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OXIDATION OF PHENANTHRENE TO PRODUCE 2,2'-DIPHENIC ACID AND ITS ESTERS

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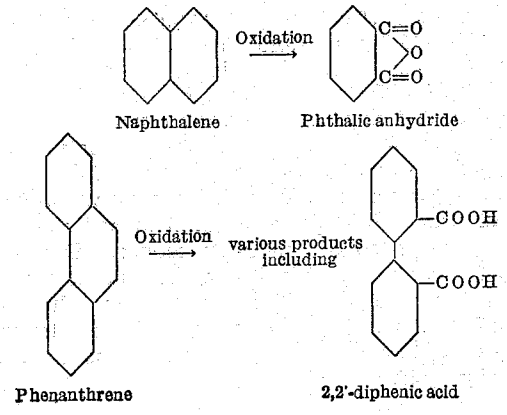
2 Claims. (Cl. 260—523)

This invention relates to the making of 2,2'-diphenic acid and to esters of the acid.

The application is a continuation in part of our application, Serial No. 289,193, filed May 21, 1952, now abandoned. Reference is made also to publications by us on allied subject matter, as follows: Journal of the American Chemical Society 73, 4044 (1951) and Industrial and Engineering Chemistry 45, 277–281 (1953).

Phenanthrene, the raw material for use in making 2,2'-diphenic acid, occurs in relatively large proportion in coal tar, to the extent of about 4% of coke oven tar. Yet phenanthrene and its derivatives have found only limited commercial use. Thus Conant and Blatt in "The Chemistry of Organic Compounds," 4th edition, p. 546 (1952) state that "Although phenanthrene may be obtained without much difficulty, it is not usually separated because neither it nor its derivatives have been found to be of sufficient commercial value to warrent the expense of their manufacture." The undiscovered potentialities of phenanthrene are recognized, however. Thus, Wilson and Wells in "Coal, Coke and Coal Chemicals," 1st edition, page 387 (1950), state "There is every reason to expect that the unique properties of phenanthrene will eventually be recognized and result in increased consumption. Experience with other coal tar chemicals indicates that some of those still used in only small amounts will eventually become of major importance and that valuable developments are still to be looked for in the coal tar field." Naphthalene, for example, derived also from coal tar to the extent of about 11%, has found an enormous and rapidly increasing use in oxidation to phthalic anhydride in the amount exceeding four hundred million pounds a year.

While the oxidation of naphthalene to phthalic anhydride with good yields is standard commercial procedure, there has been much difficulty in applying analogous methods to the production of 2,2'-diphenic acid directly from phenanthrene. A reason for the difference in oxidation of the two compounds will appear from the following simplified equations.



In the case of phenanthrene, the oxidation may affect either the middle ring or end ring or both. Phenanthrenequinone is the common product of the oxidation of phenanthrene by chemical agents, to which type of oxidizing agents with phenanthrene this application particularly relates. Thus, the Encyclopedia of Chemical Technology by Kirk and Othmer, vol. 10, page 276 (1953), states that such chemical oxidizing agents usually convert phenanthrene to the quinone "which can be further oxidized, for example, with hydrogen peroxide in acetic acid solution, to 2,2'-diphenic acid."

We have now found conditions under which the phenanthrene may be oxidized by peracetic acid in a single step process, to the 2,2'-diphenic acid, with satisfactory yield of a product that, as first separated, is almost white in color and melts sharply within about 1° C. of the melting point for the pure compound.

Briefly stated, our invention comprises forming a mixture of phenanthrene with peracetic acid of concentration below 90% and in the proportion of approximately 7–14 moles for 1 mole of phenanthrene, in a suitable solvent, maintaining the mixture at a temperature not above refluxing until heat evolution substantially ceases, and then cooling the mixture so as to decrease the formation of off-color and tarry by-products. The invention comprises also new esters of special properties and utility made from the 2,2'-diphenic acid and alcohols, the alcohols being polyhydric, C_3 and higher monohydric aliphtatic, and aromatic alcohols.

In general, the method of making 2,2'-diphenic acid is as follows: Peracetic acid is mixed cold with technical phenanthrene and a diluting solvent of which an example is ethylene glycol dimethyl ether. The temperature of the mix is raised by outside heat at the start and then in part by the exothermic reaction to about 70° C. Then the oxidation reaction, which will have begun, is continued by gentle heating to about 110° C. at which temperature refluxing occurs. Refluxing is then continued without outside heating until the oxidation subsides, usually about 2.5–3 hours. The mix is now cooled and neutralized with a solution of sodium hydroxide or like alkali. The diphenic acid and acetic acid will be present now as their salts. The neutralized solution is filtered to remove undissolved material including anthraquinone derived from the anthracene present as an impurity in the phenanthrene used. The filtrate is acidified with concentrated hydrochloric acid. The free 2,2'-diphenic acid precipitates rapidly. After standing, the mixture is filtered, giving creamy, white needles of 2,2'-diphenic acid, M. P. 228–229° C.

