TWO COMMUNICATIONS.

BY L. H. FRIEDBURG, PH.D.

I.—On a New Fat Extractor for Laboratories, by J. Graftiau, of Gembloux.

II.—On Curtius' Hydrazin.*

I.

My friend, Prof. A. Peterman, of Gembloux, Belgium, sent me a report on a new fat extractor, used in his laboratory and constructed by one of his assistants. Since I find it original and valuable enough to be described here, I do not hesitate to do so, hoping that some chemist may find it useful in his special work. I remark, that this apparatus has meanwhile been described in the November number of the Philadelphia *Textile Colorist,* from which this description is taken; it is reproduced here, as it may reach, through this journal, a different class of chemists who may wish to use it.

The different well known extractors for the analytical determination of fats and oils need not be enumerated here. The new one claims mainly two advantages over the others, particularly over those of Soxhlet and of Petermann and Simon. They are:

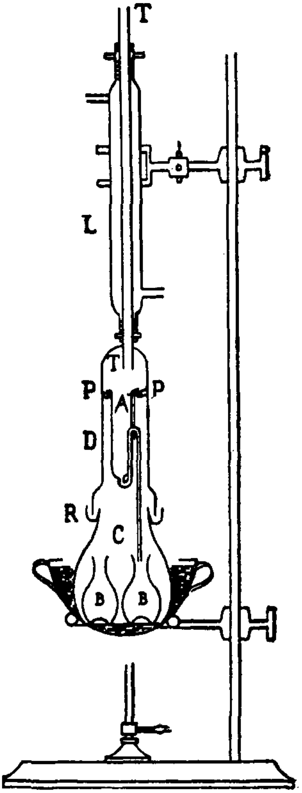
1st. No corks are used from which the solvent eventually extracts substances which would add to the weight of the fat in the sample to be extracted.

2d. At the end of the operation the ether that had been used for extraction is found in one flask, while the extracted fat, ready for weighing is contained in the flask standing alongside the first mentioned, within the same apparatus.

The apparatus consists of the following parts: 1st. A syphon digestor, A, in which the substance to be analysed is placed. The edge of the syphon has a rather broad rim, cut out symmetrically at three points.

---

*See also: Amer. Chem. Journ. Vol. XI., No. 2, Feb., 1889, pp. 142-144.



2d. Two little flasks B B, the one of which of known weight is destined to receive the extracted fat, while the other one contains the ether, or whatever solvent is used.

3d. The receiver, C, in which the two little flasks stand. Concentric with the upper end of this receiver runs a glass groove or channel R, into which the head piece D, fits. A perfect joint is secured by pouring mercury into the groove.

4th. The headpiece D, in which the digestor is fixed. It ends above in the long tube T, the condensing tube for the vapor of the solvent. At two-thirds of the height of the headpiece on its inside, three little knobs P, are attached upon which rests the rim of the digestor.

5th. The glass tube, T, is fused into the headpiece before the glass blowpipe. It runs as a condensing tube through the Liebig's condenser, L.

The mode of operation of this apparatus is as follows :

The apparatus being perfectly clean and dry, the two little flasks, one of which has been previously weighed and the other one containing ether are put into the receiver. The substance to be extracted, also weighed, enveloped in a filter is put into the digestor, which is suspended inside the headpiece. The digestor with its three cuts in the rim is given a little turn until it passes the knobs and then it is turned again slightly, now resting solidly upon them.

The headpiece is then adapted to the lower part of the apparatus and the mercury forms a joint perfectly proof against the vapors of ether. The digestor must be arranged so that the phon empties into the neck of the little weighed flask as far own as .5 to 1 cm. Heat is supplied by a water bath.

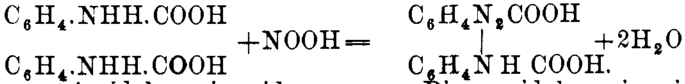
Towards the end of the extraction, when the ether does not carry any more fatty matter down from the sample into the weighed flask, the water bath is very slightly lowered (about 1 cm.) and the receiver C is given a turn half round, so that the syphon of the digestor now dips into that one of the little flasks B B, which at the beginning of the operation contained the ether. The water bath is adjusted again and the ether collected in the flask in which it was originally contained, while the extracted fatty matter alone remains in the weighed flask. This latter is allowed to dry and cool and is then weighed.

II.

Hydrazin, discovered by Dr. Theodor Curtius, of Erlangen, is, beyond doubt, one of the most interesting of compounds which have recently been made known. The reaction by means of which it is prepared is a decomposition, and an astonishing one, which offers many new suggestions. Generally speaking, the mode of formation of this substance excludes decidedly any preformed wish or intention, on the part of Curtius, of building it up. It was found in the true way of all scientific research, *i. e.*, by careful experiment in a cleverly chosen direction, with no other object than to reveal the truth by conscientious work. About four years ago Curtius began to study in this direction and he has been so fortunate as to find, in the beginning of this year, a substance more interesting than could have been anticipated.

