

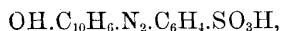
XLI.—*Contributions to the History of the Naphthalene Series.*  
*β-Naphthaquinone.* Part II.

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IN a short preliminary note published in the *Chemical News* (45, 267) some time ago, on the preparation of  $\beta$ -naphthaquinone from " $\beta$ -naphthol orange," as proposed by Liebermann (*Ber.*, 14, 131; *Annalen*, 211, 51), I pointed out the disadvantages of this method as compared with that originally described by Stenhouse and myself, and I now purpose to lay before the Society a detailed account of the experiments, and also some further contributions to the history of  $\beta$ -naphthaquinone and its derivatives.

*Preparation of β-Naphthaquinone from β-Naphthol Orange.*

In the communications referred to above, Liebermann recommends the sodium salt of  $\beta$ -naphthol-diazobenzene-sulphonic acid,



known commercially as " $\beta$ -naphthol orange," as the best material from which to prepare  $\beta$ -naphthaquinone. The process consists in treating the  $\beta$ -orange with hydrochloric acid and stannous chloride in excess, so as to decompose it and convert it into a mixture of par-amidobenzenesulphonic acid with the stannochloride\* of amido- $\beta$ -naphthol. The amido- $\beta$ -naphthol is then separated from this mixture by dissolving it in water, precipitating the tin by hydrogen sulphide,

\* It is preferable to use the term *stannochloride*, instead of "*double tin salt*," for compounds of the formula  $\text{RCl} \cdot \text{SnCl}_2$ , &c., in the same way that "*platinochloride*" is now almost universally substituted for "*double platinum salt*."

separating the stannous sulphide by filtration, and evaporating in a current of hydrogen sulphide to remove excess of hydrochloric acid; the crystalline mixture of amido- $\beta$ -naphthol hydrochloride with sulphanilic acid is then treated with a concentrated solution of sodium carbonate, and the free amido- $\beta$ -naphthol extracted by agitation with ether, of which large quantities are required, as the base is but sparingly soluble in it. On distilling off the ether, the base is left in the crystalline state, and is then converted into sulphate and oxidised to  $\beta$ -naphthaquinone in the manner described by Stenhouse and myself (*Chem. Soc. J.*, 1877, ii, 47, and *Trans.*, 1878, 415). As it seemed to me that this method of obtaining the amido- $\beta$ -naphthol sulphate was very troublesome and tedious, I carefully repeated Liebermann's experiments, and although I can confirm his statements as to the results, I must dissent from his opinion that the process affords a convenient means of preparing  $\beta$ -naphthaquinone in quantity. The decomposition of the stannochloride by hydrogen sulphide, and the subsequent evaporations, extraction with ether, &c., render the process unwieldy when any considerable quantity of material is operated on, quite irrespective of the unavoidable loss of ether. If, on the other hand, we attempt to precipitate the  $\beta$ -naphthaquinone from the solution directly by an oxidising agent, without first separating the sulphanilic acid, the product is unsatisfactory, both in quantity and in quality, whether the tin has been removed by precipitation with hydrogen sulphide or with zinc.

It was evident that in order to render Liebermann's process at all workable, some means must be devised to obviate the treatment with hydrogen sulphide, and to separate the regenerated sulphanilic acid without resorting to agitation with ether, &c. A few preliminary experiments showed that these difficulties could be overcome, the first by avoiding the use of the large excess of stannous chloride recommended by Liebermann, and the second by removing the sulphanilic acid as sodium salt. When  $\beta$ -naphthol orange is heated with stannous chloride and hydrochloric acid in slight excess over that required by the equation  $\text{OH.C}_{10}\text{H}_6\text{.N}_2\text{.C}_6\text{H}_4\text{.SO}_3\text{Na} + 2\text{SnCl}_2 + 6\text{HCl} = \text{OH.C}_{10}\text{H}_6\text{.NH}_2\text{.HCl} + \text{NH}_2\text{.C}_6\text{H}_4\text{.SO}_3\text{H} + 2\text{SnCl}_4 + \text{NaCl}$ , the diazo-compound is completely decomposed, and, on cooling, the amido- $\beta$ -naphthol crystallises out, not as stannochloride, but as hydrochloride, mixed of course with sulphanilic acid; in this way the amount of stannous chloride is reduced by 50 per cent., and the necessity for precipitating large quantities of tin as sulphide is avoided.

