[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

ORGANIC CHEMICAL REAGENTS. VI. REAGENTS FROM *n*-BUTYL ALCOHOL.

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Until two years ago, *n*-butyl alcohol was a rare organic compound. After the discovery of the method by which starch may be fermented to give acetone and *n*-butyl alcohol, however, this latter substance has become available in large quantities at a low price. It is already in technical use as a solvent but comparatively little advantage has been taken of it for scientific purposes.

In this laboratory, a number of compounds which were needed for certain scientific investigations and which previously had been extremely expensive and difficult to produce, have been easily made from *n*-butyl alcohol. The object of this communication is to point out the new reagents made available in this way and to give detailed methods for the preparation of some of the more desirable ones, such as butyl cyanide, *n*-valeric acid, ethyl *n*-valerate, *n*-amyl amine, *n*-amyl alcohol, *n*-butyl malonic ester, *n*-caproic acid, α-bromo and α-amino-*n*-caproic acids.

Butyl bromide can be made from the alcohol in almost quantitative yields and converted with ease into butyl cyanide. This product by reduction gives smoothly *n*-amyl amine; on the other hand by hydrolysis with alkali or by treatment with sulfuric acid and an alcohol, it will give respectively *n*-valeric acid or its esters, compounds which have always been difficult to obtain, particularly in a pure state. By the reduction of ethyl *n*-valerate, *n*-amyl alcohol can be produced in good yields. It is thus possible directly or indirectly to obtain the various *n*-amyl derivatives which have, up to this time, only rarely been used by the organic chemist. Another class of compounds most readily synthesized by means of *n*-butyl alcohol are *n*-caproic acid and its derivatives. Caproic acid is one of the most interesting of the lower fatty acids because of its wide distribution in many fats and oils. Its α-amino derivative known as nor-leucine is especially important on account of its occurrence among the hydrolytic products of brain protein. Pure caproic acid can be very readily prepared by condensing *n*-butyl bromide with malonic ester to give *n*-butyl malonic ester, then saponification and decomposition of this latter compound; the α-bromo caproic acid is best obtained by the bromination of *n*-butyl malonic acid and subsequent loss of carbon dioxide. Since α-amino-*n*-caproic acid or nor-leucine is made directly from the bromo acid, it is thus possible to synthesize this interesting amino acid in quantity.

***n*-Butyl Bromide, Preparation.**—The preparation of this substance has already been described in detail in a preceding paper on "Alkyl Bromides."[1]

***n*-Butyl Cyanide, Preparation.**—In a 5-liter round-bottom flask holding a reflux condenser are placed 690 g. (14 mols) of powdered sodium cyanide, 690 cc. of water, 1575 g. of 95% alcohol and 1575 g. (11.5 mols) of butyl bromide. The mixture is refluxed on a steam bath for 25–30 hours and then cooled. The sodium bromide which has separated, is filtered off by suction and the filtrate distilled with a very efficient fractionating column. The first fraction distilling at 78–85° is chiefly alcohol and can be used again in a subsequent run. The second fraction boiling from 85 to 140° and consisting of a small amount of alcohol, water and butyl cyanide is treated with calcium chloride. Two layers separate, the upper of which is dried over calcium chloride and then distilled. The portion which boils between 138 and 141° is butyl cyanide. The low boiling material if again dried over calcium chloride and redistilled, gives a further quantity of product. The total yield amounts to 720–765 g. (75–80% of the theoretical amount). The success of the whole experiment depends upon the care with which the fractionation is carried out, especially when distilling the first fraction. The complete distillation of such a run as has just been mentioned, using a 20-inch column filled with broken glass should take from 10 to 12 hours. During this process 3 times the amount of liquid should condense and flow back into the flask as distils over. In this way, the alcohol is quite efficiently separated from the other products and the butyl cyanide is then obtained in 80% yields.

Discussion of Reaction.—A few runs were attempted, using 95% alcohol in place of the water and alcohol, but in no case did the yield go above 50% of the theoretical amount.

