*Kirk-Othmer Encyclopedia of Chemical Technology.*

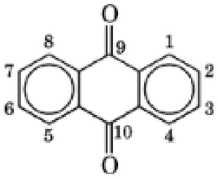
# ANTHRAQUINONE

In the early part of the nineteenth century, as a result of the use of illuminating gas for lighting purposes, huge quantities of coal tar became available. Many different compounds were isolated from this tar, one of which was anthracene. In 1840, Laurent treated anthracene with nitric acid and obtained a compound which he named "anthracenuse" indicative of its source (*anthra,* Greek for coal). Another investigator called the new compound "oxyanthracen," and it was not until 1869 that Graebe and Liebermann, in the course of their investigation on quinones, named it anthraquinone. They obtained anthraquinone by oxidizing anthracene with bichromate and sulfuric acid which later became the first commercial method for the manufacture of anthraquinone from anthracene (1).

Anthraquinone [84-65-1] has yet to be found in nature, although some of its substitution products have been known since antiquity (alizarin, kermes, cochineal, and lac dye). Of all the quinones found naturally, those derived from anthraquinone far exceed all others. Many of these are found in molds (2).

For many years, anthraquinone provided the dyestuff industry with one of the greatest and most prolific building blocks for the manufacture of valuable dyestuffs noted for their outstanding fastness properties. During the years 1941–1961, production remained fairly constant and averaged 1,305 t per year for anthraquinone and 2,477 t for its precursor, *o*-benzoylbenzoic acid (3). Since 1969, production figures have not been made public. However, in recent times, production has fallen off considerably due to the high cost of manufacturing and the discovery of other classes of dyestuffs with good fastness properties.

Anthraquinone, $C_{14}H_8O_2$, has been variously named 9,10-dihydro-9,10-diketoanthracene, 9,10-dihydro-9,10-dioxoanthracene, and 9,10-antracenedione:



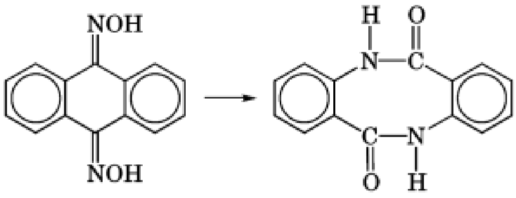
In the earlier literature, the 1,4,5,8 positions were known as alpha ($\alpha$) and the 2,3,6,7 as beta ($\beta$). The 9,10-positions are known as meso- or ms-. Other quinones of anthracene are known, but only the 9,10-quinone is of technical importance.

## 1. Physical Properties

When sublimed, anthraquinone forms a pale yellow, crystalline material, needle-like in shape. Unlike anthracene, it exhibits no fluorescence. It melts at 286°C and boils at 379°–381°C. At much higher temperatures, decomposition occurs. Anthraquinone has only a slight solubility in alcohol or benzene and is best recrystallized from glacial acetic acid or high boiling solvents such as nitrobenzene or dichlorobenzene. It is very soluble in concentrated sulfuric acid. In methanol, uv absorptions of anthraquinone are at $\lambda_{\max}$ 250 nm ($\epsilon = 4.98$), 270 nm (4.5), and 325 nm (4.02) (4). In the ir spectrum, the double allylic ketone absorbs at 5.95 $\mu$m ($1681\ cm^{-1}$), and the aromatic double bond absorbs at 6.25 $\mu$m ($1600\ cm^{-1}$) and 6.30 $\mu$m ($1587\ cm^{-1}$).

## 2. Chemical Properties

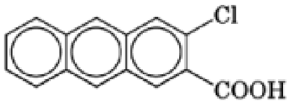
In general, anthraquinone is a relatively inert compound exhibiting stability towards oxidation. If this were not so, the commercial process for the production of anthraquinone by the oxidation of anthracene would never have achieved any technical importance. Many reactions of quinone compounds do not take place with anthraquinone or, if they do, it is only with difficulty. A monooxime is formed with hydroxylamine only by heating to a comparatively high temperature (5). A dioxime, 9,10-Autracenedione dionene $C_{14}H_{10}N_2O_2$, [7461-27-0] is formed by reaction of anthraquinone with hydroxylamine in polyphosphoric acid at 140°C (6). The dioxime undergoes the Beckmann rearrangement to give an 85% yield of dianthranilide [3266-71-5] **(1)** (7):



**(1)**

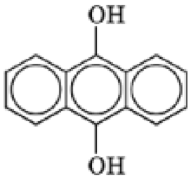
Indirect methods have also been used to form the monooxime (8) and the phenylhydrazone (9).

