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(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650(US)

(72) Inventor: **Cushman, Michael Roy c/o EASTMAN KODAK COMPANY**
Patent Department 343 State Street
Rochester New York 14650(US)
Inventor: **Lentz, Carl Michael c/o EASTMAN KODAK COMPANY**
Patent Department 343 State Street
Rochester New York 14650(US)

(74) Representative: **Parent, Yves et al**
Kodak-Pathé Département Brevets et Licences Centre de Recherches et de Technologie Zone Industrielle
F-71102 Chalon-sur-Saône Cédex(FR)

(54) Process for the electrochemicai iodination of aromatic compounds.

(57) The present invention discloses a process for the anodic electrochemical iodination of aromatic compounds to selectively and efficiently form a para-substituted iodobenzene. This process makes use of a graphitic carbon anode. Also disclosed is a process for cathodically deiodinating a diiodobenzene compound to form iodobenzene in the presence of a palladium on carbon catalyst.

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PROCESS FOR THE ELECTROCHEMICAL IODINATION OF AROMATIC COMPOUNDS

Field of Invention

The present invention relates to the electrochemical iodination of aromatic compounds to selectively and efficiently form a para-substituted iodobenzene derivative.

Background of the Invention

Iodoaromatics are desirable materials because of the wide variety of transformations they can undergo. For example, they can be catalytically carbonylated to form aromatic carboxylic acids and esters. Iodoaromatics are therefore possible starting materials for polycarbonates, polyamides, polysulfides, and polyesters. The halogenation with molecular halogen is one of the classic reactions of aromatic substitution and has been thoroughly investigated owing to its theoretical as well as synthetic value (H. P. Braendlin and E. T. McBee in Friedel-Crafts and Related Reactions ed. G. A. Olan, Wiley, New York, 1964, Volume 3, Ch. 46.) The electrophilicity of molecular chlorine and bromine allows the direct reaction of these halogens with arenes. The direct iodination of aromatic substrates with molecular iodine has proven difficult and needs the presence of an activator to be successfully carried out except for a few special cases. The most widely employed strategy consists of the use of a powerful oxidant in order to produce a strongly electrophilic species (A. Shimizu, K. Yamataka, and T. Isoya, Bull. Chem. Soc. Jap., 58, 1611 (1985) and references cited therein.). Other approaches have included polarizing I_2 with a Lewis acid, (S. Uemura, A. Onoe, and M. Okano Bull. Chem. Soc. Jap., 47(1), 147 (1974); T. Sugita, M. Idei, Y. Ishibashi, and Y. Takegami, Chem. Lett., 1481 (1982)), thallation followed by reaction with iodide ion, (A. McKillop, et al., J. Am. Chem. Soc., 93, 4841 (1971)), chloro mercuration followed by reaction with iodine, (L. F. Fieser and M. Fieser Reagents for Organic Synthesis, Wiley, New York, 1967, p 497), and diazonium salt reaction with iodide ion. (N. I. Foster, N. D. Heindell, H. D. Burns, and W. Muhr, Synthesis, 572 (1980)). All of these procedures have deficiencies.

The electrochemical iodination of aromatics has been reported. (L. L. Miller, E. P. Kujawa, and C. B. Campbell, J. Am. Chem. Soc., 92, 2821 (1970); R. Lines and U. D. Parker Acta Chem. Scand., Ser B, 34, 48 (1980)). Parker and co-workers found that the anodic oxidation of iodine in trifluoroacetic acid containing solvents produces a highly reactive iodine species. However, the selectivity of the system toward the desirable para disubstituted isomers was poor. (R. Lines and U. D. Parker Acta Chem. Scand., Ser B, 34, 48 (1980)). It would be desirable to have an electrolytic process that will afford high reactivity as well as high selectivity to the highly desirable para-disubstituted arenes.

