A Study of Some New Alkyl Hydroxylamines

A DISSERTATION

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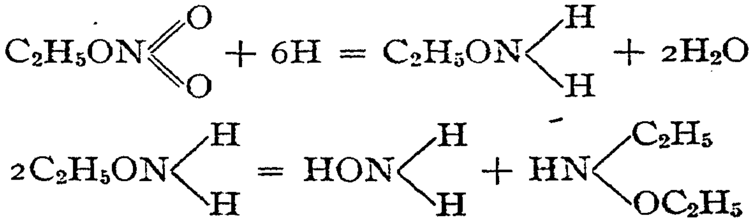
The amines have never ceased to be a center of interest since the time of their discovery by Wurtz in 1848. Although substituted hydroxylamines are nearer akin to amines than to any other class of organic compounds, they have shared only to a very minor degree in the attention paid to organic derivatives of nitrogen. Still, in many ways, the questions raised by a deductive consideration of their chemical relations are somewhat more varied and interesting than those presented by amines themselves. The present study, carried out under the direction of Dr. Lauder W. Jones, had, for its main object, the finding of methods whereby the various alkyl derivatives of hydroxylamine may be prepared in sufficient quantities and with a degree of readiness to permit of their future investigation from many other angles. Preliminary arrangements have already been made to study the electrical conductivities of water solutions of the alkylhydroxylamines described in this article.

HISTORICAL

The first representative of the alkylhydroxylamines[1] was described in 1868 by Lossen,[2] the discoverer of hydroxylamine itself. He found that one of the products of the reduction of ethyl nitrate by tin and hydrochloric acid was a base having the formula $C_4H_{11}ON$. Its properties showed that it was related to hydroxylamine, and he concluded that it was ethoxyethylamine, assuming that the following reactions took place:



$$C_2H_5ON\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O} + 6H = C_2H_5ON\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H} + 2H_2O$$

$$2C_2H_5ON\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H} = HON\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H} + HN\genfrac{}{}{0pt}{}{\diagup C_2H_5}{\diagdown OC_2H_5}$$

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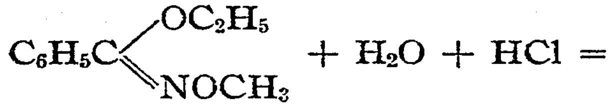
[1] Vorländer: J. prakt. Chem., N. F., **59**, 247–8. Throughout this paper the terms "alkyl" and "alphyl" are used interchangeably.

[2] Lossen: Ann. Chem. (Liebig), Suppl. **6**, 238.

Later, however, Lossen[1] showed that this compound was not ethoxyethylamine, neither is it identical with β-diethylhydroxylamine. Its constitution is doubtful.

No further study of either hydroxylamine or its derivatives was made until, in 1875, Lossen endeavored to justify the formula of hydroxylamine $\left(HON\begin{smallmatrix}H\\H\end{smallmatrix}\right)$, which had been criticized, by showing that two of the hydrogen atoms were equivalent, while the third was not. To do this, he replaced these hydrogen atoms by different groups, principally acyl groups.

The next year, Lossen and Zanni[2] prepared the hydrochloride of α-methylhydroxylamine by hydrolyzing the methyl ester of ethylbenzhydroximic acid, as shown by the equation



$$C_6H_5C\begin{matrix}\diagup OC_2H_5\\ \diagdown NOCH_3\end{matrix} + H_2O + HCl =$$

$$H_2NOCH_3HCl + C_6H_5CO_2C_2H_5$$

but they did not isolate the alkylhydroxylamine itself. Petraczek[3] obtained the same substance by hydrolyzing methylbenzaldoxime with concentrated hydrochloric acid:

$$C_6H_5CH : N.OCH_3 + H_2O + HCl = C_6H_5CHO + H_2NOCH_3HCl$$

Jones[4] also obtained this substance by hydrolyzing the α-methyl ester of carbethoxyhydroxamic acid with hydrochloric acid.

Lossen and Zanni made α-ethylhydroxylamine by a hydrolysis similar to that given above. Later Waldstein[5] prepared it from benzhydroxamic ethyl ester by heating this substance with an excess of hydrochloric acid in a sealed tube. Jones[6] obtained the hydrochloride by treating the reaction product of phosphorus pentachloride and carbethoxyhydroxamic ethyl ester with water, making this solution strongly alkaline with sodium hydroxide and distilling the hydroxylamine into dilute hydrochloric acid. This method gives almost theoretical

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[1] Lossen: Ann. Chem. (Liebig), **252**, 234.

[2] Lossen and Zanni: *Ibid.*, **182**, 225ff.

[3] Petraczek: Ber. d. chem. Ges., **16**, 827.

[4] Jones: Am. Chem. J., **20**, 41ff.

[5] Waldstein: Ann. Chem. (Liebig), **181**, 390

[6] Jones: Am. Chem. J., **20**, 41ff.

yields. α,β-Dimethylhydroxylamine and α,β-diethylhydroxylamine,[1] also α-methyl-β-ethylhydroxylamine and α-ethyl-β-methylhydroxylamine,[2] were obtained by Jones by hydrolyzing the respective esters of carbethoxyhydroxamic acid. Lossen had previously obtained the diethylhydroxylamine by alkylating α-ethylhydroxylamine with ethyl bromide.[3]

In 1888, Bewad[4] thought that he had made triethylamine oxide $(C_2H_5)_3NO$, by the action of nitroethane upon zinc ethyl, but this compound was shown later[5] to be β-ethyl-β-sec.-butylhydroxylamine. This synthesis furnishes an easy way of preparing mixed β,β-dialkylhydroxylamines, and was extensively studied by Bewad.[6]

In 1890, Behrend and Leuchs[7] published a résumé of the work done on the alkyl derivatives of hydroxylamine up to that time, and presented the results of their own investigations in that field, covering the benzyl and ethyl derivatives. Nine years later Dunstan and Goulding[8] in England, and Mamlock and Wolffenstein[9] in Germany, by the oxidation of di- and trisubstituted amines with hydrogen peroxide obtained a number of β-dialkylhydroxylamines and the so-called oxamines, or amine oxides, compounds isomeric with the trialkylhydroxylamines.

