4. The amount of alkali added to the extraction medium is not as important with fresh yeast as with dry yeast.
5. With dry yeast, 15° is a more satisfactory temperature for extraction than 30°, while with fresh yeast the reverse is true.

HARTFORD, CONNECTICUT

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

# THE PREPARATION OF β-TRIPHENYLETHYLAMINE. REARRANGEMENT OF β-TRIPHENYLPROPIONHYDROXAMIC ACID

BY LESLIE HELLERMAN

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The preparation of β-triphenylethylamine, $(C_6H_5)_3CCH_2NH_2$, was required in one of a series of researches now in progress in this Laboratory on the mechanism of the oxidation of compounds containing the primary amino group. In order to approach the problem of the exact nature of intermediate products formed when a primary amine of the type $RCH_2NH_2$, for example, is oxidized (for instance, in alkaline solution by halogen or by alkyl hypohalite) it was considered desirable to start with a substance of such structural properties that the intermediate products of its oxidation might reasonably be anticipated to possess considerable stability. A consideration of the structure of β-triphenylethylamine, where R is the triphenylmethyl group, from this point of view led to the selection of this substance as a decidedly promising starting product for investigation. It is to be noted, moreover, that this amine possesses potentially reactive hydrogen atoms only on the carbon atom adjacent to the amino group.

The synthesis of β-triphenylethylamine was first attempted by Elbs,[1] who reported that the amine resulted when triphenyl acetonitrile, $(C_6H_5)_3CC{\equiv}N$, was reduced in alcoholic solution with zinc and hydrochloric acid. Elbs gave a description of the compound, assigning a melting point of 116°, and also reported the preparation of the hydrochloride and the chloroplatinate. No melting point was given for the latter substance and no analyses whatsoever were reported. Later Biltz[2] reported that he was unable to reproduce the work of Elbs. An exhaustive study of the action of zinc upon the nitrile under varying conditions of solution, concentration and acidity failed to produce a method for the preparation of the amine. Biltz found, indeed, that the nitrile was reduced only[3]

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[1] Elbs, *Ber.*, **17**, 700 (1884).

[2] Biltz, *Ann.*, **296**, 253 (1897).

[3] Compare the stability of triphenyl acetonitrile toward hydrolysis, E. and O. Fischer, *Ann.*, **194**, 262 (1878).

by sodium in the presence of alcohol. But here triphenylmethane and hydrocyanic acid were the only products of reduction found in the reaction mixture. No amine was present.

The writer has verified the results reported by Biltz in every particular. Attempts to obtain the desired amine by reduction of triphenyl acetonitrile have resulted in complete failure. Sodium and alcohol have, as reported by Biltz, been found to effect reduction of the nitrile quantitatively to triphenylmethane and hydrocyanic acid.[4]

In view of the failure of reduction methods[5] to produce $\beta$-triphenylethylamine it was considered best to attempt the preparation of the amine by rearrangement of the corresponding halogenamide, $(C_6H_5)_3C.CH_2.CO.NH(Hal)$, or hydroxamic acid derivative, $(C_6H_5)_3C.CH_2CO.NHOH$. For this purpose it was necessary to prepare $\beta$-triphenylpropionic acid, $(C_6H_5)_3CCH_2COOH$, in suitable yield. Henderson's[6] method, which uses the action of triphenylbromomethane upon diethyl malonate with subsequent hydrolysis and loss of carbon dioxide leads to a pure acid but in unsatisfactory yield. A modification, tried in this work involving the use of cyano-acetic ester in place of malonic ester, did not lead to improved yields. By far the best way to prepare the acid is by the reaction of triphenylcarbinol and malonic acid.[7] It has been found that the yield of $\beta$-triphenylpropionic acid is not quantitative as reported, but is very good in comparison with yields given by other methods. The amide of this acid, $(C_6H_5)_3CCH_2CONH_2$, may be prepared by the usual methods. From the amide a derivative possessing the composition of a dichloro-amide is easily obtained. This, however, does not, by the methods used, lead to the desired amine. Nevertheless, it is possible to obtain from the amide an impure bromo-amide (probably a monobromo-amide). The latter compound, when rearranged in alcoholic solution with sodium ethylate,[8] yields in solution an intermediate product, probably the urethan, which upon acid hydrolysis gives $\beta$-triphenylethylamine. Analyses of the amine and its hydrochloride, chloroplati-

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[4] The latter observation is of theoretical interest. Violent reduction results, as noted, exclusively in the rupture of the carbon-carbon bond; this suggests that triphenyl acetonitrile may be minimally ionized in alcoholic solution into triphenylmethyl ion and cyanide ion.

