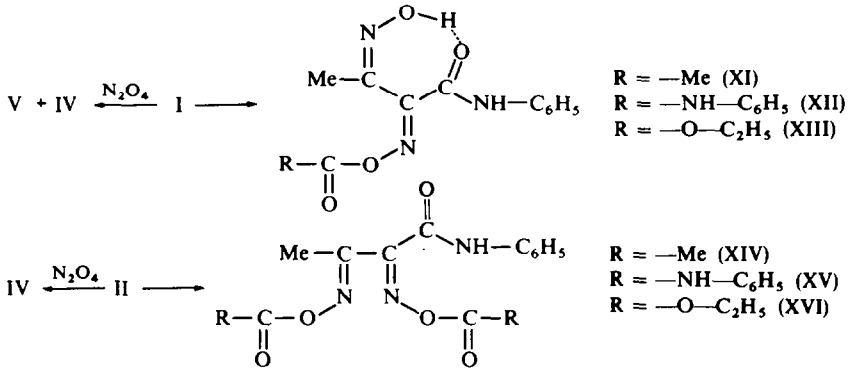
Based on the following results and observations, we may conclude that α,β-dihydroxyiminobutyranilide (I) has the *syn* and isomer II the *anti* structure.

The dioxime I does not give salts with metals: this is generally accepted in the literature as indicating a *syn* configuration.[3] This hypothesis is confirmed by the fact that an isomeric pair of furoxans (IV and V) are obtained when I is treated with nitrogen tetroxide. Although this is a property of *syn* and *anti* dioximes,[4,5] the *anti* structure cannot be taken into consideration because the product does not complex metals. Furthermore, the UV spectrum (λ_{max} 210, ε = 23,000; λ_{max} 274, ε = 7000) differs greatly from that of other aliphatic dioximes believed to be *anti* (λ_{max} around 230–240 mμ).[6]

The *syn* form is uncommon in the aliphatic series, but evidently it is stabilized in the *syn*-s-*trans* conformation by an hydrogen bond between the CO group and the hydroxyimino group in the position β to it. The s-*trans* structure favours the formation of a pseudocycle, which can explain the UV max at 274 mμ, as well as the tendency of the products of this series to recyclize.

It is known[7] that dioxime II forms a complex with nickel, in the ratio of 2:1, and therefore a compound analogous to Ni *anti*-dimethylglyoxime chelate was formulated. We have ascertained that, by removing the metal from the dilute hydrochloric acid solution of the chelate, the starting dioxime is recovered. Its UV spectrum is similar to that of *anti* dioximes (λ_{max} 239, ε = 24,000). In the reaction with N_2O_4, the dioxime II produces a single furoxan, identical with IV. This is contrary to Meisenheimer's theory, but other cases of *anti* dioximes providing a single furoxan can be found in the literature.[8]

In the reaction with OH-reagents, I gives mono derivatives, while II affords diacyl compounds. Jovtscheff *et al.*[9] have reported that *syn* ethyl α-hydroxyiminophenylpropionate, unlike the *anti* isomer, does not react with phenyl isocyanate owing to the hydrogen bond. Our results do not, as it appears, contradict this, because the hydroxyimino group held by an hydrogen bond in I is in the β position. The monoacyl derivatives should then be esters of the =NOH in α position, a hypothesis further supported by the UV max, around 273–281 mμ, of compounds XI, XII, XIII. Evidently, in dioxime II and in ethyl α,β-dihydroxyiminobutyrate, which also gives diacyl derivatives and whose *anti* structure will be discussed later, the strength of the hydrogen bond between the CO and the α=NOH is not sufficient to prevent the reaction. Thus, Jovtscheff's finding for the α-isonitroso esters cannot be applied to the α,β-dihydroxyimino derivatives of esters and amides.



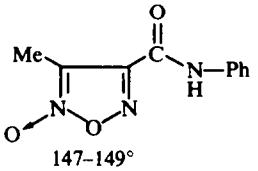
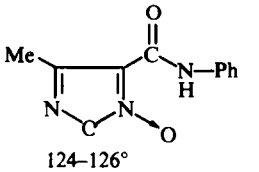
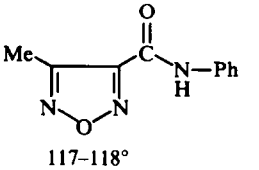
NMR spectra have also been recorded for the dioximes but, although they provide some supporting evidence of the structures, it has not been possible to ascertain the strength of the hydrogen bond, the spectra having been made in DMSO since the substances are insoluble in other suitable solvents.

