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# UNITED STATES PATENT OFFICE

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## RING CLOSURE OF AROMATIC COMPOUNDS WITH THE AID OF HYDROFLUORIC ACID

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This invention relates to the synthesis of organic compounds. More particularly, this invention relates to an improved method for ring-closing organic compounds of the type which are adapted to form a closed ring by the action of acidic dehydrating agents. Typical examples of such synthesis are the ring closure of ortho-benzoyl-benzoic acid derivatives to give anthraquinone compounds; the ring-closure of diphenyl-methane-ortho-carboxylic acid compounds to the corresponding anthrones; and the ring closure of diaraylamine-ortho-carboxylic acid compounds to acidones. Further examples, illustrating the full scope of this invention, are given in the discussion below.

It is an object of this invention to provide an improved process for effecting ring-closures, whereby to avoid undesirable side reactions such as oxidation, reduction, sulfonation, or halogenation. It is a further object of this invention to provide a process for ring-closure which is of wide applicability, and is characterized by simplicity of procedure and economy of materials. Other and further important objects of this invention will appear as the description proceeds.

These objects are accomplished, according to our invention, by the simple expedient of employing hydrofluoric acid as the ring-closing agent. More particularly, we proceed as follows: An organic compound potentially capable of being converted to a cyclic structure is dissolved or suspended in concentrated hydrofluoric acid and heated, if necessary, at atmospheric or superatmospheric pressure in an autoclave until ring-closure has taken place. The product may be recovered by pouring the reaction mixture into water, or distilling off the excess hydrofluoric acid and recovering the product from the residue.

We have discovered that concentrated hydrofluoric acid possesses the valuable quality of promoting ring-closure of such organic compounds which are adapted to form a ring when acted upon by acidic dehydrating agents, and possesses moreover additional qualities which adapt it excellently to the reaction under discussion. Hitherto it has been customary in general to employ concentrated or fuming sulfuric acid, aluminum chloride, phosphorus pentoxide, phosphorus pentachloride, or halogen sulfonic acids for the ring-closure of the open chains of various classes of organic compounds. With these reagents, however, undesirable side reactions often accompany the ring-closure to such an extent that the yield of desired product is seriously if not completely inhibited. Beta naphthyl thioglycolic acid, for instance, cannot be ring-closed satisfactorily in concentrated or fuming sulfuric without sulfonation in the naphthalene ring. The production of anthrones by the ring-closure of diphenyl-methane-2-carboxylic acids in sulfuric acid is accompanied by partial oxidation of both the starting material and the finished anthrone to anthraquinone derivatives. Aluminum chloride and phosphorus pentoxide yield tars containing only small quantities of anthrones.

Now, we have found that hydrofluoric acid is free from these defects, and accomplishes these ring-closures without reacting with the compound itself, either as an oxidizing or reducing agent or by substitution in the ring system. Diphenylmethane-2-carboxylic acid, for instance, when ring-closed in hydrofluoric acid gives a quantitative yield of anthrone of high purity. The ring-closure of beta naphthyl thioglycolic acid proceeds without sulfonation or oxidation to give good yields of 2,1-naphthio indoxyl. Other cases likewise exhibit marked advantages.

Moreover, anhydrous hydrofluoric acid is one of the best solvents for high-molecular-weight ring-systems. Therefore, ring-closure of compounds such as 1,5-dianilido anthraquinone-2',2''-dicarboxylic acid proceeds smoothly and rapidly as a single phase reaction, and gives a practically theoretical yield of 1,2,5,6-anthraquinone diacridone. Alpha naphthoyl-2-benzoic acid likewise ring-closes quantitatively to 1,2-benz-anthraquinone of high purity, whereas the same reaction if carried out in sulfuric acid is accompanied by sulfonation and low yields of the desired product.

The problem of recovery is also very simple with hydrofluoric acid. In most cases the reaction product crystallizes out when the reaction mass is diluted with cold water. A simple filtration then separates the desired reaction product from the excess hydrofluoric acid employed. In other cases, where the reaction product is too soluble in dilute acid, salting out may be resorted to by the aid of suitable fluorides, or other halides, such as ammonium fluoride, potassium chloride, calcium, barium or magnesium halides, and the like. Sodium salts, however, are to be avoided, since they would precipitate sodium fluoride which is relatively insoluble. In still other cases, where it is desired to recover the excess hydrofluoric acid, distillation, at ordinary pressure or under vacuum, may be resorted to.