Peter Griess discovered, almost 30 years ago, a class of chemical compounds called diazo compounds. Quite a number of them are well known dyes, and now largely used. Griess' reaction consisted in allowing nitrites to act on the mineral acid salts of organic, and especially of aromatic, amido compounds. Or he allowed nitrous acid to act upon the corresponding amido body, free, or combined with a mineral acid.

For example: *



$$\begin{array}{l} C_6H_4.NHH.COOH \\ C_6H_4.NHH.COOH \end{array} + NOOH = \begin{array}{l} C_6H_4N_2COOH \\ \quad\;\; | \\ C_6H_4N\,H\,COOH. \end{array} + 2H_2O$$

Amidobenzoic acid. Diazoamidobenzoic acid.

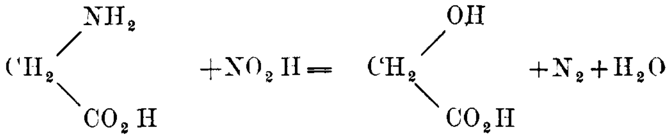
---

* Zeitschrift fur Chemie; 1866, 217.

The group which is characteristic of the diazo compounds is the bivalent group $<\text{——}N=N\text{——}>$.

Griess successfully explored this reaction in the broadest possible manner, and was followed by a number of other chemists, but no one ever tested thoroughly the consequences of this reaction in the fatty series, which is what Curtius has just done and with remarkable success.

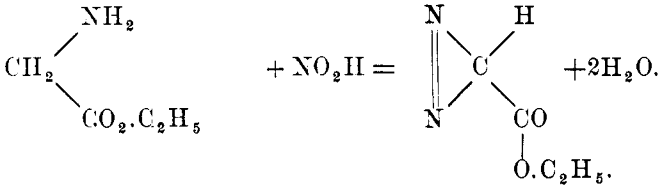
A simple amido acid of the fatty series is the amidoacetic acid, also called glycocoll, because of its sweetish taste and because it can be prepared from glue. Instead of treating glycocoll directly with nitrous acid, the hydrochloric acid salt of its ethyl ester is used, because a direct treatment of glycocoll with nitrous acid leads to the formation of an oxy-acid, thus :



$$CH_2(NH_2)(CO_2H) + NO_2H = CH_2(OH)(CO_2H) + N_2 + H_2O$$

Glycocoll. Glycollic acid.

While the ether similarly treated, yields

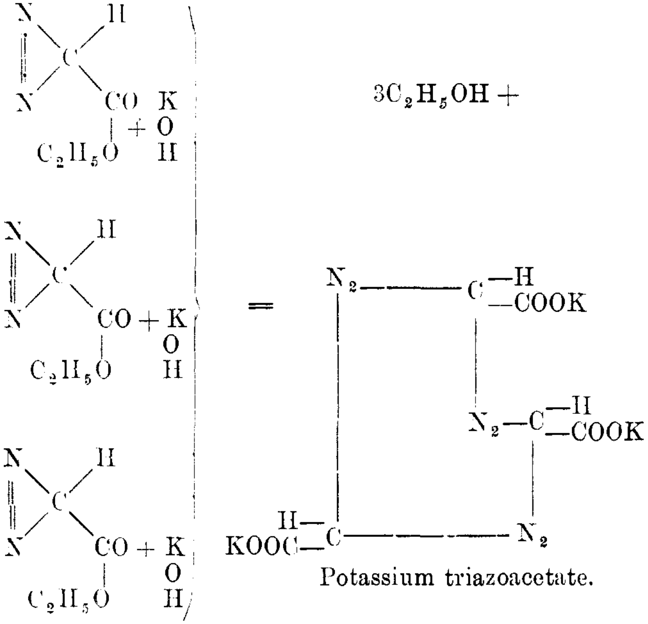


$$CH_2(NH_2)(CO_2.C_2H_5) + NO_2H = (N{=}N)C(H)(CO.O.C_2H_5) + 2H_2O.$$

Glycocoll ethyl ester (or its H Cl salt). Diazoacetic ester.

So differently runs the reaction when different attractive and repulsive chemical forces come into play, as in the substitution of C_2H_5 for one H of the carboxyl group.