Summary of the Invention

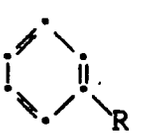
The present process is an electrolytic process that provides selective and efficient formation of a para-substituted iodobenzene derivative. This process makes use of a graphitic carbon anode. More specifically, the present invention is directed to an electrolytic process for the formation of a para-substituted iodobenzene derivative comprising contacting:

an anolyte solution of a divided electrolytic cell, wherein said divided electrolytic cell comprises:

an anode compartment comprising a graphitic carbon anode and said anolyte solution which comprises solvent and an electrolyte; and a cathode compartment comprising a cathode and a catholyte solution which comprises solvent and an electrolyte; wherein said anode compartment and cathode compartment are separated by a separator,

with

an iodine source, and a mono-substituted compound of the formula:



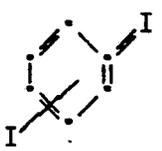
wherein R is alkyl, halo, unsubstituted aryl, or aryl substituted with up to 5 electron-donating groups such as hydroxyl, thiol, -SR′, -OR′,
wherein R′ is a C_1-C_6 alkyl, or phenyl, and applying to the anode and the cathode an electric potential; the proportions of materials, electrical potential, and other conditions being effective to form a para-substituted iodobenzene derivative in said anode compartment.

This process for the formation of a para-substituted iodobenzene derivative shall be referred to herein as "Process I."

In a preferred process of the invention benzene is used as a starting material to form iodobenzene followed by the further iodination of the iodobenzene. Therefore, the present invention also encompasses an electrolytic process for preparing iodobenzene comprising contacting:
an anolyte solution of a divided electrolytic cell, wherein said divided electrolytic cell comprises:
an anode compartment comprising a graphitic carbon anode and said anolyte solution which comprises a solvent and an electrolyte; and a cathode compartment comprising a cathode and a catholyte solution which comprises a solvent and an electrolyte; wherein said anode compartment and cathode compartment are separated by a separator,
with
an iodine source, and benzene, and applying to the anode and the cathode an electric potential; the proportion of materials, electric potential, and other conditions being effective to form iodobenzene.

This process for preparing iodobenzene shall be referred to herein as "Process II."

In carrying out the present invention, it was found that a diiodobenzene could conveniently be deiodinated cathodically, in the presence of a palladium on carbon catalyst, to iodobenzene, which facilitates a continuously run operation. Therefore, the present invention is also directed to an electrolytic process for preparing iodobenzene comprising contacting a catholyte solution of a divided electrolytic cell wherein said divided electrolytic cell comprises
an anode compartment comprising an anode and an anolyte solution which comprises a solvent and an electrolyte; and a cathode compartment comprising a cathode and a catholyte solution which comprises a solvent and an electrolyte;
wherein said anode compartment and cathode compartment are separated by a separator,
with
a diiodobenzene compound of the formula



in the presence of a catalytic amount of palladium on carbon, and applying to the anode and cathode an electric potential; the proportion of materials, electric potential, and other conditions being sufficient to form iodobenzene.

This cathodic deiodination process shall be referred to herein as "Process III."

As used herein, the term "halo" refers to chloro, bromo, fluoro or iodo; the term "alkyl" refers to C_1 to C_{16} straight, branched or cyclic alkyls; and the term "aryl" refers to aryls containing six to 14 carbon atoms.

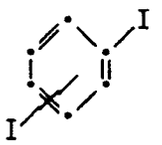
Detailed Description of the Invention

Any of Process I, Process II, or Process III can be carried out batchwise; however, for most industrial applications, it is preferred to perform these processes continuously. Therefore, it is preferred to couple Process I with Process II and/or Process III. A preferred process of the present invention is a continuous process in which Process I is performed simultaneously with Process III. This preferred process can be described as a continuous electrolytic process for the formation of para-diiodobenzene comprising:

(A) contacting
an anolyte solution of a divided electrolytic cell, wherein said divided electrolytic cell comprises:
an anode compartment comprising a graphitic carbon anode and said anolyte solution which comprises a solvent and an electrolyte, and a cathode compartment comprising a cathode and a catholyte solution which comprises a solvent and an electrolyte; wherein said anode compartment and cathode compartment are

separated by a separator, and wherein said catholyte solution and said anolyte solution are the same and comprise a tetrafluoroborate electrolyte and an acetonitrile solvent;
with
an iodine source, and iodobenzene, and applying to the anode and the cathode an electric potential; the proportions of materials, electric potential, and other conditions being effective to form para-diiodobenzene,

(B) filtering the anolyte solution containing para-diiodobenzene formed in Step (A) to obtain a solid which comprises para-diiodobenzene and a filtrate which comprises an electrolyte, a solvent and at least one diiodobenzene compound of the formula:



(C) adding the filtrate from Step (B) to said cathode compartment,

(D) deiodinating the diiodobenzene compound in the cathode compartment from Step (C) to form iodobenzene by applying to the anode and cathode an electric potential, wherein the catholyte solution and diiodobenzene compound are in the presence of a catalytic amount of palladium on carbon; the proportions of materials, electric potential, and other conditions being suficient to form iodobenzene; and

(E) recycling the iodobenzene formed by Step (D) as a starting material for Step (A).

