ted to small bulk. The salt crystallized out in small prisms. It chars when heated to 120°. Analysis: Found, Ag = 35.09, 35.14. Calculated, Ag = 35.17.

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(CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 161.)

3-AMINO-*o*-PHTHALIC ACID AND CERTAIN OF ITS DERIVATIVES.

BY MARSTON TAYLOR BOGERT AND FAREL LOUIS JOUARD.

Received February 3, 1909.

Early attempts on the part of various chemists to prepare 3-amino-*o*-phthalic acid by reduction of the corresponding nitro acid yielded only *m*-aminobenzoic acid.[1] True, it was shown that the nitro acid was actually reduced and aminophthalic acid formed when tin and hydrochloric acid were used as the reducing agents, but when the aminophthalic solution was de-tinned by hydrogen sulphide and the acid filtrate concentrated, carbon dioxide was lost and only *m*-aminobenzoic acid remained.

In 1901, Onnerz,[2] by evaporating the acid filtrate from the tin sulphide at 50° and 18 mm. pressure, and treating the residue with cold sodium hydroxide solution, obtained what he believed to be the 3-aminophthalic acid as a yellow, indefinitely crystalline meal, beginning to darken at 174°, sintering at 179–81°, and melting at 184–6° to a reddish-brown liquid with evolution of carbon dioxide. In the light of the results reported by us further on, we believe that he did actually have the aminophthalic acid in hand in an impure state. He found it impossible to purify the acid, and analyzed the best product that he could get, supporting the rather unsatisfactory figures obtained in the case of the free acid by much closer ones for certain of its salts. By reducing nitrophthalic acid with ferrous sulphate and barium hydroxide in presence of excess of ammonia, with subsequent careful addition of acetic acid, a white, crystalline precipitate separated, which he assumed to be the same aminophthalic acid, but which Kauffman and Beisswenger[3] showed to be its acid ammonium salt.

Seidel[4] reduced nitrophthalic acid with sodium sulphide and obtained a soft, yellow powder, m. p. 226°, whose analysis gave figures agreeing with those calculated for aminophthalic acid.

Various investigators have reported that 3-aminophthalic acid either decomposes spontaneously in aqueous solution,[5] is destroyed on heating

[1] Faust, *Ann.*, 160, 56 (1871). Baeyer, *Ber.*, 10, 124 (1877). Miller, *Ibid.*, 11, 992 (1878). *Ann.*, **208**, 223 (1881). Pluss, Inaug. Diss., Geneva, 1901.

[2] *Ber.*, **34**, 3745.

[3] *Ibid.*, **36**, 2494 (1903).

[4] *Ibid.*, **34**, 4351 (1901).

[5] Marignac, *Ann.*, **38**, 1 (1841).

such a solution[1] or on evaporation,[2] or is lost on re-crystallization from water.[3] Our results agree with this. The solution of the pure acid, originally colorless, gradually decomposes and turns yellow in the cold, the decomposition being hastened by warming.

We have, however, succeeded in obtaining, we believe for the first time, the pure 3-aminophthalic acid, by reducing the nitro acid with tin or stannous chloride and hydrochloric acid. It is a colorless, crystalline compound, melting at 177° (corr.) when rapidly heated, stable toward alkalies or concentrated hydrochloric acid, but losing carbon dioxide, with formation of *m*-aminobenzoic acid when heated with dilute hydrochloric acid. This great difference in behavior to concentrated and dilute hydrochloric acid is shown also by some of its derivatives. It forms an anhydride, various imides, acid and neutral salts and esters, while its amino group reacts with mineral acids, acetic anhydride or phenyl isocyanate. By suitable treatment, it can be converted into a quinazoline, like other anthranilic acids. The acid and most of its simple derivatives are crystalline compounds with definite melting-points, although on melting many of them decompose or polymerize.

In addition to the free acid, we prepared its hydrochloride, acid potassium, acid ammonium, neutral silver and neutral barium salts; its 1-methyl ester hydrochloride; dimethyl ester, its hydrochloride and acetyl derivative; anhydride and its acetyl derivative; imide and its hydrochloride, potassium, acetyl, diacetyl and phenyluramino derivatives; anil and its acetyl derivative; acetyl *o*-tolil; phenylhydrazide; tetramethyl 3-azophthalate; 2-methyl-4-quinazolone-5-carboxylic acid and its methyl ester. Of the above substances, the dimethyl acetaminophthalate is interesting on account of its strong tribo-luminescence even under water.

