Summary

1. The secondary product in the sulfonation of cinnamic acid has again been shown to be *m*-sulfocinnamic acid by its preparation from *m*-bromocinnamic acid, the identity of the products being established by the identity of numerous derivatives.

2. The true *o*-sulfocinnamic acid has been prepared (for the first time) and its difference from the foregoing compound completely demonstrated.

3. The addition of sodium bisulfite to the double bond has been shown to be a general reaction of cinnamic acid derivatives.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE STRUCTURE OF HYDROXY-UREAS AND OF CARBAMAZIDES

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RECEIVED SEPTEMBER 22, 1926 PUBLISHED JANUARY 11, 1927

It is recognized that most azides of carboxylic acids eliminate nitrogen and rearrange to isocyanates or related compounds under the influence of heat. Carbamazide, NH_2—CO—N_3, is an outstanding exception. This compound decomposes, to be sure, with the elimination of nitrogen when it is heated alone or when it is heated in such solvents as toluene, xylene or ethyl malonate, but hydrazine or its derivatives have never been found as products of such decompositions. Since the mechanism of the rearrangement of azides ($RCON_3$) to isocyanates is considered to proceed through an intermediate, hypothetical univalent nitrogen derivative, [R—CO—N=], Curtius[1] calls [NH_2—CO—N=] a "rigid residue." Such an expression is purely descriptive; it would be much more interesting to learn why the residue is rigid. The azide of phenylcarbamic acid, C_6H_5NH—CO—N_3, behaves similarly.[2] It is peculiarly inert towards boiling water or boiling alcohol. Heating under pressure with these solvents induces hydrolysis and alcoholysis, but never rearrangement.

These non-rearrangements are mysterious, inasmuch as diphenyl carbamazide does rearrange[3] with the production of carbonyl diphenylhydrazine, or of compounds which are related to it. Thus, $(C_6H_5)_2N$—$CON_3 \longrightarrow (C_6H_5)_2N$—$NCO + N_2$. There is nothing implied in the formula of the residue, [$(C_6H_5)_2N$—CO—N=], to explain why it also should not be a "rigid residue."

The cases of hydroxy-urea and of phenylhydroxy-urea, C_6H_5NH—CO—

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[1] Curtius and Schmidt, *J. prakt. Chem.*, **105**, 177 (1923). Curtius, *Ber.*, **56**, 1577 (1923).

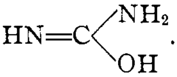
[2] Curtius and Hofmann, *J. prakt. Chem.*, [2] **53**, 530 (1896). Curtius and Burkhardt, *ibid.*, **58**, 205 (1898).

[3] Stolle, *Ber.*, **57**, 1063 (1924).

NHOH, are strictly analogous. They fail to undergo a Lossen rearrangement to hydrazine or to phenylhydrazine, yet diphenylhydroxy-urea, a compound with a supposedly analogous structure, $(C_6H_5)_2N—CO—NHOH$, forms derivatives which rearrange with exceptional ease to diphenylhydrazine.[4]

These facts suggest that the structures usually assigned to the nonrearranging compounds are incorrect. The accepted structures of the compounds which rearrange, namely, diphenyl carbamazide and diphenylhydroxy-urea, are unquestioned. Rearrangement itself is good proof of the presence of a true acid azide or of a true hydroxamic acid. Even more convincing evidence is the fact that both are formed directly from diphenyl urea chloride: $(C_6H_5)_2NCOCl + NaN_3 \longrightarrow (C_6H_5)_2NCON_3 + NaCl$; $(C_6H_5)_2NCOCl + 2NH_2OH \longrightarrow (C_6H_5)_2NCONHOH + NH_3OHCl$.

