amorphous product of the resin, can by no means be expressed by simple chemical equations.

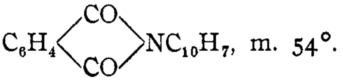
It may finally be observed that the purgative action of jalap resin is not due to any single or well-defined constituent, inasmuch as the products obtained by its successive extraction with various solvents, with the exception of the portion removed by light petroleum, appear to possess about an equal degree of physiological activity.

ACTION OF AMINES ON PHTHALIC ACID. VI.[1]

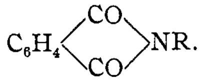
By J. Bishop Tingle and B. F. Parlett Brenton.

Received November 2, 1909.

In the course of the work described in our earlier paper, we studied the interaction of phthalic anhydride on a number of amino derivatives other than those we have already mentioned. The products which we ultimately obtained did not prove to be suitable for our intramolecular rearrangement investigations and consequently we did not carry on the work with them very far. We desire, however, to record the results which we have obtained, because we cannot continue our experiments conjointly.

Camphylamine and phthalic anhydride, when melted together, gave what is probably the *imide*,  $C_6H_4\langle{}^{CO}_{CO}\rangle NC_{10}H_7$, m. 54°. No solid hydrolysis product (amidic acid) could be obtained from it.

Benzidine and phthalic anhydride, under similar conditions, yielded a highly insoluble compound of great stability.

We made a large number of experiments with the object of "fixing" the mobile amidic hydrogen atom in the amidic acids, $RNHCOC_6H_4CO_2H$. With phosphorus pentachloride, phosphorus trichloride, or thionyl chloride, the only stable product of the reaction was the imide  $C_6H_4\langle{}^{CO}_{CO}\rangle NR$. We then directed our attention to the preparation of acylated amidic acids, such as $CH_3CONRCOC_6H_4CO_2H$. We attempted to prepare them by the action of acyl chlorides and of acid anhydrides on the amidic acids and also from acyl amines and phthalic anhydride. We found, however, that acetyl chloride or acetic anhydride either failed to react with the amidic acids, or else it transformed them into the imide, behaving in this respect exactly like the phosphorus halides mentioned above. Most of our experiments were made with phthalphenylamidic

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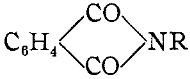
[1] The previous papers bearing on this subject have appeared as follows: Bishop Tingle and Cram, *Am. Chem. J.*, **37**, 596 (1907); Bishop Tingle and Lovelace, *Ibid.*, **38**, 642 (1907); Bishop Tingle and Rolker, THIS JOURNAL, **30**, 1882 (1908); Bishop Tingle and Brenton, *Ibid.*, **31**, 1157 (1909); Bishop Tingle and Bates, **31**, 1233 (1909).

acid. Our attempts at synthesis were carried out with phthalic anhydride and acetanilide, *p*-acetotoluidide and formo-β-naphthalide, respectively. When fractionally recrystallized, the products gave fairly sharp melting points, but further investigation showed that we were dealing with mixtures and that the phthalic anhydride, so far as it reacts at all, simply displaces the acetyl or formyl group from the amine, phthal-β-naphthylimide, for example, being produced from the above formo-β-naphthalide.

We failed to obtain any crystalline compound from 2,4-diaminophenol and phthalic anhydride, but from *m*-aminobenzoic acid we prepared the dicarboxylic acid, $HO_2\overset{1}{C}C_6H_4\overset{3}{N}H\overset{1}{C}OC_6H_4\overset{2}{C}O_2H$.[1]

The interaction of carbamide and of certain of its alkyl derivatives with phthalic anhydride has been studied previously.[2] When the mixture of the two compounds is heated in a test tube it melts, becomes solid as the temperature is raised and finally liquefies again. During the heating gas is evolved almost continuously, but chiefly towards the later stages of the experiment. The gas consists of ammonia and carbon dioxide, or in the case of a thiocarbamide, of carbon oxysulphide. The solid product of the reaction is a phthalimide,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NR$, in a fairly pure condition. After being once recrystallized it shows the correct melting point. This method of preparing the compounds in question is so easy and requires so little time that it is obviously the best to employ for the preparation, in relatively small quantity, of the imides in which $R = H, CH_3, C_2H_5$, or some other group, the amino or halide derivative of which is very volatile. We experimented with carbamide and its methyl, ethyl, benzyl and phenyl derivatives, and also with phenylthiocarbamide, obtaining phthalimide, and phthalmethyl-, ethyl-, benzyl- and phenylimides, respectively. Ethylidene carbamide gave only a tar. In the course of our experiments with phenylcarbamide we were successful in isolating phthalphenylamidic acid, $C_6H_5NHCO\ C_6H_4CO_2H$, as an intermediate product. Its formation throws some light on the mechanism of the reaction. To accomplish this was one of the chief objects of our investigation.

We have made some experiments, of a preliminary nature, on the action of aniline and 4,5-dichlorophthalic acid. The results show that the substances react in a more complicated manner than in the case of aniline and phthalic acid.

Experimental.

1. Camphylamine and Phthalic Anhydride.—When these substances

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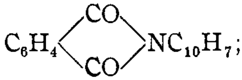
[1] Gabriel. Puitti, *Ber.*, **16**, 1320.

[2] Piutti, *Ann.*, **214**, 20. Dunlap, *Am. Chem. J.*, **18**, 337.

are fused together, in molecular proportion, water is evolved. The product appears to be *phthalcamphylimide*,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_{10}H_7$; after being recrystallized from benzene it melts at 54°.