Experimental.

3-Amino-o-phthalic Acid, $(3)H_2NC_6H_3(COOH)_2(1,2)$. *Preparation of the Free Acid.*—The following methods were tried: saponification of the dimethyl aminophthalate and of the aminophthalimide, and reduction of the nitro acid by ammonium sulphide, tin or stannous chloride and hydrochloric acid.

The saponification of the dimethyl ester apparently proceeded smoothly, but we sought vainly to get the free acid from the alkaline salt formed.

The action of alkali upon the aminophthalimide gave the anhydride instead of the free acid, so this method too was rejected. Nor did reduction of the nitro acid with ammonium sulphide give the desired product.

By reducing the nitro acid with stannous chloride (or tin) and hydrochloric acid, we believe that we have secured the perfectly pure amino-

[1] Bernthsen and Semper, *Ber.*, **19**, 164 (1886).

[2] Baeyer, *Ibid.*, 10, 124 (1877).

[3] Kahn, *Ibid.*, **36**, 2535 (1903).

phthalic acid. Using stannous chloride, the process was briefly as follows: Finely powdered 3-nitrophthalic acid was reduced at ordinary temperature with stannous chloride and hydrochloric acid. The nitro acid dissolved gradually and soon needles of the hydrochloride of the aminophthalic acid began to separate. The mixture was then thoroughly cooled in an ice-pack, the precipitate filtered out on cloth, dissolved in cold water and re-precipitated by dry hydrogen chloride. After repeating this solution and precipitation once or twice, the crystals were practically pure. Another method of purification was to recrystallize from concentrated hydrochloric acid. The crystals were then dried *in vacuo* over concentrated sulphuric acid and sodium hydroxide, to remove free hydrochloric acid, and carefully dissociated by adding the powdered crystals to water, filtering quickly as soon as the concentration rose (from successive additions of material to the cold solution) to the point where the free acid showed signs of beginning to crystallize out again, and then chilling this filtrate thoroughly. Colorless crystals of practically pure aminophthalic acid were thus obtained. The yield of free acid was approximately 25 per cent. of the hydrochloride used, but the rest of the hydrochloride was recovered by saturating with dry hydrogen chloride the filtrate from the acid.

One thing that is worth noting in this connection is that the crystalline material which separates from the acid solution upon the completion of the reduction is only the hydrochloride of the amino acid. Heretofore, it has been understood that the compound crystallizing out under these conditions was a double tin salt of hydrochloric and aminophthalic acids, as Miller so reported it. We believe that Miller was mistaken, as we have encountered no such double salt in our reductions either with tin or with stannous chloride. Miller's reports on the subject are not very convincing. He determined only the chlorine, and obtained figures which led him to assign the formula $C_6H_3(COOH)_2NH_2HCl + SnCl_2 + 2H_2O$ to it in his first article,[1] and $C_6H_3(COOH)_2(NH_2.HCl)_2 + SnCl_4 + 2H_2O$ in the later one.[2]

Properties of the Free Acid.—When freshly prepared, the pure acid is a colorless, crystalline solid. On standing, it slowly turns yellow. When heated rapidly, it melts at 177° (corr.) with effervescence, resolidifies and remelts, not very sharply, at 185°–6°. Heated slowly, it begins to soften at 177° (corr.), slowly decomposes, and melts completely at 191° (corr.).

Found: C, 53.2; H, 3.9; N, 8.0. Calculated for $C_8H_7O_4N$: C, 53.0; H, 3.9; N, 7.7.

The acid is practically insoluble in benzene, chloroform or ligroin;

[1] *Ber.*, 11, 994 (1878).

[2] *Ann.*, **208**, 223 (1881).

not very soluble in cold water; slowly soluble in ether, methyl or ethyl alcohols. It cannot, however, be crystallized from these solvents. Boiling with alcohol causes partial decomposition with marked greenish fluorescence. Boiling with water gives also a fluorescent solution which, on standing, deposits orange-yellow crystals, melting with decomposition at 240° (corr.) when rapidly heated, and containing 9.2 per cent. of nitrogen. This latter substance has not been identified. The amino acid heated with acetic anhydride gives acetaminophthalic anhydride and not an acetanthranil. Neither the acid nor its derivatives give the isonitrile reaction until fused with caustic alkali.