Only the reduction products involving the keto groups are of any academic or industrial importance. Complete reduction of the keto groups by ammonia and zinc (von Perger method) gives rise to anthracene in good yields and quality (10). This method is of importance since substituted anthracenes can be prepared from the corresponding anthraquinones. Industrially, an important dyestuff intermediate, 3-chloroanthracene-2-carboxylic acid, **(2)** is prepared by this method (11) from 3-chloroanthraquinone-2-carboxylic acid [84-32-2]

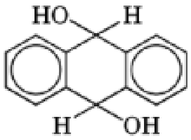


**(2)**

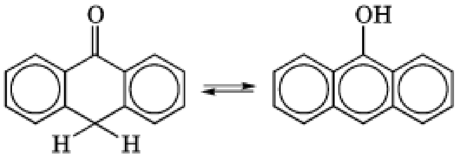
Depending on experimental conditions, sodium borohydride reduction of anthraquinone, in a lower aliphatic alcohol, results in 9,10-dihydroxyanthracene **(3)** [4981-662], 9,10-dihydro-9,10-dihydroxy-anthracene **(4)** [70143-55-4], anthrone **(5)** [90-44-8], and anthrol **(6)** [529-86-2] (12):



**(3)**

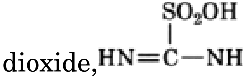


**(4)**

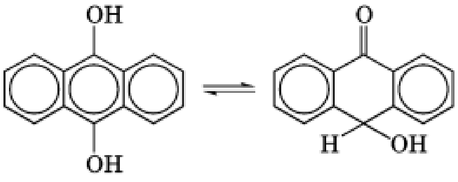


**(5)** **(6)**

Other metal hydrides and metal alkoxides have been used as well as diphenylsilane and nickel–aluminum alloy (13).

Of special interest to the dyestuff chemist is the 9,10-dihydroxyanthracene structure since its red, water-soluble sodium salt forms the basis for applying anthraquinone dyes to cotton (qv). Because the reductions were originally carried out in large tubs or vats, the operation became known as "vatting" and the dyes as "vat" dyes. The most commonly used reducing agent is alkaline hydrosulfite, also known as dithionite ($Na_2S_2O_4$). Use of thiourea dioxide,  $HN{=}\overset{SO_2OH}{\overset{|}{C}}{-}NH_2$, as a reducing agent has the advantage that the reduction can be carried out under acidic conditions (14). Because of its higher cost, its usage has been limited to a relatively few specialized cases.

Tautomeric with 9,10-dihydroxyanthracene, $C_{14}H_{10}O_2$, is oxanthrone [549-99-5] **(7)** which forms colorless needles, mp 167°C. The equilibrium mixture in alcoholic hydrochloric acid contains 97% 9,10-dihydroxyanthracene and 3% oxanthrone.



**(3)** **(7)**

With concentrated sulfuric acid, anthraquinone forms oxonium salts, thus falling into a class of compounds known as "oxygen bases" (15). In an aqueous solution, anthraquinone has an ionization constant $K_b$ equal to $7 \times 10^{-23}$ and a p$K_a$ of 7.4 (16).

Anthraquinone can be sulfonated, nitrated, or halogenated. Sulfonation is of the greatest technical importance because the sulfonic acid group can be readily replaced by an amino or chloro group. Sulfonation with 20–25% oleum at a temperature of 130–135°C produces predominantly anthraquinone-2-sulfonic acid [84-48-0]. By the use of a stronger oleum, disulfonic acids are produced. The second sulfonic acid substituent never enters the same ring; a mixture of 2,6- and 2,7-disulfonic acids is formed (Wayne-Armstrong rule). In order to sulfonate in the 1-, 1,5-, or 1,8-positions, mercury or one of its salts must be used as a catalyst.

