Patented June 2, 1931

1,808,349

# UNITED STATES PATENT OFFICE

WILLIAM J. HALE AND WESLEY C. STOESSER, OF MIDLAND, MICHIGAN, ASSIGNORS TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN

## PREPARATION OF DIPHENYLENE OXIDE

No Drawing. Application filed August 17, 1929. Serial No. 386,735.

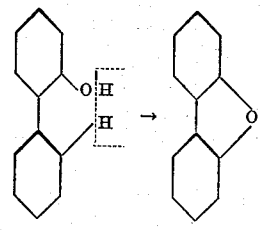
The present invention relates to methods for the preparation of compounds of the type of diphenylene oxide. This compound was discovered by Lesimple (Ann. 138; 376 (1866)) in the products of the distillation of triphenyl phosphate with lime. It has also been obtained in small amount when phenol was heated with lead oxide (Gallewsky, Ann. 264; 189 (1891)); by heating diphenyl oxide (Graebe, Ann. 174; 190 (1874)); by treating ortho-bi-phenol with zinc chloride (Kraemer & Weissgerber, Ber. 34; 1663 (1901)). Somewhat larger yields of diphenylene oxide have been obtained by the diazotization and subsequent hydrolysis of 2-amino-diphenyl oxide by Graebe and Ullmann (Ber. 29; 1876 (1896)), who obtained a 30% yield, and by the similar treatment of 2, 2'-diamino diphenyl by Täuber and Halberstadt (Ber. 25; 2745 (1892)), who obtained a yield of 75%. The latter two methods are not adapted to commercial operation due to the difficulty of obtaining and the high cost of the starting materials required, as well as the comparatively low yields returned.

The diphenylene oxide product obtained by means of any of the foregoing methods has not consisted of the pure compound, but has been contaminated by impurities imparting to it a marked discoloration. The melting point of such product has been variously reported by different investigators as 80 to 81° C., or as between 85 and 88° C. Similarly the boiling point has been variously reported at temperatures from 275° to 288° C. The lack of agreement with respect to the melting and boiling points has doubtless been due to the impurity of the product heretofore prepared.

We have now found that the aforesaid diphenylene oxide may be prepared in yield as high as 80 per cent or more and in a highly pure state by a simple and direct method which is based upon the pyrogenic decomposition of ortho-phenyl phenol, i. e., ortho-hydroxy diphenyl. The product so obtained consists of pure, white, fine crystals of triclinic form having a melting point of 82 to 83° C., and a boiling point of 283.1°–183.6° C. (corr.) at 750.5 mm. and 154°–154.5° C. (corr.) at 20 mm., therefore being a greatly superior product to that made by any of the previously known methods. The starting material for our new and improved method, e. g., ortho-phenyl phenol, may now be obtained in large quantities and in good yield, in connection with the manufacture of phenol by the alkaline hydrolysis of chlorobenzene, so that a plentiful supply of raw material is available at a cost compatible with large scale commercial production.

To the accomplishment of the foregoing and related ends the invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth certain preferred procedure whereby the principle of the invention may be used.

The reaction, whereon the present improved process is based, may be represented in diagrammatic fashion as the following:




By passing the vapors of ortho-phenyl phenol through a hot tube at a temperature between 300° and 800° C. the partial dehydrogenation thereof is caused to take place in greater or lesser amount, depending upon the actual temperature employed. The higher temperatures lead to a more rapid rate of reaction, but at the same time, are more conducive to side reactions resulting from the activity of the hydrogen liberated in the principal reaction and leading to the formation of undesirable impurities in the product.

Diphenylene oxide itself possesses exceptional stability toward reduction even under pressure and at temperatures as high as 800° C. It is well known, however, that phenols or their anhydrides are readily acted upon by hydrogen at temperatures around 500° C. or higher to form hydrogenated compounds, hydrocarbons and other reduction products (cf. Ipatiew and Orlow, Ber. 60 B; 1963

(1927)). In the present process the activity of hydrogen liberated at the high temperatures employed and in the presence of undecomposed ortho-phenyl phenol vapors apparently tends to bring about the formation of secondary reduction products of the latter which contaminate the principal reaction product and materially diminish the yield thereof.

In order to repress the formation of undesired reduction products of ortho-phenyl phenol the vapors within the reaction zone may be carried forward at a high enough velocity to prevent the hydrogen formed from diffusing backward and intermingling with the unreacted vapors entering the reaction zone. Furthermore, it is advantageous to cool rapidly the gases and vapors leaving the reaction zone, so as to lower the temperature thereof to a point below that at which hydrogenation takes place. The introduction of carbon dioxide or other inert diluent gas along with the vapors of ortho-phenyl phenol has also contributed somewhat to the regulation of the secondary reducing reactions.