Hydrochloride.—When the acid is treated with concentrated hydrochloric acid, the hydrochloride crystallizes out on cooling. If a freshly prepared alcoholic solution of the acid is saturated with dry hydrogen chloride, the hydrochloride separates in an amorphous condition. In the crystalline state it forms colorless, minute needles, melting with decomposition at 227° (corr.) when rapidly heated, or slowly decomposing from 210° to 278° when gradually heated, all being liquefied at the latter temperature. It is exceedingly soluble in water and dissociated thereby, the free acid precipitating when the solution is sufficiently concentrated. Although stable to concentrated hydrochloric acid, it is quite unstable to the dilute acid. A few minutes' boiling with hydrochloric acid of sp. gr. 1.1 suffices to break it down to *m*-aminobenzoic acid.

Salts.—The free acid dissolves in caustic alkalies and readily decomposes sodium carbonate solution.

Acid Potassium Salt.—If the acid be dissolved in ten per cent. potassium hydroxide solution and an equivalent amount of ten per cent. hydrochloric acid be added rapidly, after standing for a few minutes the amino acid reprecipitates unaltered. If, on the other hand, the neutralization be carried out slowly, or if stronger alkali and acid be used, the acid potassium salt separates as a white, curdy mass, decomposing without melting at about 300°. It is fairly soluble in water or in excess of hydrochloric acid, but the free amino acid does not precipitate from the latter solution. The acid potassium salt also decomposes sodium carbonate.

Acid Ammonium Salt.—This behaves in much the same manner as the acid potassium salt. It has already been mentioned that Onnerz mistook this compound for the free acid because it separated when he acidified with acetic acid a solution of the amino acid in excess of ammonia. It forms colorless, microscopic needles, m. p. 116–8° (corr.) with evolution of a vapor. Kauffmann and Beisswenger[1] state that the gas given off is ammonia, but we could not detect any. After melting at the above temperature, the substance resolidifies, melts with effervescence again at about 179°, again solidifies, turns red and finally decomposes at about 320°. To us, it seems most probable that these successive changes mark condensations involving elimination of water between the amino groups of some molecules and the carboxyls of others, giving imide bodies.

Silver Salt.—Colorless, pearly scales, decomposing at about 200° without melting. Onnerz[1] reports this salt also.

Barium Salt.—Heavy, granular precipitate, slightly soluble in boiling water.

Esters. 1-Methyl-3-aminophthalate Hydrochloride, $(3)HCl.H_2NC_6H_3(COOH)(2)(COOCH_3)(1)$, prepared from the 1-methyl ester of nitrophthalic acid by reduction with stannous chloride and hydrochloric acid in the same manner as the free amino

[1] *Loc. cit.*

acid, crystallizes from concentrated hydrochloric acid in colorless, pearly scales, melting with evolution of gas at 153° (corr.).

Found: N, 5.8, 6.0, 6.09. Calculated for $C_9H_{10}O_4NCl$: N, 6.04.

It is easily soluble in water or alcohol, but the free ester acid cannot be recovered from these solutions. Recrystallization from water gives the same reddish crystals, m. p. 240°, already noted as being formed by boiling aqueous solutions of the free amino acid. Like the hydrochloride of the free acid, it is stable to concentrated hydrochloric acid, but quickly decomposed by the dilute acid with formation of the hydrochloride of *m*-aminobenzoic acid. By the action of acetic anhydride, colorless needles were obtained, melting at about 175°, which were not the desired anthranil, and which have not been further investigated.

Dimethyl 3-Aminophthalate, $H_2NC_6H_3(COOCH_3)_2$.—Dimethyl 3-nitrophthalate was obtained in nearly quantitative yield by the action of dimethyl sulphate upon sodium nitrophthalate. The nitro ester was then reduced in alcoholic solution by zinc and hydrochloric acid, as described by Bogert and Renshaw[1] for the corresponding 4-nitro ester. By extraction with ether, a brown oil was obtained with a pleasant odor suggesting that of Concord grapes. On standing *in vacuo* over sulphuric acid, it solidified to a brownish waxy mass. We could not get any satisfactory melting point, nor did we succeed in further purifying the substance. On distillation at 9 mm. pressure, it decomposed. Crystallization from water, alcohol, chloroform, benzene, or benzene-ligroin, also failed to yield a good product. Its solutions in neutral solvents are fluorescent. It is easily soluble in concentrated hydrochloric acid, but if boiled with the dilute acid *m*-aminobenzoic acid is formed.