In addition to controlling the reflux temperature of the mix, the solvent-diluent moderates the reaction and assists in improving the purity of the crystals of 2,2'-diphenic acid finally obtained. The diluent used must be a co-solvent for both peracetic acid and the phenanthrene, non-oxidizing under the conditions of use, and a non-precipitant for sodium hydroxide or like alkali under the conditions of neutralization. Examples of solvents that meet these requirements and that may be used are acetic, propionic, and butyric acids and ethylene and diethylene glycol dimethyl and diethyl ethers.

The effect of the proportion of the peracetic acid to phenanthrene on the yield of 2,2'-diphenic acid is shown in Table I.

TABLE I

Moles of Peracetic Acid to 1 Mole of Phenanthrene	Yield of 2,2'-Diphenic Acid Percent of Theory based on Phenanthrene Used
4	6
6	47
8	69
10	70
12	68
20	40

These results when read or plotted show a peak in the curve for yield of 2,2'-diphenic acid in the range: 7–14 moles of the oxidizing agent.

The effect of the proportion of the peracetic acid to phenanthrene on the purity of 2,2'-diphenic acid is shown in Table II.

TABLE II

Moles of Peracetic Acid to 1 Mole of Phenanthrene	Melting Point of 2,2'-Diphenic Acid (Literature Value, M. P. 228–229° C.)
4	less than 175° C.
6	less than 200° C.
8	228–229° C.
10	229–229.5° C.
12	229–230° C.
20	229–230° C.

These results when read or plotted indicate a peak in the curve for purity of 2,2'-diphenic acid for 8–20 moles of the oxidizing agent.

As to the concentration of the peracetic acid incorporated into the oxidizing mix, a concentration of 90% or above (the remainder being mostly water) causes the production of tarry material, with resultant discoloration and loss of yield of desired product.

When the production of a product reasonably pure initially is desired, the maximum temperature of the oxidation should be at a point not substantially above 110° C. Up to such temperature, we obtain 2,2'-diphenic acid in good yield and of melting point about 229° C. (theory 228–229° C.). Oxidizing at 121° C., on the other hand, we find that both yield and purity drop somewhat. With oxidation at 162° C., the yield has fallen about 10 units from the maximum and the melting point to less than 200° C., three to six recrystallizations being required to purify the product.

Working under our critical conditions, we not only obtain good yields and purity, but also complete the oxidation reaction in time periods measured in hours, ordinarily one-half to four hours, in contrast with as many days and poorer results previously realized by certain investigators.

The invention will be described and further illustrated in connection with the following specific examples of the practice of it. Proportions here and elsewhere herein are expressed as parts by weight unless specifically stated to the contrary.

Example 1

175 parts of technical phenanthrene (90%), 1432 parts of 40% peracetic acid and 1340 parts of ethylene glycol dimethyl ether were heated slowly to about 70° C. in a reaction vessel equipped with a reflux condenser. The exothermic reaction was moderated by cooling to about 90° C. for about one hour. Thereafter the reaction mixture was refluxed vigorously for 2½–3 hours.

The mixture was then diluted with 1500–2000 parts of water and neutralized to pH 6–7 with 25% solution hydroxide solution. After filtration the solution was acidified to pH 2 with concentrated hydrochloric acid. The precipitated 2,2'-diphenic acid was separated by filtration and dried giving about 150 parts (70% of theory) of product melting at 228–229° C.

The solvent was recovered from the filtrate by distillation.

Recrystallization of the alkali insoluble portion of the product from glacial acetic acid yielded about 12 parts of anthraquinone, M. P. 383–385° C.

Example 2

In this example the peracetic acid is formed in the mix by reaction of hydrogen peroxides with glacial acetic acid.

40.6 parts of 50% hydrogen peroxide were added to a mixture of 10 parts of technical phenanthrene (90%) and 75 parts of glacial acetic acid. When slowly warmed and stirred until the exothermic reaction commenced at about 70° C., the phenanthrene paste went into solution. The resulting deep red solution was then refluxed for about one hour.

While still warm, the solution was poured into 200 parts of water and 25% sodium hydroxide solution added to pH 8–9. After being filtered, the alkaline solution was treated with charcoal, filtered again, and acidified with concentrated hydrochloric acid. On cooling, 2,2'-diphenic acid crystallized in about 70% yield and of M. P. 228–229° C.

The diphenic acid made as described is suitable for use in making esters of special properties.

In making these esters, the alcohol (hydroxy compound which it is desired to esterify) is mixed in stoichiometric proportion or in slight excess with the 2,2'-diphenic acid and a trace of esterification catalyst, as for example, 0.2–1.0% of sulfuric or other mineral acid. The mixture is warmed. The water formed in the esterification is removed, as by evaporation from an open dish when the alcohol used is high boiling or by an azeotroping liquid under other circumstances. At the end of the esterification, the acid catalyst is neutralized, as with soda ash or the like. The remaining alcohol if any is distilled away in vacuo or otherwise from the ester so produced or in some cases left in it. The finished esters may also be distilled in vacuo when their boiling point at 5 mm. is not above 250° C.