However, the basis for the structure of the compounds which fail to rearrange is much less secure. The striking point of similarity in them all is that there is at least one unsubstituted hydrogen atom on the carbamyl nitrogen. The proof of their structure has rested very largely on the assumption that the structure must be analogous to that of urea, an assumption which may, indeed, be correct. However, in the last decade or so, superlative evidence has been presented by Werner[5] to show that urea does not possess the carbamide structure, $H_2N—CO—NH_2$, but instead possesses the enolic structure,[6]



$HN{=}C\begin{matrix}\diagup NH_2\\ \diagdown OH\end{matrix}$

. Werner's proof is especially satisfactory, since he has taken precisely the evidence used many years in support of the carbamide structure, and has shown how ill-suited this evidence is for carbamide and how well adapted to the alternative structure. Perhaps the most convincing of his many arguments are the two which follow. (1) The major course of the reaction of nitrous acid with methyl urea is not one of nitrogen evolution, but is one which leads to a 90% yield of nitrosomethyl urea. This implies the presence of a secondary amino group and the absence of a primary. By this reasoning, methyl urea is $HN{=}C(OH)—NHCH_3$ and not $H_2N—CO—NHCH_3$. (2) When such ammonium carbamates as $R_2N—CO_2NH_3R$, $RNH—CO_2NH_3R$ and $H_2N—CO_2NH_3R$ are heated, urea formation is never observed from the first type, but it is always observed with the

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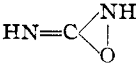
[4] Hurd, This Journal, **45**, 1472 (1923).

[5] Werner; evidence which is based on the methods of preparation of urea: *J. Chem. Soc.*, **103**, 1010 (1913); **117**, 1356 (1920); **113**, 694 (1918); **117**, 1046 (1920); evidence based on the reactions of urea: *ibid.*, **113**, 84 (1918); **117**, 1078 (1920); **111**, 863 (1917); **115**, 1093 (1919). Plimmer, *ibid.*, **127**, 2657 (1925).

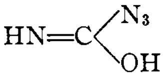
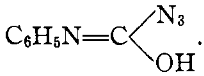
[6] An alternative formula,



$HN{=}C\begin{matrix}\diagup NH_3\\ |\\ \diagdown O\end{matrix}$

, mentioned also by Werner seems to add but little or nothing to the argument.

last two types. Water elimination, to form a "carbamide," is conceivable in all three cases, but isocyanate formation is possible only in the last two. Werner's premise is that isocyanate formation always precedes urea formation.

The adoption of such structural formulas for the above-mentioned azides and hydroxy-ureas provides a simple explanation of the peculiarities presented by these compounds. Thus, carbamazide would be  $HN{=}C\begin{smallmatrix}\diagup N_3\\ \diagdown OH\end{smallmatrix}$ and phenyl-carbamazide  $C_6H_5N{=}C\begin{smallmatrix}\diagup N_3\\ \diagdown OH\end{smallmatrix}$. From this viewpoint, these compounds are not acid azides, since they do not possess the $—CO—N_3$ group; therefore, they should not rearrange. For similar reasons, hydroxy-urea and monosubstituted derivatives of it should be assigned the structures $HN{=}C(OH)—NHOH$ and $RN{=}C(OH)—NHOH$. This type of formula possesses neither the hydroxamic nor the hydroximic acid configuration, $—CO—NHOH$ or $—C(OH){=}NOH$; therefore, these hydroxy-ureas should not, and of course they do not, rearrange.

Such formulas, to be correct, should be in harmony with all other known facts pertaining to carbamazides or to hydroxy-ureas, and such seems to be the case. The new formulas imply that in the preparation of these compounds from isocyanates by the addition of hydrazoic acid or of hydroxylamine, the addition takes place at the carbonyl group and not at the carbon-nitrogen double bond. To illustrate with phenyl isocyanate: $C_6H_5N{=}C{=}O + NH_2OH \longrightarrow C_6H_5N{=}C(OH)—NHOH$. Gilman's evidence[7] regarding the addition of the Grignard reagent isocyanates leads also to this conclusion.