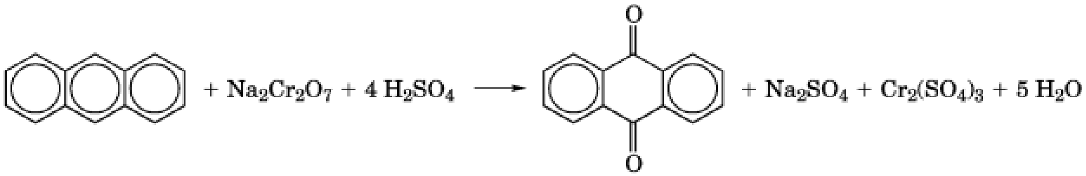
| Anthraquinone disulfonic acids | CAS Registry Number |
|---|---|
| 2,6 | [14486-58-9] |
| 2,7 | [84-49-1] |
| 1,5 | [117-14-6] |
| 1,8 | [82-48-4] |

Use of mercuric catalysts has created a serious pollution problem thereby limiting the manufacture of such acids. Other catalysts such as palladium or ruthenium have been proposed (17). Nitration of anthraquinone has been studied intensively in an effort to obtain 1-nitroanthraquinone [82-34-8] suitable for the manufacture of 1-aminoanthraquinone [82-45-1]. However, the nitration proceeds so rapidly that a mixture of mono- and dinitroanthraquinone is produced. It has not been possible, economically, to separate from this mixture 1-nitroanthraquinone in a yield and purity suitable for the manufacture of 1-aminoanthraquinone. Chlorination of anthraquinone cannot be used to manufacture 1-chloroanthraquinone [82-44-0] since polychlorinated products are formed readily. Consequently, 1-chloroanthraquinone is manufactured by reaction of anthraquinone-1-sulfonic acid [82-49-5] with sodium chlorate and hydrochloric acid (18).

## 3. Manufacture

### 3.1. Oxidation of Anthracene

Many oxidants have been described for the oxidation of anthracene [120-12-7] to anthraquinone, including nitric acid, molecular oxygen, ozone, chlorine, and dichromate (19). Industrially, only the use of dichromate achieved importance. Historically, this was the first process for converting anthracene to anthraquinone on an industrial scale (20): Water and sulfuric acid were added to an acid-proof kettle, equipped with a lead-covered steel agitator and a lead heating coil. To this was added 94–95% anthracene and a 20% solution of sodium dichromate. Under agitation and during six hours, the mixture was heated to 100°C. Frequent additions of dichromate were made until a permanent excess of dichromate was maintained for one-half hour. Then the reaction mass was filtered on an acid-proof filter box, washed free of acid, and dried. The chrome-containing filtrates were added to a large, lead-lined vessel where the chromium salts were precipitated by the addition of alkali, filtered, washed free of alkali, dried, and sold to the tanning industry as an economic credit against the cost of manufacturing the anthraquinone. Alternatively, the chromic acid may be regenerated electrochemically from the filtrates (21).



A 95% yield of pure anthraquinone was obtained. This is an almost quantitative yield based on the 100% content of the anthracene used. The crude anthraquinone was then purified. To a jacketed steel kettle, provided with an agitator, was added crude anthraquinone and nitrobenzene. Under agitation, the charge was heated at 130–140°C until a complete solution resulted. Under slow agitation, the solution was cooled to 30°C and the resulting slurry of anthraquinone was filtered on a pressure filter. The cake was washed twice with nitrobenzene, then was reslurried on the filter with nitrobenzene, sucked dry, and transferred to a vacuum dryer where the nitrobenzene was distilled. The dried anthraquinone was discharged to suitable containers. A 99% yield of pure anthraquinone was obtained equal to a recovery of approximately 90% based on the crude anthraquinone.

