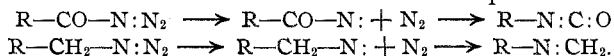


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]
REARRANGEMENTS OF SOME NEW HYDROXAMIC ACIDS RELATED TO HETEROCYCLIC ACIDS AND TO DIPHENYL- AND TRIPHENYL-ACETIC ACIDS.¹

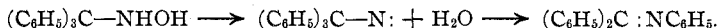
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Received July 11, 1921.

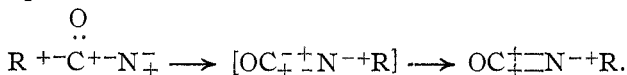
A summary of the serious attempts to explain the mechanism of the Beckmann rearrangement must necessarily include the work of Hoogewerff and van Dorp,² Hantzsch,³ Stieglitz,⁴ and Jones.^{5,6} The types of compounds generally assumed to undergo this rearrangement are the azides, mono-substituted β -hydroxylamines, monobromo-amines, oximes, amidoximes, oximido acid esters, acid halogen amides and the hydroxamic-acid derivatives. The azides are assumed to decompose as follows:



These two cases, together with the mono-substituted β -hydroxylamines presented below, furnish examples of the Beckmann rearrangement that have never been explained successfully except by the theory of Stieglitz and of Jones.



Stieglitz was the first investigator to propose the hypothesis that univalent nitrogen derivatives form the primary decomposition products in these rearrangements. His extensive experimental work has demonstrated the soundness of this postulate.⁷ Some years later, Jones formulated the reaction mechanism in a detailed manner by applying the theory of electron valence to the interpretation given by Stieglitz. The electron mechanism was represented as follows.^{5,6}



Unless there were a driving force acting to cause the transfer of the radical from carbon to nitrogen, it would still be difficult to imagine why the

¹ This paper incorporates a thesis presented by Charles D. Hurd in 1921 to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1887); **8**, 173 (1889).

³ Hantzsch, *Ber.*, **35**, 228, 3579 (1902); *ibid.*, **27**, 1256 (1894).

⁴ Stieglitz, *Am. Chem. J.*, **18**, 75 (1896); **29**, 49 (1903); Stieglitz and Earle, **30**, 399, 412 (1903); Stieglitz and Leech, *This Journal*, **36**, 272 (1914); etc.

⁵ Jones, *Am. Chem. J.*, **48**, 1 (1912); **50**, 414 (1913).

⁶ *This Journal*, **36**, 1268 (1914); etc.

⁷ The rearrangement of ketoximes, which was originally attributed by Stieglitz to the formation of univalent nitrogen derivatives, is now regarded as an exception. His present view assumes "the rearranging power of an intermediate hydrochloride of a univalent nitrogen derivative, acting in place of the ordinary free univalent nitrogen compound." See Montagne (*Ber.*, **43**, 2015 (1910)), Schroeter (*ibid.*, **44**, 1207 (1911)), and Stieglitz.

reaction should proceed, even with the explanation offered. Such a driving force is to be found in the shifting of electrons within the molecule. Jones stressed particularly that the free valences of univalent nitrogen afforded the "stage setting required to furnish a suitable environment in which the essential action," *viz.*, the transfer of the radical from carbon to nitrogen might take place. In a footnote to an article published some months later,⁴ Stieglitz stated that, in regard to the most fundamental questions of these rearrangements "postulating a shifting of electrons from carbon to nitrogen, and a migration of a positive radical, Professor Jones and the writer are happily in entire agreement."

As viewed from present day standards, this interpretation with very slight modifications, still holds. In late years, worthy evidence⁸ has been submitted to show that the positive charges possessed by an atom are centered in its nucleus. In compounds which are formed by the sharing of negative electrons, a "bond" consists of a pair of electrons held in common between two atoms. This theory of a chemical bond requires symbols in which positive charges cease to appear, except as they form an integral part of the nucleus of any atom. Such an interpretation would mean simply that a symbol, $C^{\oplus} \ddot{\vdash} N$, employed at a time when ion charges, rather than electrons in the present sense, held the attention of chemists, would now become $C : N$; that is, the carbon atom and the nitrogen atom share a single pair of electrons. This conception of paired electrons would account just as readily for the driving force necessary to bring about rearrangement. Thus, the system of symbols $C : N \longrightarrow C \vdash N$ is equivalent to $C^{\oplus} \ddot{\vdash} N \longrightarrow C^{\oplus} \ddot{\vdash} N$ previously employed.

Possibly the formula $C^{\oplus} \ddot{\vdash} N$ contains an assumption not necessarily implied by the formula $C \vdash N$ in which two pairs of electrons are shared, since the former suggests that a compound which contains such a group would not be exactly non-polar, although it should not be regarded as polar in the sense in which $Na^+ Cl^-$ must be. To meet difficulties of this kind, Lewis employs formulas in which the pairs of electrons are placed nearer one symbol than another, *e. g.*, $A : B$, which implies that the molecule AB shows some polar characteristics. With these modifications to adapt the old electronic formulas to present day practices, equations may be given to represent the rearrangement of a univalent nitrogen derivative of a hydroxamic acid.

Formulas I, Ia and Ib represent the intermediate univalent nitrogen derivative; Formulas II, IIa and IIb represent a transition stage, the rearrangement of the positive radical, R. It will be noted that, in Formula II, although the carbon atom still has its "octet" completed, the nitrogen atom has only 6 electrons in the outer shell. By the sharing of electrons, both the nitrogen and the carbon atoms may complete their octets. This

⁸ G. N. Lewis, Langmuir and others.

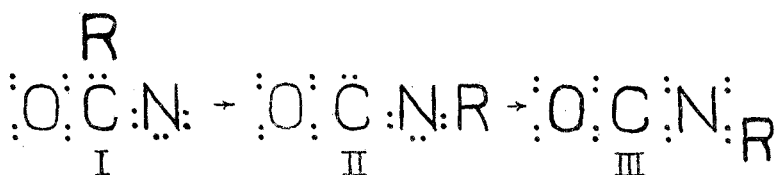


Fig. 1.

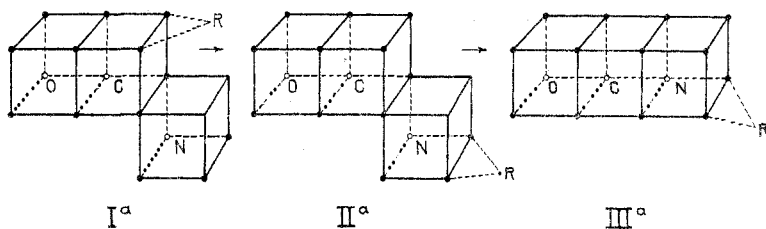
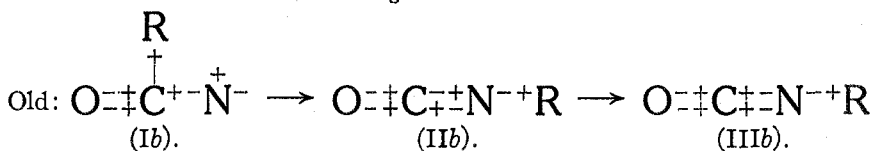


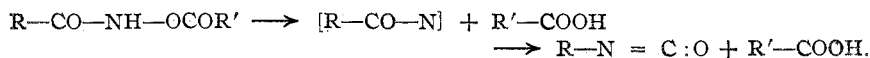
Fig. 2.



is represented in Formulas III, IIIa and IIIb, the isocyanate stage in the rearrangement.

With this conception, it is easy to understand why the radical R is able to part company with carbon and attach itself to nitrogen. No hypothesis has been offered, however, to explain why one radical R will do so with much greater readiness than some other radical R'. To seek an explanation of this factor was one of the motives that prompted the work which follows.

Chief interest in the present paper centers upon the reactions of dihydroxamic acids. They have been shown to rearrange in the following manner.



Either the action of heat, or of warm solutions of alkalis, will produce this effect. In the former case, the isocyanate is formed by dry distillation of the dihydroxamic acid, or, preferably, by heating a salt of the acid. Usually there is a fairly definite temperature at which the decomposition of the dry salt takes place. However, certain cases have proved that it is not a reliable method to use when two similar compounds are to be judged for comparative ease of rearrangement. If solutions are employed, the isocyanate generally reacts immediately with water to form the amine, or the corresponding disubstituted urea. The behavior of neutral solutions

of the sodium or of the potassium salts in water seems now to furnish a more accurate criterion by which to judge the ease of rearrangement of these particular compounds

A few years ago, phenyl-acethydroxamic acid⁹ was studied. The benzoyl ester of this acid was capable of forming salts which possessed unusual instability towards heat. Its solid potassium salt suffered Beckmann rearrangement spontaneously at room temperature. Here,



Because of this rearrangement, it was not found possible to form a clear solution of the salt in water, unless it was prepared immediately after the isolation of the salt. We have recently repeated this experiment, and found, in addition, that the clear solution, when left at room temperature for 2 hours, did not undergo a noticeable rearrangement. A small white precipitate of the urea collected in 10 hours, however. The similar potassium salt of the benzoyl ester of acethydroxamic acid, $\text{CH}_3\text{—CO—NK—OCOC}_6\text{H}_5$, did not possess this marked tendency to rearrange; so the replacement of hydrogen by phenyl must have occasioned the decrease in stability. With this in view, diphenyl- and triphenyl-acethydroxamic acid were deemed important compounds to study. The sodium or the potassium salts of their acyl esters should exhibit a greater capacity for rearrangement in solution than the similar compounds in the monophenyl series.

The univalent nitrogen compounds, $[\text{R—CO—N}]$, which have been assumed to be the primary products of decomposition, have never been isolated. The isocyanates, resulting from rearrangements which involve readjustments of electrons, are obtained instead. It was not our object in this investigation to try to isolate such derivatives. Indeed, with the groupings $[(\text{C}_6\text{H}_5)_2\text{CH—CO—N}]$, and $[(\text{C}_6\text{H}_5)_3\text{C—CO—N}]$ the tendency to rearrange to form isocyanates should be greater than in any case previously studied.

Triphenylmethyl is a group that is known to display a tendency to exist as a free radical. Certainly, then, it would seem highly probable that a derivative such as $[(\text{C}_6\text{H}_5)_3\text{C—CO—N}]$, would be far more apt to separate momentarily into $[(\text{C}_6\text{H}_5)_3\text{C—}]$ and $[\text{—CO—N}]$ than a group such as $[\text{H}_3\text{C—CO—N}]$ in which the linking of carbon to carbon is conceived to be stronger. The latter would give rise to $[\text{H}_3\text{C—}]$ and $[\text{—CO—N}]$. By no means must it be considered probable that free radicals displaying the great order of reactivity shown by triphenylmethyl could ever be isolated while in the presence of the highly reactive univalent nitrogen.

