cipitated by hydrochloric acid, washed with water, again dissolved in ammonia and reprecipitated by boiling off the ammonia. Yield, 3.5 grams (40%).

Five grams isophthalyl chloride was heated in a sealed tube with 8 grams of mercuric cyanide for 6 hours at 200°. Yield, 1.7 grams (30%).

Calculated for $C_6H_4(COCN)_2$: N, 15.2. Found: N, 15.0.

Terephthalyl Cyanide.—Ten grams terephthalyl chloride were dissolved in 25 cc. ether, 4 grams hydrogen cyanide added and 16 grams pyridine. The cyanide was purified in the same manner as the isophthalyl cyanide. Yield, 4 grams (45%).

In the sealed tube, 4 grams terephthalyl chloride and 7 grams mercuric cyanide gave 1.2 grams (30%).

Calculated for $C_6H_4(COCN)_2$: N, 15.2. Found: N, 15.2.

The first method of preparation is not recommended for phthalyl cyanide, as there is a product rich in nitrogen from which it is hard to purify it, but in the other cases it gives better yields than the preparation from mercuric cyanide.

These experiments were carried out under the direction of Professor F. B. Allan.

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ACTION OF ALCOHOLIC AMMONIA ON α,β-DIBROMOPROPIONIC ACID.

BY W. H. WARREN.

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By heating α,β-dibromopropionic acid with concentrated aqueous ammonia in a sealed tube, Klebs[1] obtained α,β-diaminopropionic acid, the yield of which never exceeded 58%, and in most cases was considerably less. Klebs suspected the presence of other products but succeeded in isolating only the product mentioned. Subsequently, Neuberg and Ascher,[2] while using the method proposed by Neuberg and Silbermann,[3] which increased the yield of α,β-diaminopropionic acid to 65%, isolated α-oxy-β-aminopropionic acid (isoserine) to the amount of 10%.

Some experiments, originally undertaken for the purpose of still further increasing the yield of α,β-diaminopropionic acid and in which α,β-dibromopropionic acid was acted upon by a cold saturated solution of ammonia in absolute alcohol, have shown that ammonia will form still another compound. Under these conditions, α,β-diaminopropionic acid is not formed but the sole product seems to be ammonium α-bromoacrylate. Since the yield of this salt is very good, it would seem to present an easy

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[1] *Z. physiol. Chem.*, **19**, 301–338 (1894).

[2] *Biochem. Z.*, **6**, 559–62 (1907).

[3] *Ber.*, **37**, 341–345 (1904).

means of preparing α-bromoacrylic acid. If heat is applied during the reaction, some α,β-diaminopropionic acid is formed, but no ammonium α-bromoacrylate, unless it be that a part of the α,β-dibromopropionic acid passes into this latter compound which at the higher temperature forms more highly unsaturated products. Such a reaction is not improbable, since Wagner and Tollens[1] obtained potassium α-bromoacrylate from α,β-dibromopropionic acid by means of hot alcoholic potassium hydroxide, a reaction analogous to that mentioned above for alcoholic ammonia. But if heat was applied too long, they obtained colloidal bodies apparently related to propiolic acid.

Experimental.

Preparation of Ammonium α-Bromoacrylate.

One hundred and twenty-five grams of 12.5% absolute alcoholic ammonia were added in small portions to a solution of 50 grams of α,β-dibromopropionic acid in 50 cc. of absolute alcohol and the mixture was kept cold and shaken from time to time. In 12 hours cubic crystals of ammonium bromide had appeared and in three to four days micaceous plates of ammonium α-bromoacrylate. The reaction was allowed to run about a week, though less time might have been sufficient. The alcoholic solution still strongly ammoniacal was poured from the crystallin deposit and spontaneously evaporated to dryness. The presence of ammonium bromide, which crystallization would not remove, was responsible for such unsatisfactory analytical results, that the following method of purification was used, though it may be dispensed with when the salt is to be used for preparing α-bromoacrylic acid.

The residue from evaporation and the crystals in the flask were dissolved in the smallest possible quantity of cold water. This solution was then vigorously shaken with powdered silver sulfate, which was added in small portions. As long as ammonium bromide was present, silver bromide settled quickly and left the solution clear. But as soon as ammonium bromide had been removed and silver sulfate was in excess, the solution remained turbid on standing. This was due to the formation of silver α-bromoacrylate.

