[Contribution from the University College of Science of Calcutta.]

REPLACEMENT OF SULFONIC GROUPS BY NITRO GROUPS BY MEANS OF NITROUS GASES.

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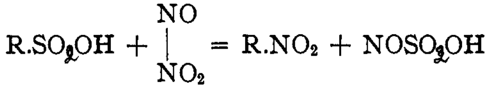
The replacement of sulfonic acid groups by nitro groups has not hitherto been studied although a few isolated instances of this sort are to be found in the literature. Thus, Neville and Winther[1] obtained dinitrocresol from *o*-, *m*-, and *p*-cresol sulfonic acids by the action of nitric acid; Werner and Kelbe[2] prepared dinitro-bromothymol from β-bromothymol sulfonic acid, and α-nitro-bromothymol from α-bromothymol sulfonic acid; Michler and Walder[3] obtained mononitro-dimethylaniline from dimethylaniline sulfonic acid by the action of sodium nitrite and sulfuric acid.

It has been found that this replacement can be effected very easily by means of nitrous gases, and that in the course of the reaction more nitro groups frequently enter the molecule with the formation of highly nitrated compounds. In fact, it has been found that those nitrations which hitherto have been achieved only by means of strong nitric acid or by means of nitric-sulfuric acid mixtures, can often be smoothly and easily brought about by the above method. Again many nitrations which cannot be brought about at all by nitric acid can be smoothly accomplished by this method.

This reaction is further useful in elucidating the constitution of nitro bodies derived from known sulfonic acids. The mechanism of the reaction may in all probability be represented thus:



$$R.SO_2OH + \begin{matrix} NO \\ | \\ NO_2 \end{matrix} = R.NO_2 + NOSO_2OH$$

The nitrous gases react upon the sulfonic acid with the formation of the nitro derivative and nitrosyl sulfuric acid. The nitrosyl sulfuric acid in aqueous medium decomposes again into sulfuric acid and nitrous gases which continue further action in the same way.

The replacement of sulfonic group by the nitro group in phenol and cresol sulfonic acids with the formation of 2,4,6-trinitrophenol and trinitrocresol, respectively, has already been described.[4]

The following general behavior can be noted: Aromatic compounds which are already substituted by hydroxyl or halogen radicals have been found to be nitrated readily with the replacement of the sulfonic group. In some cases more nitro-groups enter the ring in suitable posi-

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[1] *Ber.*, 13, 1946 (1880).

[2] *Ibid.*, 16, 617 (1883).

[3] *Ibid.*, 14, 2176 (1881).

[4] Datta and Varma, *U. S. pat.* 1,292,266 (1919).

tions. In the case of carboxylic acids of hydroxy compounds, not only the sulfonic group but also the carboxyl group is replaced with the formation of nitro-bodies. If the compound does not already contain substituted hydroxyl, and halogen groups, the replacement does not take place at all, as in the case of benzene sulfonic acid which remains unacted upon on treatment with nitrous gases.

The following detailed results have been obtained: *o*-Cresol-3-sulfonic acid and *o*-cresol-4-sulfonic acid yield 3,4-dinitro-*o*-cresol; *o*-cresol-3,5-disulfonic acid, 3,5-dinitro-*o*-cresol; *m*-cresol-6-sulfonic acid and *m*-cresol-2,6-disulfonic acid, 2,4,6-trinitro-*m*-cresol; *p*-cresol-3-sulfonic acid gives 3,5-dinitro-*p*-cresol; 1,2,4-xylenol gives 3,5-dinitro-1,2,4-xylenol; 1,3,4-xylenol yields 5-nitro-1,3,4-xylenol; 1,4,5-xylenol gives 2-nitro-1,4,5-xylenol; thymol sulfonic acid yields 6-nitrothymol; resorcinol disulfonic acid yields 2,4,6-trinitro-resorcinol; anisol and phenetol sulfonic acids give 2,4-dinitrophenol, the alkyloxyl group being hydrolyzed in both the cases; *o*-nitrophenol-4-sulfonic acid, *m*-nitrophenol sulfonic acid and *p*-nitrophenol sulfonic acid give 2,4,6-trinitrophenol. *o*-Oxybenzoic acid and *p*-oxybenzoic acid yield 2,4,6-trinitrophenol, whereas *m*-oxybenzoic acid yields 2,4,6-trinitro-resorcinol; 3,5-dinitro-*o*-cresol can be obtained from *o*-cresotonic acid (1 : 2 : 3); 2,4,6-trinitro-*m*-cresol from *m*-cresotonic acid (1 : 3 : 4); and 3,5-dinitro-*p*-cresol from *p*-cresotonic acid (1 : 4 : 3). Sulfonic acids of chlorobenzene, bromobenzene and iodobenzene yield *p*-chloronitrobenzene, *p*-bromonitrobenzene and *p*-iodonitrobenzene, respectively. *o*-Iodotoluene gives *p*-nitro-*o*-iodotoluene. Benzyl cyanide has been found to give *p*-nitrobenzyl cyanide. Anthraquinone-β-sulfonic acid yields β-nitro-anthraquinone.

