13. Aniline and 4,5-Dichlorophthalic Acid.—A number of preliminary experiments have been made with these compounds. The results show that the conditions require much more careful regulation than in the case of phthalic acid.

Summary.

1. We have studied the action of phthalic anhydride on a number of amines, including camphylamine, which gives the camphylimide; benzidine, which forms an insoluble product; and *m*-aminobenzoic acid, which yields a dicarboxylic acid.

2. The acylated amines, acetanilide, *p*-acetotoluidide and formo-β-naphthalide, eliminate the acyl group when heated with phthalic anhydride.

3. Carbamide and certain alkyl- and arylcarbamides, including phenylthiocarbamide, eliminate ammonia and carbon dioxide (or carbon oxysulphide) and form phthalimides or phthalamidic acids.

It is intended to continue the investigation of the interaction of phthalic acids and amines in this laboratory during the coming year.

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NOTE ON THE OXIDATION OF β-NAPHTHOQUINONE.

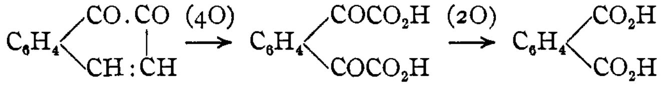
BY C. H. ROBINSON.

Received November 1, 1909.

In a series of experiments on the oxidation of naphthalene and various naphthalene derivatives, Daly[1] found some indications that in the oxidation of β-naphthoquinone by potassium permanganate in alkaline solution the reaction ceased before the amount of permanganate had been reduced which would correspond to the oxidation of the naphthoquinone to phthalonic acid and he mentions the possibility of the diketo acid, $C_6H_4(COCO_2H)_2$, being formed in the solution. Under the direction of Professor Allan, the author investigated this reaction in the hope of preparing the diketo acid in this way.

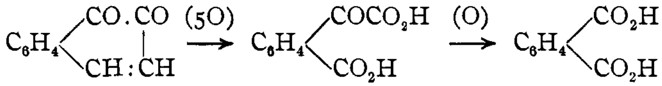
If the oxidation in alkaline solution were to the diketo acid and then in acid solution to phthalic acid the two stages of the reaction might be represented by A, but if the oxidation in alkaline solution were to phthalonic acid they would be represented by B.

A.



$$C_6H_4\left\langle\begin{array}{l}CO.CO\\ \ \ |\qquad |\\ CH:CH\end{array}\right. \xrightarrow{(4O)} C_6H_4\left\langle\begin{array}{l}COCO_2H\\ COCO_2H\end{array}\right. \xrightarrow{(2O)} C_6H_4\left\langle\begin{array}{l}CO_2H\\ CO_2H\end{array}\right.$$

B.



$$C_6H_4\left\langle\begin{array}{l}CO.CO\\ \ \ |\qquad |\\ CH:CH\end{array}\right. \xrightarrow{(5O)} C_6H_4\left\langle\begin{array}{l}COCO_2H\\ CO_2H\end{array}\right. \xrightarrow{(O)} C_6H_4\left\langle\begin{array}{l}CO_2H\\ CO_2H\end{array}\right.$$

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[1] *J. Phys. Chem.*, 11, 105.

So that the ratio of the amounts of oxygen used in the two stages of the reaction would be two according to A or five according to B.

The β-naphthoquinone was prepared by the method of Lagodzinski and Hardine[1] and purified by the method given by Boswell.[2] It is slightly soluble in decinormal sodium bicarbonate solution (0.54 g. per liter) and not more soluble in a normal solution.

