REACTIONS OF ALPHA-PHENYL-BETA-HYDROXY-UREA, AND OF ALPHA-ALPHA-DIPHENYL-BETA-HYDROXY-UREA INTERPRETED FROM THE STANDPOINT OF THEIR HYDROXAMIC ACID STRUCTURES

By CHARLES DEWITT HURD

When Beckmann, in 1886, converted benzophenone oxime[1] into benzanilide, he discovered a type of reaction that still bears his name. The term "Beckmann Rearrangement" may be given a broader meaning, however, to embrace the Hofmann rearrangement of amides to amines, the Lossen rearrangement of hydroxamic acids, and the Curtius rearrangement of azides, since an analysis of these reactions reveals that in all of them there is essentially one process, namely, the transfer of a group from carbon to nitrogen. The reaction mechanism has been analyzed from the standpoint of positive and negative valence with signal success. Last year, Jones and Hurd[2] pictured the reaction mechanism from the standpoint of modern valence relationships. Their general formulation excluded only the oximes. Thus:[3]

$$\ddot{O}\colon \overset{R}{\underset{}{C}}\colon \overset{x}{\underset{}{N}}\colon y \longrightarrow \ddot{O}\colon \overset{R}{\underset{}{C}}\colon N\colon + x\colon y \longrightarrow \ddot{O}\colon C\colon N\colon_R + x\colon y$$
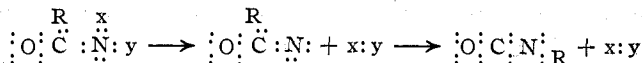
After the loss of the molecule x:y, only 6 electrons remain attached to the nitrogen atom. The driving force of the reaction is the transfer or sharing of electrons to complete the octet of the nitrogen.

This analysis implies that the group "R," which wanders, actually parts company with the rest of the molecule for a limited time. Such an idea would imply that if the carbon-to-carbon linking is to become severed with the momentary isolation of a radical, the same effect would take place much more readily than otherwise if the radical were a "free radical." Development of this thought caused Jones and Hurd[4a] to state the following hypothesis: "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."

Experimental evidence to support the hypothesis was furnished[4b] in the case of the acyl esters of triphenyl-acethydroxamic acid, $(C_6H_5)_3C$—CO—NH—O—CO—R. The sodium and the potassium salts of these esters were observed to rearrange at once without application of heat, when they were dissolved in water. A triphenylmethyl group in this case is the radical

[1] Beckmann, Ber., 19, 988 (1886).

[2] Jones and Hurd, THIS JOURNAL, 43, 2424 (1921). Here also are listed other references which bear upon the subject.

[3] See also Jones and Scott, ibid., 44, 407 (1922).

[4] Ref. 2, (a) p. 2426; (b) p. 2428.

which "wanders;" and, of course, this is also the classic illustration of a free radical.

By means of the hypothesis, it was predicted[5] that a compound bearing the formula, $(C_6H_5)_2N$—CO—NHOH, should form acyl derivatives, the salts of which should rearrange with great readiness in water solutions. The statement was based upon the fact that the radical, $(C_6H_5)_2N$, which contains divalent nitrogen, has been prepared.[6] As will be shown, the experimental evidence amply justified the prediction. The results of this work form the basis of this paper.

It was thought that it might be simpler to start with the monophenyl compound, C_6H_5—NH—CO—NHOH, which has previously been described by Fischer,[7] Kall[8] and Kjellin.[9] These investigators named the compound phenyl-hydroxy-urea; no reference was ever made to the fact that it might be a hydroxamic acid. No benzoyl or acetyl derivatives of it were attempted, so from their work it is impossible to characterize its activity.

Kjellin's method[9] of preparation was found to be the best of the methods described. He mixed free hydroxylamine with a solution of phenyl isocyanate in benzene. Chemically, phenyl-hydroxy-urea is a reducing agent, stable in the cold towards dilute solutions of alkalies. It gives the expected purple color with ferric chloride solutions, and shows a characteristic property of reverting to a more stable, higher-melting compound which possesses the empirical formula, $C_{14}H_{13}O_3N_3$. This derivative was prepared by several methods.

1. Heat an alcoholic solution of phenyl-hydroxy-urea.[9] 2. Reflux a mixture of conc. hydrochloric acid and phenyl-hydroxy-urea,[8] in which case hydroxylamine hydrochloride is also isolated. 3. Mix powdered phenyl-hydroxy-urea with phenyl isocyanate.[8] 4. Treat phenyl isocyanate with an aqueous solution of hydroxylamine.[7]

Chemically, this derivative of phenyl-hydroxy-urea is inert. Dilute solutions of sodium hydroxide fail to dissolve it. It does not reduce Fehling solution, even when the mixture is boiled. Two formulas have been assigned to represent its structure, diphenyl-hydroxy-biuret, C_6H_5—NH—CO—N(OH)—CO—NH—C_6H_5, and carbanilido-phenyl-hydroxy-urea, C_6H_5—NH—CO—NH—O—CO—NH—C_6H_5. As an argument[9] in favor of the "diphenyl-hydroxy-biuret" structure, Kjellin found that β-ethyl-(or β-methyl-)hydroxylamine reacted in ether solution with but one molecular equivalent of phenyl isocyanate to produce a compound of the formula C_6H_5NH—CO—N(OH)—C_2H_5, which gave an intense color reaction with ferric chloride. Although the structure of this is unquestioned, it should not be necessary to go into detail to explain that this com-

[5] Ref. 2, p. 2427.

[6] Wieland, "Die Hydrazine," F. Enke, Stuttgart, 1913, p. 73.

[7] Fischer, *Ber.*, **22**, 1935 (1889).

[8] Kall, *Ann.*, **263**, 263 (1891).

[9] Kjellin, *Ber.*, **26**, 2384 (1893).

pound represents a different hydroxylamine type from that which is produced by the action of two molecular equivalents of phenyl isocyanate upon hydroxylamine. The latter is a *diacylated* hydroxylamine; the former is an *alkyl-acyl* hydroxylamine. It is well known that diacylated hydroxylamines never possess the structure, $(R—CO—)_2N—O—H$, but invariably the structure, $R—CO—NH—O—CO—R$.

The fact that the latter compound, $C_6H_5NH—CO—NH—O—CO—NHC_6H_5$, has never reacted with a third molecule of phenyl isocyanate, and that the former compound, $C_6H_5NH—CO—N(OH)—C_2H_5$, has never reacted with a second molecule is no argument whatever in regard to their structure. The evidence merely shows that the compound, $C_6H_5—NH—CO—N(OH)—C_2H_5$, will not react with phenyl isocyanate in ether solution. It will be shown later (p. 1478) that there is no reaction between benzohydroxamic acid, $C_6H_5—CO—NHOH$, and phenyl isocyanate when solvents are used, although 2 molecular equivalents of the isocyanate become attached when solvents are absent. It would seem reasonable to expect that Kjellin's compound would react with a second molecule of isocyanate if no solvents were employed.

With regard to the failure of phenyl isocyanate to add to carbanilido-phenyl-hydroxy-urea, the following facts are pertinent. It has been repeatedly shown that the first 2 acyl groups add to a hydroxylamine nucleus easily, whereas a third acyl group is inserted frequently with difficulty. Thus, a customary method of acetylation for monohydroxamic acids is to add acetic anhydride, and evaporate the excess in a vacuum. To be sure, there are cases known where 2 acetyl groups enter by this method and form a trihydroxamic acid. It is more usually the case, however, that the reaction stops completely when one acetyl group has entered the molecule.