These interactions are generally effected in aqueous solutions, with the passage of nitrous gases to saturation. Finally the nitro compounds are crystallized from the solution.

Experimental.

o-Cresol. Preparation of 3,4-Dinitro-*o*-cresol and 3,5-Dinitro-*o*-cresol.

o-Cresol-3-sulfonic acid was prepared according to the method described by Claus and Jackson.[1] The crude product after sulfonation was distilled in steam to free it from unchanged *o*-cresol. To the diluted solution of *o*-cresol-3-sulfonic acid nitrous gases were added until absorption was complete. The solution was evaporated until crystals appeared and cooled, when the greater part of it crystallized. The crystals were drained, washed with a small quantity of water and finally recrystallized from absolute alcohol when they melted sharply at 89.5°. As this melting point did not correspond with that of any known nitrocompound of *o*-cresol the substance was analyzed and was found to be a dinitro-*o*-cresol:

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[1] *J. prakt. Chem.*, [2] **38**, 333 (1888).

Subs., 0.1011: 13.4 cc. N_2 at 29° and 745.5 mm.
Calc. for $C_6H_2.CH_3(OH)(NO_2)_2$: N, 14.14. Found: 14.70.

o-Cresol-4-sulfonic acid was prepared by digesting equimolecular quantities of *o*-cresol and strong sulfuric acid.[1] On treating this with nitrous gases as before the same dinitro-compound melting at 89.5° was obtained. Since this dinitro-compound is obtained both from *o*-cresol-3-sulfonic acid and *o*-cresol-4-sulfonic acid, the substance obtained is evidently 3,4-dinitro-*o*-cresol.

o-Cresol-3,5-disulfonic acid was prepared by dissolving *o*-cresol in fuming sulfuric acid and warming the mixture for some time on the water bath.[2] The crude mixture was distilled in steam to free it from unchanged cresol which otherwise chars under the influence of nitrous gases, diminishing the yield and giving an impure product. The resulting solution was saturated with nitrous gases and evaporated on the water bath until crystals separated. These were recrystallized from alcohol and then melted at 85°. This substance was identified as 3,5-dinitro-*o*-cresol. The yield was about 70% of the theoretical amount.

m-Cresol. Preparation of 2,4,6-Trinitro-*m*-cresol.

m-Cresol-6-sulfonic acid was prepared by mixing equimolecular quantities of *m*-cresol and strong sulfuric acid according to the method of Claus and Kraus.[3] The resulting product was distilled in steam to get rid of unchanged *m*-cresol. After saturating with nitrous gases and evaporating, crystals were obtained. These on recrystallization from alcohol gave pure 2,4,6-trinitro-*m*-cresol, melting at 109–10° which was further identified by analysis:

Subs., 0.1103: 17.7 cc. N_2 (28° and 746 mm.).
Calc. for $C_6H(CH_3)(NO_2)_3.OH$: N = 17.30. Found: 17.70.

The yield of trinitro-*m*-cresol was about 50% of the theoretical amount.

m-Cresol-2,6-disulfonic acid was prepared from one part of *m*-cresol and 6 parts of strong sulfuric acid, warmed for about 6 hours at 120–60°.[4] The product was purified from unchanged *m*-cresol and saturated with nitrous gases. On evaporating and cooling, crystals of 2,4,6-trinitro-*m*-cresol were obtained which on crystallization from alcohol melted at 109–10°.

p-Cresol. Preparation of 3,5-Dinitro-*p*-cresol.

p-Cresol-3-sulfonic acid was prepared by adding fuming sulfuric acid gradually to *p*-cresol, the vessel containing the mixture being cooled from time to time in cold water and the mixture all along shaken vigorously. It was distilled in steam in the usual manner to free it from un-

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[1] Engelhardt and Latschinow, *Z. Chem.*, 1869, p. 620; Haulke, *Ber.*, **20**, 340 (1887).

