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OXIDATION OF AROMATIC DERIVATIVES

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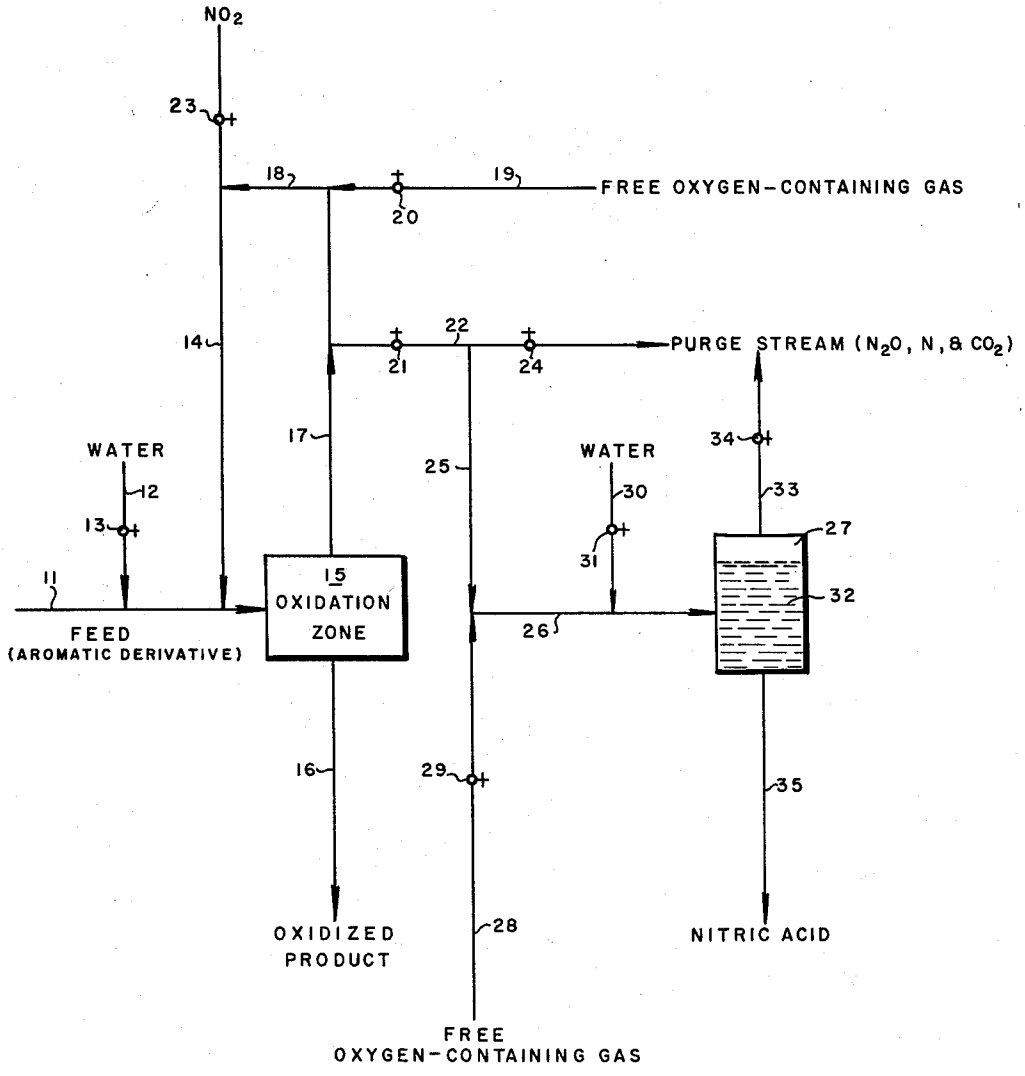


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# OXIDATION OF AROMATIC DERIVATIVES

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The present invention is directed to a method for oxidizing an aromatic derivative. More particularly, the invention is concerned with a method for producing carboxylic acid from aromatic derivatives. In its more specific aspects, the invention is concerned with the oxidation of an aromatic derivative in which a single liquid phase is maintained in the oxidation zone.