When Process I is coupled with Process II, it is preferred that such process be performed consecutively in the same electrolytic cell. As a result, the iodobenzene formed from Process II is used as a starting material for Process I.

In any of the processes of the present invention it is preferred that the electric potential applied to the anode and cathode is about 1.5 to about 2.5 volts, more preferred is about 2 volts.

It is preferred that the processes of the present invention are performed at a temperature of about 25° to about 100° C, more preferred is about 25° to about 50° C; and at a pressure of about 1 atmosphere (atm) to about 10 atm, more preferred is about 1-2 atms.

If one or more processes of the present invention is run as a batch process, typically the electric potential is applied for a period of time of about 1 to about 25 hours, preferred is about 2 to about 8 hours.

If desired, additives such as CF_3CO_2H, $(Et)_4NBF_4$, or trisbromophenyl amine can be added to the reaction medium in the processes of the present invention; however, the presence of such additives are not necessary. If one or more additives are used, they are typically present in a concentration of up to about 10 percent, based on solvent weight.

In the processes of the present invention, the cathode compartment and anode compartment are separated by a separator such as a membrane, fritted glass, and the like. Preferably this separator is a membrane. A preferred membrane is a Nafion™ membrane.

For Process I, the nature of the anode is important. It has been found that the anode must be comprised of graphitic carbon in order for the iodination process to be sufficiently effective. The graphitic anode can be comprised of spectral grade graphite or can be any other suitable graphite electrode.

The nature of the, cathode for any of the processes of the invention, is not particularly critical. The cathode can be comprised of platinum, carbon, copper, lead, tin, palladium, stainless steel, or combinations thereof. However, since Process III must proceed in the presence of palladium or carbon, it is convenient for the cathode in Process III to be comprised of palladium on carbon.

The solvents and electrolyte in the cathode and anode compartments for any of the processes of the present invention can be the same or different; however, it is usually more convenient for the electrolyte and solvents to be the same in each compartment.

Preferred solvents are polar organic aprotic or protic solvents. Examples include methanol, ethanol, acetonitrile, tetrahydrofuran, dimethylformamide, dimethylsulfoxide, dimethyl ether, diethyl ether, acetic acid (HOAc), or a mixture thereof. The most preferred solvent is acetonitrile.

The electrolyte is present in a concentration sufficient to give the total reaction medium sufficient conductivity at reaction conditions in order for the desired process to proceed satisfactorily. A preferred electrolyte is a tetrafluoroborate. Examples include substituted tetrafluoroborates such as, HBF_4, $NaBF_4$, $(Me)_4NBF_4$, $(Et)_4NBF_4$, $(Pr)_4NBF_4$, or $(Bu)_4NBF_4$ wherein Me is methyl, Et is ethyl, Pr is propyl and Bu is butyl. The most preferred electrolyte is HBF_4, $(Me)_4NBF_4$ or $(Bu)_4NBF_4$.

In Process I, in addition to the formation of said para-substituted iodobenzene derivative, typically minor

amounts of the other isomers are also formed, especially an ortho-substituted iodobenzene derivative. It is an advantage of the present invention that the yield of the para-substituted compound is greater than the yield of the ortho-substituted compound. Preferably the mole ratio of para-substituted iodobenzene derivative to ortho-substituted iodobenzene derivative after reaction is greater than about 1:1 to about 100:1.

For Process I, the following are preferred embodiments: the weight ratio of the iodine source to the mono-substituted compound to the anolyte solution is about 2.5:3.0:100 to about 1.0:15.0:100, and the weight ratio of electrolyte to solent of the anolyte solution is about 1:1 to about 1:100; said electron-donating group is alkyl, hydroxyl, thiol, -OR′, or -SR′; the iodine source is iodine (I_2) or an iodine salt such as HI, NaI, KI, or an alkyl ammonium iodide.

In Process I, most preferably R is I and the iodine source is most preferably I_2.