We found that the rate of reaction depends to a considerable extent upon the concentration

of the hydrofluoric acid employed. Thus, with anhydrous or nearly anhydrous hydrofluoric acid, reaction in many cases may proceed at ordinary temperature within a very short time, while the use of relatively dilute, aqueous hydrofluoric acid may require heating and stirring for a considerable length of time. Aside from this time factor, however, any concentration of hydrofluoric acid, down to about 43%, may be employed. In the following discussion, as well as in the claims, the phrase "concentrated hydrofluoric acid" should be construed as referring to hydrofluoric acid of from 43.2% to 100%, the lower limit being selected at 43.2% for the reason that at this concentration hydrofluoric acid forms a constant boiling mixture with water (boiling point 111° C.).

Ring-closure would probably take place also in solutions much weaker than 43.2% if elevated temperature were employed, but two factors enter here which render the process impractical, namely: With lower concentrations the rate of reaction is slow, and dilute aqueous hydrofluoric acid is extremely corrosive and it would be hard to find suitable apparatus to withstand this reaction especially at elevated temperature and pressure.

With concentrated hydrofluoric acid, the last mentioned problem is less keen. For concentrations greater than 60% hydrofluoric acid, "18–8" stainless steel, ordinary steel, nickel, Monel metal, copper, etc., are well suited. For concentrations lower than 60%, special alloys such as Electron metal are necessary. The equipment selected should be capable of withstanding pressures up to 90 atmospheres approximate pressure at the critical temperature (230° C.). The maximum pressure encountered in the preferred temperature range, namely between 20° to 150° C., is about 30 atmospheres.

The pressure during ring-closure may be the vapor pressure of the hydrofluoric acid at the operating temperature, maintained by a sealed system for temperatures above 20° C. However, the pressure may, if desired, be augmented by the addition of materials having a higher vapor pressure than hydrofluoric acid; or, on the contrary, the partial pressure of the hydrofluoric acid may be reduced by the addition of substances such as toluene, sodium fluoride, etc., which are inert to the compound being ring-closed, and which have vapor pressures lower than hydrofluoric acid.

As regards temperature, we prefer to operate in the range 20° to 150° C., but the ring-closing action of concentrated hydrofluoric acid is not confined to these limits. Practical considerations exclude other ranges; for instance, below 0° C., ring-closure proceeds very slowly, and at temperatures above 150° C. many organic compounds are decomposed. Aside from such practical factors, however, ring-closure may take place to more or less extent in anhydrous hydrofluoric acid from the freezing point, —83° C., to the critical temperature, 230° C.

The same conditions of temperature apply to dilute hydrofluoric acid, that is, the operating range extends from the freezing point to the critical temperature of any given mixture, but we prefer to use the temperature range 20° to 150° C.

In the specific examples given below, we prefer to use a ratio of 2 to 5 parts of hydrofluoric acid to each part of starting material, but these limits are arbitrary. The amount of hydrofluoric acid used, above the amount necessary to bring about ring-closure, will be determined by operating conditions, that is, the fluidity of the charge, facilities for recovery of the excess hydrofluoric acid, etc.

Without limiting our invention to any particular procedure, the following examples are given to illustrate our preferred mode of operation. Parts mentioned are by weight.

EXAMPLE 1

*Anthrone*

Into a copper vessel chilled in an ice pack are charged 27 parts of liquid, anhydrous hydrofluoric acid and 10 parts of diphenyl methane-2-carboxylic acid (melting point 115° C.). The mixture is allowed to warm to 20°–25° C., and after keeping it one hour at this temperature, the reaction mass is poured into ice. The white precipitate is filtered off, washed acid free, extracted with 100 parts of 10% sodium carbonate solution; filtered, washed alkali free and dried. A 93% yield of crude anthrone melting at 152°–156° C. is obtained.