The trend of this discussion implies that any disubstituted carbamazide or hydroxy-urea, $R_2N—CON_3$ or $R_2N—CONHOH$, should be capable of rearrangement. Until now, however, the only cases on record are the diphenyl derivatives. Although these particular cases are confirmatory, in a sense they do not contribute evidence which is wholly convincing inasmuch as the group which wanders from carbon to nitrogen in each case is diphenyl nitrogen. Since this group is potentially a free radical,[8] it is conceivable that this factor might induce a rearrangement that otherwise would be impossible. In the present investigation it was proposed to synthesize dialkylated compounds of this type and to test them for rearrangement.

Several unsuccessful attempts were made to prepare diethyl carbamazide, $(C_2H_5)_2N—CON_3$. Diethylcarbamyl chloride, which was prepared[9]

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[7] Gilman and Kinney, This Journal, **46**, 493 (1924).

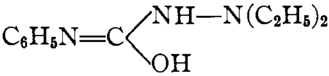
[8] Wieland, "Die Hydrazine," F. Enke, Stuttgart, **1913**, p. 73. See also Ref. 4.

[9] Michler and Escherich, *Ber.*, **12**, 1162 (1879).

by the action of diethylamine on phosgene, consistently refused to react with a suspension of sodium azide[10] in an inert solvent such as benzene. This was surprising, because azides are quite generally prepared by this method.[11] Furthermore, diethylcarbamyl chloride could not be converted into its hydrazide, diethylsemicarbazide, by reaction with a solution of hydrazine (73%) in methanol. Instead, there was decomposition to diethylammonium chloride. Again, diethyl urethan was entirely without action on hydrazine (in methanol), when heated in a sealed tube at 160°. Therefore, the attempt to prepare diethyl carbamhydrazide or diethyl carbamazide was abandoned.

Diethyl hydroxy-urea was quite readily prepared, however, by the interaction of diethylcarbamyl chloride and hydroxylamine base. It was an oil with all the properties of a hydroxamic acid. It rearranged to diethyl hydrazine by customary methods, thereby establishing the point in question.

Two satisfactory derivatives of diethylhydrazine were investigated. One of these, the derivative formed by the action of phenyl isocyanate, deserves especial mention. Instead of the anticipated addition product an anhydride of it, namely, the diethylhydrazone of phenyl isocyanate, $C_6H_5N{=}C{=}N{-}N(C_2H_5)_2$, was isolated. Very probably this dehydration was induced by the phenyl isocyanate, a conclusion which is supported by two facts. First, the derivative was formed in but 50–60% yields when molecular proportions of the hydrazine and of the isocyanate were mixed. Second, a very considerable amount of *sym.*-diphenyl urea was simultaneously produced. If phenyl diethylsemicarbazide is assumed as an intermediate product, it seems rather obvious that the enolic formula,



$C_6H_5N{=}C\begin{cases}NH{-}N(C_2H_5)_2\\OH\end{cases}$, explains its tendency for dehydration far better than the alternative ketonic formula. Here again, addition to the isocyanate molecule seems to be at the carbonyl group.

Experimental Part

For purposes of brevity, a detailed account of the attempts to prepare diethyl carbamazide and diethyl carbamhydrazide will be omitted. The results were chiefly negative.

α,α-Diethyl-β-hydroxy-urea, $(C_2H_5)_2N{-}CO{-}NHOH$

Preparation of Diethyl Hydroxy-urea in Aqueous Solution.—Directions similar to those of Hantzsch and Sauer,[12] who first prepared this compound in solution, were followed. To a solution of 2 g. of hydroxylamine hydrochloride and 4 g. of potassium

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[10] The sodium azide was generously furnished by Professor A. W. Browne, of Cornell University.

[11] Schroeter, *Ber.*, **42**, 3356 (1909). Stolle, *Ber.*, **57**, 1063 (1924).

