the two isomeric dinitrotetrachlorofluorans are formed. Tetranitrotetrachlorofluoran results when tetrachlorofluoran is nitrated in a solution of one part of nitric acid (sp. gr. 1.5) and two parts of concentrated sulfuric acid. By this method Meyer and Friedland obtained a pentanitrofluoran. However, pentanitrotetrachlorofluoran could not be made. This seems to show that one of the nitro groups in pentanitrofluoran is in the phthalic acid residue.

The solubility of tetrachlorofluoran in concentrated sulfuric acid decreases with the successive introduction of nitro groups into the molecule, while the solubility in an alcoholic solution of caustic potash increases.

Dinitrotetrachlorofluoran has been reduced and the resulting diamino compound diazotized and this solution boiled with water. *Hydroquinonetetrachlorophthalein* results showing that the nitro groups .must be in different benzene rings and occupy the *p*-positions to the pyrone oxygen atom and the *m*-positions to the tetrachlorophthalic acid residue.

Mononitrotetrachlorofluoran, when reduced and the resulting amino compound diazotized and this solution boiled with water, gives *tetrachlorofluoran* instead of the expected hydroxyl derivative.

Mono-, di-, tri-, and tetranitrotetrachlorofluorans have been reduced in an alcoholic solution of stannous chloride saturated with hydrochloric acid gas, and the corresponding aminotetrachlorofluorans have thus been prepared.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE TRANSFORMATION OF NITRILES INTO AMIDES BY HYDROGEN PEROXIDE.

BY L. MCMASTER AND F. B. LANGRECK.

Received November 20, 1916.

The first use made of hydrogen peroxide as a hydrolytic agent for converting nitriles into amides was by Radziszewski.[1] The action takes place according to the equation:

$$RCN + 2H_2O_2 = RCONH_2 + H_2O + O_2$$

Radziszewski found that the reaction took place easily in the presence of a small amount of alkali and at a temperature of about 40°. He was of the opinion that it would proceed especially well in all cases where the amide formed is insoluble in water, and gave as examples the formation of benzamide from benzonitrile and capronamide from capronitrile. Radziszewski used a 3% solution of hydrogen peroxide.

Deinert[2] applied this method to different nitriles, and obtained very fair yields of the corresponding amides from benzonitrile and *p*-tolunitrile,

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[1] *Ber.*, 18, 355 (1885)

[2] *J. prakt. Chem.*, [2] 52, 431 (1895).

poor yields from benzyl cyanide and β-naphthonitrile, very poor yields from propionitrile and α-naphthonitrile and no yield at all from *o*-tolunitrile. He thus came to the conclusion that the nitriles gave different results according to their constitution.

Bogert and Hand[1] used this same method for the direct formation of quinazolines from *o*-acylaminobenzonitriles, and Bogert and his associates have frequently used the same method since.

Keiser and McMaster[2] made use of this method to convert fumarnitrile into fumaramide. Practically a quantitative yield was obtained.

In October, 1915, we began a more thorough study of this method to see whether it could not be made of wider application and better yields obtained, particularly by the use of more concentrated solutions of hydrogen peroxide than had been previously used. Deinert used 1.8, 2.5 and 8.0% solutions but found that the 2.5% solution was the best one to use. We have applied our modification of the method to the transformation of benzonitrile, *m*-nitrobenzonitrile, *o*-tolunitrile, *p*-tolunitrile, α-naphthonitrile, β-naphthonitrile, terephthalnitrile, trichloroacetonitrile and isobutylacetonitrile into the corresponding amides. Recent abstracts give an account of some recent work by Dubsky[3] on the transformation of nitriles into amides by the Radziszewski method. Dubsky has brought about the hydrolysis of several nitriles into amides by using a large excess of a 3% solution of hydrogen peroxide. He was thus able to convert *o*-tolunitrile and α-naphthonitrile into amides, whereas Deinert found that they remained practically unchanged when treated with the usual amount of hydrogen peroxide.

We have been unable to obtain the original article of Dubsky's, and since we have worked with two of the same nitriles mentioned in the abstracts and found that the same results were obtained by using concentrated solutions of the peroxide instead of a large excess of the usual 3% solution, and since we have applied the method to a larger number of cases than Dubsky has, we thought that we should publish our results already obtained with the nitriles mentioned above. We also intend to apply the method in the case of many other nitriles.

Experimental.

Benzonitrile.—5 g. of benzonitrile were added to 50 cc. of a 6% solution of hydrogen peroxide and the mixture made slightly alkaline with sodium hydroxide. The mixture was stirred at a rather high rate of speed by means of a motor-driven apparatus to insure an intimate mixture of the substances. The temperature of the mixture was kept at 65° for 1.5

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[1] THIS JOURNAL, **24,** 1034 (1902) and following papers.