Hydrochloride.—The oily ester was dissolved in dry benzene and dry hydrogen chloride passed in. The hydrochloride forms colorless, microscopic needles, melting with decomposition at 172–4° (corr.), is hygroscopic, and is dissociated by water.

Dimethyl 3-Acetaminophthalate, $CH_3CONHC_6H_3(COOCH_3)_2$.—This was prepared from the dimethyl aminophthalate and acetic anhydride, recrystallizing the product from very dilute acetic acid. Large, brownish, transparent glassy plates or prisms, or colorless pearly scales, m. p. 92–3° (corr.).

Found: N, 5.57. Calculated for $C_{12}H_{13}O_5N$: N, 5.67.

As noted in the introduction, this compound shows remarkable tribo-luminescence, even under water. Its solutions in water, alcohol, chloroform or acetic acid, are slightly fluorescent. In glacial acetic or chloroform solution, bromine is without effect upon it at ordinary temperatures.

Other Derivatives.

3-Aminophthalic Anhydride, $H_2NC_6H_3(CO)_2O$, prepared by boiling the imide with ten per cent. potassium hydroxide solution and neutralizing exactly with ten per cent. hydrochloric acid, crystallizes from absolute alcohol in light-yellow needles, m. p. 193–4° (corr.).

Found: N, 8.62. Calculated for $C_8H_5O_3N$: N, 8.59.

It dissolves in alcohol, acetone, chloroform or ether, with strong fluorescence, but is apparently insoluble in benzene or ligroin. Dissolved in boiling water, orange-yellow crystals, m. p. 240° (corr.), are deposited, similar to those mentioned under the free amino acid and its 1-methyl ester. With hot concentrated hydrochloric acid, the hydrochloride of the acid is formed.

As the potassium salt is presumably an intermediate product in the above formation of the anhydride, it would seem that the anhydride should result whenever solutions of this salt were carefully neutralized. So far, however, we have observed only

[1] THIS JOURNAL, **28**, 618 (1906).

the free acid and the acid potassium salt separating from such solutions when acidified. Why the imide shoud give the anhydride is not clear.

Kauffmann and Beisswenger,[1] by boiling the acid ammonium salt with glacial acetic acid or by heating it dry at 110°, obtained a yellow substance, infusible at 280°, which they thought might be the anhydride since it gave the imide when boiled with ammonia. They give no analytical data and, as the imide is easily formed from the free acid and from many of its derivatives by the action of ammonia, the nature of their product is uncertain.

3-Acetaminophthalic anhydride, $CH_3CONHC_6H_3(CO)_2O$, was obtained by the action of acetic anhydride upon the free amino acid, its hydrochloride or anhydride. Colorless needles (from alcohol), m. p. 185–6° (cor.).

Found: N, 6.89. Calculated for $C_{10}H_7O_4N$: N, 6.82.

Heated with aniline, it gives 3-acetaminophthalanil. This proves that the compound is not the isomeric anthranil, for the latter should yield a quinazoline when heated with aniline.

Kahn[2] obtained this compound by the action of acetic anhydride upon the double zinc acetate and aminophthalate, and gives its melting point as 181°.

3-Aminophthalimide, $H_2NC_6H_3(CO)_2NH$.—This has been described already by Kauffmann and Beisswenger.[3] We have obtained it by reducing the nitro imide with ammonium sulphide, with zinc and hydrochloric acid, and with stannous chloride and hydrochloric acid. The latter is much the best method, giving practically quantitative yields. It crystallizes from alcohol in golden-yellow needles, m. p. 266–7° (corr.). Kauffmann and Beisswenger give the m. p. as 256–7°.

Found: N, 17.5. Calculated for $C_8H_6O_2N_2$: N, 17.3.

Its solutions are strongly fluorescent, the color of the fluorescence depending upon the solvent used. Even the crystals show a faint greenish fluorescence.

Hydrochloride.—Colorless, granular solid, melting with decomposition at 268° (corr.) when heated rapidly. Stable to concentrated hydrochloric acid, but dissociated by water.