The present invention may be briefly described as a method for oxidizing an aromatic derivative having the formula: $(CH_3)_mRX_n$, where R is an aromatic ring; X is a functional group selected from the group consisting of $—CH_2OCH_3$ and $—CH_2Cl$; $m$ is within the range of 0 to 5; and $n$ is within the range of 1 to 3. In the practice of the present invention the aromatic derivative is contacted in an oxidation zone under oxidizing conditions with $NO_2$. It has been found in accordance with the present invention that methylmethoxy and chloromethyl aromatic derivatives may be converted to carboxylic acids in high yield and purities by oxidizing with $NO_2$. Furthermore, it is preferred in the practice of the present invention to oxidize the aromatic derivatives in the presence of a small, but sufficient amount of water such that a single liquid phase is maintained in the oxidation zone.

While oxidation processes for the production of carboxylic acids have been suggested, many of these processes are not particularly satisfactory. For example, it has been suggested to employ nitric acid to oxidize aromatic compounds to the corresponding carboxylic acids. However, the use of nitric acid results in a stratification of the aromatic compound and the nitric acid into two liquid phases thus reducing contact of the oxidizing agent with the aromatic compound and also introduces into the process a difficult separation problem. It has also been suggested that nitric acid be used in the oxidation to convert chloronated derivatives of aromatic compounds to the corresponding carboxylic acid, but it has been found that this process produces two types of carboxylic acids—one containing chlorine and one having no chlorine.

According to the present invention, it has been found that the methylmethoxy and chloromethyl derivatives of benzene are oxidized selectively with $NO_2$ whereby the methylmethoxy and chloromethyl functional groups are oxidized to the carboxylic group in high yields. It has been found that the methylmethoxy and chloromethyl functional groups, while exhibiting some distinct properties, are each oxidizable to the carboxylic group by oxidizing with $NO_2$ at temperatures within the range from about 80° to about 130° C. Preferred temperatures are within the range from about 95° to about 115° C. Within the stated temperature range, the methylmethoxy and chloromethyl groups are selectively oxidized even though the benzene ring may be substituted with alkyl groups.

The aromatic derivatives which may be employed in the practice of the present invention have the formula: $(CH_3)_mRX_n$, where R is a benzene ring; X is a functional group selected from the group consisting of $—CH_2OCH_3$ and $—CH_2Cl$; $m$ is within the range of 0 to 5; $n$ is within the range of 1 to 3; and $m+n$ does not exceed 6. Illustrative of the types of compounds which may be oxidized in accordance with the present invention are those compounds having a benzene ring with a chloromethyl group or a methyl ether group attached to the ring. Further, compounds having a benzene ring with two or three chloromethyl groups or methylmethoxy groups attached to the ring may be used as feed in the



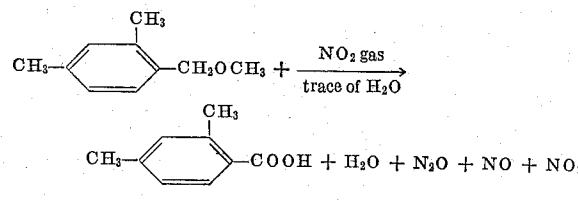
practice of the present invention. It is further contemplated that mixtures of the functional groups are also suitable. The compounds having a benzene ring may have one to five methyl groups attached to the ring plus one or more of the chloromethyl groups or methylmethoxy groups. Illustrative of the compounds which may be used as feedstocks for oxidation are: o- and p-xylyl chloride, o- and p-xylyl methyl ether, chloromethyl p-xylene, methoxymethyl p-xylene, α,α′-dichloro-p-xylene, 1,4-bis methoxymethyl) benzene, 4,6-dichloromethyl m-xylene, 4,6-dimethoxymethyl m-xylene, chloromethyl durene, methoxymethyl durene, bis methoxymethyl durene, trichloromethyl p-xylene, trimethoxymethyl p-xylene and the like.

It has been found in the practice of the present invention that the oxidation of the aromatic derivatives using $NO_2$ is enhanced by the addition of water at the start of the oxidation. The amount of water employed need only be a trace, such as 0.0001 by volume, based on the feed. However, the amount of water used should not exceed that amount wherein a phase separation exists in the oxidation zone. Thus, an amount of water is used such that a single liquid phase is maintained in the oxidation zone. This single liquid phase may be maintained by dispersing the water throughout the feed by mild mixing. It is noted that the oxidation of the aromatic derivatives employed in the present invention will produce water as a product. The necessity of adding water initially is not completely understood; however, it is thought that the oxidation of the methylmethoxy and chloromethyl groups is more rapid with nitric acid than with $NO_2$ gas. It is also contemplated that the presence of water is most beneficial when more than one functional group is to be oxidized to the corresponding carboxylic acid.