EXAMPLE 2

*Anthrone*

Into a steel pressure vessel, chilled in an ice pack, are charged 83 parts of 80% hydrofluoric acid and 21 parts of diphenyl methane-2-carboxylic acid. The mass is heated to 60° C. under its own pressure, and held at this temperature for two hours. The reaction mass is then chilled in an ice pack and poured out into ice. The flocculent white precipitate is filtered off, washed acid free and dried. A quantitative yield of anthrone melting at 149°–154° is obtained.

EXAMPLE 3

*2-methyl anthraquinone*

Into a steel pressure vessel, chilled in an ice pack, are charged 68 parts of liquid anhydrous hydrofluoric acid and 20 parts of 4'-methyl benzophenone-2-carboxylic acid. The mixture is heated under autogenous pressure to 100° C. and held at this temperature for two hours. After chilling in an ice pack, the reaction mixture is poured into ice. The crude 2-methyl anthraquinone is filtered off, washed acid-free, digested in 100 parts of 10% sodium carbonate solution; filtered, washed alkali-free and dried. An 80% yield of 2-methyl anthraquinone is obtained. It melts at 175.5° to 176.0° C. after crystallization from alcohol.

EXAMPLE 4

*2-chloranthraquinone*

Into a nickel bomb, chilled in an ice pack, are charged 70 parts of liquid, anhydrous hydrofluoric acid and 28 parts of 4'-chloro-2-benzoyl benzoyl chloride (prepared by treating 4'-chloro-benzophenone-2-carboxylic acid with thionyl chloride; melting range 65°–68° C.). The mass is heated to 130° C. under autogenous pressure and held at this temperature for two hours. It is then chilled thoroughly in an ice pack, and poured into ice. The greyish yellow precipitate is filtered off, washed acid-free, extracted with 200 parts of 10% sodium carbonate; filtered, washed alkali-free and dried. A good yield of 2-chloranthraquinone melting at 205°–206° C. is obtained.

EXAMPLE 5

*Ring-closure of 4'-chloro-2-benzoyl-benzamide*

Into a nickel bomb, chilled in an ice pack, are charged 70 parts of liquid, anhydrous hydrofluoric acid and 20 parts of 4'-chloro-2-benzoyl-

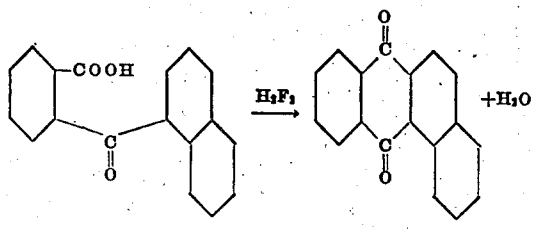
benzamide (synthesized from 4'-chloro-benzoyl-2-benzoyl chloride and aqueous ammonia; melting range 176°–181° C.). The mass is heated to 130° C. under its own pressure and held at this temperature for two hours. It is then chilled in an ice pack and poured out into ice. After allowing to stand for several hours, the precipitate is filtered off, washed acid-free, digested in 200 parts of 10% sodium carbonate solution; filtered, washed free of alkali and dried. The product is 2-chloro-anthraquinone of good quality.

EXAMPLE 6

*Ring-closure of methyl-4'-chloro-2-benzoyl-benzoate*

Into a nickel bomb, chilled in an ice pack, are charged 80 parts of liquid, anhydrous hydrofluoric acid and 27.5 parts of methyl-4'-chloro-2-benzoyl-benzoate (prepared by treating 4'-chloro-2-benzoyl benzoyl-chloride with methyl alcohol; melting range 109°–110° C.). The mass is heated to 130° C. under autogenous pressure, and held at this temperature for two hours. It is then chilled in an ice pack and poured into ice. The brown tar which precipitates out crystallizes on standing for several hours. It is filtered off and washed acid-free. The crude product is extracted with 200 parts of 10% sodium carbonate solution; filtered, washed alkali-free and dried. The unreacted methyl-4'-chloro-benzoyl-2-benzoate is removed by extracting with boiling methyl alcohol. A good yield of 2-chloro-anthraquinone is obtained.