If efficient fractionation is not carried out, the yield will drop to 60–65% of the theoretical amount. Undoubtedly with a more efficient column than the one mentioned above, the distillation could be carried on more raipdly with just as satisfactory results. In carrying out several runs, using $^1/_3$ of the quantity described above, yields of 75–80% were also obtained. The 25–30 hours refluxing is quite necessary, since 10 hours' refluxing gives only about 50% yield. A recovery of about 1800 cc. of 80% alcohol is made in each run.

The butyl cyanide always contains a fraction of 1% of isonitrile, which gives it a very objectionable odor. The amount present, however, is comparatively small and for practical purposes may be disregarded.

Butyl cyanide has already been described in the literature[2] and has been made from butyl bromide and alcoholic potassium cyanide by heating under pressure.

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[1] This Journal, 42, 299 (1920).

[2] *Ann.*, 158, 171; 159, 58 (1871).

n-**Valeric Acid, Preparation.**—In a 3-liter round bottom flask fitted with a reflux condenser are placed 245 g. (5 mols.) of powdered sodium cyanide and 245 cc. of water. After practically all of the sodium cyanide has dissolved, 548 g. of 95% alcohol and 548 g. (4 mols.) of butyl bromide are added. The mixture is refluxed for 30 hours on a steam bath and then allowed to cool. The butyl cyanide, alcohol and excess of butyl bromide are filtered by suction from the sodium bromide which has separated during the reaction. The filtrate is placed again in the 3-liter flask with 216 g. (5 mols.) of sodium hydroxide dissolved in a small amount of water. This mixture is refluxed for about 24 hours on a steam bath and then distilled in order to obtain the alcohol. When most of the alcohol has been recovered in this way, the remainder of the solution is poured into a large evaporating dish and heated over a free flame or over a steam bath for several hours longer in order to be sure that all of the alcohol has been driven off. If this is not done, the final product is invariably mixed with a small amount of ester formed during the acidification process. The sodium valerate solution is now cooled, transferred to a flask and acidified with 300 cc. of about 50% sulfuric acid. This sets free the valeric acid which then is separated, dried over calcium chloride and distilled with a fractionating column. The portion boiling between 183 and 186° is collected and amounts to 330 g. (81% of that theoretically possible). By treating the water layer after acidification with 100 cc. of ether, shaking and separating, then drying over calcium chloride and distilling, a further yield of about 7 g. of material is obtained.

Discussion of Reaction.—If all of the alcohol is not distilled off as described in the above directions, the yield of valeric acid will often drop down to as low as 60 to 65% and as much as 10 to 15% of ethyl valerate will be mixed with the product.

The low boiling fractions of material, by drying a second time with calcium chloride and redistilling, will always yield a small amount more of pure product.

An experiment using 30% sulfuric acid for the hydrolysis of the cyanide was carried out, but even after the refluxing had been carried on for 24 hours, no hydrolysis had taken place.

The early experiments on the preparation of valeric acid were carried out with pure butyl cyanide but the yields were no larger than those obtained by the above procedure. In a 3-liter round-bottom flask with reflux condenser, 230 g. of sodium hydroxide, 520 g. of water, and 250 g. of butyl cyanide are boiled for about 5 hours until the layer of butyl cyanide disappears. To the mixture is now added through the condenser 400 cc. of water, then slowly 300 cc. of 50% sulfuric acid, keeping the mixture cold during the addition. The layer of valeric acid is separated and worked up as already described.

n-Valeric acid has been mentioned many times in the literature. It has previously been produced by the action of alkali on butyl cyanide;[1] by the action of silver on a mixture of ethyl iodide and β-iodopropionic acid;[2] by the oxidation of α-oxy-*n*-caproic acid;[3] by the reduction of levulinic acid with hydriodic acid or by electrolytic reduction;[4] by the action of hydriodic acid on valero-lactone;[5] by the action of bacteria on calcium lactate;[6] by the decomposition of *n*-propyl malonic acid;[7] by the oxidation of castor oil by nitric acid;[8] by the action of enzymes on valeraldehyde;[9] by biochemical change of α-pyrollidine carbonic acid;[10] by the action of sodium ethylate on methyl-pyrazolidon.[11]

Ethyl-*n*-Valerate, Preparation.—In a 5-liter round-bottom flask fitted with a reflux condenser is placed one kg. of 95% alcohol. This is well cooled and one kg. of conc. sulfuric acid is gradually run in. To this mixture is now added 415 g. of butyl cyanide and the whole is refluxed for about 10 hours. After cooling, the reaction mixture is poured into ice water, the upper layer of alcohol and ester separated, dried over calcium chloride and distilled with a fractionating column. The portion boiling at 142–146° is collected. The low boiling fractions, after drying again and redistilling, yield a further amount of pure ester. The total yield of finished product varies between 565 and 595 g. (85–90% of the theoretical amount).