A mixture of 100 c.c. of stannous chloride solution (containing 40 grams of tin) with 110 c.c. of hydrochloric acid, sp. gr. 1.16, is poured on to 60 grams of the  $\beta$ -orange in a flask and well shaken; reduction takes place rapidly, and in about 10 minutes' time the mix-

ture becomes of a pale pink colour; 300 c.c. of boiling water is then added, and the whole boiled for a few minutes, when the product dissolves, all but a little black tar which can be separated by filtering hot, best through a vacuum filter. As the liquid cools, a mixture of amido- $\beta$ -naphthol hydrochloride with sulphanilic acid separates, whilst the tin remains in solution as stannic chloride, and may be separated by filtration. On concentrating these mother-liquors and adding strong hydrochloric acid, the remainder of the amido-compound may be recovered as hydrochloride, this being almost insoluble in strong hydrochloric acid.

In order to effect the separation of the base from the sulphanilic acid, the mixture is treated with sodic hydroxide in quantity sufficient not only to combine with the sulphanilic acid, but also to set free the amido- $\beta$ -naphthol from its hydrochloride. As the free base is almost insoluble in water, the sodium sulphanilate and chloride are easily washed out, and the free base can then be converted into hydrochloride or sulphate. The process is carried out as follows:—The crystalline product from 60 grams of the  $\beta$ -orange is collected, dissolved in 180 c.c. boiling water, and cooled quickly with agitation, so as to deposit the mixed sulphanilic acid and amido-hydrochloride in a finely divided state; 20 c.c. of a normal soda-solution (containing 40 grams NaHO in 100 c.c.) are then added with constant stirring, and after 10 minutes, 10 grams of hydrogen sodium carbonate, the object of this being to convert the excess of sodium hydroxide into carbonate. The mixture is occasionally stirred, and after the lapse of another 10 minutes, the free amido- $\beta$ -naphthol is collected on a vacuum-filter and washed with 180 c.c. water, which has been partly saturated with hydrogen sulphide, to prevent the free base from becoming oxidised during the washing; the treatment with soda and subsequent collection and washing being conducted as rapidly as possible to avoid loss by oxidation. In this way the sulphanilic acid is removed as sodium salt, and may be recovered from the filtrate by evaporating it and precipitating with hydrochloric acid. The moist amido-base may at once be converted into hydrochloride by boiling it with 200 c.c. water and 12.5 c.c. of concentrated hydrochloric acid. The yield of crystallised amido- $\beta$ -naphthol hydrochloride obtained by these means is from 35–39 per cent. of the weight of the  $\beta$ -orange. This agrees very nearly with the result obtained by Liebermann (38 per cent.) by the troublesome process of decomposing the stannochloride with hydrogen sulphide, extracting the base by agitation with ether, and subsequently converting it into the hydrochloride.

From the results formerly obtained with nitroso- $\beta$ -naphthol\*, it

\* I have retained the name *nitroso- $\beta$ -naphthol* in this paper, for although I am

seemed possible that ammonium or sodium sulphide might be employed for reducing the diazo-compound, and that this, on the small scale, would have an obvious advantage over the stannous chloride method, inasmuch as the sulphanilic acid would remain in solution as ammonium or sodium salt. The following was found to be the most advantageous mode of carrying out the process:—2 parts of the  $\beta$ -naphthol orange are dissolved by boiling in 1 part of the normal soda-solution above-mentioned diluted with 6 of water, and a rapid current of hydrogen sulphide is passed through the hot solution. At first the gas is absorbed without any apparent change, but soon the free base begins to separate in lustrous plates, and the brilliant red solution becomes of a dingy brown. The crystals rapidly increase in number, and after a time, when the red colour has entirely disappeared and the gas is no longer absorbed by the yellow solution of sodium polysulphide, the flask is tightly corked, allowed to remain for 18—20 hours, and then again saturated in the cold with hydrogen sulphide. The object of this second treatment with hydrogen sulphide is to precipitate the last portions of amido-naphthol, as it is insoluble in solutions of sodium sulphide saturated with hydrogen sulphide, although it is readily soluble if any free alkali is present.