EXAMPLE 7




Alpha naphthoyl-2-benzoic acid ⟶ 1, 2-benz-anthraquinone

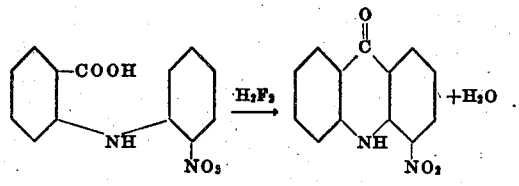
Into a steel autoclave, chilled with ice, are charged 120 parts of liquid, anhydrous hydrofluoric acid and 60 parts of alpha naphthoyl-2-benzoic acid (M. P. 165°–167° C.). Heat to 100° C. under autogenous pressure and hold at this temperature for two hours. Chill and pour the reaction mixture into ice. Filter off the dark green, flocculent product, wash acid-free, and extract with 500 parts of 5% sodium carbonate solution at 90°–95° C. Filter, wash free of alkali and dry. A quantitative yield of 1,2 benzanthraquinone is obtained. The melting range of the crude material, 150°–154° C. may be raised to 165°–167° C. by recrystallizing once from glacial acetic acid.

EXAMPLE 8

*Anthraquinone-2-sulfonic acid*

Into a nickel pressure vessel, chilled with ice are charged 75 parts of liquid, anhydrous hydrofluoric acid and 15 parts of the disodium salt of 4'-sulfo-2-benzoyl-benzoic acid. Heat to 130° C. and hold at this temperature for two hours. Chill thoroughly and pour into ice. A portion of the product may be recovered directly by filtering and the fraction remaining in solution may be recovered by salting out with ammonium fluoride or by adding a potassium salt, such as potassium chloride. A good yield of anthraquinone-2-sodium-sulfonate is obtained.

EXAMPLE 9

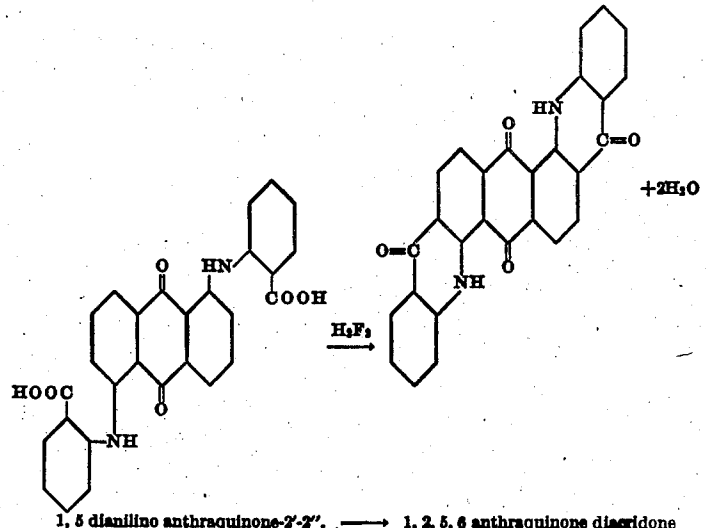



2'-nitro-diphenylamine-2-carboxylic acid ⟶ 1-nitro-acidrone

Into a steel autoclave, chilled to 0° C., charge 90 parts of liquid, anhydrous hydrofluoric acid and 24 parts of 2'-nitro-diphenylamine-2-carboxylic acid, melting range 213°–215° C. Heat to 100° C. under autogenous pressure and hold at this temperature for two hours. After chilling to 0° C., pour the reaction mixture into ice. Filter, wash acid-free, extract with 200 parts of 10% sodium carbonate solution at 90°–95° C.; filter, wash free of alkali and dry. A nearly quantitative yield of 1-nitro-acridone melting at 256°–258° C. is obtained.

EXAMPLE 10

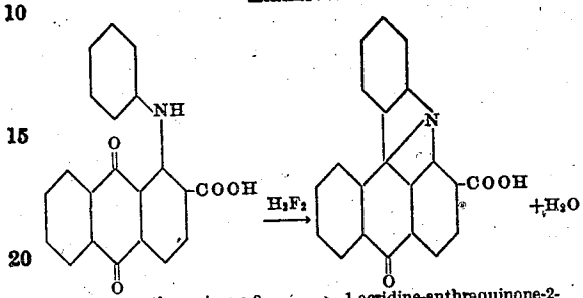
*1, 2, 5, 6 anthraquinone-diacridone; Color Index No. 1163*




1, 5 dianilino anthraquinone-2'-2'', dicarboxylic acid ⟶ 1, 2, 5, 6 anthraquinone diacridone (Indanthrene Violet BN)

Into a steel bomb, chilled in an ice pack, charge 110 parts of liquid, anhydrous hydrofluoric acid and 30 parts 1,5-dianilino-anthraquinone-2'-2'', dicarboxylic acid. Heat to 130° C. and hold at this temperature for four hours. Chill and dilute the charge in ice. Filter off the purple precipitate, wash acid free and dry. A theoretical yield of 1,2,5,6 anthraquinone diacridone is obtained.