As a result of earlier experiments, and of those included in this article,

⁹ Thiele and Pickard, *Ann.*, **309**, 189 (1899); Jones, *Am. Chem. J.*, **43**, 6 (1912).

we were led to formulate an hypothesis which may be stated as follows: the relative ease of rearrangements of the Beckmann type is dependent upon the tendency for the radical R, in the univalent nitrogen derivative, *e. g.*, [R—CO—N], to exist as a free radical.

It must be noted that this hypothesis does not deal with the ease of formation of the univalent nitrogen compound. It is essential that the group —NHX in the original molecules, R—CO—NHX, be identical when two different compounds are compared. An extreme case of the effect produced when different groups are substituted is displayed in the acyl alkyl halogen amines, *e. g.*, R—CO—NCl—C₅H₁₁. Stieglitz observed that compounds of this type show no tendency to undergo rearrangement.¹⁰

Triphenylmethyl, and other groups that are known to exist free, have been shown to exhibit polar characteristics in many of their compounds. For example, triphenylmethyl bromide displays marked conductivity when dissolved in sulfur dioxide;¹¹ this is one of the arguments which leads to the belief that an ion, or a pseudo-ion, (C₆H₅)₃C⁺, must exist in the solution. Furthermore, it has been shown that triphenylmethyl is formed in the cathode chamber when triphenylmethyl bromide is electrolyzed. In fact, appropriate solutions of triphenylmethyl, itself, conduct the electric current.¹² These are important facts in support of our hypothesis.

From the standpoint of our hypothesis, it would seem that the tendency for the phenylmethyl radical, C₆H₅—CH₂, to exist free is greater than for methyl, CH₃. The allusion is to the experimental fact that the derivatives of phenyl-acethydroxamic acid suffer rearrangement more easily than those of acethydroxamic acid. On the basis of this hypothesis, also, the observation made by McCoy and Stieglitz,¹³ and supplemented by van Dam,¹⁴ that dibromo-salicylic-bromo-amide rearranges even at —12°, is evidence for the tendency of the radical C₆H₂Br₂.OH to exist free. Other bromo-amides that have been studied exhibit a more stable character.

From this same standpoint, it may be predicted that any substituted acethydroxamic acid containing a tri-aryl methyl group will undergo rearrangement with great ease. For example, tri-bisphenyl-acethydroxamic acid, (C₆H₅—C₆H₄)₃C—CO—NHOH, should form derivatives that are even more unstable than triphenyl-acethydroxamic acid. The group tribisphenylmethyl, in contrast to triphenylmethyl, is one that has been shown to exist exclusively in the monomolecular form at room

¹⁰ Stieglitz, *Am. Chem. J.*, **29**, 49 (1903).

¹¹ Gomberg, *Ber.*, **35**, 2397 (1902).

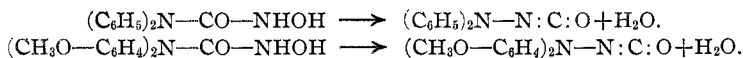
¹² Gomberg and Cone, *ibid.*, **37**, 2403 (1904); Schlenk, Weichel, and Herzenstein, *Ann.*, **372**, 10 (1910).

¹³ McCoy and Stieglitz, *Am. Chem. J.*, **21**, 116 (1899).

¹⁴ Van Dam, *Rec. trav. chim.*, **18**, 408 (1899); **19**, 318 (1900).

temperature.¹⁵ Therefore, in the univalent nitrogen derivative, $[(C_6H_5-C_6H_4)_3C-CO-N]$, there should be a pronounced tendency for the momentary existence of tribisphenylmethyl, and the ultimate formation of the isocyanate.

The applications of this hypothesis need not be restricted to one class of radicals that show a tendency to exist free. Since certain radicals which contain divalent nitrogen¹⁶ have been prepared, a hydroxamic acid which could furnish such a group might also rearrange with considerable ease. Illustrations would be,



Benzophenone when it is treated in ether solution with potassium develops an intense color.¹⁷ Since the boiling point of the ether is unchanged after complete solution of the metal, a trivalent carbon radical, $(C_6H_5)_2C(OK)-$, is assumed to exist in solution. In this connection, therefore, the hydroxamic acid of benzilic acid, $(C_6H_5)_2C(OH).CO.NHOH$, should present a somewhat complicated, but, nevertheless, a highly interesting case to develop.¹⁸

Our assumptions were corroborated to a large extent by the experimental evidence submitted in this paper. Unexpected difficulties presented themselves in the attempts to prepare the sodium and potassium salts in the diphenyl-acethydroxamic acid series. If the customary procedure, *viz.*, the addition of an alcoholic solution of sodium ethylate to an alcohol-ether solution of the benzoyl ester of the acid, *e. g.*, $(C_6H_5)_2CH-CO-NH-OCOC_6H_5$, was followed, no precipitation of the salt occurred, even when a very large excess of ether was used. The existence of the salt in solution was proved, but the salt could not be obtained pure. Evaporation of the alcohol and ether *in vacuo* always left a mixture of the salt with its products of decomposition and rearrangement; *viz.*, diphenylmethyl isocyanate, diphenylmethyl urethane, sodium benzoate and, also, *sym.* bi-diphenylmethyl urea, if any water was present. When this residue was extracted with cold water, and the solution filtered and boiled, there was an immediate precipitation of some *sym.* bi-diphenylmethyl urea, which is the normal reaction for salts of this character.

Similar difficulties arose in the study of triphenyl-acethydroxamic acid. The sodium or the potassium salts of the benzoyl ester could not be formed pure. The acetyl ester seemed to yield a potassium

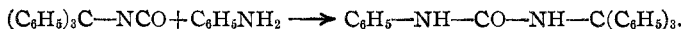
¹⁵ Schlenk, Weichel and Herzenstein, *Ann.*, **372**, 11 (1910).

¹⁶ Wieland, "Die Hydrazine," F. Enke, Stuttgart, **1913**, p. 73.

¹⁷ Schlenk and Thal, *Ber.*, **46**, 2843 (1913); Schlenk and Weichel, *ibid.*, **44**, 1183 (1911).

¹⁸ Jones and Neuffer (*THIS JOURNAL*, **39**, 659 (1917)), have studied the rearrangements of lact-hydroxamic acid, $CH_3-CHOH-CO-NHOH$, and of mandel-hydroxamic acid, $C_6H_5CH(OH).CO.NHOH$.

salt insoluble in ether; but subsequent tests showed that it was mixed to a large extent with triphenylmethyl isocyanate. This isocyanate, not previously described, possesses a remarkable stability, even in the presence of boiling water. Thus, when the precipitate containing the potassium salt was taken up in water, and heated, only the isocyanate separated. The cause of its sluggishness may be attributed to its insolubility in water. It reacts normally with aniline in ether to form the urea derivative.



The evidence obtained proves that there is an increase in the ease of rearrangement of the molecule as more phenyl groups are added. In solution, the potassium salt of the benzoyl or acetyl ester of monophenyl-acethydroxamic acid was comparatively stable at room temperature; a similar solution of the diphenyl compound became turbid in a short time; whereas the triphenyl derivative showed rearrangement almost immediately when it was treated with water. In the diphenyl or in the triphenyl series, it was found to be impossible to obtain a sodium or a potassium salt which failed to show the effects of extensive decomposition. For this reason, the temperature of decomposition of the pure dry salts could not be determined accurately.

The silver salts, made by the action of aqueous silver nitrate upon the cold ether solutions of the sodium or potassium salts were somewhat soluble,¹⁹ but precipitated for the most part. Chromo-isomerism was displayed here. The silver salt of the benzoyl ester of diphenyl-acethydroxamic acid, when first formed, was bright yellow. In a short time, the yellow substance changed to a pure white salt. The similar salt in the triphenyl series precipitated as a white solid, but changed soon to a brilliant yellow salt.²⁰

¹⁹ The exact cause of the solubility of the sodium and of the potassium salts in alcohol with a large excess of ether is purely a matter of conjecture. There may be tautomeric forms, one soluble and the other insoluble, such as $(\text{C}_6\text{H}_5)_2\text{CHC}-\text{O}-\text{NK}-\text{OCOCCH}_3$ and $(\text{C}_6\text{H}_5)_2\text{CH}-\text{C}(\text{OK})\text{:N}-\text{OCOCCH}_3$. It may be caused by the addition of a molecule of alcohol; thus, $(\text{C}_6\text{H}_5)\text{CH}-\text{C}(\text{OK})(\text{OC}_2\text{H}_5)-\text{NH}-\text{OCOCCH}_3$. These are suggestions, which may be correct. Salts of the alkali metals which are soluble in ether are very uncommon but not unknown. Sodium iodide behaves in this manner. Loeb, *THIS JOURNAL*, **27**, 1020 (1905).

²⁰ There are many chromo-isomers on record; such, for example, as silver violurate (Hantzsch, *Ber.*, **42**, 969 (1909); Henrich, "Theorien der Org. Chem.," **1918**, p. 364) which is colorless when precipitated, and gradually changes through green to a dark brown. Titherley (*J. Chem. Soc.*, **71**, 468 (1897); **79**, 408 (1901)), reported silver benzamide to exist in an orange and in a white modification. Jones and Oesper (*THIS JOURNAL*, **36**, 2208 (1914)), found chromo-isomeric silver salts among acyl derivatives of hydroxy-urethanes; *e. g.*, $\text{C}_6\text{H}_5\text{CO}-\text{O}-\text{NAg}-\text{CO}-\text{OR}$. These salts, yellow when prepared were easily transformed into white modifications, especially if R represents *iso*-butyl, *iso*-amyl, or benzyl.

vinyl ketene, $\text{CH}_2 : \text{CH}-\text{C}(\text{CH}_3) : \text{CO}$; ethyl ketene carboxylic ester, $\text{OC} : \text{C}(\text{C}_2\text{H}_5)-\text{COOC}_2\text{H}_5$; carbon suboxide, C_3O_2 ; and ketene, itself, with hydroxylamine, or substituted hydroxylamines, should lead to interesting results.