Summing up, we see that up to the present time there is only a single representative of the α-monoalkylhydroxylamines known, for although Lossen and Zanni obtained the hydrochloride of α-methylhydroxylamine, they did not isolate the base. There is a similar paucity of data on the α,β-dialkylhydroxylamines, only two compounds containing like groups and two compounds containing unlike groups being known.

In the present paper are described two new α-monoalkylhydroxylamines, six new α,β-dialkylhydroxylamines, and the intermediate products in their preparation, many of which

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[1] Jones: Am. Chem. J., **20**, 41ff.
[2] Jones: *Ibid.*, **38**, 253ff.
[3] Lossen: Ann. Chem. (Liebig), **252**, 234.
[4] Bewad: Ber. d. chem. Ges., **21**, Ref. 479.
[5] Bewad: J. Russ. Phys. Chem. Soc., **32**, 455.
[6] Bewad: J. prakt. Chem., N. F., **63**, 94ff. and 193ff.
[7] Behrend and Leuchs: Ann. Chem. (Liebig), **257**, 203ff.
[8] Dunstan and Goulding: J. Chem. Soc., **75**, 799ff., 1004ff.
[9] Mamlock and Wolffenstein: Ber. d. chem. Ges., **33**, 159.

are new. Four of these dialkylhydroxylamines are isomeric with each other and with the β,β-ethylpropylhydroxylamine described by Bewad. It is intended to study all of these compounds and others, including the sixth isomer, β-ethyl-β-isopropylhydroxylamine, yet to be made, from the standpoint of their electrical conductivities in water solution.

The method suggested by Jones[1] of introducing successively into hydroxyurethan two different alkyl groups and subsequently hydrolyzing the resulting product was followed in the preparation of the α,β-dialkylhydroxylamines. An alcoholic solution of hydroxyurethan mixed with the theoretical amount of alkyl halide was treated with the calculated amount of an alcoholic solution of potassium hydroxide. This formed a mixture of the mono- and dialkyl esters of carbethoxyhydroxamic acid. One might expect that some of the oxygen ester ($C_2H_5O.C(OR) : NOR$) would be formed at the same time, but none was observed. These two substances were then separated by shaking the ether solution with dilute alkali. By this treatment, the monoalkyl derivative was converted into its salt, which dissolved in the water, while the dialkyl derivative, having no acid properties, remained dissolved in the ether. The alkali salt of the monoalkyloxyurethan was easily decomposed by dilute acids to give the free ester, which was extracted with ether, and then obtained in the free state by fractional distillation.

When a mixed α,β-dialkylhydroxylamine was to be made, a mixture of one mole of monoalkylcarbethoxyhydroxamic ester and one mole of alkyl halide was treated with the calculated amount of sodium ethylate dissolved in alcohol. After the dialkyl ester was extracted with ether, it was shaken with dilute alkali to remove any unchanged monoalkyl ester, then dried and fractionated.

The hydrolysis of these esters was accomplished uniformly by heating the ester with a considerable excess of potassium hydroxide solution in a sealed tube for fifteen to sixty hours at temperatures varying from 100° to 200°. To separate the hydroxylamine, the mixture from the hydrolysis was distilled

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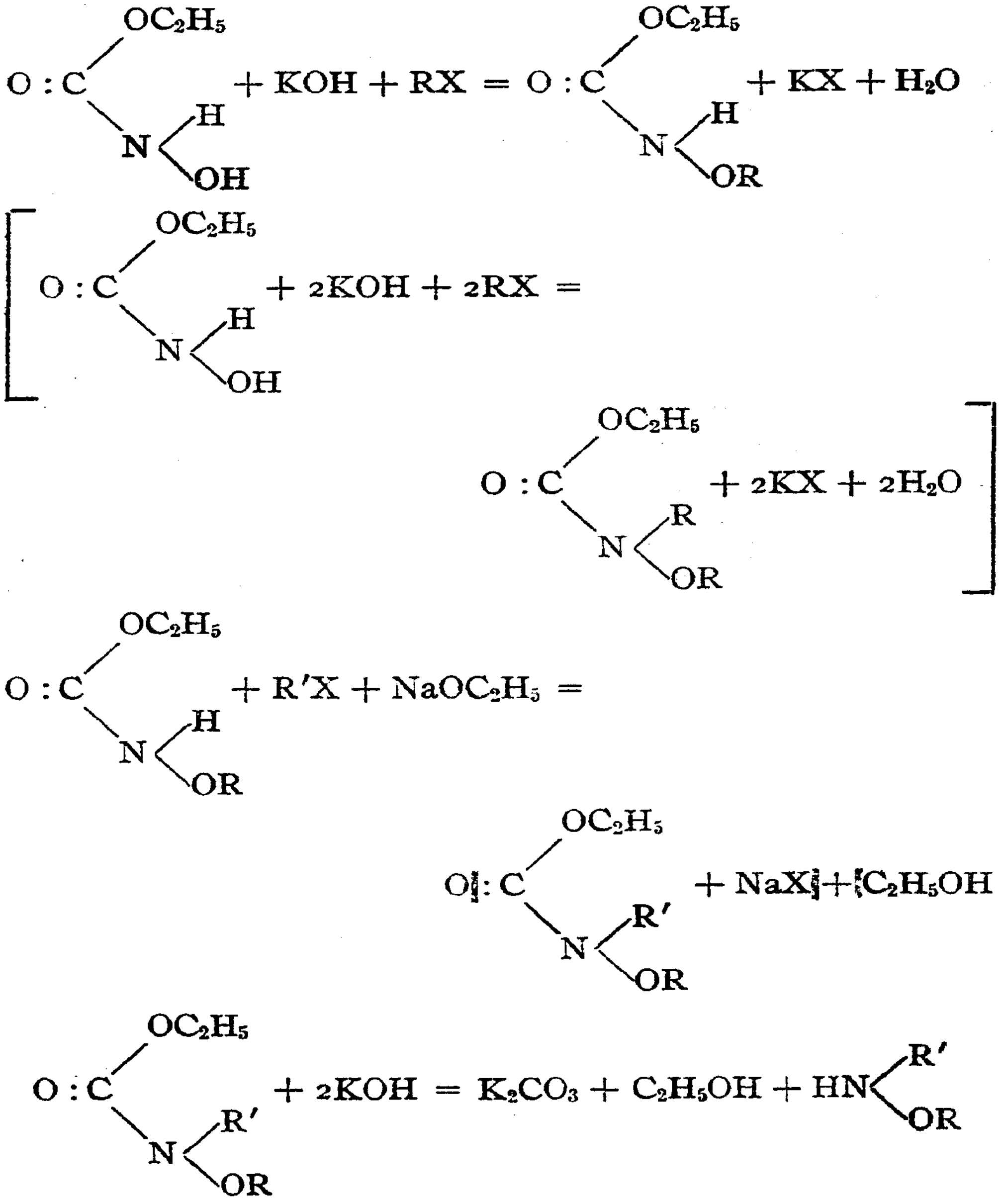
[1] Jones: Am. Chem. J., **38**, 253ff.

and the free base collected in dilute hydrochloric acid. The hydrochloride formed was recrystallized, decomposed with potassium hydroxide and the vapors of the free alkylhydroxylamine condensed.