[5] A recent paper by Rupe and Gisiger [*Helv. Chim. Acta* [4] **8**, 343 (1925)] describes the reduction of triphenyl acetonitrile by means of hydrogen in the presence of catalytic nickel. The results of this experiment were somewhat uncertain since 15 g. of the nitrile yielded only 0.1 to 0.2 g. of a hydrochloride, the melting point of which was stated to be 214° (m. p. of $\beta$-triphenylethylamine hydrochloride observed in the present work, 239–240°).

[6] Henderson, *J. Chem. Soc.*, **51**, 226 (1887).

[7] Fosse, *Compt. rend.*, **145**, 197 (1907).

[8] This procedure is based upon that of Lengfeld and Stieglitz, *Am. Chem. J.*, **16**, 370 (1894).

nate, benzoyl derivative and ethyl urethan derivative establish the identity of the compound. The melting point of the amine is 132° as compared with 116° reported by Elbs for his product. Curiously, the nitrate of β-triphenylethylamine is rather difficultly soluble in water.

Because of the unsatisfactory yields given by the bromo-amide procedure, it was deemed valuable to study the preparation of the amine starting with the hydroxamic acid derivative. For this purpose the benzoyl derivative of β-triphenylpropionhydroxamic acid, $(C_6H_5)_3C.CH_2.CO.NHOCOC_6H_5$, was synthesized. When this substance is dropped upon a hot aqueous solution of alkali it is practically quantitatively rearranged, yielding β-triphenylethylamine and *sym.*-di-β-triphenylethylurea, $[(C_6H_5)_3CCH_2NH]_2CO$. The urea is the chief product of the reaction. From it β-triphenylethylamine is easily obtained in good yield by means of hydrolysis under pressure with alcoholic hydrochloric acid. The relationship of the urea to the amine is further established from the observation that the former compound is produced by the action of phosgene upon the amine.

## Experimental Part

### Preparation of β-Triphenylpropionic Acid

(A) **By Henderson's Method.**[6]—As stated earlier in the paper, the yields obtained by this method (of the order of 5–10%) were inadequate for the preparation of the considerable quantity of acid required for this work.

(B) **By the Condensation of Cyano-ethyl Acetate and Triphenylbromomethane.**—When sodiocyano-ethyl acetate (suspended in either alcohol or ether) was treated with triphenylbromomethane under conditions similar to those described by Henderson for the analogous operation with sodiodiethyl malonate, the ultimate product was found to consist of yellow needles, probably cyanotriphenylmethylethylacetate, $(C_6H_5)_3C.CH(CN).COOC_2H_5$, m. p. 215–216°, in very poor yield. The product resisted hydrolysis with 50% sulfuric acid at the boiling point of the acid. Because of the low yields no further attempts were made to hydrolyze the product and the method was abandoned for the preparation of β-triphenylpropionic acid.

(C) **By the Method of Fosse.**—Since Fosse[7] does not give detailed directions for his preparation of β-triphenylpropionic acid, the following procedure which was found to give excellent results in this work is submitted.

Triphenylcarbinol, 100 g., is intimately mixed in a round-bottomed flask with malonic acid, 65 g. The mixture is heated in an oil-bath, at first *cautiously* at 140–150°, and is maintained within that temperature range until the first vigorous evolution of gas has subsided somewhat. The temperature is then brought to 160° and is maintained there for three hours. The melt is transferred to a beaker and treated with an excess of sodium hydroxide, and about 1.5 liters of water. The mixture is heated in order to hasten solution and unchanged (almost pure) triphenylcarbinol is removed by filtration of the hot mixture. The cooled filtrate is treated with an excess of hydrochloric acid; β-triphenylpropionic acid precipitates,—usually in perfectly pure condition; the yield varies, 65 to 75 g.