The evidence, therefore, is against the "diphenyl-hydroxy-biuret" structure. Kall[8] suggested the name carbanilido-phenyl-hydroxy-urea, and although the omission of a bond in "—NHO—" of his structural formula, $C_6H_5NH—CO—NHO—CO—NHC_6H_5$, causes ambiguity, a study of his article makes it plain that the hydrogen is joined directly to the nitrogen and not to the oxygen. Kall's argument for his structure, however, was rather ineffective. He merely cited the fact that the substance is insoluble in solutions of sodium hydroxide. Phenyl-hydroxy-urea may be named phenyl-carbam-hydroxamic acid; carbanilido-phenyl-hydroxy-urea would then be the phenyl-carbamyl ester of phenyl-carbam-hydroxamic acid.

It has been assumed[10] that when carbanilido-phenyl-hydroxy-urea was formed by heating an alcoholic solution of phenyl-hydroxy-urea, or by other similar methods, there was an intermediate decomposition into phenyl isocyanate and hydroxylamine. The equation would be $C_6H_5NH—CO—NHOH \longrightarrow C_6H_5—NCO + NH_2OH$. This molecule of phenyl isocyanate

[10] Ref. 8, p. 266.

would then be free to react with unchanged phenyl-hydroxy-urea as follows:
C_6H_5NH—CO—$NHOH$ + C_6H_5—NCO ⟶ C_6H_5—NH—CO—NH—O-—CO—NHC_6H_5.

A few experiments were attempted in order either to prove or to disprove this reaction mechanism. In the first place, phenyl isocyanate, if formed, should be free to react with the solvent as well as with the solute. Phenyl-urethane, C_6H_5—NH—CO—OC_2H_5, would be the by-product if phenyl isocyanate reacted with the solvent, alcohol. A fruitless search was made for this low-melting compound. Following this, a second experiment was planned which differed from the first only by the addition of aniline to the mixture of alcohol and phenyl-hydroxy-urea. In this case, there would be three competing reactions if phenyl isocyanate were liberated. Besides the two reactions expected in the first test, there would also be formed *sym*-diphenyl-urea due to the reaction between aniline and phenyl isocyanate. The results of this experiment showed no points of difference from the first test, in which aniline was absent. Some carbanilido-phenyl-hydroxy-urea was formed, and some unchanged phenyl-hydroxy-urea was still present. The aniline was unused. This meant conclusively that either the suggested mechanism is untenable or phenyl isocyanate reacts ever so much more quickly with phenyl-hydroxy-urea than it does with alcohol or with aniline. In order to decide the latter point, molecular equivalents of phenyl-hydroxy-urea and aniline were dissolved in ethyl acetate. To this solution 1 molecular equivalent of phenyl isocyanate was added. There was an immediate precipitation of nearly the quantitative amount of *sym*-diphenyl-urea. Only phenyl-hydroxy-urea was present in the filtrate. There is no basis, therefore, for the assumption that phenyl-hydroxy-urea dissociates into phenyl isocyanate and hydroxylamine when it is heated in alcoholic solution. The probable course of the reaction is that 2 molecules of phenyl-hydroxy-urea react with each other, with the liberation of hydroxylamine. The equation follows.

C_6H_5NH—CO—NH—O⫶H + HO—NH⫶CO—NHC_6H_5 ⟶ NH_2OH +
C_6H_5NH—CO—NH—O—CO—NHC_6H_5.
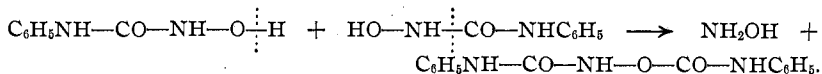
Brief mention will be made of hydroxy-urea,[11] NH_2—CO—$NHOH$, because of its relation to the compounds under discussion in this paper. An alcoholic solution of hydroxy-urea is unstable, and in a reaction that parallels the behavior of phenyl-hydroxy-urea, "hydroxy-biuret" is formed. Dresler and Stein, who discovered the compound, assigned only an empirical formula to it. In Beilstein's 4th "Handbuch," however, two possible structures are given,[12] namely, H_2N—CO—NH—CO—$NHOH$

[11] (a) Dresler and Stein, *Ann.*, **150**, 242 (1869). (b) Francesconi and Parozzani, *Gazz. chim. ital.*, [2] **31**, 334 (1901).

[12] Beilstein, "Handbuch der organischen Chemie," [4] **1921**, Julius Springer, Berlin, 3, p. 96.

and H_2N—CO—N(OH)—$CONH_2$. Both of these structures seem inadequate. Ferric chloride would impart an intense color to solutions of hydroxy-biuret if either of these formulas were correct. As a matter of fact, no color whatever is produced. The structure, NH_2—CO—NH—O—CO—NH_2, is, therefore, suggested since it is in harmony with all of the known reactions of this substance. It is in accord with the formulas for other di-acylated hydroxylamines. It expresses the fact that hydroxy-urea may be obtained from it by hydrolysis. It states why ferric chloride produces no coloration. A name in accord with this formula would be either dicarbam-hydroxamic acid, or the carbamyl ester of carbam-hydroxamic acid.

The parallelism between this compound and the phenyl-carbamyl ester of phenyl-carbam-hydroxamic acid is evident. Both are formed by the addition of isocyanate to a monohydroxamic acid. The addition takes place at the α-hydroxylamino hydrogen, rather than at the β-hydroxylamino-, or at the amido-hydrogen. A general equation is

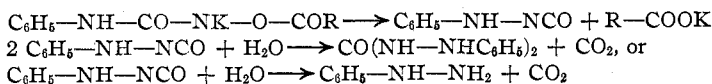$$R—CO—NH—O\!\vdots\!H + R'—NCO \longrightarrow R—CO—NH—O—CO—NH—R'$$
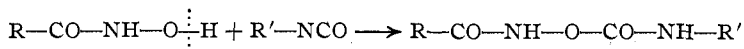
Evidence was recently published which showed that ketene reacts with hydroxamic acids in precisely a similar fashion.[13] The close relationship between isocyanates and ketenes has been pointed out frequently by various authors.

Hydroxy-urea has been assumed to undergo dissociation[14] in solution into hydroxylamine and isocyanic acid. Although no experimental work has been done in this connection, it seems reasonable to infer from the evidence submitted with phenyl-hydroxy-urea that there is no such dissociation. Dresler and Stein, who suggested the above mechanism, also suggested the optional scheme that hydroxy-biuret may have been formed by the interaction of 2 molecules of hydroxy-urea. This idea is probably the correct one. The equation would be

$$NH_2CONHO\!\vdots\!H + HONH\!\vdots\!CONH_2 \longrightarrow NH_2OH + NH_2CONHOCONH_2$$
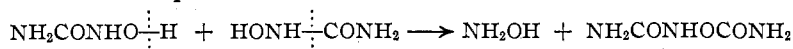
Little difficulty was presented in the preparation of the acetyl or the benzoyl esters of phenyl-carbam-hydroxamic acid (α-phenyl-β-hydroxy-urea). These two esters showed no tendency whatever to rearrange. The following reactions, which would have been customary for dihydroxamic acids, did *not* occur.

C_6H_5—NH—CO—NK—O—COR $\longrightarrow C_6H_5$—NH—NCO + R—COOK
2 C_6H_5—NH—NCO + $H_2O \longrightarrow CO(NH—NHC_6H_5)_2 + CO_2$, or
C_6H_5—NH—NCO + $H_2O \longrightarrow C_6H_5$—NH—$NH_2$ + CO_2

A very careful search was made for diphenyl carbazide and for phenyl-

[13] Hurd and Cochran, THIS JOURNAL, **45**, 515 (1923).