The above method may be summarized in the following equations:

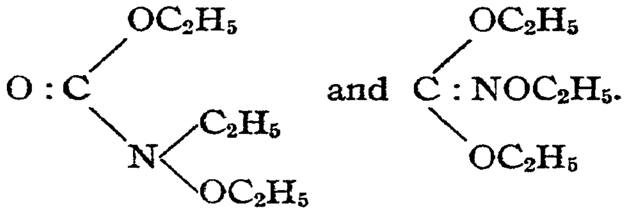


Concentrated hydrochloric acid was tried as the hydrolyzing agent, but gave poor yields of a very impure salt. The α-monoalkyl esters were easily hydrolyzed by the potassium hydroxide solution, but the dialkyl esters with two like groups were decomposed much more slowly. Furthermore, the ease with which the α-monoalkyl esters were hydrolyzed seemed to increase with increasing molecular weight. This is probably partly responsible for the low yields obtained in making the α-monoalkyl esters of carbethoxyhydroxamic acid.

EXPERIMENTAL PART

Action of Ethyl Iodide on the Potassium Salt of Carbethoxyhydroxamic Acid

The carbethoxyhydroxamic acid, which served as the starting point in the preparation of the following compounds, was prepared according to Jones's modification of Hantzsch's method.[1] This was then converted into the ethyl ester by treatment with ethyl iodide and potassium hydroxide,[2] and the mono- and di-esters separated as described above. The monoethyl ester was used in the preparation of mixed dialkylcarbethoxyhydroxamic esters. The ether solution of the diethyl ester was dried with anhydrous sodium sulphate and the ether was removed by distillation, under diminished pressure. The oil which was left was impure, as was that obtained by Jones. It was, therefore, fractionated, and two approximately equal fractions, one boiling at 107° to 112° (70 mm. pressure) and the other boiling at 129° to 133° (70 mm. pressure) were obtained. It was at first thought that these two fractions might be two tautomeric forms, viz.:



$$O:C{<}^{OC_2H_5}_{N{<}^{C_2H_5}_{OC_2H_5}} \quad \text{and} \quad C{<}^{OC_2H_5}_{OC_2H_5}:NOC_2H_5.$$

This could, of course, be determined easily, for the first should give α-diethylhydroxylamine on hydrolysis with potassium

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[1] Jones: Am. Chem. J., **20**, 41ff.

[2] *Ibid.*

hydroxide, while the second should give α-monoethylhydroxylamine. However, the nature of the impurity was determined without this step. An analysis of the higher boiling fraction gave the following results:

0.3987 gram gave 39.2 cc. N_2 at 21° and 747.8 mm. (uncorr.).

	Calc. for α-diethyloxyurethan $C_7H_{15}O_3N$	Calc. for α-monoethyloxyurethan $C_5H_{11}O_3N$	Found
N	8.69	10.52	10.95

The boiling point of this fraction was found to be 194° to 196° under 750 mm. pressure. The boiling point of α-monoethylcarbethoxyhydroxamic ester is 195° to 196°.[1]

The following results were obtained from an analysis of the other fraction:

0.2258 gram gave 0.4299 gram CO_2 and 0.1873 gram H_2O.

	Calc. for $C_7H_{15}O_3N$	Found
C	52.11	52.00
H	9.39	9.29

From this it is seen that the impurity which contaminated the neutral portion obtained from the action of ethyl iodide upon the potassium salt of carbethoxyhydroxamic acid was α-ethylcarbethoxyhydroxamic ester.

Action of Ethyl Iodide on α-Ethylcarbethoxyhydroxamic Ester

An alcoholic solution containing the theoretical amount of sodium ethylate was gradually added to a mixture of 14 grams of α-ethylcarbethoxyhydroxamic ester and 16.4 grams of ethyl iodide. The mixture grew warm and sodium iodide soon began to crystallize. After standing at room temperature for two days, the mixture was heated on the water bath at 80° for two hours. Most of the alcohol was then removed by distillation and the residue filtered from the dense precipitate of sodium iodide. The solution was then diluted with water, and extracted repeatedly with ether. The ether solution was shaken several times with dilute alkali to remove unchanged α-ethylcarbethoxyhydroxamic ester, dried with anhydrous sodium sulphate and fractionated. Twelve and one-half

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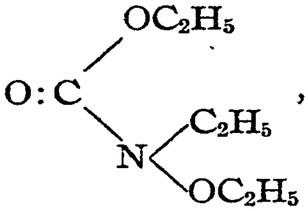
[1] Jones: Am. Chem. J., **20**, 41ff.

grams of the diethyl ester, boiling at 72°–74° under 12 mm. pressure, were obtained. The yield was 76 per cent. of the theoretical. The oil prepared in this way was identical in every respect with that obtained as the by-product in ethylating hydroxyurethan with ethyl iodide and potassium hydroxide.

α-Diethylcarbethoxyhydroxamic ester,  , is a colorless oil, with a disagreeable odor suggesting an isocyanide. It is very slightly soluble in water, and is soluble in all proportions in alcohol and ether. It gives no color test with ferric chloride, and does not reduce ammoniacal silver nitrate or Fehling's solution.