[2] Claus and Jackson, *Loc. cit.*

[3] *Ber.*, **20**, 3089 (1887).

[4] Claus and Kraus, *Loc. cit.*

changed cresol. On passing nitrous gases, a precipitate began to form, the quantity increasing with the passing of the gas. During the absorption of the gas much heat was developed and it was necessary to keep the mixture cold by immersing the vessel in cold water. The product was collected and recrystallized from absolute alcohol when it melted at 84°, and was identified as 3,5-dinitro-*p*-cresol. If the passing of the nitrous gases be continued for a sufficiently long time, much oxalic acid is formed as a result of destructive oxidation.

1,2,4-Xylenol. **Preparation of 3,5-Dinitro-1,2,4-xylenol.**

1,2,4-Xylenol sulfonic acid was prepared by heating on the water bath for about $^1/_2$ hour 10 g. of xylenol and 20 cc. of conc. sulfuric acid. The product was then diluted with water and treated with nitrous gases. The solution turned dark in color at once and a black, resinous mass was deposited on the surface, some dark-colored, thick liquid settling at the bottom of the vessel. A considerable quantity of heat was developed. The passing of the nitrous gases was continued for nearly an hour when the black, resinous mass and the separated oil were transformed gradually into a yellow solid product which on crystallization from alcohol gave bright yellow crystals melting at 125–6° and identified as 3,5-dinitro-1,2,4-xylenol. The yield was nearly quantitative.

1,3,4-Xylenol. **Preparation of 5-Nitro-1,3,4-xylenol.**

1,3,4-Xylenol sulfonic acid was obtained by heating on the water bath for 2 to 3 hours 10 cc. of the xylenol with 25 cc. of a mixture of equal quantities of fuming and conc. sulfuric acids. The mixture was distilled in steam to free it from unchanged xylenol, diluted with water and then treated with nitrous gases. The solution began to turn turbid and the color changed from dark to yellow, clearing in 30 to 40 minutes, when a considerable quantity of yellow solid product collected on the surface of the liquid. This solid, crystallized from alcohol, gave beautiful crystals melting at 72°, which were identified as 5-nitro-1,3,4-xylenol.

1,4,5-Xylenol. **Preparation of 2-Nitro-1,4,5-xylenol.**

1,4,5-Xylenol was sulfonated by mixing 10 g. of xylenol and 20 cc. of conc. sulfuric acid and heating on the water bath for about an hour. The product was diluted with water and treated with nitrous gases. The solution was at first dark green in color, an emulsion-like product being formed; but after some time the solution became clear with the separation of a yellow, solid product which on crystallization from benzene yielded light yellow crystals melting at 116–7°, identified as 2-nitro-1,4,5-xylenol. The yield was quantitative.

Thymol. **Preparation of 6-Nitrothymol.**

Thymol sulfonic acid was prepared by heating thymol with fuming sulfuric acid at 160–80° on a paraffin bath for about two hours and a half.[1] A dark-colored, viscid mass was obtained. This was mixed with a small quantity of water and allowed to stand, when it solidified on cooling. The solid was removed and purified by suction. The product was dissolved in water and the treatment with nitrous gases continued for 3 hours since the reaction is very sluggish. The solution was evaporated on the water bath when an oil separated which solidified on cooling. This, when recrystallized from alcohol, melted at 130° and was identified as 6-nitrothymol. The mother liquor, after the separation of crystals, gave a small yield of oxalic acid due to exhaustive oxidation.

Resorcinol. Preparation of 2,4,6-Trinitro-resorcinol.

Resorcinol disulfonic acid was prepared by adding one part of resorcinol to about two parts of fuming sulfuric acid and heating on the water bath for about an hour.[2] The dark-colored product after diluting with water was treated with nitrous gases when the color cleared to yellow at the end of the reaction. On evaporating on the water bath crystals were obtained which on recrystallization from alcohol gave fine, yellow crystals, melting at 175–6°. This was identified as 2,4,6-trinitro-resorcinol. The yield was good.

Anisol. Formation of 2,4-Dinitrophenol.

Equal volumes of anisol and sulfuric acid were thoroughly mixed and heated on the water bath for about an hour. The liquid obtained was then diluted with water and nitrous gases were passed into it for about an hour and a half. The resulting solution was concentrated on the water bath until on cooling the liquid partly solidified. The substance was separated and recrystallized from alcohol when it melted sharply at 115°. It was identified as 2,4-dinitro-phenol.