As an alternative to the above described procedure for making the esters, we substitute an equimolar proportion of the anhydride of 2,2'-diphenic acid for the acid itself.

The anhydride for this other use, we make to advantage by heating the 2,2'-diphenic acid with an excess of acetic anhydride, continuing the warming for an hour or so, and then cooling the mix, whereupon the anhydride of 2,2'-diphenic acid crystallizes.

The disodium salt of 2,2'-diphenic acid may be reacted with alkyl halides in making esters. This salt is made by neutralization of 2,2'-diphenic acid with a sodium hydroxide solution to a phenolphthalein end point. The solution is vacuum distilled to remove the water, the disodium diphenate that separates being then oven dried to remove the last traces of the solvent, water.

Example 3.—Di-n-butyl diphenate

To 12.1 parts (0.05 mole) of 2,2'-diphenic acid there were added 13.7 parts (0.15 mole) of n-butyl alcohol, 50 parts toluene and 1% by weight of the whole mix of sulfuric acid. The mix was brought to a boil and the water formed during the reaction was removed azeotropically by the toluene and collected in a calibrated water trap. Reflux was continued for 10 hours until the formation of water ceased. The reaction mixture was neutralized with sodium carbonate solution and extracted with water, to remove the salts formed. Di-n-butyl diphenate was recovered in 78% yield from the residual mixture by distillation through a Vigreux column at reduced pressure. The boiling point of the ester was 195°–197° C. at 1–2 mm. The product was a moderately oily liquid.

The dipropyl and the di-isopropyl esters are made by replacing the butanol by equivalent weights of n- and isopropanol, respectively.

Example 4.—Dihexyl diphenate

To 11.2 parts (0.05 mole) of diphenic anhydride there were added 18.7 parts (0.15 mole) of n-hexyl alcohol and 1 part of concentrated sulfuric acid. The mixture was refluxed for 5 hours. It was then extracted with a 5% sodium carbonate solution, until the water-insoluble portion gave an alkaline reaction to litmus. Upon cooling the water-insoluble mixture to −10° C., white crystals of di-n-hexyl diphenate were obtained, melting point 43–44° C. The yield was 80% theoretical.

Example 5.—Dibenzyl diphenate

To 14.3 parts (0.05 mole) of powdered disodium diphenate mixed with 17.3 parts (0.15 mole) of benzyl chloride there were added 0.5 part of triethylamine as catalyst. The mixture was vigorously stirred and heated slowly to 100° C., at which time the temperature rose immediately to 130° C. This temperature was maintained for ½ hour. After cooling, the reaction mass was extracted with ether. The ether extracts were combined and vacuum distilled, to remove ether and unreacted benzyl chloride. The dibenzyl diphenate was then distilled at 316–318° C./20–22 mm.

This high molecular weight diester remained in a fluid state for four months at temperatures of −10° C.

The esters of Examples 3–5 are useful as substantially non-volatile solvent plasticizers for pyroxylin and other plastics such as polyvinyl chloride and as lubricant additives.

Example 6.—Glyceryl diphenate

To 12.1 parts (0.05 mole) of 2-2'-diphenic acid there were added 4.6 parts (0.05 mole) of glycerol. The mixture was heated with stirring until the mass was molten, at which time 0.1 part of concentrated sulfuric acid was added. The reaction mixture was maintained at a temperature of 200° C. for one hour, at which time all water formed in the reaction had evaporated. The glyceryl diphenate ester was cooled and fibers were drawn from the cooling mass. The drawn fibers were elastic and of high tensile strength.

The synthetic resin fibers of Example 6 may be and suitably are compounded with plasticizers or toughenners of which dibutyl phthalate, dioctyl sebacate, glycol o- or p-phthalate in the poly form, and polyacrylonitrile are examples, each being introduced in the proportion of 10%–70% of the whole composition. The compounding

is effected by blending all of the ingredients in fluid state before the fibers are drawn.

Example 7

The procedure of Example 3 is followed with the substitution of the butanol by an equimolecular proportion of another primary or secondary alcohol, as, for example, amyl alcohol, sec.- or isobutyl, n-hexanol, or a secondary hexyl alcohol.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What we claim is:

1. In making 2,2'-diphenic acid, the process which comprises forming a mixture of 7–14 moles of peracetic acid of concentration 40% to 90%, 1 mole of phenanthrene, and an organic liquid diluent that is a co-solvent for the acid and phenanthrene and is non-oxidizing in contact with the acid and maintaining the mixture at a temperature at least as high as about 70° C. but not substantially above 110° C. until the reaction is practically complete, whereby 2,2'-diphenic acid is formed.

2. The process of claim 1 which includes the use of phenanthrene in the form of technical phenanthrene and adding, to the reaction product, aqueous alkali in the amount to neutralize the acidity, filtering the resulting solution in hot condition to remove material undissolved at this stage, acidifying the filtrate by the addition of an acid, and then recrystallizing the 2,2'-diphenic acid from the resulting solution by cooling the acidified filtrate to a temperature below the saturation point of 2,2'-diphenic acid, the said co-solvent being a non-precipitant of the said alkali.

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