Potassium Derivative, $H_2NC_6H_3(CO)_2NK$, from the imide and anhydrous alcoholic potassium hydroxide solution, was obtained as a cream-colored precipitate, hydrolyzed by water. When it was treated with dimethyl sulphate and then neutralized with sodium carbonate, a compound was isolated, crystallizing from alcohol in yellow needles, melting at about 145°, which appeared to be an impure 3-dimethylaminophthalmethylimide.

3-Acetaminophthalimide, $CH_3CONHC_6H_3(CO)_2NH$, from the imide and acetic anhydride, crystallizes from alcohol or ethyl acetate in colorless granules, or from boiling water in needles, m. p. 242° (corr.).

Found: N, 13.9. Calculated for $C_{10}H_8O_3N_2$: N, 13.7.

Heated with dilute caustic alkali, it condenses to 2-methyl-4-quinazolone-5-carboxylic acid. Bromine is without effect upon its glacial acetic solution.

3-Diacetaminophthalimide, $(CH_3CO)_2NC_6H_3(CO)_2NH$, prepared by boiling the imide with excess of acetic anhydride, and recrystallizing from absolute alcohol, forms colorless prisms, m. p. 152–4° (corr.).

Found: N, 11.6. Calculated for $C_{12}H_{10}O_4N_2$: N, 11.4.

Boiling water partly hydrolyzes it to the monacetyl derivative.

3-Phenyluraminophthalimide, $C_6H_5NHCONHC_6H_3(CO)_2NH$, from the imide and

[1] *Loc. cit.*

[2] *Ber.*, **36**, 2536 (1903).

[3] *Ibid.*, **36**, 2494 (1903); **37**, 2612 (1904).

phenyl isocyanate, crystallizes from 30–40 per cent. alcohol in pearly scales which sinter at about 260° (corr.) and melt, with darkening, at about 335° (corr.).

Found: N, 15.2. Calculated for $C_{15}H_{11}O_3N_3$: N, 14.9.

3-Aminophthalanil, $H_2NC_6H_3(CO)_2NC_6H_5$.—Kauffmann and Beisswenger[1] prepared this compound by reducing the nitro anil, and gives its melting point as 185–7°. We have obtained it by heating the free amino acid, its anhydride or amide, with aniline. It crystallizes from alcohol in pale yellow needles, m. p. 186–8° (corr.).

3-Acetaminophthalanil, $CH_3CONHC_6H_3(CO)_2NC_6H_5$, has also been prepared previously by Kauffmann and Beisswenger[2] by acetylating the anil. We have obtained it by heating dimethyl 3-acetaminophthalate with excess of aniline. Recrystallized from alcohol, it forms pale yellowish needles, m. p. 195.5° (corr.). Kauffmann and Beisswenger give its melting point at 191°.

3-Acetaminophthal-o-tolil, $CH_3CONHC_6H_3(CO)_2NC_6H_4CH_3(o)$, from dimethyl 3-acetaminophthalate and *o*-toluidine, crystallizes from methyl alcohol in coarse, straw-colored prisms, or may be precipitated from its acetone solution in cream-colored needles by diluting with water. It melts at 214–5° (corr).

Found: N, 9.7. Calculated for $C_{17}H_{14}O_3N_2$: N, 9.5.

3-Aminophthalphenylhydrazide, $H_2NC_6H_3(CO)_2NNHC_6H_5$, prepared by heating the imide with phenylhydrazine, crystallizes from 60 per cent. alcohol in yellow scales, melting with decomposition at 284–5° after previous softening.

Found: N, 16.52. Calculated for $C_{14}H_{11}O_2N_3$: N, 16.60.

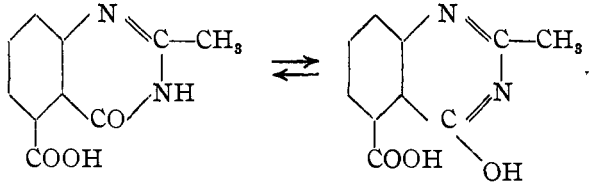
Repeated crystallization from dilute alcohol or dilute acetone causes it to turn gradually dark green. It reacts vigorously with acetic anhydride, giving yellow needles, which on recrystallization from alcohol melt at 223–4° (corr.). As these crystals contain 16.3 per cent. nitrogen, they cannot be the simple acetyl derivative of the aminohydrazide (14.2 per cent. nitrogen). They have not been further investigated.