Subs., 0.1216: 17.4 cc. N_2 (30° and 760 mm.).
Calc. for $C_6H_3(NO_2)_2OH$: N = 15.22. Found: 15.92.

Besides the usual replacement and nitration, the methoxyl group is here hydrolyzed to hydroxyl under the influence of nitrous gases.

Phenetol. Formation of 2,4-Dinitrophenol.

Equal volumes of phenetol and sulfuric acid were heated on the water bath, and the product mixed with water and treated with nitrous gases. The resulting solution on concentration partially solidified. The solid was collected and recrystallized from alcohol when it melted at 115–6° and was identified as 2,4-dinitrophenol. The reaction here is strictly analogous to the one with anisol.

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[1] Engelhardt and Latschinow, *Z. Chem.*, **1869**, p. 44. Lieberman (*Ber.*, 10, 612 (1817)) prepared 6-nitrothymol by the action of nitric acid on an aqueous solution of the corresponding sulfonic acid.

[2] Tideschi, *Ber.*, **21**, 1267 (1888).

o-Nitrophenol. Formation of 2,4,6-Trinitrophenol.

o-**Nitrophenol** was sulfonated by adding in small quantities at a time one and a half molecular weight of comparatively weak fuming sulfuric acid to one molecular weight of the substance. During the addition of the acid much heat was evolved and the vessel was cooled from time to time to prevent any loss by charring and other side reactions. When the addition of the acid was complete, the mixture was heated for nearly an hour on the water bath. It was diluted with water, filtered to separate the few black particles present and treated with nitrous fumes. The solution obtained after sulfonating the nitrophenol was yellow in color. During the passage of the gases very little change in color of the solution took place. The solution was then evaporated on a water bath till a solid incrustation had formed. On cooling, more solid precipitate was obtained. This was separated, dried and recrystallized from alcohol. It was identified as 2,4,6-trinitrophenol. The theoretical yield was obtained.

m-Nitrophenol. Formation of 2,4,6-Trinitro-resorcinol.

m-**Nitrophenol** was sulfonated by mixing one molecular weight of nitrophenol with one and a half molecular weights of fuming sulfuric acid the latter being added drop by drop. During the addition, the mixture was kept cooled by cold water. When the whole of the acid had been added, the mixture was heated on the water bath for half an hour. It was diluted with water, filtered from the few black particles present, and then submitted to the action of nitrous gases for nearly two hours. The solution, originally dark in color, changed gradually to pale yellow, and when the action was complete, was evaporated on the water bath until a crust formed on the surface. More solid was obtained on cooling which was separated by filtration, dried and crystallized from absolute alcohol, when it melted sharply at 174–5° and was found to be trinitro-resorcinol. The yield was quantitative.

p-Nitrophenol. Formation of 2,4,6-Trinitrophenol.

p-**Nitrophenol** was dissolved in a little more than the equimolecular quantity of fuming sulfuric acid and the mixture heated on the water bath for about half an hour. The product was dissolved in water and the undissolved solid particles were removed by filtration. The solution thus obtained was dark-colored and was, therefore, treated with animal charcoal. Nitrous gases were passed through the filtrate for about 45 minutes and were readily absorbed, the color changing from dark to greenish yellow and finally yellow. The solution was concentrated on the water bath and allowed to cool, when solid crystals were obtained which melted at 122° after recrystallization from alcohol. This substance has been identified as 2,4,6-trinitrophenol. The yield was good.

o-Oxybenzoic Acid. Formation of 2,4,6-Trinitrophenol.

Salicylic acid was dissolved in conc. sulfuric acid (one molecular weight of the former with one and a half molecular weights of the latter) and the mixture heated on the water bath for nearly one hour. The solution thus obtained was diluted with water to 3 times its volume and nitrous fumes were passed into it for nearly two hours. The dark-colored solution changed gradually to yellow. During the passage of the fumes through the solution there was considerable evolution of carbon dioxide. The solution obtained was concentrated by heating on the water bath and cooling, giving beautiful, yellow crystals which proved on drying and crystallizing from alcohol to be 2,4,6-trinitrophenol, melting at 122.5°. A quantitative yield was obtained.

m-Oxybenzoic Acid. Formation of 2,4,6-Trinitro-resorcinol.

m-Oxybenzoic acid does not appear to form a sulfonic acid very easily with conc. sulfuric acid. The oxybenzoic acid was dissolved in fuming sulfuric acid and the mixture heated on a water bath for nearly 3 hours. The dark-colored liquid thus obtained was diluted with water and treated with nitrous fumes until no more heat was evolved and the formation of gas in the solution had practically ceased. The solution was then concentrated until a crust formed. It was then cooled when a large quantity of yellow product was obtained, which on separation and crystallization was identified as 2,4,6-trinitro-resorcinol, melting at 175.5°. The yield was good.

p-Oxybenzoic Acid. Formation of 2,4,6-Trinitrophenol.