The second new method of preparing hydroxamic acids is a modification of the long established method in which acid chlorides are employed. Heretofore, the chloride has been allowed to act upon an aqueous solution of hydroxylamine. This always leads to side reactions, which lower the yield and augment the difficulty of purification of the desired product. When the acid chloride was dissolved in a neutral solvent, such as benzene, and a trifle more than 2 mols of free hydroxylamine was added, it was found that a quantitative yield of monohydroxamic acid resulted.



This reaction was modified later so that the preparation of free hydroxylamine was avoided. Two equivalents of pyridine or of sodium carbonate crystals was used with one equivalent of hydroxylammonium chloride in a benzene or an ether solution of the acid chloride. A quantitative yield was obtained here also.

Two heterocyclic hydroxamic acids were studied, one a derivative of furane, and the other of thiophene. The former (I) will be called



pyromucyl-hydroxamic acid; and the latter (II), α -thenhydroxamic acid.²³ Previous work with heterocyclic hydroxamic acids is very slight. Pyromucyl-hydroxamic acid was prepared by Pickard and Neville,²⁴ and by Rimini,²⁵ but was not extensively studied. A few isolated examples in the pyrone series are known.²⁶ *Anti*-ethyl-thenhydroximic acid, $\text{C}_4\text{H}_3\text{S}-\text{C}(\text{OC}_2\text{H}_5) : \text{NOH}$, has been studied by Douglas.²⁷ It was not found possible to isolate this in the *syn* form. One object of our investigation was to

²³ Other names such as α -thienyl formhydroxamic acid, or α -thenoyl- β -hydroxylamine suggest themselves. Both of these names have their shortcomings. Essentially, the compound is a derivative of thiophene, not of formhydroxamic acid; to call it a "hydroxylamine," conceals the acid nature of the substance. The difficulty could be avoided easily, if thiophene- α -carboxylic acid possessed a simple name. It would be entirely in keeping with both its chemical and physical properties to assign it a name similar to benzoic acid. Inasmuch as the grouping "*thenoyl*," $\text{C}_4\text{H}_3\text{S}-\text{CO}-$ is in common usage already, the name *thenoic* acid is suggested. The prefix "*then*" corresponds to "*benz*," and just as $\text{C}_6\text{H}_5-\text{CONHOH}$ is benzhydroxamic acid, so $\text{C}_4\text{H}_3\text{S}-\text{CONHOH}$ is α -thenhydroxamic acid.

²⁴ Pickard and Neville, *J. Chem. Soc.*, 79, 847 (1901).

²⁵ Rimini, *Gazz. chim. ital.*, [2] 31, 90 (1901).

²⁶ Oliveri-Mandala, *J. Chem. Soc.*, 100, 916 (1905); 88, 428 (1911); *Atti. accad. Lincei*, [5] 14, ii, 162 (1905).

²⁷ Douglas, *Ber.*, 25, 1312 (1892).

study the chemical behavior of pyromucyl-, and of thenhydroxamic acids, since they are typical members of a legion of unstudied heterocyclic compounds.

Pickard and Neville²⁴ stated "an aqueous solution of the sodium salt" of the benzoyl ester of pyromucyl-hydroxamic acid, $C_4H_3O-CO-NNa-O-COC_6H_5$, "when boiled with water evolves carbon dioxide and an oil (containing nitrogen) is obtained when the solution is evaporated. The oil is presumably difurfuran-carbamide, but decomposes completely when hydrolyzed. No better success was obtained on attempting to prepare the carbamates by boiling the sodium salt with alcohols."

A year later, Curtius and Leimbach²⁸ tried to isolate *sym.* difuryl urea, $CO(NH-C_4H_3O)_2$, from the azide, $C_4H_3O-CO-N_3$, and met with only partial success. Crystals melting at 229° , and at 220° were obtained. The former was found to contain 12.01% of nitrogen, the latter 12.13%. The calculated percentage for difuryl urea is 14.56%.

In the present study, it was found that when the potassium salt, $C_4H_3O-CO-NK-OCOC_6H_5$, was warmed gently in water solution, and cooled at the first evidence of precipitation, the precipitate formed was the free benzoyl ester, $C_4H_3O-CO-NH-OCOC_6H_5$. This compound is produced by hydrolysis, not by rearrangement. When this same filtrate was heated to boiling, much carbon dioxide was evolved, and a red resinous mass precipitated; after purification, it melted at about 210° . This material is similar to the product found by Curtius and Leimbach.

Thenhydroxamic acid derivatives were observed to undergo a slight hydrolysis also, but rearrangement to form *sym.* di-thienyl urea was a simple matter. Curtius and Thyssen²⁹ obtained this same urea from the azide, $C_4H_3S-CO-N_3$. The properties of their compound check with those of ours in all respects. The normal reaction, then, is as follows,



This behavior is entirely analogous to that of the salts of dibenzhydroxamic acid.

It will be noticed that the benzoyl ester of thenhydroxamic acid is isomeric with the thenoyl ester of benzhydroxamic acid. The latter compound was prepared, so that comparative properties of the two might be observed. Melting points of the pure substance, and the temperatures at which the potassium and the silver salts decomposed were for the former 144° , 125° and 168° ; for the latter, 133° , 135° and 165° , respectively. The ease of rearrangement of the potassium or the sodium salts in aqueous solution was nearly identical. Too much stress should not be laid upon the temperature of decomposition of the solid salts. The figures are of importance, but the method of applying heat to determine the temperature

²⁸ Curtius and Leimbach, *J. prakt. Chem.*, [2] 65, 37 (1902).

²⁹ Curtius and Thyssen, *ibid.*, [2] 65, 17 (1902).

of decomposition influences them very much. For example, when the potassium salt of the latter compound is heated slowly there is no visible action until about 160° . However, if the tube containing the salt is suddenly thrust in a bath at 135° , there is violent decomposition. With most of the salts, however, there is a fairly definite temperature at which they explode when heat is applied gradually.

The physical and some of the chemical properties of thiophene compounds are very similar to those of corresponding benzene compounds. Thenhydroxamic acid is no exception. It melts at 124° , while benzhydroxamic acid also melts at 124° . It is of interest to note that di-thenhydroxamic acid melts much lower than di-benzhydroxamic acid. The former was found to exist in two modifications, one melting at $105\text{--}107^{\circ}$, and the other at $83\text{--}86^{\circ}$. Dibenzhydroxamic acid is reported by Lossen³⁰ to melt at 145° . Both of these heterocyclic hydroxamic acids resemble benzhydroxamic acid in that they form an acid ammonium salt,³¹ $(R\text{--CO--NH--O})_2\text{H.NH}_4$, which is difficultly soluble in water.

Experimental Part.

1. Preparation of Diphenyl-acethydroxamic acid, $(C_6H_5)_2CH.CO.NHOH$.

First Method. From Ethyl Diphenyl-acetate.—Thirty g. of ethyl diphenyl-acetate was dissolved in 180 cc. of methanol which contained a little more than the calculated amount of free hydroxylamine. The hydroxylamine was liberated from 15 g. of its hydrochloride by a solution of sodium methylate, which contained 4.8 g. of sodium. To this mixture a solution of 3.3 g. of sodium in 60 cc. of methanol was added. After 10 hours, the mixture was diluted with one liter of water, and the hydroxamic acid was precipitated with dil. sulfuric acid. The filtrate, separated from this precipitate, contained a little diphenyl-acethydroxamic acid. By the addition of a solution of copper acetate to this filtrate, 4 g. of the green copper salt was obtained.

A solution of sodium carbonate was used to purify the crude diphenyl-acethydroxamic acid, since it was found to dissolve all of the diphenyl-acetic acid present, but none of the hydroxamic acid. The insoluble part was removed and washed several times with water, and when dry, weighed 35 g. The crude material melted between 145° and 158° . Recrystallization from ethyl acetate formed needle-shaped crystals melting at 172° .

Diphenyl-acethydroxamic acid is soluble in acetone, in ethyl acetate, in ethyl alcohol, and in a warm solution of sodium hydroxide. It is insoluble in water, in a solution of sodium carbonate (hot), in ligroin, in benzene, in ether, or in chloroform. An alcoholic solution yields the characteristic red color with ferric chloride.

Analyses. Subs., 0.1470, 0.1589; CO_2 , 0.3962, 0.4321; H_2O , 0.0767, 0.0852. Calc. for $C_{14}H_{13}O_2N$: C, 73.98; H, 5.77. Found: C, 73.53, 74.18; H, 5.84, 6.00.

Subs., 0.3042; N, 16.8 cc. (24° and 743.3 mm. (17.5°)) 30% KOH sol. used. Calc. N, 6.17. Found: 6.08.

Diphenyl-acethydroxamic acid could not be prepared in quantity by the action of ethyl diphenyl-acetate upon free hydroxylamine. Enough was formed to give a purple coloration with ferric chloride, but in order to obtain a satisfactory yield, one mol. of sodium methylate (or its equivalent) seemed essential.

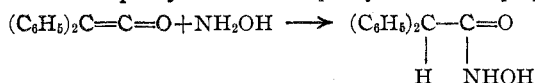
³⁰ Lossen, *Ann.*, **161**, 347 (1872).

³¹ Lossen, *ibid.*, **231**, 172 (1894).

Second Method. From Diphenyl-acetyl Chloride.—Diphenyl-acetylhydroxamic acid was also prepared from diphenyl-acetyl chloride, although the method was less satisfactory because of side reactions. A solution of 1.9 g. of hydroxylammonium chloride in a small amount of water, was mixed with a solution of 2.8 g. of sodium carbonate. After carbon dioxide had escaped, 6 g. of diphenyl-acetyl chloride crystals was added and the mixture was shaken vigorously. When the reaction had apparently ceased, the product was warmed to 60°, then filtered to collect the solid. When the filtrate was acidified, half a gram of diphenyl-acetic acid (m. p. 145°) precipitated.

The residue obtained by filtration (5 g.) gave a double melting point, 155–160°, and 215–230°. Recrystallization from ethyl acetate led to the separation of diphenyl-acetylhydroxamic acid (m. p. 172°), and *sym.* bi-diphenylmethyl urea (m. p. 269–270°), $\text{CO}(\text{NH}.\text{CH}(\text{C}_6\text{H}_5)_2)_2$, which will be described later. Yield of the hydroxamic acid, 2 to 3 g.

Third Method. From Diphenyl Ketene.—Diphenyl ketene was prepared by Schroe-



ter's method.³² Azibenzil, formed by the oxidation of 29 g. of benzil hydrazone dissolved in 120 cc. of dry benzene, was warmed to 60° in a current of dry carbon dioxide for about 3 hours, until evolution of nitrogen had ceased.