The free base, which is mixed with more or less sulphur, but is quite free from sulphanilic acid, is collected on a vacuum filter, and washed with 200 c.c. dilute hydrogen sulphide solution, to remove the sodium sulphide and sodium sulphanilate; it may then be converted into the hydrochloride in the manner already described, using the same proportions of hydrochloric acid and water. The yield of hydrochloride is from 35—37 per cent. of the weight of the  $\beta$ -orange. If the experiment of reducing the  $\beta$ -orange with hydrogen sulphide is made on a small scale—10 to 15 grams—it is advisable to keep the vessel hot by immersing it in a water-bath, at all events until the free base begins to crystallise out; with larger quantities, however, this is unnecessary, as the heat developed during the reaction is sufficient to maintain the temperature. The reduction may also be effected by passing hydrogen sulphide into the  $\beta$ -orange mixed with aqueous ammonia, but it is less convenient, for the reaction does not take place as readily as with sodium hydrogen sulphide; moreover, the volatility of the ammonium sulphide is an objection.

*Preparation of Amido- $\beta$ -Naphthol from Nitroso- $\beta$ -Naphthol.*

Nitroso- $\beta$ -Naphthol.—In a former paper (*Chem. Soc. J.*, 1877, ii, 47) a method was given for preparing nitroso- $\beta$ -naphthol, which inclined to regard it as belonging to the class of hydroximido- or isonitroso-compounds, the evidence we have as to its constitution is inconclusive at present.

yielded very satisfactory results. At the present time, nearly pure sodium nitrite is made on the large scale for use in the coal-tar colour industry, and it would obviously be an advantage if a commercial article like this could be employed, instead of nitrosyl sulphate which has to be made in the laboratory. A few preliminary trials rendered it evident that nitroso- $\beta$ -naphthol might be prepared by this means with the greatest ease, even on the large scale. A solution of sodium  $\beta$ -naphthol and sodium nitrite is first made by boiling 4 parts of  $\beta$ -naphthol with 3 parts by measure of the normal soda-solution and 8 parts of water, until the naphthol has completely dissolved, and adding it to a solution of 3 parts of sodium nitrite in 300 of cold water. This solution is then poured, with constant stirring, into 5 parts by measure of sulphuric acid, diluted with 2000 of water; the mixture assumes a deep orange colour, then a black tarry scum separates on the surface, but on continuing to stir for a few minutes, the deep yellow nitroso-compound is formed, and the scum disappears. The mixture is stirred occasionally during the next hour or so, and then allowed to remain until the next day, when the crude nitroso- $\beta$ -naphthol may be collected, and washed with a little water. In order to purify it, the moist paste is made up to 140 parts with water, mixed with 4 parts normal soda-solution previously diluted with 140 of water, and filtered (on the large scale it is better to employ a Taylor's bag filter with a head of 6—8 feet of the liquid). It is important to dissolve the crude product precisely in the manner described, as if concentrated soda-solution is added to the mixture, more or less of the green crystalline sodium-derivative of nitroso- $\beta$ -naphthol is at once precipitated, and dissolves again with great difficulty; this does not occur if the soda-solution is dilute. The clear filtrate (280 parts) containing sodium nitroso- $\beta$ -naphthol is then mixed with 16 parts of the normal soda-solution; this throws down the sodium-derivative as a bright green crystalline powder, as it is but very sparingly soluble in solutions containing free sodium hydroxide. The green precipitate is collected, and if necessary purified by washing it with dilute soda-solution (4 parts of the normal solution to 40 of water). When decomposed by dilute hydrochloric acid, it yields nearly pure nitroso- $\beta$ -naphthol, which may be further purified by crystallisation in the manner previously described (*loc. cit.*).

In dissolving the crude nitroso-derivative in soda-solution, it is advisable to use ordinary river or well water, as the small quantity of insoluble calcium nitroso- $\beta$ -naphthol formed greatly facilitates the filtration; when considerable quantities are operated on, it is worth while to recover this from the insoluble residue by treating it with dilute hydrochloric acid at the ordinary temperature for a day or two, washing until nearly free from acid, and extracting the nitroso-

naphthol with very dilute soda-solution. It may then be precipitated by acid and purified along with a fresh batch of the crude nitroso.