[2] *Am. Chem. J.*, **49,** 81 (1913).

[3] *J. Soc. Chem. Ind.*, **35,** 829 (1916); *J. Chem. Soc.*, **110,** I, 550 (1916); from *J. prakt. Chem.*, [2] **93,** 137 (1916).

hours, during which time the amide separated out as white flakes. The stirring was now interrupted and the mixture surrounded by ice and salt, whereupon more of the amide separated. It was filtered off, washed with cold water, dried over sulfuric acid for 48 hours and crystallized from absolute ethyl alcohol. The yield was about 92% of the theory. M. p. 128°. The m. p. recorded[1] in the literature is 128°.

Calc. for $C_6H_5CONH_2$: 11.59%. Found: 11.50% N.

***m*-Nitrobenzonitrile.**—1 g. of *m*-nitrobenzonitrile was added to 15 cc. of an approximately 20% solution of hydrogen peroxide, the mixture made slightly alkaline and warmed to 65°. The mixture was shaken vigorously, placed in the dark, and allowed to stand, with occasional shaking, for 24 hours. At the end of 1 hour a thin layer of white crystals formed at the surface of contact of the hydrogen peroxide solution and the nitrile which floated on the surface. The solution became a bright yellow-green in color. At the end of 24 hours the pale yellow crystals, which had separated and fallen to the bottom of the tube, were filtered off, washed with cold water and dried on a suction filter. The crystals were dissolved in a minimum amount of hot absolute ethyl alcohol and the amide freed from any unchanged nitrile by suddenly cooling the hot alcoholic solution in a freezing mixture. The nitrile, being less soluble than the amide in the alcohol, crystallized out first and was filtered off. On allowing the alcohol to evaporate, the amide crystallized out. This process was repeated several times until a product of m. p. 141° was finally obtained. The recorded[2] m. p. of *m*-nitrobenzamide is 140-142°. The final recrystallization yielded beautiful white needles, some of which were 4 cm. in length. The crystals of the amide formed were rather difficultly soluble in ethyl alcohol, ether, benzene, petroleum ether and water. The yield obtained was 80% of the theory.

Calc. for $C_6H_4(NO_2)CONH_2$: 16.87%. Found: 16.97% N.

***o*-Tolunitrile.**—Deinert[3] could not transform this nitrile into the corresponding amide by the use of hydrogen peroxide. Dubsky[3] found that 2.5 g. of the nitrile in 50 cc. of methyl alcohol gave a yield of 2.1 g. of *o*-toluamide on treatment at 40-60° with 200 cc. of 3% hydrogen peroxide and 10 cc. of *N* sodium hydroxide solution, the reaction product being neutralized, evaporated to dryness and extracted with alcohol.

We added 10 cc. of a 15% hydrogen peroxide solution to 1.1 g. of the nitrile in a large test tube, and, after making the mixture slightly alkaline, it was warmed to 65° and shaken vigorously. After standing 24 hours, a white crystalline mass had formed at the surface of the liquid. On warming the mixture again, the unchanged nitrile separated from the

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[1] Schiff and Tassinari, *Ber.*, 10, 1785 (1877).

[2] Reichenbach and Beilstein, *Ann.*, 132, 141 (1864).

[3] *Loc. cit.*

enclosing crystalline mass. The contents of the tube were again heated to 65°, shaken and allowed to stand for another 24 hours, whereupon more of the amide was formed. On further similar treatment no more amide formed. The crystals were filtered off on a suction filter, dried and taken up in absolute ethyl alcohol. From the third recrystallization the amide separated as white, semitransparent needles, readily soluble in ethyl alcohol, moderately soluble in ether and quite insoluble in cold water. The crystals obtained melted at 138°. Weith[1] found that *o*-toluamide melts at 138°. The yield was 90% of the theory.

Calc. for $C_6H_4(CH_3)CONH_2$: 10.37%. Found: 10.42% N.

***p*-Tolunitrile.**—Deinert obtained from 2 g. of this nitrile, dissolved in alcohol, 2 g. of amide (instead of 2.3 g.) which melted at 155°. We added 1 g. of the nitrile to 10 cc. of a 15% solution of hydrogen peroxide, made the mixture slightly alkaline and warmed it to 60°. The nitrile melted to a yellow oil. After shaking the mixture for some time, it was allowed to stand for 24 hours. The amide was filtered off, dried and crystallized from absolute ethyl alcohol. The crystals melted at 155°.