Two g. of freshly distilled hydroxylamine was suspended in a mixture of 50 cc. of absolute ether and 20 cc. of ethyl acetate, which had been carefully purified to remove traces of alcohol, water, or acetic acid. To this mixture, 100 cc. of the benzene solution of diphenyl ketene was added, while air was excluded carefully by maintaining an atmosphere of dry hydrogen gas.³³ Ether was employed to increase the solubility of hydroxylamine, which is insoluble in benzene. A better yield would be obtained, no doubt, if an ether solution of diphenyl ketene were used, but in this preparation the yield was of secondary interest.

After the mixture had been shaken thoroughly, the product gradually darkened. From time to time, the stopper of the flask was lifted momentarily to release the pressure, probably caused by the decomposition of some hydroxylamine. After two hours, very little pressure accumulated; so the flask was left overnight. The solvent was then distilled at the temperature of a water-bath and the residue was poured into an Erlenmeyer flask to crystallize. The crystals secured in this way were crystallized from ethyl acetate and petroleum ether. Yield, 4 g. After one recrystallization, the melting point was 169–172°.

To establish the identity of this compound and diphenyl-acetylhydroxamic acid prepared above, the benzoyl esters of both were made and found to possess identical properties. Both preparations melted at 140°. (See below.)

Fourth Method. From the Copper Salt.—Apparently, there are two forms of monophenyl-acetylhydroxamic acid. By the decomposition of the copper salt with hydrogen sulfide, Thiele and Pickard⁹ obtained a compound melting at 121°. Phenyl-acetylhydroxamic acid which melted at 145° was prepared by Jones by the interaction of free hydroxylamine and ethyl phenyl-acetate. It was thought probable that a second form of diphenyl-acetylhydroxamic acid might be obtained, if the copper salt should be suspended in alcohol and decomposed by hydrogen sulfide, but such was not found to be the case.

Benzoyl Ester: $(\text{C}_6\text{H}_5)_2\text{CH}.\text{CO}.\text{NHO}-\text{CO}.\text{C}_6\text{H}_5$.—Three and five-tenths g. of diphenyl-acetylhydroxamic acid was dissolved in a warm solution of potassium hydroxide

³² Schroeter, *Ber.*, **42**, 2345 (1909); Staudinger, *Ref.* **21**, p. 144.

³³ CO_2 reacts with NH_2OH .

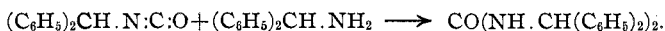
just sufficient to cause the solution of the acid. Benzoyl chloride (1.65 cc.) was added in 4 portions. The reaction mixture was constantly agitated, while a stream of cold water was played over the flask. This gave 6 g. of crude dry product. Crystallization of this material from alcohol yielded plates which melted at 139.5–141°. Three recrystallizations caused the compound to have a sharp melting point, 140–140.5°. This ester is soluble in acetone, in ethyl acetate, in chloroform and in hot alcohol; slightly soluble in ether and in benzene, and insoluble in water, in ligroin and in a cold solution of sodium hydroxide. When the solution of sodium hydroxide is warmed, rearrangement takes place. When the ester was heated a little above its melting point, the odor of isocyanate became noticeable at once.

Analysis. Subs., 0.5417:N, 20.6 cc. (over 40% KOH, at 26° and 740.1 mm.) Calc. for $C_{21}H_{17}O_3N$:N, 4.22. Found: 4.13.

Potassium Salt. $(C_6H_5)_2CH.CO.NK.O.CO.C_6H_5$.—First Method. Alcoholic potassium hydroxide was prepared of such a strength that 1 cc. \approx 0.113 g. of KOH. One cc. of this reagent was added to a solution of 0.67 g. of the benzoyl ester in a mixture of 15 cc. of absolute alcohol and 10 cc. of dry ether, previously cooled to -15° . There was no precipitation when a sample of the solution was diluted largely with ether, or with petroleum ether. Part of the solution was treated with silver nitrate to form the silver salt (see p. 2435). The rest was evaporated *in vacuo* over conc. sulfuric acid. For convenience, the residue left after evaporation of the solution will be called "R."

This residue (R) was shown to consist of a mixture of the desired potassium salt, together with diphenyl-methyl isocyanate, diphenyl-methyl urethane, and potassium benzoate. The part of (R) which was soluble in ether was extracted and half of this ether solution was evaporated. A residue remained which melted at 90° to 100° . Two recrystallizations of this material from benzene and ligroin resulted in the isolation of the urethane, $(C_6H_5)_2CH.NH.CO.OC_2H_5$, melting at 124° . The properties of this compound were confirmed by its preparation from diphenyl-acetamide, (see below).

The other half of the portion soluble in ether was shown to contain the isocyanate, $(C_6H_5)_2CH.NCO$, since an ether solution of benzhydryl-amine added to it, caused an immediate precipitate of the urea, m. p. 268–270°, according to the equation,



Benzhydryl-amine is without action upon an ether solution of the urethane.

The residue left from (R) after ether extraction was also divided into two parts. One part was analyzed and was found to contain a much greater percentage of potassium than that calculated for the potassium salt, $(C_6H_5)_2CH.CO.NK.O.CO.C_6H_5$.

Analysis. Subs., 0.1385: K_2SO_4 , 0.0441. Calc. for $C_{21}H_{16}O_3NK$:K, 10.58. Found: 14.30.

This would indicate the presence of potassium benzoate as an impurity.

The other part dissolved in water to give a clear solution. A portion of the solution was boiled; this caused an immediate precipitation of *sym.* bi-diphenylmethyl urea, which confirms the presence of some potassium salt of the benzoyl ester. The remainder of the solution, acidified with dil. hydrochloric acid, gave a precipitate which, by fractional crystallization from alcohol, was resolved into the original benzoyl ester of diphenyl-acethydroxamic acid, m. p. 140° , and benzoic acid, m. p. 121° .

Second Method. A solution of potassium ethylate prepared from metallic potassium instead of potassium hydroxide gave no different results.

An interesting observation was made concerning the extreme solubility of the potassium salt. When 0.33 g. of the benzoyl ester was suspended in a cold mixture of 3 cc. of alcohol, and 6 cc. of ether, the undissolved ester went into solution when alcoholic potash was added.

Third Method. About 0.36 g. of silver salt, $(C_6H_5)_2CH.CO.NAg.O.CO.C_6H_5$ (see preparation, below) suspended in 4 cc. of ice-water, was treated with 0.12 g. of potassium bromide, dissolved in a little water. The mixture was stirred frequently. After an hour, the precipitate had assumed the yellow color of silver bromide. Ample proof of metathesis was furnished when a little of the solution was filtered, and heated. A heavy crystalline precipitate of *sym.* bi-diphenylmethyl urea (m. p. 268–270°) separated. There appears to be no record of the use of silver salts in the preparation of alkali salts of hydroxamic acid.

The reaction mixture was kept at 0° overnight. Little, if any, decomposition occurred. One-third of the solution, after filtration, was acidified. The benzoyl ester precipitated in quantity. When a second portion of this solution was allowed to stand at room temperature, a gradual precipitation of the urea took place.

A portion of the solution containing the potassium salt was treated with silver nitrate, copper acetate, and cobalt nitrate solutions. The colors of the three precipitates were white, light green, and light pink respectively. These salts were not studied further.

Sodium Salt. $(C_6H_5)_2CH.CO.N.Na.O.CO.C_6H_5$.—A convenient solution of sodium ethylate to employ is one in which 1 cc. \approx 0.023 g. of sodium. To a solution of 0.3 g. of benzoyl ester in 4 cc. of absolute alcohol and 15 cc. of ether, 0.9 cc. of the sodium ethylate solution was added. (The ester was in slight excess.) Just as with the potassium salt, here, also, no precipitate could be obtained. One portion of this solution was saved for the preparation of the silver salt, (see below) while a second portion of the solution was evaporated rapidly, and the residue extracted with water. Filtration from the insoluble matter left a clear solution that soon became turbid. A precipitate of the urea derivative was formed by boiling the solution.

The remainder of the ether-alcohol solution was evaporated *in vacuo* over conc. sulfuric acid. Ether caused the extraction of a large amount of the urethane, m. p., 123–124°. The portion insoluble in ether was shown by analysis to be chiefly sodium benzoate.

Analysis. Subs., 0.0558: Na_2SO_4 , 0.0251. Calc. for $C_{21}H_{16}O_3NNa$: Na, 6.51. Calc. for $C_6H_5.COONa$: Na, 15.97. Found: 14.56.

Silver Salt. $(C_6H_5)_2CH.CO.NAg.O.CO.C_6H_5$.—First Method: from the potassium salt. The ether-alcohol solution of the potassium salt (see p. 2434) was treated with an aqueous solution of silver nitrate. The ether layer instantly assumed a deep yellow color, but remained clear. When this solution was shaken, a *pure white* precipitate of the silver salt formed, and the yellow color of the ether layer disappeared simultaneously.

Analysis. Subs., 0.1164; Ag, 0.0285. Calc. for $C_{21}H_{16}O_3NAg$: Ag, 24.62. Found: 24.49.

A little of the white salt, suspended in ether, did not cause the ether to assume a yellow color, even when alcohol was added. Here, again, as with the sodium or the potassium salt, there is evidence of the existence of two modifications, one of which is soluble in ether and alcohol, and the other insoluble. Gradual rearrangement occurred when the salt was heated gently; the odor of isocyanate was very marked. In a small tube the salt decomposed with a puff at about 145°.

Second Method: from the sodium salt. A similar procedure was followed with an ether-alcohol solution of the sodium salt (see above). In this case, the ether layer became yellow in color, and the precipitate which formed was yellow as well. The color of the salt gradually changed to pure white, and, in so doing, formed needle-shaped crystals. This change of color was hastened by scratching the precipitate with a glass rod. That the color change commenced at the surface was proved; for

yellow clumps that had apparently turned white, were found still to be yellow at the center. This material, when heated on a spatula, decomposed with a puff to form the isocyanate and a residue of metallic silver was left after ignition.

Di-acetyl Ester, $(C_6H_5)_2CH.CO.N(CO.CH_3).O.CO.CH_3$.—Apparently, the normal reaction of acetic anhydride and diphenyl-acethydroxamic acid leads to the formation of the di-acetyl ester, a trihydroxamic acid, instead of the mono-acetyl ester, even when half a mol. of acetic anhydride is used. In this case, a mixture of mono- and di-acetyl derivatives is obtained. By recrystallization from alcohol, the mixture was separated only with the greatest difficulty.