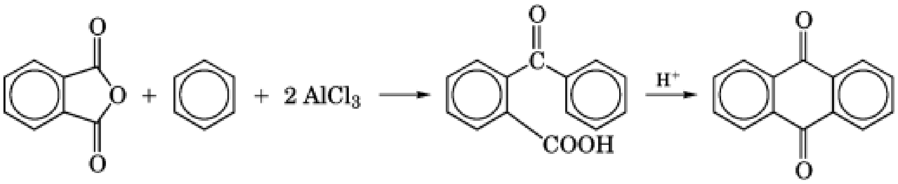
In Europe, where an abundant supply of anthracene has usually been available, the preferred method for the manufacture of anthraquinone has been, and still is, the catalytic oxidation of anthracene. The main problem has been that of obtaining anthracene, $C_{14}H_{10}$, practically free of such contaminants as carbazole and phenanthrene. Many processes have been developed for the purification of anthracene. Generally these follow the scheme of taking the crude anthracene oil, redistilling, and recrystallizing it from a variety of solvents, such as pyridine (22). The purest anthracene may be obtained by azeotropic distillation with ethylene glycol (23).

The catalytic oxidation of anthracene has received more attention than any other method for converting anthracene to anthraquinone. This is evident from the great number of patents issued on this method (24). Catalysts proposed for the oxidation generally utilize vanadium, either as its oxide or in the form of metal vanadates, in combination with the salts of other metals (iron, manganese, potassium, etc) supported on an inert carrier such as silica gel or aluminum hydroxide. The patent literature indicates that the ideal catalysts is one that does not require regeneration too frequently, that is not poisoned by impurities in anthracene, and that allows the oxidation of large volumes of anthracene per unit of time without the attendant production of appreciable quantities of phthalic anhydride. Unless the quality of the anthracene and the operating conditions are carefully controlled, the resulting anthraquinone may be contaminated. Such contaminants have been isolated and identified (25). Crude anthraquinone may be purified by various methods, such as sublimation (26).

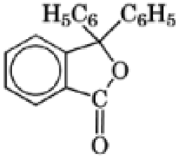
The vapor-phase catalytic oxidation of anthracene to anthraquinone was first described in 1916 and was the basis for a plant operated at Ludwigshafen (27). In 1940, a smaller plant at Milan, Italy incorporated the latest information available at the time and was believed to be far in advance, technically, of the Ludwigshafen plant. The entire plant was designed exclusively for the manufacture of anthraquinone from anthracene (28). The main feature of the plant was the so-called "contact oven" where the oxidation of the anthracene occurred. The oven was a cylindrical iron vessel about 5.8 m high and 2.4 m in diameter. Within the oven were nine perforated sheet-iron shelves placed one on top of the other. On each shelf was a layer of iron vanadate catalyst (29) embedded in high pressure coils which heated and cooled the reaction mass during the oxidation. In conjunction with the contact oven were a number of auxiliary pieces of equipment: a preheater for heating an air–stream mixture, a vaporizer containing molten anthracene, various metering and temperature control devices, several heat exchangers, and a Dowtherm heating system. Briefly, 93% anthracene was vaporized at 318°C by means of the preheated air–steam mixture. The steam was incorporated to minimize the possibility of an explosion during the oxidation; several had occurred at the Ludwigshafen plant. The vaporized anthracene–air–steam mixture was carefully metered into the contact oven containing the catalyst at 390°C. From here, the anthraquinone–air–steam reaction mixture passed through several heat exchangers and finally into a cold room where the anthraquinone was deposited. The yield of anthraquinone was about 82% of theory and had a purity of 99.6%. Although the yield was lower than that obtained by the dichromate oxidation, the vapor-phase catalytic oxidation had the advantage that no by-products were formed. A pilot plant has been described for the fluid-bed, vapor-phase catalytic oxidation of anthracene. The process gave a 96% yield of anthraquinone having a purity greater than 90% (30). Anthracene has been oxidized to anthraquinone electrolytically using ceric sulfate as a catalyst. Quantitative yields have been claimed (31). Laboratory procedures have been described for oxidizing anthracene to anthraquinone (32).

### 3.2. Friedel-Crafts Reaction

Until quite recently, the manufacture of anthraquinone in the United States was by the Friedel-Crafts reaction: benzene [71-43-2] and phthalic anhydride [85-44-9] condense in the presence of anhydrous aluminum chloride to give *o*-benzoylbenzoic acid [85-52-9] which, on treatment with concentrated sulfuric acid, is converted into anthraquinone in high yields and purity (33).