**Amido- $\beta$ -naphthol Hydrochloride**,  $\text{OH.C}_{10}\text{H}_6\text{.NH}_3\text{Cl}$ . — This may be prepared from the sodium-derivative of nitroso- $\beta$ -naphthol, by reducing it with ammonium or sodium sulphide in the same way as described for the  $\beta$ -orange. The sodium salt from 1 part  $\beta$ -naphthol is mixed with 8 of water, a little ammonia or soda-solution added, and a slow current of hydrogen sulphide is passed into it, heating gently to about  $40^\circ$ , at first, to start the reaction; when the liquid is nearly saturated with the gas, the temperature is raised to  $100^\circ$ , and the rest of the operation conducted precisely as in the case of the diazo-compound. This method, although very convenient for obtaining small quantities of the free base, is not adapted for the preparation of the hydrochloride on the large scale, firstly, owing to the large quantities of hydrogen sulphide required, and secondly, the product is almost always more or less coloured, apparently by the product of a secondary reaction between the free amido-base and the nitroso-derivative in alkaline solution. On the small scale, however, the base is obtained in almost colourless crystals.

When the hydrochloride is required in quantity, the best method is to act on the sodium nitroso-naphthol with hydrochloric acid and stannous chloride, using sufficient merely to reduce it to the amido-derivative without forming the stannochloride. For this purpose it is unnecessary to prepare the nitroso-naphthol from its sodium-derivative; in fact, the latter being a somewhat dense crystalline powder, is far more convenient to operate upon than the felted mass of fine needles in which the free nitroso-compound separates from its metallic derivatives. The moist sodium-derivative from 4 parts  $\beta$ -naphthol, prepared in the manner already described, is made up with water until the bulk is 80 parts, and the thin creamy liquid thus obtained is poured in a slender stream with constant stirring into a mixture of 15 parts by measure of hydrochloric acid, sp. gr. 1.16, with 14 of a solution of stannous chloride (100 c.c. = 40 grams Sn) in a capacious beaker. The first portions dissolve completely, the solution acquiring a brownish tint; but as more of the sodium salt is added, white crystals begin to form, the mixture becomes warm, and the sodium salt is reduced and converted into the amido-naphthol hydrochloride, as fast as it comes in contact with the acid solution. Care must be taken, however, to add the solution gradually and with constant stirring, otherwise dark-coloured secondary products will be formed, which are very difficult to remove. The mixture is left to itself for an hour with occasional stirring, and the beaker is then heated in the water-bath until the crystals are dissolved, and nothing but a small quantity of a dark-coloured flocculent substance is left

suspended in the liquid; owing to its mucilaginous nature, it is, however, practically impossible to remove this by filtering the *hot* solution, and a somewhat indirect method of separating it has to be adopted. The hot solution is therefore allowed to cool slowly; next day a cake of crystals will be found at the bottom of the beaker resting on the finely divided impurities; the supernatant clear liquid is then syphoned or poured off, and the crystals are freed from the impurities by elutriation, using for this purpose successive quantities of the clear liquid which has been poured off; when the washings are clear, the crystals of amido-naphthol hydrochloride may be collected. A large proportion of the substance, however, still remains in solution; this is filtered, concentrated by evaporation, and the crystals are collected and washed with dilute hydrochloric acid, in which they are almost insoluble. The yield of crude amido-hydrochloride is from 100 to 105 per cent. of the weight of the  $\beta$ -naphthol originally employed. As it oxidises somewhat rapidly when exposed to the air in the moist state, it should either be at once converted into  $\beta$ -naphthaquinone, or preserved under a dilute aqueous solution of sulphur dioxide in a well closed bottle nearly filled with the substance. If the pure hydrochloride is carefully dried at  $100^{\circ}$ , and introduced into a well stoppered bottle while hot, it may be preserved without undergoing oxidation, but heat appears to have caused some change, as the  $\beta$ -naphthaquinone prepared from it is dark coloured; this impurity is removed by recrystallisation from water, but is again formed on drying the crystals at  $100^{\circ}$ .

In order to purify the amido- $\beta$ -naphthol hydrochloride, it is dissolved in 8 parts of boiling water, a little sulphurous acid solution added, the liquid is filtered, and to the boiling filtrate is added about 5 per cent. of its bulk of strong hydrochloric acid. As the hydrochloride is but sparingly soluble in dilute hydrochloric acid, the greater part separates in the crystalline state as the solution cools; that which remains dissolved may be recovered by boiling the solution down rapidly without access of air. The hydrochloride is much less soluble in cold than in hot water, and requires nearly 15 parts of boiling spirit to dissolve it.