Discussion of Reaction.—Several runs by the method just described were made and in practically every instance very good yields were obtained. An attempt was made to see whether ethyl-*n*-valerate could not be produced from the crude reaction mixture containing butyl cyanide, instead of isolating the pure butyl cyanide. A number of experiments, however, showed that as good results could not be obtained in this way. A very brief description of the procedure is given below because it is possible that this method might be developed into a more satisfactory one. A mixture of 115 g. of powdered sodium cyanide and 115 g. of water with 265 g. of 95% alcohol and 265 g. of butyl bromide was made and refluxed for 30 hours. The layer of butyl cyanide and alcohol was separated from the salt and water, treated with 570 g. of conc. sulfuric acid and the

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[1] *Ann.*, **159**, 58 (1871); *Ibid.*, 233, 272 (1886).

[2] *Z. Chem.*, **5**, 342 (1869).

[3] *Ber.*, **9**, 1840 (1876); **10**, 231(1877).

[4] *Ann.*, **206**, 236; **208**, 110 (1881); *Z. Electrochem.*, **17**, 571 (1911).

[5] *Ann.*, **226**, 346 (1884).

[6] *Ber.*, **13**, 1309 (1880); **14**, 1084 (1881).

[7] *Ibid.*, **17**, 2504 (1884).

[8] *Ibid.*, [2] **22**, 438 (1889).

[9] *Biochem. Z.*, **28**, 289 (1910).

[10] *Ibid.*, **37**, 490 (1911).

[11] *Ann.*, **394**, 99 (1912).

mixture refluxed about 10 hours. The product was worked up as described under the preparation using pure butyl cyanide. The yield amounted to about 120 to 125 g. (47–49% of the theoretical amount, based on butyl bromide, or 68–71% based on the butyl cyanide which actually can be obtained from the butyl bromide).

Ethyl-*n*-valerate has already been made by the electrolysis of sodium propionate and potassium ethyl succinate;[1] by the action of alcohol upon *n*-propyl-*n*-butyryl acetic ester;[2] by the esterification of valeric acid with sulfuric acid and ethyl alcohol.[3]

***n*-Amyl Amine, Preparation.**—In a 5-liter round-bottom flask fitted with a rubber stopper holding a reflux condenser, dropping funnel and efficient mechanical stirrer are placed 276 g. of sodium and 1000 cc. of toluene. The mixture is heated until the toluene commences to boil, at which point the molten sodium is stirred vigorously, a procedure which soon produces an emulsion. A mixture of 166 g. (2 mols.) of butyl cyanide and 300 g. of absolute alcohol is now added to the flask through the dropping funnel (one hour). During this addition and subsequent addition of alcohol and water, the stirring should be vigorous and the temperature regulated so that refluxing is continuous; in general the heat of reaction is all that is required. After all of the butyl cyanide solution has been added, 300 g. more of absolute alcohol is gradually added. To decompose any sodium which may still be present, the reaction mixture is treated slowly with 200 g. of 95% alcohol and then 100 g. of water. About 3.5 hours are required up to this point. The contents of the flask are now steam distilled (3 hours) and the distillate treated with 200 cc. of conc. hydrochloric acid. The toluene is removed and the water, hydrochloric acid, alcohol, amyl amine hydrochloride layer is distilled until most of the alcohol has been removed. As soon as this has been completed, the contents of the flask are poured into an open porcelain dish and evaporated to dryness, the last portion of liquid being removed best on a steam bath. The amyl amine hydrochloride which is obtained is treated with a concentrated solution of 200 g. of sodium hydroxide. The amyl amine separates as a layer, is removed, dried over sodium hydroxide and distilled. The portion boiling at 102–105° is collected as pure material. The low boiling fraction after drying again over sodium hydroxide and redistilling gives an additional amount of amine. From a number of runs, the yields varied between 100 and 120 g. of pure amyl amine (57–68% of that theoretically possible).