Unless two moles of anhydrous aluminum chloride are used per mole of phthalic anhydride, the yields of *o*-benzoylbenzoic acid are low due to the formation of diphenylphthalide **(8)** 596-29-2] (34):



**(8)**

Both a ball mill and a solvent process have been described for the manufacture of *o*-benzoylbenzoic acid. In the latter method (35), an excess of dry benzene is charged into a jacketed, cast-iron reactor at room temperature. Granulated anhydrous aluminum chloride is added under agitation, followed by the addition of phthalic anhydride. Heat is evolved and is controlled until a temperature of 50–60°C is reached. The hydrogen chloride evolved is passed through a condenser in order to remove entrained benzene and finally into an alkaline scrubber which removes the hydrogen chloride. Heating is continued at 50–60°C until the evolution of hydrogen chloride has practically ceased. At this point, the charge is transferred to an acid-proof kettle containing dilute sulfuric acid. Here, the aluminum chloride complex of *o*-benzoylbenzoic acid decomposes giving a benzene solution of *o*-benzoylbenzoic acid and an aqueous solution of aluminum salts. After separation, the solution of aluminum salts may be used as a coagulant in the water-treatment plant. The benzene solution is transferred to another acid-proof vessel where the benzene is steam-stripped off, resulting in a slurry of *o*-benzoylbenzoic acid. This is filtered, washed acid-free, and dried. A very pure product is obtained in practically a quantitative yield. A typical unit for the manufacture of *o*-benzoylbenzoic acid is shown in Figure 1.