**β-Triphenylpropionamide,** $(C_6H_5)_3CCH_2CONH_2$.—When β-triphenylpropionic acid (1 mole) is treated with pure thionyl chloride (3 moles), reaction readily takes place in the cold. The action is completed by means of heating just below the boiling point. The solution is allowed to cool slowly, when the acid chloride precipitates in beautifully crystalline form. It is removed by filtration and dried in a vacuum over sodium hydroxide. More may be obtained by means of evaporation of the filtrate at room temperature in a vacuum desiccator over sodium hydroxide; yield, excellent; m. p. of crude product, 132°. The crude product is now cautiously added to a well-agitated, concentrated solution of ammonia. The mixture is heated and is allowed to boil for several minutes; it is then cooled and the solid product, after careful trituration with water, is dried and crystallized two or three times from alcohol. The amide crystallizes from alcohol in white, plate-like crystals, sometimes cubical, resembling sodium chloride in form. It is soluble in benzene, acetone and other common organic solvents; m. p., 192° (corr.).

*Anal.*[9] Subs., 0.3102: N, 12.8 cc. (over 50% KOH; 21°, 749.0 mm.). Calcd. for $C_{21}H_{19}ON$: N, 4.65. Found: 4.63.

**N-Dichloro-β-Triphenylpropionamide,** $(C_6H_5)_3CCH_2CONCl_2$.—This was obtained in slightly impure form when β-triphenylpropionamide, 4.5 g., was dissolved in 300 cc. of ethyl alcohol, treated at 5° with a concentrated solution of sodium hypochlorite (prepared from a solution of 15 g. of sodium carbonate and the calculated quantity of chlorine at −5°) and to the resulting solution chlorine water (saturated) was added little by little until a permanent precipitate was obtained. It was collected at once, washed with ice-cold chlorine water and dried in a vacuum over phosphorus pentoxide. The crude product melted at 116°; when purification was attempted by means of crystallization from chloroform and ligroin, the melting point dropped 13° and the active chlorine content decreased 0.6%.

*Anal.* Subs., 0.1192: 9.36 cc. of 0.1281 *N* $Na_2S_2O_3$. Calcd. for $C_{21}H_{18}ONCl$: Cl, 10.6. Calcd. for $C_{21}H_{17}ONCl_2$: 19.2. Found: 17.9.

When a portion of the dichloro-amide was heated, chlorine was evolved and the cooled product was a "glass" which seemed to contain no definite chemical individual capable of easy isolation. Only a negligible amount of primary amine salt could be obtained in solution by treatment of the "glass" with hot, dil. hydrochloric acid. Treatment of the chloro compound with soda lime or with sodium ethylate in absolute alcohol likewise failed to yield an amine (after treatment of the resulting mixture with acid). The behavior of this dichloro-amide will be investigated more fully at a later date. It is of interest that the dichloro-amide readily oxidizes cold ethyl alcohol to acetaldehyde; chlorine is evolved at the same time and the parent amide is easily obtainable from solution in pure form: $(C_6H_5)_3CCH_2CONCl_2 + CH_3CH_2OH \longrightarrow (C_6H_5)_3CCH_2CONH_2 + CH_3CHO + Cl_2$.

**Preparation of an Impure N-Bromo-amide,** $(C_6H_5)_3CCH_2CONHBr$ (?).—Because of the insolubility of β-triphenylpropionamide in water it was found not possible to prepare the corresponding N-bromo-amide

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[9] The writer acknowledges with pleasure the generous assistance rendered by Drs. Andrew M. Neff and T. L. McMeekin in connection with some of the analytical work recorded in this paper.

by the usual procedure for this type of compound. The directions which follow were found to give a product which, when subjected to rearrangement by the Lengfeld-Stieglitz method,[8] led to β-triphenylethylamine. The bromo-amide mixtures from successive preparations based on these directions were by no means uniform, varying in active bromine content from 9.1% to 13.0%; calcd. for $C_{21}H_{18}ONBr$: Br, 21.0.

To 3 g. of β-triphenylpropionamide dissolved in 200 cc. of ethyl alcohol and cooled to 0°, was added a ten-fold excess of potassium hypobromite in concentrated solution (prepared at −5°). Bromine water at 0° was added at once to precipitate the bromo-amide. This was collected, rapidly freed from mother-liquor, washed with cold bromine water and dried in a vacuum over phosphorus pentoxide. The product, a white powder, was found to be very reactive with hydriodic acid and with other reducing agents.