We have discovered, however, that certain catalysts may also be employed in the present process which apparently perform a dual function of facilitating the dehydrogenation of ortho-phenyl phenol and of opposing or counteracting the formation of secondary reduction products, whereby a purer principal product is obtained. As catalysts the most serviceable have been found to be the refractory acidic oxides, such as alumina, silica, thoria, zirconia, tungsten and molybdenum oxides, pumice, etc. Basic oxides have also been observed to exhibit a catalytic action, although to a less extent than the acidic oxides, and such action among basic oxides appears to increase as the basicity thereof decreases. For example, strongly basic oxides or hydroxides, such as sodium hydroxide, are less effective than the weaker basic oxides, such as lime, magnesia, strontia, baryta, or the oxides of iron, copper and other heavy metals. The relative activity of the various catalysts varies, however, to an appreciable degree with the temperature. While at lower reaction temperatures, e. g. 500° to 600° C. or below, the yields obtained using acidic oxides as catalysts are distinctly greater, at higher temperatures, e. g. around 700° C., this distinction is not so apparent.

Still further, we have found that when a basic oxide, or a mixture of two or more such oxides, is associated with one or more acidic oxides a compound catalyst is provided which is more effective than either an acidic or a basic oxide alone. For example, commercial bauxite, which normally contains a small amount of iron oxide, is more effective than pure alumina. The oxides of calcium, magnesium, strontium, barium and of the heavy metals, such as copper, nickel or silver, when admixed with an acidic oxide form highly effective catalysts. For example, copper silicate, which may be regarded as a mixture of silica and copper oxide, has been employed in the present process with good results.

In this connection it may be noted that, where metallic oxides are employed which are reducible with hydrogen at the reaction temperature, there naturally ensues a certain amount of reduction at the expense of the hydrogen liberated in the process. Under such circumstances it will be advisable to withdraw a portion of the catalyst mass, either continuously or intermittently, and to replace the same with fresh catalyst, while such reduced catalyst may be reoxidized and reintroduced into the process later. In fact such procedure may be applied so as to accomplish the removal of all or a part of the hydrogen liberated in the principal reaction.

In addition to the aforementioned metallic oxides, certain of the metals, e. g. copper, nickel, silver, etc., have been observed to exert a catalytic effect upon the present reaction, particularly when such metals are deposited upon a porous substratum so as to provide an extensive surface exposed to contact with the vapors passed thereover.

The following detailed examples describe in typical fashion the application of our improved process, but such examples are not to be considered as a limitation upon the invention.

*Example 1.*—Ortho-phenyl phenol was liquefied by warming to a temperature at which it flowed freely and allowed to flow gradually into the upper end of an inclined silica tube heated to a temperature of approximately 650° C. The vapors issuing from the lower end of the heated tube were condensed and treated with dilute caustic soda solution whereby unreacted ortho-phenyl phenol was dissolved and the crude diphenylene oxide formed a crystalline precipitate. The precipitated material was separated and distilled, the diphenylene oxide fraction passing over at 280°–288° C. was collected and recrystallized from alcohol, yielding shining white crystals, M. P. 82°–83° C. From 22.7 grams condensate 5.5 grams diphenylene oxide were recovered, the conversion being 24 per cent at one passage.

In similar manner but increasing the reaction temperature to 700° C. the conversion was 52 per cent.

*Example 2.*—The procedure was the same as in Example 1, except that the silica reaction tube was filled with a catalytic material consisting of commercial bauxite crushed to approximately ¼ inch mesh. The conversion in one passage at 650° C. reaction temperature was 42 per cent, at 700° C. 65 per cent and at 750° C. 77 per cent.

*Example 3.*—Following likewise the pro-

cedure as in Examples 1 and 2 and employing as catalyst copper silicate in a coarse pulverulent form the conversion to diphenylene oxide in one passage at 598° C. reaction temperature was 21 per cent, at 675° C. 50.8 per cent and at 720° C. 65.5 per cent.

*Example 4.*—A quantity of 23.6 grams ortho-phenyl phenol was passed through a reaction tube filled with a catalyst consisting of aluminum oxide deposited upon pumice, and heated to a temperature of approximately 700° C., the time required being 15 minutes. The product was worked up as in Example 1, from which 10.4 grams diphenylene oxide were recovered, the conversion being 44 per cent.

*Example 5.*—Employing a catalyst consisting of calcium oxide deposited on pumice, a quantity of 20.7 grams ortho-phenyl phenol passed through the reaction tube during 15 minutes at a temperature of 710° C. yielded 10.6 grams diphenylene oxide, or 51 per cent of theoretical.