When the hydrochloride of the base is oxidised by passing a current of air through its cold aqueous solution (1 part in 40 of water) by means of an aspirator, a bluish-black substance is formed, which is insoluble in hydrochloric acid, but dissolves in concentrated sulphuric acid with blue colour, and is reprecipitated on adding water to the solution. It is oxidised by nitric acid and by chromic mixture, but without formation of  $\beta$ -naphthaquinone, and when treated with alcoholic stannous chloride, it is reduced and dissolved. The nature of this substance has not as yet been investigated.

Amido- $\beta$ -naphthol sulphate, formed by dissolving the base in warm



dilute sulphuric acid crystallises easily, but is less soluble than the hydrochloride. The base does not seem to form salts with acetic or oxalic acid.

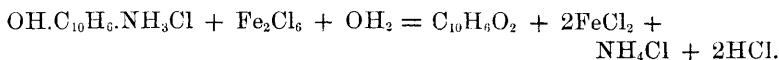
*β-Naphthaquinone.*

Details of a method for preparing β-naphthaquinone by the oxidation of amido-β-naphthol sulphate with dilute chromic mixture were given in a former paper (Trans., 1878, 415), but I find it is more advantageous to employ ferric chloride, as this may be used in excess and left for some time in contact with the precipitate without causing any change; whereas with chromic mixture the quinone is attacked, and soon becomes contaminated with brown amorphous products.

The best method of proceeding is as follows:—1 part of powdered amido-β-naphthol hydrochloride is placed in a flask, 2 parts of a saturated solution of sulphur dioxide is added, and then 40 parts of boiling water; the mixture is agitated until the hydrochloride is entirely dissolved, and the flask is then corked and left to cool. When cold, the solution is filtered from the small quantity of undissolved impurity, and the clear filtrate poured at once into 12 to 14 parts of a solution of ferric chloride (100 c.c. = 10 grams Fe<sub>2</sub>O<sub>3</sub>). The mixture becomes momentarily darker in colour, and immediately afterwards deposits the β-naphthaquinone in orange-yellow microscopic needles. After the lapse of half an hour the quinone is collected on a vacuum-filter, and must be carefully washed to remove the iron salts and free acid; this is best done by removing the precipitate from the filter, stirring it up thoroughly with 20 parts water, allowing it to remain for 20 minutes with occasional stirring, and again collecting; repeating the washing a second time in the same way, and finally drying the product at a gentle heat in an atmosphere free from acid fumes. The quinone obtained in this way is pure and of a deep golden colour. The yield is from 70—72 per cent. of the weight of the hydrochloride taken, or 73—75 on the β-naphthol originally employed.

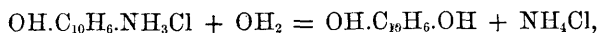
Now, as the commercial value of β-naphthol is not more than half that of β-naphthol orange, and as the former yields 100 parts quinone for 40 obtained from an equal weight of the β-orange, it follows that to produce a given quantity of β-naphthaquinone by Liebermann's process, the cost for raw material will be at least five times as great as by the one just described, and what is of far more importance in the laboratory, the latter method is comparatively simple and involves but little trouble.

The reaction in this case may be thus expressed:—





The amount of ammoniac and ferrous salts found in the solution after reaction is sensibly that required by the above equation. There can be but little doubt, however, that under the influence of the oxidising agent the  $\text{NH}_2$ -group is first replaced by  $\text{OH}$ , thus:—



and that the quinol is immediately oxidised to the quinone. The reaction is analogous to that which I observed to take place when trichloroquinol,  $\text{C}_6\text{MeCl}_3(\text{OH})_2$ , is treated with an oxidising agent in alkaline solution, one of the chlorine atoms being replaced by  $\text{OH}$  and the quinol oxidised to the quinone,  $\text{C}_6\text{MeCl}_2(\text{OH})\text{O}_2$ . The conversion of trichlorophenol into dichloroquinone by nitric acid is another instance of the same kind.

#### *Nitro-β-Naphthaquinol.*

In a former paper (*Trans.*, 1878, 416) the preparation and properties of nitro-β-naphthaquinone were fully described, and it was mentioned that two compounds were obtained from it by the reducing action of hydriodic acid and phosphorus—apparently nitro-β-naphthaquinol and amido-β-naphthaquinol. Since then I have more carefully examined these two substances, which may be conveniently prepared by employing stannous chloride as the reducing agent; the nitro-quinol being obtained with a cold dilute solution of the tin salt, whilst the more energetic action of a hot concentrated solution converts the nitro- into an amido-group.