Hydrogen sulfide was passed through the filtered solution, silver sulfide was removed by filtration and the filtrate was spontaneously evaporated to dryness. This residue should be thoroughly dried, since the separation of ammonium α-bromoacrylate from ammonium sulfate is brought about by means of absolute alcohol in which the latter salt is practically insoluble. The finely powdered residue was extracted with boiling absolute alcohol from which nearly pure ammonium α-bromoacrylate crystallized. From 50 grams of α,β-dibromopropionic acid as much as 30 grams (83% yield) of the salt and sometimes more, was obtained. Twice crys-

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[1] *Ann.* 171, 340-355 (1874).

tallized from absolute alcohol, this compound gave the following results upon analysis:

Subst., 0.3596; CO_2, 0.2799; H_2O, 0.1223. Subst., 0.2153; N, 20.2 cc.; 19 degrees; 752 mm. Subst., 0.2534; AgBr, 0.2844.

Calculated for $C_3H_6O_2NBr$: C, 21.43; H, 3.57; N, 8.33; Br, 47.61.
Found: C, 21.23; H, 3.80; N, 8.53; Br, 47.76.

Wagner and Tollens,[1] who first prepared ammonium α-bromoacrylate by neutralizing the free acid with gaseous ammonia, describe the salt as crystallizing in leaflets. This compound, obtained as described above, crystallized from absolute alcohol in shining micaceous plates which began to sinter at 144° and melted at about 148° with decomposition. Less soluble in cold absolute alcohol, it is freely soluble in hot; and very soluble in water and in ordinary alcohol. It is not soluble in ether, acetic ether, benzene or chloroform to any appreciable extent. Aqueous solutions of the salt are acid to litmus.

That this compound was α-bromoacrylate was not at once determined, for the acidity of its aqueous solutions and the fact that an aminobromopropionic acid would have given the same result upon analysis led to the supposition that this compound might be an intermediate product between dibromo- and diaminopropionic acids. Since Gabriel[2] has described the hydrobromide of α-bromo-β-aminopropionic acid, an attempt was made to prepare a hydrobromide and compare its properties with those given by Gabriel. As stated in another place, two products were obtained, namely, ammonium bromide and α-bromoacrylic acid. Further experiments showed that the supposed aminobrompropionic acid could not be converted into a bromolactic acid by means of nitrous acid and that its aqueous solution, when heated with sodium hydroxide solution, gave a strong test for ammonia. These and other results showed clearly that the compound was an ammonium salt and not an aminobromopropionic acid.

Silver α-Bromoacrylate.

As an additional means of identifying the compound just described, the silver salt was prepared and analyzed. A concentrated aqueous solution of two grams of silver nitrate was added to an aqueous solution of pure ammonium α-bromoacrylate. The white, crystallin precipitate, which appeared immediately, was filtered by suction, washed with water and alcohol, and then dried in the dark *in vacuo* over sulfuric acid. Upon analysis this salt gave the following results:

Subst., 0.2688; AgBr, 0.1958 (Ag. pptd. by HBr). Subst., 0.3469; AgBr, 0.2521 (by Carius method).

Calculated for $C_3H_2O_2BrAg$: Ag, 41.86; Br, 31.01.
Found: Ag, 41.84; Br, 30.93.

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[1] *Loc. cit.*

[2] *Ber.*, 41, 242–250 (1908).

An analysis of this salt for nitrogen gave a negative result, which was further evidence that it could not be the silver salt of an aminobromopropionic acid. Wagner and Tollens[1] prepared this same silver salt by precipitating an aqueous solution of potassium α-bromoacrylate. They describe the salt as shining leaflets difficultly soluble in water. The salt prepared from the ammonium salt answered to this description. A further statement that it rapidly darkens upon exposure to the light might be made.

Isolation of α-Bromoacrylic Acid.

The isolation of α-bromoacrylic acid resulted from a previously mentioned attempt to convert ammonium α-bromoacrylate into a hydrobromide by dissolving it on the water bath in 34% hydrobromic acid. The compound that crystallized as the solution cooled, when freed from mother liquor and recrystallized, was found, upon analysis, to be ammonium bromide. An ether extract of the mother liquor gave, upon evaporation, an entirely different substance, which, after several crystallizations from a very small quantity of water, had the constant melting point 69° and gave the following results upon analysis:

Subt., 0.2738; CO_2, 0.2367; H_2O, 0.0579. Subst., 0.2634; AgBr, 0.3274.