Decomposition of α-Diethylcarbethoxyhydroxamic Ester with Potassium Hydroxide

A mixture of 12.5 grams of the diethyl ester and 20 grams of potassium hydroxide dissolved in water was heated together in a sealed tube at 100° for 30 hours. The contents of the tube were then distilled, and the distillate passed into a dilute solution of hydrochloric acid. Since the distillate did not all dissolve in the hydrochloric acid, the solution was extracted with ether. Five grams of the undecomposed ester were recovered from the ether by fractionation. The acidified distillate was concentrated on the water bath and the last portions of water and hydrochloric acid were removed by placing the thick liquid in a vacuum desiccator containing concentrated sulphuric acid and pieces of solid potassium hydroxide. After some time the liquid had solidified to a mass of white crystals. identical with those obtained by Jones.[1] The free base can be obtained by heating a mixture of the dry salt and potassium hydroxide. It was first prepared by Lossen[2] from the oxalate, and was fully described by him.

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[1] Jones: Am. Chem. J., **20**, 41ff.

[2] Lossen: Ann. Chem. (Liebig), **252**, 234.

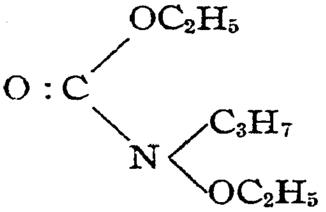
I. α-Ethyl-β-propylhydroxylamine

(*a*) *Action of Normal Propyl Iodide on α-Ethylcarbethoxyhydroxamic Ester.*—The action of a mixture of normal propyl iodide and sodium ethylate upon α-ethylcarbethoxyhydroxamic ester proceeds very slowly in the cold, but quite rapidly at higher temperatures. Thus, a solution of 35.5 grams of α-ethylcarbethoxyhydroxamic ester, 45.5 grams of normal propyl iodide and the theoretical amount of sodium ethylate in absolute alcohol gave a slight precipitate of sodium iodide after standing at room temperature for four days. The precipitate was filtered from the solution, and this was then heated on the water bath at 80° for half an hour. A dense precipitate formed, which was removed. After the solution had been diluted with water, it was extracted a number of times with ether. The little free iodine which was present was removed with sodium thiosulphate, the ether solution was dried and 33 grams of the α-ethyl-β-propylcarbethoxyhydroxamic ester were obtained by fractionation. The yield was 71 per cent. of the theoretical.

0.4076 gram gave 29 cc. N_2 at 18° and 750 mm. (uncorr.).

	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.11

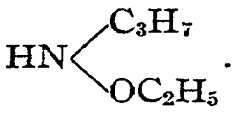
α-Ethyl-β-propylcarbethoxyhydroxamic ester,



$O:C{<}^{OC_2H_5}_{N{<}^{C_3H_7}_{OC_2H_5}}$

, is a colorless oil boiling at 189° under 740 mm. pressure. It has an odor similar to nicotine, and is soluble in water, alcohol and ether. It gives no reaction with ferric chloride, ammoniacal silver nitrate or Fehling's solution.

(*b*) *Preparation of α-Ethyl-β-propylhydroxylamine,*



$HN{<}^{C_3H_7}_{OC_2H_5}$

.—The hydrolysis of the corresponding ester of carbethoxyhydroxamic acid was accomplished most easily as follows: Fifteen grams of the ester, mixed with an aqueous solution containing 30 grams of potassium hydroxide, were heated in a sealed tube at about 120° for twenty-four hours. The product from the hydrolysis was then treated in the same way as described under α-diethylcarbethoxyhydroxamic ester (see page 10).

α-Ethyl-β-propylhydroxylamine hydrochloride crystallizes in large plates melting at 72°.5–73°. This salt is easily soluble in alcohol, benzene, chloroform and toluene. It is not soluble in ether and very slightly soluble in carbon bisulphide. An alcoholic solution of platinic chloride with an alcoholic solution of the hydrochloride gave a solution of the chloroplatinate. By the addition of dry ether to the solution the salt was precipitated as brilliant, deep yellow crystals, which melted at 150°.2.

0.2490 gram gave 0.0794 gram platinum.

	Calc. for $C_{10}H_{28}O_2N_2PtCl_6$	Found
Pt	32.19	31.88

To prepare α-ethyl-β-propylhydroxylamine, the hydrochloride was distilled with an excess of concentrated sodium hydroxide solution, and the vapors passed over pieces of solid sodium hydroxide heated to 95° before they were condensed. It is a clear, colorless liquid boiling at 83°.8–84° and has a sharp ammoniacal odor and a sweet, biting taste. It reduces ammoniacal silver nitrate solution slowly in the cold, and very rapidly when warmed. It does not reduce Fehling's solution in the cold, but does so slowly on being heated. It gives no color reaction with ferric chloride. It is slightly soluble in water, and is soluble in all proportions in alcohol. Its specific gravity is 0.8033 (25°/25°). Its index of refraction at 25° is 1.39426.

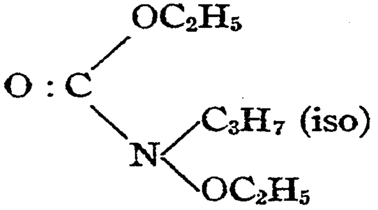
II. α-Ethyl-β-isopropylhydroxylamine

(a) Action of Isopropyl Iodide and Sodium Ethylate on α-Ethylcarbethoxyhydroxamic Ester

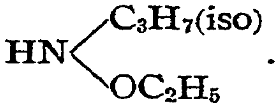
Isopropyl iodide reacts with α-ethylcarbethoxyhydroxamic ester in the presence of sodium ethylate just as its isomer does. Thus, 28 grams of the α-ethyl ester of carbethoxyhydroxamic acid and 36 grams of isopropyl iodide, when treated with the calculated amount of sodium ethylate dissolved in alcohol, gave a fine, white precipitate of sodium iodide after standing for several days at room temperature. This precipitation was hastened by warming the solution on the water bath. The alcoholic solution was filtered, diluted with water and extracted with ether. The ether solution was then shaken with dilute potassium hydroxide solution, dried and fractionated. Twenty-four grams of α-ethyl-β-isopropylhydroxamic ester were obtained. The yield was 66 per cent. of that required by theory.

0.3015 gram gave 23 cc. N_2 at 24° and 739 mm. pressure (uncorr.).