The amount of $NO_2$ employed in the practice of the present invention may range from about 1 to 5 moles per mole of the aromatic derivative having one mono-functional group. If the aromatic derivative has more than one functional group, then the amount of $NO_2$ employed is increased according to the number of functional groups. Therefore, a preferred range is from about 1 to about 3 moles per mole of an aromatic derivative having one mono-functional group; whereas, the range is from 2 to 6 moles per mole of an aromatic derivative having 2 functional groups and a range from about 3 to 9 moles per mole of an aromatic derivative having 3 functional groups.

In practicing the present invention, there is maintained in the oxidation zone a single liquid phase, and only oxidized product and off gases are withdrawn. The off gases contain NO and are suitably admixed with air or other free oxygen-containing gas to convert the NO to $NO_2$ which then may be employed to contact the aromatic derivative in the oxidation zone. From time to time or continuously, it may be desirable to withdraw a purge stream since the off gas contains a small amount of $N_2O$. An amount of $NO_2$ sufficient to compensate for the withdrawn $N_2O$ may be added to the system.

In practicing the present invention, aromatic derivatives of the nature illustrated hereinbefore are oxidized to carboxylic acid using $NO_2$ gas. Only a trace of water is needed in the reaction mixture to start the reaction as illustrated in the following equation:



The present invention will be further illustrated by reference to the flow diagram in which the single figure is a flow sheet of a preferred mode. Referring now to the drawing, numeral **11** designates a charge line through which a feed aromatic derivative is introduced into the system from a source, not shown. If the feed does not contain dissolved water, a trace of water is added to the feed through line **12** by opening valve **13**. The feed flowing in line **11** has admixed with it $NO_2$ introduced by way of line **14**, and the mixture of $NO_2$, water, and feed is then discharged into an oxidation zone **15** maintained at a temperature in the range from about 80° to 130° C. The $NO_2$ may be introduced in an alternate manner into the bottom of the oxidation zone by a separate line not shown. This alternative may be preferred to prevent solids from forming in the feed line to the oxidation zone. In oxidation zone **15** a single liquid phase is maintained and, as a result of the oxidation occurring in zone **15**, there is withdrawn by way of line **16** the oxidized product, and by way of line **17**, the off gases.

The oxidation in zone **15** is conducted over a period of time ranging from about 0.5 to about 20 hours. A satisfactory time for the oxidation to proceed may be suitably in the preferred range from about 1 to 8 hours. The off gases in line **17** are discharged into line **18** and have admixed therewith a free oxygen-containing gas such as air which is introduced by line **19** controlled by valve **20**. The free oxygen-containing gas oxidizes NO in the off gases to $NO_2$, and these gases are then discharged into line **13** for recycling to the oxidation zone **15**. Since the gases withdrawn by line **17** contain $N_2O$, it is necessary to withdraw either intermittently or continuously a purge stream; and, this is done by opening valve **21** in purge line **22**. When the purge stream is taken off by line **22**, it will be necessary to compensate for the amount of $N_2O$ that is discharged and to compensate therefor; valve **23** in line **14** is opened, introducing a small, but additional amount of $NO_2$ into the system.

The purge stream in line **22** may be discharged from the system by opening valve **24** or the purge stream may be routed by way of lines **25** and **26** into a zone **27**. When this is desirable, the purge stream in line **25** has admitted thereto a free oxygen-containing gas which is admitted by line **28** controlled by valve **29**. Water is added to line **26** by way of line **30** controlled by valve **31** to form nitric acid which is accumulated as a body **32** in drum **27**. A purge stream may be withdrawn from drum **27** by way of line **33** controlled by valve **34**. Nitric acid is withdrawn from drum **27** by line **35**.

The invention may be illustrated by the following examples:

*Example I*

Into a 500 cc. flask equipped with a water condenser is placed 100 g. (0.66 mole) of 2,4-dimethyl methylmethoxybenzene containing a trace of water. The ether is warmed to a constant temperature of about 80° C., and then $NO_2$ gas is bubbled into the flask. During the reaction, the temperature rises to about 107° C.; and, the reaction proceeds for about 3½ hours. The introduction of $NO_2$ is then stopped; and when the reaction mixture is cooled to room temperature, the whole mass crystallizes except for a small amount of oily matter.

