UNITED STATES PATENT OFFICE.

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PRODUCTION OF DICARBOXYLIC ACIDS.

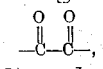
1,423,980. Specification of Letters Patent. Patented July 25, 1922.

No Drawing. Application filed March 22, 1921. Serial No. 454,479.

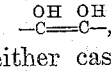
To all whom it may concern:

Be it known that I, ARTHUR G. WILLIAMS, a citizen of the United States, residing at Grantwood, in the county of Bergen and State of New Jersey, have invented certain new and useful Improvements in the Production of Dicarboxylic Acids, of which the following is a specification.

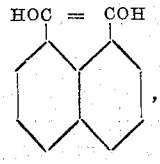
This invention relates to a process whereby certain dicarboxylic acids are obtained from appropriate compounds in a much more convenient, rapid and efficient manner than has hitherto been practicable and in yields which in certain cases far surpass those formerly obtainable. It relates more particularly to the production of dicarboxylic acids from aromatic compounds containing the diketonic group,



or the corresponding double bonded dihydroxy group,



such group in either case to form a part of a carbocyclic ring structure. These compounds are for the most part known as orthoquinones and hydroquinones, respectively, being generally either true quinones and hydroquinones or quinones and hydroquinones so-called. Examples (not to be exhaustive) of such compounds are phenenthraquinone, acenaphthene-quinone, retenequinone, fluoranthene-quinone, chrysenequinone, picene-quinone and the corresponding double bonded dihydroxy compounds. I have discovered that in the case of the diketonic compounds, preliminary reduction, as by sodium hydrosulfite in alkaline solution, for example, followed by oxidation in alkaline solution by means of a suitable oxidizing agent, as by sodium peroxide, hydrogen peroxide, or, where feasible, air, leads to the production of the corresponding dicarboxylic acids. I have discovered in the case of the dihydroxy compounds that their solution in aqueous alkali followed by oxidation by means of a suitable oxidizing agent, as by sodium peroxide, hydrogen peroxide or, where feasible, air, leads likewise to the production of the corresponding dicarboxylic acids. Thus, from phenanthraquinone and phenanthrenehydroquinone, diphenic acid is obtained, while from acenaphthenequinone and 7, 8-dihydroxyacenaphthylene,



naphthalic acid is produced. Suitable substituted derivatives of the parent compounds, substituents being, for example, alkyl, halogen, hydroxyl, sulfo, may likewise be employed for the production of the corresponding substituted dicarboxylic acids.

Inasmuch as phenanthrene and acenaphthene are comparatively plentiful, the invention will be illustrated and described specifically in connection with them and their derivaties, but it is to be understood that the invention is not restricted to these particular substances.

The usual products of the direct oxidation of phenanthrene are phenanthraquinone and, from this, diphenic acid. Inasmuch as phenanthraquinone is a higher oxidation product of phenanthrene than is phenanthrene-hydroquinone and is therefore nearer in state of oxidation to diphenic acid than is the hydroquinone, it has not been obvious that the acid may be produced much more readily from phenanthrene-hydroquinone, the intermediate production of which from phenanthraquinone represents in a sense a backward step, not to be foreseen, yet found desirable, in the production of diphenic acid.

I have found, for example, that the action of an oxidizing agent such as sodium peroxide on an alkaline reduced solution of phenanthraquinone or on an alkaline solution of phenanthrene hydroquinone results directly in a substantially quantitative conversion to the dicarboxylic acid, here diphenic acid, and that this oxidation will take place at comparatively low temperatures. The conversion takes place almost immediately between 50°–60°C. and re-

quires only a short time at a temperature of about 35°C. This unexpected result is one of the unforeseen consequences of my invention. The sensitiveness of hydroquinones to oxidation to the corresponding quinones is well known and it was therefore wholly unexpected that certain oxidizing agents should have shown a preference for another course. Experimentation shows, for example, that alkaline potassium permanganate, the oxidant most generally used in alkaline solution, regenerates the quinone when allowed to act on phenanthrene-hydroquinone. Further, Anschütz and Japp found (Ber. vol. 11 page 211) that alkaline permanganate at 100° gave with phenanthraquinone diphenylene-ketone and only traces of diphenic acid. Inasmuch, however, as their oxidation was applied to the quinone unreduced, it is in no wise comparable to the peroxide process.