It is also an advantage of Process I that the purity of the para-substituted iodobenzene derivative is typically greater than about 98 weight percent, preferably greater than about 99 weight percent, after isolation by standard techniques. When forming para-diiodobenzene, this compound can be isolated simply by cooling the electrolysis mixture until the desired compound becomes a solid, typically less than about 15 °C, followed by filtering. By this simple isolation procedure, typically greater than about 80 weight percent of the available para-isomer can be obtained. It is also preferred that the yield of para plus ortho derivatives is greater than about 60 percent preferably greater than about 90 percent, based on the weight of consumed iodine source. Typical by-products formed include iodonium salts.

For Process I, the selectivity for para substitution appears to be independent of the working potential. It is not desired to be bound by any particular theory or mechanism; however, it is believed that the independence of para selectivity from working potential, together with the advantages of using a graphitic carbon anode, suggests that the mechanism of iodination may be more complex than a simple electrophillic attack on an "I+" species.

For Process II, it is preferred that the weight ratio of the iodine source to benzene to the anolyte solution is about 1.25:2.0:100 to about 2.5:1.0:100, the weight ratio of electrolyte to solvent in the anolyte and catholyte solutions is about 1:10 to about 1:100, and that the iodine source is iodine.

For Process III, it is preferred that the weight ratio of the diiodobenzene compound:catholyte solution is about 1:10 to about 1:100; the weight ratio of electrolyte: solvent in the anolyte and catholyte solutions is about 1:10 to about 1:100; and that the diiodobenzene starting material is ortho-diiodobenzene.

Process III must be performed in a catalytic amount of palladium on carbon catalyst. Such a catalytic amount is typically at least about 0.001%, based on the weight of diiodobenzene starting material, preferably about 0.01%.

For the examples that follow, the following experimental conditions were used: Electrolysis was performed in an H-type cell where the anode and cathode were separated by a Nafion membrane. In each case, the cathode was a spectroscopic (UltraCarbon, U50) carbon rod. All reactions were run at the indicated constant potential by way of an ESC Model 410 potentiostatic controller. The electrochemical apparatus was fitted with an ESC Model 630 digital coulometer and, in each case, the theoretical number of coulombs was collected. The cell temperature was not controlled and usually rose to about 28 °C in the course of an experiment.

The following examples illustrate the invention but should not be interpreted as a limitation thereon.

EXAMPLES

Example 1 - Iodination of Toluene

To the anode side of a laboratory H cell fitted as previously described is added 100 milliliters (mL) of a solution made up by adding sufficient 50% aqueous HBF_4 to acetic anhydride/acetic acid so the final concentration of HBF_4 is 10% by weight and the water concentration is from 1% to 3% by weight. To this solution is added 2.54 grams (g) (0.01 mole) iodine and 3.0 g (0.031 mole) toluene. The cell is fitted with the various anodes as shown in Tables 1 and 2. To the cathode compartment is added the same acetic acid/tetrafluoroboric acid solution as in the anode. The cathode is a carbon rod in each case. The potential is set at 2.00 volts versus SCE (saturated calomel electrode), and current is passed through the electrolysis solution. The electrolysis is stopped after 1930 coulombs are passed. The product is isolated by pouring the anode solution into 500 mL of water and extracting three times with 50 mL of methylene chloride each time. The extracts are combined and washed with 100 mL of water. The organic layer is dried over

magnesium sulfate and the solvent is removed in vacuo to afford 4.3 g of a light color oil. The product is analyzed by capillary gas chromatograph versus authentic samples to establish the yield and ortho-para ratio.

Example 2 - Iodination of Iodobenzene

The electrolysis apparatus employed is as previously described. The catholyte and anolyte solutions are prepared as described for the electrolysis of toluene. To the anode compartment is added 1.26 g of iodine (5 mmols) and 2.04 g of iodobenzene (10 mmols). The system is electrolyzed at a constant potential of 1.7 volts versus SCE. After passing 965 coulombs, the electrolysis is stopped. The anode mixture is cooled to 15°C and the resulting solid isolated by filtration. After water wash and air drying, the solid weighs 2.1 g (64% isolated yield) and is shown by capillary gas chromatography to be 100% p-diiodobenzene.