Discussion of Reaction.—Although it is quite necessary to have good absolute alcohol, the yield does not drop off so markedly in this experiment

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[1] *Ber.*, 28, 2434 (1895).

[2] *Ann. chim. phys.*, [8] 19, 204 (1910).

[3] *Ibid.*, 165, 117 (1873); 233, 273 (1886).

as it does in the reduction of ethyl-*n*-valerate when even the smallest amount of water is present.

In distilling amyl amine, it is advisable to have the side arm of the flask extend a considerable distance into the condenser. This prevents the vapors from coming in contact with the cork and becoming colored.

Stirring should be efficient so as to prevent the caking in the reaction flask when the cyanide-alcohol mixture or subsequent alcohol addition is made.

n-Amyl amine has already been prepared by the action of sodium hypobromite upon *n*-caproic acid amide;[1] by the action of phosphorus pentachloride upon benzoyl-piperidine and then subsequent reduction and hydrolysis.[2]

***n*-Amyl Alcohol.**—In a 5-liter round-bottom flask, the stopper of which is fitted with a large Y-tube, one branch holding an efficient reflux condenser and the other closed with a stopper, are placed 156 g. of ethyl-*n*-valerate and 2500 cc. of absolute alcohol ($d^{25.5}$ 0.785). To this mixture is added through the Y-tube 280 g. of sodium in small pieces at such a speed that vigorous refluxing is continuous. This requires 50 to 60 minutes. The mixture is now refluxed for 2 to 3 hours longer in an oil bath to be certain that all of the sodium has dissolved. The reflux apparatus is replaced by an efficient fractionating column (at least a 20-inch column filled with broken glass) and condenser set downward for distillation. The mixture is distilled from an oil bath; in this way 700 cc. of absolute alcohol is recovered. The residue consisting of amyl alcohol and sodium ethylate is treated with 1000 cc. of water and the distillation carried on again until the temperature of the vapors reaches 83°, indicating that practically all the alcohol is removed. The oil bath must be heated to about 110 or 120° in order to cause the liquid to distil over. In this way between 1800 and 1900 cc. of about 90% alcohol is recovered. The procedure thus far requires 1–1$^1/_2$ days' time. The fractionating column is now removed and the amyl alcohol steam distilled from the reaction mixture, about 500 to 600 cc. of distillate coming over before all the alcohol is removed. This requires about 1.5 hour. The alcohol is separated, dried over potassium carbonate, and distilled. It is quite necessary to dry carefully in order to get a clean product which boils at the right point. By drying again the low fraction from the first distillation a few more grams of good material is always obtained. The yield amounts to 97–105 g. (56–61% of the theoretical amount).

Discussion of Reaction.—The alcohol used for the reduction must be absolute. A lower grade causes the yield to drop very rapidly with a large increase in amount of valeric acid formed.

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[1] *Ber.*, **15**, 770 (1882); *Ann.*, **233**, 253 (1886); *J. Russ. Phys. Chem. Soc.*, **29**, 455 (1897).

[2] *Ber.*, **43**, 3596 (1910).

By distilling the 90% alcohol again through a good column and fractionating the residue, 6 or 8 g. more of pure amyl alcohol is obtained. The original distillation must be carried out very carefully and slowly or else a large part of the amyl alcohol comes over with the ethyl alcohol and is consequently lost. Undoubtedly a more efficient frationating column would give a somewhat better yield and in a shorter period of time.

The alkaline solution after the distillation of the *n*-amyl alcohol may be cooled and acidified. Valeric acid separates, is dried and distilled. The yield amounts to 15–25 g.