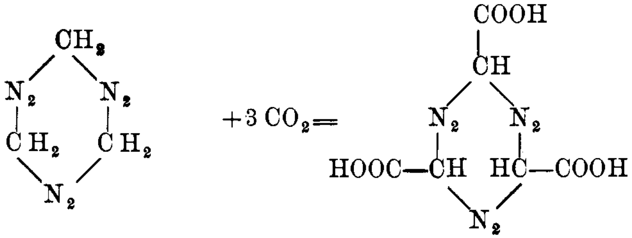
When the newly formed diazo compound is treated with caustic alkalies, *i.e.*, is saponified, we obtain salts of triazoacetic acid, $C_3H_3N_6(COOM)_3$, as follows :



Potassium triazoacetate.

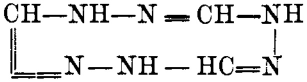
The free acid crystallizes in golden yellow leaflets or in glittering orange colored prisms, melting at 151°. The molecular size of the compounds was ascertained by means of the triazoacetic ethers. The salts of the acid have the normal composition, $C_3H_3N_6(CO_2R)_3$. The potassium salt, for instance, forms orange-yellow prisms of any size. Triazoacetamid is formed by directly heating diazo acetic ether with concentrated aqueous ammonia ; it crystallizes in yellow leaves, which do not melt at 300°.

Already at 60° triazoacetic acid splits off its carboxyl groups in the form of carbon dioxide. There remains a substance, $C_3H_6N_6$, crystallizing from a mixture of ether and alcohol in long, colorless hygroscopic needles. The molecular weight of this substance was also determined. Triazoacetic acid can therefore be considered as the tri-carbon acid of this substance, $C_3H_6N_6$ and, more exactly as tri-carbon acid of triazotrimethylene.



Triazotrimethylene. Triazoacetic acid.

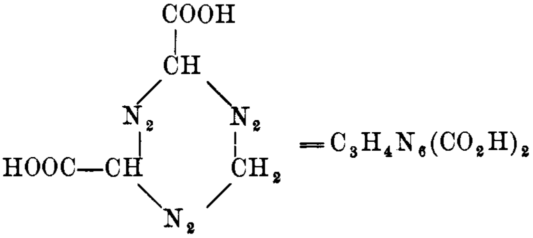
But, since the substance obtained from triazoacetic acid by loss of carbon dioxide, is a *colorless* one, it does *not* contain any diazo-groups. We can assume that one hydrogen atom of the methylene groups has been attracted by the nitrogen, so that the formula for the body $C_3H_6N_6$ finds the following expression :



The behavior of this substance compels the admission that it contains imido groups. It forms with argentic nitrate and with mercuric chloride well characterized double salts of the composition

$$C_3H_6N_6 + 2NO_3\,Ag \text{ and } C_3H_6N_6 + 3HgCl_2.$$

When triazoacetic acid is treated with alkali, carbon dioxide is split off, and, as an intermediate product, a dicarbo acid is formed;



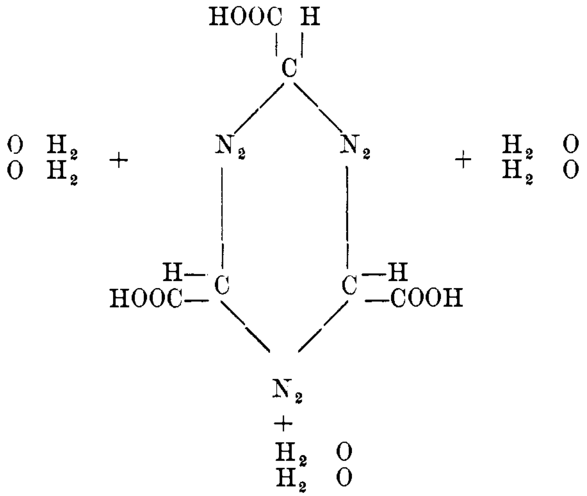
$$= C_3H_4N_6(CO_2H)_2$$

but eventually a substance forms that has, for the simplest expression of its composition, the formula $(C\,N_2\,H_2)_x$, but which is not identical with the body $C_3 H_6 N_6$. The substance forms a normal, colorless silver salt $(CN_2 Ag_2)_x$, being an entirely different body from cyanamid.

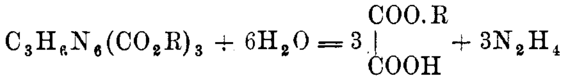
An entirely new reaction takes place when triazoacetic acid is boiled with water or with dilute mineral acids. The condensation ring is then broken and the products of decomposition are carbon dioxyde, formic acid and *hydrazin.*

$$C_3H_3N_6(COOH_3) + 6H_2O = 3CO_2 + 3H.COOH + 3N_2H_4$$

or better, graphically :



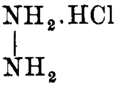
Triazoacetic ether is correspondingly decomposed according to the equation



$$C_3H_6N_6(CO_2R)_3 + 6H_2O = 3 \begin{array}{l} COO.R \\ | \\ COOH \end{array} + 3N_2H_4$$

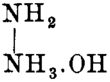
i.e., into oxalic ether and hydrazin.