Reactions with *o*-chloroaniline and *o*-toluidine are similar in every respect and produce only small quantities of the dioximes noted as having the *anti* configuration,[7] whereas the main product of each appears to have properties corresponding to *syn* α,β-dihydroxyiminobutyranilide.

No traces of *anti* isomers could be found in the reactions with isonicotinoyl-hydrazine and with hexylamine, and the single product obtained had similar physical and chemical characteristics to the anilide I.

As a further result of this investigation, it was possible to ascribe the respective structures to the isomeric furoxans (IV and V). The one with the higher m.p. (see Table 1) was obtained by Ponzio[10] in the Beckmann rearrangement of the oxime of 3-methyl-4-benzoyl-furoxan,[11] but its structure was not specified. The author postulated

TABLE 1. DATA FOR FUROXANS IV and V AND FURAZAN VI

	IV	V	VI
			
M.p.	147–149°	124–126°	117–118°
R_f(TLC SiO_2–benzene)	0·59	0·68	0·70
δ_{Me} ($CDCl_3$)	2·44	2·65	2·63
δ_{NH} ($CDCl_3$)	8·52	9·54	8·66
ν_{NH} ($CHCl_3$)	3400	3320	3410
ν_{CO} ($CHCl_3$)	1703	1695	1703
UV (EtOH)	233 (10,500)	232·5 (12,500)	223 (7920)
λ_{max} mμ (ε)	282 (9800)	262 (7500)	274 (4980)

structure IV instead of that which we can now attribute on the basis of a direct comparison of the chemical and physical properties (especially the NMR spectra) of both furoxans and of the corresponding furazan (VI), which we prepared by reducing V. From the data in Table 1, the structure of 3-methyl-furoxan(2)-4-carboxy-anilide can be assigned to IV and that of 3-methylfuroxan(5)-4-carboxyanilide to V. In fact, the NMR and IR spectra indicate that the NH in V is more closely bound than in IV or in VI, because an intramolecular hydrogen bond is possible; the position of the NH-signal and of the IR band of the NH are almost identical for both IV and VI. The UV spectra show that the conjugation between furoxan and anilide chromophores is weaker in V than in IV and therefore the latter can assume an extended and flattened conformation. An analysis of the NMR spectra has confirmed that the N → O group has a long-range shielding effect on the protons of the Me group, as was recently noted[12] in the case of 3,4-dimethylfuroxan, based on the studies of methylazoxy-compounds.[13]

We have tried to reduce furoxans IV and V to dioximes with the aim of preparing *amphi* dioximes, which—by exclusion—would provide additional confirmation of the structures of I and II. Although the reduction of IV occurs very rapidly, the product formed is not the required dioxime but 2,5-dimethyldihydropirazine-3,6-dicarboxyanilide[14] obtained by reducing α-isonitroso-acetoacetanilide.[15] On the other hand, it has been possible to isolate furazan VI by reduction of isomer V under similar conditions.

As small amounts of dioximes I and II are obtained together with III, by warming aniline with ethyl α,β-dihydroxyiminobutyrate, we were interested to know the structure of the starting ester, but the information available concerning this is somewhat confusing. According to Nussberger,[1a] the product obtained by Ceresole[1b] is the *syn* form, which can be isomerized to an *amphi* form with gaseous HCl in ether. Bouveault *et al.*[16] deny the existence of the *amphi* isomer, affirming that it is the result of cyclization and that there was but one isomeric ethyl α,β-dihydroxyimino-butyrate to which, however, they assigned no structure.