The reduction should be run as rapidly as possible in order to prevent the caking of the sodium ethylate which is formed.

n-Amyl alcohol has already been made by several methods, the reduction of valeraldehyde by sodium amalgam;[1] by the hydrolysis of amyl chloride with potassium acetate;[2] the fermentation of glycerine;[3] by the action of silver nitrite upon *n*-amyl amine hydrochloride;[4] by the action of enzymes upon valeraldehyde;[5] by the action of silver oxide upon amyl iodide;[6] by the reduction of acetopropyl alcohol with zinc amalgam and hydrochloric acid.[7]

n-**Butyl Malonic Ester, Preparation.**—In a 5-liter round-bottom flask fitted with a rubber stopper holding a reflux condenser, separatory funnel, and mechanical stirrer, is placed 2.5 liters of absolute alcohol. To this alcohol is added gradually 115 g. of sodium cut into thin slices. The sodium alcoholate solution is cooled somewhat and 825 g. of malonic ester allowed to flow in slowly through the separatory funnel. Stirring is then started and 685 g. of *n*-butyl bromide is gradually run in. The reaction starts almost immediately and refluxing takes place during the addition of the halide, due to the heat of the reaction. Up to this point, the time required is about one hour. The reaction flask is now placed upon a steam bath and the mixture refluxed until neutral to moist litmus. This point is reached within 2 to 3 hours. The stopper of the flask is removed, a new one holding a condenser set for downward distillation is attached and the alcohol distilled off from a water bath. About half a day is required for this distillation and about 2 liters of alcohol is recovered.

An equal volume of water is added to the residue, the layer of *n*-butyl malonic ester separated and distilled under diminished pressure. A low boiling portion comes over first, consisting of a little alcohol, water and butyl bromide, then a small intermediate fraction of unchanged malonic

[1] *Ann.*, **159**, 70 (1871).

[2] *Ibid.*, **161**, 268 (1872).

[3] *Bull. soc. chim.*, [2] **48**, 803 (1887).

[4] *Ann.*, **233**, 253 (1886).

[5] *Biochem. Z.*, **28**, 289 (1910).

[6] *Ann. chim. phys.*, [8] **25**, 260 (1912).

[7] *Ber.*, **47**, 686 (1914).

ester and finally pure *n*-butyl malonic ester boiling at 144–145° at 40 mm. The yield is 960–990 g. (89–92% of the theoretical amount) of material collected over 5°. Under ordinary pressure the *n*-butyl malonic ester boils at 235–240°.

Discussion of Reaction.—The quality of the alcohol used has a very marked effect on the yield of product. It should be absolute. A trial run with alcohol of 98.4% purity gave a 66% yield.

***n*-Caproic Acid, Preparation.**—In a 5-liter round-bottom flask fitted with a stopper holding a reflux condenser and separatory funnel, 500 g. of potassium hydroxide is dissolved in 500 cc. of water. To this hot solution with frequent shaking, 500 g. of *n*-butyl malonic ester is added slowly through the separatory funnel. The hydrolysis proceeds rapidly and by the time the butyl malonic ester has been added, the saponification is practically complete and the solution is clear. The stopper is removed and the flask heated for 1 or 2 hours on a water bath to drive off most of the alcohol and to insure complete hydrolysis. The stopper, with reflux condenser and separatory funnel, is again attached and the reaction mixture is then acidified with 1500 cc. of conc. hydrochloric acid (sp. gr. 1.19), the acid being added slowly enough to prevent foaming over. This mixture is then refluxed for 4–5 hours, after which time the reaction is nearly complete and a layer of caproic acid appears on the surface. The condenser is set downward for distillation and the solution distilled until practically all of the liquid has come over. From the distillate, the upper layer of caproic acid is separated and 300 to 400 cc. of the water layer is added to the main flask and again distilled off. The caproic acid is again separated and the total aqueous solutions combined and salted out with calcium chloride. About 4 g. of caproic acid per liter of aqueous solution is thus obtained. The distillation as described requires about half a day. The caproic acid is dried over calcium chloride and distilled. It boils at 200–205°. The yield is 200 g. (74% of the theoretical amount).