[12] Hantzsch and Sauer, *Ann.*, **299**, 86 (1898).

carbonate was gradually added 3.8 g. of diethylcarbamyl chloride. Because of the experience of Hantzsch and Sauer, no attempts were made to isolate the hydroxy-urea as such. However, it was considered probable that the benzoyl ester of it could be isolated, by means of a Schotten-Baumann reaction with benzoyl chloride and alkali. A large excess of benzoyl chloride was found to be necessary before a negative ferric chloride color test was obtainable. The solid which separated was collected, pressed dry and washed with two 10cc. portions of ether, after which it weighed 3.58 g. From this, by recrystallization from alcohol, 0.5 g. of white needles was obtained; m. p., 101–102°. The filtrate was found to contain a considerable quantity of dibenzohydroxamic acid, m. p. 156–157°, and a high-melting (above 270°) residue. The latter was not investigated.

Anal. (of the 101–102° material). Subs., 0.1088: N_2, 6.32 cc. (over 40% KOH; 24.5°; 747.3 mm.). Calcd. for $(C_2H_5)_2NCONHOCOC_6H_5$: N, 11.86. Calcd. for $C_6H_5CONHOCOC_6H_5$: N, 5.80. Found: 6.42.

The analysis and the reactions proved that the 102° material was not the anticipated benzoyl ester of diethyl hydroxy-urea. It behaved more like dibenzohydroxamic acid. Thus, instead of obtaining diethylhydrazine by rearrangement of its sodium salt, *sym.*-diphenyl urea was formed instead. No evidence of the hydrazine was observed by the test with warm Fehling solution.

The formation of dibenzohydroxamic acid was due to the reaction of benzoyl chloride and hydroxylamine. The presence of hydroxylamine may be explained either by an original excess, or by hydrolysis of the hydroxy-urea.

Rather than do more work with the products from an aqueous solution of diethyl hydroxy-urea, it was decided to prepare the compound in non-aqueous media. For this reason, the 102° material was not investigated further.

Preparation of Diethyl Hydroxy-urea.—A solution of 30.8 g. of freshly distilled diethylcarbamyl chloride in 50 cc. of ethyl acetate was added to 11.8 g. of hydroxylamine base.[13] The stoppered flask was shaken vigorously. Heat of reaction was immediately apparent, so the flask was cooled in an ice-bath. After two hours, the ice-cold solution was filtered free from the precipitated hydroxylamine hydrochloride, which weighed 8 g. This hydrochloride was washed with two 10cc. portions of ethyl acetate and the washings were added to the filtrate. The latter was evaporated in a vacuum to a volume of 30 cc., and 120 cc. of low-boiling petroleum ether was added. This gave 7.6 g. of an oil that gave a strong ferric chloride reaction in aqueous solution. Attempts were made to purify the oil by solution in ethyl acetate, followed by precipitation with petroleum ether, but the product which was obtained in this way seemed to have gained nothing in purity.

Diethyl hydroxy-urea was also prepared with benzene as a solvent instead of ethyl acetate, but the method was poorer due to the fact that the oily hydroxy-urea was much less soluble in benzene.

Diethyl hydroxy-urea dissolved readily in water, and gave a pronounced violet color reaction with a solution of ferric chloride. This is characteristic of hydroxamic acids.

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[13] This was prepared in 34% yield by the method of Hurd and Brownstein, THIS JOURNAL, **47**, 67 (1925).

Thermal Decomposition of Diethyl Hydroxy-urea.—About 1.5 g. of the crude oil (obtained by the benzene method) was placed in a 10cc. Claisen distilling flask. The flask was evacuated to 25 mm. and was heated in an oil-bath. The material decomposed when distillation started; the temperature of the bath was 150–160°, and of the vapor, 130°.

The charred residue in the flask was extracted with ethyl acetate. An oil was precipitated by the addition of petroleum ether. This oil, which gave only a slight ferric chloride color reaction, was treated with 3 g. of sodium hydroxide and 10 cc. of water. The volatile portion from this was distilled into a flask which contained 5 cc. of concd. hydrochloric acid, and this distillate was evaporated to dryness. The residue reduced warm Fehling solution. As will be explained in more detail below, this reduction is evidence of the formation of diethylhydrazine. This could not be due to hydroxylamine, since the latter does not distil under the same conditions, as shown by a blank test. This indicates the following reactions: $(C_2H_5)_2N—CO—NHOH \longrightarrow (C_2H_5)_2N—NCO + H_2O$; $(C_2H_5)_2N—NCO + 2NaOH \longrightarrow (C_2H_5)_2N—NH_2 + Na_2CO_3$.