	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.27

α-Ethyl-β-isopropylcarbethoxyhydroxamic ester,  , is a clear, colorless oil boiling at 182° under 748 mm. pressure (84°–87° under 14–15 mm.). It has a strong odor resembling parsnips. Its aqueous solution does not reduce ammoniacal silver nitrate, and gives no coloration with ferric chloride.

(*b*) *Preparation of α-Ethyl-β-isopropylhydroxylamine,*



$$HN\begin{cases} C_3H_7(\text{iso}) \\ OC_2H_5 \end{cases}.$$

A mixture of 15 grams of α-ethyl-β-isopropylcarbethoxyhydroxamic ester and 25 grams of potassium hydroxide dissolved in water were heated in a sealed tube at 120°–160° for 36 hours. The aqueous solution of the free base, thus formed, was distilled, and the distillate passed into dilute hydrochloric acid. All of the ester had been hydrolyzed. Another tube, charged in the same way and heated to 110° for forty hours, gave five grams of unhydrolyzed ester on extraction of the acidified distillate with ether. The solution of the hydrochloride was concentrated by evaporation on the water bath, and then placed in a vacuum desiccator containing concentrated sulphuric acid and potassium hydroxide. The salt had not crystallized from the liquid after one month, so the liquid was placed in a vacuum desiccator over phosphorus pentoxide and kept at room temperature for one week, then at 0° for a week. By this treatment a syrupy liquid, intermixed with a few tiny crystals (probably ammonium chloride), was obtained. A mixture of 3 grams of this syrupy hydrochloride with 6 grams of powdered potassium hydroxide was dry distilled and gave 1.90 grams of the free base.

α-Ethyl-β-isopropylhydroxylamine is a clear, colorless liquid boiling at 78°. It has an odor very much like that of ethylamine. Its specific gravity (25°/25°) is 0.8132. The base is soluble in a large amount of water and this solution does not reduce ammoniacal silver nitrate in the cold, but does so rapidly when warmed. It does not reduce Fehling's solution when hot or cold.

An alcoholic solution of platinic chloride precipitated the chloroplatinate from a hot alcoholic solution of the hydrochloride as small lemon-yellow crystals. These decomposed without melting when heated.

0.2060 gram gave 0.0660 gram Pt.

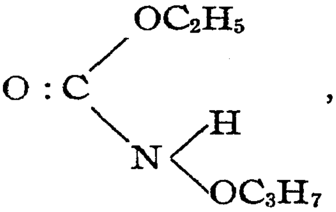
	Calc. for $C_{10}H_{28}O_2N_2PtCl_6$	Found
Pt	32.19	32.04

III. α-Propylhydroxylamine, $H_2NOC_3H_7$

(*a*) *Action of Normal Propyl Iodide on the Potassium Salt of Hydroxyurethan.*—When an alcoholic solution containing 33.6 grams of potassium hydroxide was slowly added, with constant shaking, to a mixture of 64 grams of normal propyl bromide, 13.6 grams of normal propyl iodide and 63 grams of hydroxyurethan, the mixture became turbid and the temperature rose slightly. The flask was, therefore, cooled to prevent, as far as possible, the hydrolysis of the mono ester by the potassium hydroxide. After standing for a week at room temperature, the mixture was heated for one-half hour at 80°. The salt which had precipitated was removed by filtration, most of the alcohol was distilled off, the remaining solution was diluted with water and extracted repeatedly with ether. The ether solution was then shaken with the calculated amount of a dilute solution of potassium hydroxide. The ether solution which was left contained the dipropylcarbethoxyhydroxamic ester (see below), and the water solution contained the monopropylcarbethoxyhydroxamic ester in the form of the potassium salt. To obtain the free ester, the alkaline solution was acidified with 10 per cent sulphuric acid, and extracted with ether. The ether solution was colored by a little free iodine, which was removed with sodium thiosulphate solution. The ether solution was dried and then fractionated under diminished pressure, since the ester decomposes somewhat when distilled under atmospheric pressure. The yield was 32 grams, only 36.3 per cent. of the theoretical yield.

0.3119 gram gave 28.3 cc. N_2 at 23°.5 and 733.8 mm.

	Calc. for $C_6H_{13}O_3N$	Found
N	9.55	9.84

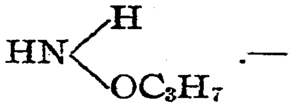
α-Propylcarbethoxyhydroxamic ester,  , is a colorless oil boiling at 109°–111° under 15 mm. pressure. At atmospheric pressure it boils between 200° and 210° with slight decomposition. It is not appreciably soluble in water, but is soluble in all proportions in alcohol and in ether. It has a faint, pleasant odor.

The ether solution of the dipropylcarbethoxyhydroxamic ester (see above) was dried with anhydrous sodium sulphate and fractionated. Nine and one-half grams (8.5 per cent. of the theoretical) of dipropylcarbethoxyhydroxamic ester were obtained. It is a clear, colorless oil, insoluble in water, boiling at 107°.5–108° under 20 mm. pressure. It has an odor resembling roasted chestnuts.

0.3192 gram gave 23 cc. N_2 at 22° and 740 mm. pressure.

	Calc. for $C_9H_{19}O_3N$	Found
N	7.40	7.80

(*b*) *Preparation of α-Propylhydroxylamine,*



$HN\begin{matrix}H\\OC_3H_7\end{matrix}$.—

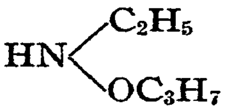
Ten grams of α-propylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide dissolved in water formed a homogeneous mixture. This mixture was heated in a sealed tube at 100° for 12 hours. The resulting products from the hydrolysis were distilled and the distillate collected in dilute hydrochloric acid. This was concentrated by evaporation on the water bath, and then placed in a vacuum desiccator containing concentrated sulphuric acid and solid potassium hydroxide. α-Propylhydroxylamine hydrochloride crystallized from the solution in large, thin, transparent white plates, which melted at 140°–141°. The salt is very soluble in water and in alcohol, but insoluble in ether. It is not deliquescent. An alcoholic solution of platinic chloride precipitated the chloroplatinate as light yellow crystals from an alcoholic solution of the hydrochloride.

0.1103 gram gave 0.0408 gram Pt.