Discussion of Reaction.—In place of the potassium hydroxide for the saponification of the butyl malonic ester, sodium hydroxide was used in one or two experiments. Under these conditions, the hydrolysis did not proceed nearly so rapidly and it was necessary to boil it under a reflux condenser for 2 to 3 hours to be certain of the completion of the reaction. The difficulty with sodium hydroxide is due to the fact that an organic sodium salt separates, yielding a semi-solid mass, thus making several hours refluxing a necessary procedure to be sure all the ester is saponified. The difference in the price of potassium hydroxide and sodium hydroxide is inconsiderable in comparison with the price of the caproic acid and it is, therefore, advisable to use potassium hydroxide.

After the butyl malonic ester has been saponified to the butyl malonic acid, several ways of decomposing it to caproic acid besides the method described above were carried out. First, the solution of the potassium salt of the butyl malonic acid was acidified, cooled and extracted twice with ether. This ether solution was dried with calcium chloride and the solvent evaporated. Butyl malonic acid remained behind, which by heating to 160–170°, decomposed rapidly and gave off carbon dioxide. Care had to be taken to condense all the caproic acid which was carried along with the carbon dioxide. Starting with 250 g. of ester, 154 g. (57% of the theoretical amount) of acid thus resulted. Second, the potassium salt of the butyl malonic acid was acidified, refluxed in the way described above and then after cooling, the caproic acid was extracted directly with ether. Under these conditions, some tarry products were always obtained with the caproic acid and the yield of pure material amounted to not over 63% of the theoretical amount. Third, the potassium butyl malonate was made and acidified as in the second procedure just described. Instead of extracting with ether at this point, a steam distillation was carried out until no more caproic acid came over. It required a distillate of 3 to 4 liters before all of the caproic acid was obtained. This distillate was salted out with calcium chloride, the caproic acid separated and dried in the usual way, then distilled. Not over 66% of the theoretical amount resulted. The larger yields of about 75% when the procedure is carried out as in the main experiment, may be due to the longer heating with the acid, during the process of distilling off the caproic acid after it is first formed. At any rate this method, giving the best yields, is at the same time the most convenient one.

If the butyl malonic ester is not heated 1 to 2 hours with alkali, a little acid ester remains undecomposed. This yields upon acidification and decomposition ethyl caproate, a substance which can not be removed easily from the caproic acid by simple distillation.

The methods for the production of caproic acid described in the literature are of two types, that by fermentation and that by synthetic reactions. Thus in the fermentation process for the production of butyric acid, a considerable amount of caproic acid is obtained as a by-product;[1] also good yields of caproic acid result from the fermentation of bran with *mycrozyma*.[2] These methods, however, require a long period of time and particular care in the regulation of the conditions of the reaction. As laboratory procedures they are practically useless. Moreover, there are obtained in these reactions other acids and by-products which are difficult to remove. The synthetic methods described in the literature give in practically every case a clean product, but the cost of the raw material makes these methods almost prohibitive. Thus *n*-amyl cyanide on hy-

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[1] *Z. Chem.*, 1868, p. 522.

[2] *Ibid.*, 1868, p. 430; 1869, p. 308.

drolysis[1] gives very good results; to produce this cyanide, however, requires starting with *n*-valerianic acid, a substance none too common, converting it first into the aldehyde, then to the alcohol, next to the halide and finally to the cyanide. A second synthetic process has appeared which involves the oxidation of *n*-hexyl alcohol,[2] but here the same difficulty, namely, the scarcity of hexyl alcohol, presents itself. A more recent method using certain decomposition reactions of piperidine[3] is almost as impractical as the preceding ones. Finally, the oxidation of castor oil[4] with nitric acid yields an appreciable amount of caproic acid. This method, however, gives only a small yield of product and at the same time a mixture of substances from which the pure acid must be fractionated.