The solid is broken into fine particles and washed with petroleum ether and then with ethyl ether. A snow white solid (68.4 g.) is recovered having a melting point of 123–126° C. and neutral equivalent of 150.3. The melting point and neutral equivalent for 2,4-dimethyl benzoic acid are 126-127° C. and 150, respectively. Upon further extraction, an additional 22.7 g. of high purity 2,4-dimethyl benzoic acid is recoverable. The conversion of 2,4-dimethyl methylmethoxybenzene to 2,4-dimethyl benzoic acid is about 91%.

*Example II*

Into a 500 cc. flask equipped with a water condenser and a stirrer is placed 75.25 g. (0.5 mole) of dry 2,4-dimethyl chloromethylbenzene. The chloromethyl compound is warmed to a constant temperature of about 80° C. and then $NO_2$ gas is bubbled into the flask. The temperature is allowed to increase over a period of about four hours to 150° C., and the introduction of $NO_2$ is continued for another four hours at about a temperature within the range of about 145° to 155° C. Introduction of $NO_2$ is then stopped, and the reaction mixture is cooled to room temperature. Upon cooling, a semi-solid mixture is formed which contained only a small amount of acid.



*Example III*

In the same manner as in Example II, 51.2 g. (0.333 mole) of 2,4-dimethyl chloromethylbenzene and 5 cc. of water is placed into a 500 cc. flask. After warming to about 80° C., $NO_2$ gas is bubbled into the chloromethyl compound; and, the reaction temperature rises to about 95° to 105° C. The reaction is allowed to proceed for a total reaction time of about 7½ hours. The reaction mixture is then cooled to room temperature and consists mostly of a white solid with a small amount of oily material on top of the solid.

The reaction mixture is treated with an excess of sodium carbonate solution and extracted with ether to remove neutral materials. The aqueous sodium carbonate phase is acidified with $HNO_3$ and extracted a second time with ether to dissolve the carboxylic acid. The second ether solution is washed free of the mineral acid, dried, filtered, and all solvents evaporated off whereupon 2,4-dimethylbenzoic acid is recovered.

It can be seen from a comparison of Examples I, II, and III, that it is more beneficial in the oxidation of a chloromethyl group to have a significant amount of water present during the oxidation. The addition of water appears to make the reaction more rapid and complete. It is further noted that if the reaction mixture is maintained in a single liquid phase and that the reaction proceeds rapidly, the oxidation is selective in that only the methylmethoxy and chloromethyl functional groups are oxidized. In Example II it is noted that the oxidation is not selective when the reaction with $NO_2$ is incomplete giving undesirable products and the temperature is allowed to rise above 130° C. whereby the tendency to produce nitrated acids is increased.

*Example IV*

A 500 cc. flask is equipped with a stirrer and a reflux condenser. Into the flask is added 48.5 g. (0.25 mole) of 4,6-dimethoxymethyl m-xylene and 120 g. (2 moles) of glacial acetic acid. The charge is warmed to a constant temperature of about 80° C., and then $NO_2$ gas is bubbled into the mixture. During the addition, the temperature rises to about 120° C. The addition of $NO_2$ proceeds for about 7 hours. At this time, 10 cc. of water are added to the reaction mixture, and $NO_2$ is added for another 8 hours. The reaction mixture is stirred to maintain a single liquid phase after the addition of water, and finely divided solids are observed in less than one hour after the addition of water.

The reaction mixture is diluted with approximately an equal volume (170 cc. of water) and cooled in ice water to about 40° C. and filtered. Snow white solid is recovered which after washing and drying is the 4,6-dimethyl isophthalic acid of 90–95% purity.

The addition of the acetic acid to the reaction mixture in the oxidation of 4,6-dimethoxymethyl m-xylene is to maintain the intermediate aldehyde acid in solution. Thus, when the aromatic derivatives of the present invention contain more than one mono-functional group, it is preferred that the oxidation take place in the presence of a solvent, such as acetic acid, which will maintain all the reaction materials in a single liquid phase.