EXAMPLE 11




1-anilino-anthraquinone-2-carboxylic acid ⟶ 1-acridine-anthraquinone-2-carboxylic acid

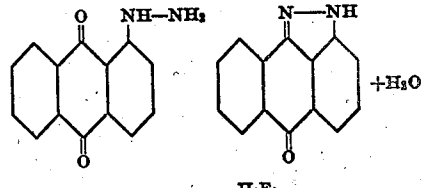
Into a steel pressure vessel, chilled with ice, charge 110 parts of liquid, anhydrous hydrofluoric acid and 30 parts of 1-anilino-anthraquinone-2-carboxylic acid. Heat to 100° C. under pressure and hold at this temperature for four hours. Chill and pour the reaction mixture into ice. Filter off the deep red precipitate, wash acid free and dry. The 92% yield of crude product may be purified by dissolving in a large volume of hot, dilute sodium hydroxide and reprecipitating in a mixture of ice and excess hydrochloric acid. The product is insoluble in all but the higher boiling solvents; gives a red-brown color in concentrated sulfuric acid; and vats in warm, alkaline sodium hydrosulfite. These properties of the product correspond to 1-acridine-anthraquinone-2-carboxylic acid as described in Germ. Pat. No. 262,469 (Friedlaender XI, 687).

EXAMPLE 12

*Ring-closure of 1-beta-naphthyl-amino anthraquinone-2-carboxylic acid*

1-beta naphthyl amino anthraquinone-2-carboxylic acid under conditions similar to those described in Example 11 gives a high yield of material possessing properties closely resembling 1-acridine-anthraquinone-2-carboxylic described in Example 11.

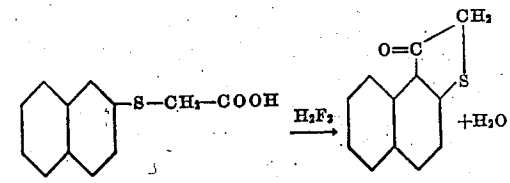
EXAMPLE 13




1-anthraquinonyl-hydrazine ⟶ Pyrazole anthrone

Into a steel bomb, chilled in an ice pack, charge 110 parts of liquid, anhydrous hydrofluoric acid and 36 parts of 1-anthraquinonyl-hydrazine, melting at 233°–235° C. Heat to 100° C. under pressure and hold at this temperature for two hours. Chill and pour the charge into ice. Filter the brown precipitate and wash acid free. A high yield (86%) of pyrazole-anthrone, melting at 247°–250° C., is obtained. The product yields a light brown color with strong, yellow fluorescence in concentrated sulfuric acid. A known sample of pyrazole-anthrone melted at 248°–252° C. and showed similar color in concentrated sulfuric acid. A mixed melting point showed no depression.

EXAMPLE 14



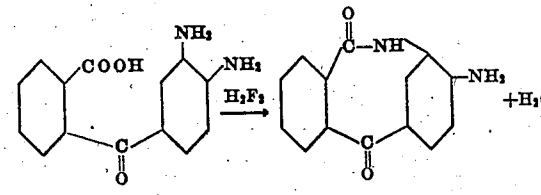

Beta-naphthyl-thioglycollic acid ⟶ 2, 1-naphthio-indoxyl

Into an "18–8" stainless-steel bomb, chilled in an ice pack, charge 70 parts of liquid, anhydrous hydrofluoric acid and 20 parts of beta-naphthyl-thioglycollic acid, melting range 91°–92.5° C. Heat to 98°–99° C. and hold at this temperature for fifteen minutes. Chill at once and pour onto ice (approximately 300 parts). Filter, wash acid-free, and either dry the crystals or oxidize the paste directly in the usual manner, to bisnaphtho-thiophene-indigo. A 54% yield of crude color is obtained by the oxidation of the crude thio-indoxyl.