A mixture of 10 g. of *p*-oxybenzoic acid dissolved in 20 cc. of fuming sulfuric acid was heated on a water bath for about two hours and a half. The product was dissolved in water and treated with nitrous gases until no more heat was evolved. Gas was evolved from solution, and at a certain stage the evolution was so rapid as to give the appearance of brisk boiling. During this period the color of the solution changed from dark to greenish and finally yellowish green. In about an hour and a half the operation was stopped and the solution concentrated till a solid incrustation formed on the surface of the liquid. On cooling, crystals separated which on recrystallization from water melted at 122.5° and were identified as 2,4,6-trinitrophenol. The yield was quantitative.

o-Cresotonic Acid (1:2:3). Formation of 3,5-Dinitro-*o*-cresol.

A mixture of 10 g. of *o*-cresotonic acid with 30 cc. of fuming sulfuric acid was thoroughly shaken and heated on a water bath for about one hour and a half. The dark-colored liquid thus obtained was dissolved in water very carefully by adding small quantities to cold water. Nitrous gases were then passed through this dark-colored solution when gas evolution set up gradually, and in less than half an hour the solution became turbid and a yellow precipitate began to form. In an additional half hour the precipitation was found to be complete, leaving a clear solution. The solid was dried and recrystallized from alcohol when it melted at 85–6° and was identified as 3,5-dinitro-*o*-cresol. The yield was quantitative.

m-Cresotonic Acid (1:3:4). Formation of 2,4,6-Trinitro-*m*-cresol.

The sulfonic acid derivative of this substance was prepared by dissolving 10 g. of *m*-cresotonic acid in 20 cc. of fuming sulfuric acid and heating the mixture on a water bath for one hour and a half only. The dark-colored liquid was added drop by drop to cold water and the resulting solution submitted to the action of nitrous gases, when as in the case of *o*-cresotonic acid, effervescence commenced, heat was evolved, and the solution became turbid. In an additional half hour the formation of the yellow precipitate was complete, the passing of the gases being continued until no more heat evolution could be noticed. The product was concentrated on the water bath when the precipitate dissolved, but it reprecipitated in copious quantity on cooling. It was filtered and crystallized from alcohol 3 times when it melted sharply at 109–10°, and was identified as 2,4,6-trinitro-*m*-cresol.

p-Cresotonic Acid (1:4:3). Formation of 3,5-Dinitro-*p*-cresol.

By the action of nitrous fumes on the sulfonic acid derivative of *p*-cresotonic acid, 3,5-dinitro-*p*-cresol was obtained in theoretical yield in a high state of purity. The sulfonic acid derivative consists of colorless, fine, needle-shaped crystals not quite so easily soluble as the sulfonic acid derivatives of the other cresotonic acids. It was prepared by dissolving 10 g. of the *p*-cresotonic acid in 20 cc. of fuming sulfuric acid and heating the mixture for nearly two hours on a water bath. When the action was complete the product was mixed with water and at once solidified to a mass of fine crystals, which were dissolved in water and submitted to the action of nitrous fumes. A solid formed on the surface of the liquid with the liberation of much heat and the evolution of minute bubbles of gas. When no sign of further reaction could be noticed, the operation was stopped and the solid separated, dried on a porous plate and crystallized from alcohol. The mother liquor was concentrated on the water bath and more solid obtained on cooling. These beautiful, yellow crystals proved to be 3,5-dinitro-*p*-cresol, melting at 84°.

Chlorobenzene. Preparation of *p*-Nitrochlorobenzene.

Equal volumes of chlorobenzene and strong sulfuric acid were mixed and heated on the water bath for about two hours. Nitrous fumes were then bubbled through the solution for nearly two hours after which no more action between the substances could be noticed. The action in this case was slower than in the case of iodo and bromobenzene sulfonic acids.

No solid appeared in this case, but by pouring the liquid in cold water, a solid separated from solution. It was filtered off, dried and recrystallized from alcohol, when it melted sharply at 82–3°, and has been identified as *p*-nitrochlorobenzene.

Bromobenzene. Preparation of *p*-Nitrobromobenzene.