To prepare the di-acetyl ester, diphenyl-acethydroxamic acid (3 g.) was dissolved in a large excess of acetic anhydride (10 cc.). This solution was kept warm for 2 hours, and the excess of acetic anhydride was then evaporated in a vacuum desiccator containing powdered alkali. The solid ester, after recrystallization from alcohol, melted at 95.5–97.5°. It is soluble in hot alcohol, in ethyl acetate, in chloroform, in acetone and in benzene. It is but slightly soluble in ether, and is insoluble in water, in ligroin, or in a solution of sodium hydroxide.

Analysis. Subs., 0.5008: N, 19.8 cc. (over 40% KOH at 25° and 743.8 mm. (26°)). Calc. for $C_{18}H_{17}O_4N$: N, 4.50. Found: 4.34.

Two g. of the di-acetyl ester was distilled in a small flask heated by a metal bath. A liquid that weighed 0.45 g. was collected when the temperature of the bath rose to between 200° and 300°. This liquid all redistilled between 120° and 138°; this fraction consisted chiefly of acetic anhydride. When the residue in the flask was heated with a free flame, a liquid distilled at about 300° and left resinous materials in the flask. When the distillate was treated with an ether solution of benzhydriyl-amine to detect any diphenylmethyl isocyanate and then diluted with an equal quantity of petroleum ether, a tardy precipitate resulted; m. p. 136–137°. This was identified as benzhydriyl-amine acetate; no *sym.* bi-diphenylmethyl urea could be found.

Benzhydriyl-amine Acetate, $(C_6H_5)_2CH.NH_2O.COCH_3$.—A sample of benzhydriyl-amine acetate was prepared by mixing an ether solution of benzhydriyl-amine with glacial acetic acid. White crystalline plates separated, which melted at 138°. The salt dissolved readily in water.

Mono-acetyl Ester, $(C_6H_5)_2CH.CO.NH—O—CO.CH_3$.—In order to avoid the formation of the di-acetyl ester, precautions had to be taken to destroy the acetic anhydride as soon as the reaction mixture showed no mono-hydroxamic acid. Ferric chloride was used as an indicator. Three g. of diphenyl-acethydroxamic acid was dissolved rapidly in an excess of warm acetic anhydride (10 cc.), and, after about 30 seconds, the reaction was stopped by the addition of 50 cc. of cold water. A white precipitate, chiefly the mono-acetyl ester, resulted. Two recrystallizations gave crystalline plates of pure substance melting at 113–113.5°.

The acetyl ester dissolves in acetone, in chloroform, in ethyl acetate, in benzene and in alcohol. It is insoluble in a cold solution of sodium hydroxide and in ligroin, and only slightly soluble in ether. When the solution of sodium hydroxide is warmed, rearrangement takes place.

Analysis. Subs., 0.3046: N, 14.1 cc. (over 40% KOH at 23.5° and 738.8 mm. (19°)). Calc. for $C_{18}H_{15}O_2N$: N, 5.20. Found: 5.09.

Potassium Salt.— $(C_6H_5)_2CH.CO.NK.O.CO.CH_3$.—One-third of a gram of acetyl ester dissolved quite readily in 5 cc. of cold alcohol. The solution was diluted with 10 cc. of ether and was then chilled to -10° by means of a freezing mixture of ice and conc. sulfuric acid. To this solution, 0.6 cc. of alcoholic potash solution (see p. 2434) was added. Here again, no precipitate formed, even when an excess of ether was

added. Part of the liquid was evaporated; the residue was extracted with ether, dried and analyzed.

Analysis. Subs., 0.0929: K_2SO_4 , 0.0293. Calc. for $C_{16}H_{14}O_3NK$: K, 12.72. Found: 14.15.

This high result is explained by the presence of potassium acetate, a decomposition product.

The remainder of the solution, which still contained the potassium salt, was diluted with 10 cc. of petroleum ether. There was no precipitate. If it was shaken with a dil. solution of silver nitrate in water, a white silver salt was obtained (see below).

Sodium Salt.—About 0.3 g. of the acetyl ester was dissolved in 2 to 3 cc. of absolute alcohol, and diluted to 15 cc. with ether. This solution, cooled with ice, was treated with 0.8 cc. of sodium ethylate solution (see p. 2435). There was a tardy precipitation that gradually became quite heavy. The addition of ether hastened its formation. This material, collected and washed with ether, was dried and analyzed. Its sodium content was found to be midway between that required for $(C_6H_5)_2CH.CO.NNa.O.COCH_3$ and that for sodium acetate.

Analysis. Subs., 0.0634: Na_2SO_4 , 0.0346. Calc. for $C_{16}H_{14}O_3NNa$: Na, 7.90. Calc. for $CH_3.COONa$: Na, 28.05. Found: 17.67.

Silver Salt.—The ether-alcohol solution of the potassium salt, when mixed with aqueous silver nitrate, formed a pure white precipitate. It was found best not to wash the salt with alcohol, since that frequently caused it to turn dark. The white precipitate was washed carefully with water, dried, and analyzed. When it was heated in a small tube, it decomposed between 103° and 110° . The isocyanate, recognized by its characteristic odor, distilled.

Analysis. Subs., 0.0738: Ag, 0.0213. Calc. for $C_{16}H_{14}O_3NAg$: Ag, 28.69. Found: 28.86.

In order to establish the identity of the products of rearrangement isolated in these reactions, they were prepared in a different manner. Some of them represent new compounds, not previously described.

Diphenylmethyl Urethane, $(C_6H_5)_2CH.NH.COOC_2H_5$.—A method, similar to that developed by Stieglitz and his students,³⁴ was employed successfully in the preparation of this urethane. A solution of sodium ethylate was made by the action of 3.42 g. of sodium upon 160 cc. of alcohol. Nine g. of diphenyl-acetamide was suspended in it, and caused to dissolve by the rapid addition of 4.1 cc. of bromine. Without filtration to remove sodium bromide, the neutral mixture was boiled for 10 minutes, after which the alcohol was distilled. The urethane was precipitated by the addition of an excess of water. Yield, 8 g. Nothing except sodium bromide was found in the filtrate. The precipitate was extracted with 50 cc. of hot benzene. One g. of material, later proved to be *sym.* bi-diphenylmethyl urea, was insoluble. When the benzene became cool, 1.8 g. of unchanged amide (m. p. 161°) precipitated. The benzene filtrate contained nearly pure diphenylmethyl urethane. After evaporation of the solvent, the residue was pressed on a clay plate. Yield, 4.2 g. It may be recrystallized from a mixture of benzene and ligroin, or of alcohol and water; m. p. 122 – 123° . It is soluble in alcohol, in chloroform, in acetone, in ethyl acetate, and in benzene, but insoluble in water and in ligroin.

Analysis. Subs., 0.4130: N, 20.69 cc. (over 40% KOH at 20° and 763.9 mm. (16°)). Calc. for $C_{16}H_{17}O_2N$: N, 5.49. Found: 5.64.

Diphenylmethyl urea chloride, $(C_6H_5)_2CH.NH.CO.Cl$.—Two g. of the urethane

³⁴ Jeffreys, *Ber.*, 30, 898 (1897); *Am. Chem. J.*, 22, 27 (1899); Folin, *Am. Chem. J.*, 19, 324 (1897).

and 1.63 g. of phosphorus pentachloride were dissolved in 10 to 15 cc. of dry chloroform. This mixture was warmed, and a current of dry hydrogen chloride was bubbled through the solution. This served to expel phosphorus oxychloride and also to prevent the decomposition of the urea chloride which would yield the more volatile isocyanate. Chloroform was added twice as the solution evaporated. Finally, when the solvent was nearly exhausted, petroleum ether was added, and the entire solution was poured through a filter. A solid mixed with oil resulted when the filtrate was evaporated.

Diphenylmethyl Isocyanate, $(C_6H_5)_2CH.NCO$.—The crude urea chloride was extracted with benzene, and the solution filtered. Some calcium oxide was placed in the flask, and the mixture was left in the stoppered flask for 3 hours. This solution contained the isocyanate (see below). After filtration, it was not purified further, but was treated at once with benzhydriyl-amine to form the urea.

Benzhydriyl-amine, $(C_6H_5)_2CH.NH_2$.—This compound was prepared by reducing benzophenone oxime with metallic sodium and alcohol. It has been prepared from benzophenone oxime by Goldschmidt,³⁵ who employed sodium amalgam, and also by Michaelis³⁶ from benzophenone-phenylhydrazone with metallic sodium and alcohol.

Five g. of dry benzophenone oxime was suspended in 50 cc. of absolute alcohol. The mixture was poured through a reflux condenser upon a piece of sodium which weighed 12 g. The oxime dissolved at once, and enough heat was generated to melt the sodium. A little alcohol was introduced from time to time. After 40 minutes, when all the sodium had dissolved, most of the alcohol was recovered by distillation, and water was added to the residue. After partial neutralization of the alkaline solution, benzhydriyl-amine was extracted by means of ether, and the ether solution was dried over potassium hydroxide. To precipitate benzhydriyl-amine hydrochloride, it was only necessary to add conc. hydrochloric acid to the ether solution. Between 5.5 and 6 g. of the salt was collected.

Sym. bi-diphenylmethyl Urea, $CO(NH.CH(C_6H_5)_2)_2$.—The benzene solution of the isocyanate (see above) was treated with an ether solution of benzhydriyl-amine. There was a tardy precipitation of solid which was collected after a few hours and shown to consist of a mixture of benzhydriyl-amine hydrochloride, and the urea. The former, produced because of some unchanged urea chloride, was soluble in very dilute hydrochloric acid; it melted at 276–280°. The portion insoluble in the acid melted at 266°. It was rather soluble in hot acetone and in hot ethyl acetate. Recrystallization from either of these solvents produced fine needle-shaped crystals of the urea which melted at 269.5–270°.

Analysis. Subs., 0.3246: N, 19.90 cc. (20° and 763.9 mm. (16°)). Calc. for $C_{27}H_{24}ON_2$: N, 7.14. Found: 7.07.

2. Triphenyl-acethydroxamic Acid.



Triphenyl-acetyl chloride, $(C_6H_5)_3C.COCl$.—Schmidlin and Hodgson³⁷ prepared triphenyl-acetyl chloride from triphenyl-acetic acid, acetyl chloride and phosphorus pentachloride. In the same year Bistrzycki and Landtwig³⁸ described a method of preparation in which phosphorus oxychloride was used as a solvent, instead of acetyl chloride.