	Calc. for $(C_3H_{10}ON)_2PtCl_6$	Found
Pt	35.48	36.89

When a mixture of 2.67 grams of α-propylhydroxylamine hydrochloride and 6 grams of finely powdered potassium hydroxide was subjected to dry distillation, 1.35 grams of a clear, colorless liquid, having a sweetish, ammoniacal odor, were obtained. The yield was 75 per cent. of the theoretical. α-Propylhydroxylamine boils at 86°.6–87°. Its specific gravity (25°/25°) is 0.8687. Its aqueous solution rapidly reduces ammoniacal silver nitrate and Fehling's solution in the cold.

IV. α-Propyl-β-ethylhydroxylamine,

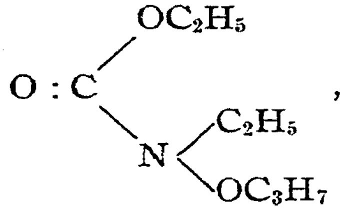


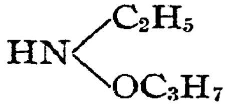
$HN\begin{matrix}C_2H_5\\OC_3H_7\end{matrix}$

(*a*) *Action of Ethyl Iodide on α-Propylcarbethoxyhydroxamic Ester.*—Five grams of sodium dissolved in alcohol were slowly added to an alcoholic solution containing 32 grams of α-propylcarbethoxyhydroxamic ester and 35 grams of ethyl iodide. The mixture was allowed to stand at room temperature for a week, and was then heated to 70° for four hours to complete the reaction. Most of the alcohol was then distilled off, the solution was diluted with water and extracted with ether. The ether extract was shaken with dilute potassium hydroxide solution to remove free iodine and any unchanged monopropyl ester present, then dried with sodium sulphate. After a few hours, the solution became dark brown, due to free iodine. Repeated shaking with sodium thiosulphate solution was necessary to remove all of the color. The solution was again dried and fractionated under 750 mm. pressure. Thirty grams of α-propyl-β-ethylcarbethoxyhydroxamic ester were obtained. The yield was 79 per cent. of the theoretical.

0.3512 gram gave 27 cc. N_2 at 27° and 750.4 mm. pressure.

	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.33

α-Propyl-β-ethylcarbethoxyhydroxamic ester,  $\mathrm{O:C{<}^{OC_2H_5}_{N{<}^{C_2H_5}_{OC_3H_7}}}$, is a colorless liquid which boils at 191° under 750 mm. pressure without decomposition (92°.5 under 20 mm.). It has an odor similar to α,β-diethylcarbethoxyhydroxamic ester. It is not soluble in water, but is very soluble in alcohol and in ether.

(*b*) *Preparation of α-Propyl-β-ethylhydroxylamine,*  $\mathrm{HN{<}^{C_2H_5}_{OC_3H_7}}$.—A mixture of 10 grams of α-propyl-β-ethylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide dissolved in water was heated in a sealed tube at 130° for 24 hours. The contents of the tube were then treated in the customary manner, and the hydrochloric acid solution extracted with ether. One-half gram of unhydrolyzed ester was recovered from the ether extract. The acid solution was concentrated on the water bath. During this operation considerable α-propyl-β-ethylhydroxylamine hydrochloride was lost by volatilization. Only 1.7 grams of α-propyl-β-ethylhydroxylamine hydrochloride was obtained. This was purified by precipitation with ether from an alcoholic solution. It forms large, lustrous crystals, resembling benzoic acid in appearance, which melt without decomposition at 96°.2. It is moderately soluble in cold chloroform and readily soluble in boiling chloroform, from which it crystallizes on cooling. It is very deliquescent. Its aqueous solution does not reduce ammoniacal silver nitrate or Fehling's solution, either cold or hot. An alcoholic solution of platinic chloride precipitated the chloroplatinate from an alcoholic solution of the hydrochloride as small, light yellow crystals, which decomposed when melted.

When 1.14 grams of the hydrochloride were mixed with 4 grams of finely powdered potassium hydroxide and distilled, 0.31 gram of a clear, colorless liquid, having an odor similar to its isomer, was obtained. α-Propyl-β-ethylhydroxylamine is moderately soluble in water, and this solution reduces ammoniacal silver nitrate slowly in the cold and rapidly on warming. It does not reduce Fehling's solution either hot or cold. The free base is very volatile.

V. *α-Dipropylhydroxylamine*

(*a*) *Hydrolysis of α,β-Dipropylcarbethoxyhydroxamic Ester.*—Fifteen grams of dipropylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide were heated together in a sealed tube at 130° for 40 hours. The contents of the tube were then treated in the usual way, and the hydrochloride of α-dipropylhydroxylamine obtained as white crystals, mixed with a little ammonium chloride. The salt was easily purified by dissolving the impure product in absolute alcohol, filtering from the ammonium chloride, and then adding absolute ether. This precipitated the salt as small, lustrous crystals, which melted at 146°.6. These crystals were extremely soluble in water but were not at all deliquescent. When an alcoholic solution of platinic chloride was added to an alcoholic solution of the hydrochloride, deep yellow crystals of the chloroplatinate were precipitated.

0.1634 gram gave 0.0498 gram Pt.

	Calc. for $C_{12}H_{32}O_2N_2PtCl_6$	Found
Pt	30.29	30.47

By distillation of 3 grams of the hydrochloride with finely powdered potassium hydroxide, 1.76 grams of α,β-propylhydroxylamine were obtained. The yield is 77 per cent. of the theoretical. It is a clear, colorless liquid boiling at 85°–86°. Its specific gravity (25°/25°) is 0.8141. It is somewhat soluble in water, and this solution instantly reduces ammoniacal silver nitrate solution in the cold, but has no effect upon Fehling's solution even when boiled with it.