In preparing nitro-β-naphthaquinol,  $\text{C}_{10}\text{H}_5(\text{NO}_2)(\text{OH})_2$ , 10 parts of β-naphthaquinone are converted into the nitro-derivative, and the moist product (equal to 8 parts dry nitro-β-naphthaquinone) is mixed with 40 of water; on to this is poured 15 parts, by measure, of a solution of stannous chloride (100 c.c. = 40 grams Sn) previously mixed with 15 of concentrated hydrochloric acid and 80 of water. The liquid immediately becomes of a deep red from solution of part of the nitro-β-naphthaquinone, but in a few minutes it again becomes paler from separation of the quinol. It is allowed to remain for two hours with occasional stirring, then collected, washed with 40 parts water, in which it is almost insoluble, and dried. The nitro-quinol may be purified by crystallising it from acetic acid or alcohol, in which it is readily soluble, or from benzene. It separates from benzene and from alcohol in crimson rhomboidal plates, and from acetic acid in long prisms. The yield is from 80 to 90 per cent. of the β-naphthaquinone taken.

It is reconverted into nitro-β-naphthaquinone by treatment with dilute chromic mixture, and warm dilute nitric acid has the same action, but if it is boiled with the acid for any length of time it is

oxidised to phthalic acid in the same way that naphthaquinone itself is, thus proving the  $\text{NO}_2$ -group to lie in the same ring as the quinonic ( $\text{O}_2$ )"-group. On adding ferric chloride solution to a warm alcoholic or acetic solution of the quinol, it is not reconverted into the quinone, but the red colour is at once changed to a yellowish-green, and the solution soon deposits *nitro- $\beta$ -naphthaquinhydrone* in minute prisms; this compound is also formed by the action of an aqueous solution of ferric chloride on the quinol, but it is not produced on boiling an acetic or alcoholic solution containing the nitroquinol and nitroquinone in equal molecular proportions. The quinkhydrone is of a dark bronze-green colour when dry: it is soluble in alcohol and in acetic acid, but only sparingly in ether, and almost insoluble in benzene.

*Amido- $\beta$ -Naphthaquinol.*

$\beta$ -Naphthaquinone may be converted into the amido-derivative by submitting it to the action of energetic reducing agents, such as tin and hydrochloric acid, or hot concentrated stannous chloride solution. It is far better, however, to convert it first into the nitro- $\beta$ -naphthaquinol and to act on this with tin and hydrochloric acid. The moist nitro-quinol from 10 parts of  $\beta$ -naphthaquinone, prepared in the manner just described, is placed in a capacious beaker with 15 parts of finely divided tin (such as is obtained by precipitation with zinc) and 40 of concentrated hydrochloric acid is poured on to it. The beaker is now immersed in boiling water and well stirred, when a violent reaction sets in, which, unless the quantity operated on is small, must be moderated by removing the beaker and plunging it into cold water. In a very short time the red colour entirely disappears, and the reaction is completed. When cold, the crystals are collected and purified by recrystallisation from hot water, in which they are easily soluble. The *amido- $\beta$ -naphthaquinol hydrochloride*,  $\text{C}_{10}\text{H}_5(\text{OH})_2\cdot\text{NH}_3\text{Cl}$ , forms large pale yellow crystals, which, like those of amido- $\beta$ -naphthol hydrochloride, are rapidly oxidised on exposure to the air.

In conclusion, I wish to draw attention to the fact that, although in a paper published in conjunction with the late Dr. Stenhouse, I mentioned the production of amido- $\beta$ -naphthaquinone by the action of reducing agents (*Annalen*, 194, 203), and in a notice in the *Berichte*, (14, 1659), especially addressed to Prof. Liebermann, I stated that I was engaged in an investigation "of nitro- $\beta$ -naphthaquinone and the products obtained from it by the action of reducing agents," a student in the "örg Laboratorium d. tech. Hochschule," working under Prof. Liebermann's direction, has recently published a note in which he describes the reduction of nitro- $\beta$ -naphthaquinone to amido- $\beta$ -naphthaquinone without the slightest reference to its having been already done.