It may be prepared much more simply with thionyl chloride as the chlorinating agent. Three g. of triphenylacetic acid and 10 cc. of thionyl chloride were placed

³⁵ Goldschmidt, *Ber.*, **19**, 3233 (1886).

³⁶ Michaelis, *ibid.*, **26**, 2168 (1893).

³⁷ Schmidlin and Hodgson, *ibid.*, **41**, 438 (1908).

³⁸ Bistrzycki and Landtwig, *ibid.*, **41**, 687 (1908).

in a small flask equipped with an air condenser, and gently warmed until solution was complete. The liquid was boiled for about 5 minutes after gas evolution (sulfur dioxide and hydrogen chloride) had ceased. Then, it was cooled and poured upon crushed ice to decompose any excess of thionyl chloride. (If larger quantities were employed, it would be better of course, to recover the thionyl chloride by distillation.) The solid triphenylacetyl chloride was filtered, washed with a little cold water, pressed upon a porous plate, and then dried in a vacuum desiccator. Without further treatment, the material obtained was pure enough for most purposes. It melted at 127°. The yield was practically quantitative.

Thionyl chloride readily dissolved both triphenylacetyl chloride, and ethyl triphenylacetate, and it was without action upon either one.

Triphenylacethydroxamic Acid.—Two and five-tenths g. of triphenylacetyl chloride was dissolved in 40 cc. of dry benzene. This was poured into a flask containing 2.5 g. of free hydroxylamine. The mixture was agitated at frequent intervals during an hour, and then was put aside until the next day. Since there was no precipitation of hydroxamic acid, the benzene layer was decanted from the excess of hydroxylamine, placed in a distilling flask, and the solvent was distilled. An oil remained which crystallized readily when it became cool. Petroleum ether caused an additional precipitate. More than 2 g. of crystals was obtained. The crude substance melted at 172°.

Triphenylacethydroxamic acid is soluble in a warm solution of sodium hydroxide, in benzene, in acetone, in ethyl acetate and in alcohol. It is insoluble in ligroin, and in water. Recrystallization from ether produced a pure product which melted at 175–176°.

An alcoholic solution, treated with ferric chloride, gave the usual red color reaction. Furthermore, copper acetate formed a light green copper salt.

Analysis. Subs., 0.3858: N, 16.14 cc. (over 40% KOH at 21.8° and 758.9 mm. (18°)). Calc. for $C_{20}H_{17}O_2N$: N, 4.62. Found: 4.75.

Attempts to prepare triphenylacethydroxamic acid by the action of free hydroxylamine upon ethyl triphenylacetate, $(C_6H_5)_3C.CO.OC_2H_5$, resulted in failure. There was no action, even when an excess of sodium ethylate was present. In all cases the ester was recovered unchanged.

When triphenylacetyl chloride was employed with a mixture of hydroxylamine and sodium carbonate in water, it was very difficult to purify the triphenylacethydroxamic acid.

Benzoyl Ester, $(C_6H_5)_3C.CO.NH.O.CO.C_6H_5$.—First Method. One-tenth g. of triphenylacethydroxamic acid was fused with a considerable excess of benzoic anhydride until a sample gave no reaction with ferric chloride. The excess of anhydride was then extracted several times with warm ligroin (50°). An oil was left which refused to solidify in the course of a week. It was extracted with a very dilute, cold solution of sodium hydroxide. This solution was filtered and acidified immediately. A white solid precipitated, m. p. 40–50°. When this process was repeated the benzoyl ester was obtained in a somewhat purer state. It melted between 44° and 47° for the most part, but there was a little that did not melt until the temperature reached 70°. It is highly probable that, even at this low temperature, the ester decomposed to a slight extent into benzoic acid and triphenylmethyl isocyanate, which may account for the anomalous melting point (see p. 2429).

This low-melting ester was found to be extremely soluble in organic solvents. From benzene solution, petroleum ether precipitated it as an oil which could not be made to crystallize, even after the removal of the solvent.

By careful hydrolysis with alkalis, it was possible to convert part of the ester into triphenylacethydroxamic acid. The greater tendency by far, however, was

rearrangement of the salt in solution, not to form the urea derivative, as would be anticipated, *but to give the isocyanate*, $(C_6H_5)_3C.NCO$.

Second Method. Because of the instability of the sodium salt of the benzoyl ester of triphenylacetylhydroxamic acid, this method (Schotten-Baumann reaction) is less successful than the first method. One and six-tenths g. of triphenylacetylhydroxamic acid was dissolved in 15 cc. of water that contained 0.23 g. of sodium hydroxide. The solution was cooled in a stream of tap water, and 0.6 cc. of benzoyl chloride was added in 3 portions.

No attempt was made to purify the sticky solid. Instead, it was washed thoroughly with water, then dried, and converted into its salts.

Potassium Salt. $(C_6H_5)_3C.CO.NK.O.CO.C_6H_5$.—The crude benzoyl ester was dissolved in 1.5 cc. of absolute alcohol. This solution was treated with a solution of potassium hydroxide (0.11 g.) in alcohol. Since 20 cc. of ether caused no precipitation of salt, a solution of silver nitrate in water was added. This gave the silver salt.

Silver Salt. $(C_6H_5)_3C.CO.NAg.O.CO.C_6H_5$.—A white precipitate formed, which turned canary-yellow in a short time. It was filtered and washed thoroughly with water, and with ether. In a small tube, this salt became gray in color at 120° ; it was black at 160° ; and at 195° it melted with much decomposition.

Analysis. Subs., 0.1444: Ag, 0.0300. Calc. for $C_{27}H_{20}O_4NAg$: Ag, 20.98. Found: 20.85.

Acetyl Ester, $(C_6H_5)_3C.CO.NH.O.CO.CH_3$.—A large excess of warm acetic anhydride (about 3 cc.) was used to dissolve 0.6 g. of triphenylacetylhydroxamic acid. In about half a minute a test with ferric chloride showed that the reaction was complete. In order to stop any further action which might lead to the formation of a di-acetyl ester, 10 cc. of cold water was added to decompose any unused anhydride. In a short time, the acetyl ester solidified to form a white solid. It was filtered and dried. Very few impurities were present in this crude material. One recrystallization from a mixture of 2 cc. of benzene and 10 cc. of ligroin gave a pure product that melted at 133.5 – 134° . The ester was very soluble in most common organic solvents. The yield was quantitative.

Analysis. Subs., 0.2156: N, 7.62 cc. (20° and 762.2 mm.). Calc. for $C_{22}H_{19}O_3N$: N, 4.06. Found: 4.08.

Potassium Salt. $(C_6H_5)_3C.CO.NK.O.CO.CH_3$.—When 0.38 g. of the acetyl ester was dissolved in a small quantity of absolute alcohol and neutralized with 0.55 cc. of alcoholic caustic potash (0.062 g. of potassium hydroxide), a little ether caused the separation of a gelatinous precipitate, which was collected upon a filter. The material would not dissolve to give a clear solution in cold water. It was evident that the unstable potassium salt suffered rearrangement in solution, because the solution, turbid at first, rapidly became white and opaque. When the solution was boiled, the potassium salt was decomposed completely; triphenylmethyl isocyanate was precipitated. The dry salt decomposed slightly at 112° . At 165° there was a vigorous evolution of gas.

Analyses. Subs., 0.0400, 0.1253; K_2SO_4 , 0.0080, 0.0252. Calc. for $C_{22}H_{18}O_3NK$: K, 10.19. Found: 8.98, 9.03.

Sodium Salt.—Sodium ethylate and ether did not cause a precipitate when added to a solution of the acetyl ester in alcohol. Accordingly, the solution was treated with an aqueous solution of silver nitrate to form the silver salt.

Silver Salt.—This was thrown down at once as a yellow precipitate, but the quantity was insufficient to warrant an analysis. When heated upon a spatula it decomposed at a fairly high temperature and left a residue of metallic silver.

Triphenylmethyl Isocyanate, $(C_6H_5)_3C.NCO$.—When a solution of the potassium

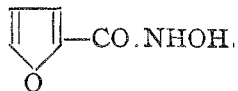
salt of the acetyl ester of triphenylacethydroxamic acid was boiled for a short time with water, an oil was formed. In the course of a few hours this oil solidified. It was collected, and washed with water. The isocyanate was very soluble in organic solvents, even in ligroin. It was dissolved in petroleum ether, filtered into an open dish, and most of the solvent evaporated in a vacuum desiccator. White crystals were formed in this manner, m. p. 85–87°.

Analysis. Subs., 0.1518: N, 6.72 cc. (17° and 757 mm. (18°)). Calc. for $C_{22}H_{15}ON:N$, 4.91. Found: 5.12.

The solubility in petroleum ether, and the low melting point are sufficient evidence that this compound could not be *sym.* bi-triphenylmethyl urea, $CO(NH.C(C_6H_5)_2)_2$. Although E. von Meyer and P. Fischer⁸⁹ claim to have prepared this urea, none of its properties, not even the melting point, was described. It can be predicted, however, that the melting point is very high.

In order to prove that the material in hand was the isocyanate, it was dissolved in ether, and treated with the calculated quantity of aniline, also dissolved in ether. Upon evaporation of the ether, a white solid was left which melted sharply at 242°. This was anticipated, since phenyl-triphenylmethyl urea, $C_6H_5.NH-CO.NH.C(C_6H_5)_2$, which has been prepared⁸⁹ previously, was known to melt at that temperature.

3. Pyromucyl-hydroxamic Acid.



The procedure described by Pickard and Neville²⁴ for the preparation of pyromucyl-hydroxamic acid employed ethyl pyromucate and hydroxylamine in alcoholic solution. It was purified through the medium of the insoluble copper salt. Our modification of the method consists in the addition of a mol of sodium ethylate, and the direct recovery of the hydroxamic acid without the intermediate formation of the copper salt.

Thirty g. of methyl pyromucate was poured into 150 cc. of a methanol solution of free hydroxylamine which had been liberated from 19.5 g. of its hydrochloride by a solution of sodium methylate containing 6.4 g. sodium. A solution of 5.4 g. of sodium in 70 cc. of methanol was then added to the mixture and, after 10 hours, as light excess of conc. hydrochloric acid was introduced. Sodium chloride was separated and the methanol removed by distillation *in vacuo*. An oil was left which solidified after a few hours in a vacuum desiccator. One crystallization from water brought the melting point to 119–122°. Twenty-four g. of this material was obtained. Three g. of the copper salt was precipitated from the solvent used in recrystallization.