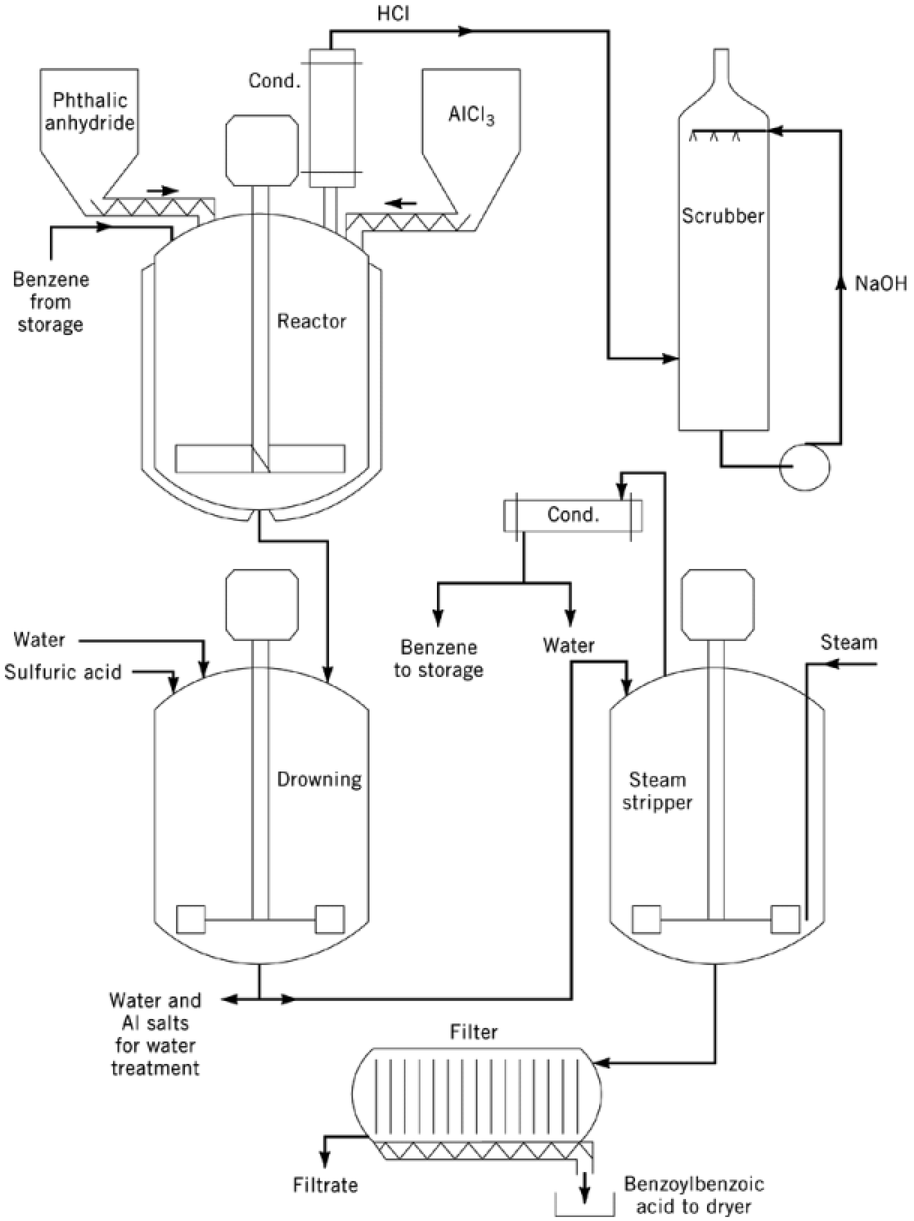


**Fig. 1.** *o*-Benzoylbenzoic acid manufacture.

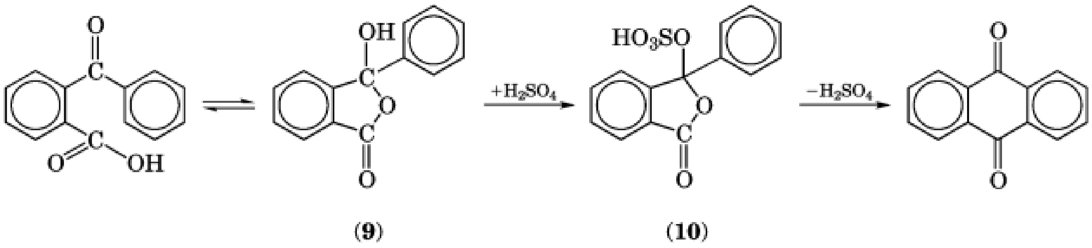
In the ball mill process (36), an iron, horizontal rotary-type reactor is used for the condensation. The mill is equipped with a calibrated vessel for feeding in benzene, an outlet pipe through which hydrogen chloride escapes from the mill into an alkaline scrubber, and a manhole for adding solid material. Inside the mill are iron balls or rods which stir the reactants during the condensation. Benzene, phthalic anhydride, and anhydrous aluminum chloride are charged into the mill in the molecular ratio of 1:1:2. These are slowly heated to 50–60°C and held there until no more hydrogen chloride is evolved. During the condensation, the hydrogen chloride mixes in the viscous mass causing it to form a spongelike material which fills the entire mill. As stirring continues, the aluminum chloride complex of *o*-benzoylbenzoic acid is ground into a powdery material which is discharged through a coarse sieve into suitable containers. Decomposition of the aluminum complex follows the same procedure as that described in the solvent process. The yield and quality of the product are equal to that obtained by the solvent process.

There are advantages and disadvantages in both processes: the solvent process requires no special equipment but uses an excess of benzene whose recovery adds to the cost of the product. The ball mill method uses no excess benzene but requires special equipment which has frequent mechanical problems.

Benzene and phthalic anhydride may be condensed to *o*-benzoylbenzoic acid using hydrofluoric acid and boron trifluoride instead of anhydrous aluminum chloride (37).

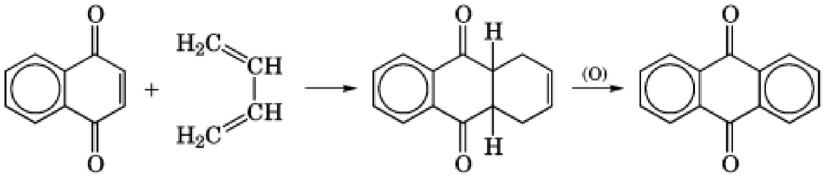
Ring closure of *o*-benzoylbenzoic acid is accomplished by the use of concentrated sulfuric acid or a weak oleum (5–20%) solution at a temperature ranging from 100–110°C. Practically, a quantitative yield of very pure material is obtained (38). Also, the conversion can be accomplished by heating *o*-benzoylbenzoic acid at 200–300°C in the presence of a Lewis-type catalyst. High yields of anthraquinone are claimed (39). A one-step process has been described in which benzene is acylated by phthalic anhydride followed by ring closure of the resulting *o*-benzoylbenzoic acid. Briefly, in an atmosphere of nitrogen and carbon dioxide and at a temperature of 430°C, benzene and phthalic anhydride are passed over a catalyst consisting of magnesia, silica, metal oxides, and metal sulfates. A 90% conversion of the phthalic anhydride results giving an 88% yield of anthraquinone (40).