Example 3 - Iodination of Benzene

The electrolysis apparatus is as previously described. The catholyte and anolyte solutions are prepared as described for the electrolysis of toluene. To the anode compartment is added 2.54 g (0.01 mole) iodine and 2.42 g (0.031 mole) benzene. The system is electrolyzed at a constant potential of 2.0 volts vs SCE. The electrolysis is stopped after 1950 coulombs are passed. The product is isolated by pouring the anode solution into 500 mL water and extracting three times with 50 mL of methylene chloride. The extracts are combined and washed with 100 mL water. The organic layer is dried over magnesium sulfate and the solvent removed in vacuo to afford 4.1 g of a light yellow oil. The product is analyzed by capillary gas chromatography to afford iodobenzene chemical yield of 95% based on iodine.

Example 4 - Iodination of Toluene

The procedure of Example 1 is substantially repeated except that the working potential is varied. The para selectivity versus working potential is shown in Table 3.

TABLE 1

Electrochemical Iodination of Toluene in HoAc/10% HBF_4[1]					
Anode	Iodine Source	Additives	Products - % Yield[2]		op + pp[4] Iodonium Salt
			p-Iodotoluene	o-Iodotoluene	
Graphitic Carbon	I_2	None	53.8	32.1	8.4
Graphitic Carbon	HI	None	62.0	32.6	1.2
Graphitic 8.0 Carbon	I_2	Et_4NBF_4	40.8		38.5
Graphitic 29.7 Carbon	I_2	CF_3CO_2H	9.2		5.5
Pt 2.8	I_2	CF_3CO_2H	1.0		0.4
RVC[3]	I_2	None	3.9	2.5	-
Pt/Ir/Ti	I_2	None	2.9	1.8	-
Graphitic Carbon	I_2	Trisbromophenyl Amine	54.0	32.9	7.2
Ebonex[5]	I_2	None	10.6	6.0	-
Footnotes:					
[1]All reactions were run in a divided cell with a Nafion membrane at 2.00 volts versus SCE.					

[2]Isolated yield based on iodine.
[3]RVC = reticulated vitreous carbon.
[4]op + pp = ortho para and para para.
[5]Ebonex is a trade name for conductive TiO_2.

TABLE 2

Electrochemical Iodination of Toluene in Various Solvents[1]					
Anode	Solvent	Supporting Electrolyte	Iodine Source	Products - % Yield[2]	
				p-Iodotoluene	o-Iodotoluene
Pt/Ir/Ti	CH_3OH/H_2O	$NaBF_4$	KI	0	0
Pt/Ir/Ti	CH_3CN	$(Me)_4NBF_4$	$(Et)_4NI$	0	0
Pt/Ir/Ti	H_2O/CH_2Cl_2	$(Me)_4NBF_4$	I_2	10.0	2.1
Graphitic Carbon	CH_3CN	$(Me)_4NBF_4$	I_2	72.5	8.2
Graphitic Carbon	CH_2Cl_2/CF_3CO_2H	$(Bu_4)_4NBF_4$	I_2	18.0	14.1
Footnotes:					
[1]All reactions were run in a divided cell with a Nafion membrane at 2.00 volts versus SCE.					

[2]Isolated yield based on iodine.

TABLE 3

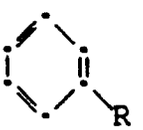
Para Selectivity of Toluene Iodination Versus Working Potential[1]	
Working Potential[2]	% Para Iodotoluene
1.7 v	62%
1.8 v	61%
1.9 v	66%
2.0 v	65%
2.1 v	62%

[1]At carbon anode in a divided cell.
[2]Potential versus SCE.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. An electrolytic process for the formation of a para-substituted iodobenzene derivative comprising contacting:
an anolyte solution of a divided electrolytic cell, wherein said divided electrolytic cell comprises:
an anode compartment comprising a graphitic carbon anode and said anolyte solution which comprises solvent and an electrolyte; and a cathode compartment comprising a cathode and a catholyte solution which comprises solvent and an electrolyte; wherein said anode compartment and cathode compartment are separated by a separator,
with
an iodine source, and a mono-substituted compound of the formula:



wherein R is alkyl, halo, unsubstituted aryl, or aryl substituted with up to 5 electron-donating groups, and applying to the anode and the cathode an electric potential; the proportions of materials, electrical potential, and other conditions being effective to form a para-substituted iodobenzene derivative in said anode compartment.