Preparation of the Acetyl Ester of Diethyl Hydroxy-urea, $(C_2H_5)_2N—CO—NH—O—COCH_3$.—To 7.6 g. of crude diethyl hydroxy-urea, prepared by the ethyl acetate method, was added the theoretical amount (6 g.) of acetic anhydride. The two liquids mixed readily, with a noticeable heat of reaction. After two hours, the solution still gave a deep color with ferric chloride. A further amount of acetic anhydride (4 g.) was added and the solution, placed in a desiccator, was allowed to stand overnight. It then failed to give a ferric chloride test, showing that the reaction was complete. A few crystals of hydroxylamine hydrochloride appeared in the solution. The excess of acetic anhydride and acetic acid was evaporated by evacuating the desiccator, which contained both solid sodium hydroxide and concd. sulfuric acid. The oily residue was taken up in carbon tetrachloride and was filtered from the small amount of insoluble hydroxylamine hydrochloride.

To the filtrate was added 20 cc. of petroleum ether (b. p., 34–45°) and the mixture was cooled to $-15°$ by ice and salt. An oily layer settled out. This was separated and washed with 5 cc. of petroleum ether. Acetic acid and acetic anhydride were removed from the oil by this process.

The oil was taken up in 15 cc. of technical ethyl acetate and reprecipitated by 45 cc. of petroleum ether. Even this amount of the hydrocarbon did not precipitate more than half of the original oil. Two g. precipitated. Analysis showed that the oil was still impure, as did also the presence of a slight ferric chloride reaction.

Anal. Calcd. for $C_7H_{14}O_3N_2$: N, 16.1. Found (Dumas): 18.1.

From the ethyl acetate–petroleum ether mixture which was decanted from the oil an additional amount of oil settled out in the course of two days. This made a total weight of 3.87 g. Upon adding 15 cc. of absolute ethyl acetate, a precipitate of fine white flakes appeared. Twenty cc. of dry ether gave an additional amount of the crystals. These weighed 1.07 g. and melted at 214–215°; they proved to be diethylammonium chloride.

Anal. Calcd. for $C_4H_{12}NCl$: N, 12.6. Found (Dumas): 12.4.

The filtrate was evaporated in a vacuum desiccator. The resulting oil showed a slight ferric chloride test, and possessed an odor of acetic acid. It may be that water in the technical ethyl acetate caused a partial hydrolysis.

Attempted Preparation of the Sodium Salt of the Acetyl Ester.—Three cc. of absolute alcohol was used as solvent for 0.14 g. of the acetyl ester, and 0.8 cc. of sodium ethylate solution (0.020 g. of sodium) was added. The addition of 13 cc. of ether followed by 8 cc. of petroleum ether gave 0.04 g. of a salt. Another run gave a sufficient amount to analyze. It was found to be sodium acetate.

Anal. Subs., 0.0763: Na_2SO_4, 0.0643. Calcd. for $C_2H_3O_2Na$: Na, 28.0. Found: Na, 27.3.

Examination of the Filtrate from the Sodium Salt for Products of Rearrangement.—The above sodium acetate may have resulted in part from the trace of free acetic acid which was already present, but also from a rearrangement of the sodium salt of the acetyl ester. Thus, $(C_2H_5)_2N\text{—}CO\text{—}N(Na)\text{—}OCOCH_3 \longrightarrow CH_3CO_2Na + (C_2H_5)_2N\text{—}NCO$, and $(C_2H_5)_2N\text{—}NCO + C_2H_5OH \longrightarrow (C_2H_5)_2N\text{—}NH\text{—}COOC_2H_5$.