If we boil with dilute sulphuric acid, the hydrazin sulphate, which is very insoluble, separates at once in glittering prisms. The hydrazin forms beautifully crystallizing salts of which the bichlorhydride forms, like ammonium chloride, regular octahedrons. If this latter salt be heated to 170°, a monochlorhydride is formed, crystallizing in long needles of the formula



$$\begin{array}{l} NH_2.HCl \\ | \\ NH_2 \end{array}$$

The composition gives the molecular weight of hydrazin. Free hydrazin (or diamide) is formed when salts of hydrazin are heated with caustic alkali in a silver still, the vapors being conducted over quicklime. It is a gas of peculiar odor, and but very feebly suggesting ammonia. Since hydrazin attracts water in a very high degree it readily forms a hydrate, which fumes in contact with air, boils without decomposition at 119° and corresponds to the formula



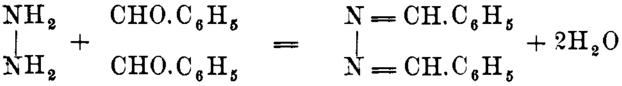
$$\begin{array}{l} NH_2 \\ | \\ NH_3.OH \end{array}$$

Hydrazin is the strongest reducing agent known ; it separates the heavy metals even from their *neutral* salt solutions, for instance, platinum from the solution of its chloride.

In all these reactions the nitrogen escapes as a gas.

If hydrazin sulphate be heated to its melting point (254°), the sulphuric acid radical is not only reduced to sulphur, but even to hydrogen sulphide, and this reaction takes place with explosive force.

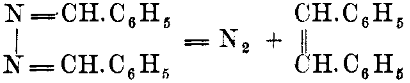
Since hydrazin possesses two amido groups of even value, it combines with two molecules of aldehydes. The resulting compounds are bodies of beautiful crystalline form, almost insoluble in water, and are represented as follows :



$$\begin{array}{l} NH_2 \\ | \\ NH_2 \end{array} + \begin{array}{l} CHO.C_6H_5 \\ \\ CHO.C_6H_5 \end{array} = \begin{array}{l} N = CH.C_6H_5 \\ | \\ N = CH.C_6H_5 \end{array} + 2H_2O$$

Benzaldehyde. Benzal-azin.

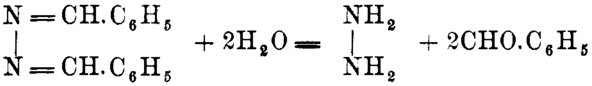
This benzal-azin is the best form of obtaining hydrazin pure from mixtures. The benzal-azin crystallizes from alcohol in long, light yellow needles, which melt at 93°, and which, when subjected to distillation, decompose evenly into nitrogen and stilbene :



$$\begin{array}{l}\mathrm{N=CH.C_6H_5}\\ |\\ \mathrm{N=CH.C_6H_5}\end{array} = \mathrm{N_2} + \begin{array}{l}\mathrm{CH.C_6H_5}\\ \|\\ \mathrm{CH.C_6H_5}\end{array}$$

Benzal-azin. Stilbene.

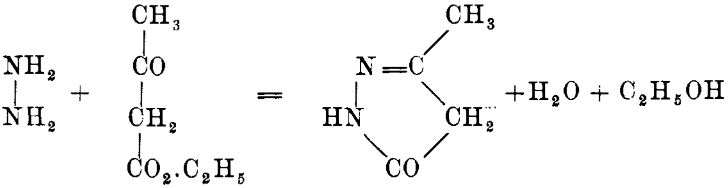
When benzal-azin is boiled with acids the aldehyde is regenerated and the corresponding salt of hydrazin is formed :



$$\begin{array}{l}\mathrm{N=CH.C_6H_5}\\ |\\ \mathrm{N=CH.C_6H_5}\end{array} + \mathrm{2H_2O} = \begin{array}{l}\mathrm{NH_2}\\ |\\ \mathrm{NH_2}\end{array} + \mathrm{2CHO.C_6H_5}$$

A quite analogous behavior is shown by all the other compounds of aldehydes with hydrazin.

On the other hand, acetacetic ether combines with one molecule of hydrazin, simultaneously losing water and alcohol, to form methyl-pyrazolon, a substance crystallizing in colorless prisms and melting at 216°, thus :



Acetacetic ether. Methyl-pyrazolon.

In methyl-pyrazolon the hydrogen of the imido group can be replaced by silver.

Hydrazin will also unite to form crystallizing compounds with ketones, such as acetophenon or benzil.

College of the City of New York, November, 1888.*

---

* Printed in October number because of previous delay in publication.