On repeating Nussberger and Bouveault's experiments, we also only obtained 3-methyl-4-hydroxyiminoisoxazolin-5-one. Since the dioxime in question is obtained from ethyl α-isonitrosoacetoacetate, for which Taylor[17] established that the =NOH is *anti* to the ketonic CO, the further reaction with hydroxylamine, under non-isomerizing conditions, may give rise to an *amphi* or *anti* dioxime. Consequently, it may be assumed that the structure of the product is *anti*. It, in fact, forms a dark red nickel complex (with a 2:1 ratio), soluble in organic solvents.[18] The ester-dioxime has an IR spectrum in which a single band for the two $\rangle C{=}N-$ groups may be noted and its UV spectrum is very similar to that of the dioximes for which the *anti* form has been ascertained. All these properties agree with those of Ungnade *et al.*[6] and earlier authors,[3] when determining the *anti* structure of dioximes. Moreover, from the ester and from its diacetyl derivative, it is possible to obtain both 3-methyl-4-hydroxyiminoisoxazolinone and α,β-dihydroxyiminobutyric acid,[1a] which means that no decarboxylation and dehydration to nitrile occurs; which would be contrary for *anti*-carboxyl oximes.[19] A dicarbamate XIX is produced with phenyl isocyanate and a bis-(ethyl carbonate) XX with ethyl chlorocarbonate: thus the ester-dioxime behaves like II.

In the reaction of the ester with aniline, isomerization is thus necessary for the formation of I, but this should not be surprising, since the reaction takes place at 90–95° with excess aniline, which is often used as an isomerizing agent for oximes,[20] while high temperatures also have the same effect.[21] Finally the *anti*-structure of the β-hydroxyimino group is not in contrast with the facility with which the ester cyclizes to isoxazolinone, as this cyclization is known to occur even with a *trans* elimination.[22] On the other hand, under the reaction conditions, the intermediate step may well be the transposition. The production of N-phenylformydroxamamide,[23] as a result of the reaction between ester and aniline, and its extension to other dioximes and amines will form the subject of a future paper.

EXPERIMENTAL

M.ps are uncorrected. NMR spectra were determined at 60-Mc on a Varian A-60 spectrometer, with TMS as internal standard. UV spectra were recorded on a Unicam model SP 800 spectrophotometer and IR spectra on a Unicam model SP 200. Microanalyses were performed by Dr. G. Valentini.

3-Methyl-4-hydroxyiminoisoxazolin-5-one

Although this product has been prepared,[1] the following method, gives better yields.

To a soln of 3-methyl-2-isoxazolin-5-one[2a] (12·5 g) in 2N HCl (60 ml), 10·8 g $NaNO_2$ were added slowly with stirring and cooling. After about ½ hr a solid separated, which was extracted with ether. After removal of ether, the residue was crystallized from a mixture of ether and pet ether: m.p. 147° (dec). This was identical with a sample prepared according Nussberger.[1a]

General method for the reaction between 3-methyl-4-hydroxyiminoisoxazolin-5-one and bases

The isoxazolinone was dissolved in EtOH and one mole of the base was added at room temp; a red coloration immediately appeared which gradually turned yellow. In some cases an intensely red ppt formed—the salt of isoxazolinone with the amine—which on warming the mixture went into soln. The crystalline product which finally separated was recrystallized from a suitable solvent.

syn *α,β-Dihydroxyiminobutyranilide* (I)

The above reaction, carried out with aniline, gave after a few hr a white crystalline product consisting of I and a small amount of the *anti* isomer II, appearing as a slight yellow ppt with Ni^{+2}. The latter was removed by crystallization from EtOH in which II is much more soluble, yielding I as white shiny plates, m.p. 143–144° (dec). (Found: C, 54·30; H, 5·30; N, 18·86. $C_{10}H_{11}N_3O_3$ requires: C, 54·29; H, 5·01; N, 19·00%); UV: λ_{max}^{EtOH} 210 mμ (ε = 23,000), 274 mμ (ε = 7000). IR (Nujol): ν = 1665 (CO), 3150 (OH bonded), 3300 cm^{-1} (NH). NMR (DMSO): signals at δ = 12·15 ppm and δ = 10·84 ppm (OH); signal at δ = 9·99 ppm (NH); signal at δ = 1·96 ppm (CH_3); multiplet between 7 and 7·8 ppm (5 aromatic protons).

Chromatography of the combined recrystallization and reaction liquors on a silica column and elution with AcOEt–cyclohexane (80:20) yielded a small amount of product m.p. 185° (dec), identical by mixed m.p. with a pure sample of *anti* α,β-dihydroxyiminobutyranilide (II) obtained by Knorr's method.[2] The UV and IR spectra and the property of precipitating Ni^{+2} were also the same. UV: λ_{max}^{EtOH} 239 mμ (ε = 24,000). IR (Nujol): 1670 (CO), 3180 (OH bonded), 3290 cm^{-1} (NH). NMR (DMSO): singlet at δ = 11·71 ppm (two hydroxyimino protons), singlet at δ = 10·24 ppm (NH), singlet at δ = 1·98 ppm (CH_3), multiplet between 7 and 7·7 ppm (5 aromatic protons).