Calculated for $C_3H_3O_2Br$:	C, 23.84; H, 1.99; Br, 52.98.
Found:	C, 23.58; H, 2.37; Br, 52.89.

Two bromoacrylic acids have been described, the α-acid, melting at 69°–70°, prepared by Wagner and Tollens,[1] and the β-acid, melting at 115°–116°, prepared by Wallach.[2] The compound just mentioned must be the former. Its properties fully agree with those given by Wagner and Tollens for their acid. It crystallizes in beautiful shining plates that often attain a considerable size. Upon standing in a desiccator over sulfuric acid, it loses hydrobromic acid and turns brown in the light. If the substance which has stood in the desiccator is treated with water, a product is formed which is insoluble in water and alcohol.

The formation of ammonium α-bromoacrylate may explain the low yields of α,β-diaminopropionic acid. It is not surprising that this ammonium salt is not obtained when heat is used, for the reaction is probably carried further. Wagner and Tollens have shown, and the same thing has been observed during this investigation, that α-bromoacrylic acid is decomposed even by standing over sulfuric acid. A gelatinous compound of unknown molecular weight, whose simplest formula is $C_3H_4O_3$, or propiolic acid plus a molecule of water, is formed. That is to say, α-bromoacrylic acid by loss of hydrobromic acid passes into propiolic acid which may polymerize and form the gelatinous substance in question.

It has also been observed that a considerable quantity of a gelatinous

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[1] *Loc. cit.*

[2] *Ann.*, **193**, 55 (1878).

substance answering the description given by Wagner and Tollens is formed by the action in sealed tube of cold, liquid, anhydrous ammonia upon α,β-dibromopropionic acid. The latter fact points to the possibility of decomposing the dibromopropionic acid by ammonia and forming polymeric compounds of colloidal nature by passing through α-bromoacrylic and propiolic acids.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE OXIDATION OF PROPYLENEGLYCOL. I. THE ACTION OF ALKALIN POTASSIUM PERMANGANATE GIVING CARBONIC, ACETIC AND OXALIC ACIDS.

BY WILLIAM LLOYD EVANS AND EDGAR J. WITZEMANN,

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The purpose at the beginning of these experiments was to find some conditions under which lactic aldehyde, $CH_3.CHOH.CHO$, is formed by the oxidation of propyleneglycol, $CH_3.CHOH.CH_2OH$. Lactic aldehyde has never been prepared by direct oxidation. It was, however, synthesized in 1908, by A. Wohl and M. Lange.[1] They took dichloroacetic acid which with sodium ethylate gave ethyl diethoxyacetate; this, when condensed with piperidine, gave a piperidide, which on treatment with $MgICH_3$ by Grignard's · general method, gave methylglyoxalacetal, $CH_3COCH : (OC_2H_5)_2$. The glyoxal derivative reduced with sodium gave the acetal of lactic aldehyde, which, when hydrolyzed with 0.1*N* sulfuric acid, gave the free aldehyde. The derivatives and properties of lactic aldehyde recorded by these workers make the identification of lactic aldehyde relatively simple. Lactic aldehyde has also been synthesized more recently by Dr. Cyrill Krauz of Prague,[2]. He took *unsym*-dichloroacetone from which pyruvic aldehyde acetal was prepared. This, on reduction of the ketone group and on subsequent hydrolysis gave lactic aldehyde. In cases where it is impossible to find lactic aldehyde in the oxidation products it would be interesting to learn if this substance represents one of the intermediate stages of oxidation.

In the accompanying table the possible oxidation products of propyleneglycol are given. No reference was found in the literature concerning the oxidation of propyleneglycol to glycerol. The second stage, glyceric aldehyde and dihydroxyacetone from glycerol, has been brought about variously by the action of nitric acid, platinum black, hydrogen peroxide in the presence of ferrous iron, bromine and soda, bromine vapor on lead glycerate, action of quinone on aqueous solutions in the sunlight or the illumination

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[1] *Ber.*, 41, 3612.

[2] *Chemicke Listy*, 5, 323–7; *C. A.*, 6, 739.