Ring closure of *o*-benzoylbenzoic acid to anthraquinone is an unusual reaction in that normally it is not predicted to occur ortho to a keto group. Several theories have been proposed to explain the mechanism whereby this could possibly occur. One involves a complex ionization of *o*-benzoylbenzoic acid (41), the other favors the intermediate formation of 3-hydroxy-3-phenyl-1(3*H*)isobenzofuranone **(9)** [64693-03-4] and 3-phenylphthalidyl sulfate **(10)** (42):



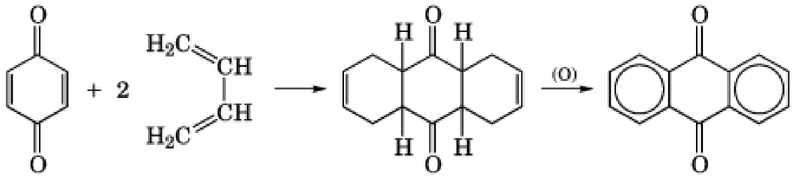
### 3.3. Diels-Alder Reaction

In 1928, Diels and Alder discovered that 1,3-unsaturated organic compounds reacted with quinoid systems to give partially hydrogenated, cyclic compounds. In the course of their work, they found that 1 mol of 1,4-naphthoquinone [130-15-4] reacted readily with 1 mol of 1,3-butadiene [106-99-0] to give a partially hydrogenated anthraquinone **(11)** 1,4,4a,9a-tetrahydro-9,10-anthracenedione [56136-14-2] which, on oxidation with chromic oxide, produced anthraquinone (43):



**(11)**

Although a patent was issued for the manufacture of anthraquinone by this method (44), it was never put into practice because, at that time, butadiene and naphthoquinone were not available at a reasonable price. However, during World War II there was a great demand for 1,3-butadiene in the manufacture of synthetic rubber. This resulted in the development of processes whereby it became a readily available intermediate at a fairly low cost. 1,4-Naphthoquinone is formed to some extent during the vapor-phase oxidation of naphthalene to phthalic anhydride. By varying the nature of the catalyst and other variables, it is possible to produce increasingly larger amounts of 1,4-naphthoquinone (45). American Cyanamid found that an impure 1,4-naphthoquinone, as obtained directly from the phthalic anhydride converter, could be condensed with 1,3-butadiene to give anthraquinone in almost theoretical yields and excellent purity (46). Based on this, American Cyanamid erected a plant for the manufacture of anthraquinone by the Diels-Alder reaction. Unforeseen technological problems developed which terminated the manufacture of anthraquinone by this method. European manufacturers also investigated the manufacture of anthraquinone by the Diels-Alder reaction. CIBA utilized a variation of the American Cyanamid patent (47) while BASF used *p*-benzoquinone [106-51-4] instead of 1,4-naphthoquinone (48). In this method, *p*-benzoquinone condenses with 2 mol 1,3-butadiene to give octahydroanthraquinone **(12)** [33982-93-3] which is then oxidized by oxygen, under pressure and in the presence of alkali, to give anthraquinone:



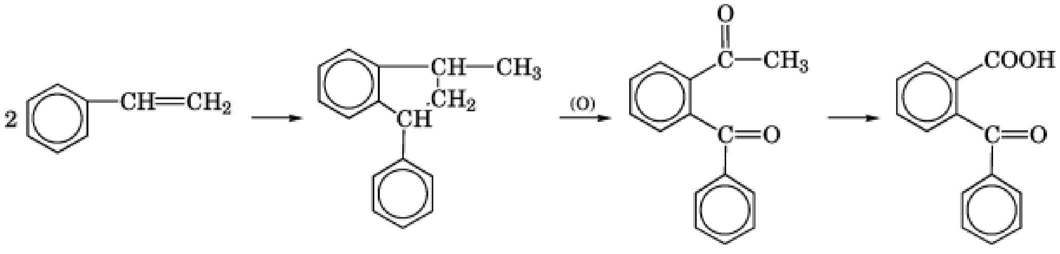
**(12)**

A continuous process has been described for the manufacture of anthraquinone by the Diels-Alder reaction (49).