*Example V*

Into a 500 cc. flask is added 48 g. (0.2 mole) of 2,3,5-

trimethoxymethyl p-xylene, 120 g. (2 moles) of glacial acetic acid and 10 cc. of water. The charge is warmed to a constant temperature of about 80° C., and then $NO_2$ gas is bubbled into the mixture. Temperature rises during the addition to about 120–130° C. Then, $NO_2$ gas is added for a period of about 15 hours. The reaction mixture is constantly stirred to maintain a single liquid phase; and after the end of the reaction, the reaction mixture is cooled. From the reaction mixture is obtained 3,6-dimethyl trimellitic acid in high purity and yield.

The present invention is quite advantageous and useful since it eliminates entirely the addition of nitric acid for the oxidation medium substituting therefor $NO_2$. In other words, the invention is useful because the cost of nitric acid is eliminated, and the cost of $NO_2$ as compared thereto is only a small amount. Moreover, by virtue of using $NO_2$ and a trace of water, it is possible to reduce the size and therefore the cost of the oxidation zone with an attendant reduction in corrosion problems since the $NO_2$ and water are not as corrosive as the dilute nitric acid ordinarily employed. Furthermore, it is possible in the practice of the present invention to use higher temperatures, where such may be desirable; whereas, heretofore the temperatures usable in the oxidation of aromatic derivatives employing aqueous nitric acid were limited by the reflux temperature of the aqueous nitric acid unless pressure equipment is employed.

An unexpected and most desirable feature of the present invention is due to the fact that the $NO_2$ gas and the trace of water that is used is miscible with the charge stocks. In other words, whereas hot aqueous nitric acid is only slightly soluble in the feedstock, the $NO_2$ gas and trace of moisture are miscible. Thus, in the practice of the present invention, a single liquid phase is maintained in the oxidation zone assuring good contact and substantially complete reaction.

A further advantage of the present invention and an unexpected and unobvious result is that the recovery of products is essentially 100 percent since the product is recovered as the carboxylic acid directly; there is no problem such as with aqueous nitric acid where a significant amount of the product remains in solution in the aqueous acid and must be removed by extraction with a solvent, evaporation, and the like. In short, the practice of the present invention is quite advantageous and useful.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and secure by Letters Patent is:

1. A method for oxidizing an aromatic derivative having the formula: $(CH_3)_mRX_n$, where R is a benzene ring; X is a functional group selected from the group consisting of $—CH_2OCH_3$ and $—CH_2Cl$; *m* is within the range of 0 to 5; and *n* is within the range of 1 to 3 which comprises contacting said aromatic derivative in an oxidizing zone under oxidizing conditions which include a temperature within the range from about 80° to about 130° C. with $NO_2$ in the presence of water such that a single liquid phase is maintained in said zone wherein said functional group is selectively oxidized to form the corresponding carboxylic acid in a time period of less than 20 hours.

2. A method in accordance with claim 1 wherein said aromatic derivative is methoxymethyl xylene and said time period is less than 8 hours.

3. A method in accordance with claim 1 wherein said aromatic derivative is chloromethyl xylene and said time period is less than 8 hours.

4. A method in accordance with claim 1 in which the oxidizing conditions include a temperature within the range from about 95° to about 115° C.

5. A method for oxidizing an aromatic derivative having the formula: $(CH_3)_mRX_n$, where R is a benzene ring; X is a functional group selected from the group consisting of $—CH_2OCH_3$ and $—CH_2Cl$; *m* is within the range of 0 to 5; and *n* is within the range of 1 to 3 which comprises contacting said aromatic derivative in an oxidizing zone under oxidizing conditions which include a temperature within the range from about 80° to about 130° C. with $NO_2$ for a time period of less than 20 hours in the presence of water such that a single liquid phase is maintained in said zone, separately withdrawing the oxidized product and the gas-containing NO and $N_2O$ from said zone, said oxidized product comprising the corresponding carboxylic acid formed by the oxidation of said functional group consisting of $—CH_2OCH_3$ and $—CH_2Cl$ of said aromatic derivative, admixing with said gas a free oxygen-containing gas to convert said NO to $NO_2$ and then employing said last named $NO_2$ to contact said aromatic derivative.


**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,298,387 | 10/42 | Kenyon et al. | 260—523 X |
| 2,561,350 | 7/51 | Eichel | 260—523 X |
| 2,821,551 | 1/58 | Katzschmann | 260—523 X |
| 3,068,280 | 12/62 | Katzschmann | 260—523 X |

FOREIGN PATENTS

| | | |
|---|---|---|
| 730,474 | 5/55 | Great Britain. |
| 823,437 | 11/59 | Great Britain. |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