The acid is soluble in alcohol, in ethyl acetate, and in water. In benzene, in chloroform, in carbon disulfide, in ligroin, and in ether it is insoluble.

Ammonium Salt. $(C_6H_5O.CO.NH.O)_2H.NH_4$.—Ammonium hydroxide caused the precipitation of beautiful crystalline plates, when added to an aqueous solution of pyromucyl-hydroxamic acid. (Cf. p. 2444.) This precipitate was soluble either in an excess of ammonium hydroxide, or in dilute acid, which indicated that the salt is the acid salt and not the normal salt. In the former case, the normal salt is undoubtedly obtained, whereas with acids, the soluble pyromucyl-hydroxamic acid is restored. The salt melted at 130–131°, with considerable gas evolution. The analysis gave the same values whether the salt was prepared in this manner, or in the absence of water, by the action of dry ammonia upon an alcohol-ether solution of pyromucyl-hydroxamic acid.

⁸⁹ von Meyer and Fischer, *J. prakt. Chem.*, [2] **82**, 521 (1910).

Analyses. (I) Prepared in the presence of water. Subs., 0.1114: N, 15.9 cc. (over 40% KOH at 27° and 737.9 mm.); (II) prepared in the absence of water; subs., 0.2126: N, 27.58 cc. (17.3°, and 772.6 mm. (15°)). Calc. for $C_{10}H_{18}O_6N_3$; N, 15.49. Found: (I) 15.41, (II) 15.30.

Benzoyl Ester, $C_6H_5O.CO.NH.OCO.C_6H_5$.—Pickard and Neville⁴⁰ stated that this derivative "is precipitated when an aqueous solution of the hydroxamic acid is shaken with the calculated quantity of benzoyl chloride, and sodium acetate." Potassium hydroxide was found to be far superior to sodium acetate. Three g. of pyromucyl-hydroxamic acid, and 1.3 g. of potassium hydroxide were dissolved in 20 cc. of water, and 2.7 cc. of benzoyl chloride was added in 4 portions. A quantitative yield of the benzoyl ester resulted. After recrystallization from alcohol, the compound melted at 140°. ⁴¹

Preparation of Salts.—The following general method was employed in the preparation of the potassium and the sodium salts of the esters. Alcoholic solutions of sodium ethylate, or of potassium ethylate were added to concentrated alcoholic solutions of the esters. The salt usually precipitated at once. It was found advantageous to add the alcoholate in a slight excess. Three or four volumes of ether were added to effect a complete separation of the salt.

To prepare the silver salts, it was necessary only to add a solution of silver nitrate in water, to an aqueous solution of the potassium salt. In most cases this could be done at room temperature, but in a few cases a lower temperature was required to inhibit any hydrolysis.

Potassium Salt. $C_4H_3O.CO.NK.O.CO.C_6H_5$.—The appearance of the dry salt was unchanged after 8 months. In a small tube, it puffed at 125°.

Analysis. Subs., 0.4337: K_2SO_4 , 0.1380. Calc. for $C_{12}H_3O_4NK$; K, 14.52. Found: 14.28.

*Sodium Salt.*⁴²—This salt was white when first formed, but in 3 months the color was distinctly yellow.

Silver salt.—The silver salt was pure white.

Analysis. Subs., 0.1289: Ag, 0.0413. Calc. for $C_{12}H_3O_4NAg$; Ag, 31.92. Found: 32.04.

All of these salts showed a decided tendency to undergo hydrolysis. The potassium salt, dissolved in cold water, gave a ferric chloride color test in a very short time. Similarly, a little of the silver salt suspended in boiling water, caused a separation of black silver, a reaction characteristic of monohydroxamic acids.

When a 0.5 *M* solution of the potassium salt was warmed carefully to about 70°, crystals were precipitated which were unmistakably identified as the benzoyl ester. By careful application of heat, the filtrate gave a still more abundant yield of the same ester. If the filtrate from this precipitate was heated to boiling, a red resinous mass accompanied by the evolution of much carbon dioxide, was formed. This was dried, and then recrystallized twice from a mixture of alcohol and ether. After this treatment, it was still colored. The material darkened at 180°, and melted at 210° with decomposition. This is presumably *sym.* difuryl urea, although enough was not obtained for analysis.

If the solution of the potassium salt was heated immediately to boiling, the same resinous mass was produced, but the separation of the benzoyl ester did not occur.

Acetyl Ester, $C_4H_3O.CO.NH.O.COCH_3$.—Three g. of pyromucyl-hydroxamic acid

⁴⁰ Ref. 24, p. 848.

⁴¹ That obtained by Pickard and Neville melted at 134°.

⁴² This salt was previously prepared by Pickard and Neville.

and copper acetate, it reacts in the normal manner, to give respectively, a purple colored liquid, and a grass-green copper salt. The acid is soluble in alcohol, in hot toluene, in hot benzene, in chloroform, and in water. It is insoluble in ether and in ligroin. With isatin, and warm sulfuric acid the red color characteristic of thiophene derivatives is produced.

Analysis. Subs., 0.2259; N, 19.12 cc. (over 40% KOH at 18.5° and 757.8 mm.). Calc. for $C_6H_5O_2NS$: N, 9.78. Found: 9.74.

Isolation of thenhydroxamic acid through the medium of the copper salt and hydrogen sulfide was found to be successful, but the procedure is not to be recommended.

The Preparation of α -Thenoyl Chloride, $C_4H_3S.COCl$.—Thenoyl chloride has always been prepared from thenoic acid by the action of phosphorus pentachloride.⁴³ A much simpler, and smoother preparation follows if thionyl chloride, $SOCl_2$, is employed instead of the phosphorus compound.

Six g. of α -thenoic acid was warmed with 16 cc. of thionyl chloride until the gas evolution showed that the reaction was complete, when the two chlorides were separated by fractional distillation. Thenoyl chloride all distilled between 206° and 210°; yield, 6 g.

α -Thenhydroxamic Acid. Second method.—A solution of 0.3 g. of sodium carbonate, and 0.2 g. of hydroxylammonium chloride in 2.5 cc. of water was shaken with 0.3 g. of thenoyl chloride. Di-thenhydroxamic acid $C_4H_3S.CO.NH.O.CO.C_4H_3S$ (see p. 2445) precipitated from the solution, whereas thenhydroxamic acid did not. To recover the latter, the filtrate was made slightly acid with acetic acid, and treated with copper acetate solution. The light green copper salt precipitated, although the green color of the solution showed that it possessed a rather high degree of solubility. The filtrate still gave an intense ferric chloride reaction.

The precipitate of di-thenhydroxamic acid was recrystallized from alcohol and water. It melted at 105–107°. We did not try to prepare thenhydroxamic acid by our new method, *viz.*, by the action of free hydroxylamine and a benzene solution of thenoyl chloride. No side reactions would be anticipated in this case.

Ammonium Salt. $(C_4H_3S.CO.NH.O\text{---})_2H.NH_4$.—This difficultly soluble acid salt was prepared in exactly the same way as the similar furan salt, (p. 2441) and showed the similar property of dissolving either in ammonia, or in hydrochloric acid. For analysis, the salt was precipitated from an alcohol-ether solution of thenhydroxamic acid by dry ammonia. It melted, with decomposition, at 142–143°.

Analysis. Subs., 0.1172; N, 13.95 cc. (21° and 769 mm. (20°)). Calc. for $C_{10}H_{12}O_4N_2S_2$: N, 13.85. Found: 13.75.

Benzoyl Ester, $C_4H_3S.CO.NH.O.CO.C_6H_5$.—Two g. of thenhydroxamic acid, and 0.8 g. of potassium hydroxide were dissolved in 10 cc. of water. This solution, agitated with 1.7 cc. of benzoyl chloride, gave a precipitate which was recrystallized from alcohol. The needle shaped crystals so obtained melted sharply at 143–144°, with decomposition. It is soluble in alcohol, in acetone and in ethyl acetate, and is insoluble in ligroin, or in cold water.

Analysis. Subs., 0.4336 g.; N, 21.97 cc. (at 21° and 758.6 mm. (at 19°)). Calc. for $C_{12}H_9O_3NS$: N, 5.67. Found: 5.77.

Potassium Salt.—The general method described upon p. 2422, was used also to prepare the salts in this series. The potassium salt was pure white. When it was heated in a small dry tube, it became yellow at 121° and decomposed with a faint puff at 125–127°.

Analysis. Subs., 0.5313; K_2SO_4 , 0.1626. Calc. for $C_{12}H_9O_3NSK$: K, 13.71. Found: 13.73.

⁴³ V. Meyer and Kreis, *Ber.*, 16, 2174 (1883); Peter, *Ber.*, 18, 543 (1885).

Sodium Salt.—When slowly heated, the sodium salt decomposed mildly between 155° and 160°.

Analysis. Subs., 0.2388: Na₂SO₄, 0.0631. Calc. for C₁₂H₈O₃NSNa: Na, 8.54. Found: 8.55.

Silver Salt.—The silver salt decomposed between 163° and 168°. Above this temperature thienyl isocyanate distilled from the tube.

Analysis. Subs., 0.2364: Ag, 0.0723. Calc. for C₁₂H₈O₃NSAg: Ag, 30.47. Found: 30.58.

Rearrangement of the Salts.—A 0.5*M* solution of the potassium salt in water was boiled. The solution darkened, and di-thienyl urea precipitated as a gray-violet crystalline mass.⁴⁴ It was collected and recrystallized from acetic acid. The melting point was 224–225°.

The filtrate was acidified and the precipitate obtained was crystallized fractionally from dilute alcohol. Crystals melting at 140–144° separated at first. This material was the benzoyl ester, which must have been formed by hydrolysis of the salt. Benzoic acid was left in the filtrate. The ratio of the urea to the benzoyl ester was about 4:1.

Acetyl Ester, C₄H₈S.CO.NH.O.CO.CH₃.—Three-tenths g. of pure thenhydroxamic acid was warmed in an open glass dish with 0.2 g. of acetic anhydride. As soon as solution had taken place, the dish was placed in a vacuum desiccator to remove the excess of anhydride. The white solid obtained was recrystallized from benzene. The melting point was sharp at 96.5–97°; yield, quantitative. The ester is soluble in alcohol, in ethyl acetate, and in hot benzene, but is insoluble in cold benzene and in ligroin.

Analysis. Subs., 0.3242: N, 21.47 cc. (over 40% KOH at 17.8° and 760.3 mm. (15°)). Calc. for C₇H₇O₃NS: N, 7.57. Found: 7.66.