Equal volumes of bromobenzene and fuming sulfuric acid were mixed and heated on the water bath for about an hour. The solution was then slightly diluted with water and treated with nitrous gases for half an hour, when crystals began to form on the sides of the vessel. The solution was shaken from time to time and to prevent too much rise of temperature, the vessel was cooled by immersing in cold water. When the action slackened, the liquid was poured into a large volume of water whereupon the solid product precipitated. The whole operation did not take more than an hour. The solid on crystallization from glacial acetic acid proved to be *p*-nitrobromobenzene, melting at 116–27°.

Iodobenzene. Preparation of *p*-Nitroiodobenzene.

Iodobenzene sulfonic acid was prepared by shaking thoroughly equal volumes of iodobenzene and fuming sulfuric acid and heating the mixture on a water bath for an hour. It was cooled and then submitted to the action of nitrous gases. In a few minutes a copious precipitate formed, to which water was added to effect a complete separation of the solid. The latter was separated by decantation, dried on a porous plate and crystallized from benzene. It melted sharply at 170–1° and was identified as *p*-nitroiodobenzene.

o-Iodotoluene. Preparation of *p*-Nitro-*o*-iodotoluene.

o-Iodotoluene was mixed with twice its volume of fuming sulfuric acid and heated for 4 hours, when the reaction seemed to be complete. It was then diluted with water and submitted to the action of nitrous fumes for 2 to 3 hours. The action was comparatively slow, and when no more heat was evolved the current of nitrous gases was discontinued, the mixture shaken thoroughly and poured into a large volume of water, when a solid product was obtained which on repeated crystallization melted at 102°. It was identified as *p*-nitro-*o*-iodotoluene. The yield was good although not quantitative, due probably to the incomplete formation of the sulfonic acid.

Benzyl Cyanide. Preparation of *p*-Nitrobenzylcyanide.

By the action of nitrous gases on benzyl cyanide dissolved in strong sulfuric acid, *p*-nitrobenzylcyanide was obtained. This compound has been previously obtained by the action of 5 parts of nitric acid on one part of benzyl cyanide.

A mixture of 10 cc. of strong sulfuric acid and 10 cc. of benzyl cyanide was well shaken for about 15 minutes and then heated on a water bath for an hour. The action was very vigorous at first and the solution became a dark-colored, viscous mass. This was dissolved in water and treated with nitrous gases, when much heat was evolved with the formation of a dark, oily product. This oil was separated and allowed to stand until the change into a yellow product was complete. On recrystallization from acetic acid the substance melted at 83°, and was identified as *p*-nitrobenzylcyanide.

Anthraquinone. Preparation of β-Nitro-anthraquinone.

A mixture of 10 g. of anthraquinone and 10 cc. of fuming sulfuric acid was heated on a paraffin bath for about 2 hours, and the product dissolved in water and treated with nitrous gases. When reaction was complete, the solution was evaporated and a yellow solid obtained. It was soluble in chloroform and acetone, from which on crystallization a product melting at 180° was obtained, which was identified as β-nitro-anthraquinone.

Additional investigations along similar lines are being made.

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TETRAPHENYLDIARSINE.

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The earliest attempt to prepare tetraphenyldiarsine was made by LaCoste and Michaelis[1] who heated diphenylchloroarsine, $(C_6H_5)_2AsCl$, with zinc in a sealed tube at 100°. The crystalline body they obtained melted at 154°, and analyses showed 53.01% carbon instead of 62.88%, the theoretical value. Lack of material prevented them from making further examination of this body.

Two years later Michaelis and C. Schulte[2] reported the preparation of tetraphenyldiarsine by heating tetraphenyldiarsine oxide, $(C_6H_5)_4As_2O$, in absolute ethyl alcohol with phosphorous acid. It was found to be a crystalline body, melting at 135°. The substance oxidized readily in the air forming the anhydride of diphenyl arsenic acid, $(C_6H_5)_4As_2O_3$.

Later, Michaelis[3] reported its preparation by heating an alcoholic solution of diphenylarsenic acid, $(C_6H_5)_2AsOOH$, for 10 hours with a large excess of phosphorous acid. It was described as a crystalline body spontaneously combustible in air. The oxidation product of the substance in a stream of carbon dioxide containing some oxygen was identified as tetraphenyldiarsine oxide.

More important work was done by Schlenk[4] who determined the

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[1] *Ann.*, **201**, 222 (1880).

[2] *Ber.*, **15**, 1952 (1882).

[3] *Ann.*, **321**, 148 (1902).

[4] *Ibid.*, **394**, 216 (1912).