The solvents were distilled off on the steam-bath; b. p., 35–78°. The residue in the flask was dissolved in 5 cc. of alcohol, after which 5 cc. of 20% sodium hydroxide solution was added. This served to complete the rearrangement and also to hydrolyze any products of rearrangement to diethyl hydrazine, which is volatile. The solution was distilled almost to dryness into 5 cc. of concd. hydrochloric acid. Evaporation of the acid distillate yielded a slight amount of crystalline salts. This residue was washed with water into 5 cc. of Fehling solution. No visible reduction occurred on standing for ten minutes in the cold, but cuprous oxide soon precipitated when the solution was heated to incipient boiling and allowed to stand. Treatment of a known sample of diethylhydrazine hydrochloride in the same way gave identical results. The necessity of warming the Fehling solution was originally noted by Fischer.[14] Because there are no other possible products in the residue which would behave in this manner, this constitutes ample proof of the presence of diethylhydrazine.

The other possible products in this residue are diethylammonium chloride and possibly hydroxylamine hydrochloride. The latter, however, would reduce Fehling solution in the cold. Further proof of its absence was furnished by the fact that hydroxylamine did not distil under these conditions, nor did it produce other compounds which were capable of reducing Fehling solution. This was shown by a distillation test on pure hydroxylamine hydrochloride in the presence of a solution of sodium hydroxide. No material was formed which would reduce warm Fehling solution. Similarly, a blank on the original diethylammonium chloride, which was used as the source of the diethylamine for the preparation of the diethyl hydroxy-urea, gave negative results.

Rearrangement of the Acetyl Ester of Diethyl Hydroxy-urea.—To 0.81 g. of acetyl ester dissolved in 20 cc. of water, the calculated amount of sodium hydroxide (0.19 g.) which was necessary to form the sodium salt, was added. The solution was refluxed for two hours to accomplish rearrangement of the sodium salt. To prevent any possible

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[14] Fischer, *Ann.*, **199**, 311, 319 (1879).

loss of diethylhydrazine during the process, a tube was fitted at the top of the condenser to deliver any uncondensed vapors into a flask containing 10 cc. of hydrochloric acid. The solution was then cooled, and an excess of sodium hydroxide added to it. Then it was distilled into the same hydrochloric acid that was mentioned above. The acidified distillate was evaporated nearly to dryness. It yielded a quantity of crystalline salts.

A stirring rod was dipped into the moist salts to extract a small portion of them. This was transferred into 5 cc. of Fehling solution, and here again no reaction occurred on standing in the cold, but a visible amount of cuprous oxide soon precipitated after the boiling temperature was reached. As was shown earlier, the reduction of hot Fehling solution is excellent proof of the formation of diethyl hydrazine and thus a proof of the rearrangement of the acetyl ester of α,α-diethyl-β-hydroxy-urea, which was the point in question.

Derivatives of Diethylhydrazine.—Diethyl semicarbazide is apparently the only recorded organic derivative of diethylhydrazine. Fischer's directions[15] for making this were very meager indeed; no reference was made to the quantities taken. Attempts to prepare it from the small amount of diethylhydrazine hydrochloride formed in the above experiments, or from an equivalent sample of material formed by the reduction of diethyl nitrosamine, were unsuccessful. It was found, after some trial, that good results were obtained from small quantities by the following modification.

One g. of potassium cyanate was dissolved in 2 cc. of dil. acetic acid (1:1), then 1 cc. of diethylhydrazine was added. There was frothing as the mixture was warmed, after which a clear solution resulted. On cooling to the temperature of tap water, 0.6 g. (dry weight) of crystalline diethyl semicarbazide separated. Fischer's method of purification, that is, recrystallization from a small amount of water, was found satisfactory.

In a search for other derivatives, it was found that the diethylhydrazones of benzaldehyde, *m*-nitrobenzaldehyde, benzophenone and cyclohexanone were all non-crystallizable oils.

Diethylhydrazone of Phenyl Isocyanate, $C_6H_5N{=}C{=}N{-}N(C_2H_5)_2$.—This compound may be recommended as a derivative of diethylhydrazine. It crystallizes well and is easily prepared from phenyl isocyanate.