N found, 5.67; calculated, 4.94 per cent.

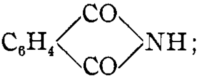
The substance was warmed with an aqueous solution of sodium carbonate and the clear solution acidified; this caused the deposition of an oil.

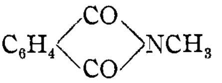
2. *Benzidine and Phthalic Anhydride.*—When melted together these substances combine. The resulting compound is very sparingly soluble in all the ordinary media. It was dissolved in nitrobenzene and precipitated by benzene, but we are uncertain as to its purity because it remained unmelted at 300°. Our specimen contained 7.37 per cent. of nitrogen. It failed to react with benzoyl chloride, by the Schotten-Baumann method. In a similar experiment, employing 2 mols. of base : 1 mol. of anhydride, the product appeared to be similar to that obtained in the first experiment, or identical with it.

3. *Acetanilide, p-Acetotoluidide, Formo-β-Naphthalide and Phthalic Anhydride.*—As explained in the theoretical part of this paper, our experiments with these substances were carried out in the hope of preparing disubstituted phthalamidic acids, $RR'NCOC_6H_4CO_2H$, in which one of the groups, R or R′, could be easily removed. The acylated bases were melted with the anhydride, and the heating continued during varying periods ranging from a few minutes to 1.5 hours. The resulting materials, after recrystallization, usually melted within 1°, but, in each case, further purification caused the melting point to vary widely from that shown at first and the analytical results were not constant. From formo-β-naphthalide we were able to isolate and identify phthal-β-naphthylimide and to prove that formic acid was evolved during the heating. It is evident, therefore, that the phthalyl group merely replaces the acyl already linked to the nitrogen of the amine.

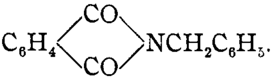
4. *2,4-Diaminophenol and Phthalic Anhydride.*—A considerable number of experiments were carried out with these substances, but no definite compound could be isolated.

5. *m-Aminobenzoic Acid and Phthalic Anhydride.*—We prepared the dicarboxylic acid, $HO_2\overset{1}{C}C_6H_4\overset{3}{N}H\overset{1}{C}OC_6H_4\overset{2}{C}O_2H$, in the manner described above and purified it by means of its sodium salt from the strongly colored materials which are produced during its formation. It dissolved readily in ethyl alcohol (40 per cent.), but the deposited material failed to exhibit crystalline structure. It was recovered unchanged by boiling with acetic anhydride and also by treatment with benzoyl chloride, by the Schotten-Baumann method.

6. Carbamide and Phthalic Anhydride.—When these substances are mixed in equimolecular proportion and heated they melt, then after a time solidify and, finally, as the temperature is raised, become liquid again. During the heating ammonia and carbon dioxide are evolved vigorously. The product consists of phthalimide,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$; it was fully identified by its melting point and analytical results. The same substance was obtained by the use of 2 molecular proportions of carbamide, under otherwise similar conditions. The yield was almost quantitative.

7. Methylcarbamide and Phthalic Anhydride.—These substances, when treated in the same manner as the carbamide, behaved similarly, giving phthalmethylimide,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NCH_3$ (m. p. 132°), carbon dioxide and ammonia. The yield was almost quantitative.

8. Ethylcarbamide and Phthalic Anhydride.—The product in this case was phthalethylimide. The yield was relatively small.

9. Benzylcarbamide and Phthalic Anhydride.—These substances reacted like the methylcarbamide, the product being phthalbenzylimide,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NCH_2C_6H_5$. The yield was good. An unsuccessful attempt was made to isolate the intermediate compound, the formation of which is indicated by the molten mass becoming solid. The only materials which could be identified were the mother-substances.

10. Phenylcarbamide and Phthalic Anhydride.—When these substances are melted together and the heating stopped as soon as they solidify, the product consists of phthalphenylamidic acid, $C_6H_5NHCOC_6H_4CO_2H$, which was fully identified. In another experiment the heating was continued until all reaction had ceased. In this case the only substance which was obtained was phthalphenylimide.

11. Phenylthiocarbamide and Phthalic Anhydride.—These substances behaved exactly like the phenylcarbamide mixture, except that the gases which were evolved were ammonia and carbon oxysulphide.

12. Ethylidenecarbamide and Phthalic Anhydride.—The product from this experiment was tarry.

The results recorded above show that the preparation of phthalimide and its alkyl derivatives is carried out far more easily by means of the carbamides than by the use of the amines, or from the alkyl halides and potassium phthalimide, provided that only relatively small quantities of material are required (5–10 grams) and that the amine or alkyl derivative is so volatile as to require the use of a sealed tube or autoclave.

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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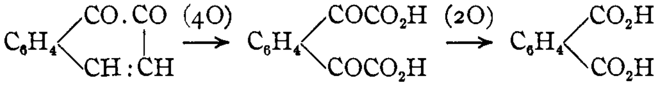
NOTE ON THE OXIDATION OF β-NAPHTHOQUINONE.

By C. H. Robinson.

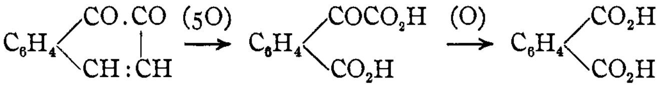
Received November 1, 1909.

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.


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

B.


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

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