[14] Ref. 11a, **1869**, p. 249.

hydrazine in the products of reaction, but no trace of either could be found. This is in perfect agreement with the non-rearrangement[15] of the azide of phenyl carbamic acid, C_6H_5—NH—CO—N_3. This azide was peculiarly inert towards boiling water or boiling alcohol. Heating under pressure with these solvents caused hydrolysis and alcoholysis, but never rearrangement.

With this in view, the behavior of carbanilido-phenyl-hydroxy-urea, C_6H_5—NH—CO—NH—O—CO—NHC_6H_5, towards alkaline solutions is not difficult to understand. Although its structure is that of a dihydroxamic acid, a type of compound which is known to rearrange in the presence of a hot alkaline medium, actually, a hot solution of sodium hydroxide will hydrolyze it to form *sym*-diphenyl-urea, aniline, hydroxylamine and carbon dioxide. Rearrangement to form phenylhydrazine never occurs. Strangely enough, this fact was never used as an argument in favor of the diphenyl-hydroxy-biuret formula as opposed to the dihydroxamic acid structure. It is seen now that, since the acetyl and the benzoyl esters of the same acid behave similarly, such an argument would have become invalid. Of course, it might be suggested that the structure of the acetyl or of the benzoyl ester is not correctly represented, that the structure, C_6H_5NH—CO—N(OH)—CO—R, is the correct one. A reply to this would be to suggest the behavior of the azide, C_6H_5NH—CO—N_3. In this case, there is no possibility of a different structure, and yet it does not rearrange. There is little doubt, then, that the dihydroxamic acid structure is the correct one, in spite of the anomaly of non-rearrangement.

It could be predicted that acyl esters of hydroxy-urea, NH_2—CO—NH—O—CO—R, would show no tendency to rearrange to form hydrazine, but no work has been done towards that end.

It was stated above that the potassium salt of the benzoyl ester of phenyl-carbam-hydroxamic acid could not be made to rearrange. Very briefly, this is what did happen instead. When the salt was dissolved in water there was no reaction in the cold but a copious precipitate of *sym*-diphenyl-urea resulted when the solution was boiled. This would indicate the reaction, $C_6H_5NHCONKOCOC_6H_5 + H_2O \longrightarrow KHCO_3 + CO(NHC_6H_5)_2$.
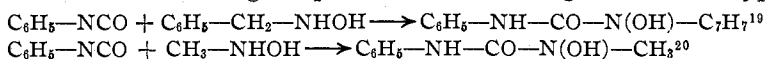
Neither the potassium nor the sodium salt of the acetyl ester, C_6H_5—NH—CO—NH—O—$COCH_3$, decomposed in a similar manner. *Sym.*-methyl-phenyl-urea would have been the product of reaction, but it was never isolated. Carbanilido-phenyl-hydroxy-urea, and an unidentified compound melting at 161°, were found instead. The latter compound was converted into carbanilido-phenyl-hydroxy-urea by solution in concd. sulfuric acid followed by dilution with water. No trace of phenylhydrazine was found. It was thought at first that the material melting at 161°

[15] Curtius and Hofmann, *J. prakt. Chem.*, [2] **53**, 530 (1896). Curtius and Burkhardt, *ibid.*, [2] **58**, 205 (1898).

was sym-diphenyl-carbazide, $CO(NH—NHC_6H_5)_2$, which is reported to melt at $163°$[16] and at $169°$.[17] It was conclusively shown, however, that there was no resemblance in the chemical properties of the two. Although the mechanism of what really does occur is somewhat undetermined as yet, it is definitely established that the products of rearrangements are absent. The carbanilido-phenyl-hydroxy-urea was probably produced as a result of hydrolysis of the original salt to phenyl-hydroxy-urea. It has been shown that this parent compound will decompose under favorable influences to form carbanilido-phenyl-hydroxy-urea.

The reaction between benzohydroxamic acid, which contains 2 available hydrogens, and phenyl isocyanate received some study. When ethyl acetate was employed as a solvent there was no reaction. Marquis[18] reported that when pyridine was used as solvent, one of the 2 hydrogens became attached. The resultant compound, $C_6H_5CO—NH—O—CO—NHC_6H_5$, is isomeric with $C_6H_5NH—CO—NH—O—COC_6H_5$, which has been described. Marquis' compound melted at $209°$, but little more was said of its properties. It was found in the present study that when no solvent was employed, both hydrogens of the benzohydroxamic acid became reactive and the trihydroxamic acid, $C_6H_5CO—N(CO—NHC_6H_5)—O—CO—NH-C_6H_5$, formed quantitatively.

Considerable attention has been directed to the reactions of phenyl isocyanate and the alkyl or aryl hydroxylamines, $R—NHOH$. When 1 molecule of isocyanate is added, it is always the β-hydrogen of the hydroxylamine which is affected. Ferric chloride will give a pronounced color reaction with the resulting compound. The following reactions are typical.

$C_6H_5—NCO + C_6H_5—CH_2—NHOH \longrightarrow C_6H_5—NH—CO—N(OH)—C_7H_7$[19]

$C_6H_5—NCO + CH_3—NHOH \longrightarrow C_6H_5—NH—CO—N(OH)—CH_3$[20]

Kjellin[19] reported that β-methyl-hydroxylamine and β-ethyl-hydroxylamine would not react with 2 molecular equivalents of phenyl isocyanate. That it is not universally true that the α-hydrogen is inert is evident from the work of Beckmann and Schönermark[21] who reported that phenyl isocyanate will react with $C_6H_5NH—CO—N(OH)—C_7H_7$ to give a compound which has no color reaction with ferric chloride. The same authors reported the isolation of an addition compound of $C_6H_5NH—CO—N(OH)—CH_2—C_6H_4—OCH_3$ and phenyl isocyanate which also gives no reaction with ferric chloride.

Very limited work, however, has been done with the addition products of phenyl isocyanate and hydroxamic acids. Phenyl-benzohydroxamic

[16] Heller, Ann., **263**, 276 (1891).

[17] Cazeneuve and Moreau, Compt. rend., **129**, 1256 (1899).

[18] Marquis, ibid., **143**, 1163 (1906).

[19] Beckmann and Felrath, Ann., **273**, 28 (1893).

[20] Ref. 9, p. 2382.

[21] Beckmann and Schönermark, J. prakt. Chem., [2] **56**, (a) 75, (b) 84, (c) 81 (1897).

acid[20] forms C_6H_5CO—$N(C_6H_5)$—O—CO—NHC_6H_5, and benzyl-benzo-hydroxamic acid forms a similar addition compound. The methyl ester of formohydroxamic acid[22] unites with phenyl isocyanate to yield H—CO—$N(OCH_3)$—CO—NHC_6H_5. Werner and Subak[23] obtained a similar result with methyl benzohydroximic acid (either *syn* or *anti*). In this case, C_6H_5—$C(OCH_3):NOH$ produced C_6H_5—$C(OCH_3):NOCO$—NHC_6H_5.

The study of diphenyl-carbam-hydroxamic acid, $(C_6H_5)_2N$—CO—NH-OH, revealed the fact that it behaves exactly as anticipated from its hydroxamic acid structure. Therefore, the reactions of the monophenyl compound, C_6H_5NH—CO—$NHOH$, possessed but little similarity.

Diphenyl-carbam-hydroxamic acid (or α,α-diphenyl-β-hydroxy-urea) is quite stable in a boiling solution of alcohol. There was no decomposition to form the diphenyl-carbamyl ester of diphenyl-carbam-hydroxamic acid, $(C_6H_5)_2N$—CO—NH—O—CO—$N(C_6H_5)_2$. The acetyl ester and the benzoyl ester of the monohydroxamic acid were prepared in the customary manner. The esters are white crystalline compounds that show no tendency to decompose at ordinary temperatures.