The mechanism of the Diels-Alder reaction is not as simple as usually depicted. This may, in part, explain some of the problems encountered when this reaction has been applied on an industrial scale. A number of different theories have been proposed for this reaction (50).

### 3.4. Manufacture of *o*-Benzoylbenzoic Acid from 1-Methyl-3-phenylindane

In 1909 it was reported that treatment of styrene with concentrated sulfuric acid resulted in its dimerization (51). However, the wrong structure was assigned to this dimer (52). Years later it was suggested, without proof, that the dimer consisted primarily of 1-methyl-3-phenylindane **(13)** [6416-39-3] and some 1,3-diphenyl-1-butene (53). In 1950, oxidative studies on the dimer proved that this supposition was correct (54):



**(13)**

Under the oxidative conditions used, only low yields of *o*-benzoylbenzoic acid were obtained since this underwent further oxidation.

In the early 1970s, styrene was a fairly inexpensive intermediate (55); also 1-methyl-3-phenylindane could be obtained from styrene [100-42-5] in high yields (56). These facts, and the fact that supplies of anthracene were dwindling, led BASF to invest over three million dollars in research in an effort to develop a practical process for the oxidation of 1-methyl-3-phenylindane to *o*-benzoylbenzoic acid (57). Various oxidative techniques were developed: oxygen under pressure along with a catalyst (58), nitrogen dioxide and selenium (59), a solution of nitric and hydrochloric acids (60), and a combination of nitric acid and a dichromate (61). The latter method gave the highest yield of *o*-benzoylbenzoic acid—about 92% of theory. By 1972, BASF had a pilot in operation for the oxidation of 1-methyl-3-phenylindane to anthraquinone; however, unforeseen dermatological problems prevented the continuation of the operation (57).

## 4. Economic Aspects

In the dyestuff industry, anthraquinone still ranks high as an intermediate for the production of dyes and pigments having properties unattainable by any other class of dyes or pigments. Its cost is relatively high and will remain so because of the equipment and operations involved in its manufacture. As of May 1991, anthraquinone sold for $4.4/kg in ton quantities. In the United States and abroad, anthraquinone is manufactured by a few large chemical companies (62). At present, only two processes for its production come into consideration: manufacture by the Friedel-Crafts reaction utilizing benzene, phthalic anhydride, and anhydrous aluminum chloride, and by the vapor-phase catalytic oxidation of anthracene; the latter method is preferred.

## 5. Health, Safety, and Environmental Factors

Anthraquinone is a comparatively safe compound: $LD_{50}$ (rat) is 3500 mg/kg. It is a mild allergen and, as a fine powder, may cause skin irritation. It presents only a slight fire hazard on exposure to heat.

Of the two processes used for the manufacture of anthraquinone, the one involving the vapor-phase catalytic oxidation of anthracene has the least effect on health and the environment. On the other hand, the use of benzene in the Friedel-Crafts process presents serious safety and health problems: benzene is a highly flammable liquid having a flash point of $-11^\circ C$. It has an upper explosive limit of 7.1% and a lower one of 1.3%. By OSHA standards, the average 8-h exposure limit is 10 ppm. Exposure to 3,000 ppm may be tolerated for only 30–60 min after which irritation of the nose, throat, and lungs may occur along with headaches, dizziness, and slurred speech. Exposure for 5–10 min at a concentration of 20,000 ppm results in death. Benzene is a known leukemogen (63). The workplace should be well ventilated and equipped with respirators capable of handling different concentrations of benzene.

Disposal of the solutions of aluminum salts generated in the Friedel-Crafts process presents an environmental problem unless use can be found for them as coagulants in a water treatment plant.

## 6. Uses

Aside from its major use in the manufacture of intermediates for anthraquinone dyes and pigments, anthraquinone is finding increasing interest as a catalyst in the pulping of wood (64), in the polymerization of various materials for plastics (65), and in the isomerization of vegetable oils (66). It has been used to make seeds distasteful to birds (67) and as an accelerator in nickel electroplating (68).

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A. J. COFRANCESCO

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