2. The process of Claim 1 wherein said electric potential applied is about 1.5 to about 2.5 volts.

3. The process of Claim 1 wherein said electric potential is applied for a period of time of about 1 to about 25 hours, at a temperature of about 25° to about 100° C and at a pressure of about 1 atm to about 10 atm.

4. The process of Claim 1 wherein the weight ratio of the iodine source to the mono-substituted compound to the anolyte solution is about 2.5:3.0:100 to about 1.0:15.0:100, and the weight ratio of electrolyte to solvent of the anolyte solution is about 1:1 to about 1:100.

5. The process of Claim 1 wherein the anolyte solution and the catholyte solution are the same.

6. The process of Claim 5 wherein the solvent is comprised of a polar organic aprotic or protic solvent and the electrolyte is present in a concentration sufficient to give the total reaction medium sufficient conductivity at reaction conditions.

7. The process of Claim 6 wherein said iodine source is iodine or an iodine salt and said electrolyte is a

tetrafluoroborate.

8. The process of Claim 1 wherein R is I.

9. The process of Claim 6 wherein said electrolyte is HBF_4, $(Me)_4NBF_4$ $(Et)_4NBF_4$, $(Pr)_4NBF_4$, or $(Bu)_4NBF_4$; and said solvent is methanol, ethanol, acetonitrile, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, dimethyl ether, diethyl ether, or acetic acid.

10. The process of Claim 1 wherein said electron-donating groups are alkyl, hydroxyl, thiol, -OR′, -SR′, wherein R′ is a C_{1-6} alkyl, or phenyl; said separator is a membrane; and said cathode is comprised of platinum, carbon, copper, lead, tin, palladium, or stainless steel.

11. The process of Claim 1 wherein the yield of said para-substituted iodobenzene derivative is greater than the yield of an ortho-substituted iodobenzene derivative.

12. The process of Claim 11 wherein the mole ratio of para-substituted iodobenzene derivative to ortho-substituted iodobenzene derivative after reaction is about greater than 1:1 to about 100:1.

13. The process of Claim 1 run continuously.

14. An electrolytic process for the formation of para-diiodobenzene comprising contacting:
an anolyte solution of a divided electrolytic cell, wherein said divided electrolytic cell comprises:
an anode compartment comprising a graphitic carbon anode and said anolyte solution which comprises a solvent and an electrolyte; and a cathode compartment comprising a cathode and a catholyte solution which comprises a solvent and an electrolyte; wherein said anode compartment and cathode compartment are separated by a separator, and wherein said catholyte solution and said anolyte solution are the same and comprise a tetrafluoroborate electrolyte and an acetonitrile solvent;
with an iodine source, and iodobenzene, and applying to the anode and the cathode an electric potential; the proportions of materials, electric potential, and other conditions being effective to form para-diiodobenzene.

15. The process of Claim 14 wherein said electric potential applied is about 1.5 to about 2.5 volts, for a period of time of about 1 to about 25 hours, at a temperature of about 25° to about 100° C, and at a pressure of about 1 atm to about 10 atm.

16. The process of Claim 14 wherein the weight ratio of the iodine source to iodobenzene to the anolyte solution is about 1.25:2.0:100 to about 2.5:1:100, and the weight ratio of tetrafluoroborate to acetonitrile is about 1:10 to about 1:100.

17. The process of Claim 16 wherein said iodine source is iodine and said electrolyte is HBF_4, $(Me)_4NBF_4$, $(Et)_4NBF_4$, $(Pr)_4NBF_4$, or $(Bu)_4NBF_4$.

18. The process of Claim 16 wherein said separator is a membrane, and said cathode is comprised of platinum, carbon, copper, lead, tin, palladium or stainless steel.

19. The process of Claim 16 wherein the yield of para-diiodobenzene is greater than the yield of ortho-diiodobenzene.

20. The process of Claim 19 wherein the mole ratio of para-diiodobenzene to ortho-diiodobenzene after reaction is about 1:1 to about 10:1.

21. The process of Claim 14 wherein the purity of para-diiodobenzene is greater than about 98 percent after isolation by standard techniques.

22. An electrolytic process for preparing iodobenzene comprising contacting:
an anolyte solution of a divided electrolytic cell, wherein said divided electrolytic cell comprises:
an anode compartment comprising a graphitic carbon anode and said anolyte solution which comprises a solvent and an electrolyte; and a cathode compartment comprising a cathode and a catholyte solution which comprises a solvent and an electrolyte; wherein said anode compartment and cathode compartment are separated by a separator,
with
an iodine source, and benzene, and applying to the anode and the cathode an electric potential; the proportion of materials, electric potential, and other conditions being effective to form iodobenzene.