The experiment was repeated by treating 2 g. of the nitrile with 50 cc. of a 10% hydrogen peroxide solution and warming the mixture to 60°. Instead of shaking the mixture, we stirred it for 1 hour, at the end of which time the reaction was complete. The voluminous, flaky mass of amide on the surface of the liquid was filtered off, washed with water, dried and crystallized from ethyl alcohol. The crystals were found to melt at 155°. The literature records various melting points for *p*-toluamide. Fischli[2] gives 151°, Gatterman and Schmidt[3] give 156°, while Holleman[4] gives 158-159°. Deinert[5] records 155°. The amide is described as fine needles when crystallized from alcohol (Fischli) or large plates when crystallized from water (Gatterman and Schmidt). We obtained monoclinic needles of about 5 mm. in length. The yield obtained was about 90% of the theoretical.

Calc. for $C_6H_4(CH_3)CONH_2$: 10.37%. Found: 10.30% N.

α-Naphthonitrile.—Deinert observed practically no change in this nitrile when treated with hydrogen peroxide. Dubsky was able to convert it into the amide by means of a large excess of the reagent, but the abstracts of the article above referred to do not state the amount obtained. By treating 1 g. of the nitrile with 20 cc. of 10% hydrogen peroxide and making the mixture slightly alkaline, we were able to obtain a 20% yield after allowing the mixture to stand one week, with occasional

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[1] *Ber.*, **6**, 42 (1873).

[2] *Ibid.*, **12**, 615 (1879).

[3] *Ann.*, **244**, 51 (1888).

[4] *Rec. trav. chim.*, **6**, 78.

[5] *Loc. cit.*

shaking and warming. The mass which formed was filtered off, washed with cold water and placed on a porous plate. It contained some unchanged nitrile which would probably have changed to the amide had we continued to add hydrogen peroxide and allowed the mixture to stand longer. The porous plate was placed in a water oven and warmed to 45°. The greater portion of the unchanged nitrile (m. p. 36°) was absorbed by the plate and the amide remained as white, crystalline flakes. The amide was then freed from the remaining traces of nitrile by refluxing the mixture with a very small amount of ethyl alcohol and suddenly cooling it. The amide, being less soluble in alcohol than the nitrile, separates first and can be filtered off. The amide, recrystallized from alcohol, melted at 202°. The literature records[1] 202° as the m. p. of α-naphthoamide.

Calc. for $C_{10}H_7CONH_2$: 8.18%. Found: 8.16% N.

β-Naphthonitrile.—1 g. of β-naphthonitrile was added to 25 cc. of 10% hydrogen peroxide solution, the mixture made alkaline and warmed to 70°. The mixture was shaken vigorously and then allowed to stand. At the end of 1 hour fine, white needles began to form. The hydrogen peroxide decomposed very rapidly and the solution became bright yellow in color, later changing to bright red and finally to brown. Hydrogen peroxide was added from time to time and after 24 hours the transformation seemed to be complete. The solid mass, which had formed, was filtered off and washed first with water and then with alcohol to remove any unchanged nitrile. The amide is difficultly soluble in alcohol and remained on the filter. It was, however, recrystallized from alcohol and allowed to stand over sulfuric acid. Small rhombohedral plates of m. p. 192-193° resulted. There was a slight sublimation during the determination of the melting point. Vieth and Leone[2] record 192° as the melting point of β-naphthoamide.

Calc. for $C_{10}H_7CONH_2$: 8.18%. Found: 8.27% N.

From 2 g. of β-$C_{10}H_7CN$ Deinert obtained 0.8 g. of β-$C_{10}H_7CONH_2$ instead of the calculated amount, 1.12 g. From 1 g. of the nitrile we obtained 0.9 g. of the amide.

Terephthalnitrile.—The dicyanide of terephthalic acid, purified from boiling alcohol, was treated with hydrogen peroxide solution and a small amount of alkali. The mixture was warmed to 40° and a vigorous action took place. A white, amorphous compound, with a yellowish tinge, formed. This was separated from any unchanged nitrile by boiling alcohol in which the nitrile is soluble, while the amide is insoluble. Terephthalamide[3] is insoluble in all ordinary solvents. We found our product to be insoluble in

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[1] Hofmann, *Compt. rend.*, 66, 476 (1868); Leone, *Gazz. chim. ital.*, 14, 122 (1914).

[2] *Gazz. chim. ital.*, 14, 123.

[3] de la Rue and Müller, *Ann.*, 121, 90 (1862).

all such solvents. The compound, thus prepared, melted above 250°, and gave off ammonia when treated with potassium hydroxide solution. The yield was not determined.

Calc. for $C_6H_4(CONH_2)_2$: 17.07%. Found: 17.10% N.