**Rearrangement.**—The crude bromo-amide was added to a solution of sodium ethylate (prepared from 1.3 g. of sodium) in 50 cc. of dry ethyl alcohol. The solution was boiled for three quarters of an hour, when a test proved that active bromine was absent. The solvent was allowed to evaporate on a water-bath. The residual viscous mass was washed with water, dissolved in a boiling mixture consisting of 200 cc. of alcohol, and 150 cc. of concd. aqueous hydrochloric acid, and the boiling was continued for five hours. The solvents were then allowed to evaporate; the residue was treated with hot water and the mixture filtered. When sodium hydroxide solution was added to the cooled filtrate a white precipitate resulted. This was taken up in ether, recovered by distillation of the ether, treated with a little concd. hydrochloric acid and the acid mixture was evaporated to dryness. The residual white needles were purified by dissolving in absolute alcohol and reprecipitating with dry ether. A mat of finely twined needles resulted; m. p., 239–240°. Analysis indicated that the product was β-triphenylethylamine hydrochloride. The hydrochloride is moderately soluble in alcohol and in water.

*Anal.* (Volhard). Calcd. for $C_{20}H_{20}NCl$: Cl, 11.4. Found: 11.5.

**β-Triphenylethylamine, $(C_6H_5)_3CCH_2NH_2$.**—The hydrochloride, prepared as described in the preceding section, is identical with that obtained after rearrangement of the benzoyl derivative of β-triphenylpropionhydroxamic acid (see below). The free amine was prepared directly in pure condition by adding a small excess of concd. ammonia water to an aqueous solution of the hydrochloride. The precipitate which resulted was collected, washed with water and dried. When viewed under the microscope it was found to consist of crystals which may be described simply but inadequately as elongated hexagonal platelets; m. p., 132° (corr.). When the amine is crystallized from ligroin (purified, b. p. 60–80°) the melting point does not change; the crystal form likewise is unchanged. The amine is soluble in hot ligroin, cold ether and benzene, moderately soluble in acetone and ethyl alcohol, and almost insoluble in water. It gives, with chloroform and potassium hydroxide, the carbylamine reaction.

*Anal.* Subs., 0.0695: N, 3.1 cc. (over 50% KOH; 20°, 755 mm.). Calcd. for $C_{20}H_{19}N$: N, 5.1. Found: 5.0.

SALTS OF THE AMINE.—The hydrochloride has already been described (see above). The dichromate (?) precipitates when a solution of a soluble dichromate is added to a solution of amine hydrochloride. The nitrate comes down in very characteristic manner when aqueous solutions of the hydrochloride and nitric acid are mixed. Under the microscope the salt is seen to consist of thin, elongated hexagonal plates. The salt may be crystallized from alcohol; decomposition point, 237°. Its solubility in water at 20° is approximately of the order 1:1000. None of the following ions, chlorate, perchlorate, oxalate, sulfate, interferes with the precipitation of the nitrate. Analysis and more complete solubility data will be submitted later.

CHLOROPLATINATE, $[(C_6H_5)_3CCH_2NH_3]_2PtCl_6$.—When a small excess of chloroplatinic acid solution is added to β-triphenylethylamine hydrochloride dissolved in a small volume of absolute alcohol, the chloroplatinate soon precipitates in yellow-orange crystals, which have the appearance of rhomboids under the microscope; m. p., 183°, with decomposition.

*Anal.* Subs., 0.1598: Pt, 0.0317. Calcd. for $C_{40}H_{40}PtCl_6$: Pt, 20.41. Found: 19.84.

BENZOYL DERIVATIVE, $(C_6H_5)_3CCH_2NHCOC_6H_5$.—The benzoyl derivative is formed when some β-triphenylethylamine hydrochloride in aqueous solution is shaken with a slight excess of benzoyl chloride in the presence of an excess of sodium carbonate. The product, a solid, is washed with water and crystallized from ethyl alcohol (platelets); m. p., 157.0° (corr.).

*Anal.* (Micro-Kjeldahl).[10] Calcd. for $C_{27}H_{23}ON$: N, 3.7. Found: 3.6, 3.6.

URETHAN, $(C_6H_5)_3CCH_2NHCOOC_2H_5$.—This is formed when some β-triphenylethylamine is shaken with a small excess of ethyl chlorocarbonate in the presence of an excess of sodium carbonate. When all of the chlorocarbonate has been decomposed (with the aid of sodium hydroxide solution, if necessary) the urethan is taken up with ether, dried with sodium sulfate, recovered by evaporation of the ether, and crystallized from ligroin (b. p., 60–80°); m. p., 94°.

*Anal.* (Micro-Kjeldahl). Calcd. for $C_{23}H_{23}O_2N$: N, 4.1. Found: 4.2.