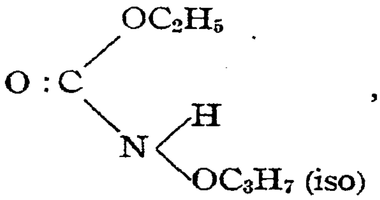
VI. α-Isopropylhydroxylamine

(*a*) *Action of Isopropyl Halides on the Potassium Salt of Carbethoxyhydroxamic Acid.*—Isopropyl halides react with difficulty with the sodium and potassium salts of carbethoxyhydroxamic acid. When the usual method for carrying out the reaction between isopropyl halides and carbethoxyhydroxamic acid in the presence of potassium hydroxide was tried, it was found impossible to increase the yield of the monoisopropylcarbethoxyhydroxamic ester much above 20 per cent. Usually the yield was lower than this. The following data represent an average experiment: Thirty-one grams of isopropyl bromide and 40 grams of isopropyl iodide were added to 51 grams of carbethoxyhydroxamic acid dissolved in 25 cc. of absolute alcohol. The mixture was cooled and then an alcoholic solution of potassium hydroxide, containing a little less than the theoretical amount, was slowly added, with constant shaking of the mixture. The mixture was kept cool for a day, then allowed to stand at room temperature for three days, and finally heated to 90° for fifteen minutes to complete the reaction. The alcoholic solution was then treated in the usual manner, and 13 grams of α-isopropylcarbethoxyhydroxamic ester were obtained. The yield was 18.3 per cent. of the theoretical.

The next method which was tried was to isolate the sodium salt of hydroxyurethan and suspend it in alcohol. The theoretical quantity of isopropyl halide was added, and the mixture was then boiled under a reflux condenser for a day. The reaction mixture was then worked up, but a smaller yield of the ester was obtained than before.

The following method gave the best results: A mixture of 25 grams of hydroxyurethan, 29.3 grams of isopropyl bromide and about 15 grams of alcohol was boiled under a reflux condenser. An alcoholic solution of 13.3 grams of potassium hydroxide was added very slowly to the boiling solution. A heavy precipitate separated out. The resulting solution was then treated in the usual manner. Six grams of unchanged isopropyl bromide were recovered. Ten grams of α-monoisopropylcarbethoxyhydroxamic ester were obtained, representing a yield of 36 per cent.

α-Isopropylcarbethoxyhydroxamic ester,



, is a colorless oil boiling at 102°–103° under 12 mm. pressure. It is slightly soluble in water, and does not reduce ammoniacal silver nitrate solution. It colored ferric chloride purple, due to a trace of hydroxyurethan which was carried over with it. Unlike the other alkyl derivatives of carbethoxyhydroxamic acid, it has practically no odor.

0.3098 gram gave 0.5482 gram CO_2 and 0.2158 gram H_2O.

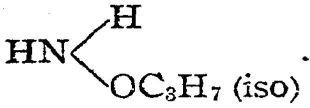
	Calc. for $C_6H_{13}O_3N$	Found
C	48.91	48.30
H	8.91	9.02

The ether solution containing the α,β-diisopropylcarbethoxyhydroxamic ester, which was left after the mixture of the mono- and diisopropyl esters had been extracted with potassium hydroxide solution, was dried and fractionated. An oil boiling at 101°–101°.5 under 15 mm. pressure was obtained. Eight and a half per cent. of the carbethoxyhydroxamic acid had been converted into the dialkyl derivative.

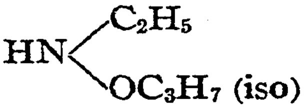
0.2760 gram gave 0.5754 gram CO_2 and 0.2524 gram H_2O.

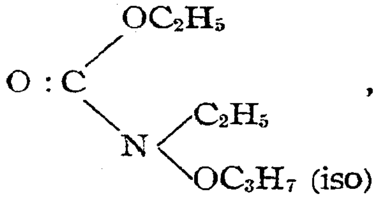
	Calc. for $C_9H_{19}O_3N$	Found
C	57.09	56.85
H	10.13	11.76

α,β-Diisopropylcarbethoxyhydroxamic ester is slightly soluble in water. This solution gives no reaction with ferric chloride, ammoniacal silver nitrate or Fehling's solution. It has a pleasant odor, very much like that of phenylacetic ester.

(*b*) *Preparation of α-Isopropylhydroxylamine,*  $HN\langle^{H}_{OC_3H_7\,(iso)}$.—The hydrolysis of the α-isopropylcarbethoxyhydroxamic ester was accomplished in the customary manner. Five and one-half grams of the ester, mixed with a solution containing 10 grams of potassium hydroxide, were heated at 100° for twenty-four hours. The free base was distilled from the aqueous solution and collected in dilute hydrochloric acid. This solution was concentrated and placed in a vacuum desiccator with potassium hydroxide and sulphuric acid. After two weeks α-isopropylhydroxylamine hydrochloride had crystallized out as white plates, melting at 84°.8, which were deliquescent. (Compare the isomeric *n*-propylhydroxylamine hydrochloride.) It is soluble in water and alcohol, but not soluble in ether. Its aqueous solution rapidly reduces silver nitrate and Fehling's solution in the cold.

Free α-isopropylhydroxylamine was obtained by distilling a mixture of 2 grams of the hydrochloride and 4 grams of dry potassium hydroxide. It is a colorless liquid boiling at 72°.2 (uncorr.). It has a disagreeable, pungent odor. Its specific gravity (25°/25°) is 0.8459. Its aqueous solution reduces ammoniacal silver nitrate solution and Fehling's solution.

VII. α-Isopropyl-β-ethylhydroxylamine,  $HN\langle^{C_2H_5}_{OC_3H_7\,(iso)}$

(*a*) *Action of Ethyl Iodide on α-Isopropylcarbethoxyhydroxamic Ester.*—A solution of 4.22 grams of sodium in absolute alcohol was slowly added to an alcoholic solution containing 27 grams of α-isopropylcarbethoxyhydroxamic ester and 28.6 grams of ethyl iodide. No noticeable change occurred. The mixture was allowed to stand for two weeks at room temperature, and was then heated to 70° for several hours. The small amount of fine precipitate was removed, most of the alcohol was distilled off, and after diluting the solution with water it was extracted with ether. The ether extract was shaken with dilute potassium hydroxide solution, and then shaken repeatedly with sodium thiosulphate solution to remove the free iodine which was present. It was then dried and fractionated under 748 mm. pressure. Twenty grams of α-isopropyl-β-ethylcarbethoxyhydroxamic ester,  $O:C(OC_2H_5)-N(C_2H_5)(OC_3H_7)$ (iso), boiling at 181°–182° were obtained. The yield was 62.5 per cent. of the theoretical.

0.3499 gram gave 26 cc. N at 20° and 743.5 mm. pressure.

	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.29

α-Isopropyl-β-ethylcarbethoxyhydroxamic ester is soluble in water, alcohol and ether. It gives no reaction with either ammoniacal silver nitrate, Fehling's solution or ferric chloride. It has a biting odor resembling phosgene.