To find the ratio between the amount of permanganate required to oxidize the naphthoquinone in alkaline solution and the permanganate required to complete the oxidation in acid solution to phthalic acid, 110 cc. of a saturated solution of the quinone in decinormal sodium bicarbonate was added to 50 cc. decinormal permanganate solution and left at laboratory temperature for twenty-four hours. In 50 cc. of this solution the residual permanganate was determined by adding a solution of 0.4 g. potassium iodide and 2 g. sulphuric acid in 100 cc. water and titrating the iodine set free. To another 50 cc. of the solution two per cent. sulphuric acid and a few drops of manganese sulphate solution were added, and after two minutes, by which time the oxidation to phthalic acid was complete, the solution of potassium iodide and sulphuric acid was added and the iodine determined. Since the oxidizing power of the permanganate is 1.66 times greater in acid solution than in alkaline solution, the permanganate used in oxidizing the solution to phthalic acid was multiplied by 1.66 so that the amounts of permanganate would be in proportion to their oxidizing value.

	I.	II.
$\frac{\text{Permanganate reduced in alkaline solution}}{\text{Permanganate reduced in acid solution}}$	4.65	4.75

This shows conclusively that the oxidation is as represented above in B and that the reaction in alkaline solution proceeds to phthalonic acid, but it is still possible that there is a rapid oxidation to the diketo acid and then a slower oxidation to phthalonic acid.

Some experiments were made to determine the constituents of the solution at various stages of the oxidation by adding small amounts of permanganate to the quinone solution, allowing the reaction to proceed till all the permanganate was reduced, acidifying the solution and ethering out. As the residual quinone is so much more insoluble in water than the products of the reaction, the residue obtained by the evaporation of the ether contained little else than quinone.

A = initial weight of quinone in the solution.
B = cc. permanganate used to 50 cc. quinone solution.
C = weight of residue from ether.
D = weight of quinone which would be left if oxidation were direct to phthalonic acid.

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[1] *Ber.*, **27**, 3075.

[2] THIS JOURNAL, **29**, 230.

E = weight of quinone which would be left if oxidation were to diketo acid.

A. Gram.	B. cc.	C. Gram.	D. Gram.	E. Gram.
0.0226	1	0.0209	0.0210	0.0206
0.0226	6	0.0126	0.0131	0.0108
0.0226	8	0.0110	0.0100	0.0068
0.0226	10	0.0087	0.0069	0.0023

The results given in this table are not very good because the method was inaccurate but they confirm the conclusion arrived at from the previous experiments that there is no intermediate stage in the oxidation of β-naphthoquinone to phthalonic acid in alkaline solution. A series of experiments, in which the rate of oxidation of the quinone in alkaline solution was determined, also gave no indication of the existence of an intermediate product.

Further experiments to prepare the diketo acid by the saponification of phthalyl cyanide are now being carried out.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 174.]

RESEARCHES ON QUINAZOLINES (TWENTY-FOURTH PAPER). ON OXALYL ANTHRANILIC COMPOUNDS AND QUINAZOLINES DERIVED THEREFROM.[1]

BY MARSTON TAYLOR BOGERT AND ROSS AIKEN GORTNER.

Received November 27, 1909.

In 1883, Kretschy[2] obtained by oxidation of kynurine, or of kynurenic acid, an acid which he called "kynuric acid." The succeeding year[3] he showed that this "kynuric acid" was oxalyl anthranilic acid.

The following pages describe various derivatives of oxalyl anthranilic acid and condensation products obtained therefrom.

Mauthner and Suida[4] have recorded the fact that when anthranilic acid is heated with ethyl oxalate, both oxalyl dianthranilic acid and ethoxalyl anthranilic acid are produced:

$$\mathrm{HOOC.C_6H_4.NH_2 + ROOC.COOR = HOOC.C_6H_4.NHCOCOOR + ROH,}$$

$$\mathrm{2HOOC.C_6H_4.NH_2 + ROOC.COOR = HOOC.C_6H_4.NHCOCONH.C_6H_4.COOH + 2ROH,}$$

and we have used this method for the preparation of these substances, as well as for the methoxalyl anthranilic acid. Oxalyl dianthranilic

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[1] Read at the meeting of the New York Section, March 5, 1909.

[2] *Monatsh. Chem.*, 4, 157 (1883).

[3] *Ibid.*, 5, 30 (1884).

[4] *Monatsh. Chem.*, 9, 743 (1888).