**Preparation of β-Triphenylpropionhydroxamic Acid,** $(C_6H_5)_3CCH_2CONHOH$.[11]—A solution of 8 g. of crude β-triphenylpropionyl chloride (see section on preparation of β-triphenylpropionamide, above) in 100 cc. of ether is treated with 2.65 g. of sodium carbonate (anhydrous) and 1.75 g. of hydroxylamine hydrochloride. About 7 cc. of water is added and the mixture is shaken violently until all action has ceased (care: carbon dioxide is evolved). The solid product is brought upon a filter and washed with a little ether; it is thoroughly digested with hot water (to remove inorganic impurities), collected, and dried in a vacuum. The product so obtained is almost pure β-triphenylpropionhydroxamic acid; yield, 90%. It may be crystallized from ethyl acetate. The substance melts and decomposes at 182.5°; it is readily soluble in alcohol, acetone, hot ethyl acetate and hot benzene; it is not soluble in ligroin. It gives, in alcohol solution, the usual color reaction with ferric chloride.

*Anal.* (Kjeldahl). Calcd. for $C_{21}H_{19}O_2N$: N, 4.42. Found: 4.23.

BENZOYL DERIVATIVE, $(C_6H_5)_3CCH_2CONHOCOC_6H_5$.—To a portion of the hydroxamic acid (the "crude" product may be used) to which has been added a small excess of 5% potassium hydroxide solution, is added slightly more than an equivalent amount of benzoyl chloride. The mixture is shaken vigorously. Suspended solid matter must be maintained in finely divided form or the benzoylation will not be complete. When reaction is complete, potassium hydroxide solution is added, if necessary, until the small quantity of benzoic acid which floats near the surface is just dissolved. The product is collected, washed with water, dried and crystallized from alcohol; m. p., 171.5°; yield, almost quantitative. The substance gives no color reaction with ferric chloride.

*Anal.* (Kjeldahl). Calcd. for $C_{28}H_{23}O_3N$: N, 3.33. Found: 3.29.

**Rearrangement of the Benzoyl Derivative: Preparation of β-Triphenylethylamine.**—The uncrystallized benzoyl derivative prepared from 24 g. of β-triphenyl-

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[10] Koch and McMeekin, THIS JOURNAL, **46**, 2066 (1924).

[11] The method is similar to one of those recommended by Jones and his co-workers, THIS JOURNAL, **43**, 2430 (1921); **44**, 412 (1922).

propionhydroxamic acid was added slowly in finely divided form to a gently boiling solution of 190 g. of potassium hydroxide in 500 cc. of water contained in a 2-liter flask. A vigorous reaction took place, accompanied by change of the organic substance to a white, caked mass which floated upon the surface. The mixture was refluxed for 40 minutes, diluted somewhat, cooled and filtered. The residue was washed well with water and then stirred with hot hydrochloric acid. The acid mixture was filtered and the residual solid washed with water and dried at 100°. From the filtrate 2.5 g. of β-triphenylethylamine was obtained by the addition of an excess of aqueous ammonia. The amine, after being dried over potassium hydroxide in a vacuum was practically pure, as indicated by its melting point. Its identity with the product previously obtained by rearrangement of the bromo-amide derivative was further established by conversion to the hydrochloride and the benzoyl derivative.

Analysis and the properties of the residual solid (from the acid treatment; see above) indicated that it was sym.-di-β-triphenylethyl-urea, $[(C_6H_5)_3CCH_2NH]_2CO$. The yield of crude urea was practically that calculated; m. p., 216–218°. When twice crystallized from alcohol the substance was pure and consisted of clumps of long, slender needles; m. p., 218.5–219°. It readily dissolves in benzene from which it may be precipitated by the addition of ligroin. The urea is completely converted to the parent amine by the procedure outlined in the following section.

*Anal.* Calcd. for $C_{41}H_{36}ON_2$: N, 4.90. Found (Kjeldahl): 4.84, 4.97; (Micro-Kjeldahl) 5.0, 5.0.

**Hydrolysis of the Urea.**—In sealed Pyrex "bomb" tubes (length, about 58 cm.; internal diameter, 1.7 cm.) the urea (5 g.) is heated with a mixture of 10 cc. of hydrochloric acid (d., 1.18–1.19) and 10 cc. of ethanol (95%) for 12 hours at 150°. The mixture thus obtained is concentrated to remove alcohol, diluted with water and filtered. To the filtrate ammonia is carefully added. Just beyond the "neutral point" a small amount of slightly colored matter precipitates. This is almost pure β-triphenylethylamine. An excess of ammonia is then added; the amine precipitates as a white solid in practically pure form. It is collected and dried. For complete purification it is dissolved in dry ether and the solution is treated with hydrogen chloride. The precipitate is collected, washed with ether and dried. The salt is dissolved in water and ammonia is then added to precipitate the amine.