23. The process of Claim 22 wherein said electric potential applied is about 1.5 to about 2.5 volts, for a period of time of about 1 to about 25 hours, at a temperature of about 25° to about 100° C, and at a pressure of about 1 atm to about 10 atm.

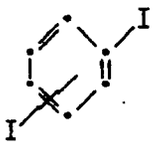
24. The process of Claim 22 wherein the weight ratio of the iodine source to benzene to the anolyte solution is about 1.25:2.0:100 to about 2.5:1.0:100, and the weight ratio of electrolyte to solvent in the anolyte and catholyte solutions is about 1:10 to about 1:100.

25. The process of Claim 22 wherein said iodine source is iodine; the anolyte solution and the catholyte solution are the same; said electrolyte is HBF_4, $(Me)_4NBF_4$, $(Et)_4NBF_4$, $(Pr)_4NBF_4$, or $(Bu)_4NBF_4$; and said solvent is acetonitrile.

26. The process of Claim 14 wherein the iodobenzene is formed by the process of Claim 22.

27. The process of Claim 26 wherein the formation of iodobenzene and the formation of para-diiodobenzene are performed consecutively in the same electrolytic cell.

28. An electrolytic process for preparing iodobenzene comprising contacting a catholyte solution of a divided electrolytic cell wherein said divided electrolytic cell comprises
an anode compartment comprising an anode and an anolyte solution which comprises a solvent and an electrolyte; and a cathode compartment comprising a cathode and a catholyte solution which comprises a solvent and an electrolyte;
wherein said anode compartment and cathode compartment are separated by a separator, with
a diiodobenzene compound of the formula



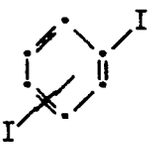
in the presence of a catalytic amount of palladium on carbon, and applying to the anode and cathode an electric potential; the proportion of materials, electric potential, and other conditions being sufficient to form iodobenzene.

29. The process of Claim 28 wherein the cathode comprises palladium on carbon.

30. The process of Claim 28 wherein said electric potential applied is about 1.5 to about 2.5 volts, the weight ratio of the diiodobenzene compound catholyte solution is about 1:10 to about 1:100, and the weight ratio of electrolyte: solvent in the anolyte and catholyte solutions is about 1:10 to about 1:100.

31. The process of Claim 28 wherein the analyte solution and the catholyte solution are the same; said electrolyte is HBF_4, $(Me)_4NBF_4$, $(Et)_rNBF_4$, $(Pr)_4NBF_4$, or $(Bw)_4NBF_4$; said solvent is acetonitrile; and said diiodobenzene compound is ortho-diiodobenzene.

32. A continuous electrolytic process for the formation of para-diiodobenzene comprising:
(A) contacting
an anolyte solution of a divided electrolytic cell, wherein said divided electrolytic cell comprises:
an anode compartment comprising a graphitic carbon anode and said anolyte solution which comprises a solvent and an electrolyte, and a cathode compartment comprising a cathode and a catholyte solution which comprises a solvent and ana electrolyte; wherein said anode compartment and cathode compartment are separated by a separator, and wherein said catholyte solution and said anolyte solution are the same and comprise a tetrafluoroborate electrolyte and an acetonitrile solvent;
with
an iodine source, and ioodobenzene, and applying to the anode and the cathode an electric potential; the proportions of materials, electric potential, and other conditions being effective to form para-diiodobenzene,
(B) filtering the anolyte solution containing para-diiodobenzene formed in step (A) to obtain a solid which comprises para-diiodobenzene and a filtrate which comprises an electrolyte, a solvent and at least one diiodobenzene compound of the formula:



(C) adding the filtrate from step (B) to said cathode compartment,
(D) deiodinating the diiodobenzene compound in the cathode compartment from step (C) to form iodobenzene by applying to the anode and cathode an electric potential, wherein the catholyte solution and diiodobenzene compound are in the presence of a catalytic amount of palladium on carbon; the proportions of materials, electric potential, and other conditions being sufficient to form iodobenzene; and
(E) recycling the iodobenzene found by step (D) as a starting material for step (A).