Potassium Salt.—No precautions were necessary to prepare the potassium salt

Analysis. Subs., 0.3099: K₂SO₄, 0.1215. Calc. for C₆H₆O₃NSK: K, 17.51. Found 17.49.

Sodium Salt.—Ice-cold solutions were essential in the preparation of the sodium salt. Otherwise, alcoholysis to yield the monohydroxamic acid occurred.

Analysis. Subs., 0.0609: Na₂SO₄, 0.0209. Calc. for C₇H₆O₃NSNa: Na, 11.10. Found: 11.11.

Silver Salt.—Because of hydrolysis, a water solution of the sodium salt could not be used to prepare the silver salt. A black precipitate of silver always resulted. With the potassium salt, however, the preparation was entirely successful.

Analysis. Subs., 0.1481: Ag, 0.0548. Calc. for C₇H₆O₃NSAg: Ag, 36.94. Found: 37.00.

These salts all puffed at a comparatively high temperature. A pronounced odor of thienyl isocyanate was always noticed. When water solutions of the salts were boiled, di-thienyl urea separated instantly. However, this was always accompanied by an unavoidable hydrolysis to form the acetyl ester and a second hydrolysis to give thenhydroxamic acid.

Thenoyl Ester, (Di-thenhydroxamic Acid), C₄H₈S.CO.NH.O.CO.C₄H₈S.—One preparation of this ester (Cf. p. 2444) which resulted in the high-melting modification (see below) has already been described.

Three g. of thenhydroxamic acid, and 1.18 g. of potassium hydroxide were dissolved in 15 cc. of water. The ice-cold mixture was treated with 3 portions (1 g. each)

⁴⁴*Sym.* di-thienyl urea was found by Curtius and Thyssen²⁹ to be gray-violet in color, even after 7 recrystallizations from solvents with animal charcoal; m. p. 224°.

of thenoyl chloride. A precipitate which weighed 2.7 g. was collected; m. p. between 80° and 88°.

The filtrate was found to be acid in reaction, and to contain some unchanged thenhydroxamic acid. It was therefore made slightly alkaline with sodium hydroxide and treated with 2 cc. of thenoyl chloride. The resulting precipitate melted at 90–100° and weighed 1.4 g. When the filtrate was acidified, an appreciable quantity of thenoic acid separated.

The crude precipitates, (m. p. 80–100°) were combined and recrystallized from benzene. Crystals which melted between 83° and 86° were obtained. Later a re-determination of the melting point of this same sample indicated that a transformation to a higher-melting modification had taken place. The melting point ranged from 100° to 104°.

When alcohol was used as the solvent, the high melting modification separated first. There was an indication of softening at 95°, but the melting point at 102–104° was quite distinct.

Both of these compounds responded to all the reactions expected of di-thenhydroxamic acid.⁴⁵ They both formed salts; neither one gave a color test with ferric chloride, but after hydrolysis both showed an intense purple color with this reagent. The purest sample of the high-melting form melted at 105–107°. Its isomer melted at 83–86°. Both were soluble in alcohol, in ethyl acetate, and in hot benzene. In water and in ligroin they were insoluble.

Analyses. (I) Low-melting modification; subs., 0.3339: N, 16.90 cc. (16.5° and 762.0 mm.); (II) high-melting modification; subs., 0.4288: N, 19.60 cc. (18.5° and 769.1 mm. (16°)). Calc. for C₁₀H₇O₃NS₂: N, 5.53. Found: (I) 5.90, (II) 5.35.

Potassium Salt. C₄H₃S.CO.NK—O.CO.C₄H₃S.—The salts were all prepared from di-thenhydroxamic acid melting at 102–104°. In a small tube, the temperature of decomposition of the potassium salt was 122°.

Analysis. Subs., 0.1988: K₂SO₄, 0.0584. Calc. for C₁₀H₆O₃NS₂K: K, 13.42. Found: 13.18.

Sodium Salt.—There was no evident alcoholysis, when this last was prepared at room temperature. At 142° the dry salt decomposed.

Analysis. Subs., 0.0797: Na₂SO₄, 0.0206. Calc. for C₁₀H₆O₃NS₂Na: Na, 8.36. Found: 8.37.

Silver Salt.—An abundant white precipitate of the silver salt of di-thenhydroxamic acid resulted when aqueous solutions of the potassium salt and silver nitrate were mixed. It decomposed at 155°.

Analysis. Subs., 0.1253: Ag, 0.0376. Calc. for C₁₀H₆O₃NS₂Ag: Ag, 29.96. Found: 30.01.

When boiled with water, both the potassium and the sodium salts gave a dense precipitation of *sym.* di-thienyl urea. Water solutions of the pure salts did not readily undergo hydrolysis or rearrangement.

5. Benzhydroxamic Acid.

The new method of preparation of hydroxamic acids, (see p. 2430) namely, by the use of the acid chloride in benzene, was successfully employed in the preparation of benzhydroxamic acid from benzoyl chloride.

First Method.—Six and five-tenths g. of benzoyl chloride was dissolved in 70 cc. of dry benzene. Upon the addition of 3.3 g. of free hydroxylamine a dense precipitate of benzhydroxamic acid was formed. The reaction mixture was shaken vigorously,

⁴⁵ Lossen, *Ann.*, **281**, 289 (1894).

and then set aside for a few hours until the odor of benzoyl chloride had disappeared. Less than half a gram of benzhydroxamic acid was recovered from the benzene filtrate. One recrystallization of the solid from hot toluene removed hydroxylammonium chloride and yielded a pure product, m. p. 124°. This is identical with the material described by Lossen.³⁰ No evidence of the higher melting di-benzhydroxamic acid was observed.

Second Method.—Benzhydroxamic acid was also prepared in excellent yields, from benzoyl chloride, dissolved in organic solvents, with hydroxylammonium chloride instead of free hydroxylamine. An intimate mixture of anhydrous sodium carbonate (2.1 g.) and hydroxylammonium chloride (1.4 g.) was suspended in 50 cc. of ether. When 2.8 g. of benzoyl chloride was added there was little action, but it became more vigorous when 3.5 cc. of water was added. In about half an hour the reaction was complete. The ether solution was filtered into a distilling flask, and most of the solvent was removed. When this residue was cooled, an abundant crystalline mass precipitated. This was filtered, washed with a little ether, and pressed upon a porous plate. The benzhydroxamic acid melted at 124–125° without further purification. Yield, nearly quantitative.

Similarly, benzhydroxamic acid was obtained in quantitative yields when pyridine was substituted for sodium carbonate. Benzene was used instead of ether in this case.

Thenoyl Ester of Benzhydroxamic Acid, C₆H₅.CO.NH.O.CO.C₄H₉S.—Two and a half g. of benzhydroxamic acid dissolved in 25 cc. of water was neutralized with 0.7 g. of potassium hydroxide. Three portions of 1 g. each of thenoyl chloride were added to this solution. The precipitate was filtered, and washed with water; yield, 2 g. When it was recrystallized from ethyl acetate, it gave white needles which melted at 133.0–133.5°. The ester is soluble in alcohol, in acetone, in ethyl acetate and in hot benzene. It is insoluble in cold benzene, in ligroin and in water.

Analysis. Subs., 0.1547: N, 7.70 cc. (over 40% KOH at 15° and 763 mm.). Calc. for C₁₂H₉O₃NS: N, 5.67. Found: 5.85.

Potassium Salt. C₆H₅.CO.NK.O.CO.C₄H₉S.—When 0.32 g. of the thenoyl ester was dissolved in a mixture of 2 cc. of alcohol and 1 cc. of ether, the potassium salt was precipitated by the addition of 0.7 cc. of an alcoholic solution of potassium hydroxide (0.08 g. KOH). Five cc. of ether caused further precipitation.

A water solution of this salt became turbid in a short time, when left at room temperature. When the solution was boiled, a crystalline precipitate of *sym.* diphenyl urea, m. p. 236–238°, was formed.

The dry potassium salt puffed vigorously at 135–140°, providing the tube containing it was thrust into a bath previously heated to that temperature. However, when the tube was gradually warmed, a mild decomposition took place. There was no noticeable action until 160°, although phenyl isocyanate was undoubtedly being evolved at a temperature somewhat below that.

Analysis. Subs., 0.1788: K₂SO₄, 0.0538. Calc. for C₁₂H₉O₃NSK: K, 13.70. Found: 13.50.

Silver Salt.—When silver nitrate, in water solution, was added to a solution of the potassium salt in water, a voluminous white precipitate of the silver salt resulted. It blackened near 165°.

Analysis. Subs., 0.0897; Ag, 0.0274. Calc. for C₁₂H₉O₃NSAg: Ag, 30.47. Found: 30.54.

Summary.

An interpretation of the mechanism of the Beckmann rearrangement has been proposed, based upon the modern conception of chemical bonds

and electrons. The transfer of electrons for all stages in the process has been pictured in a detailed manner.

The following hypothesis has been advanced: the relative ease of rearrangements of the Beckmann type is dependent upon the tendency for the radical R in the univalent nitrogen derivative, *e. g.*, (R.CO.N), to exist as a free radical.

The hypothesis was tested successfully with the sodium and the potassium salts of the acyl esters both of diphenylacethydroxamic acid and of triphenylacethydroxamic acid. Rearrangement of the salts in solution was found to be more reliable for purposes of comparison than rearrangement of the solid salts. In agreement with the hypothesis, the relative ease of rearrangement was greater with triphenylacethydroxamic acid derivatives than with the similar compounds in the diphenyl series. When water solutions of the salts in the triphenyl series were heated, the product of rearrangement was triphenylmethyl isocyanate, and not *sym.* bi-triphenylmethyl urea. This is a singular fact. The phenomenon of chromo-isomerism was displayed by the silver salts of the diphenyl series, as well as those of the triphenyl series.

Diphenyl ketene and hydroxylamine were found to react readily in a neutral solvent to form diphenylacethydroxamic acid. Modifications of this new reaction between ketenes and hydroxylamine, or substituted hydroxylamines, should be valuable in future synthetic work.

The properties of pyromucyl-hydroxamic acid, and of α -thenhydroxamic acid have been determined. The latter resembles benzhydroxamic acid very closely. The former is similar to benzhydroxamic acid in many respects, but its derivatives differ materially in rearrangement. These two compounds, which are representatives of the furane and of the thiophene types, prepare the way for further investigations of heterocyclic hydroxamic acids.

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