Mono-acetate of I (XI). α-Acetoxyimino-β-hydroxyiminobutyranilide was produced in the reaction of I with excess Ac_2O at room temp. The product was isolated by decomposing excess Ac_2O in water and then neutralizing with Na_2CO_3 aq; it was crystallized from EtOH–water, m.p. 150–151° (dec). (Found: C, 54·81; H, 5·15; N, 16·18. $C_{12}H_{13}N_3O_4$ requires: C, 54·75; H, 4·98; N, 15·96%); UV: λ_{max}^{EtOH} 221·5 mμ (ε = 14,000), 280 mμ (ε = 5800).

Monophenylcarbamate of I (XII). The α-phenylcarbamate was obtained by refluxing I with excess phenyl isocyanate for about 15 min. The crude product was washed with ligroin and crystallized from acetone– pet. ether: m.p. 254–258° (dec). (Found: C, 59·72; H, 5·02; N, 16·29. $C_{17}H_{16}N_4O_4$ requires: C, 59·99; H, 4·74; N, 16·46%); UV: λ_{max}^{EtOH} 232·5 mμ (ε = 27,400); 273 mμ (ε = 5100).

Mono-ethyl carbonate of I (XIII). The reaction of I with ethyl chlorocarbonate was carried out in anhydrous pyridine with excess reagent (2·2 mole), on a water bath for 1 hr. The mixture was then poured into cold 2N HCl and extracted with ether. The extract was dried and evaporated and the residue crystallized from EtOH–water as white needles m.p. 152–153°. (Found: C, 52·97; H, 4·93; N, 14·58. $C_{13}H_{15}N_3O_5$ requires: C, 53·24; H, 5·16; N, 14·33%); UV: λ_{max}^{EtOH} 217 mμ (ε = 14,400); 281 mμ (ε = 5500).

Bis-acetate of II (XIV). *anti* α,β-Diacetoxyiminobutyranilide was obtained by treating II with excess Ac_2O at room temp. It crystallized as white needles from EtOH–water, m.p. 145–146° (dec). (Found: C, 55·19; H, 5·21; N, 14·06. $C_{14}H_{15}N_3O_5$ requires: C, 55·08; H, 4·95; N, 13·77%.)

Bis-phenylcarbamate of II (XV). II was heated with excess phenyl isocyanate on a water bath for about 10 min. The mixture was well washed with ligroin and the residue crystallized from EtOH–water. The product consisted of white needles, m.p. 143–145° (dec). (Found: C, 62·53; H, 4·45; N, 15·45. $C_{24}H_{21}N_5O_5$ requires: C, 62·74; H, 4·61; N, 15·24%.)

Bis-ethyl carbonate of II (XVI). This product was obtained from II using the method for XIII from I. It crystallized as white needles from EtOH–water, m.p. 159–160° (dec). (Found: C, 52·72; H, 5·39; N, 11·51. $C_{16}H_{19}N_3O_7$ requires: C, 52·60; H, 5·24; N, 11·50%.)

Reaction between syn *α,β-dihydroxyiminobutyranilide* (I) *and* N_2O_4

Slightly more than the theoretical quantity of N_2O_4 was passed through a suspension of I (2 g) in anhyd benzene (50 ml), while cooling. The mixture was allowed to stand overnight, after which period all the

product went into soln. After washing with $NaHCO_3$ aq and water, the solvent was removed under vacuum; the white residue was subjected to chromatography on silica column, using benzene for elution. The first fraction (about 0·4 g) consisted of a white powder which recrystallized from EtOH, m.p. 124–126° (dec). This was *3-methylfuroxan-(5)-4-carboxyanilide* (V). (Found: C, 54·80; H, 4·18; N, 19·44. $C_{10}H_9N_3O_3$ requires: C, 54·79; H, 4·14, N, 19·17%); UV: λ_{max}^{EtOH} 232·5 mμ (ε = 12,500); 262 mμ (ε = 7500); shoulder at about 300 mμ. IR ($CHCl_3$): ν = 1695 (CO), 3320 (NH), 860, 1000, 1045 cm^{-1} (furoxan cycle).[25] NMR ($CDCl_3$): flattened signal equivalent to one proton at δ = 9·54 ppm (NH), singlet at δ = 2·65 ppm (Me), multiplet at δ = 7·2–7·8 ppm (5 aromatic protons).