Essentially the same results are obtained when the charge is heated at 30° C. for six hours in a nickel bomb. The crude thio-indoxyl has a melting range of 98° to 104° C.

EXAMPLE 15

*Ring-closure of 3',4'-diamino-2-benzoyl benzoic acid*

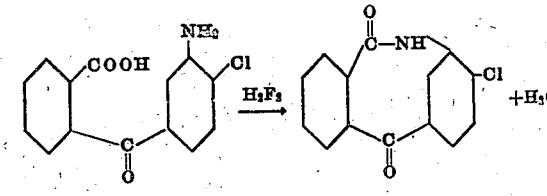



(Probable reaction)

Into a steel pressure vessel, chilled with ice, charge 40 parts of liquid, anhydrous hydrofluoric acid and 10 parts of 3',4'-diamino-2-benzoyl-benzoic acid (M. P. 190° C.). Heat to 100° C. and hold at this temperature for two hours. Chill thoroughly and pour into ice. Filter off the light brown product, wash acid-free and dry. The product is insoluble in cold dilute alkali, but slowly dissolves in dilute, boiling sodium hydroxide. A small amount of anthraquinone bodies is present. The predominating product is probably an internal lactam of 3',4'-diamino-2-benzoyl benzoic acid (Br. Pat. No. 22,440 of 1912).

EXAMPLE 16

*Ring-closure of 3'-amino-4'-chloro-2-benzoyl-benzoic acid*




(Probable reaction)

Into a steel bomb, chilled in an ice pack, charge 50 parts of liquid anhydrous hydrofluoric acid and 20 parts of 3'-amino-4'-chloro-2-benzoyl benzoic acid. Heat to 100° C. under pressure and hold at this temperature two hours. Chill thoroughly and pour onto ice. Filter off the grey precipitate, wash acid free and dry. The product

is insoluble in warm sodium carbonate or dilute sodium hydroxide. Prolonged boiling in dilute sodium hydroxide dissolves the product, however. Very little vat formation takes place in warm, alkaline sodium hydrosulfite solution. The product is probably an internal lactam of 3'-amino-4'-chloro-2-benzoyl benzoic acid.

The advantages of our invention will now be readily understood. Hydrofluoric acid as a ring-closing agent provides the following advantageous conditions:

1. It is a non-oxidizing and non-reducing medium.

2. It is a powerful dehydrating agent.

3. Anhydrous hydrofluoric is one of the best solvents for high molecular weight organic compounds, especially the complex vat dyestuffs.

4. Hydrofluoric acid may be recovered by simple distillation at low temperature (boiling point at atmospheric pressure is 20.4° C.).

5. Ease of manipulation. No special equipment is necessary. An ordinary, high-pressure, steel autoclave with brine-jacketed steel condenser is adequate.

6. The use of concentrated hydrofluoric eliminates objectional sulfonation which is encountered in the use of concentrated sulfuric acid, oleum or halogen sulfonic acids as ring-closing agents.

Concentrated hydrofluoric acid provides the best medium discovered to date for the ring-closure of compounds which are easily oxidized, both in the initial stage and the finished product stage, e. g., diphenylmethane-2-carboxylic acid. Since organic compounds in general are very soluble in anhydrous hydrofluoric acid, ring-closure proceeds smoothly and rapidly as a single phase reaction. When the reaction is finished, the charge may be run into ice and the product isolated by filtration; or better, the hydrofluoric acid may be simply distilled off and reused. In cases where water is the by-product only a very small amount of hydrofluoric acid is lost to the process as a constant boiling mixture containing 43% $H_2F_2$.

It will be observed that although we referred in the introduction to organic compounds adapted to form a closed ring under the action of acidic dehydrating agents, our invention is by no means restricted to ring-closures by the elimination of $H_2O$. On the contrary, as illustrated by the above specific examples, hydrofluoric acid may be successfully employed as a ring-closing agent in many cases where the elements split off are those of hydrochloric acid (Example 4), ammonia (Example 5), alkali metal hydroxide (Example 8) or a lower alcohol (Example 6). This is particularly true when one deals with the ring-closures of diaryl-methane-ortho-carboxylic acids and diaryl-ketone-ortho-carboxylic acids. To put it in different words, according to our observations hydrofluoric acid will operate successfully as ring-closing agent whether the side chain involved in the ring-closure is a free carboxylic acid group or a functional derivative thereof such as metal salt, alkyl ester, amide or chloride.