Tetramethyl 3-azophthalate, $(CH_3OCO)_2C_6H_3N:NC_6H_3(COOCH_3)_2$, from the nitrophthalic ester and aluminum amalgam in alcoholic solution, crystallizes from alcohol in pale salmon needles, m. p. 224–5° (corr.).

Found: N, 7.04. Calculated for $C_{20}H_{18}O_8N_2$: N, 6.76.

The process is slow and the yield of azophthalate poor.

2-Methyl-4-quinazolone-5-carboxylic Acid (*2-Methyl-4-hydroxyquinazoline-5-carboxylic Acid*),



This was obtained by heating dimethyl 3-acetaminophthalate with excess of ammonia at 150°, at the close of the reaction boiling with potassium hydroxide solution to expel any excess of ammonia, and then carefully neutralizing with dilute hydrochloric acid. A simpler way is to boil the acetaminophthalimide with a slight excess of five per cent. potassium hydroxide solution and then faintly acidify with dilute hydrochloric acid, when the quinazoline will crystallize out on cooling. It was purified by treating with bone-black and recrystallizing from boiling water, and then appeared in colorless

[1] *Ber.*, **37**, 2611 (1904).

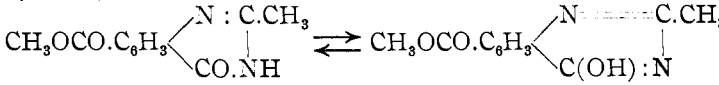
[2] *Loc. cit.*

needles, melting with decomposition at 342° (corr.). It is soluble in alkalies and reprecipitated on acidification.

Found: C, 58.9; H, 4.0; N, 13.95. Calulated for $C_{10}H_8O_3N_2$: C, 58.8; H, 3.9; N, 13.72.

It is difficultly soluble in boiling water and crystallizes therefrom with a molecule and a half of water of crystallization, which is driven off at 110°.

Methyl Ester,



This ester was prepared from the sodium or potassium salt of the above acid with the calculated amount of dimethyl sulphate. It crystallizes from alcohol in colorless silky needles, very light and bulky, m. p. 273–4° (cor.).

Found: N, 12.9. Calculated for $C_{11}H_{10}O_3N_2$: N, 12.8.

INVESTIGATION OF THE ESSENTIAL CONSTITUENT OF TURKEY-RED OIL AND ITS DERIVATIVES.

BY AD. GRÜN AND M. WOLDENBERG.

Received July 10, 1909.

Turkey-red oil, obtained by the action of concentrated sulphuric acid on castor oil, and dissolving the resulting product in ammonia or soda solution, is a very complicated mixture of derivatives of ricinoleic acid, $C_{17}H_{32}(OH)COOH$.

It contains (in the form of salts): free ricinoleic acid, the sulphuric ester and the sulphuric ester of castor oil;[1] perhaps also a mixed diricinoleic-acid-sulphuric glyceride,[2] sulphuric ester of dioxystearic acid,[3] ricinoleic acid anhydride,[4] polyricinoleic acids,[5] and other complicated compounds.

The reaction of sulphuric acid on ricinoleic acid or its glyceride has been often investigated. Regardless of this fact, however, the course of the reaction in relation to time is still very uncertain; the most important product of this reaction, the ricinoleic-acid-sulphuric ester, has not been thoroughly investigated (not even isolated in pure form) and has never been characterized through its derivatives.

The following research has been undertaken with the object of joining the numerous bits of information on this subject, which are at hand, and filling in such gaps as may present themselves, so as to leave the problem, if possible, conclusively solved. The reaction of gram-molec-

[1] Benedikt and Ulzer, *Monatsh. Chem.*, 8, 208 (1887). Scheurer-Kestner, *Bull. soc. ind. Mulhouse* (1891). See also Wilson, *J. Soc. Chem. Ind.*, 26 (1891).

[2] Bogajewski, *Chem. Centrbl.*, 1897, II, 335. See also Liechti, *Ber.*, 16, 2453 (1883).

[3] Fuillard, *Bull. soc. chim.*, 1891, 6; 1894, 280. Fuillard, *Bull. soc. ind. Mulhouse*, 1892, 415.

[4] Fuillard, *Loc. cit.*

[5] Scheurer-Kestner, *Loc. cit.* Fuillard, *Loc. cit.*