The amide was then boiled with alcoholic potassium hydroxide until ammonia was no longer evolved (10 hours). The alcohol was allowed to evaporate spontaneously, leaving the white salt of terephthalic acid. The salt thus formed was dissolved in water and treated with dilute hydrochloric acid, but not enough to neutralize the solution for the free acid, which would form, is difficultly soluble in water. A concentrated solution of barium chloride was now added to the solution and also more hydrochloric acid to make the mixture more nearly neutral. White barium terephthalate formed, which was washed on a suction filter and dried at 150-160° for 2 days.

Calc. for $C_6H_4(CO_2)_2Ba$: 45.58%. Found: 45.52% Ba.

It was thus proved that we had prepared the pure terephthalamide from the nitrile.

Trichloroacetonitrile.—2 g. of trichloroacetonitrile were added to 40 cc. of 3% hydrogen peroxide solution. The mixture was treated with a few drops of sodium hydroxide solution, and stirred at a high rate of speed for 5 minutes. An energetic action took place and some free chlorine was liberated. The mixture was then set aside in the dark. At the end of 2 hours a few fine, white needles had separated, but at the end of 24 hours a mass of white needles, some of which were 2 cm. in length, had separated. These were filtered off, washed with water and then with 50% alcohol. The nitrile is very soluble in alcohol, while the amide is only fairly soluble in this solvent. The needle-like crystals of the amide were recrystallized from *cold* alcohol and placed over sulfuric acid for one week. They melted at 137°. Zincke[1] records the m. p. as 141°.

Calc. for CCl_3CONH_2: 8.62%. Found: 8.55% N.

From 2 g. of the nitrile we obtained 0.9 g. of the amide.

Isobutylacetonitrile.—1 g. of the nitrile was added to 50 cc. of 3% hydrogen peroxide solution, the mixture made *very slightly* alkaline and stirred at a high rate of speed for 1 hour, the temperature being maintained at 20°. It was found in preliminary experiments that a 6%, or stronger, solution of hydrogen peroxide caused oxidation to isocaproic acid and the presence of even 2 or 3 cc. of a 10% solution of sodium hydroxide brought about the same result. The alkalinity of the solution continually tended to disappear and frequent additions of a drop of sodium hydroxide solution were necessary. At the end of 1 hour the stirring was interrupted and the mixture allowed to stand for 24 hours. The mixture

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[1] *Ber.*, 33, 241 (1901).

was then cooled to 10°, when a small amount of precipitate formed. This was filtered off and crystallized from alcohol. M. p. 121°. The filtrate was evaporated to dryness on the water bath and the residue taken up in hot absolute alcohol. On cooling the alcoholic solution, flaky crystals of isobutylacetamide formed. This process was repeated several times. The crystals melted at 121°, with a slight sublimation at 118.5°. The recorded[1] m. p. is 120°. The yield was about 70% of the theory.

Calc. for $(CH_3)_2CH(CH_2)_2CONH_2$: 12.17%. Found: 12.22% N.

Conclusions.

1. We have thus prepared 9 amides in the pure condition from the corresponding nitriles. Their analyses (for nitrogen) have been made and some of their properties studied.
2. We have found that some of the nitriles, which formerly could not be transformed into amides by the ordinary concentration of hydrogen peroxide, can be transformed by more concentrated solutions of the peroxide.
3. It has been shown that the change of nitriles into corresponding amides by hydrogen peroxide, under stated conditions, is a generally applicable method.

ST. LOUIS, MO.

[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

THE PREPARATION OF GLYCOLLIC ACID.

BY EDGAR J. WITZEMANN.

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Perhaps the simplest and most inexpensive method of obtaining glycollic acid hitherto has been the method of Hölzer[2] in which monochloroacetic acid is boiled in aqueous solution with somewhat more than the calculated quantity of calcium carbonate until no more goes into solution. The solution is then filtered and allowed to cool and crystallize. The crystals of calcium glycollate ($Ca(C_2H_3O_2)_2.4H_2O$) are washed until free from calcium chloride. Sometimes a double salt of calcium chloride and glycollate separates as a lower layer. In any case the subsequent crops are contaminated with this double salt and washing and recrystallization must be continued until all calcium chloride has been removed. These latter processes are very time-consuming. In order to obtain the free glycollic acid the calcium is precipitated quantitatively from the solution of the pure calcium glycollate with the calculated amount of oxalic acid and the solution thus obtained evaporated and crystallized. The preparation of glycollic acid may be much simplified by using barium carbonate

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[1] Hofmann, *Ber.*, 17, 1411 (1884).

[2] *Ber.*, 16, 2955 (1883).