It will be recalled that the primary object of this investigation was to test the hypothesis of Jones and Hurd[24] by means of rearrangements in this series. Because of the diphenyl nitrogen, a potential free radical, such solutions should rearrange readily and should furnish direct evidence for or against the hypothesis. Just as was true in the case of the salts of the acyl esters of triphenyl-acethydroxamic acid[25] or of diphenyl-acethydroxamic acid, here also, the salts could not be obtained pure. Water solutions could be obtained, however, which started to decompose immediately *at room temperature*. *Unsym*-diphenylhydrazine was isolated in quantity as a reaction product. The following reaction expresses this fact: $(C_6H_5)_2$-N—CO—$N(Na)$—O—COR + H_2O ⟶ $(C_6H_5)_2N$—NH_2 + R—COO-Na + CO_2. Inasmuch as this is *rearrangement*, and not hydrolysis, it affords striking agreement with the hypothesis. As a further confirmation of the hypothesis, a small amount of *sym*-tetraphenyl-carbazide, CO-$(NH$—$N(C_6H_5)_2)_2$, was isolated from the filtrate out of which the sodium salt originally precipitated. This must have resulted from the rearrangement of the salt while it was still in solution.

It was noticed that although *unsym*-diphenylhydrazine separated rapidly from a water solution of the salt at room temperature, it was necessary to keep it at room temperature to prevent a secondary reaction. When the solution was boiled, diphenylamine precipitated instead. Concerning its formation, two possibilities are suggested. First, diphenylhydrazine

[22] Biddle, *Am. Chem. J.*, **33**, 65 (1905).

[23] Werner and Subak, *Ber.*, **29**, 1157 (1896).

[24] Ref. 2, p. 2426.

[25] Ref. 2, p. 2434.

is an intermediate product which decomposes in boiling water to form diphenyl-urea. Chattaway and Aldridge[26] report that diphenylamine, ammonia and nitrogen are formed when diphenylhydrazine is heated at high temperatures for a long time. $3 (C_6H_5)_2N—NH_2 \longrightarrow 3 (C_6H_5)_2$-$NH + N_2 + NH_3$. The details of a control reaction of diphenylhydrazine and water will be given later (see p. 1488). The results showed conclusively that no diphenylamine was formed by this method until at least 2 or 3 weeks had elapsed. Thus, it would seem inconsistent to assume that the diphenylamine, which in the original experiment was formed instantly, could have been formed through the medium of diphenylhydrazine.

The second possibility is that diphenylamine was formed directly from the salt by hydrolysis. At present, it is impossible to decide whether the cleavage plane for the hydrolysis is at $(C_6H_5)_2N—CO\vdots N(Na)—OCO-$ CH_3 or at $(C_6H_5)_2N\vdots CO—N(Na).OCOCH_3$. The first would form $(C_6H_5)_2N—COOH$, which breaks at once into carbon dioxide and diphenylamine. If hydrolysis occurred in accordance with the second scheme, it would be the result of diphenyl nitrogen playing its part as free radical. Our customary means of representation of the Beckmann rearrangement is to assume the intermediate formation of a univalent nitrogen derivative, $(R—CO—N)$. The radical R then momentarily separates from the carbon, later to become attached to the very reactive, univalent nitrogen. Although it never has been done, it should not be impossible to find compounds of this type in which the radical R is sufficiently reactive to force its separation whether the univalent nitrogen atom has been formed or not. In the absence of univalent nitrogen, the radical would react with water. It may be that this is exactly what happens here. This would be the first bit of recorded evidence in support of the theory that in the Beckmann rearrangement there is an actual cleavage of a radical from the carbon in the univalent nitrogen derivative, $(R—CO—N)$. A pertinent fact to remember is that diphenyl nitrogen is not formed[27] at temperatures below $90°$. In order to obtain the diphenylamine by the method described above, the temperature of boiling water was necessary.

The diphenyl nitrogen grouping which is present in some compounds described in this paper made it possible to secure additional data for the "diphenylamine reaction." The following compounds have been known for some time to give a blue reaction product with conc. sulfuric acid: $(C_6H_5)_2N—NH_2$, $(C_6H_5)_2N—OH$, $(C_6H_5)_2N—N(C_6H_5)_2$, and $(C_6H_5)_2N—$ NO. Such compounds as diphenylamine and tetraphenyl-carbazide, $CO(NH—N(C_6H_5)_2)_2$, dissolve in conc. sulfuric acid without the production of color. An intense blue is formed at once, however, upon the addition of

[26] Chattaway and Aldridge, *J. Chem. Soc.*, **99**, 404 (1911).

[27] Ref. 6, p. 77.

certain oxidizing agents, notably nitric acid.   So also, in the list which follows, I have found that an oxidizing agent in addition to sulfuric acid is necessary to produce the familiar blue coloration.   The list includes $(C_6H_5)_2N$—COCl, $(C_6H_5)_2N$—NH—CO—C_6H_5, $(C_6H_5)_2N$—CO—NHOH, $(C_6H_5)_2N$—CO—NH—OCOCH$_3$, and $(C_6H_5)_2N$—CO—NH—O—COC$_6H_5$. The scope of this paper does not include a discussion of this type of color reactions. . However, a partial list of references[28] is given to this interesting subject.

Experimental Part

Phenyl-hydroxy-urea, C_6H_5—NH—CO—NHOH.—The two methods available for the preparation of this compound were both employed.   Kall's method[8] used phenyl isocyanate and an aqueous solution of hydroxylamine.   In Kjellin's procedure,[9] free hydroxylamine was added to a solution of phenyl isocyanate in benzene.   The latter method was found to give excellent yields of material in a high state of purity.

Phenyl-hydroxy-urea was recrystallized by suspension in an excess of ethyl acetate, warming, filtering and diluting the solution with 2 or 3 times the volume of petroleum ether after it had cooled.   The resulting crystals were collected and washed with petroleum ether; m. p., 140°.   During this process there was no noticeable decomposition to form the higher-melting derivative, carbanilido-phenyl-hydroxy-urea.

An alcoholic solution of phenyl-hydroxy-urea was mixed with an alcoholic solution of copper acetate.   A green copper salt precipitated abundantly.   The filtrate from this still gave a color reaction with ferric chloride.

Benzoyl Ester, C_6H_5NH—CO—NH—O—COC$_6H_5$.—First Method.   A partial solution of 1.5 g. of phenyl-hydroxy-urea in 0.5 g. of sodium hydroxide in 20 cc. of water was prepared by heating the mixture upon the steam-bath for some time.   To the well-cooled solution was added 1.2 cc. of benzoyl chloride in 2 portions with constant agitation.   When the reaction was completed the white solid was collected on a filter, washed and dried.

The solution of the phenyl-hydroxy-urea was not perceptibly hastened by the use of twice as much sodium hydroxide (1 g.) or potassium hydroxide, but the hydrolysis was increased.   When the filtrate from which the benzoyl ester had been removed was carefully neutralized a white precipitate formed which consisted chiefly of dibenzo-hydroxamic acid, C_6H_5CO—NH—OCOC$_6H_5$.   An excess of hydrochloric acid precipitated benzoic acid.   Dibenzo-hydroxamic acid was formed by the action of benzoyl chloride upon hydroxylamine.   The latter was separated by hydrolysis from phenyl-hydroxy-urea by the hot alkaline solution.   To avoid separation, therefore, no more than an equivalent of base should be employed.