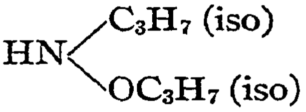
(*b*) *Preparation of α-Isopropyl-β-ethylhydroxylamine.*—Ten grams of the ester were treated in the usual manner with 20 grams of potassium hydroxide dissolved in water. The hydrochloride of α-isopropyl-β-ethylhydroxylamine, which was formed, remained as an oil upon evaporating the aqueous solution and drying in a desiccator over sulphuric acid. The aqueous solution of the salt reduced ammoniacal silver nitrate in the cold. Platinic chloride precipitated the chloroplatinate as a light yellow crystalline powder from an alcoholic solution of the hydrochloride.

0.1328 gram gave 0.0436 gram Pt.

	Calc. for $C_{10}H_{28}O_2N_2PtCl_6$	Found
Pt	32.19	32.83

When the hydrochloride is distilled with potassium hydroxide it gives α-isopropyl-β-ethylhydroxylamine. This is a colorless liquid boiling at 82°. It has an ammoniacal odor, and is not very soluble in water. Its aqueous solution reduces ammoniacal silver nitrate in the cold and Fehling's solution when heated. Its specific gravity (25°/25°) is 0.8730.

VIII. α-Diisopropylhydroxylamine,



$$HN\begin{cases} C_3H_7 \text{ (iso)} \\ OC_3H_7 \text{ (iso)} \end{cases}$$

A mixture of 13 grams of α,β-diisopropylcarbethoxyhydroxamic ester and 25 grams of potassium hydroxide dissolved in water were heated at 120° in a sealed tube for 36 hours. The contents of the tube were then distilled, and treated as usual. The hydrochloride of diisopropylhydroxylamine slowly crystallized out, mixed with ammonium chloride. The salt was recrystallized from alcohol. It formed flat plates, which melted at 74°.8.

Ten grams of powdered potassium hydroxide were poured over 5 grams of the hydrochloride contained in a distilling flask, and the mixture was warmed. Three and one-tenth grams of the free base were obtained. The yield was 82 per cent. of the theoretical. α-Diisopropylhydroxylamine is a colorless liquid boiling at 76.°6–77°. It has an ammoniacal odor mixed with that of an isocyanide. It is readily soluble in water, and rapidly reduces ammoniacal silver nitrate in the cold. It does not reduce Fehling's solution. Its specific gravity (25°/25°) is 0.8525.

The following table summarizes the properties of these compounds:

	Esters of hydroxyurethan	Alkylhydroxylamines		
		Free base		Hydrochloride.
	B. p.	B. p.	Sp. gr.	M. p.
α-Ethyl	195°–196° 95°–97° at 17 mm.	68° (Lossen)	0.8827 (Lossen) 7°.5	128° E. (Lossen)
α-Propyl	200°–210° E. 109°–111° at 15 mm.	86°.6–87°	0.8687	140°–141°
α-Isopropyl	102°–103° at 12 mm.	72°.2	0.8459	84°.8
α,β-Diethyl	72°–74° at 12 mm.	83° (Lossen)	0.829 at 0° (Lossen)	123°–124° (Jones)
α,β-Dipropyl	107°.5–108° at 20 mm.	85°–86°	0.8141	146°.6
α,β-Diisopropyl	101°–101°.5 at 15 mm.	76°.6–77°	0.8525	74°.8
α-Ethyl-β-propyl	189°	83°.8–84°	0.8033	72°.5–73
α-Ethyl-β-isopropyl	182° 84°–87° at 15 mm.	78°	0.8132	oil
α-Propyl-β-ethyl	92°.5 at 20 mm. 191°			96°.2
α-Isopropyl-β-ethyl	181°–182°	82°	0.8730	oil

SUMMARY

1. In the present paper methods of preparing the ethyl, propyl and isopropyl esters and mixed ethyl propyl and ethyl isopropyl esters of carbethoxyhydroxamic acid are described and the compounds studied. These esters are all high boiling oils with a characteristic odor. None of them reduce ammoniacal silver nitrate or Fehling's solution.

2. α-Propylhydroxylamine, α-isopropylhydroxylamine, and the different possible α-dialkylhydroxylamines containing ethyl, propyl and isopropyl groups, also their hydrochlorides and chloroplatinates, have been made and studied.

3. It has been shown that the esters of carbethoxyhydroxamic acid suffer hydrolysis with potassium hydroxide, the more easily the higher the molecular weight of the substituting group.[1]

4. The specific gravity of the dialkyl derivatives of hydroxylamine is less than the specific gravity of the monoalkyl derivatives of hydroxylamine, and all are specifically lighter than water. All boil between 70° and 90°.

5. The monoalkylhydroxylamines and the dialkylhydroxylamines containing two like groups are soluble in water, while the mixed dialkylhydroxylamines require a large amount of water for solution.

6. The aqueous solutions of the α-monoalkylhydroxylamines are energetic reducing agents. A second alkyl group in the molecule diminishes the reducing action.

In conclusion, I desire to express my sincere thanks to Dr. Lauder W. Jones, under whose direction the present work was carried out, for his kindly interest and many helpful suggestions and criticisms.

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[1] Experiments made in this laboratory by Miss Leonora Neuffer on the secondary butyl derivatives confirm this statement.

VITA.

Charles Henry Hecker was born in Cincinnati, Ohio, on May 15, 1886. He received his early education in the Cincinnati Public Schools, and graduated from Woodward High School in 1905. In the fall of 1905 he entered the Engineering College of the University of Cincinnati, and received the degree of Chemical Engineer from this institution in 1909. His graduating thesis was "Piping and Segregation in Steel Ingots." From 1909 to 1913 he was a student in the Graduate School of the University of Cincinnati, receiving from it in 1911 the degree of Master of Arts (the thesis for this degree was "An Account of the Alkyl Derivatives of Hydroxylamine") and in 1913 the degree of Doctor of Philosophy. During the year 1908–9 he was Student Assistant in Chemistry, in 1909–10 Graduate Assistant in Chemistry, and from 1910–13 Assistant in Chemistry. His major work for the Doctor's degree was in Chemistry, his first minor in Applied Mathematics and his second minor in Physics.