*Example 6.*—Similarly, passing vapors of ortho-phenyl phenol at a temperature of 750° C. for 15 minutes over a catalyst composed of sodium hydroxide deposited on pumice, 32.3 grams of product were obtained which contained 17.4 grams diphenylene oxide, corresponding to a yield of 54 per cent at one passage.

*Example 7.*—With a catalyst consisting of metallic copper deposited upon pumice and at a temperature of approximately 650° C. 84 grams of product were collected which contained 56.6 grams diphenylene oxide, the yield being 67 per cent of theory.

In the foregoing examples the reacting material was caused to traverse the heated reaction tube only once, giving the yield indicated in each case with but one passage therethrough. By returning the initial product to the reaction zone, thus recycling the reaction mass, an equivalent conversion of unreacted ortho-phenyl phenol may be obtained at each repetition of the reaction cycle, thereby increasing the yield after two or more such additional passages through the reaction tube to a figure approaching a quantitative conversion. The extreme stability of diphenylene oxide readily permits of such repeated exposure to an elevated temperature without decomposition or deterioration of the product already formed. Likewise, by utilizing a longer reaction tube, or decreasing the rate of flow of material to the reaction or by any other suitable means for increasing the time factor for the reaction, the percentage yield may be increased over the figures as given in the examples.

The crude diphenylene oxide product as obtained directly by means of our improved process is relatively pure, is only slightly colored and is remarkably free from tarry decomposition products or carbon. After purification by distilling and recrystallizing from alcohol, or other solvent, the product notably exceeds in purity any similar product heretofore prepared by other methods. In consequence thereof we are enabled to demonstrate a discrepancy in the hitherto published figures for the melting and boiling points of diphenylene oxide, such figures undoubtedly in all cases having been determined upon an impure material. Whereas the melting point, as already stated, has been reported either as 80° to 81° C., or as between 85° and 88° C., we have definitely established the corrected melting point of our purified product as 82° to 83° C., which, we believe, represents the true melting point of the pure compound. The crystals sublime slowly at room temperature and readily at 100° C. We have also established the boiling point of our purified product which is 283.1°–283.6° C. (corr.) at 750.5 mm. and 154°–154.5° (corr.) at 20 mm. pressure.

In its broad aspects, the present improved process involves the preparation of diphenylene oxide by heating the vapors of ortho-phenyl phenol by any suitable means at an elevated temperature within the general range of 300° to 800° C., with or without the presence of a catalyst capable of facilitating the reaction. Other methods of heating the vapors than that already described may be employed, if desired. For example, the vapors may be bubbled through a bath of molten lead or other readily fusible metal, or a molten salt bath may be similarly employed.

The present method may likewise be adapted for the preparation of other compounds of the type of diphenylene oxide, such as the aryl or alkyl substituted derivatives thereof, by means of the pyrogenic decomposition of the vapors of the corresponding substituted derivatives of ortho-phenyl phenol whereby an intramolecular dehydrogenation thereof takes place involving the hydrogen atom of the hydroxy group and the ortho-hydrogen atom of the conjoined aromatic nucleus.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. The method of making diphenylene oxide which comprises heating the vapors of ortho-phenyl phenol at a temperature between 300° and 800° C.

2. The method of making diphenylene oxide which comprises heating the vapors of ortho-phenyl phenol at a temperature between approximately 300° and 800° C. in the

presence of a catalyst capable of promoting the dehydrogenation thereof.

3. The method of making diphenylene oxide which comprises heating the vapors of ortho-phenyl phenol at a temperature between approximately 300° and 800° C. in the presence of a refractory metallic oxide catalyst.

4. The method of making diphenylene oxide which comprises heating the vapors of ortho-phenyl phenol at a temperature between approximately 300° and 800° C. in the presence of a catalyst including an acidic oxide and a basic oxide.

5. The method of making diphenylene oxide which comprises heating the vapors of ortho-phenyl phenol at a temperature between approximately 300° and 800° C. in the presence of a catalyst containing aluminum oxide.

6. The method of making diphenylene oxide which comprises heating the vapors of ortho-phenyl phenol at a temperature between approximately 300° and 800° C. in the presence of a catalyst consisting substantially of bauxite.

7. The method of making diphenylene oxide which comprises heating the vapors of ortho-phenyl phenol at a temperature between approximately 300° and 800° C. in the presence of a catalyst containing aluminum oxide and a basic metallic oxide.

Signed by us this 13th day of August, 1929.

WILLIAM J. HALE.
WESLEY C. STOESSER.