The second fraction (about 0·9 g) m.p. 147–149° (dec) after crystallization from EtOH was identical with the product described by Ponzio,[3] and was obtained as the sole product when II was treated with N_2O_4 in the same way as I. Chemical and physical evidence showed the product to be *3-methylfuroxan-(2)-4-carboxyanilide* (IV) which did not lower the m.p. of the isomer V; UV: λ_{max}^{EtOH} 233 mμ (ε = 10,500), 282 mμ (ε = 9800). IR ($CHCl_3$): ν = 1703 (CO), 3400 (NH), 870, 1000, 1050 cm^{-1} (furoxan cycle). NMR ($CDCl_3$): flattened signal at δ = 8·52 ppm (NH); singlet at δ = 2·44 ppm (Me); multiplet between 7·1–7·8 ppm (5 aromatic protons).

Reduction of furoxans IV *and* V.

(a) To a soln of IV (0·6 g) in 30 ml abs EtOH containing a little ether, 2 g Zn powder and a soln of glacial AcOH (1·5 ml) in 10 ml abs EtOH were added under stirring. The reaction was followed by TLC and after 15 min the original product had completely disappeared. The liquid was filtered and evaporated under red press. The residue was chromatographed on a silica column: the AcOEt eluate furnished a pale yellow substance, which was crystallized from EtOH, m.p. 215–216°. This substance was identical to the product obtained by reduction of α-isonitrosoacetoacetanilide,[15] i.e. to *2,5-dimethyldihydropirazine-3,6-dicarboxy-anilide*.

(b) *3-Methyl-furazan-4-carboxyanilide* (VI). To a soln of V (1·6 g) in a mixture of 50 ml abs EtOH and 15 ml ethyl ether, 4 g Zn powder and 1·5 ml glacial AcOH, diluted with 10 ml EtOH were added with stirring. A yellow colour formed immediately and the intensity of the colour increased with time. After 40 min the mixture was filtered and the solvent removed by evaporation under reduced press. The residue was subjected to chromatography on a silica column, eluting with AcOEt–cyclohexane (50:50); the product VI was isolated which, when crystallized from the same solvent mixture, melted at 117–118°. (Found: C, 59·38; H, 4·71; N, 20·52. $C_{10}H_9N_3O_2$ requires: C, 59·10; H, 4·46; N, 20·68%); UV: λ_{max}^{EtOH} 223 mμ (ε = 7920), 274 mμ (ε = 4980). IR ($CHCl_3$): ν = 1703 (CO), 3410 cm^{-1} (NH). NMR ($CDCl_3$): δ = 8·66 ppm (NH); singlet at δ = 2·63 ppm (Me); multiplet between δ = 7·1–7·8 ppm (5 aromatic protons).

o-Toluidide of syn *α,β-dihydroxyiminobutyric acid* (VII)

This compound was obtained by the general method, from 3-methyl-4-hydroxyiminoisoxazolin-5-one and *o*-toluidine, diluting with water after a day. The white solid was collected and crystallized from EtOH; m.p. 148–149° (dec). It did not precipitate Ni^{+2}. (Found: C, 56·19; H, 5·82; N, 18·09. $C_{11}H_{13}N_3O_3$ requires: C, 56·16; H, 5·57; N, 17·86%); UV: λ_{max}^{EtOH} 262·5 mμ (ε = 4600). IR (Nujol): ν = 3295 (NH, OH); 1665 cm^{-1} (CO).

Small amounts of *o-toluidide* of anti *α,β,-dihydroxyiminobutyric acid* (VIII) were obtained by subjecting the combined reaction and crystallization liquors of the above preparation to chromatography on a silica column, eluting with AcOEt–cyclohexane (60:40). The product did not lower the m.p. when mixed with a sample of authentic material obtained in another manner.[12] The IR and UV spectra and the characteristic of precipitating Ni^{+2} were also the same. UV: λ_{max}^{EtOH} 232·5 mμ (ε = 18,200). IR (Nujol): ν = 3230 (NH, OH); 1665 cm^{-1} (CO).

o-Chloroanilide of syn *α,β-dihydroxyiminobutyric acid* (IX)

This was obtained by the general method as a white solid by diluting with water after 2–3 days. It melted at 143–144° (dec), after crystallization from EtOH, and did not precipitate Ni^{+2}. (Found: C, 46·75; H, 4·03; N, 16·32. $C_{10}H_{10}ClN_3O_3$ requires: C, 46·97; H, 3·99; N, 16·43%); UV: λ_{max}^{EtOH} 220 mμ (ε = 25,600), 276 mμ (ε = 9150). IR (Nujol): ν = 1678 (CO), 3300–3400 cm^{-1} (OH, NH).