Hitherto diphenic and naphthalic acids have been made by the oxidation of phenanthrene and acenaphthene, respectively, or the corresponding quinones, by the action in acid medium of chromic acid or of sodium or potassium dischromate. In the case of the production of diphenic acid from phenanthrene, there is obtained by the usual oxidation procedure a mixture of unchanged phenanthrene, phenanthraquinone, and diphenic acid, and if the phenanthrene is not pure, as is usually the case, other products including acids are produced, thus forming a mixture from which the separation of a diphenic acid of a high degree of purity is a matter of considerable difficulty. If the oxidation is carried far enough to oxidize all of the phenanthrene and phenanthraquinone, much of the diphenic acid is itself destroyed. The yield of acid in either case is very low.

If diphenic acid is produced from phenanthraquinone, there is obtained by the usual oxidation procedure a mixture of unchanged phenanthraquinone and diphenic acid, and if the quinone is crude, other products including acids will be produced, thus forming a mixture requiring a separation of the diphenic acid from other products, thereby making even much more difficult the production of a diphenic acid of a high degree of purity. Here too, in the case of the use of phenanthraquinone, the yield is comparatively small. Thus Oyster and Adkins (J. Am. Chem. Soc. 43,208—1921—), even by improvement on the previously described procedures, were able by the usual chromate oxidation to secure a yield of only 53% of diphenic acid from phenanthraquinone that had been purified by means of sodium bisulfite.

In the case of the production of naphthalic acid from acenaphthene, the direct oxidation process is a prolonged operation subject to practically the same difficulties as in the case of phenanthrene, and unless acetic acid is used as the menstruum for the reaction, thereby greatly increasing the cost of production and this still with a prolonged operation, the naphthalic acid is only difficultly obtainable and the yield is very small.

By my process the principal difficulties of other processes are not encountered and the production of the acid may be had rapidly, in high degree of purity, and without the necessity of separations from troublesome by-products. Moreover, the yield is very high, the essential reaction being in all probability quantitative. Thus, a yield of 86% and upwards may be obtained from purified phenanthraquinone and a yield of 52% may be obtained even from a crude phenanthraquinone which had been made by chromate oxidation from a phenanthrene of but 70% purity. This crude phenanthraquinone had been prepared only by being washed with a soda solution. It is a very great improvement over all other processes for the production of diphenic acid to have obviated the desirability of using a purified phenanthraquinone, or of a highly pure phenanthrene in the production of the former. The purification of a crude phenanthraquinone requires large amounts of sodium bisulfite in a leeching or digesting operation.

I have discovered that the preliminary reductions in the case of the diketonic compounds or the starting with the corresponding double bonded dihydroxy compounds, and the oxidation in alkaline solution with certain specific agents, such as sodium peroxide, hydrogen peroxide, or where feasible, air, are highly advantageous. The following are given as specific examples illustrating the invention:

10 parts of phenanthraquinone may be warmed until it dissolves in a solution of 100 parts of 20% sodium hydroxide and 20 parts of solid sodium hydrosulfite. The final solution may be poured onto ice and 45 parts of sodium peroxide rapidly and thoroughly stirred into the cold ice-containing solution. The resultant system may then be warmed to about 40°–50°, or until the green color which it possessed has disappeared. The solution may then be filtered and the filtrate acidified with hydrochloric acid, thus causing the diphenic acid to be precipitated. The copiously precipitated diphenic acid may be filtered off and washed with water. The yield has been found to be about 86.2% of theoretical yield.

Naphthalic acid, for another example, may be made in an exactly analogous manner. In the case of the production of this acid either from acenaphthenequinone or from 7, 8-dihydroxy-acenaphthylene, blow-

ing with air may be substituted for the use of the peroxide.