**Formation of the Urea from the Amine.**—Some β-triphenylethylamine was treated with an excess of a solution of phosgene in toluene. Reaction was completed and the excess of phosgene removed on the water-bath. Slightly more than the same amount of amine dissolved in benzene was added to the reaction mixture (which presumably contained β-triphenylethylcarbamyl chloride), the solvents were evaporated, and the residual solid was digested with dil. hydrochloric acid to remove the excess of amine. The white solid obtained by filtration of the acid mixture was washed well and dried. Its melting point was 218° and was not lowered by admixture with some di-β-triphenylethyl-urea obtained from rearrangement of the hydroxamic acid derivative.

## Summary

1. The synthesis of β-triphenylethylamine has been accomplished by the rearrangement of the benzoyl derivative of β-triphenylpropionhydroxamic acid and also by the rearrangement of an N-bromo derivative of β-triphenylpropionamide. The properties of the amine and those of several derivatives have been described; the properties of the amine and its derivatives have been found to differ from those set forth by Elbs, who stated that he prepared the substance by the reduction of triphenyl-

aceto nitrile, a procedure which could not be confirmed in the present work.

2. Among other new compounds described in this work are β-triphenylpropionamide, β-triphenylpropionhydroxamic acid and its benzoyl derivative, and *sym.*-di-β-triphenylethyl-urea.

3. Detailed directions for the preparation of β-triphenylpropionic acid by the method of Fosse are submitted.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

# THE OXIDATION OF COMPOUNDS POSSESSING THE PRIMARY AMINO GROUP. I. DIPHENYLMETHYLAMINE

BY LESLIE HELLERMAN AND AGNES GRAHAM SANDERS[1]

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The mechanism of oxidation of compounds possessing an amino group linked to a primary or secondary carbon atom ($RCH_2NH_2$; $RR'CHNH_2$) is a problem of considerable interest to organic chemists, and is also of importance in biological chemistry, particularly in connection with the important question of the oxidation of amino acids. Because of the electronic relationship of amino derivatives to hydroxylated compounds,[2] it has seemed interesting to inquire to what extent oxidation of amino compounds may, in general, produce substances of the types (that is, aldehydes and ketones as the ultimate products) which are obtained when the corresponding hydroxy derivatives are oxidized. From a theoretical point of view, the question of intermediate compounds formed during the course of an oxidation reaction is of additional importance.

Considerable work is recorded[3] in which amino derivatives of types (1) $RCH_2NH_2$, (2) $RR'CHNH_2$ and (3) $RR'R''CNH_2$ have been subjected to oxidation with agents related to hydrogen peroxide. Bases of the

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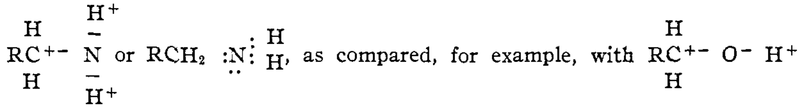
[1] This preliminary paper is an abstract of part of a dissertation submitted to the University of Chicago by Agnes Graham Sanders, in partial fulfilment of the requirements for the degree of Master of Science, August, 1925. Presented before the Virginia Section of the American Chemical Society, April, 1926.

[2] 
$\overset{H}{\underset{H}{RC}}{}^{+-}\ \overset{\overset{H^+}{-}}{\underset{\underset{H^+}{-}}{N}}$ or $RCH_2\ :\overset{\cdot}{\underset{\cdot\cdot}{N}}\!\!:{}^{H}_{H}$, as compared, for example, with $\overset{H}{\underset{H}{RC}}{}^{+-}\ O^-\ H^+$ or $RCH_2\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\ H$. The valence sign $^-$ as used here indicates the relative polarity of an atom resulting from the approach of a valence electron pair : , and the sign $^+$ the corresponding polarity of the other atom held by the doublet bond.

[3] (a) Bamberger and Seligman, *Ber.*, **36**, 701 (1903). (b) Bamberger and Tschirner, *Ber.*, **32**, 1675 (1899). For other references consult Houben-Weyl, "Methoden," Georg Thieme, Leipzig, **1922**, vol. 2, p. 144.