α-Bromocaproic Acid, Preparation.—In a 1.5-liter round-bottom flask, 216 g. of potassium hydroxide is dissolved in 216 cc. water. To the hot solution 216 g. (1 mol.) of butyl malonic ester is added in portions (10–15 min.), shaking after each addition. The saponification proceeds rapidly. The reaction mixture is then heated for 1.5 hours on a steam bath to complete the reaction and to remove the alcohol which is formed. The flask is set in an ice-salt bath and cooled to 0°, after which the solution is made acid to congo red paper by adding conc. hydrochloric acid (about 500 cc. of acid of sp. gr. 1.19). The butyl malonic acid is now extracted with ether, 3 portions of 200–250 cc. each being used. The ether solution without drying is placed in a flask under a reflux condenser and 50 cc. of bromine (1 mol) is gradually run in (1.5 hr.). The reaction is started at room temperature but the temperature soon rises until the ether boils. The ether solution is now washed with water to remove the hydrobromic acid, dried over calcium chloride and then distilled until all the ether is removed. The crude bromobutyl malonic acid is heated in an oil bath to 125–130° until no more carbon dioxide is given off and the bromocaproic acid thus formed is distilled under diminished pressure. A very small fraction of low boiling material, probably caproic acid, and then the main fraction of α-bromocaproic acid boiling at 148–153° at 30 mm. are obtained. Practically no higher boiling fraction remains. On the first vacuum distillation it often happens that a little carbon dioxide comes off, making it almost impossible to get a constant pressure. Hence, it is advizable to distil all the material over first and then redistil with careful fractionation. The yield of product is 140 g. (71% of the theoretical amount.)

Discussion of Reaction.—α-Bromocaproic acid has thus far been made by the action of bromine on caproic acid in a sealed tube at 140–145°[5]

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[1] *Ann.*, **159**, 75 (1871).

[2] *Ibid.*, 163, 199 (1872).

[3] *Ber.*, **43**, 3599 (1910).

[4] *Bull. soc. chim.*, [3] 11, 99 (1894).

[5] *Ann. Suppl.*, **2**, 78 (1862); *J. prakt. Chem.*, [2] **1**, 6 (1870).

or by the action of bromine and phosphorus on caproic acid and subsequent hydrolysis of the acid bromide,[1] but neither of these methods is as easy as the one just described.

α-Aminocaproic Acid.—Several experiments were carried out to produce α-aminocaproic acid from α-bromocaproic acid. The exact method of Abderhalden[2] was used, 140 g. of the bromo acid being employed in each run. The yield of pure product amounted to about 61 g. The first crop of crystals was about 45 g. and the second crop obtained by concentration of the mother liquors to crystallization and addition of an equal volume of alcohol gave 16 g. Further treatment of the mother liquors as described by Abderhalden did not increase the yield appreciably. The material, after washing with alcohol, is practically pure; if small amounts of colored products are present, they are easily removed by crystallization from water.

Discussion of Reaction.—This preparation has already been described in several communications and has been made by the action of ammonia on α-bromocaproic acid,[3] the details being given in the paper by Abderhalden.[4] This investigator claims 100% yields but in the experiments carried out in this laboratory following his directions, only 65% yields of pure product were obtained.

Summary.

1. It has been pointed out that the commercially available *n*-butyl alcohol is a valuable material for the preparation of (A) *n*-amyl derivatives, and (B) *n*-caproic acid and its derivatives.

2. Detailed directions are given for the production of *n*-butyl cyanide, *n*-valeric acid, ethyl *n*-valerate, *n*-amyl amine, *n*-amyl alcohol, *n*-caproic acid, α-bromo-*n*-caproic acid and α-amino-*n*-caproic acid.

URBANA, ILL.

NEW BOOKS.

Notes on Qualitative Analysis. By LOUIS AGASSIZ TEST AND H. M. MCLAUGHLIN. Ginn and Company, 1919. iv + 92 pp. 13.5 × 19.5 cm. Price, $0.80.

The book contains 24 pages given to the development of the theory of solutions and the law of mass action, followed by directions for experiments on the reactions of the common metallic and non-metallic radicals and tables for use in systematic analysis. A list of 162 questions for students is appended, based upon the practice and theory of qualitative analysis. The periodic table of the elements and a table of atomic weights conclude the volume.

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[1] *Z. physiol. Chem.*, **16**, 454 (1913).

[2] *Ibid.*, **86**, 454 (1913).

[3] *J. prakt. Chem.*, [2] **1**, 6 (1870); *Ber.*, **33**, 2370 (1900); *Z. physiol. Chem.*, **86**, 454 (1913).

[4] *Z. physiol. Chem.*, **86**, 454 (1913).