The identity of the dibenzo-hydroxamic acid was carefully established because of the proximity of its melting point to that of diphenyl-carbazide, a possible product had re-.arrangement occurred.   It was recrystallized twice from alcohol.   A mixed melting point with a known sample of dibenzo-hydroxamic acid which had been recently prepared and purified showed no change.   Ferric chloride solutions failed to produce a color reaction; copper sulfate solutions were likewise without effect.   Diphenyl-car-

[28] Ref. 2, pp. 32–36; 59–81.   Wieland and his students, *Ber.*, **45**, 494 (1912); **43**, 3263 (1910); **39**, 1503 (1906).   Kehrmann and St. Micewicz, *ibid.*, **45**, 2641 (1912); *Helvetica Chim. Acta*, **4**, 949 (1921).   Kehrmann and Roy, *Ber.*, **55B**, 156 (1922). Blom, *Helvetica Chim. Acta*, **4**, 625, 1036 (1921).   Rupe and Labhardt, *Ber.*, **33**, 246 (1900).

bazide[29] is known to form an intensely colored solution with either of the two salts. Finally, the compound was analyzed to establish its nature without question.

Analysis. Subs., 0.1702: N, 9.8 cc. (over water, 32°, 747.3 mm.). Calc. for $C_{14}H_{11}O_3N$: N, 6.06. Found: 5.92.

Alcohol, ethyl acetate, acetone or hot benzene dissolves the benzoyl ester of phenyl-carbam-hydroxamic acid. Ether, petroleum ether, dilute acids or dil. alkali fails to do so. A warm solution of sodium hydroxide does hydrolyze it slowly, however, for ferric chloride, uncolored at first, gradually produces the purple coloration. The ester was recrystallized from a mixture of ethyl acetate and ligroin. The heavy crystalline clumps melted at 179°, with decomposition.

Analysis. Subs., 0.1736: N, 18.08 cc. (over 30% KOH; 28.5°, 746.2 mm. (26°)). Calc. for $C_{14}H_{12}O_3N_2$: N, 10.92. Found: 11.15.

Second Method.—Phenyl-hydroxy-urea was fused at 50° with quite an excess of benzoic anhydride for 5 hours. The excess of anhydride was extracted several times with warm ligroin, and triturated with dil. sodium hydroxide solution. The insoluble portion was washed with water, dried, and recrystallized from a mixture of ethyl acetate and ligroin.

POTASSIUM SALT, C_6H_5NH—CO—NK—O—CO—C_6H_5.—About 0.1 g. of the benzoyl ester was dissolved in 5 cc. of absolute alcohol, and to the solution was added a small volume of alcohol in which was dissolved about 0.05 g. of potassium hydroxide. After a few minutes, a sandy, white precipitate developed. The addition of ether increased the yield somewhat.

The salt blackened between 160° and 180°, but did not change further below 240°. For the most part, the salt dissolved in water. A small amount of material melting at 125–137° was filtered and discarded. The filtrate seemed stable in the cold, but when it was boiled white crystals formed which were identified as *sym*-diphenyl-urea. With no further purification they melted sharply at 236°.

There was no evidence of the presence of phenylhydrazine.

Acetyl Ester, C_6H_5—NH—CO—NH—O—$COCH_3$. A solution of 1.5 g. of phenyl-hydroxy-urea in 10 cc. of acetic anhydride, was prepared on the steam-bath. After 5 minutes there was still a pronounced ferric chloride reaction. After 2 hours the test was negative and the reaction was stopped by adding an excess of water. In the course of an hour the oil solidified, at which time the solid was collected, washed and dried. It was recrystallized twice from a mixture of benzene and ligroin; m. p., 121–123°. A gas was formed at 135°, and at 160° the material darkened.

Analysis. Subs., 0.1893: N, 25.46 cc. (over 30% KOH; 28°, 747.7 mm. (26°)). Calc. for $C_9H_{10}O_3N_2$: N, 14.42. Found: 14.46.

The acetyl ester is soluble in benzene, alcohol, acetone or ethyl acetate. It is insoluble in ligroin, carbon tetrachloride, ether, or a dilute solution of sodium hydroxide.

ACID SODIUM SALT, $(C_6H_5NH$—CO—N(OCOCH_3))_2H$—Na.—Three cc. of hot absolute alcohol dissolved 0.38 g. of the acetyl ester. No precipitate formed when the solution was cooled. Previously, a solution of sodium methylate in methanol had been prepared of such strength that 1 cc. was equivalent to 0.023 g. of sodium. Two cc. of this solution was added to the alcoholic solution of the ester. There was no precipitation, neither was there an apparent heat of reaction. The mixture was diluted at once with 6 cc. of absolute ether, and a precipitate was soon obtained. The yield was increased to 0.25 g. by the addition of 5 cc. of petroleum ether.

Analysis. Subs., 0.0910: Na₂SO₄, 0.0157. Calc. for $C_{18}H_{19}O_6N_4Na$: Na, 5.61. Found: 5.60.

[29] Skinner and Ruhemann, *J. Chem. Soc.*, **53**, 554 (1888).

The acid salt was subjected to 3 definite behavior tests toward: (1) very dilute sodium hydroxide solution, (2) cold water and (3) boiling water. The sodium hydroxide dissolved the acid salt readily, especially when the mixture was warmed somewhat. When this solution was acidified, the original acetyl ester was *not* regenerated but, instead, a compound, m. p. 174–177°, was formed. Towards cold and boiling water the behavior was much the same. The solubility was not great in either case. The solutions were filtered and divided into 2 parts, of which one was acidified. Acids always precipitated a solid which melted at 177°. At least 2 possible derivatives of phenyl-hydroxy-urea melt at 177–179°: (A) carbanilido-phenyl-hydroxy-urea, (B) the benzoyl ester of phenyl-carbam-hydroxamic acid. Mixed melting points of the 177°-material, obtained from the acetyl ester, were taken with both of these compounds: mixture with (A), m. p. 177–178°; mixture with (B), m. p. 155–168°. The evidence is good, then, that carbanilido-phenyl-hydroxy-urea is the product of the reaction.

The other part was allowed to stand for 2 days. Little change occurred after the first day, at which time the solutions became an opaque white. The precipitate was collected and purified by recrystallization from a mixture of ethyl acetate and ligroin. The needle-shaped crystals melted at 160–161°, with decomposition. An added yield of the 177°-material was precipitated when the aqueous filtrate was acidified. No trace of aniline, a possible product of hydrolysis, could be found in the filtrate.

The nature of this compound is still undetermined. It is soluble in alcohol, ethyl acetate or ether. It is insoluble in benzene or ligroin; it is also insoluble in dil. acids or alkalies. As yet, sufficient substance has not been isolated for an analysis. By the method of mixed melting points it was established that it was not dibenzo-hydroxyamic acid (see above, p. 1481). The melting point of the mixture was 145–148°. This compound was also far more soluble in alcohol than was dibenzo-hydroxamic acid. Comparison also proved that it could not be *sym*-diphenyl-carbazide. Heller's method[30] was used to prepare the latter. The mixed melting point of the two was 150–152° with much decomposition. Pure diphenyl-carbazide melted without decomposition. The 161°-crystals dissolved easily in conc. sulfuric acid. From such a solution, water precipitated a white solid; m. p., 175–177°. Recrystallization from dil. alcohol gave a purer product, carbanilido-phenyl-hydroxy-urea; m. p., 176–177°.

POTASSIUM SALT, C_6H_5—NH—CO—NK—O—$COCH_3$.—The precipitation of the potassium salt by an alcoholic solution of potassium hydroxide was much slower than in the case of the sodium salt, in spite of the fact that a larger quantity of petroleum ether was added to the alcohol-ether mixture. The salt was partly soluble in water. The insoluble part was boiled with very dilute hydrochloric acid, filtered and dried; m. p., 161°. The soluble portion gave no precipitate when boiled. To a part, ferric chloride solution was added, without action. A green copper salt was produced when copper acetate was added to a second portion. A white silver salt was precipitated from a third sample with silver nitrate; this rapidly turned dark in color. Analysis showed that the potassium salt was not precipitated in the pure state.