I claim:

1. The process of producing a dicarboxylic acid from an aromatic compound containing a diketonic group,

forming part of a carbocyclic ring structure, which comprises dissolving the said compound in a suitable alkaline reducing solution, and oxidizing the solution.

2. The process of producing a dicarboxylic acid from an aromatic compound containing a double bonded dihydroxy group,

forming part of a carbocyclic ring structure, and having an existent corresponding diketonic compound, which comprises dissolving the said dihydroxy compound in an alkaline solution, and oxidizing the solution.

3. The process of producing a dicarboxylic acid from an aromatic compound containing a diketonic group,

forming part of a carbocyclic ring structure, which comprises dissolving the said compound in a suitable alkaline reducing solution, and oxidizing the solution by means of a peroxide.

4. The process of producing a dicarboxylic acid from an aromatic compound containing a double bonded dihydroxy group,

forming part of a carbocyclic ring structure and having an existent corresponding diketonic compound, which comprises dissolving the said dihydroxy compound in an alkaline solution, and oxidizing the solution by means of a peroxide.

5. The process of producing a dicarboxylic acid from an aromatic compound containing a diketonic group,

forming part of a carbocyclic ring structure, which comprises dissolving the said compound in an alkaline hydrosulfite solution and oxidizing the solution by means of a peroxide.

6. The process of producing diphenic acid from phenanthraquinone which comprises dissolving the said quinone in a suitable alkaline reducing solution, and oxidizing the solution.

7. The process of producing diphenic acid from phenanthraquinone, which comprises dissolving the said quinone in an alkaline hydrosulfite solution, and oxidizing the solution.

8. The process of producing diphenic acid from phenanthraquinone, which comprises dissolving the said quinone in an alkaline reducing solution, and oxidizing the solution by means of a peroxide.

9. The process of producing diphenic acid from phenanthraquinone, which comprises dissolving the said quinone in an alkaline hydrosulfite solution, and oxidizing the solution by means of a peroxide.

10. The process of producing diphenic acid from phenanthraquinone, which comprises dissolving the said quinone in an alkaline hydrosulfite solution, and oxidizing the solution by means of sodium peroxide.

11. The process of producing diphenic acid from phenanthrene-hydroquinone, which comprises dissolving the said hydroquinone in an alkaline solution, and oxidizing the solution.

12. The process of producing diphenic acid from phenanthrene-hydroquinone, which comprises dissolving the said hydroquinone in an alkaline solution, and oxidizing the solution by means of sodium peroxide.

13. The process of producing naphthalic acid from acenaphthene-quinone, which comprises dissolving the said quinone in an alkaline reducing solution, and oxidizing the solution.

14. The process of producing naphthalic acid from acenaphthene-quinone, which comprises dissolving the said quinone in an alkaline hydrosulfite solution, and oxidizing the solution.

15. The process of producing naphthalic acid from acenaphthene-quinone, which comprises dissolving the said quinone in an alkaline reducing solution, and oxidizing the solution by means of a peroxide.

16. The process of producing naphthalic acid from acenaphthene-quinone, which comprises dissolving the said quinone in an alkaline hydrosulfite solution, and oxidizing the solution by means of a peroxide.

17. The process of producing naphthalic acid from acenaphthene-quinone, which comprises dissolving the said quinone in an alkaline hydrosulfite solution, and oxidizing the solution by means of sodium peroxide.

18. The process of producing naphthalic acid from 7, 8-dihydroxy-acenaphthylene which comprises dissolving the said 7, 8-dihydroxy-acenaphthylene in an alkaline solution and oxidizing the solution.

19. The process of producing naphthalic acid from 7, 8-dihydroxy-acenaphthylene, which comprises dissolving the said 7, 8-dihydroxy-acenaphthylene in an alkaline solution, and oxidizing the solution by means of sodium peroxide.

In testimony whereof I affix my signature.

ARTHUR G. WILLIAMS.