Working up the mother liquors as previously described, some *o-chloroanilide* of anti *α,β-dihydroxyimino-butyric acid* (X) was obtained; the eluting mixture was AcOEt–cyclohexane (40:60). The product was identical (mixed m.p., UV, IR) with that synthesized by Dave *et al.*[12] and precipitated Ni^{+2}; UV: λ_{max}^{EtOH} 235 mμ (ε = 20,450). IR (Nujol): ν = 1680 (CO), 3260–3400 cm^{-1} (NH, OH).

N- syn α,β-*Dihydroxyiminobutyroyl*), N'-*isonicotinoylhydrazine* (XVII)

This product was obtained by reaction of isonicotinoylhydrazine with 3-methyl-4-hydroxyimino-isoxazolin-5-one at room temp, after several days. The white crystalline product was washed with water and EtOH and was analysed in this form since it decomposed on recrystallization: m.p. 134–135° (dec). (Found: C, 45·67; H, 4·27; N, 26·21. $C_{10}H_{11}N_5O_4$ requires: C, 45·28; H, 4·18; N, 26·41%); UV: λ_{max}^{EtOH} shoulder at 270 mμ. IR (Nujol): ν = 1670, 1700 (CO); 3280, 3420 cm^{-1} (NH, OH).

When treated with acids the product hydrolysed and cyclized to the original isoxazolinone.

N-*Hexylamide of* syn α,β-*dihydroxyiminobutyric acid* (XVIII)

This was obtained in the usual way after one day at room temp. The white solid was collected and crystallized from EtOH, m.p. 140–142° (dec). (Found: C, 52·02; H, 8·20; N, 18·13. $C_{10}H_{19}N_3O_3$ requires: C, 52·38; H, 8·35; N, 18·33%); UV: λ_{max}^{EtOH} 215 mμ (ε = 24,700). IR (Nujol): ν = 1650 (CO); 3150–3320 cm^{-1} (NH, OH).

Derivatives of ethyl anti α,β-*dihydroxyiminobutyrate*

The original ester was obtained according to Ceresole's method [1b] by reaction of hydroxylamine chlorhydrate and ethyl α-isonitrosoacetoacetate.

Bis-phenylcarbamate (XIX). 1 g of ester was heated on a water bath for 15–20 min with 1·35 g phenyl isocyanate. The mixture was then thoroughly washed with ligroin; the residue was dissolved in cold AcOEt and some pet. ether was added. White needles crystallized in the cold, m.p. 151–153°. (Found: C, 57·98; H, 5·09; N, 13·85; $C_{20}H_{20}N_4O_6$ requires: C, 58·25; H, 4·89; N, 13·58%).

Bis-ethyl carbonate (XX). Compound XX was obtained by the method used for XIII; white needles from EtOH–water, m.p. 159–160°. (Found: C, 45·51; H, 5·52; N, 8·88. $C_{12}H_{18}N_2O_8$ requires: C, 45·28; H, 5·70; N, 8·80%.)

Reaction between ethyl anti- α,β-*dihydroxyiminobutyrate and aniline*

Equimolecular quantities of ester and aniline were heated at 90–95° for 1 hr. A mixture of various products were obtained, which could be separed in the following manner.

A solid consisting of a non-identified product and *syn* α,β-dihydroxyiminobutyranilide (I) was obtained by washing the mixture with ether. By chromatography I could be purified. The residue of the ether soln was subjected to chromatography on silica column; by elution with AcOEt–cyclohexane (80:20), various fractions were obtained. These consisted of traces of the starting products, small quantities of *anti*-II and greater amounts of a product which proved to be III. In fact it does not lower the m.p. when mixed with an authentic sample obtained by another method.[23] The IR spectra are also identical.

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