Analysis. Subs., 0.0947: K_2SO_4, 0.0279. Calc. for $C_9H_9O_3N_2K$ (normal potassium salt): K, 16.8. Calc. for $C_{18}H_{19}O_6N_4K$ (acid potassium salt): K, 9.17. Found: 13.2.

Carbanilido-phenyl-hydroxy-urea.—In order to learn more concerning the mechanism of the reaction "phenyl-hydroxy-urea ⟶ carbanilido-phenyl-hydroxy-urea" by heating phenyl-hydroxy-urea in alcohol, Kjellin's experiment[9] was repeated with modifications. About 1 g. of phenyl-hydroxy-urea was dissolved in absolute alcohol and refluxed for 2 hours. Atmospheric moisture was excluded by means of a soda-lime tube. A sandy precipitate melting at about 174° crystallized readily when the solution was cooled. The filtrate contained only a mixture of this derivative and of the original phenyl-hy-

30 Heller, *Ann.*, 263, 276 (1891).

droxy-urea, m. p. 140°. There was no indication whatever of the formation of phenyl-urethan, which possesses an unmistakably low melting point of 51°.

When a solution which contained 0.7 g. of phenyl-hydroxy-urea and 0.8 cc. of aniline in 10 cc. of absolute alcohol was boiled for 1 hour and cooled, crystals of pure carbanilido-phenyl-hydroxy-urea appeared. They melted at 178° after washing with alcohol and ether. These crystals were suspended for 5 minutes in alcohol (25°) and then filtered. Ferric chloride did not give a color reaction with the filtrate. Evaporation of the original filtrate showed the presence of more carbanilido-phenyl-hydroxy-urea, some unused phenyl-hydroxy-urea, and nearly all of the aniline. Several recrystallizations of the solids failed to reveal the presence of any *sym*-diphenyl-urea. This should have been formed had there been any phenyl isocyanate liberated during the process.

To determine whether phenyl isocyanate reacts more readily with aniline or with phenyl-hydroxy-urea, a warm solution of 1.52 g. of phenyl-hydroxy-urea in 10 cc. of ethyl acetate was filtered, and to the warmed filtrate 0.93 g. of aniline was added, followed by 1.19 g. of phenyl isocyanate. A voluminous white precipitate formed at once, which failed to dissolve when the solution was boiled. The precipitate was washed thrice with ethyl acetate, and then twice with petroleum ether; m. p., dry, 234-235°. Therefore, it was *sym*-diphenyl-urea in a high state of purity; yield, 2 g.

When ligroin was added to the filtrate another white precipitate formed, which was practically pure phenyl-hydroxy-urea. It was filtered by suction, and washed with petroleum ether. The crystals melted quite sharply at 140°. It seems well established, therefore, that aniline reacts much more readily with phenyl isocyanate, than is the case with phenyl-hydroxy-urea.

Addition Compound of Phenyl Isocyanate and Benzohydroxamic Acid.—*With solvents.*—To a solution of 0.8 g. of benzohydroxamic acid in 10 cc. of ethyl acetate,[31] petroleum ether was added cautiously so as to cause no precipitation, followed by 1.5 cc. of phenyl isocyanate, a great excess. The flask was corked at once to exclude moisture. At the end of 10 hours, even in the presence of the excess of isocyanate, a sample from the solution showed the intense ferric chloride reaction characteristic of benzo-hydroxamic acid. A small, white, crystalline precipitate of diphenyl-urea, m. p. 236°, indicated that the solvents employed were not anhydrous. This was separated by filtration. There was no other evidence of reaction. The filtrate was diluted with ligroin. Crystalline plates formed, m. p. 123°, which were soluble in water; this solution was colored strongly by ferric chloride. About 0.6 g. of pure benzohydroxamic acid was recovered.

Without solvents.—The 0.6 g. of benzohydroxamic acid which was recovered in the preceding experiment was warmed with 5 cc. of phenyl isocyanate until it dissolved. The flask was then cooled and corked. After several hours, 80 cc. of petroleum ether was added to dissolve the excess of phenyl isocyanate. An oil gradually settled to the bottom and the corked flask was surrounded by a freezing mixture for 0.5 hour, before the petroleum ether layer was decanted. The oily residue was washed twice with more petroleum ether and then was set aside for 3 days in a vacuum desiccator to crystallize. The excess of phenyl isocyanate was recovered from the petroleum ether by fractional distillation.

The white solid was purified by solution in 8 cc. of warm benzene. A small quantity of undissolved diphenyl urea was removed by filtration after the mixture was cooled. The filtrate was diluted with 15 cc. of ligroin. There was no immediate precipitation, but there was supersaturation because in the course of 15 minutes practically all of the solute had separated; m. p., 115-116°.

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[31] Benzene, as a neutral solvent, cannot be used, since it fails to dissolve benzo-hydroxamic acid, even at boiling temperature.

The material was again recrystallized from benzene-ligroin and analyzed; m. p., 113–114°. The compound is soluble in ordinary organic solvents, but insoluble in petroleum ether. An alcoholic solution does not color a solution of ferric chloride.

Analysis. Subs., 0.1127: N, 12.1 cc. (over 40% KOH; 32°, 744.5 mm. (29.5°)). Calc. for $C_{21}H_{17}O_4N_3$: N, 11.2. Found: 11.4.

It was found possible to convert this material into *sym*-diphenyl-urea by 2 methods, namely, by heating and by the action of sodium methylate. (1) The pure material resolidified after melting at about 125°; at 145°, gas was evolved. Heating was continued carefully in a small free flame. A small amount of charred matter remained at the bottom, while a liquid distilled up the tube and solidified. The tube was then opened at the bottom and sealed at the top and the melting point of this decomposition product determined to be 234°. It was *sym*-diphenyl-urea. (2) Equimolecular parts of a concd. solution of the ester in absolute alcohol and sodium methylate in solution were mixed. The mixture was diluted with absolute ether and petroleum ether, when a precipitate formed which was filtered and washed with water. The insoluble portion melted at 236°. The water-soluble portion liberated bubbles of a gas when it was acidified, presumably because of the presence of ethyl sodium carbonate. This would seem to indicate that carbon dioxide can be extracted from the molecule by alkali as well as by heat. To make certain that the material precipitated was a mixture and not a "salt" in which sodium had replaced an amido hydrogen, it was analyzed.

Analysis. Subs., 0.1046: Na_2SO_4, 0.0217. Calc. for $C_{21}H_{16}O_4N_3Na$: Na, 5.95. Found: 6.72.

Diphenyl-carbam-hydroxamic Acid ($\alpha.\alpha$-Diphenyl-β-hydroxy-urea),

$$(C_6H_5)_2N—CO—NH—OH$$

Preparation. First Method: From diphenyl-urea chloride and free hydroxylamine.— This method is an application of the general method of preparing hydroxamic acids developed by Jones and Hurd.[32] Twenty-three g. of diphenyl-urea chloride was dissolved in 120 cc. of dry benzene. To this was added 6.5–7 g. of free hydroxylamine. The flask was then stoppered and shaken vigorously. In the course of a few minutes, considerable heat of reaction developed. The mixture was left for an hour to insure complete reaction, and the white crystalline mass which had formed was then collected and pressed upon a porous plate; yield, 11 g. Most of the hydroxylamine hydrochloride formed during the reaction remained in the flask as a viscous oil, which after a few hours had solidified. It weighed about 3 g.