Two g. of diethylhydrazine, dissolved in 10 cc. of absolute ether, was added to a solution of 3 g. of phenyl isocyanate in 20 cc. of dry ether. Because of the vigor of the reaction, too rapid mixing of the solutions is to be avoided. The ether was evaporated, and the solid residue taken up in 15 cc. of warm ethyl acetate. About 0.25 g. of *sym.*-diphenyl urea, m. p. 236°, failed to dissolve and an additional 0.1 g. separated from the solution. By slow and undisturbed evaporation of the filtrate, crystals of two different forms appeared. Diphenyl urea crystallized in slender needles, whereas the crystals of the desired product were much more massive. The latter (3 g.) were separated by hand with no difficulty, and were dissolved in 10–15 cc. of ethyl acetate. Five cc. of petroleum ether failed to cause immediate precipitation, but large crystals again appeared on standing overnight in a loosely covered Erlenmeyer flask. They melted at 125–125.5°.

For analysis, a portion of these was again recrystallized from ethyl acetate—petroleum ether. Crystallization was rapidly induced, when cool, by scratching. These crystals were dried in a desiccator over sulfuric acid; m. p., 125.5–126°.

Anal. Calcd. for $C_{11}H_{15}N_3$: N, 22.2. Found (Dumas): 22.3.

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[15] Ref. 14, p. 312.

Due to the ease of decomposition of this substance in the combustion tube, it was found necessary to remove the iron supports underneath that part of the tube which contained the sample.

The crystals of this substance were examined by Professor A. J. Walcott, of the Department of Mineralogy of Northwestern University, who submitted the following report.

1. Biaxial crystals, apparently monoclinic.
2. Optically positive (+).
3. Indices of refraction: $\alpha = 1.515 \pm 0.005$; $\beta = 1.535 \pm 0.005$; γ = between 1.635 and 1.740, but nearer 1.740 than 1.635.
4. Pronounced dispersion of optic axes. Red greater than violet ($\rho > \nu$). Strong birefringence.

Diethylbenzohydrazide, $C_6H_5CO—NH—N(C_2H_5)_2$.—Considerable effort was spent on the reaction product of diethylhydrazine and benzoyl chloride. Because of the difficulties encountered in the purification of this substance, it cannot be recommended as a derivative of diethylhydrazine. Therefore, the details regarding this work will be omitted.

Summary

Carbamazide, hydroxy-urea or their monosubstituted derivatives $RNH—CO—N_3$ and RNH—CO—NHOH, fail to undergo the rearrangements which are so customary in compounds that contain the groupings $—CO—N_3$ or —CO—NHOH. It is pointed out that these non-rearrangements would be anticipated from the structures $RN{=}C(OH)—N_3$ and RN=C(OH)—NHOH, which are proposed for these compounds. Other arguments are cited in support of the formulas, and no facts are known which contradict them.

α,α-Diethyl-β-hydroxy-urea was found to rearrange to diethylhydrazine. This is the first dialkylated derivative of this type to be investigated. Inasmuch as diarylated compounds are known also to rearrange, it may be inferred that the accepted structures are correct and that disubstituted hydroxy-ureas or azides in general, $R_2N—CO—NHOH$ and $R_2N—CO—N_3$, will rearrange to produce a nitrogen-to-nitrogen linkage, It was not found possible to prepare diethylcarbamazide or -diethylcarbamhydrazide by general methods, from diethylcarbamyl chloride or from diethyl urethan.

Crystalline derivatives of diethylhydrazine have been prepared from potassium cyanate, by modifying Fischer's directions, and from phenyl isocyanate. The diethylhydrazone of phenyl isocyanate was formed in the latter reaction. A crystallographic description of this curious derivative is given. All of the diethylhydrazones of aldehydes or ketones which were investigated were found to be oils. Although diethyl benzohydrazide is crystalline, it is not to be recommended as a derivative because of the difficulty encountered in its purification.

EVANSTON, ILLINOIS