In this particular respect, hydrofluoric acid is not singular, since concentrated sulfuric acid and other acidic dehydrating agents are likewise capable of ring-closing ortho-benzoyl-benzoic acid derivatives regardless whether the carboxylic acid group is free or in the form of a functional derivative of the same. It will be understood therefore that where we speak of acidic dehydrating agents in the claims below, we are not attempting to limit this invention to the case of splitting off water, but are merely trying to identify a group of reagents which are normally employed for ring-closure and which by their capacity of effecting ring-closure define the organic materials to which this invention is applicable.

It will be understood that although we reported above a number of specific procedures with great particularity, many variations and modifications are permissible in our preferred mode of procedure, without departing from the spirit of this invention.

We claim:

1. In the process of ring-closing an aromatic compound of the type which is adapted to form a closed ring by treatment with acidic dehydrating agents, the improvement which comprises use of a proportion of concentrated hydrofluoric acid sufficient to effect ring-closure and leave an acid residue containing not less than 43% strength hydrofluoric acid.

2. In the process of ring-closing an aromatic compound of the type which is adapted to form a closed ring by treatment with acidic dehydration agents, the improvement which comprises employing an amount of 80% hydrofluoric acid sufficient to effect ring-closure and leave an acid residue containing not less than 43% strength hydrofluoric acid.

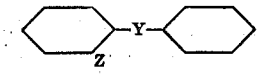
3. A process according to claim 2 in which the ring-closing agent is anhydrous hydrofluoric acid.

4. The process of ring-closing an organic compound of the type which is normally adapted to form a closed ring by reaction with an acidic dehydrating agent, which comprises mixing said compound with concentrated hydrofluoric acid, promoting reaction by the usual expedients of warming and agitation as necessary and recovering the closed-ring reaction product, said concentrated hydrofluoric acid being used in sufficient amount to assure residual acid of at least 43% strength.

5. The process of ring-closing an organic compound of the type adapted to form a closed ring by the elimination of water, which comprises treating such compound with sufficient concentrated hydrofluoric acid to effect ring-closure and leave an acid residue containing not less than 43% strength hydrofluoric acid.

6. In a process of synthesizing an organic compound by eliminating the elements of water from a related compound, with the formation of a closed ring, the improvement which comprises effecting the elimination and ring-closure by the aid of an amount of concentrated hydrofluoric acid sufficient to effect ring-closure and leave a residual acid of not less than 43% strength.

7. The process of ring-closing an organic compound of the general formula




wherein Y is a member of the group consisting of CO, $CH_2$ and NH and Z is a member of the group consisting of the carboxylic acid radical and functional derivatives thereof, which comprises reacting said compound with a proportion of concentrated hydrofluoric acid sufficient to effect ring-closure and leave an acid residue containing not less than 43% strength hydrofluoric acid.

8. The process of producing an anthrone com-

pound, which comprises ring-closing a corresponding diphenyl-methane-o-carboxylic acid compound by the aid of concentrated hydrofluoric acid in amount sufficient to effect ring-closure and leave an acid residue of at least 43% strength hydrofluoric acid.

9. In the process of ring-closing a diarylmethane compound which possesses an unsubstituted ortho position on one aryl radical and a reactive ortho carboxyl group on the other aryl radical, the improvement which comprises effecting the ring-closure by the aid of a proportion of concentrated hydrofluoric acid sufficient to effect ring-closure and leave an acid residue of at least 43% strength hydrofluoric acid.

10. The process of producing a cyclic organic ketone compound, which comprises ring-closing a corresponding ortho-benzoyl-benzoic acid compound in a medium consisting of concentrated hydrofluoric acid in amount sufficient to effect ring-closure and leave an acid residue of at least 43% strength hydrofluoric acid.

11. The process of producing an acridone compound which comprises ring-closing a diphenylamine-2-carboxylic acid by the aid of concentrated hydrofluoric acid in amount sufficient to effect ring-closure and leave an acid residue of at least 43% strength hydrofluoric acid.

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