An additional 4 g. of diphenyl-carbam-hydroxamic acid was obtained when the benzene filtrate was distilled to half its volume; yield, 15 g. Recovery of more from the filtrate was not attempted. $(C_6H_5)_2NCOCl + 2 NH_2OH \longrightarrow (C_6H_5)_2NCONHOH + NH_4OCl$.

Ethyl acetate was an excellent solvent for recrystallization. A small amount of insoluble hydroxylamine hydrochloride was removed from the hot solution. When the filtrate had cooled, the acid crystallized in beautiful colorless needles; m. p., 134–134.5° with slight decomposition; at 150°, the decomposition became vigorous.

Diphenyl-carbam-hydroxamic acid is very soluble in acetone, hot alcohol, or hot ethyl acetate. It is only moderately soluble in cold alcohol, hot benzene or hot carbon tetrachloride; it is slightly soluble at room temperature in ether, ethyl acetate or benzene, and insoluble in petroleum ether or water. Enough dissolves in boiling water, however, to give an intense purple coloration when ferric chloride is added. It is insoluble in a solution of sodium carbonate, but a solution of sodium hydroxide readily dissolves it. From the latter, it can be precipitated in crystalline form by dil. acids. Concd. sulfuric

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[32] Ref. 2, p. 2430.

acid dissolves the substance easily. The resulting solution is colorless, but when a drop of nitric acid is added an intense blue develops.

Analysis. Subs., 0.1693: N, 19.85 cc. (over 30% KOH; 27.5°, 741.3 mm. (25°)). Calc. for $C_{13}H_{12}O_2N_2$: N, 12.3. Found: 12.5.

Second Method: From diphenyl-urea chloride and an alcoholic solution of hydroxylamine.—This method was tried since there is no reaction between diphenyl-urea chloride and methanol, even when heated. It is even recommended to recrystallize diphenyl-urea chloride from alcohol.

The customary means for the preparation of hydroxylamine in alcoholic solution is to start with the hydrochloride. It was learned that hydroxylamine sulfate could be used with results nearly as satisfactory,[33] in spite of the fact that the sulfate does not dissolve in alcohol. To a solution of 32 g. of hydroxylamine sulfate (50% pure) in 16 cc. of hot water, was gradually added with constant agitation a solution of sodium methylate (4.3 g. of sodium to 60 cc. of methanol). The heat of reaction, was considerable and an abundant precipitate of sodium sulfate was formed. The mixture was cooled rapidly in tap water,[34] diluted with 60 cc. of methanol, and filtered upon a Büchner funnel.

A solution of 13 g. of diphenyl-urea chloride in 60 cc. of warm methanol was added to the hydroxylamine solution. The resulting solution gave an intense purple ferric chloride reaction. The flask was stoppered and left at a freezing temperature overnight. No precipitate formed, except a small amount of water-soluble inorganic material, which was separated and discarded. Most of the methanol was removed by distillation in a vacuum. The crude residue, which weighed 9.5 g., was rinsed twice with hot ligroin (80°) to remove unchanged diphenyl-urea chloride, and was then dissolved in hot ethyl acetate, treated with animal charcoal and filtered. A small volume of ligroin was added to the filtrate, causing an abundant crystallization as the solution cooled. Very pure diphenyl-carbam-hydroxamic acid was formed as the result of a second recrystallization.

Of the two, the first method offers fewer obstacles during the purification of the product, but it suffers because of the trouble in the preparation of free hydroxylamine.

Acetyl Ester, $(C_6H_5)_2N$—CO—NH—O—COCH$_3$.—The details of this preparation paralleled those given for the acetyl ester of the monophenyl compound (p. 1482). The solubilities also were similar, the chief difference being that this ester is soluble in warm water. The yield was quantitative. Crystallization from a mixture of ethyl acetate and ligroin produced white needles; m. p., 126.5–127°.

This ester dissolved in a dil. sodium hydroxide solution. Hydrolysis, evidenced by the recurrence of the ferric chloride reaction, took place when the alkaline solution was boiled. At the same time, products of rearrangment were formed and were suspended as an oil throughout the solution. The ester dissolved in concd. sulfuric acid without coloration, but the addition of nitric acid caused an intense blue color.

Analysis. Subs., 0.1578: N, 15.62 cc. (over 40% KOH; 33°, 743.6 mm. (30°)). Calc. for $C_{15}H_{14}O_3N_2$: N, 10.37. Found: 10.47.

Sodium Salt, $(C_6H_5)_2N$—CO—N.Na—O—CO—CH$_3$.—To a solution of 0.27 g. of the acetyl ester in 4 cc. of absolute alcohol, 1 cc. of the prepared sodium methylate solution

[33] Hydroxylamine hydrochloride is preferable always, especially if an anhydrous medium is better. The method of conversion of the sulfate to the chloride by means of acetone oxime [Semon, THIS JOURNAL, **45,** 188 (1923)] is very satisfactory. The older method, which precipitates the sulfate by BaCl$_2$ or by NaCl, is extremely tedious and uncertain.

[34] Theoretically, 16.8 g. of water may be withdrawn from the solvent at this point in the precipitate of Na$_2$SO$_4$.10H$_2$O, which would leave the solvent chiefly alcohol.

was added (see above p. 1482). There was a noticeable heat of reaction. At the same time the solution darkened somewhat in color, towards a brown. It was diluted with 5 cc. of absolute ether followed by 50 cc. of petroleum ether. A voluminous precipitate soon formed, which was collected upon a filter, washed with petroleum ether, and dried in a vacuum. Analysis revealed that sodium acetate was present to a considerable extent in this material. Concd. sulfuric acid charred the white salt at once, and liberated a vapor that smelled strongly of acetic acid.

Analysis. Subs., 0.1150: Na_2SO_4, 0.0436. Calc. for $C_{15}H_{13}O_3N_2Na$: Na, 7.87. Calc. for CH_3COONa: Na, 28.1. Found: 12.28.

The filtrate was evaporated in an open dish at room temperature. The residue was soluble in concd. sulfuric acid, giving an intense blue solution. The remainder of this residue was washed with ether, and an oil extracted and discarded, leaving a white insoluble solid which melted at 235–237°. In the course of a week the solid became blue. It was shown to be identical with tetraphenyl-carbazide, $CO(NH-N(C_6H_5)_2)_2$; m. p., 239°. This must have been formed from the sodium salt by rearrangement. Tetraphenyl-carbazide was prepared for purposes of comparison by the action of phosgene upon *unsym*-diphenylhydrazine.[35]

Attempted Preparation of the Silver Salt.—A clear water solution of the sodium salt was mixed with a solution of silver nitrate. For a moment there was no action, and then the whole mass became black.

REARRANGEMENT OF THE SODIUM SALT.—About 0.1 g. of the sodium salt was added to 5 cc. of water; most of it dissolved instantly, but enough remained insoluble so as to make the solution look milky. It was left at room temperature, 30°, overnight and in the morning the oily precipitate which had formed was removed. The filtrate was boiled for 2 minutes. There was a small evolution of gas. The clear solution rapidly became cloudy when cooled, and after about a day the precipitate had solidified. The crystalline plates which resulted were collected, washed and dried; m. p., 53–54°; a mixture of this material with pure diphenylamine melted sharply at 53°. The substance gave the "diphenylamine test" for nitric acid. It dissolved without color in concd. sulfuric acid, but an intense blue developed when a trace of nitric acid was added. These properties are characteristic only of diphenylamine.

The filter paper which contained the original oily precipitate was washed with ether to remove the oil and the latter recovered by evaporation. It was *unsym*-diphenyl hydrazine, $(C_6H_5)_2N-NH_2$, as shown conclusively by the following tests. (1) It did not solidify when cooled to 0°.[36] (2) A drop of the oil added to concd. sulfuric acid resulted in an intense blue coloration. Aqua regia produced a similar coloration.

The above tests, while satisfactory for diphenylhydrazine, would also respond with the isocyanate,[35] $(C_6H_5)_2N-NCO$, which must be an intermediate product. The following tests clearly indicate that the isocyanate is not present. (1) The oil was immiscible with water. The addition of a very little dil. hydrochloric acid changed the oil to a white solid which gradually dissolved. Evaporation of this solution gave thin, white, needle-shaped crystals, whose color in the course of a few hours changed to a blue. The action is characteristic of diphenylhydrazine hydrochloride. (2) A sample of pure *unsym*-diphenylhydrazine (liquid) was mixed with an equal volume of the oil; there was no reaction. If the oil had been the isocyanate, *sym*-tetraphenyl-carbazide, a solid, would have been formed. (3) To a solution of the oil in absolute ether was added a drop of benzoyl chloride. Crystals formed immediately, which were shown to be chiefly *unsym*-diphenylhydrazine hydrochloride. They were soluble in water which contained a little

[35] Acree, *Ber.*, **36**, 3154 (1903).

[36] Diphenylhydrazine is known to melt at 34.5°. To obtain the solid from the oil, considerable supercooling is necessary.

hydrochloric acid. The reaction expected was 2 $(C_6H_5)_2N$—NH_2 + C_6H_5—COCl —→ $(C_6H_5)_2N$—NH—COC_6H_5 + $(C_6H_5)_2N$—NH_3Cl. The ether filtrate was evaporated, and the residue was washed with three 1cc. portions of ether to remove benzoyl chloride or benzoic acid. The residue was dissolved in ethyl acetate and evaporated. The white product melted sharply at 192°, known[37] to be the melting point of benzoyl-diphenylhydrazine, $(C_6H_5)_2N$—NH—CO—C_6H_5. Concd. sulfuric acid dissolved this material without the appearance of color. A drop of nitric acid, when added to this solution, produced a brilliant blue.

   Unsym-Diphenylhydrazine and Water.—A drop of diphenylhydrazine in 4 cc. of water was boiled for 10 minutes and then set aside for a week. Very little change was noticed, except that the immiscible drop of diphenylhydrazine was colored somewhat. Fehling solution, even when boiled, was without effect upon the mixture. In 3 weeks' time, the oil had solidified to a blue-black solid. Fehling solution still had no effect upon the mixture. The solid, when filtered and dried, melted at 40–50°. It was suspended in boiling water and filtered. After 10 hours, white crystalline plates of diphenyl-urea were present in the filtrate. They gave no color with concd. sulfuric acid previous to the addition of a drop of nitric acid.

   Benzoyl Ester, $(C_6H_5)_2N$—CO—NH—O—CO—C_6H_5. First Method.—The essential points of difference between this preparation and that of the benzoyl ester of the monophenyl compound (p. 1481) are as follows: (1) two g. of diphenyl-carbam-hydroxamic acid dissolved quite readily in 20 cc. of a solution which contained 0.35 g. of sodium hydroxide; (2) the benzoyl ester, as it precipitated, was tinged a lavender color; yield, 2 g.; (3) it was recrystallized from boiling toluene; ethyl acetate, even when heated, did not dissolve it readily; otherwise, the solvent action, even in sodium hydroxide solutions, was similar. The ester dissolved readily in concd. sulfuric acid without coloration, but the addition of a drop of nitric acid developed an intense blue.

   Analysis. Subs., 0.1357: N, 11.2 cc. (over 40% KOH; 32.5°, 741.3 mm. (30°)). Calc. for $C_{20}H_{16}O_3N_2$: N, 8.44. Found: 8.7.

   Second Method.—Diphenyl-carbam-hydroxamic acid was dissolved in an excess of benzoic anhydride, ferric chloride being used as an indicator to denote the completion of the reaction. The excess of anhydride was extracted at room temperature with benzene leaving an insoluble, dark oil at the bottom of the tube. This was crystallized from hot toluene.

   The results obtained by the first method are more satisfactory.

   SODIUM SALT, $(C_6H_5)_2N$—CO—N.Na—O—COC_6H_5.—This was prepared as was the sodium salt of the acetyl ester, (p. 1487). The precipitation took several hours to produce half the theoretical amount of salt, even when a very large excess of petroleum ether was present. Ether itself, without petroleum ether, precipitated nothing. When such a solution was evaporated, the benzoyl ester seemed unchanged, except for the presence of base which was removed with water. The salt, precipitated by petroleum ether, was easily charred by concd. sulfuric acid. The white cloud of vapor which arose at the same time possessed a characteristic isocyanate odor.

   Analysis. Subs., 0.1186: Na_2SO_4, 0.0377. Calc. for $C_{20}H_{15}O_3N_2Na$: Na, 6.50. Calc. for C_6H_5COONa: Na, 15.97. Found: 10.30.

   This analysis is high, as was the case with the sodium salt of the acetyl ester (p. 1487).

The Reaction between β-Phenyl-hydroxylamine and Phenyl Isocyanate

   The directions of Beckmann and Schönermark[21b] were followed. N-hydroxy-diphenyl-urea, C_6H_5—NH—CO—N(OH)—C_6H_5, m. p., 125°, formed readily and in good

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[37] Fischer, *Ann.*, **190**, 178 (1878).

yields. There was no evidence of the formation of the isomeric, higher-melting compound, diphenyl-carbam-hydroxamic acid. The latter would have been formed, had β-phenyl-hydroxylamine possessed any tendency to dissociate at the phenyl linking, C_6H_5—NHOH.

Summary

Evidence is submitted that supports the hypothesis of Jones and Hurd, which stated that if the radical "R," which "wanders" in a Beckmann rearrangement, is potentially a free radical, the rearrangement occurs with greater ease than otherwise. Diphenyl-carbam-hydroxamic acid derivatives are discussed in this connection; diphenyl nitrogen is the "free radical."

Derivatives of monophenyl-carbam-hydroxamic acid (phenyl-hydroxy-urea) could not be made to rearrange. The structure of carbanilido-phenyl-hydroxy-urea is discussed and is preferred to the optional "diphenyl-hydroxy-biuret" structure. It is definitely proved that the assumption that phenyl-hydroxy-urea dissociates into phenyl isocyanate and hydroxylamine, is untenable.

Hydroxy-urea, and hydroxy-biuret are similarly discussed in this connection.

A preliminary study has been made of the reaction between phenyl isocyanate and monohydroxamic acids. The addition seems to be at the α-hydroxylamino hydrogen rather than at the β.

Additional data are obtained for the "diphenylamine reaction."

A method is given which uses hydroxylamine sulfate in the preparation of hydroxylamine in alcoholic solution, when hydroxylamine hydrochloride is not available.

URBANA, ILLINOIS

A SYNTHESIS OF THYMOL FROM PARA CYMENE.   II

BY MAX PHILLIPS

In an earlier article published from this Laboratory[1] a synthesis of thymol from p-cymene was described. The yields obtained according to the method outlined in that paper were far from satisfactory. In the present article certain modifications and improvements in the process are given.

It will be noted from the results presented in this paper that, aside from certain improvements in the yields of some of the intermediates used in this synthesis, the present method differs primarily from the previous one in the manner in which the amino group of cymidine-sulfonic acid is eliminated. Instead of converting the cymidine-sulfonic acid into diazocymene-sulfonic

[1] J. Ind. Eng. Chem., 12, 733 (1920).